The development and chemistry of novel phosphacarbons and their derivatives

A thesis submitted to the University of Sussex for the degree of Doctor of Philosophy

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Declaration

I hereby declare that this thesis has not been and will not be, submitted in whole or in part to another University for the award of any other degree.

Signed ……..

Amy Jane Saunders

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Summary

The exploration of low-coordinate phosphorus chemistry resulted in the synthesis of a range of novel phosphorus species which were duly characterised and subjected to extensive reactivity studies; potential applications and implications for the field are outlined.

The group 14 chloropropargyls $R_3EC{\equiv}CCH_2Cl$ (E = Si, Sn; R = ^{n}Bu, Ph, Me_2Ph, ^{n}Pr, ^{i}Pr) were prepared from $HC{\equiv}CCH_2Cl$ and the respective R_3ECl. While attempts to convert $R_3EC{\equiv}CCH_2Cl$ to $R_3EC{\equiv}CCH_2PX_2$ (X = Cl, NEt_2) *via* the Grignard reaction and addition of $ClPX_2$ were unsuccessful, reactions with $LiPR'_2$ effected conversion to group 14 propargylphosphines $R_3EC{\equiv}CCH_2PR'_2$ (E = Si, Sn; R_3 = ^{n}Bu$_3$, Ph_3, Me_2Ph, ^{n}Pr$_3$, ^{i}Pr$_3$; R' = Ph, $SiMe_3$). The addition of neat I_2 to $R_3SiC{\equiv}CCH_2P(SiMe_3)_2$ afforded impure samples of $R_3SiC{\equiv}CCH_2PI_2$ (R_3 = Me_2Ph, ^{n}Pr$_3$, ^{n}Bu$_3$) that could not be isolated from pentane solutions; attempts to convert $R_3SiC{\equiv}CCH_2P(SiMe_3)_2$ to $R_3SiC{\equiv}CC{\equiv}P$ with AgOTf and DABCO were unsuccessful. The synthesis of $PhC{\equiv}CCH_2PR'_2$ (R' = Ph, $SiMe_3$) was achieved by reaction with $LiPR'_2$, while the Grignard reaction followed by addition to $ClP(NEt_2)_2$ afforded the novel allene $Ph((NEt_2)_2P)C{=}C{=}CH_2$; reactions with HCl and MeI occurred exclusively at phosphorus.

The syntheses of phosphaalkenes C_6H_4(1-C(OSiMe$_3$)=PR')(R) (R = 2-Me, 3-Me, 3-CN, 4-CN, 4-CO_2Me, 4-COCl; R' = H, $SiMe_3$) were attempted by Becker condensation of C_6H_4(1-COCl)(R) and R'P$(SiMe_3)_2$. These reactions were studied in some detail in order to ascertain the principle reaction products, for which tentative identities were assigned. Phosphaalkenes *E*-/*Z*-C_6H_4(1-C(OSiMe$_3$)=PSiMe$_3$)(2-Me) and *E*-/*Z*-C_6H_4(1-C(OSiMe$_3$)=PSiMe$_3$)(3-Me) were isolated and characterised spectroscopically.

A library of *meta*- and *para*-substituted phosphomides C_6H_4(R)C(O)PPh_2 (R = 3-Me, 3-CN, 3-CH_2Cl, 4-CN, 4-CO_2Me) was synthesised by reaction of $HPPh_2$ with the respective acyl chlorides C_6H_4(R)COCl. Following standard literature methods for assessing electronic characteristics, IR data evidenced extensive delocalisation of the phosphorus lone pair into the carbonyl region in all cases, though coordination chemistry evidenced coordination exclusively *via* the phosphorus lone pair, indicative of little delocalisation. Novel di-phosphomides C_5H_3E(2,6-C(O)$PPh_2)_2$ (E = CH, N) were generated by addition of $C_5H_3E(COCl)_2$ to $HPPh_2$ and their behaviour as tridentate pincer ligands assessed by reaction with transition metals. The reaction of $MeP(SiMe_3)_2$ with C_5H_3E(2,6-C(O)$PPh_2)_2$ (E = CH, N) generated unprecedented diphosphametacyclophanes {3-CO-C_6H_4-C(O)PMe}$_2$ and {2-CO-C_5H_3N-C(O)PMe}$_2$; {3-CO-C_6H_4-C(O)PMe}$_2$ is the first example of a metacyclophane that incorporates multiple phosphorus centres within the ligand skeleton, and was characterised crystallographically.

Contents

Abbreviations

δ	Chemical shift
[18]crown-6	1,4,7,10,13,16-hexaoxacyclooctadecane
acac	Acetylacetone
Ad	Adamantyl
Ar	Aryl
BINAP	2,2'-bis(diphenylphosphino)-1,1'-binaphthyl
Bipy	2,2'-bipyridine
^{n}Bu	^{n}butyl
^{t}Bu	^{t}butyl
br	Broad
calcd.	Calculated
cat.	Catalytic
cot	Cyclooctatetraene
Cp	Cyclopentadienyl
Cp*	$(1,2,3,4,5\text{-}Me)_5$-cyclopentadienyl
Cy	Cyclohexyl
d	Doublet
dba	Dibenzylideneacetone
dd	Doublet of doublets
dt	Doublet of triplets
DABCO	1,4-diazabicyclo[2.2.2]octane
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DCM	Dichloromethane
DCPB	Diphosphinidenecyclobutene
Deg	Degrees
DEAD	Diethyl azodicarboxylate

DFT	Density functional theory
DIAD	Diisopropyl azodicarboxylate
dme	Dimethoxyethane
dppe	1,2-bis(diphenylphosphino)ethane
EI	Electron ionisation
ESI-MS	Electrospray ionisation mass spectrometry
Elem. Anal.	Elemental analysis
Et	Ethyl
HMBC	Heteronuclear multiple bond correlation
HOMO	Highest occupied molecular orbital
HSQC	Heteronuclear single quantum correlation
Hz	Hertz
i	Ipso
IR	Infra-red
J	Scalar coupling
LDA	Lithium diisopropylamide
LUMO	Lowest unoccupied molecular orbital
m	Multiplet
m	Meta
M	Molar
mA	Milliamps
mbar	Millibar
Me	Methyl
Mes	Mesitylene
Mes*	Supermesitylene
MHz	Megahertz
mol	Moles
MS	Mass spectrometry

NBO	Natural bond order
NICS	Nucleus-independent chemical shift
NLO	Nonlinear optic
nm	Nanometres
NMR	Nuclear magnetic resonance
Np	Neopentyl
NR	Neutralisation-reionisation
o	Ortho
OAc	Acetate
OLED	Organic light emitting diode
OTf	Trifluoromethanesulfonate
OTs	Tosylate
p	Para
Ph	Phenyl
ppm	Parts per million
PPV	Poly(-phenylenevinylene)
^{n}Pr	^{n}propyl
^{i}Pr	^{i}propyl
q	Quartet
quin	Quintet
r.t.	Room temperature
t	Triplet
TBAF	Tetra-n-butylammonium fluoride
THF	Tetrahydrofuran
TMS	Trimethylsilyl
TON	Turnover number
UV/Vis	Ultraviolet/ visible
VGSR	Vacuum gas solid reaction

1. Introduction

1.1 Phosphorus: "The Devil's Element"

Phosphorus ("phos" meaning "light" in Greek) was first isolated from urine by alchemist Hennig Brandt in 1669; as the 13th element to be discovered, it has been referred to as "the Devil's element."[1] Phosphorus is in period 2 of the pnictogen group, which also contains nitrogen (period 1), arsenic (period 3), antimony (period 4) and bismuth (period 5). The only stable isotope of phosphorus, of a total of twenty-three, is ^{31}P. As such, it is 100% naturally abundant, and with a nuclear spin of ½ is NMR active.

The phosphorus atom 'P' and the 'CH' fragment are isolobal and isoelectronic; they possess similar frontier molecular orbitals and electronic configurations, giving rise to the term "carbon-copy," with reference to phosphorus.[2] Phosphorus and carbon also have similar Pauling electronegativities (2.5 for carbon, 2.1 for phosphorus). Given these facts, phosphacarbons R_3P and hydrocarbons R_3CH often share similar reactivities, although disparities do arise due to the polar $^{\delta-}C\text{-}P^{\delta+}$ bond of phosphacarbons compared with the apolar C-C bond of hydrocarbons. Analogies between organophosphorus and organonitrogen compounds are less frequent since the increased electronegativity of nitrogen (3.0) reverses the bond polarity ($^{\delta+}C\text{-}N^{\delta-}$ and $^{\delta-}C\text{-}P^{\delta+}$), thus altering the reactivity in many cases.[3]

Organophosphorus compounds might reasonably be divided into the following categories in accordance with their coordination number (σ) and valency (λ) (Figure 1); **λ^5-σ^5**) phosphoranes, **λ^5-σ^4**) phosphine oxides, **λ^4-σ^4**) phosphonium salts, **λ^3-σ^3**) phosphines, **λ^3-σ^2**) phosphaalkenes and **λ^3-σ^1**) phosphaalkynes.

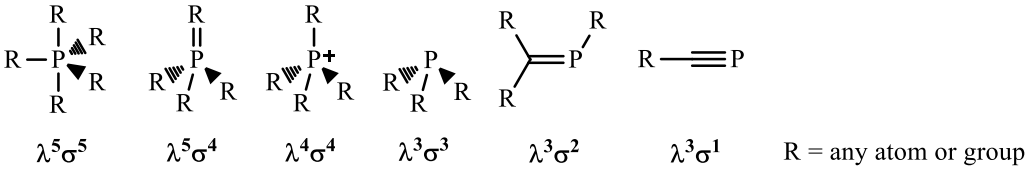


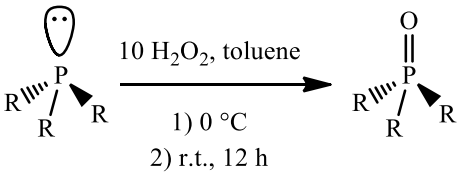
Figure 1. Categories of organophosphorus compounds

Given that this project focuses primarily on tri-, di- and monovalent organophosphorus species, the key literature regarding phosphines, phosphaalkenes and phosphaalkynes will be reported, including defining characteristics, synthetic methodologies, reactivity and applications.

1.2 Phosphines

1.2.1 General considerations

Phosphines are neutral two electron-donor compounds of the general formula R_3P, analogous to amines, NR_3, which adopt trigonal pyramidal geometries with the phosphorus lone pair occupying the fourth vertex. The R-C-P angles vary dependent upon the substituents, although always remain less than 109.5°. Many phosphines oxidise readily upon exposure to air to form phosphine oxides $R_3P{=}O$;[4] controlled synthetic routes towards phosphine oxides are also well-established and typically feature reaction of the phosphine with excess H_2O_2 (Scheme 1).[5]



Scheme 1. Oxidation of R_3P to $R_3P{=}O$ [5]

1.2.2 Phosphine subcategories

Phosphines and phosphites are one of the most frequently reported phosphorus-containing species in the literature, and might reasonably be divided into the following sub-categories; **i**) primary, secondary and tertiary, **ii**) bis-phosphines, **iii**) phosphomides, **iv**) pincer ligands, **v**) phosphiranes, **vi**) phospholes, **vii**) phosphites (Figure 2).

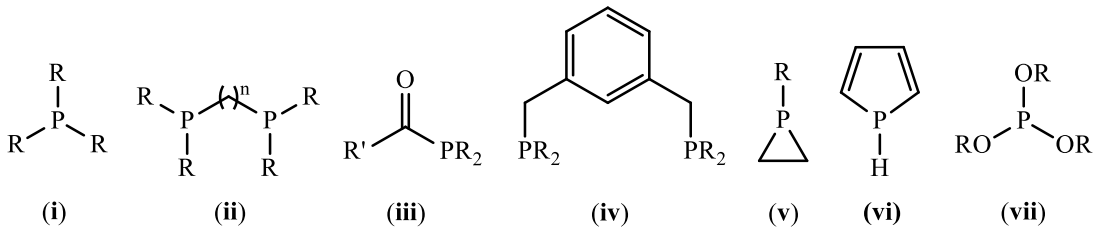
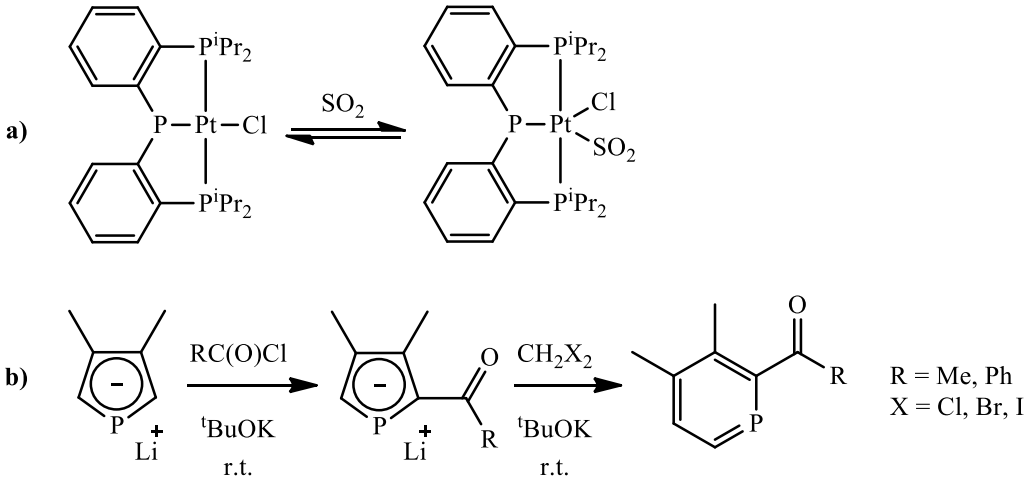


Figure 2. Categories of phosphines

The applications of phosphines are extremely varied and well-documented; types **i**,[6,7] **ii**,[8,9] **iii**,[10,11] **iv**,[12–17] **vi**,[18] and **vii** are all used primarily as ligands in catalysis due to the ease with which their

steric and electronic properties can be tuned,[19] although type **i** phosphines are also used as reducing agents for oxygen extraction.[20,21] Type **iv** phosphine complexes find additional applications as gas sensors (Scheme 2 **a**),[22–24] biomarkers,[25] and molecular switches,[26,27] while phosphines of the type **vi** find further applications in the synthesis of π-conjugated materials,[28–30] and the generation of β-functionalised phosphabenzene derivatives, achieved by lithiation of phospholes to phospholides and subsequent reaction with a strong base (Scheme 2 **b**).[31] The instability of phosphiranes (type **v**) has thus far limited most reports to novel chemical processes,[32–34] although a handful of reports have described exploration of their use as ligands in transition metal catalysis.[35]



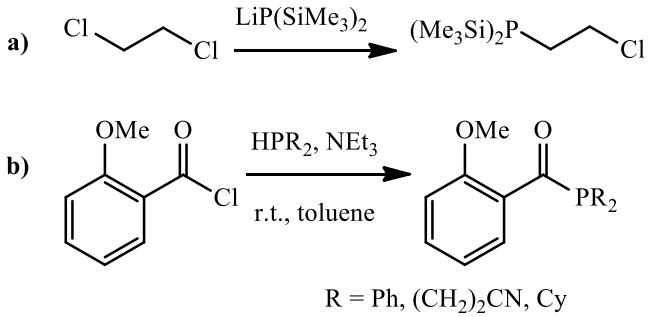
Scheme 2. a) Type **iv** phosphines as gas sensors,[24] **b**) type **vi** phosphines for the generation of phosphabenzene derivatives [31]

1.2.3 Synthetic methodologies

The synthesis of organophosphorus compounds stems from the ready availability of the precursor phosphines, PH_3, PX_3 (X = Cl, Br) and $P(SiMe_3)_3$. The primary phosphine PH_3 is produced industrially from the reaction of P_4 with MOH (M = Na, K), while the halophosphines PX_3 are synthesised by reaction of P_4 with X_2.[36] Silylphosphines such as $P(SiMe_3)_3$ are accessed *via* the reflux of P_4 with Na/K followed by addition of Me_3SiCl; the resulting phosphine $P(SiMe_3)_3$ can be converted to $HP(SiMe_3)_2$ upon stoichiometric addition of MeOH.[37]

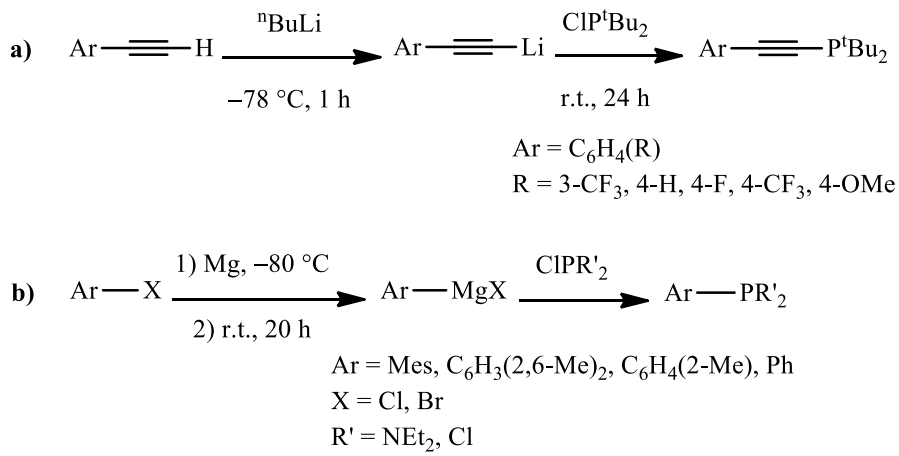
A wide variety of routes are available for the preparation of organophosphorus compounds, although several feature in the literature more frequently than others, including the reaction of phosphides with halocarbons. For instance, the lithium phosphide $LiP(SiMe_3)_2$ reacts with $C_2H_4Cl_2$ at ambient temperature to produce the phosphine $(Me_3Si)_2P(CH_2)_2Cl$, which was

identified by a ^{31}P NMR resonance at −175 ppm, with trace levels (<10 %) of the phosphirane $(CH_2)_2PSiMe_3$ evidenced by a characteristic resonance at −318 ppm (Scheme 3 **a**).[38] Another common route towards phosphines is the reaction of secondary or silylated phosphines with acyl chlorides (with or without a base).[39,11,40] Clarke prepared a series of acyl phosphines by the addition of the acyl chloride C_6H_4(1-COCl)(2-OMe) to the respective secondary phosphines HPR_2 (R = Ph, $(CH_2)_2CN$, Cy) in the presence of NEt_3 (Scheme 3 **b**);[11] the acyl phosphines C_6H_4(1-C(O)PR_2)(2-OMe) were isolated in high yields (>88 %) after filtration and removal of the solvent under reduced pressure.



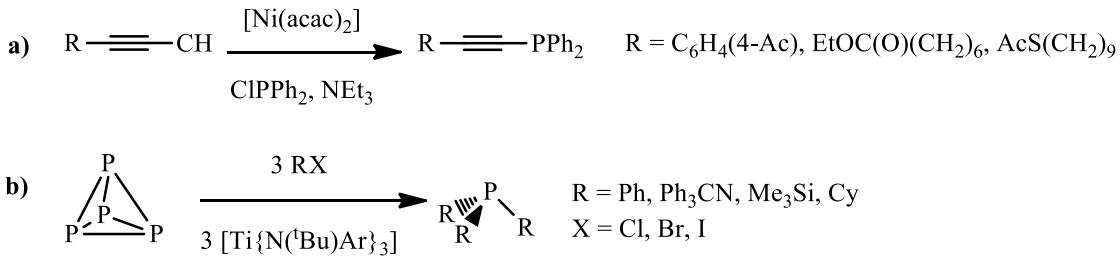
Scheme 3. Phosphine syntheses; **a**) reaction of phosphides with halocarbons,[38] **b**) reaction of secondary phosphines with acyl chlorides [11]

Phosphines have also frequently been accessed by the reaction of halophosphines with organolithium reagents. The reaction of ArC≡CLi with ClP^tBu_2 afforded the respective alkynylphosphines ArC≡CP^tBu_2 in good yields (>50 %) after purification by column chromatography (Scheme 4 **a**).[41] The reliability of this route is demonstrated by the wide range of phosphines produced by it, including PhC≡CPPh_2,[42] and $Me_3SiCH_2P^tBu_2$.[43] The reaction of Grignard reagents, such as ArMgX, with chlorophosphines of the type ClPR'$_2$ also provide access to the respective phosphines ArPR'$_2$ with elimination of XMgCl (Scheme 4 **b**).[44]



Scheme 4. Phosphine syntheses; **a**) reaction of chlorophosphines with organolithium reagents,[41] **b**) reaction of chlorophosphines with Grignard reagents [44]

Less frequently reported routes to phosphines include the use of transition metal catalysis. Thus, the reaction of RC≡CH with $ClPPh_2$ in the presence of NEt_3 was catalysed by $[Ni(acac)_2]$ (3 mol %) to afford the corresponding phosphine, $RC{\equiv}CPPh_2$ (Scheme 5 **a**).[45] Although the yields were variable, ranging from 30 - 70 %, the route held particular value for the synthesis of phosphines comprising labile substituents such as C_6H_4(4-Ac), $EtOC(=O)(CH_2)_6$ and $AcS(CH_2)_9$. A particularly rare route towards phosphines includes the radical reaction of elemental phosphorus. The reaction of P_4 with RX in the presence of a radical initiator such as $[Ti\{N(^tBu)Ar\}_3]$ has been documented to afford phosphines of the type PR_3. Yields were typically in excess of 70 % (up to 97 %), although the reaction failed with PhCl (Scheme 5 **b**).[46]



Scheme 5. Phosphine syntheses; **a**) transition metal catalysed,[45] **b**) cleavage of P_4 [46]

1.2.4 Reactivity traits

Coordination chemistry

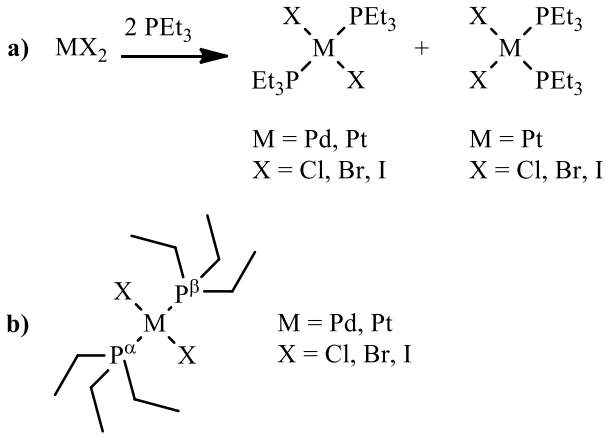
The influence of substituent steric profiles upon the coordination reactions of phosphines was first described by Tolman in 1970,[47,48] and reviewed succinctly in 1976.[49] Tolman reported that the coordination behaviour of phosphines to $[Ni(CO)_4]$ could not be explained by electronic effects alone. Thus, despite the significantly increased basicity of P^tBu_3 over PMe_3 (assessed by comparison of the IR stretching frequencies of $[Ni(CO)_3P^tBu_3]$; $\nu_{(C=O)}$ 2056 cm^{-1}, $[Ni(CO)_3PMe_3]$; $\nu_{(C=O)}$ 2064 cm^{-1}), PMe_3 was found to coordinate to $[Ni(CO)_4]$ preferentially ahead of P^tBu_3. This was rationalised in terms of steric crowding at the bonding face of the phosphorus centre of P^tBu_3, wherein the bulky ^{t}Bu substituents clash with the CO ligands of the metal complex to a greater extent than the more compact Me groups. The Tolman cone angle was devised to compare the steric influences of phosphine substituents and is defined as "the apex angle of a cylindrical cone, centred 2.28 Å from the centre of the phosphorus atom, which just touches the van der Waals radii of the outermost atoms of the model."[49] It has since become a standard tool when discussing phosphine complexes.

Table 1. Tolman cone angles of phosphine complexes $[Ni(CO)_3PR_3]$ [49]

Phosphine (PR_3)	Cone angle / °
PH_3	93.8
PF_3	96.3
PMe_3	98.9
PCl_3	100
PPh_3	103
P^tBu_3	106

The coordination chemistry of phosphines is dominated by lone pair donation,[50,45,51] although bridging coordination has also been documented (see section **1.2.5**), as has coordination of the phosphorus lone pair to bridge two,[52] and three metal centres.[53] Literature reports have noted that the prevalence of *cis*- or *trans*- isomers within bis-phosphine di-halide metal complexes is often directed by the radius of the metal nuclei.[54] Despite the comparable atomic radii of palladium and platinum (137 pm for palladium; 139 ppm for platinum), square planar palladium complexes of the type $[PdX_2(PEt_3)_2]$ (X = Cl, Br, I) typically adopt the *trans*-configuration, while square planar platinum complexes $[PtX_2(PEt_3)_2]$ (X = Cl, Br, I) adopt either *cis*- or *trans*-geometries when formed under the same conditions (Scheme 6 **a**).[55]

While the *cis*-/*trans*-isomers of $[PtX_2(PEt_3)_2]$ may be distinguished by the characteristic magnitude of platinum satellites (typically $^1J_{P\text{-}Pt}$ 3500 - 3900 Hz for *cis*-complexes, 2200 - 2800 Hz for *trans*-complexes), virtual coupling effects are an invaluable tool for distinguishing between *cis*-/*trans*-$[PdX_2(PEt_3)_2]$, which do not exhibit characteristic satellites due to the lack of a suitable spin-active isotope.[56] Virtual coupling can be explained by considering *trans*-$[MX_2(PEt_3)_2]$, for which the phosphine ligands are chemically equivalent but magnetically inequivalent; thus, the carbon atoms bound to the α-phosphorus couples to both the α- and β-phosphorus centres (Scheme 6 **b**), which are separated by one and three bonds respectively, and the couplings become apparently identical, resulting in a virtual triplet signal instead of two doublets. The same virtual triplet is exhibited by the PCH_2 protons, with the coupling resulting from two-bond and four-bond proton-phosphorus separations. For instance, the PCH_2 groups of *trans*-$[PdCl_2(PEt_3)_2]$ show an apparent six line pattern in the ^1H NMR spectrum, due to the quartet being further split as a virtual triplet, at 1.80 ppm ($J_{H\text{-}P}$ 7 Hz), while the $^{13}C\{^1H\}$ NMR spectrum shows a virtual triplet resonance at 13.8 ppm ($J_{C\text{-}P}$ 26.9 Hz).[55] Virtual coupling effects are not typically observed in *cis*-$[MCl_2(PR_2CH_3)_2]$ complexes.

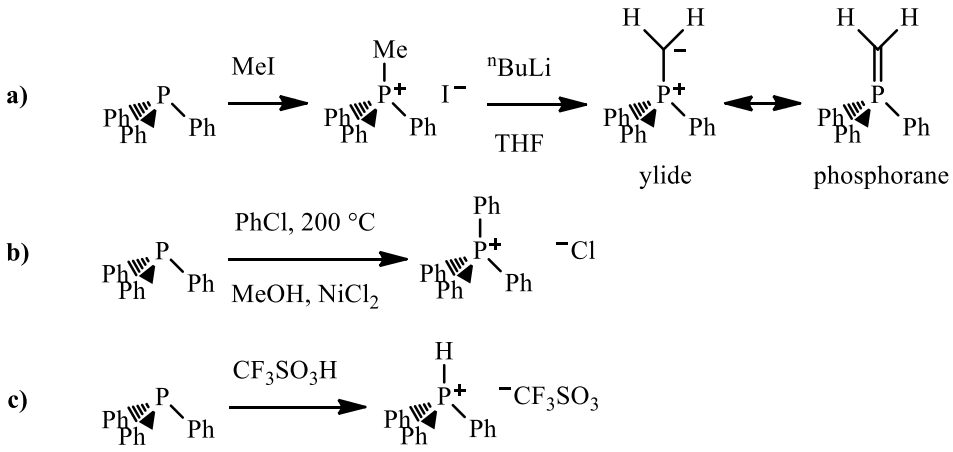


Scheme 6. Phosphine coordination chemistry; **a**) syntheses of *cis*-/*trans*-$[MX_2(PEt_3)_2]$, [55] **b**) virtual coupling effects of *trans*-$[MX_2(PEt_3)_2]$ [56]

Nucleophilic reactions

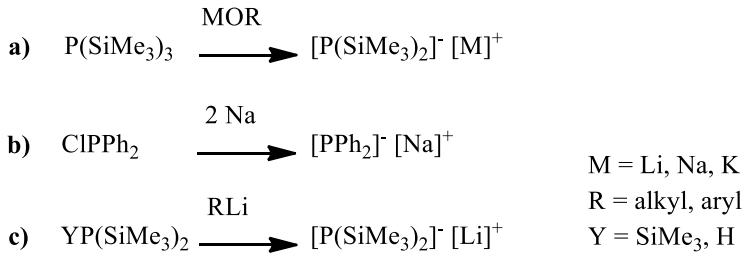
Phosphines undergo several reactions in which they behave as nucleophiles, including quarternisation reactions to afford phosphonium ions of the general formula PR_4^+. One particularly important example is Ph_3P^+Me, which is the precursor to the Wittig reagent (Ph_3PCR_2). The phosphonium ion Ph_3P^+Me is synthesised by reaction of PPh_3 with MeI; conversion to Ph_3PCR_2 is achieved by the addition of a strong base, often PhLi or ^{n}BuLi (Scheme 7 **a**).[57] Tetraphenylphosphonium chloride $[Ph_4P]^+[Cl]^-$, which is frequently used in

phase transfer catalysis,[58] is afforded from the reaction of PPh_3 with PhCl in the presence of a nickel catalyst (Scheme 7 **b**).[59] Phosphonium salts like $[R_3P^+H][CF_3SO_3]^-$ are synthesised by the addition of acids, such as CF_3SO_3H, to R_3P (Scheme 7 **c**).[60]



Scheme 7. Synthesis of phosphonium salts; **a**) **[**$Ph_3P]^+[Me]^-$,[57] **b**) $[Ph_4P]^+[Cl]^-$,[59] **c**) $[R_3P^+H][CF_3SO_3]^-$ [60]

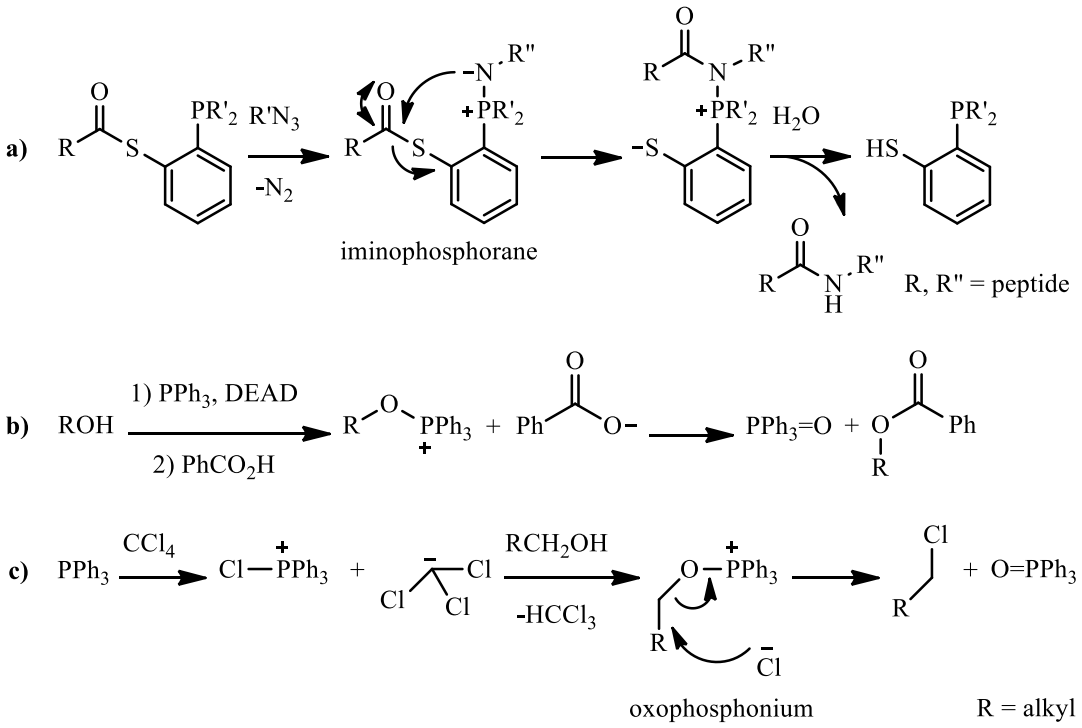
One common application of phosphines is the synthesis of phosphides $[R_2P]^+[M]^-$, which play a key role in the formation of new carbon-phosphorus bonds; examples include the reaction of $LiP(SiMe_3)_2$ with $Cl(CH_2)_2Cl$, which affords $Cl(CH_2)_2P(SiMe_3)_2$.[38] Phosphide synthesis can be achieved by several routes, including **a**) addition of alkoxides to $P(SiMe_3)_3$,[61,62] **b**) addition of alkali metals to chlorophosphines,[63] **c**) addition of alkyllithium reagents to secondary phosphines $YP(SiMe_3)_2$ (Y = $SiMe_3$, H) (Scheme 8).[64]



Scheme 8. Syntheses of phosphides; **a**) addition of MOR to $P(SiMe_3)_3$,[61] **b**) addition of alkali metals to chlorophosphines,[63] **c**) addition of alkyllithium reagents to $YP(SiMe_3)_2$ [64]

Reduction reactions

Due to the ease with which phosphines are oxidised, they are commonly employed as reducing agents.[65] The Staudinger ligation,[66] a variation of the Staudinger reaction,[21] enables the reduction of azides using tertiary phosphines *via* an iminophosphorane intermediate that ultimately generates amides (Scheme 9**a**).[67] The Mitsunobu reaction is another example of the application of phosphines as reducing agents, in which primary and secondary alcohols are converted to esters, ethers, thioethers, imides or azides with PPh_3 and an azodicarboxylate,[20] typically DEAD or DIAD (Scheme 9 **b**).[68,69] The Appel reaction also incorporates a phosphine as a reducing agent; the PPh_3 is initially oxidised to a chlorophosphonium salt $[ClPPh_3]^+[CCl_3]^-$ by the addition of CCl_4 (Scheme 9 **c**).[70] Then the salt reacts with an alcohol to afford an oxyphosphonium intermediate $[RCH_2OPPh_3]^+[Cl]^-$, followed by spontaneous conversion to an alkylhalide.



Scheme 9. Phosphines as reducing agents; **a**) the Staudinger ligation,[67] **b**) the Mitsunobu reaction, [68] **c**) the Appel reaction [70]

1.2.5 Significant phosphines and their chemistry

Coordination complexes in catalysis

Among the vast collection of phosphine complexes, several stand out for their prevalent use in catalysis, in which the phosphines typically act as spectator ligands. Well-established examples include Wilkinson's catalyst [$Rh(PPh_3)_3Cl$] (**1.A**) for the hydrogenation of alkenes,[6] "Grubbs catalyst" (of which many variations are known, such as [$Ru(PCy_3)_2(CHR)Cl_2$]) (**1.B**) for olefin metathesis,[7] [$Pd(PPh_3)_4$] (**1.C**) for the Heck reaction,[71] Stille coupling,[72] Suzuki coupling,[73] Sonogashira coupling,[74] and chiral [RuHX(BINAP)] (**1.D**) for the Noyori hydrogenation in the enantioselective hydrogenation of ketones, aldehydes and imines (Figure 3).[9]

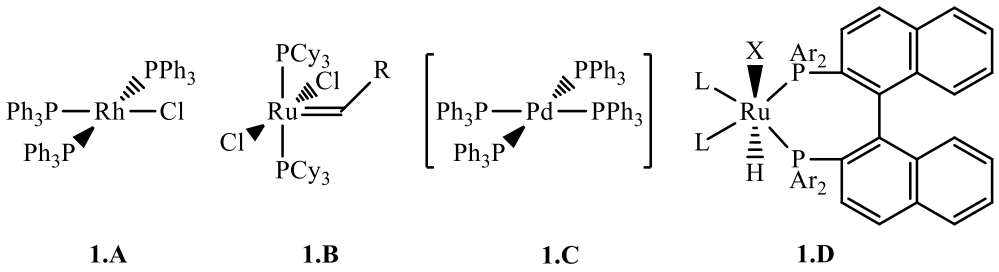


Figure 3. Transition metal phosphine complexes in catalysis; Wilkinsons catalyst (**1.A**),[6] "Grubbs catalyst" (**1.B**),[7] [$Pd(PPh_3)_4$] (**1.C**),[71–74] [RuHX(BINAP)] (**1.D**) [9]

Pincer ligand complexes, although less well-established than any featured in Figure 3, are becoming increasingly popular in catalysis due to their highly tunable electronic and steric properties,[75] which are achieved *via* alterations to the pendant arms (AR_2), the heteroatom (E), the metal centre (M) and the metal substituent (X) (Figure 4).

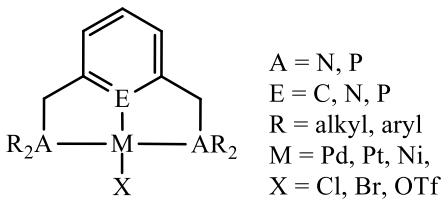
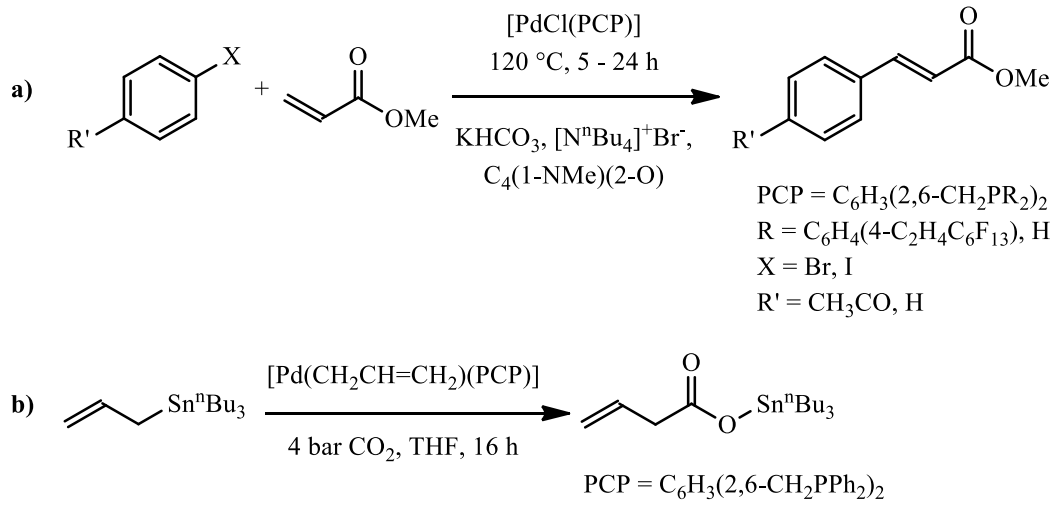


Figure 4. Pincer ligands possess highly tunable electronic and steric properties

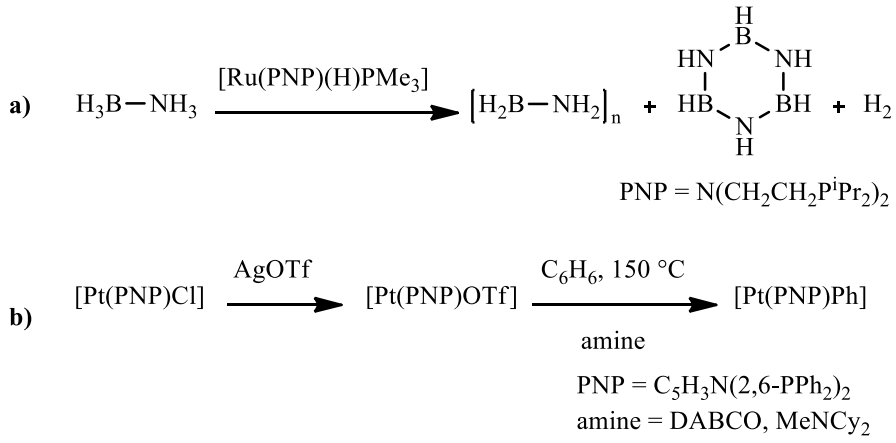
PCP pincer complexes such as [PdCl(PCP)] (PCP = $\{C_6H_3(2,6\text{-}CH_2PR_2)_2\}$ (R = C_6H_4, $C_6H_4CH_2C_6F_{13}$), H) have been used to catalyse the Heck reaction of $C_6H_4(1\text{-}R')(4\text{-}X)$ (R' =

CH_3CO, H; X = Br, I) with $H_2C{=}CHCO_2Me$ at 120 °C (Scheme 10 **a**),[13] generating the coupled product $C_6H_4(1\text{-}R')(4\text{-}(HC)_2CO_2Me)$ in yields of 57 - 98 %. The perfluoroalkylated PCP pincer complex (where R = $C_6H_4CH_2C_6F_{13}$) was recovered in 96 % yield by solid-phase extraction and re-used up to four times with little diminishment of catalytic activity. The catalytic carboxylation of allylstannane $^nBu_3SnCH_2CH{=}CH_2$ has also been achieved by the use of a PCP pincer complex [Pd($CH_2CH{=}CH_2$)(PCP)] (3.5 mol %) (PCP = {$C_6H_3(2,6\text{-}CH_2PPh_2)_2$}) (Scheme 10 **b**).[16] The carboxylate $^nBu_3SnOC(O)CH_2CH{=}CH_2$ was generated in 80 % yield after 16 h, though the yield was increased to 94 % after 40 h. The results are comparable with the traditional system, which uses [$Pd(PPh_3)_4$] (8 mol %) with 33 bar of CO_2 to generate $^nBu_3SnOC(O)CH_2CH{=}CH_2$ in 90 % yield after 24 h, though the reduced levels of catalyst required in the former is an advantage.



Scheme 10. PCP pincer complexes for; **a**) the Heck reaction,[13] **b**) allylstannane carboxylation [16]

As for PCP pincer complexes, PNP complexes are also frequently used to effect catalytic conversions. The ruthenium complex [Ru(PNP)(H)PMe_3] (PNP = $N(CH_2CH_2P^iPr_2)_2$) has been applied in the catalytic dehydrogenation of ammonia-borane with an unprecedented turnover number (TON) (8300 with 0.01 mol % catalyst) (Scheme 11 **a**),[76] while the platinum complex [Pt(PNP)OTf] (PNP = $C_5H_3N(2,6\text{-}PPh_2)_2$) has effected stoichiometric C-H bond activation (Scheme 11 **b**).[77]



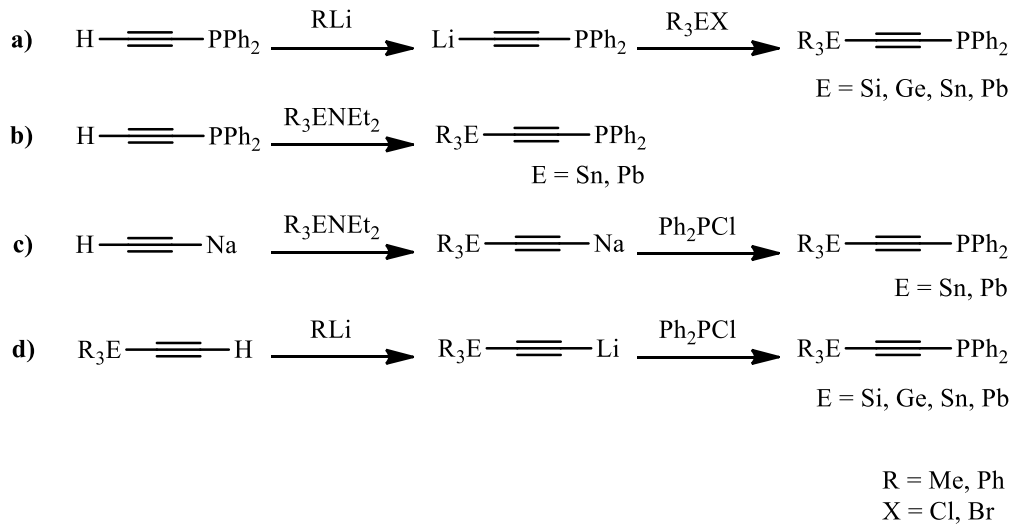
Scheme 11. PNP pincer complexes for; **a**) dehydrogenation of H_3B-NH_3,[76] **b**) C-H bond activation [77]

Alkynyl- and propargylphosphines

Alkynylphosphines are extremely well-documented throughout the literature, often exhibiting unusual reactions with transition metals due to the π-system. Carty synthesised a library of alkynylphosphines RC≡CPR'$_2$ by reaction of the respective lithiated alkynes RC≡CLi with ClPR'$_2$ (see above, Scheme 4 **a**), and noted that unlike phosphines of the type R_3P, alkynylphosphines RC≡CPR'2 do not readily oxidise upon exposure to air due to the "stabilising effect of α-acetylenic substituents."[78] Several of the alkynylphosphines exhibited IR absorbances at the lower end of the typical range for alkynes (RC≡CR; $\nu_{(C\equiv C)}$ 2300 - 2175 cm^{-1}) (Table 2), which Carty postulated may be attributed to π-conjugation between the phosphorus lone pair and the alkyne. Among the collection of Carty's alkynylphosphines, $Ph_2AsC{\equiv}CPPh_2$ was the first example of a mixed phosphine-arsine to be reported, while $Ph_2PC{\equiv}CP(C_6F_5)_2$ and $Ph_2PC{\equiv}CP(NEt_2)_2$ were the first examples of asymmetric alkynyldiphosphines. Reports of main group alkynylphosphines $R_3EC{\equiv}CPR_2$ (R = Si, Ge, Sn, Pb) are limited to a handful of examples, most of which were reported by Siebert, who used four different synthetic routes, depending on the identity of E (Scheme 12).[79] As for Carty's examples, the IR absorbances for $R_3EC{\equiv}CPPh_2$ were at relatively low frequencies.

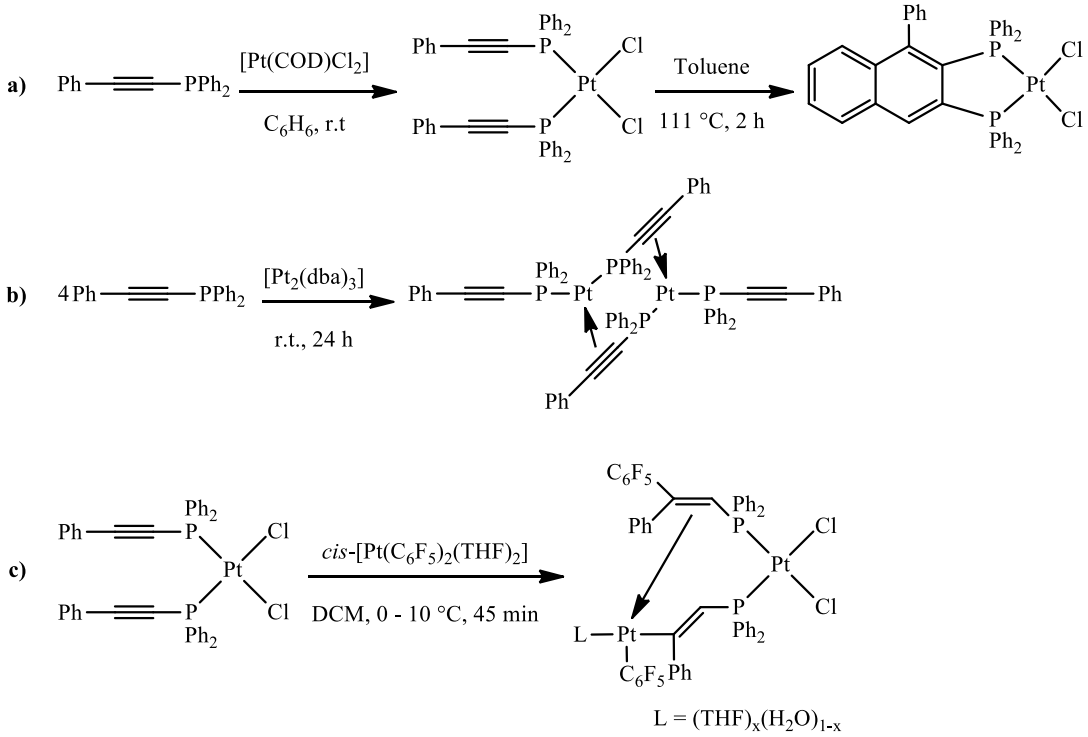
Table 2. Selected IR absorbances of alkynylphosphines

Compound	$\nu_{(C\equiv C)}$ / cm^{-1}	Source
$CF_3C{\equiv}CPPh_2$	2200	78
$MeC{\equiv}CPPh_2$	2195	78
$MeC{\equiv}CP(C_6F_5)_2$	2200	78
$PhC{\equiv}CP(C_6F_5)_2$	2170	78
$Me_3SiC{\equiv}CPPh_2$	2105	79
$Me_3GeC{\equiv}CPPh_2$	2115	79
$Me_3SnC{\equiv}CPPh_2$	2078	79
$Ph_3SiC{\equiv}CPPh_2$	2101	79
$Ph_3GeC{\equiv}CPPh_2$	2105	79
$Ph_3SnC{\equiv}CPPh_2$	2084	79



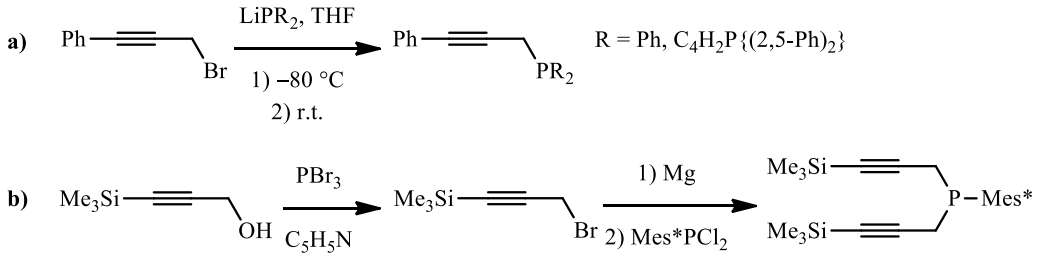
Scheme 12. Synthesis of main group alkynylphosphines [79]

The postulated π-conjugation between the phosphorus centre and alkyne prompted an in-depth study into the reactivity of $PhC{\equiv}CPPh_2$ by several groups. Carty reported that *cis*-$[PtCl_2(PhC{\equiv}CPPh_2)_2]$ could be induced to cyclise upon heating (Scheme 13 **a**),[80] and rationalised the process with the close proximity (3.110(10) Å) of the phosphorus centre to the alkynic π-system of the second ligand, ascertained by single crystal X-ray diffraction. Lalinde demonstrated that both the phosphine and alkyne moieties of $PhC{\equiv}CPPh_2$ could be promoted to coordinate to platinum (Scheme 13 **b**),[81] while Forniés successfully generated a new carbon-carbon bond between the alkyne and C_6F_5 by reaction of *cis*-$[PtCl_2(PhC{\equiv}CPPh_2)_2]$ with *cis*-$[Pt(C_6F_5)_2(THF)_2]$ (Scheme 13 **c**).[82]



Scheme 13. Novel coordination chemistry of $PhC{\equiv}CPPh_2$ and its complexes; **a**) cyclisation of *cis*-$[PtCl_2(PhC{\equiv}CPPh_2)_2]$,[80] **b**) synthesis of $[\{Pt(PPh_2C{\equiv}CPh)(\mu\text{-}\kappa P{:}\eta^2\text{-}PPh_2C{\equiv}CPh)\}_2]$,[81] **c**) addition of *cis*-$[PtCl_2(PhC{\equiv}CPPh_2)_2]$ across a Pt-C_6F_5 bond [82]

In contrast to the prevalent reports of alkynylphosphines in the literature, propargylphosphines remain extremely rare, the only documented examples being $Ph_2PCH_2C{\equiv}CCH_2PPh_2$,[83] $MeC{\equiv}CCH_2PPh_2$,[84] $Mes^*P(CH_2C{\equiv}CSiMe_3)_2$,[85] $HC{\equiv}CCH_2PPh_2$,[84] $PhC{\equiv}CCH_2PPh_2$ and $PhC{\equiv}CCH_2P\{C_4H_2P(2,5\text{-}Ph)_2\}_2$.[86] Synthesis has been achieved *via* two routes, including the reaction of the respective lithium phosphide $LiPR_2$ (R = Ph, $\{C_4H_2P(2,5\text{-}Ph)_2\}$) with propargyl bromide $PhC{\equiv}CCH_2Br$ (Scheme 14 **a**), which afforded the propargylphosphines $PhC{\equiv}CCH_2PPh$ and $PhC{\equiv}CCH_2P\{C_4H_2P(2,5\text{-}Ph)_2\}$ in 42 % and 60 % yields in turn.[86] Furthermore, the Grignard reaction of propargyl bromide $Me_3SiC{\equiv}CCH_2Br$ and subsequent addition of Mes^*PCl_2 generated $Mes^*P(CH_2C{\equiv}CSiMe_3)_2$ in 80 % yield (Scheme 14 **b**).[85]



Scheme 14. Propargylphosphine syntheses; **a**) *via* lithium phosphides,[86] **b**) by chlorophosphine [85]

1.3 Phosphaalkenes

1.3.1 General considerations

Phosphaalkenes possess the general formula $R_2C{=}PR$ and are isoelectronic with alkenes, $R_2C{=}CR_2$, resulting in similar reactivity profiles; both undergo polymerisation, addition reactions and cyclisation reactions. Large disparities in bond angles between typical phosphaalkenes, alkenes and imines exist, whereby phosphaalkenes typically possess contracted angles around the double bond (Table 3). This can be rationalised by the low degree of 3p character possessed by the lone pair of phosphaalkenes, in contrast to the lone pair of imines and the σ-bond of alkenes, both of which experience a much greater contribution from the 3p orbitals. Phosphaalkenes are polarised as $^{\delta-}C{=}P^{\delta+}$, in contrast to imines $^{\delta+}C{=}N^{\delta-}$, due to the relative electronegativity differences between C/P and C/N; quantification by NBO calculations resulted in heteroatom charges of +0.42 and −0.59 for $H_2{}^{\delta-}C{=}P^{\delta+}H$ and $H_2{}^{\delta+}C{=}N^{\delta-}H$ in turn, rationalising their frequently different reactivities.[87] The bond polarity of phosphaalkenes may, however, be inverted by installing electron-withdrawing substituents, such as amines, at the carbon centre, typically resulting in elongation of the double bond ($(Me_2N)_2C{=}PH$; 1.740(1) Å), a slight change to the C=P-A angle ($(Me_2N)_2C{=}PH$; 103(1) °), and modified reactivities.[3]

Table 3. Bond lengths, C=P-A angles (A = H, C), heteroatom charges and lone pair characteristics of phosphaalkenes, imines and alkenes

Compound	*d* C=P / Å	C=P-A / °	Source	Heteroatom charge / e	3s / %	3p / %	Source
$H_2C{=}PH$	1.67	100	88	+0.42	66	34	87
$H_2C{=}NH$	1.26	120	89	−0.59	39	61	87
$H_2C{=}CH_2$	1.337	117.3	90	0	33	67	-

As for classical alkenes, the HOMO and HOMO−1 of phosphaalkenes are associated with the π-system and lone pair (σ-bond for alkenes) respectively. However, the situation is reversed for imines, in which the HOMO relates to the nitrogen lone pair and the HOMO−1 refers to the π-system (Figure 5).[91] The HOMO and HOMO−1 ionisation energies of H_2C=PH are −10.3 and −10.7 eV respectively,[92] as determined by photoelectron spectroscopy, are close to previously calculated values (−9.63 and −10.43 eV).[92] The phosphaalkene H_2C=PH possesses a significantly smaller HOMO - HOMO−1 energy gap (0.4 eV) than the imine H_2C=NH (1.87 eV), which allows phosphaalkenes to react at both the π-system and the lone pair, while imines typically react *via* the nitrogen lone pair.

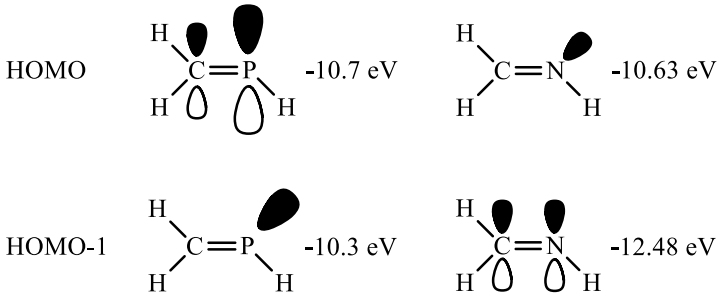
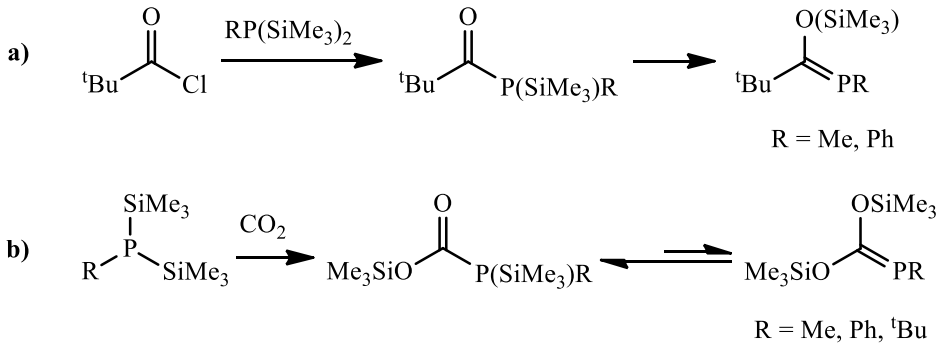


Figure 5. The HOMO and HOMO−1 ionisation energies of H_2C=NH,[91] H_2C=CH_2 [93]

1.3.2 Synthetic methodologies

Becker condensation

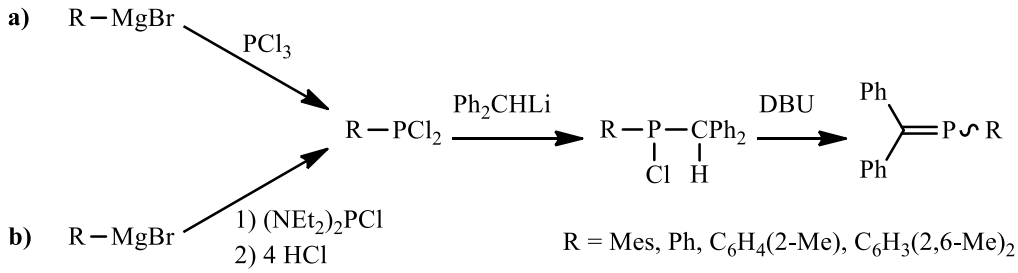
One of the most frequently reported methodologies for the synthesis of phosphaalkenes is now referred to as the Becker synthesis. The reaction requires the addition of a silylated phosphine $RP(SiMe_3)_2$ (R = Me, Ph) to an acyl chloride (^{t}BuCOCl) (Scheme 15 **a**).[94] The resulting acyl phosphine intermediate is only detected on rare occasions,[95] as it usually undergoes a spontaneous [1,3]-silatropic rearrangement to form the phosphaalkene, reportedly driven by the oxophilicity of silicon. Appel demonstrated the influence of temperature on the [1,3]-silatropic rearrangement step in 1984. The reaction of $RP(SiMe_3)_2$ (R = Me, Ph, ^{t}Bu) with CO_2 afforded the acyl phosphine ^{t}BuC(O)P$(SiMe_3)_2$ as the only product at "low temperature" (unspecified) (Scheme 15 **b**), with a ^{31}P NMR resonance at −86.9 ppm.[95] Upon warming to ambient temperature, a new ^{31}P NMR resonance was observed at −17.9 ppm, attributed to ^{t}BuC$(OSiMe_3)$=P$(SiMe_3)$, prompting Appel to postulate the existence of an equilibrium between ^{t}BuC(O)P$(SiMe_3)_2$ and ^{t}BuC$(OSiMe_3)$=P$(SiMe_3)$.



Scheme 15. Becker condensation of phosphaalkenes; **a**) synthesis of ^{t}BuC(OSiMe$_3$)=PR,[94] **b**) the equilibrium between ^{t}BuC(O)P(SiMe$_3$)$_2$ and ^{t}BuC(OSiMe$_3$)=P(SiMe$_3$) [95]

Dehydrohalogenation

The first example of a thermally stable phosphaalkene was reported by Bickelhaupt in 1978. Synthesis of the dichlorophosphine precursor MesPCl$_2$ was achieved by reaction of MesMgBr with PCl$_3$. The addition of Ph$_2$CHLi afforded MesP(Cl)C(H)Ph$_2$, which was then dehydrohalogenated *via* reaction with DBU to generate the phosphaalkene Ph$_2$C=PMes in 50 % yield (Scheme 16 **a**).[96] The methodology was subsequently applied to the syntheses of Ph$_2$C=PR (R = Ph, C$_6$H$_4$(2-Me), C$_6$H$_3$(2,6-Me)$_2$) in 1984, the precursor chlorophosphines being obtained by an alternative route (Scheme 16 **b**),[44] for which improved overall yields were reported (63 - 83 %).

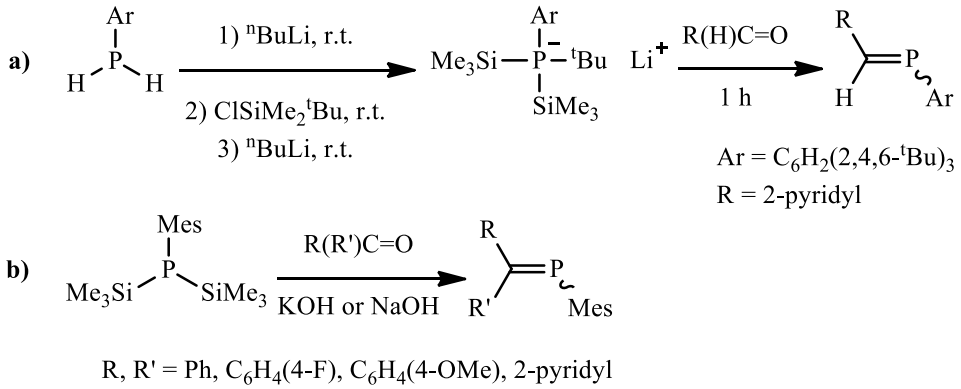


Scheme 16. Syntheses of Ph$_2$C=PR by the dehydrohalogenation methodology *via* route **a**),[96] route **b**) [44]

Alternate synthetic routes

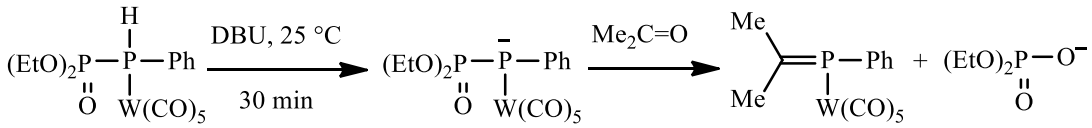
One of the less commonly documented routes towards phosphaalkenes is the Phospha-Peterson reaction. The successive addition of ^{n}BuLi and ClSiMe$_2$^{t}Bu converted ArPH$_2$ to the lithium salt [(Me$_3$Si)$_2$P(Ar)^{t}Bu]$^{-}$[Li]$^{+}$; the subsequent addition of R(H)C=O produced the phosphaalkenes *E*/*Z*-R(H)C=PAr as a mixture of isomers (Scheme 17 **a**).[97] The phosphaalkenes were purified by

column chromatography, although separation of the isomers was not reported. Alternate variations of the Phospha-Peterson reaction have also been documented. Yam reported the synthesis of a collection of phosphaalkenes *E*/*Z*-R(R')C=PMes using catalytic quantities of KOH or NaOH to initiate the reactions (Scheme 17 **b**).[98] The products were isolated by either vacuum distillation or recrystallisation in yields that ranged from 43 - 72 %. The scope of the reaction might be considered to be limited, given that attempts to synthesise the *P*-adamantyl-phosphaalkenes *E*/*Z*-R(R')C=PAd were unsuccessful.



Scheme 17. Phospha-Peterson reaction variations; **a**) traditional,[97] **b**) base-initiated [98]

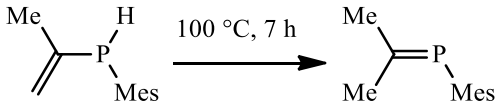
The Phospha-Wittig-Horner reaction was adapted from the Wittig reaction, whereby the reaction of a phosphaylide with aldehydes or ketones affords alkenes;[99] however, in the Phospha-Wittig-Horner variation a Phospha-Wittig reagent like $[(EtO)_2P(=O)P(Ph)W(CO)_5]^-$ is reacted with aldehydes or ketones to produce phosphaalkene complexes (Scheme 18).[100] The resulting complexes were themselves unstable and as such were trapped *via* reaction with methanol or dienes and characterised as the products of those reactions.



Scheme 18. The Phospha-Wittig-Horner reaction [100]

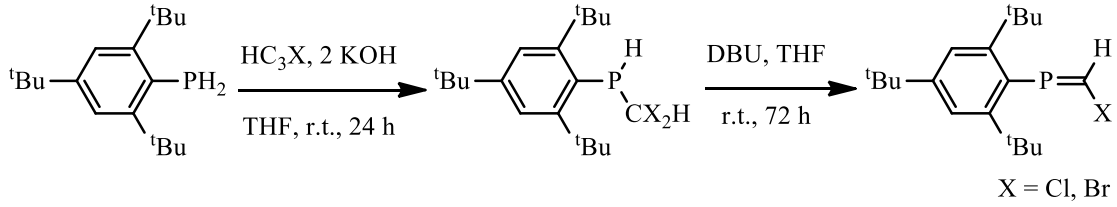
Another route to phosphaalkenes involves the thermal rearrangement of secondary vinyl phosphines. Heating $H_2(Me)C=CP(H)Mes$ to 100 °C for 7 h converted > 80 % to the corresponding phosphaalkene, $Me_2C=PMes$ (Scheme 19),[101] though this could not be separated

from unreacted $H_2(Me)C{=}CP(H)Mes$, its presence being confirmed solely by NMR spectroscopy.



Scheme 19. Thermally-induced rearrangement of vinyl phosphines [101]

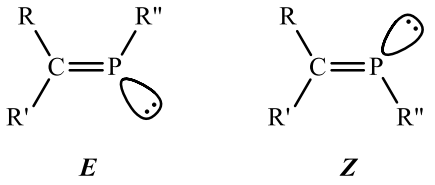
Phosphaalkenes can also be accessed *via* the insertion of an *in situ* generated dihalocarbene into the P-H bond of primary phosphines RPH_2 and subsequent base-induced dehydrohalogenation. Thus, the stepwise reaction of Mes^*PH_2 with HCX_3 (X = Cl, Br) in the presence of KOH afforded the phosphine $Mes^*P(H)C(H)X$, which was dehydrohalogenated to the phosphaalkenes *E*/*Z*-$Mes^*P{=}C(H)X$ upon addition of DBU (Scheme 20).[102] A single isomer was isolated by chromatography followed by recrystallisation, though its stereochemistry was not determined.



Scheme 20. Phosphaalkene synthesis *via* carbene insertion into a primary phosphine [102]

Phosphaalkene isomerism

Phosphaalkenes exist as both *E*- and *Z*-isomers due to lack of free rotation about the double bond (Figure 6). The atom bound directly to the C=P carbon centre determines the *E*/*Z*-assignment on the basis of molecular mass; for example, $OSiMe_3$ is prioritised above C_6H_5, given that the molecular mass of oxygen is 16, while for carbon the value is 12. Given the almost negligible mass of the phosphorus lone pair (2/1837 of a proton's mass), it is always the lower priority substituent on the phosphorus centre.



E ***Z***

R' = highest priority group

Figure 6. *E*-/*Z*-phosphaalkenes

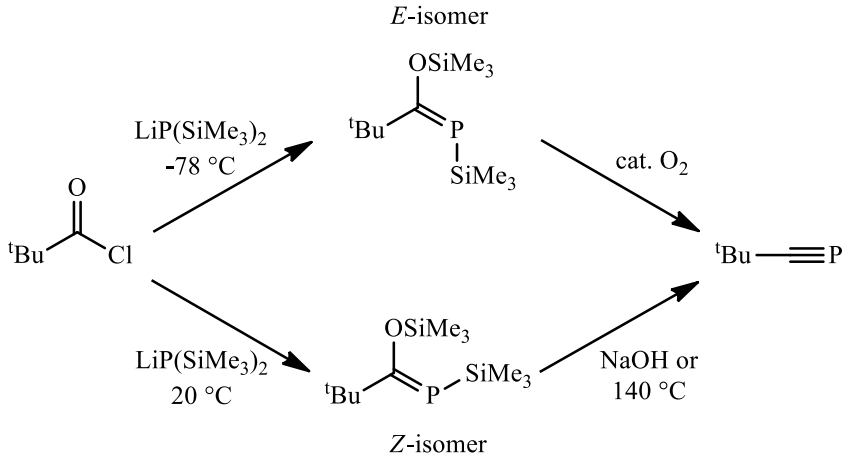
While the absolute stereochemistry of an isomerically pure sample of a phosphaalkene cannot be determined purely on the basis of spectroscopic data, where both isomers are present, it has been determined that the *Z*-isomer exhibits a higher-field chemical shift in both the ^{31}P and $^{13}C\{^{1}H\}$ NMR spectra, and the phosphaalkenic carbon centre shows a larger carbon-phosphorus coupling constant.[103] This trend was demonstrated by phosphaalkenes *E*/*Z*-{C_6H_2(2,6-Mes)$_2$(4-Br)}P=C(H){C_6H_4(4-Br)}, the isomer configurations being determined by X-ray diffraction; the C=P bond length of *E*-{C_6H_2(2,6-Mes)$_2$(4-Br)}P=C(H){C_6H_4(4-Br)} was marginally elongated compared to *Z*-{C_6H_2(2,6-Mes)$_2$(4-Br)}P=C(H){C_6H_4(4-Br)}, providing a rationale for the smaller one-bond carbon-phosphorus coupling constant of the *E*-isomer, which also possessed a significantly smaller C=P-C angle (Table 4).[104] This report is the only known single crystal X-ray diffraction study of both the *E*- and *Z*-isomers of the same phosphaalkene. UV/Vis spectroscopy showed that the C=P π-π* transition was blue-shifted in *Z*-{C_6H_2(2,6-Mes)$_2$(4-Br)}P=C(H){C_6H_4(4-Br)} to 330 nm, compared with 345 nm for *E*-{C_6H_2(2,6-Mes)$_2$(4-Br)}P=C(H){C_6H_4(4-Br)}.

The isomeric preference of phosphaalkenes is a topic to which much research has been dedicated. Regitz reported that formation of *E*-RC($OSiMe_3$)=P$SiMe_3$ is favoured when R is a primary or secondary substituent, while *Z*-RC($OSiMe_3$)=P$SiMe_3$ is favoured for tertiary substituents.[105] However, Kostitsyn highlighted the existence of exceptions, as for *E*/*Z*-RC($OSiMe_3$)=P$SiMe_3$ (R = 2,2-dichloro-l-methylcyclopropyl), for which the *E*-isomer dominated (62:38).[106] The propensity of phosphaalkenes to undergo isomerisation has also been reported. The isomerically pure phosphaalkene *E*-Mes*P=C(H)Ph was photoisomerised to a mixture of *E*/*Z*-Mes*P=C(H)Ph by irradiation with a 100 W medium pressure mercury lamp for 6 h at 0 °C;[107] this could not be effected thermally. Separation of the isomers was achieved by column chromatography and the spectroscopic characteristics of each isomer was in line with known trends (Table 4),[103] including a significantly larger carbon-phosphorus one-bond coupling constant for *Z*-Mes*P=C(H)Ph.

Table 4. Selected data of *E*/*Z*-ArP=C(H)Ar' (Ar = C_6H_2(2,6-Mes)$_2$(4-Br), Ar' = C_6H_4(4-Br)),[104] *E*-/*Z*-Mes*P=C(H)Ph [107]

Compound	**^{31}P NMR / ppm**	**^{13}C{^{1}H} NMR / ppm**	**$^1J_{C\text{-}P}$ / Hz**	***d* C=P / Å**	**C=P-C / °**	**λ_{max} ($\pi\rightarrow\pi^*$) / nm**
E-ArP=C(H)Ar'	241	179	39.7	1.682(3)	101.57(14)	345
Z-ArP=C(H)Ar'	235	-	-	1.666(3)	107.30(14)	330
E-Mes*P=C(H)Ph	259	176	34.8	-	-	-
Z-Mes*P=C(H)Ph	242	163	48.8	-	-	-

Cowley demonstrated that the reaction conditions have a significant effect on isomeric preference in the reaction of LiP(SiMe$_3$)$_2$ with ^{t}BuCOCl, which at 20 °C afforded isomerically pure *Z*-^{t}BuC(OSiMe$_3$)=PSiMe$_3$, while at −78 °C only *E*-^{t}BuC(OSiMe$_3$)=PSiMe$_3$ was produced. Once formed, both isomers were stable to interconversion (Scheme 21).[108] The isomers were markedly different in their reactivity profiles; a "novel catalytic oxygenation" converted *E*-^{t}BuC(OSiMe$_3$)=PSiMe$_3$ to ^{t}BuC≡P (though no mechanism was proposed), while the same conversion of *Z*-^{t}BuC(OSiMe$_3$)=PSiMe$_3$ required the addition of NaOH, or heating to 140 °C in the absence of solvent. Both isomers were converted to ^{t}BuC≡P upon addition of stoichiometric [Fe$_2$(CO)$_9$]. The authors proposed an intermediate η^2-phosphaalkene [Fe(CO)$_4$] complex that decomposed to a phosphaalkyne, although no evidence was provided.



Scheme 21. Syntheses and reactivity profiles of *E*/*Z*-^{t}BuC(OSiMe$_3$)=PSiMe$_3$ [108]

1.3.3 Reactivity traits

Coordination chemistry

There are five known coordination modes for phosphaalkenes. The η^1-coordination mode (type **i**) is the most well-documented, although η^2-complexes (type **ii**) are also relatively common (Figure 7). This is attributed to the small energy gap between the HOMO and HOMO−1 typical of phosphaalkenes. The η^1,η^2-coordination mode (type **iii**) was slow to emerge, although many examples have since been reported. In contrast, examples of $\eta^1(\mu_2)$-complexes (type **iv**) and $\eta^2(\mu_3)$-complexes (type **v**) remain rare.

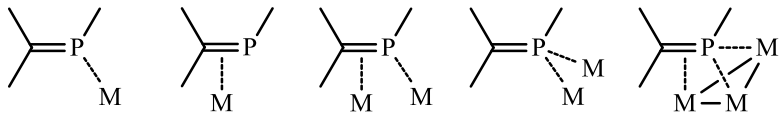
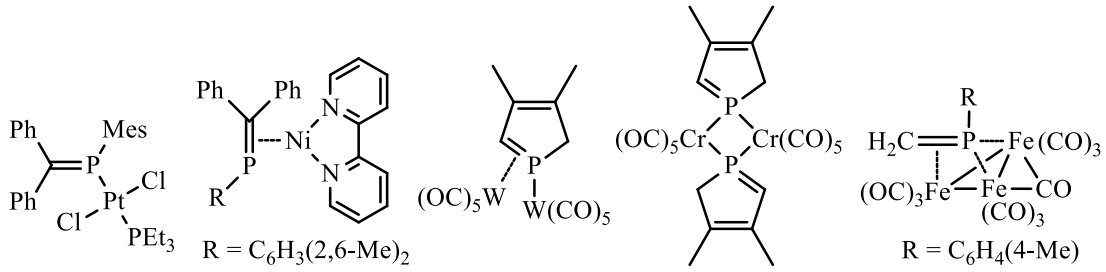


Figure 7. Coordination modes of phosphaalkenes

The first examples of coordinated phosphaalkenes were described by Nixon in 1981, who reported several η^1-complexes, including [Pt{P(Mes)=CPh$_2$}(PEt$_3$)Cl$_2$] (Figure 8 **1.E**).[109] The η^2-complexes were reported shortly after, and typically possessed elongated C=P bonds [Ni{η^2-P(R)=CPh$_2$}(bipy)];1.832(6) Å, Figure 8 **1.F**), indicative of a large degree of π-back-bonding from the metal centre.[110] Holand reported the first η^1,η^2-complex in 1984 (Figure 8 **1.G**), identified unambiguously by X-ray crystallography, which demonstrated a lesser degree of carbon-phosphorus double bond elongation (1.78(1) Å) than the η^2-complexes.[111] The same publication also documented the first example of an $\eta^1(\mu_2)$-coordinated phosphaalkene [{Cr(CO)$_5$(PC$_4$H$_3$(3,4-Me)$_2$)}$_2$] (Figure 8 **1.H**),[111] which was isolated in 55 % yield from the reaction of the metallate ion [Cr(CO)$_5$(PC$_4$H$_2$(3,4-Me)$_2$)]$^-$ [Li]$^+$ with H$_2$O. As one of the earliest examples of an $\eta^2(\mu_3)$-complex, [(H$_2$C=PR)Fe$_3$(CO)$_9$(μ_2-CO)] (R = C$_6$H$_4$(4-Me)) was studied crystallographically and found to possess a carbon-phosphorus double bond length of 1.76(1) Å (Figure 8 **1.I**),[112] comparable to the η^1,η^2-complex **1.G** (1.78(1) Å).

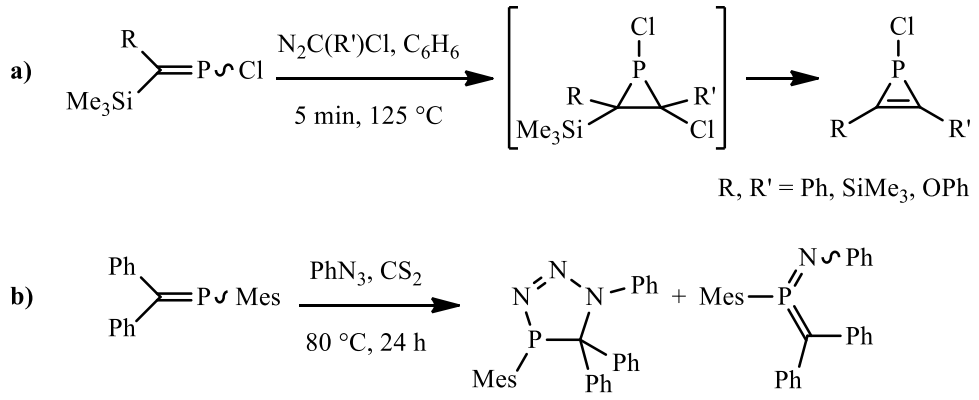


1.E **1.F** **1.G** **1.H** **1.I**

Figure 8. Phosphaalkene complexes; $[Pt(MesP{=}CPh_2)(PEt_3)Cl_2]$ (**1.E**),[109] $[Ni(bipy)(RP{=}CPh_2)]$ (**1.F**),[110] $[(C_4H_3P(3,4\text{-}Me)_2)\{W(CO)_5\}_2]$ (**1.G**),[111] $[\{Cr(CO)_5(PC_4H_3(3,4\text{-}Me)_2)\}_2]$ (**1.H**),[111] $[(H_2C{=}PR)Fe_3(CO)_9(\mu_2\text{-}CO)]$ (**1.I**) [112]

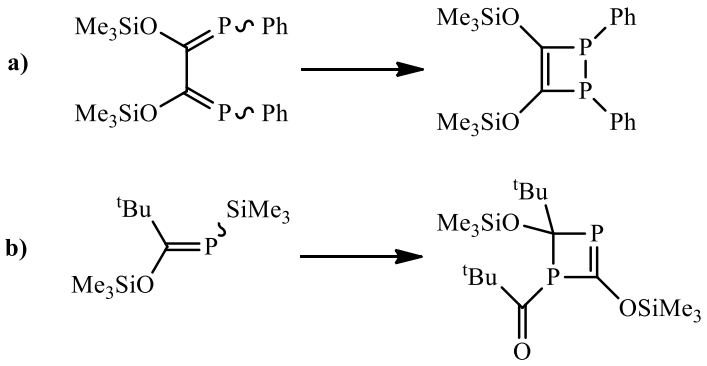
Cycloaddition reactions

Cycloadditions are a widely-reported reactivity for phosphaalkenes, with many variations documented. One example of the [2+1] cycloaddition reaction provides a rare route to 1-chlorophosphirenes by reaction of $Me_3Si(R)C{=}PCl$ with the *in-situ* generated chlorocarbenes C(R')Cl (Scheme 22 **a**).[113] Meanwhile, [2+3] cycloadditions of phosphaalkenes with [1,3]-dipoles provide access to heterophospholes, as for the reaction of $Ph_2C{=}PMes$ with PhN_3, which was found to be solvent sensitive; when the reagents were refluxed in C_6H_6 or $CHCl_3$ the only product was the phosphorane $Ph_2C{=}P(Mes){=}NPh$, but when the same reaction was performed in CS_2 at 80 °C the heterophosphole was afforded in 90 % yield, with $Ph_2C{=}P(Mes){=}NPh$ present only as a minor by-product (Scheme 22 **b**).[114]



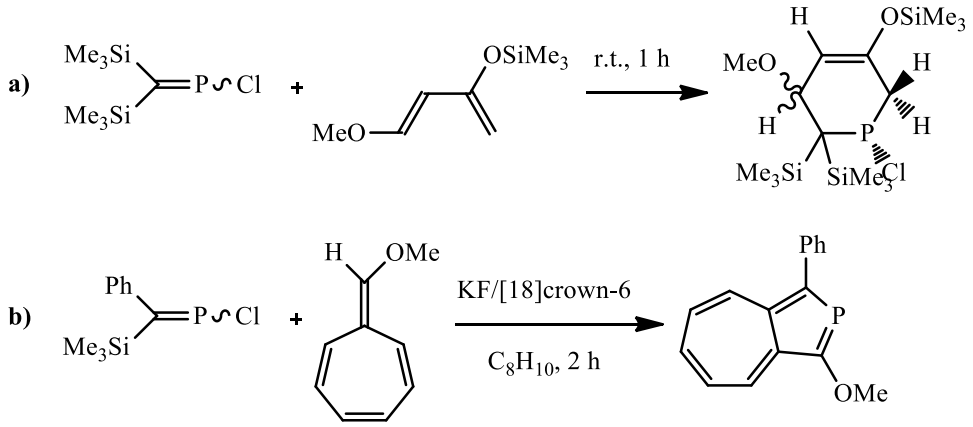
Scheme 22. Cycloaddition reaction of phosphaalkenes; **a**) [2+1] cycloaddition with a carbene, [113] **b**) [2+3] cycloaddition with PhN_3 [114]

Both intermolecular and intramolecular [2+2] cycloaddition reactions of phosphaalkenes are also well-documented, generating a variety of species that contain the [C_2P_2] unit. Significant examples include the intramolecular head-to-head dimerisation of a diphosphaalkene that affords [1,2]-diphosphacyclobutene (Scheme 23 **a**),[115] and the intermolecular head-to-tail dimerisation of two phosphaalkenes affording [1,3]-diphosphacyclobutene (Scheme 23 **b**).



Scheme 23. [2+2] cycloadditions of phosphaalkenes afford; **a**) [1,2]-diphosphacyclobutene, **b**) [1,3]-diphosphacyclobutene [115]

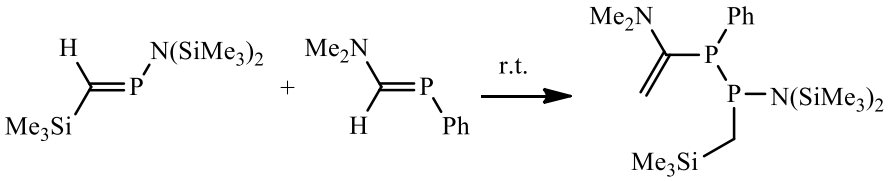
The [4+2] cycloaddition reactions (Diels-Alder reactions) of phosphaalkenes are a viable synthetic route to phosphabenezenes. For instance, the reaction of $(SiMe_3)_2C{=}PCl$ with either electron-rich or electron-poor dienes provides quantitative conversion to functionalised phosphabenzenes under mild conditions (Scheme 24 **a**).[116] Other aromatic systems have been obtained from the [2+8] cycloaddition of $SiMe_3C(Ph){=}PCl$ with a conjugated alkene, which afforded a 2-phosphaazulene (Scheme 24 **b**),[117] and which represents the only [2+8] phosphaalkene cycloaddition reaction reported to date.



Scheme 24. Cycloaddition reaction of phosphaalkenes; **a**) [4+2] cycloaddition with dienes,[116] **b**) [2+8] cycloaddition with a conjugated alkene [117]

Other reactions

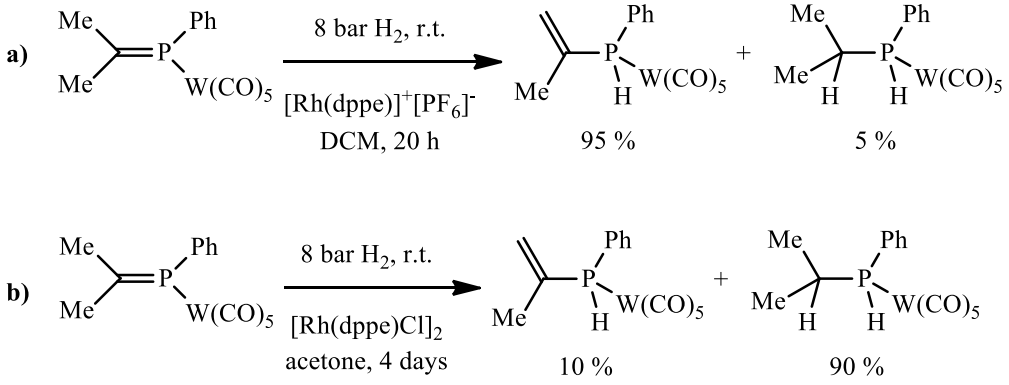
As for classical alkenes,[118] phosphaalkenes have been documented to participate in 'ene' reactions. The first example of type II ene reactions of phosphaalkenes, incorporating *C*-aminophosphaalkenes, was reported in 1997, wherein the phosphaalkene adopts the role of the H-donor.[119] The reaction occurred at ambient temperature, but took several days to afford the diphosphine, which was isolated in 64 % yield as a diastereomeric mixture following distillation (Scheme 25).



Scheme 25. Phosphaalkenes in 'ene' reactions [119]

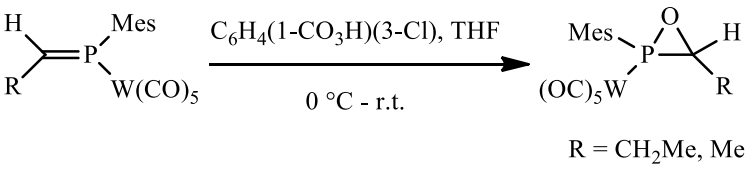
While the reactivity of classical alkenes is often mimicked by phosphaalkenes, in some instances the phosphorus lone pair can hinder reactions. As such, protection of the lone pair allows further classical alkene reactions, such as hydrogenations, to be performed for phosphaalkenes. Although hydrogenation of the protected phosphaalkene $[W\{P(Ph)=CMe_2\}(CO)_5]$ to the hydrogenated phosphine $[W\{P(H)(Ph)C(H)Me_2\}(CO)_5]$ was only achieved in 5 % yield with the ionic $[Rh(dppe)]^+[PF_6]^-$ catalyst (Scheme 26 **a**), the use of [Rh(dppe)Cl] as the active catalyst, which was derived from the reaction of [Rh(COD)Cl] with dppe, afforded the hydrogenated phosphine in 90 % yield (Scheme 26 **b**).[120] The authors

postulated that the Lewis acidity of both the solvent and catalyst caused the disparate results, supported by 99 % conversion of the phosphaalkene to the hydrogenated phosphine when the reaction was performed in acetone over 4 days. The catalytic hydrogenation was not attempted without prior protection of the phosphorus lone pair, as the authors reasoned that the lone pair would likely coordinate to the catalyst.



Scheme 26. Catalytic hydrogenation of phosphaalkenes [120]

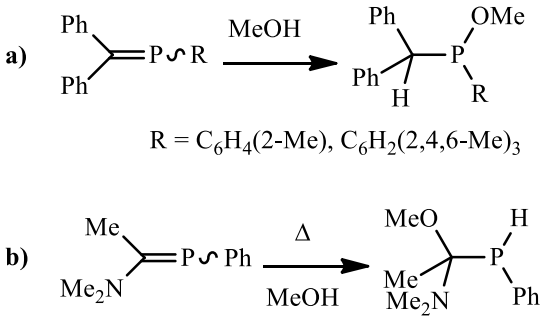
Phosphaalkenes can also be epoxidised following the protection of the phosphorus lone pair; the authors noted the propensity of phosphaalkenes to oxidise preferentially at the phosphorus centre over the π-system, rendering protection of the phosphorus lone pair necessary.[121] Following the protection of the phosphaalkenes RC(H)=PMes (R = CH_2Me, Me) by coordination to $[W(CO)_6]$, the resulting complexes $[W\{P(Mes)=C(H)R\}(CO)_5]$ underwent epoxidation upon addition of $C_6H_4(1\text{-}CO_3H)(3\text{-}Cl)$ (Scheme 27).[122] The oxaphosphirane products were isolated in 86 % and 40 % yields for the R = CH_2Me and R = Me variants respectively following recrystallisation.



Scheme 27. The epoxidation of phosphaalkenes [122]

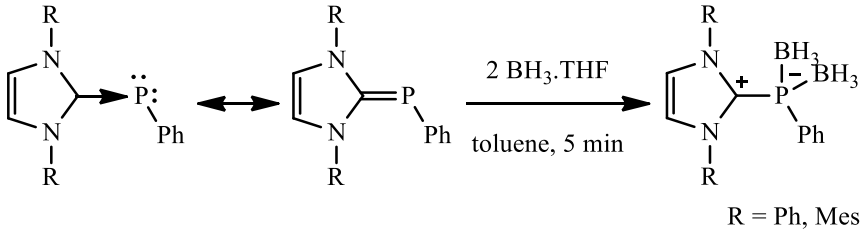
As for classical alkenes, phosphaalkenes react with protic reagents such as MeOH to afford saturated species, the regiospecificity being governed by the phosphaalkene polarisation. Thus,

selection of appropriate substituents allows the proton to be added to either the carbon centre (Scheme 28 **a**),[96] or the phosphorus centre (Scheme 28 **b**).[123]



Scheme 28. Phosphaalkenes react with MeOH to install the proton at; **a**) the carbon centre,[96] **b**) the phosphorus centre [123]

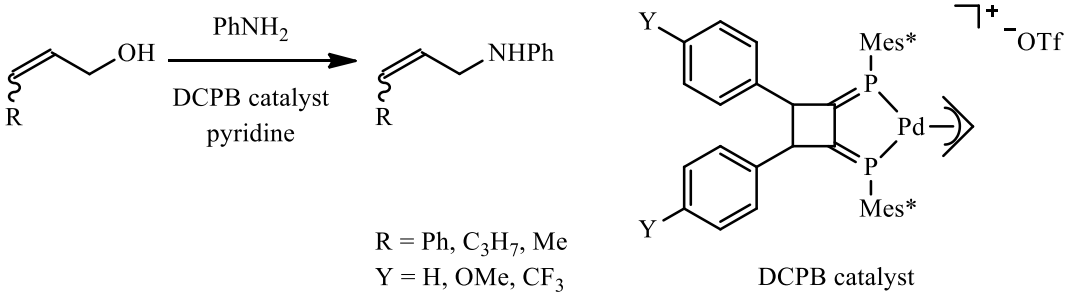
Reports of phosphaalkene quarternisation are infrequent. Where such reactions are documented, they are slow,[124] though when the phosphaalkene is inversely polarised the process is significantly more facile (Scheme 29).[125] The reaction of the phosphaalkene $\{C_3(3,4\text{-}H)_2(2,5\text{-}NR)_2\}$=PPh with two equivalents of BH_3.THF rapidly generated the quarternised adduct $\{C_3(3,4\text{-}H)_2(2,5\text{-}NR)_2\}^+P^-(BH_3)_2Ph$, confirmed by single crystal X-ray diffraction, which showed a P-C bond length of 1.856(2) Å, in the expected range for carbon-phosphorus single bonds.



Scheme 29. Phosphaalkene quarternisation [125]

Another uncommon reaction of phosphaalkenes, in this instance the diphosphaalkenes diphosphinidenecyclobutenes (DCPB), is as ligands in catalysis, aided by their poor σ-donor properties but excellent π-acceptor characteristics. Catalytic processes that have been documented to use DCPB include the polymerisation of ethylene,[126] the amination of aryl bromides,[127] and the condensation of allylic alcohols and amines (Scheme 30).[128] While the traditionally used catalyst system for the latter condensation, which comprises

$[Pd(OAc)_2]/4PPh_3$ (1 mol %) and $[Ti(O^iPr)_4]$ (25 mol %), requires the reaction mixture to be heated to between 50 and 80 °C, the reaction catalysed by the DCPB palladium complex occurs at ambient temperature, with as little as 0.1 mol % catalyst loading, and affords the allylaniline products in high yields (>82 %).



Scheme 30. Catalytic conversion of allylic alcohols with aniline to allylaniline [128]

1.3.4 Significant phosphaalkenes

Conjugated phosphaalkenes

Studies regarding the incorporation of phosphorus moieties into extended conjugated systems have been well-documented in recent years as their electronic characteristics make them ideal for use in molecular scale electronics.[129] Gates reported the synthesis of *E*/*Z*-$[(C_6H_4)P=C(OSiMe_3)(C_6Me_4)C=P]_n$ (Figure 9 **1.J**) by reaction of $C_6Me_4(1,4\text{-}COCl)_2$ with $C_6H_4(1,4\text{-}P(SiMe_3)_2)$, as the first example of a π-conjugated polymer that contained between 5 and 21 phosphaalkenic units in the polymer backbone.[130] UV/Vis spectroscopy showed a red-shifted π-π* absorbance (λ_{max} 328 - 338 nm) for the C=P bond when compared to the model phosphaalkenes $MesC(OSiMe_3)=PSiMe_3$ (λ_{max} 310 nm) and $C_6Me_4(1,4\text{-}C(OSiMe_3)=PSiMe_3)_2$ (λ_{max} 314 nm); this was deemed to signify an increase in conjugation. The polyphosphaalkene *Z*-$[(C_6Me_4)P=C(OSiMe_3)(C_6H_4)C=P]_n$ (Figure 9 **1.K**) also possessed increased π-conjugation compared to $C_6H_4\{1,4\text{-}C(OSiMe_3)=PMes\}_2$ (λ_{max} 388 nm) and $C_6Me_4(1,4\text{-}P=C(OSiMe_3)C_6H_5)_2$ (λ_{max} 394 nm).[103]

Recently, Ott's group demonstrated that the incorporation of phosphaalkenes into conjugated systems, such as the octatetrayne-linked bis-phosphaalkene **1.L** (Figure 9),[131] provides compounds which possess lower HOMO - LUMO band gaps than the all-carbon-containing analogues. The UV/Vis spectra of phosphorus-containing poly(-phenylenevinylene) (PPV) oligomers **1.M** – **1.O** showed that increasing the chain length afforded increasingly red-shifted π-π* absorbances,[132] signifying increased through-chain conjugation. Additionally, these

oligomers possessed more red-shifted absorbances than their all-carbon-containing analogues (λ_{max} 317 nm for **1.M**^{C}, λ_{max} 354 nm for **1.N**^{C}, λ_{max} 385 nm for **1.O**^{C}), confirming that incorporation of phosphorus moieties into the oligomers also resulted in increased conjugation. The authors postulated that such compounds might find application within the development of materials with "interesting (opto)electronic properties," such as NLO devices.[133]

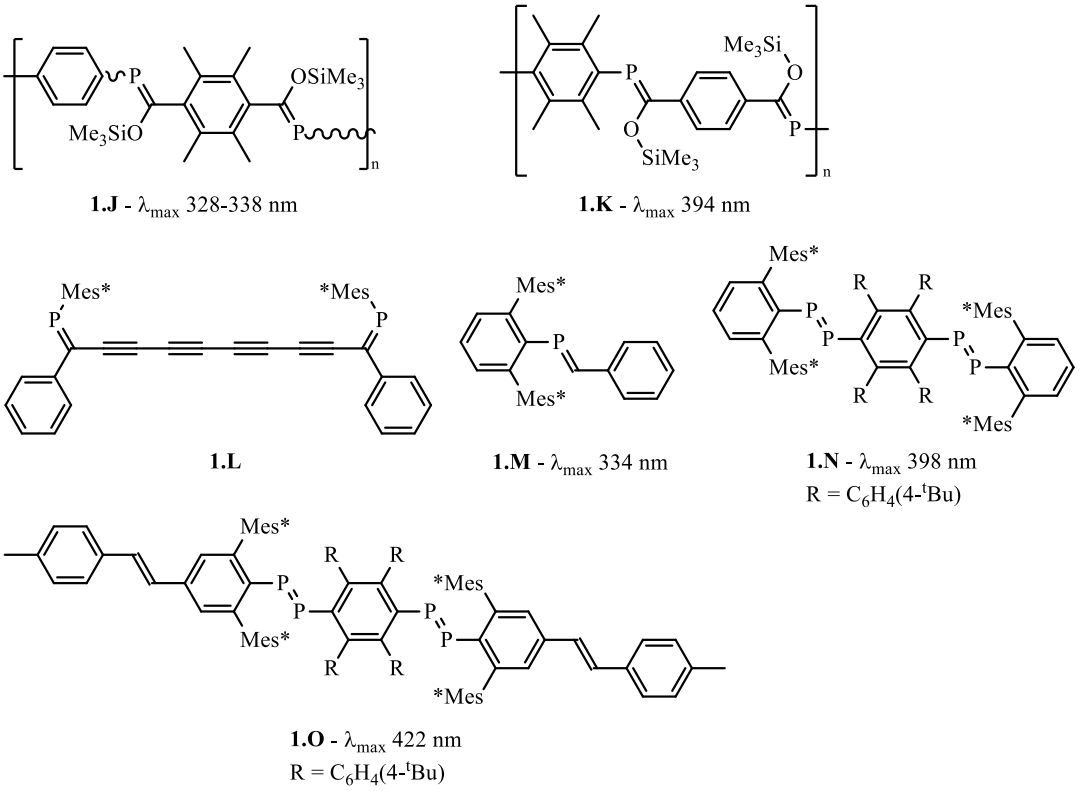


Figure 9. Conjugated phosphaalkenes; *E*/*Z*-phospha-PPV (**1.J**),[130] *Z*-phospha-PPV (**1.K**),[103] acetylenic phosphaalkene (APA) (**1.L**),[131] phospha-PPV oligomers (**1.M** - **1.O**) [132]

Metallophosphaalkenes

Metallophosphaalkenes are phosphaalkenes in which one of the substituents on either the carbon or phosphorus centre is replaced with a metal fragment. Four types have been documented throughout the literature (Figure 10);[134] **i**) *P*-metallophosphaalkenes, **ii**) *C*-metallophosphaalkenes, **iii**) *C*,*C*-dimetallophosphaalkenes, **iv**) *C*,*P*-dimetallophosphaalkenes, with types **i** and **ii** the most frequently reported. Type **v**, the *C*,*C*,*P*-trimetallophosphaalkene, has been proposed but remains to be demonstrated. Both *C*- and *P*-metallophosphaalkenes possess C=P bond lengths that are comparable to traditional phosphaalkenes, but possess significantly larger C=P-A (A = C, M) angles (Table 5). The disparity in bond angles is attributed primarily to the increased 3p character of the phosphorus lone pair of metallophosphaalkenes compared to

traditional phosphaalkenes. The increased 3p character also results in a large decrease in the phosphorus lone pair ionisation energy, which sees the phosphorus lone pair promoted to the HOMO orbital, while the π-system becomes the HOMO-1.[135]

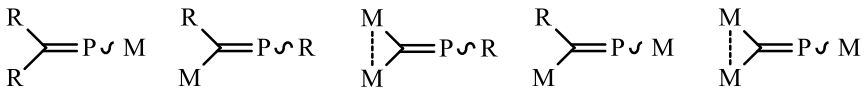
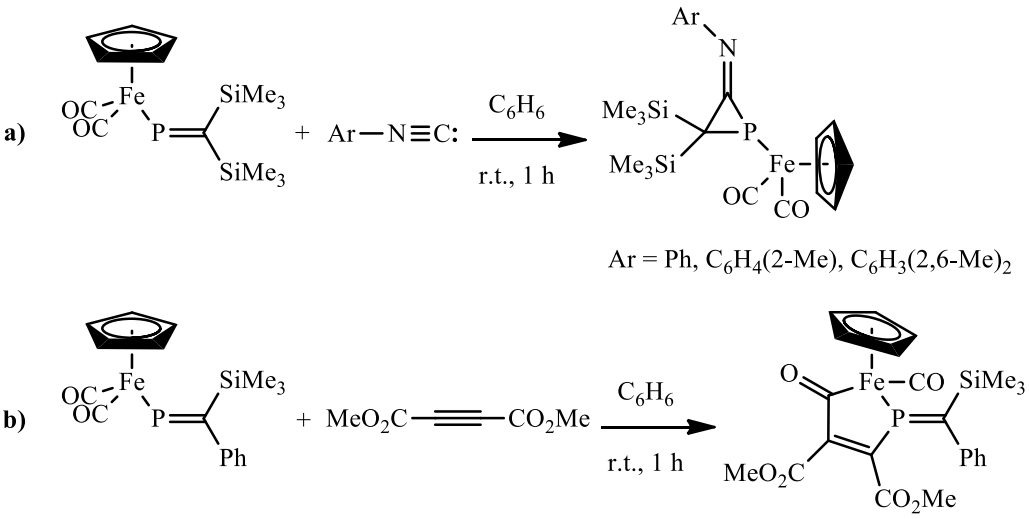


Figure 10. Categories of metallophosphaalkenes

Table 5. Bond lengths and C=P-A angles of traditional phosphaalkenes and *C*- and *P*-metallophosphaalkenes (A = C, Fe)

Type	**Compound**	***d* C=P / Å**	**C=P-A / °**	**Source**
Phosphaalkene	$Ph_2C(OSiMe_3)$=PMes	1.692(3)	107.5	44
C-metallophosphaalkene	[ReCp*(CO)(NO){$C(OSiMe_3)=P^tBu$}]	1.704(4)	112.3(2)	136
P-metallophosphaalkene	[$FeCp^*(CO)_2${$P=C(OSiMe_3)_2$}]	1.680(9)	126.2(3)	137

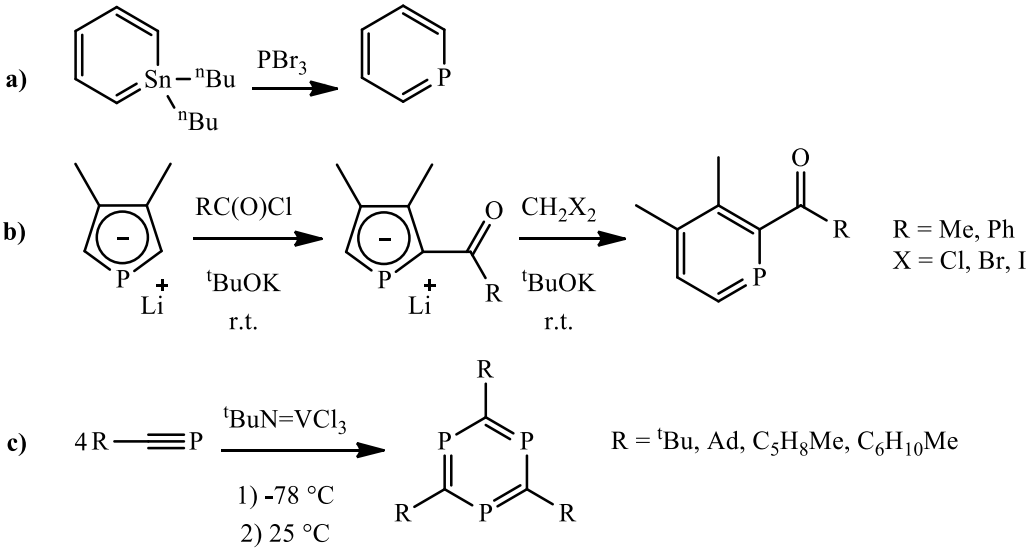
The synthesis of metal-functionalised phosphaalkenes has been well-documented, with multiple pathways available for each type,[137,138] including the reaction of phosphaalkynes with transition metals,[139] and the oxidative addition of halogenated phosphaalkenes $(Me_3Si)_2C$=PX (X = Cl, I) to transition metals.[140] As for traditional phosphaalkenes, their reactivity profiles are dominated by coordination chemistry, with η^1-,[141] η^2-,[142] and η^1,η^2-coordination complexes reported,[143] and cycloaddition reactions; 2-imino-*P*-metallophosphiranes were afforded from the [2+1] cycloaddition of type **i** *P*-metallophosphaalkenes with aryl isocyanides (Scheme 31 **a**),[144] while metallaheterocycles result from the [3+2] cycloadditions of type **i** *P*-metallophosphaalkenes with electron-deficient alkynes (Scheme 31 **b**).[145]



Scheme 31. Cycloaddition reactions of *P*-metallophosphaalkenes; **a**) [2+1],[144] **b**) [3+2] [145]

1.3.5 Phosphinines

Phosphinines are planar six-membered rings that contain one or more phosphorus centres and are tangentially related to phosphaalkenes. As for benzene, phosphinines are aromatic, though the calculated nucleus-independent chemical shift (NICS) values are somewhat lower for phosphinines (C_5H_5P; −8.1 ppm, $C_3H_3(1,3,5\text{-}P)_3$; −5.9 ppm, C_6H_6; −9.7 ppm), indicative of reduced aromaticity.[146,147] The parent phosphabenzene, C_5H_5P, was first isolated from the reaction of $C_5H_5Sn(^nBu)_2$ with PBr_3 (Scheme 32 **a**),[148] although modern synthetic methods include the reaction of phospholides with acyl chlorides (Scheme 32 **b**).[31] Triphosphabenzenes have also been generated by cyclotrimerisations of the corresponding phosphaalkyne RC≡P (R = ^{t}Bu, Ad, C_5H_8Me, $C_6H_{10}Me$) in the presence of ^{t}BuN=VCl_3 (Scheme 32 **c**). The ^{31}P NMR spectra of phosphabenzenes are typical of phosphaalkenes; $C_5H_2(3,4\text{-}Me)_2(2\text{-}C(O)R)P$ exhibits resonances at 187 (R = Ph) and 189 ppm (R = Me).



Scheme 32. Synthetic methodologies for phosphinines; **a**) phosphabenzene,[148] **b**) phosphabenzene derivatives,[31] **c**) triphosphabenzenes [149]

1.4 Phosphaalkynes

1.4.1 General considerations

Phosphaalkynes are the phosphorus-containing analogues of alkynes RC≡CR and nitriles RC≡N, with the general formula RC≡P. Phosphaalkynes possess near linear C-C≡P bond angles (Table 6), and triple bond lengths in the region of 1.533 - 1.548 Å.[150]

Table 6. Bond lengths and C-C≡P angles of selected phosphaalkynes

Compound	*d* C≡P / Å	C-C≡P angle / °	Source
{C_6H_3(2,6-Mes)$_2$}C≡P	1.539(6)	176.6(4)	151
{C_6H_2(2,6-^{t}Bu)$_2$(4-NMe_2)}C≡P	1.533(3)	178.7(3)	152
Ph_3CC≡P	1.538(2)	178.5(2)	153
^{t}BuC≡P	1.548(1)	179.5(1)	154

In contrast to phosphaalkenes, phosphaalkynes possess energetically low-lying lone pairs and large energy gaps between the HOMO (π-system) and HOMO−1 (phosphorus lone pair) (HC≡P, 2.07 eV; ^{t}BuC≡P, 1.83 eV;[155] PhC≡P, 1.89 eV;[155] H_2C=PH, 2.07 eV),[156] which rationalises their propensity to react primarily *via* the π-system. The HOMO - HOMO−1 energy gap is much smaller for nitriles than phosphaalkynes (HC≡P, 2.07 eV;[156] HC≡N, 0.40 eV),[157] though the HOMOs relate to the π-system in both alkynes and nitriles (Figure 11). The triple bonds of

phosphaalkynes and nitriles are heavily polarised; in phosphaalkynes, the electron density is localised at the carbon centre ($R^{\delta-}C{\equiv}P^{\delta+}$), while the reverse is true for nitriles ($R^{\delta+}C{\equiv}N^{\delta-}$), rationalising their different reactivities.

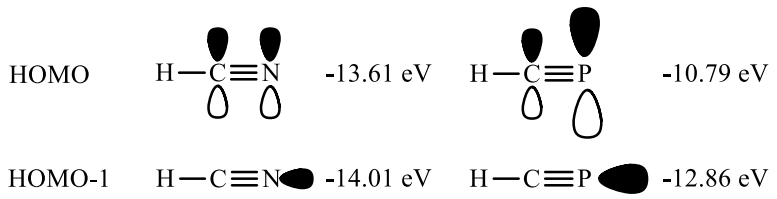


Figure 11. The HOMO and HOMO−1 ionisation energies of HC≡N,[157] and HC≡P [156]

1.4.2 Synthetic methodologies

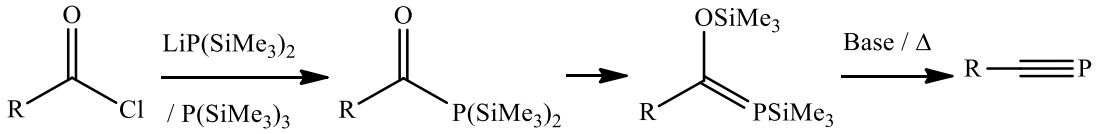
The first confirmed example of a phosphaalkyne, HC≡P, was reported by Gier in 1961 and was synthesised as a colourless gas by passing PH_3 through a rotating arc between graphite electrodes.[158] The gaseous products, a 4:1 mixture of C_2H_2 and HC≡P, were quenched in traps at −196 °C. The phosphaalkyne polymerised above −130 °C, and microanalysis of the polymeric species $(HC{\equiv}P)_n$ was performed after prolonged standing; elemental proportions were close to the calculated values (Calcd for $(HCP)_z$: H, 2.27 %; C, 27.28 %; P, 70.45 %. Found: H, 2.95 %; C: 26.77 %; P, 71.07 %). IR spectroscopy performed at −196 °C revealed absorbances consistent with HC≡P at $\nu_{(CH\ bend)}$ 671, $\nu_{(C{\equiv}P)}$ 1265 and $\nu_{(CH\ bend)}$ 3180 cm^{-1}, comparable with HC≡N $\nu_{(CH\ bend)}$ 830, $\nu_{(C{\equiv}N)}$ 2120 and $\nu_{(CH\ bend)}$ 3120 cm^{-1} (Table 7), in addition to a notable lack of absorbance between 2350 - 2440 cm^{-1} (the P-H stretch region), supporting the identity of HC≡P above the theoretical isomer C≡PH. Further evidence was obtained by reaction of the proposed HC≡P with excess HCl at −110 °C, which afforded a pure sample of CH_3PCl_2. Since 1961 the development of new synthetic routes for phosphaalkynes has been reported; two primary routes, the Becker condensation and the double dehydrohalogenation method, being most prevalent.

Table 7. Selected IR absorbances of HC≡P and HC≡N [158]

Compound	**$\nu_{(C{\equiv}E)}$ / cm^{-1}**	**$\nu_{(C\text{-}H)}$ (stretch) / cm^{-1}**	**$\nu_{(C\text{-}H)}$ (bend) / cm^{-1}**
HC≡P	1265	3180	671
HC≡N	2120	3120	830

Becker condensation

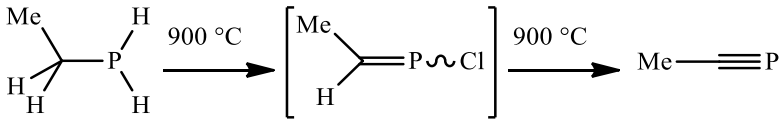
In 1981 Becker first reported what is now known as the Becker synthesis of phosphaalkynes;[159] the precursor phosphaalkene $RC(OSiMe)_3{=}PSiMe_3$ was synthesised *via* the Becker condensation, followed by conversion to the phosphaalkyne R-C≡P by the addition of a base, or heating in the absence of solvent, inducing the loss of $O(SiMe_3)_2$ (Scheme 33).[105]



Scheme 33. Becker synthesis of phosphaalkynes RC≡P [159]

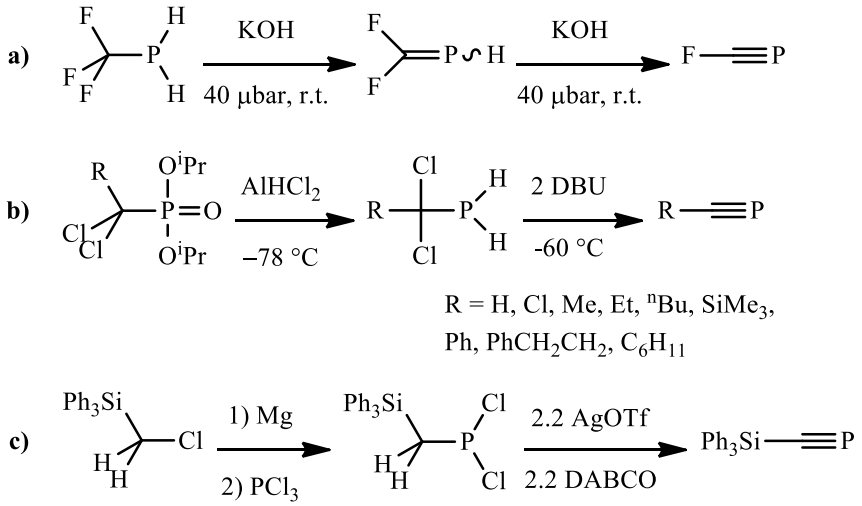
Double dehydrohalogenation

The double dehydrohalogenation route was first achieved using flash pyrolysis in 1976 (Scheme 34).[160] A vapour of the chlorophosphine $MeCH_2PCl_2$ was passed through a quartz tube at 900 °C and the outflow gas was analysed in a microwave spectrometer; a mixture of products was thus identified, including MeC≡P.



Scheme 34. The synthesis of MeC≡P *via* flash pyrolysis double dehydrohalogenation [160]

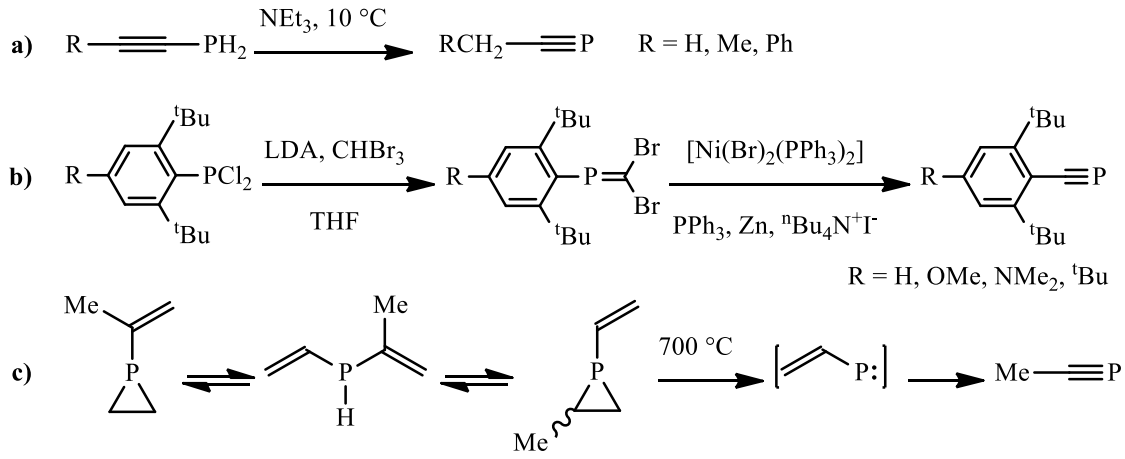
The first example of an ambient temperature, based-induced double dehydrohalogenation was reported in 1978 (Scheme 35 **a**);[161] CF_3PH_2 vapour was passed over KOH pellets at 40 x 10^{-6} bar through a 40 cm spiral glass tube (1 cm bore). The resulting phosphaalkyne, FC≡P, was identified by gas-phase IR absorbances at $\nu_{(C\equiv P\ stretch)}$ 1725 and $\nu_{(F\text{-}C\ stretch)}$ 760 cm^{-1}. The use of a shorter glass tube or higher flow rate both resulted in the generation of $F_2C{=}PH$, as determined by IR spectroscopy of the product. Double dehydrohalogenation reactions are now usually performed in solution and with DBU (Scheme 35 **b**),[162] or AgOTf/DABCO (Scheme 35 **c**).[163,164]



Scheme 35. Double dehydrohalogenation syntheses of; **a**) FC≡P,[161] **b**) RC≡P,[162] **c**) $Ph_3SiC{\equiv}P$ [163]

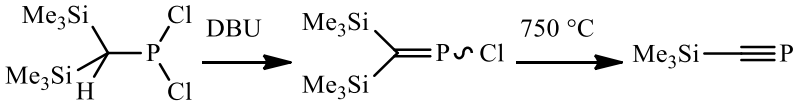
Alternate synthetic routes

Rearrangement reactions have been employed sporadically *en route* to phosphaalkynes. One example includes the base-induced rearrangement of primary alkynylphosphines (Scheme 36 **a**);[165] though initially achieved with NEt_3, this rearrangement could also be achieved by addition of DBU at −90 °C, or the ambient temperature Vacuum Gas Solid Reaction (VGSR) with K_2CO_3. Phosphaalkynes like $C_6H_2(2,6\text{-}^tBu)_2(4\text{-}R)C{\equiv}P$ have also been afforded from the metal-catalysed rearrangement of dibromomethylenephosphines $C_6H_2(2,6\text{-}^tBu)_2(4\text{-}R)P{=}CBr_2$ (Scheme 36 **b**),[152] in addition to the thermally-induced elimination-rearrangements of 1-phosphiranes, wherein heating the 1-vinylphosphirane to 700 °C afforded $MeC{\equiv}P$ (Scheme 36 **c**).[166] Finally, Cummins showed that phosphaalkynes $RC{\equiv}P$ (R = ^{t}Bu, Ad) could also be accessed by reaction of the terminal niobium phosphide anion $[PNb\{N(Np\}Ar)_3]^-$ (Np = neopentyl, Ar = $C_6H_3(3,5\text{-}Me)_2$) with acyl chloride reagents RCOCl.[167]



Scheme 36. Rearrangement reactions for the syntheses of phosphaalkynes have been induced by; **a**) bases,[165] **b**) transition metal catalysis,[152] **c**) heat [166]

Phosphaalkynes have also been generated by the thermally-induced elimination of $ClSiMe_3$ from phosphaalkenes, partially driven by the affinity of chlorine for silicon. The dichlorophosphine $(Me_3Si)_2HCPCl_2$ was converted to the corresponding phosphaalkene $(Me_3Si)_2C{=}PCl$ upon addition of DBU, which when heated to 750 °C generated the phosphaalkyne $Me_3SiC{\equiv}P$ (Scheme 37).[168]



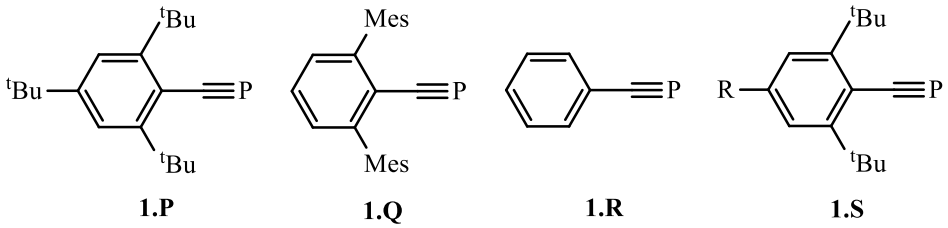
Scheme 37. Phosphaalkyne synthesis by thermally-induced elimination of $ClSiMe_3$ [168]

1.4.3 Significant phosphaalkynes

Conjugated phosphaalkynes

In contrast to phosphaalkenes, phosphaalkynes that bear extended conjugation are limited to eight examples in the literature (Figure 12 **1.P** – **1.S**, Figure 13 **1.T**). Compounds **1.P** – **1.R** were accessed *via* the Becker condensation, while **1.S** were produced by transition metal catalysis (Scheme 36 **b**). Both **1.P** and **1.Q** are relatively stable over time at ambient temperature by virtue of their bulky substituents. In contrast, **1.R** was reported to have a half-life of 7 min at 0 °C, and was characterised exclusively by a singlet resonance at −31.8 ppm in the ^{31}P NMR spectrum. The phosphaalkyne $C_6H_3(2,6\text{-}^tBu)_2C{\equiv}P$ (**1.Q**) was reportedly stable for

more than one week when exposed to air, while $C_6H_2(2,6\text{-}^tBu)_2(4\text{-}NMe_2)C{\equiv}P$ (**1.S**) was highly air sensitive.



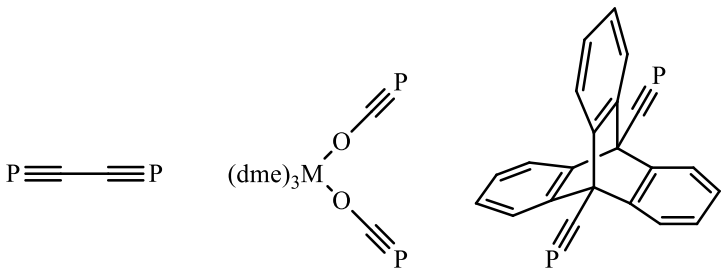
1.P **1.Q** **1.R** **1.S**

R = H, OMe, NMe_2

Figure 12. Conjugated phosphaalkynes Mes*C≡P (**1.P**),[169] $C_6H_3(2,6\text{-Mes})_2C{\equiv}P$ (**1.Q**),[151] PhC≡P (**1.R**),[170] $C_6H_2(2,6\text{-}^tBu)_24\text{-R})C{\equiv}P$ (**1.S**) [152]

Diphosphaalkynes and phosphadiynyls

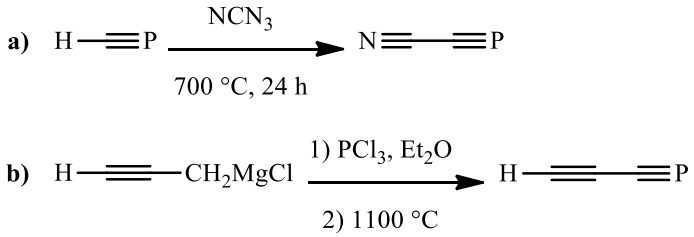
To date only six examples of diphosphaalkynes exist (Figure 13); the radical cationic species $P{\equiv}CC{\equiv}P^{\cdot+}$ was generated by EI ionisation of either $Cl_2PC{\equiv}CPCl_2$ or $Cl_2PCH_2P(Cl)CH_3$ in the mass spectrometer and inferred from a signal at *m/z* = 86. The cation $P{\equiv}CC{\equiv}P^{\cdot+}$ was subsequently converted to the diphosphaalkyne P≡CC≡P (Figure 13 **1.T**) by a neutralisation-reionisation (NR) experiment with Xe as the neutralisation gas and O_2 as the reionisation gas. The NR spectra of the gaseous product showed a signal at *m/z* = 86 for P≡CC≡P.[171] Diphosphaalkynes **1.U** were synthesised by reaction of $M\{P(SiMe_3)_2\}_2$ with $(MeO)_2C{=}O$,[172] while **1.V** was synthesised *via* the Becker condensation of $LiP(SiMe_3)_2$ with $Cl(O)CC(C_6H_4)_3CC(O)Cl$ and subsequent reaction with catalytic KOH.[173] While compounds **1.U** were found to be unstable to solvent removal, **1.V** was isolated as an air and moisture stable solid, which was characterised crystallographically.



1.T **1.U** - M = Mg, Ca, Sr, Ba **1.V**

Figure 13. Diphosphaalkynes P≡CC≡P (**1.T**),[171] $[M(dme)_3(OC{\equiv}P)_2]$ (**1.U**),[172] bis(phosphaethynyl)triptycene (**1.V**) [173]

Including the diphosphaalkyne P≡CC≡P, only three phosphadiynyls are known, including N≡CC≡P, which was generated by the flash pyrolysis of HC≡P and NCN_3 at 700 °C (Scheme 38 **a**),[174] while diphosphaalkyne HC≡CC≡P was generated by flow-pyrolysis at 1100 °C of the products of the reaction of $HC{\equiv}CCH_2MgCl$ with PCl_3 (Scheme 38 **b**).[175] Both phosphadiynyls were characterised by microwave spectroscopy.



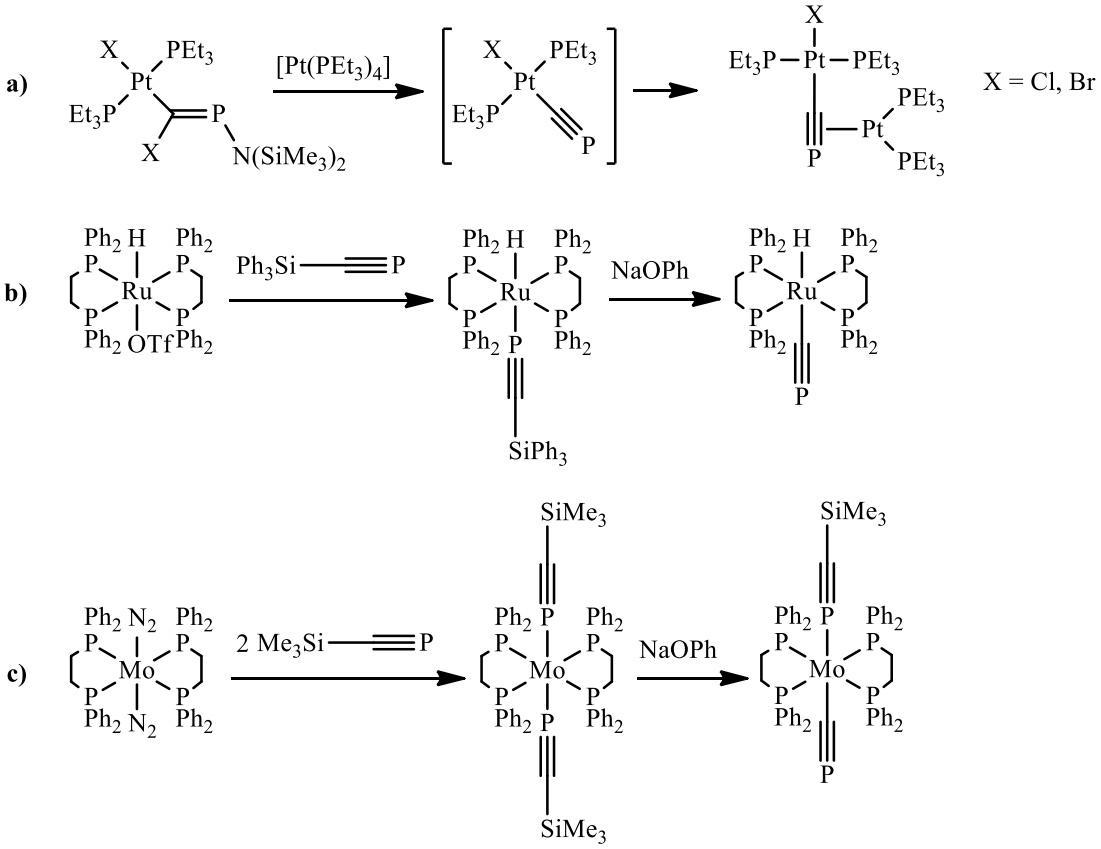
Scheme 38. Synthesis of phosphadiynyls; N≡CC≡P,[174] HC≡CC≡P,[175]

Cyaphides

Cyaphides are the long sought-after analogues of cyanides ($^{-}C{\equiv}N$),[176] which are σ-bound to metal centres *via* the phosphaalkynic carbon. The first evidence of a cyaphide complex ($[Pt(\eta^1,\eta^2\text{-}P{\equiv}C)(PEt_3)_2X]$) was reported in 1994 by Angelici as part of an inseparable mixture of products that rapidly decomposed upon attempted isolation;[177] the cyaphide was trapped by reaction with $[Pt(PEt_3)_4]$ to form the η^2-complex $[PtX(PEt_3)_2(C{\equiv}P)Pt(PEt_3)_2]$ (Scheme 39 **a**), the identity of which was confirmed by single crystal X-ray diffraction. The first irrefutable example of an isolated terminal cyaphide complex was reported by Grützmacher in 2006 and its identity confirmed by X-ray crystallography;[163] the precursor $Ph_3SiC{\equiv}P$ was coordinated to the ruthenium centre to afford $[Ru(H)(dppe)_2\{P{\equiv}CSiPh_3\}]$ and subsequently converted to the cyaphide complex $[Ru\{C{\equiv}P\}(H)(dppe)_2]$ upon addition of NaOPh (Scheme 39 **b**). The ^{31}P NMR resonance at 111 ppm for $Ph_3SiC{\equiv}P$ was shifted significantly downfield to 144 ppm upon coordination, and shifted further downfield to 165 ppm upon rearrangement to the cyaphide.

More recently, Russell presented inconclusive evidence for the synthesis of a mixed phosphaalkyne-cyaphide complex $[Mo(Me_3SiC{\equiv}P)(C{\equiv}P)(dppe)_2]^{-}$ (Scheme 39 **c**), generated by addition of NaOPh to $[Mo(Me_3SiC{\equiv}P)_2(dppe)_2]$;[178] the ^{31}P NMR quintet resonance at 172 ppm, attributed to the phosphaalkyne units of $[Mo(Me_3SiC{\equiv}P)_2(dppe)_2]$, disappeared and were replaced by two mutually coupled complex multiplets at 183 and 198 ppm. Additionally, the resonance assigned to the dppe ligands was transformed from a triplet at 62.8 ppm in $[Mo(Me_3SiC{\equiv}P)_2(dppe)_2]$ to a doublet of doublets at 65.5 ppm, consistent with, but not definitive of $[Mo(Me_3SiC{\equiv}P)(C{\equiv}P)(dppe)_2]^{-}$. The only other examples of cyaphide complexes

in the literature are those published during this report, which include *trans*-[Ru{C≡P}(dppe)$_2$(C≡CR)] (R = CO_2Me, C_6H_4(4-OMe)), and those prepared by co-workers that are currently unpublished.[179–181]



Scheme 39. Synthesis of cyaphides and complexes; **a**) ([PtX(PEt$_3$)$_2$(C≡P)] and [PtX(PEt$_3$)$_2$(C≡P)Pt(PEt$_3$)$_2$],[177] **b**) [RuH(dppe)$_2$C≡P],[163] **c**) [Mo(Me$_3$SiC≡P)(C≡P)(dppe)$_2$]$^-$ [178]

1.4.4 Reactivity traits

Coordination chemistry

As for phosphaalkenes, several coordination modes are known for phosphaalkynes; however, in contrast to the prevalence of η^1-phosphaalkene complexes, η^2-phosphaalkyne complexes are the most commonly observed (Figure 14, type **i**). This is attributed to the significantly higher energy of the π-system compared with the energetically low-lying phosphorus lone pair in phosphaalkynes. Additional coordination modes of phosphaalkynes include the less common η^1-complexes (type **ii**), the rare η^1, η^2- complexes (type **iii**), and μ-bridging phosphaalkyne complexes (types **iv** - **v**) (Figure 14).

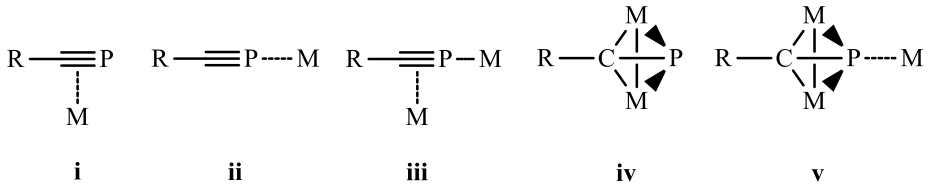


Figure 14. Coordination modes of phosphaalkynes

The first example of an η^2-phosphaalkyne complex was reported by Nixon in 1981 (Figure 15 **1.W**);[182] a single crystal X-ray diffraction study of the product highlighted a significant increase in C≡P bond length (1.672(17) Å) from typical free phosphaalkynes (^{t}BuC≡P; 1.548(1) Å),[154] due to back-bonding from the platinum centre. Numerous further examples of η^2-phosphaalkyne complexes have been described since.[183,184] The η^1-coordination mode is less common, and requires the employment of bulky ligands around the metal centre to create a channel into which the phosphaalkyne can only enter end-on. The first examples were reported by Nixon in 1987 (Figure 15 **1.X**),[185] while further examples include *trans*-[FeH(P≡C^{t}Bu)(dppe)$_2$],[186] and [MH(dppe)$_2$P≡CCPh$_3$]OTf (M = Fe, Ru).[153] The η^1, η^2-coordination mode is quite rare, although Carmichael's report includes three examples that were synthesised by addition of excess [M(CO)$_6$] to [Pt(P≡C^{t}Bu)(dppe)$_2$] (Figure 15 **1.Y**).[187] The first example of μ,η^1-bridging phosphaalkyne complexes were reported in 1994 (Figure 15 **1.Z**),[188] although several have since followed.[189,190]

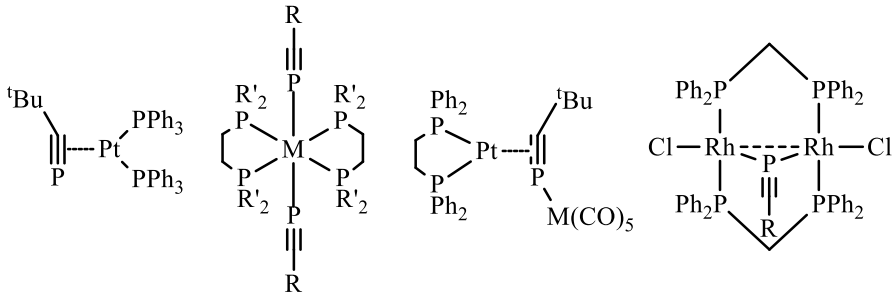
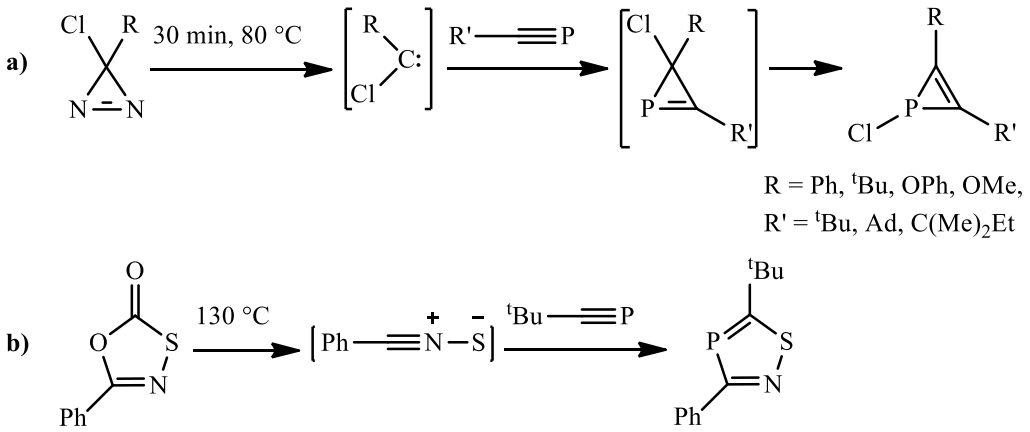


Figure 15. Phosphaalkyne complexes; [Pt(P≡C^{t}Bu)(PPh$_3$)$_2$] (**1.W**),[182] *trans*-[M(P≡CR)$_2$(R'$_2$PCH$_2$CH$_2$PR'$_2$)$_2$] (**1.X**),[185] [Pt(dppe)$_2$(^{t}BuC≡P)M(CO)$_5$] (**1.Y**),[187] [Rh$_2$Cl$_2$(μ-dppm)$_2$(RC≡P)] (**1.Z**) [188]

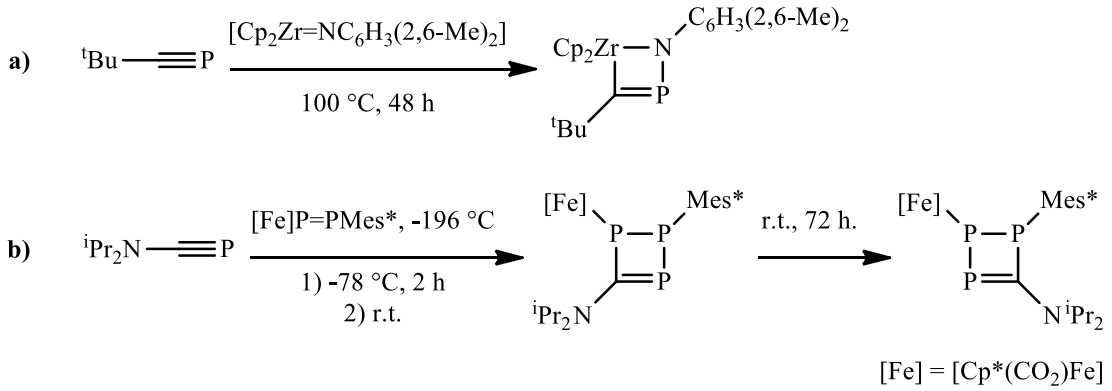
Cycloaddition reactions

The cycloaddition reactions of phosphaalkynes are extremely common. Phosphaalkynes undergo [2+1] cycloadditions with 1-chlorocarbenes, providing an excellent synthetic route towards 1-chlorophosphirenes (Scheme 40 **a**);[191] the final step of the reaction is a spontaneous [1,3]-chlorine shift. The resulting 1-chlorophosphirene readily undergoes nucleophilic substitution to install N^iPr_2, $P(SiMe_3)_2$, $C{\equiv}C^tBu$ or N_3 substituents at the phosphorus atom. The [2+3] cycloaddition reactions of phosphaalkynes with unsaturated species, such as nitrile oxides, azides and nitrile sulphides, provide facile access to heterophospholes (Scheme 40 **b**).[192]



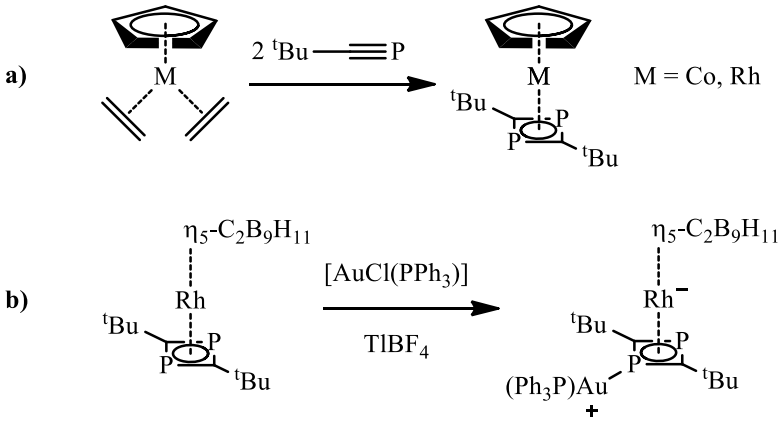
Scheme 40. Cycloadditions of phosphaalkynes; **a**) [2+1],[191] **b**) [2+3] [192]

The [2+2] cycloaddition reactions of phosphaalkynes have been reported only sporadically throughout the literature. Cloke and Nixon demonstrated the [2+2] cycloaddition of $^tBuC{\equiv}P$ with $[Cp_2Zr{=}NC_6H_3(2,6\text{-}Me)_2]$ affording $[Cp_2Zr(P{=}C(^tBu)NC_6H_3(2,6\text{-}Me)_2]$ (Scheme 41 **a**), which was characterised crystallographically.[193] Such [2+2] cycloaddition reactions have also been documented to involve diphosphenes such as [Cp*(CO$_2$)FeP=PMes*] with $^iPr_2NC{\equiv}P$, which initially generated the 1,2-dihydro-1,2,3-triphosphetene that isomerised over 72 h (Scheme 41 **b**).[194] The geometry of the final product was confirmed by single crystal X-ray diffraction.



Scheme 41. The [2+2] cycloadditions of phosphaalkynes; **a**) with [Cp_2Zr=Nar],[193] **b**) with [$Cp^*(CO)_2$Fep=PMes*] [194]

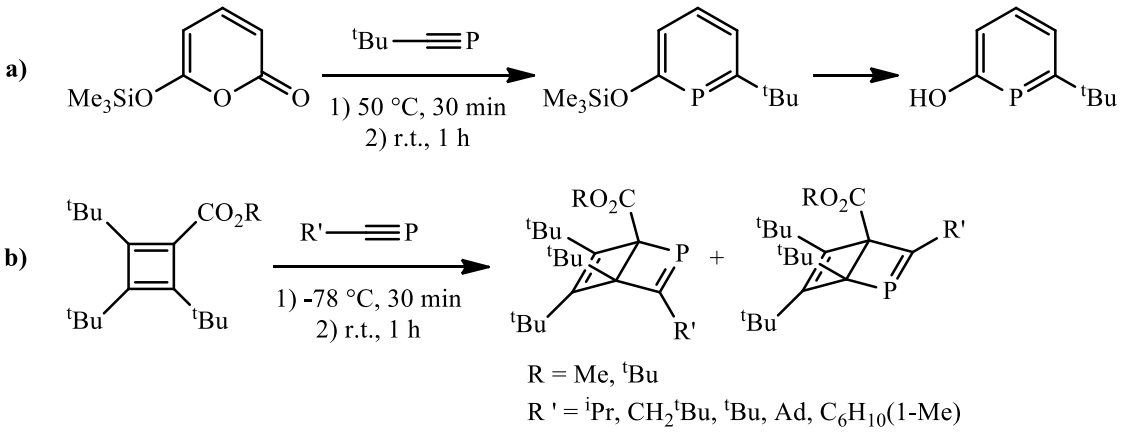
Similar to the reactivity displayed by classical alkynes,[195] phosphaalkynes readily undergo cyclodimerisation reactions within the coordination sphere of transition metals to afford coordinated diphosphacyclobutadienes. The first example was reported in 1986 (Scheme 42 **a**),[196] and was soon followed by examples that feature iron or cobalt mediated [2+2] cycloadditions.[197,198] Diphosphacyclobutadiene complexes have also been further coordinated *via* the phosphorus lone pair to additional metal centres,[199] providing access to mixed-metal bonded complexes (Scheme 42 **b**).[200]



Scheme 42. a) [2+2] cycloaddition reaction of ^{t}BuC≡P within the coordination sphere of a metal,[196] **b**) synthesis of mixed-metal complexes [200]

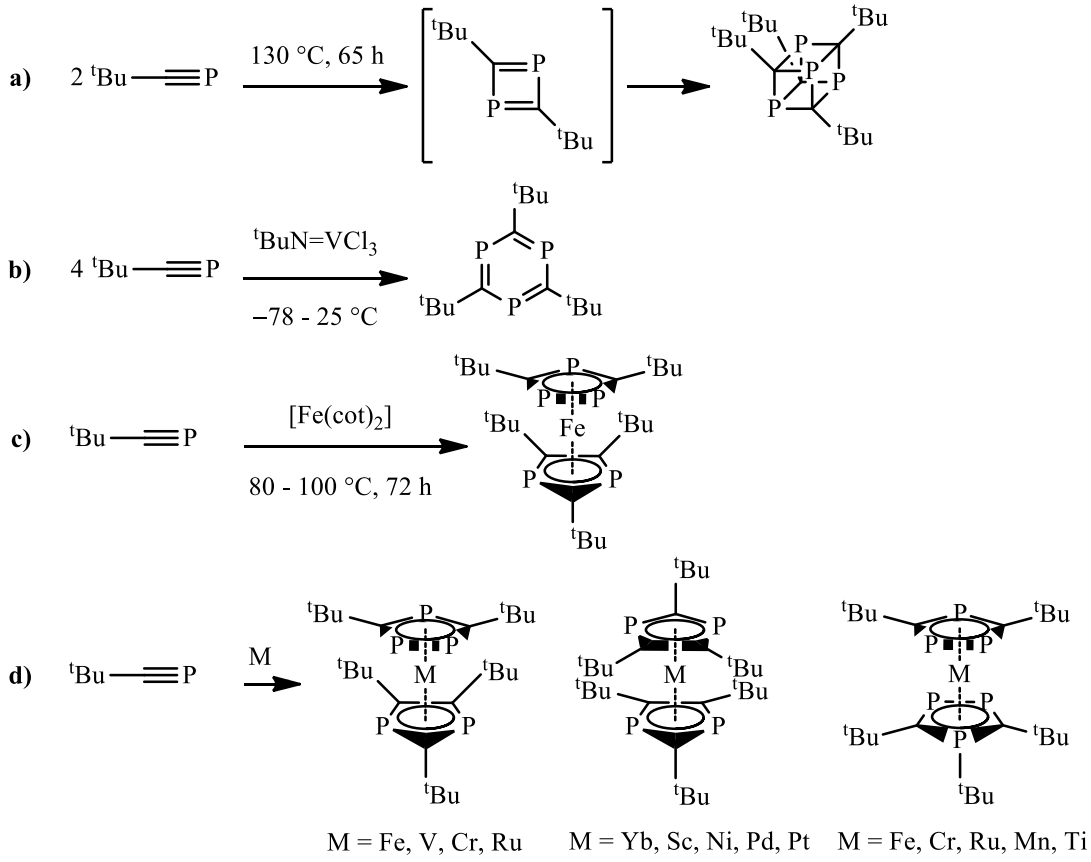
The [2+4] cycloaddition reactions of phosphaalkynes with pryones afford phosphinines under mild conditions (Scheme 43 **a**);[201] similarly, a [4+2] cycloaddition reaction of phosphaalkynes with cyclobutadienes generated the first documented examples of 1- and 2-Dewar phosphinines (Scheme 43 **b**),[202] which exhibit extremely low-field ^{31}P NMR resonances in the region of 312

to 317 ppm and small one-bond carbon-phosphorus coupling constants that range from $^{1}J_{C\text{-}P}$ 17.0 to 19.6 Hz.



Scheme 43. Cycloadditions of phosphaalkynes; **a**) [2+4],[201] **b**) [4+2] [202]

Phosphaalkynes also undergo cyclooligomerisation reactions to produce cage compounds; the first thermally induced example resulted from heating neat ^{t}BuC≡P at 130 °C for 65 h, followed by distillation to afford tetraphosphacubane (Scheme 44 **a**).[203] A resonance consistent with an AX_3Y spin system was observed at −29.1 ppm in the $^{13}C\{^{1}H\}$ NMR spectrum, while the ^{31}P NMR spectrum showed a multiplet signal at 257 ppm. In the presence of a Lewis acid 'cyclotrimerisation reagent' ^{t}BuC≡P cyclooligomerised to form triphosphabenzene (Scheme 44 **b**),[149] while the reaction of ^{t}BuC≡P with $[Fe(cot)_2]$ produced the phosphaferrocene (Scheme 44 **c**).[204] Nixon and Cloke demonstrated that numerous metallocenes could be accessed *via* metal vapour synthesis with ^{t}BuC≡P (Scheme 44 **d**).[205–213]

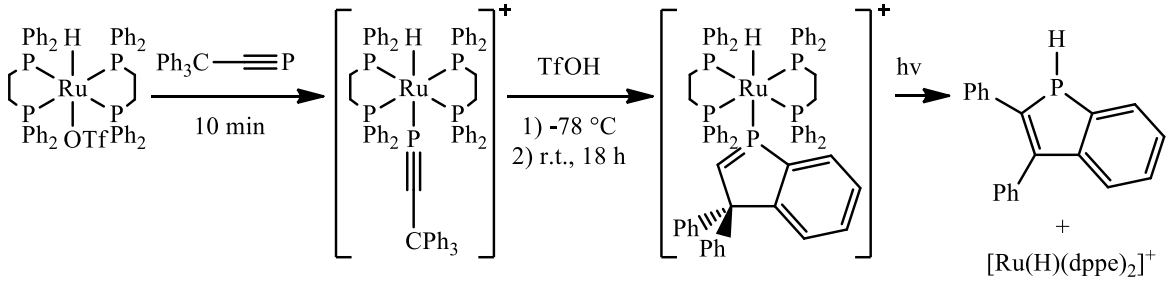


Scheme 44. Cyclooligomerisation of ^{t}BuC≡P produces; **a**) tetraphosphacubane, [203] **b**) triphosphabenzene,[149] **c**) phosphaferrocene, [204] **d**) metallocenes [205–213]

Other reactions

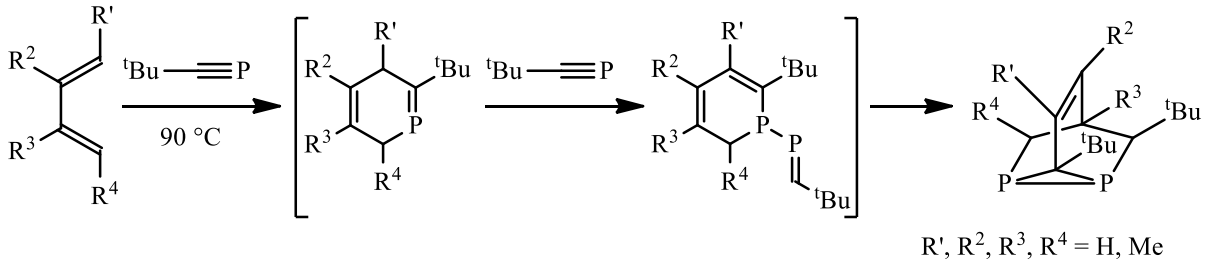
As for classical alkynes,[214] phosphaalkynes are prone to polymerisation, with PhC≡P polymerising spontaneously upon warming to ambient temperature, with 20 % of unreacted PhC≡P remaining after 9 h.[215] The ^{31}P NMR spectrum showed two minor sharp resonances at 190 and 196 ppm, attributed to low molecular weight polymeric phosphaalkenes, while a very broad major signal at 60 ppm was assigned to a high molecular weight phosphaalkane polymer.

Coordinated phosphindoles, which are commonly used for transition metal catalysis, can be accessed *via* the coordination of phosphaalkynes to transition metal centres followed by reaction with strong acids such as TfOH or TsOH (Scheme 45).[153] The free phosphaindole is generated from photolysis of the precursor complex following removal of the volatile products, which was necessary to prevent degradation. Similar photo-induced cyclisation reactions have been observed for 4,4-diphenylcyclohexanones.[216]



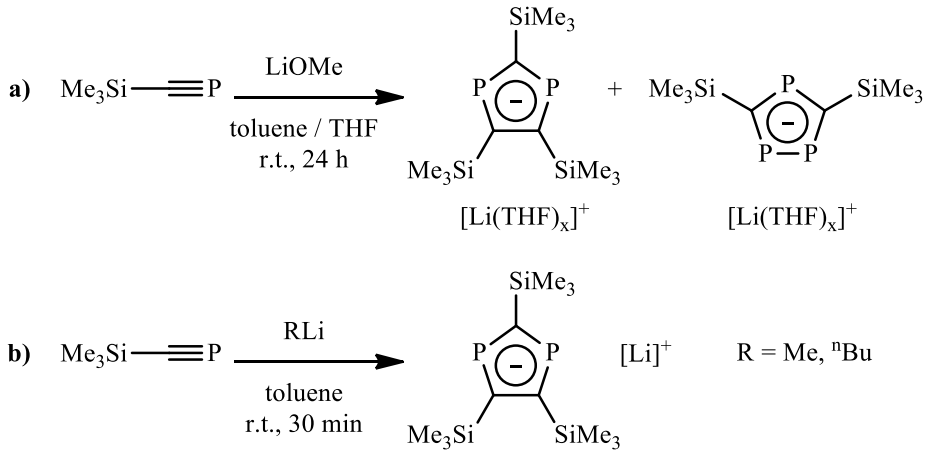
Scheme 45. Synthesis of phosphindoles from phosphaalkynes [153]

Homo-Diels-Alder reactions of phosphaalkynes with 1,3-dienes have been sparsely documented; in Fuchs' example the reagents were heated to 90 °C and the products were distilled as isomeric mixtures, attributed to a lack of regioselectivity of the Diels-Alder reaction.[217] The author postulated that the reaction occurred *via* an initial Diels-Alder step, followed by an 'ene' reaction with a second equivalent of ^{t}BuC≡P, and finally a [4+2] cycloaddition reaction to yield the bicyclic products (Scheme 46).



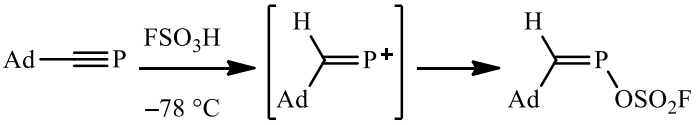
Scheme 46. Homo-Diels-Alder reactions of ^{t}BuC≡P with 1,3-dienes [217]

The reaction of $Me_3SiC{\equiv}P$ with LiOMe afforded the diphospholide and triphospholide anions in a 1:2 ratio respectively (Scheme 47 **a**), identified by ^{31}P NMR resonances at 270 ppm for the diphospholide anion and mutually coupling signals at 316 and 327 ppm ($^{2}J_{P\text{-}P}$ 30.2 Hz) for the triphospholide anion.[164] Notably, the reaction of $Me_3SiC{\equiv}P$ with alkyllithium afforded the diphospholide anion exclusively (Scheme 47 **b**); the same conversion was achieved by the reaction of $Me_3SiC{\equiv}P$ with K, Na or Li, reminiscent of the reaction of ^{t}BuC≡P with Na/Hg that was originally documented by Bartsch and Nixon in 1989.[218]



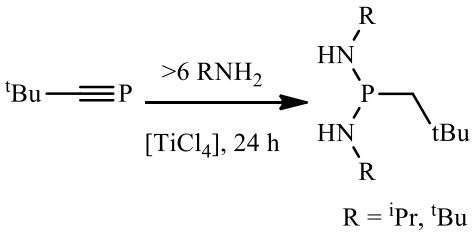
Scheme 47. Synthesis of phospholide anions [164]

The protonation of classical alkynes by superacids is well-documented, and proceeds *via* a vinyl cation intermediate;[219] similarly, the reaction of superacids, namely FSO_3H or SO_2ClF, with AdC≡P induces protonation exclusively at the carbon centre to generate an isomerically pure sample of phosphaalkene *Z*-Ad(H)C=P(OSO_2F) (Scheme 48).[220] The intermediate cation was proposed solely by comparison with the analogous reactions with alkynes.



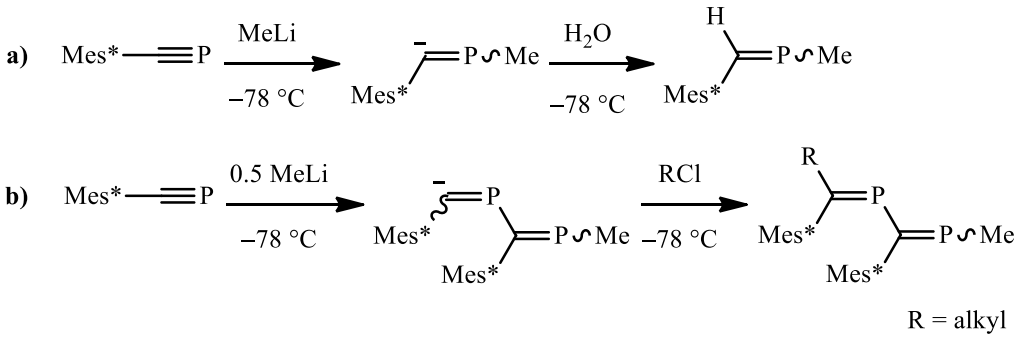
Scheme 48. Superacid protonation of phosphaalkynes [220]

The dihydroamination of alkynes has historically been achieved by transition metal or lanthanide catalysts, as the reactions are otherwise kinetically unfavourable due to high activation barriers.[221,222] This methodology was similarly effective for the first catalytic dihydroamination of a phosphaalkyne, achieved by addition of excess RNH_2 to $^tBuC{\equiv}P$ in the presence of [$TiCl_4$] (Scheme 49).[223] The resulting diaminophosphine $^tBuCH_2P(N(H)R)_2$ was afforded in >90 % yield after 24 h following purification by sublimation.



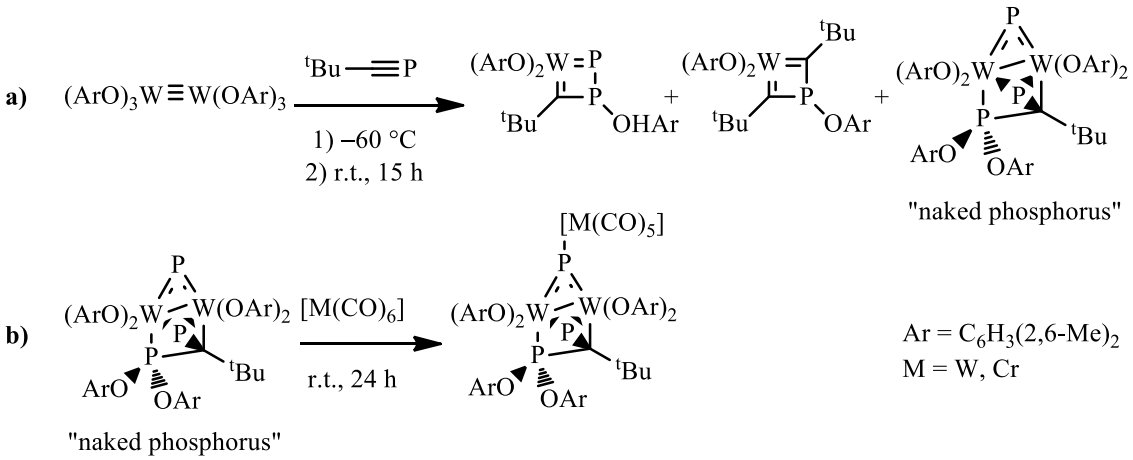
Scheme 49. Catalytic dihydroamination of phosphaalkynes [223]

The reaction of phosphaalkynes with nucleophilic reagents was first probed by Arif in 1988, and was found to be quite different from the analogous reactions of nitriles; whereas nucleophiles react with the electrophilic carbon centre of nitriles ($R^{\delta+}C{\equiv}N^{\delta-}$),[224] phosphaalkynes react with nucleophiles at the electrophilic phosphorus centre ($R^{\delta-}C{\equiv}P^{\delta+}$).The reaction of Mes*C≡P with MeLi provided facile access to phosphaalkene Mes*(H)C=PMe *via* an intermediate phosphaalkenic anion (Scheme 50 **a**).[225] In contrast, reaction of Mes*C≡P with half an equivalent of MeLi afforded a novel [1,3]-diphosphabutadienyl anion, which could be converted to the corresponding [1,3]-diphosphabutadiene by treatment with RCl (Scheme 50 **b**).



Scheme 50. Reactions of Mes*C≡P with **a**) MeLi, **b**) 0.5 MeLi [225]

The reaction of ^{t}BuC≡P with $[(ArO)_3W{\equiv}W(OAr)_3]$ affords a mixture of cyclic complexes that included the first example of "naked phosphorus as a bent bridging ligand," which was characterised by single crystal X-ray diffraction (Scheme 51 **a**).[226] The authors postulated that the "naked phosphorus" complex was formed by the reaction of two phosphide units $[(ArO)_3W{\equiv}P]$ with one free phosphaalkyne ^{t}BuC≡P. A ^{31}P NMR resonance at 832 ppm was attributed to the naked phosphorus centre. The naked phosphorus lone pair provided further reactivity by coordination to an additional metal centre (Scheme 51 **b**), resulting in an up-field shift of the ^{31}P NMR resonance (M = W, 651 ppm; M = Cr, 715 ppm).



Scheme 51. The cyclisation reaction of ^{t}BuC≡P with [$(ArO)_3W{\equiv}W(OAr)_3$] afforded the first example of phosphorus as a "naked bridging ligand" [226]

1.5 Summary

Although phosphines, phosphaalkenes and phosphaalkynes are well-documented species, much scope for further investigation remains. Reports of alkynylphosphine chemistry are limited to reactions with transition metals and examples of propargylphosphines are extremely limited, while the electronic characteristics of conjugated phosphaalkynes, diynes, and diphosphaalkynes are undocumented.

Phosphorus has long been used as an n-type dopant to enhance the electronic properties of conducting polymers,[227,228] and recent years have seen a surge in the application of conjugated species in molecular electronics *viz.* molecular wires,[129,229] and organic light emitting diodes (OLEDs).[230] Gates and Ott have independently demonstrated that conjugated phosphaalkenes possess enhanced electronic communicative abilities *viz.* reduced HOMO - LUMO band gaps and increased through-chain conjugation compared with the all-carbon containing analogues.[130,131] However, such studies have yet to be extended to systems containing phosphaalkynes.

Herein are described attempts to develop low coordinate phosphorus species bearing extended conjugation, which may prove particularly valuable in the field of molecular wire research. The synthesis of linear conjugated phosphaalkynes such as $R_3EC{\equiv}CC{\equiv}P$ may ultimately provide access to coordinated complexes $[M\{P{\equiv}CC{\equiv}CER_3\}(H)(dppe)_2]$ and 1-phosphadiynyls $[M\{C{\equiv}CC{\equiv}P\}(H)(dppe)_2]$ *via* use of the main group fragment as a transfer reagent. The synthesis of phosphaalkynes in conjugation with aromatic systems that incorporate additional functional groups, as for $C_6H_4(1\text{-}C{\equiv}P)(R)$, was also approached, with the knowledge that developing a synthetic route that is tolerant of additional ring substituents may ultimately allow access to conjugated polyphosphaalkynes $C_6H_4(1,3\text{-}C{\equiv}P)_2$ and $C_6H_4(1,3,5\text{-}C{\equiv}P)_3$. Such species are envisaged to possess novel electronic properties and provide value in the on-going development of NLO devices.

2. The development of chloropropargyls and propargylphosphines

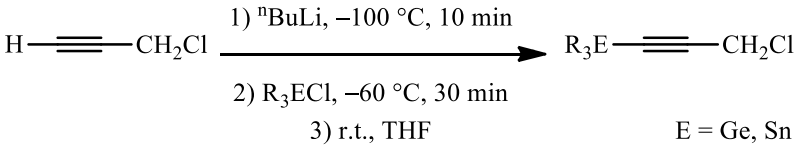
2.1 Introduction

Unlike the relatively common bromopropargyl compounds,[231–243] main group chloropropargyls of the type $R_3EC{\equiv}CCH_2Cl$ have been reported only sporadically in literature,[244–247] with germanium and tin variants particularly poorly documented (Table 8);[248,249,246] main group iodopropargyls are similarly rare.[250–253,240] Two new examples of chloropropargyls, $^{n}Bu_3SnC{\equiv}CCH_2Cl$ and $Me_2PhSiC{\equiv}CCH_2Cl$, have been reported since work on this project commenced.[243,254]

Table 8. Main group halopropargyls previously reported in literature

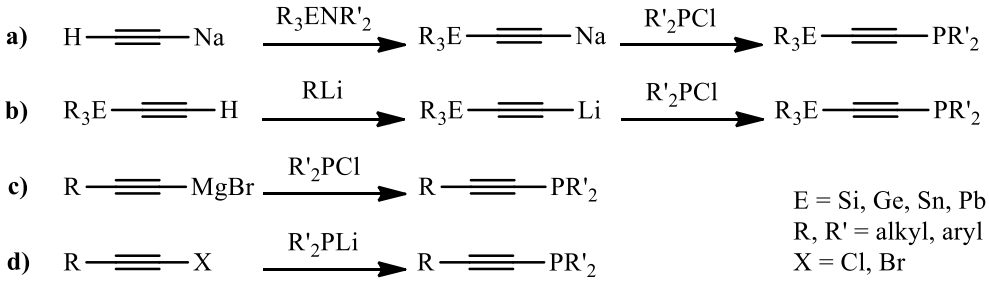
Compound	R_3	Source
$R_3SiC{\equiv}CCH_2Cl$	Me_3	247
$R_3SiC{\equiv}CCH_2Cl$	$Me_2{}^{t}Bu$, Et_3	245
$R_3SiC{\equiv}CCH_2Cl$	Me_2Ph, $Me_2(C_6H_4$2-Me)	254
$R_3GeC{\equiv}CCH_2Cl$	Ph_3	246
$R_3SnC{\equiv}CCH_2Cl$	Me_3, Et_3, Ph_3, $^{n}Bu_3$	248,249,246,243
$R_3SiC{\equiv}CCH_2Br$	Et_3, $^{i}Pr_3$, $Me_2(PhCH_2)$	233,232,236
$R_3SiC{\equiv}CCH_2Br$	$Me_2(C_3H_6Cl)$, $Me_2{}^{t}Bu$	238
$R_3SiC{\equiv}CCH_2Br$	Ph_2Me, $^{t}BuPh_2$, Ph_3, $Ph_2(H_2C{=}CHCH_2)$, $PhMe(H_2C{=}CHCH_2)$	237
$R_3SiC{\equiv}CCH_2Br$	$Me_2(H_2C{=}CH)$, Me_2Ph, Me_3	231
$R_3GeC{\equiv}CCH_2Br$	Me_3	240
$R_3SnC{\equiv}CCH_2Br$	Me_3, Et_3, $^{n}Bu_3$	241-243
$R_3SiC{\equiv}CCH_2I$	Me_2Ph, Et_3, $Me_2{}^{t}Bu$	253,251,255
$R_3SiC{\equiv}CCH_2I$	Me_3, $Me_2(H_2C{=}CH)$	252
$R_3SnC{\equiv}CCH_2I$	Me_3	240

The syntheses of main group halopropargyls can be achieved *via* a number of routes; Ruitenberg's approach featured the reaction of $LiC{\equiv}CCH_2Cl$ (generated by addition of $^{n}BuLi$ to $HC{\equiv}CCH_2Cl$) with R_3ECl (Scheme 52).[246]



Scheme 52. Literature synthesis of $R_3EC{\equiv}CCH_2Cl$ [246]

The conversion of main group halopropargyls to main group propargylphosphines $R_3EC{\equiv}CCH_2PR'_2$ has not previously been described in literature, although the synthesis of main group phosphinoacetylenes $R_3EC{\equiv}CPPh_2$ (R = Ph, Me, E = Si, Ge, Sn, Pb) has,[79] as has the synthesis of propargylphosphines of the type $RC{\equiv}CCH_2PPh_2$ (R = H,[84] Me,[256] Ph,[86]). The synthesis of alkynylphosphines has historically been achieved by a variety of routes, including **a**) addition of $R_3EC{\equiv}CNa$ to R'_2PCl,[79,41] **b**) addition of $R_3EC{\equiv}CLi$ to R'_2PCl,[79] **c**) addition of R'_2PCl to $RC{\equiv}CMgBr$,[257] **d**) addition of R'_2PLi to $RC{\equiv}CX$ (Scheme 53).[84,256,86]

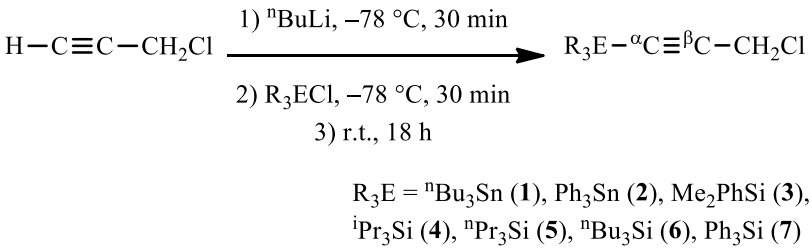


Scheme 53. Literature syntheses of alkynylphosphines

Herein the synthesis of a comprehensive library of main group chloropropargyls is reported, and further transformation to main group propargylphosphines thoroughly explored. An investigation of reactivity profiles and coordination chemistry will be described, and the synthesis and reactivity of selected carbocentric counterparts also reported.

2.2 Syntheses of $R_3EC{\equiv}CCH_2Cl$

Following from Ruitenberg's synthetic methodology for the production of tin chloropropargyls,[246] $R_3EC{\equiv}CCH_2Cl$ (**1** – **7,** Scheme 54) were synthesised by addition of ^{n}BuLi to $HC{\equiv}CCH_2Cl$ at −78 °C, followed by the subsequent addition of R_3ECl. Compounds **1** - **7** were isolated in good yields (>60 %) as yellow oils after purification by washing with pentane (**1** - **2**), fractional distillation (**3** - **6**) or sublimation (**7**), although complete solvent removal (THF) for **2** was not achieved.



Scheme 54. Syntheses of $R_3EC{\equiv}CCH_2Cl$ (**1** - **7**)

The ^{1}H NMR spectra for **1** - **2** show singlet resonances at ca. 3.70 ppm ($^{4}J_{H\text{-}Sn}$ ca. 9.9 Hz) that are assigned to the CH_2Cl protons and display satellites (^{119}Sn, I = ½, 8.59 %) that are characteristic in magnitude of a four-bond proton-tin separation.[258,259] The analogous CH_2Cl protons of compounds **3** - **7** are located at 3.49 to 3.56 ppm; although no silicon satellites are resolved, long-range correlations between the CH_2Cl proton resonances and silicon centres in the range of −28.8 to −1.7 ppm are evident from the ^{1}H-^{29}Si HMBC NMR spectra (Table 9). The signals assigned to the CH_2Cl protons for compounds **1** - **7** each integrate to two protons when compared to the remaining resonances of the R substituents in their respective ^{1}H NMR spectra, consistent with the product assignments. The $^{13}C\{^{1}H\}$ NMR spectra of **1** - **7** show singlet resonances at ca. 30.6 ppm for the CH_2Cl carbons and two further singlet signals at ca. 89.4 and ca. 104 ppm, attributed to the $^{\alpha}C$ ($R_3E\underline{\mathbf{C}}{\equiv}CCH_2Cl$) and $^{\beta}C$ ($R_3EC{\equiv}\underline{\mathbf{C}}CH_2Cl$) alkynic carbon centres respectively. The alkynic assignments are made by comparison with $^{n}Bu_3SnC{\equiv}CCH_2Cl$, ($\delta_C$ 97.2 for $^{\alpha}C$, 104 for $^{\beta}C$).[243] The difference in chemical shifts between the $^{\alpha}C$ and $^{\beta}C$ centres is consistent with polarisation of the triple bond when relative electron-donor/acceptor strengths of the respective termini are considered; compounds **3** - **7** exhibit smaller chemical shift differences between the $^{\alpha}C$ and $^{\beta}C$ centres ($\Delta\delta_C$ + ca. 13.3) than **1** - **2** ($\Delta\delta_C$ +13.9 for **1**, $\Delta\delta_C$ +18.3 for **2**) as there is less electron-donor/acceptor strength disparity between the terminal groups. The $^{119}Sn\{^{1}H\}$ NMR spectra show singlet signals at −65.1 and −169 ppm for **1** and **2** respectively; the chemical shifts of similar tin species (R_4Sn) typically span −150 to +50 ppm,[260] and while the shift of **2** falls marginally outside of this window, literature reveals similar data for compounds of the type R_4E when R = Ph.[261,262]

Table 9. Selected NMR data for $R_3EC{\equiv}CCH_2Cl$ (**1** - **7**)

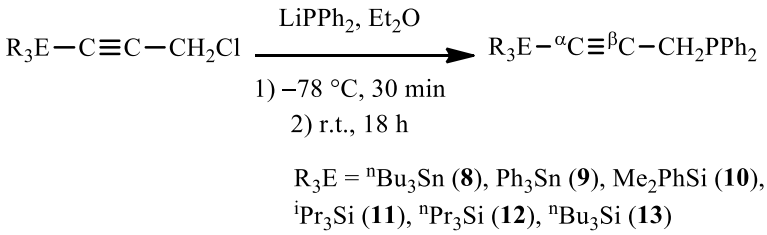
	R_3E	$^{119}Sn\{^1H\}$ / ppm	$^{29}Si\{^1H\}$ / ppm	^1H CH_2Cl / ppm	$^4J_{H\text{-}Sn}$ / Hz	$^{13}C\{^1H\}$ CH_2Cl / ppm	$^{13}C\{^1H\}$ $^{\alpha}C$ / ppm	$^{13}C\{^1H\}$ $^{\beta}C$ / ppm
1	$^nBu_3Sn$	−65.1	-	3.70	9.2	31.2	91.1	105
2	Ph_3Sn	−169	-	3.67	10.5	30.3	88.1	106
3	Me_2Ph	-	−21.6	3.51	-	30.1	89.7	102
4	$^iPr_3Si$	-	−1.7	3.53	-	30.2	88.0	102
5	$^nPr_3Si$	-	−13.0	3.55	-	30.7	90.2	102
6	$^nBu_3Si$	-	−11.3	3.56	-	30.7	90.3	102
7	Ph_3Si	-	−28.8	3.49	-	30.4	87.6	105

2.3 Syntheses and reactions of $R_3EC{\equiv}CCH_2PPh_2$

2.3.1 Syntheses of $R_3EC{\equiv}CCH_2PPh_2$

The addition of $R_3EC{\equiv}CCH_2Cl$ (**1** - **6**) to $LiPPh_2$ afforded $R_3EC{\equiv}CCH_2PPh_2$ (**8** - **13**) as red or brown oils in good yields (78 - 99 %) (Scheme 55). While compounds **10** - **13** were isolated in analytical purity, compound **8** was generated alongside significant quantities of $^nBu_4Sn$ (identified by comparison to literature data, δ_{Sn} −12.0),[263] from which isolation could not be achieved by washing or crystallisation; distillation resulted in the degradation of **8** to an intractable mixture. Similarly, **9** was obtained with trace contaminants, including $^nBuPh_3Sn$,[264] thus compounds **8** and **9** were characterised only spectroscopically.

In all cases the solvent identity proved to be of the utmost importance to the success of the reaction; when performed in THF, the regeneration of $HPPh_2$ was observed, and none of the desired product was detected by multinuclear NMR spectroscopy. Interestingly, the analogous reaction of $LiPCy_2$ with $R_3SiC{\equiv}CCH_2Cl$ was unsuccessful irrespective of the solvent and reaction conditions, with only free $HPCy_2$ detected by ^{31}P NMR spectroscopy.



Scheme 55. Syntheses of $R_3EC{\equiv}CCH_2PPh_2$ (**8** - **13**)

With the exception of the $^{119}Sn\{^{1}H\}$ NMR data, the multinuclear NMR characteristics of **8** and **9** are similar (Table 10), with each resonance (^{1}H and $^{13}C\{^{1}H\}$) exhibiting significantly high-field chemical shifts compared to **1** and **2**. The ^{31}P NMR spectra show broad resonances at ca. −13.3 ppm ($w_{½}$ ca. 21.7 Hz) that are consistent in chemical shift with comparable tin-containing phosphines ($Me_3Sn(CH_2)_3PPh_2$, δ_P −17.2).[265] The ^{1}H NMR studies show doublet signals at 2.87 ppm ($^{2}J_{H\text{-}P}$ ca. 2.4 Hz) that are assigned to the CH_2P protons, with two-bond proton-phosphorus coupling constants similar to previously reported values (Me_3P, $^{2}J_{H\text{-}P}$ 2.7 Hz;[266] Ph_2MePh, $^{2}J_{H\text{-}P}$ 4.0 Hz;[267] $Ph_2PCH_2PPh_2$, $^{2}J_{H\text{-}P}$ 1.9 Hz).[267] The CH_2P resonance of compound **9** also exhibits both ^{117}Sn and ^{119}Sn satellites ($^{4}J_{H\text{-}Sn}$ 15.0 Hz and 9.1 Hz). The $^{13}C\{^{1}H\}$ NMR spectra of **8** and **9** show doublet signals at ca. 20.3 ppm ($^{1}J_{C\text{-}P}$ ca. 19 Hz) for the CH_2P carbon centres, with carbon-phosphorus coupling constants consistent with one-bond carbon-phosphorus separations ($Me_2(Cl)Sn(CH_2)_3P^{n}Bu_2$, $^{4}J_{Sn\text{-}P}$ 19.5 Hz),[265] in addition to doublet resonances at ca. 83.9 ($^{3}J_{C\text{-}P}$ ca. 6.3 Hz) and 108 ppm ($^{2}J_{C\text{-}P}$ ca. 4.2 Hz), attributed to the alkynic carbon atoms $^{\alpha}C$ and $^{\beta}C$. Compounds **8** and **9** exhibit doublet signals at −68.4 ($^{4}J_{Sn\text{-}P}$ 14.5 Hz) and −168 ppm ($^{4}J_{Sn\text{-}P}$ 13.9 Hz) respectively in the ^{119}Sn NMR spectra; the tin-phosphorus coupling constants are consistent with four-bond tin-phosphorus separations in the literature ($Me_2(Cl)Sn(CH_2)_3PCy_2$, $^{4}J_{Sn\text{-}P}$ 14.5 Hz).[265]

The ^{31}P NMR spectra of $R_3SiC{\equiv}CCH_2PPh_2$ (**10** - **13**) show broad resonances at ca. −13.5 ppm ($w_{½}$ ca. 22.5 Hz), which correlate with doublets (confirmed by ^{1}H-^{31}P HMBC NMR studies) in the ^{1}H NMR spectra at ca. 2.76 ppm ($^{2}J_{H\text{-}P}$ ca. 2.5 Hz) that are assigned to the CH_2P protons (Table 10). For each compound the doublet signal integrates as two protons when compared to the resonances assigned to the respective R groups. Doublet signals that are assigned to the CH_2P, $^{\alpha}C$ and $^{\beta}C$ centres are located at ca. 19.9 ($^{1}J_{C\text{-}P}$ ca. 20 Hz), ca. 84.7 ($^{3}J_{C\text{-}P}$ ca. 5.1 Hz), and ca. 104 ppm ($^{2}J_{C\text{-}P}$ ca. 3.9 Hz) in the $^{13}C\{^{1}H\}$ NMR spectra, with coupling constants and chemical shifts comparable to those exhibited by **8** and **9**.

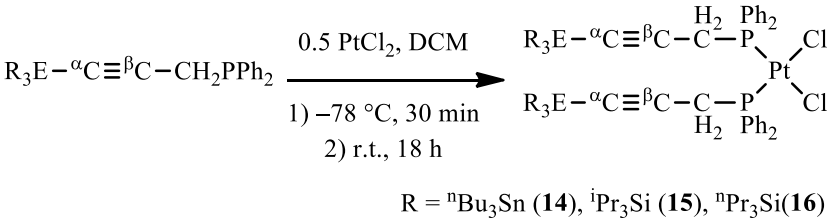
Table 10. Selected NMR data for $R_3EC{\equiv}CCH_2PPh_2$ (**8** - **13**)

	R_3E	^{31}P / ppm	^{1}H CH_2P / ppm	$^{13}C\{^{1}H\}$ CH_2P / ppm	$^{1}J_{C\text{-}P}$ / Hz	$^{13}C\{^{1}H\}$ $^{\alpha}C$ / ppm	$^{3}J_{C\text{-}P}$ / Hz	$^{13}C\{^{1}H\}$ $^{\beta}C$ / ppm	$^{2}J_{C\text{-}P}$ / Hz
8	$^{n}Bu_3Sn$	−13.4	2.87	20.4	18.5	85.0	6.7	107	4.9
9	Ph_3Sn	–13.2	2.87	20.2	20.5	82.8	5.9	109	3.4
10	Me_2PhSi	−13.5	2.76	19.8	20.7	84.7	4.9	105	3.6
11	$^{i}Pr_3Si$	−13.5	2.75	19.9	19.3	83.3	5.2	105	4.2
12	$^{n}Pr_3Si$	−13.6	2.76	19.9	19.9	85.4	5.2	103	4.0
13	$^{n}Bu_3Si$	−13.5	2.76	19.9	19.8	85.5	4.8	104	4.1

2.3.2 Coordination reactions of $R_3EC{\equiv}CCH_2PPh_2$

Syntheses of *cis/trans*-$[PtCl_2(R_3EC{\equiv}CCH_2PPh_2)_2]$

Complexes of the type *cis*-$[PtCl_2(R_3EC{\equiv}CCH_2PPh_2)_2]$ (**14 - 16**) were synthesised in high yields (>75 %) *via* addition of $PtCl_2$ to the respective phosphine $R_3EC{\equiv}CCH_2PPh_2$ (R_3E = $^{n}Bu_3Sn$, $^{i}Pr_3Si$, $^{n}Pr_3Si$) (Scheme 56). Complexes **15 - 16** could also be accessed by addition of [Pt(1,5-COD)Cl_2] to $R_3SiC{\equiv}CCH_2PPh_2$, with comparable yields (76 - 86 %) of analytically pure solids. In contrast, **14** could not be generated by addition of [Pt(1,5-COD)Cl_2] to $^{n}Bu_3SnC{\equiv}CCH_2PPh_2$, nor could it be isolated from significant levels of contaminants, the identities of which remain elusive. Washing and recrystallisation both proved ineffective, although **14** was the predominant product (>50 % determined by integration of the resonances in the ^{31}P NMR spectrum), which enabled spectroscopic characterisation.

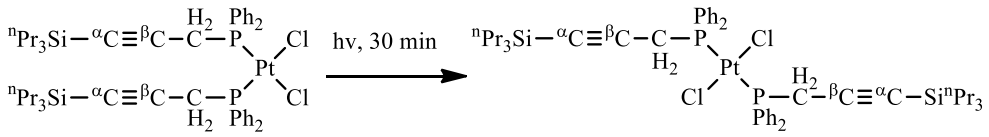


Scheme 56. Syntheses of *cis*-$[PtCl_2(R_3EC{\equiv}CCH_2PPh_2)_2]$ (**14 - 16**)

The ^{31}P NMR spectrum of **14** shows a broad resonance at 6.0 ppm ($^{1}J_{P\text{-}Pt}$ 3611 Hz, $w_{½}$ ca. 45.1 Hz), while complexes **15 - 16** show broad signals at ca. 5.9 ppm ($^{1}J_{P\text{-}Pt}$ ca. 3610 Hz, $w_{½}$ ca. 45.1 Hz) (Table 11). The magnitude of the platinum satellites for **14 - 16** are consistent with *cis*-coordinated bisphosphine di-halide complexes.[268] For complex **14**, twelve additional signals that range from −5.2 to 52.8 ppm are located in the ^{31}P NMR spectrum, although none can be identified due to the relatively small quantities of each present (ca. 47.3 % by integration of the ^{31}P NMR spectrum). The $^{195}Pt\{^{1}H\}$ NMR spectra of **14 - 16** show triplet resonances at ca. −4404 ppm ($^{1}J_{Pt\text{-}P}$ ca. 3610 Hz), consistent with coordination of two equivalent phosphorus atoms to each platinum centre. The ^{1}H NMR spectrum of **14** shows a multiplet resonance at 3.78 ppm ($^{2}J_{H\text{-}P}$ 10.9 Hz) that is assigned to the CH_2P protons and integrates as four protons when compared to the remaining signals in the spectrum. The analogous CH_2P protons for complexes **15 - 16** are located as doublet signals in the ^{1}H NMR spectra at ca. 3.85 ppm ($^{2}J_{H\text{-}P}$ ca. 9.8 Hz), and correspond to their respective phosphorus resonances *via* ^{1}H-^{31}P HMBC NMR studies. The $^{13}C\{^{1}H\}$ NMR spectrum of **14** shows unresolved multiplet signals for the alkynic carbon centres $^{\alpha}C$ and $^{\beta}C$ at 88.7 ($^{3}J_{C\text{-}P}$ 7.8 Hz) and 104 ppm ($^{2}J_{C\text{-}P}$ 12.2 Hz), similar to those exhibited by **15 - 16** at ca. 86.9 ($^{3}J_{C\text{-}P}$ 3.2 Hz) and ca. 102 ppm ($^{2}J_{C\text{-}P}$ ca. 6.2 Hz). The resonance assigned to the

CH_2P carbon of **14** is observed as a multiplet at 23.8 ppm ($^1J_{C\text{-}P}$ 42.1 Hz) in the $^{13}C\{^1H\}$ NMR spectrum, shifted significantly down-field ($\Delta\delta_C$ +3.40 ppm) from free $^nBu_3SnC{\equiv}CCH_2PPh_2$ (**8**), with a greatly increased carbon-phosphorus coupling constant ($\Delta^1J_{C\text{-}P}$ +23.6 Hz). Complexes **15 - 16** also exhibit multiplet resonances attributed to the CH_2P carbon centres in a similar region (δ_P 23.9 ($^1J_{C\text{-}P}$ ca. 44.2 Hz)) that possess increased carbon-phosphorus coupling constants compared with the free propargylphosphines **11 - 12**. These trends are characteristic of phosphine coordination complexes in the literature; *cis*-$[PtCl_2(PEt_3)_2]$ exhibits a multiplet at 1.9 ppm ($^1J_{C\text{-}P}$ 42.0 Hz) in the $^{13}C\{^1H\}$ NMR spectrum,[269] while free PEt_3 shows a doublet at 18.0 ppm ($^1J_{C\text{-}P}$ 11.5 Hz).[270]

In order to gain access to *trans*-$[PtCl_2(^nPr_3SiC{\equiv}CCH_2PPh_2)_2]$ (***trans*-16**), thermal and photo-isomerisations of ***cis*-16** were attempted by reflux and irradiation with a 500 MW full spectrum mercury lamp, in line with literature precedent.[271] The reflux of ***cis*-16** proved ineffective at inducing isomerisation, with only ***cis*-16** observed spectroscopically. However, UV irradiation afforded a mixture of *cis*-/*trans*-$[PtCl_2(^nPr_3SiC{\equiv}CCH_2PPh_2)_2]$ (57.5 % ***cis*-16**, 42.5 % ***trans*-16**) after 30 min (Scheme 57). Further irradiation over 3 h failed to convert the remaining ***cis*-16**, rendering it necessary to characterise ***trans*-16** in equilibrium with ***cis*-16**.



***cis*-16** ***trans*-16**

Scheme 57. Synthesis of *trans*-$[PtCl_2(^nPr_3SiC{\equiv}CCH_2PPh_2)_2]$ (**16**)

The ^{31}P NMR spectrum of ***trans*-16** shows a broad resonance at 11.5 ppm ($^1J_{P\text{-}Pt}$ 2217 Hz) (Table 11), with platinum satellites characteristic in magnitude of a *trans*-geometry at the metal centre. This signal couples (as determined by ^1H-^{31}P HMBC NMR spectroscopy) to a triplet resonance in the ^1H NMR spectrum at 3.77 ppm ($^2J_{H\text{-}P}$ 4.6 Hz),[56] which is assigned to the CH_2P group and integrates as four protons when compared to the remaining alkyl and aryl resonances (Figure 16). The $^{195}Pt\{^1H\}$ NMR spectrum shows a triplet signal at −3993 ppm ($^1J_{Pt\text{-}P}$ 2217 Hz), shifted significantly from that of ***cis*-16** (δ_{Pt} −4403 ($^1J_{Pt\text{-}P}$ 3608 Hz)). The signals in the $^{13}C\{^1H\}$ NMR spectrum are assigned by comparison with those recorded for ***cis*-16**, from which only minor deviations are noted. A triplet resonance at 23.8 ppm ($^1J_{C\text{-}P}$ 23.8 Hz) is assigned to the CH_2P centre, while the alkynic carbons $^{\alpha}C$ and $^{\beta}C$ are found respectively as an unresolved multiplet and triplet signal at 88.1 and 101 ppm ($^2J_{C\text{-}P}$ 4.9 Hz).

Table 11. Selected NMR data for $[PtCl_2(R_3SiC{\equiv}CCH_2PPh_2)_2]$ (**14 - 16**)

	Complex	^{31}P / ppm	$^{1}J_{P\text{-}Pt}$ / Hz	$^{195}Pt\{^{1}H\}$ / ppm	^{1}H CH_2P / ppm	$^{2}J_{H\text{-}P}$ / Hz	$^{13}C\{^{1}H\}$ CH_2P / ppm	$^{1}J_{P\text{-}C}$ / Hz	$^{13}C\{^{1}H\}$ $^{\alpha}C$ / Hz	$^{3}J_{P\text{-}C}$ / Hz	$^{13}C\{H\}$ $^{\beta}C$ / Hz	$^{2}J_{P\text{-}C}$ / Hz
14	*cis*-$[PtCl_2(^{n}Bu_3SnC{\equiv}CCH_2PPh_2)_2]$	6.0	3611	−4407	3.78	10.9	23.8	42.1	88.7	7.8	104	12.2
15	*cis*-$[PtCl_2(^{i}Pr_3SiC{\equiv}CCH_2PPh_2)_2]$	5.8	3618	−4399	3.87	10.0	23.9	42.3	85.8	3.1	102	6.3
***cis*-16**	*cis*-$[PtCl_2(^{n}Pr_3SiC{\equiv}CCH_2PPh_2)_2]$	5.9	3608	−4403	3.82	9.6	23.9	46.1	88.0	3.3	101	6.0
trans-16	*trans*-$[PtCl_2(^{n}Pr_3SiC{\equiv}CCH_2PPh_2)_2]$	11.5	2217	−3993	3.77	4.6	23.8	23.8	88.1	-	101	4.9

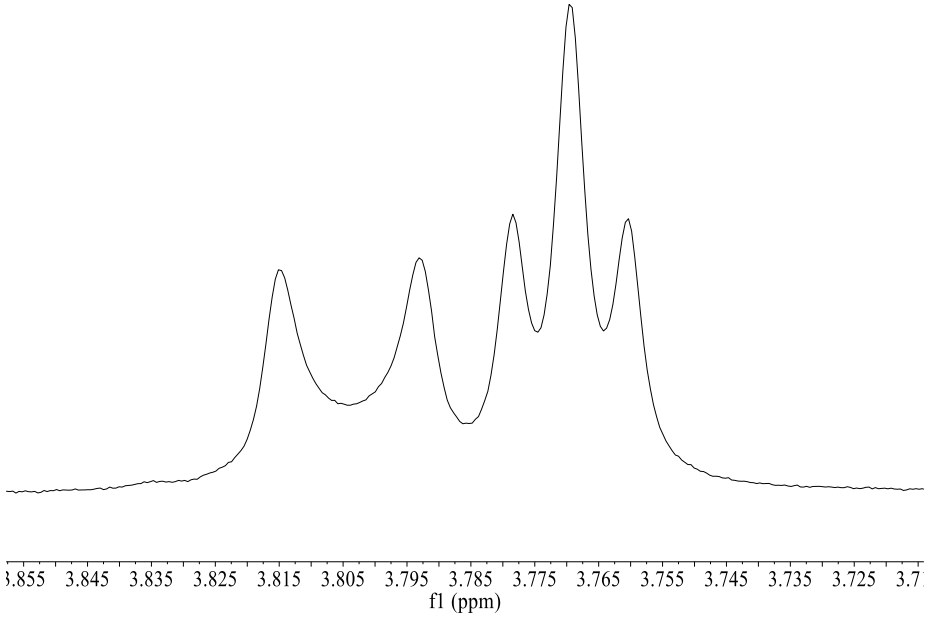
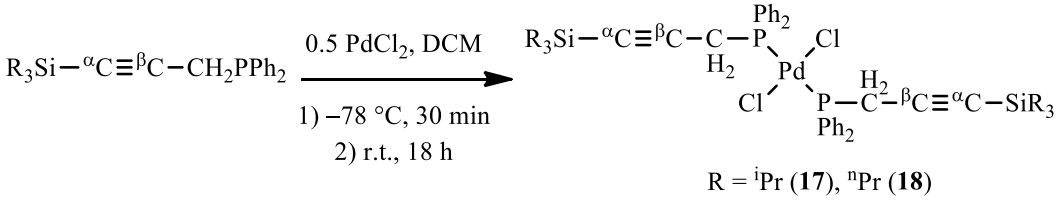


Figure 16. Selected section (3.71 - 3.85 ppm) of the ^{1}H NMR spectrum of *cis*-/*trans*-$[PtCl_2(^{n}Pr_3SiC{\equiv}CCH_2PPh_2)_2]$ (**16**); the triplet resonance is for the *trans*-isomer

Syntheses of *trans*-[$PdCl_2(R_3SiC{\equiv}CCH_2PPh_2)_2$]

The syntheses of *trans*-[$PdCl_2(R_3SiC{\equiv}CCH_2PPh_2)_2$] (**17** - **18**) were achieved by addition of $PdCl_2$ or [Pd(1,5-COD)Cl_2] to $R_3SiC{\equiv}CCH_2PPh_2$ (Scheme 58), with both routes producing high yields of solid products (>85 %).



Scheme 58. Syntheses of *trans*-[$PdCl_2(R_3SiC{\equiv}CCH_2PPh_2)_2$] (**17** - **18**)

The ^{31}P NMR spectra show resonances at ca. 15.9 ppm ($w_{½}$ ca. 24.2 Hz) that correspond (as determined by ^{1}H-^{31}P HMBC NMR spectra) to triplet signals in the ^{1}H NMR spectrum at ca. 3.75 ppm ($^{2}J_{H\text{-}P}$ ca. 3.9 Hz), assigned to the four CH_2P protons (Table 12). The phosphorus centres of **17** and **18** resonate at significantly lower frequencies than the free phosphines **11** and **12**, consistent with known bisphosphine di-halide palladium complexes.[272] Triplet resonances for the $^{\alpha}C$ and $^{\beta}C$ alkynic carbon centres at ca. 86.6 ($^{3}J_{C\text{-}P}$ ca. 2.9 Hz) and 101 ppm ($^{2}J_{C\text{-}P}$ 5.6 Hz) in the $^{13}C\{^{1}H\}$ NMR spectra are similar to ***trans*-16**. The CH_2P and CH_3 centres of **17** overlap, precluding resolution of the carbon-phosphorus couplings, however, the CH_2P carbon atom is located as a triplet signal for **18** at 18.8 ppm ($^{1}J_{C\text{-}P}$ 13.1 Hz).

Table 12. Selected NMR data for *trans*-[$PdCl_2(R_3SiC{\equiv}CCH_2PPh_2)_2$] (**17** - **18**)

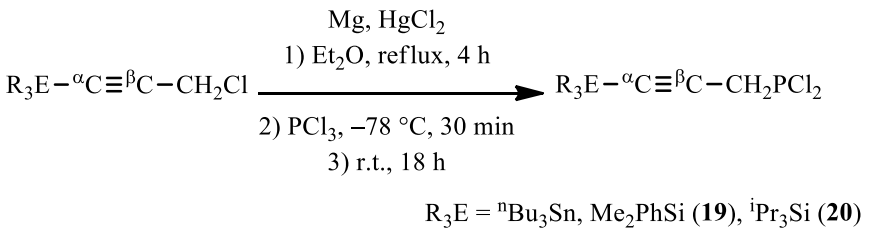
	R	^{31}P / ppm	^{1}H CH_2P / ppm	$^{2}J_{H\text{-}P}$ / Hz	$^{13}C\{^{1}H\}$ CH_2P / ppm	$^{1}J_{C\text{-}P}$ / Hz	$^{13}C\{^{1}H\}$ $^{\alpha}C$ / ppm	$^{3}J_{C\text{-}P}$ / Hz	$^{13}C\{^{1}H\}$ $^{\beta}C$ / ppm	$^{2}J_{C\text{-}P}$ / Hz
17	iPr	15.9	3.74	3.9	18.4	-	85.3	3.0	101	5.6
18	nPr	15.9	3.75	3.8	18.8	13.1	87.9	2.9	101	4.7

2.4 Reactions of $R_3EC{\equiv}CCH_2Cl$ with chlorophosphines

The syntheses of propargyl dihalophosphines $R_3EC{\equiv}CCH_2PX_2$ (X = Cl, I) were pursued as a potential intermediate *en route* to conjugated phosphaalkynes, $R_3EC{\equiv}CC{\equiv}P$. The double dehydrohalogenation of dichlorophosphines to afford phosphaalkynes is well-established,[163,164,162] and may provide a viable route for the synthesis of phosphaalkynes incorporating extended conjugation. Dichlorophosphines of the type $RC(H)_2PCl_2$ are typically produced from the reaction of "$RC(H)_2MgCl$" (generated from the Grignard reaction of chlorocarbons $RC(H)_2Cl$) with chlorophosphines, usually PCl_3.[44]

2.4.1 Reactions of $R_3EC{\equiv}CCH_2Cl$ with PCl_3

The syntheses of $R_3EC{\equiv}CCH_2PCl_2$ (**19 - 20**) were attempted by addition of $R_3EC{\equiv}CCH_2Cl$ to activated magnesium with an initiator; however, no evidence for initiation was apparent and the products obtained from the addition to PCl_3 did not exhibit any resonances in the ^{31}P NMR spectra save for that assigned to unreacted PCl_3. Initiation was therefore achieved by reflux and after 4 h the resulting mixtures were filtered into cold PCl_3 (Scheme 59). The products isolated upon workup were determined to be complex mixtures that could not be improved upon by alterations of i) solvent (Et_2O, pentane, THF, toluene), ii) initiator ($HgCl_2$ or I_2), iii) time at reflux (2 – 8 h), or iv) temperature of addition to PCl_3 (−78 °C, −20 °C, ambient temperature). Isolation by washing (with pentane or hexane) or distillation proved equally unsuccessful.



Scheme 59. Attempted syntheses of $R_3EC{\equiv}CCH_2PCl_2$ (**19 - 20**)

$^{n}Bu_3SnC{\equiv}CCH_2Cl$

The attempted synthesis of $^{n}Bu_3SnC{\equiv}CCH_2PCl_2$ afforded a brown oil that was identified as a mixture of compounds, including $^{n}Bu_3SnC{\equiv}CCH_2Cl$ (**1**) and $^{n}Bu_3SnCl$, identified by singlet resonances at −65.1 and 146 ppm in the $^{119}Sn\{^1H\}$ NMR spectrum;[273] comparison with the ^1H NMR spectroscopic data (chemical shift of the ^{n}Bu groups for $^{n}Bu_3SnCl$ and CH_2Cl protons in **1**) corroborate these assignments and no further tin-containing products are observed. The ^{31}P

NMR spectrum shows just one broad signal of low intensity at 48.8 ppm ($w_{½}$ ca. 38.5 Hz) that remains unassigned, being inconsistent with either chlorophosphines (Ph_2PCl, δ_P 82.3, $^tBuP(C{\equiv}CPh)Cl$ δ_P 71.9),[274,275] or dichlorophosphines ($C_6H_5PCl_2$ δ_P 166).[276] A corresponding multiplet (located by ^1H-^{31}P HMBC NMR spectroscopy) is observed in the ^1H NMR spectrum at 3.45 ppm. Additional multidimensional spectroscopy experiments (^1H-^{119}Sn HMBC, ^1H-^{13}C HMBC and ^1H-^{13}C HSQC NMR) do not provide evidence of further correlation of this signal, and distillation of the brown oil affords the same product mixture but as a colourless oil.

$Me_2PhSiC{\equiv}CCH_2Cl$

The attempted synthesis of $Me_2PhSiC{\equiv}CCH_2PCl_2$ (**19**) afforded an orange solid that exhibits three resonances in the ^{31}P NMR spectrum, *viz.:* a broad signal at −27.4 ppm ($w_{½}$ ca. 32.1 Hz) that remains unassigned, a multiplet at 81.8 ppm that is tentatively attributed to $(Me_2PhSiC{\equiv}CCH_2)_2PCl$, and a triplet at 170 ppm ($^2J_{P\text{-}H}$ 14.6 Hz) that is assigned to compound **19** (Table 13). The ^1H-^{31}P HMBC NMR spectrum shows that the triplet resonance correlate to a doublet signal in the ^1H NMR spectrum at 2.57 ppm ($^2J_{H\text{-}P}$ 14.6 Hz), while the multiplet resonance in the ^{31}P NMR spectrum at 81.8 ppm corresponds to a complex multiplet resonance centred at 2.7 ppm in the ^1H NMR spectrum. The ^1H and ^{31}P NMR data of **19** are similar to $PhCH_2PCl_2$ (δ_P 179 (t, $^2J_{P\text{-}H}$ 15.7 Hz), δ_H 3.51),[277] which while not directly comparable does contain the CH_2PCl_2 unit.

$^iPr_3SiC{\equiv}CCH_2Cl$

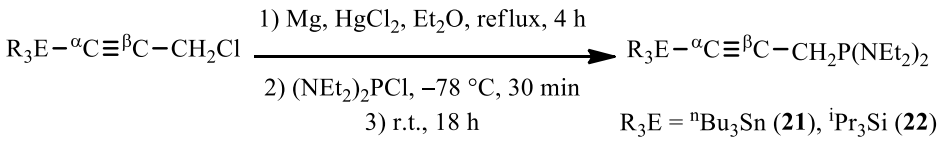
The attempted synthesis of $^iPr_3SiC{\equiv}CCH_2PCl_2$ (**20**) produced a yellow oil that was a similar mixture of products to **19**. The ^{31}P NMR spectrum exhibits five resonances, including a triplet signal at 171 ppm ($^2J_{P\text{-}H}$ 14.8 Hz) with a corresponding doublet signal at 2.5 ppm ($^2J_{H\text{-}P}$ 14.8 Hz) in the ^1H NMR spectrum (Table 13), and is tentatively attributed to **20**. A broad ^{31}P NMR resonance at 81.4 ppm (w½ ca. 24.2 Hz) is tentatively assigned to the bis-substituted compound $(R_3SiC{\equiv}CCH_2)_2PCl$, although the associated protons are not observed in the ^1H NMR spectrum due to the high number of overlapping signals Attempts to isolate any of the species by fractional distillation were unsuccessful; the liquid distils as a single fraction that exhibits an altered product mixture, including a singlet resonance at 3.53 ppm in the ^1H NMR spectrum, consistent with $^iPr_3SiC{\equiv}CCH_2Cl$ (**5**). The ^{31}P NMR spectrum exhibits new signals at –2.9 and 33.9 ppm, in addition to each of the species encountered prior to distillation.

Table 13. Selected spectroscopic data for $R_3SiC{\equiv}CCH_2PCl_2$ (**19** - **20**)

	R_3	^{31}P / ppm	^{1}H CH_2P / ppm	$^{2}J_{H\text{-}P}$ / Hz
19	Me_2Ph	170	2.57	14.6
20	$^{i}Pr_3$	171	2.55	14.8

2.4.2 Reactions of $R_3EC{\equiv}CCH_2Cl$ with $(NEt_2)_2PCl$

The installation and subsequent chlorination cleavage of the terminal $P(NEt_2)_2$ group is a well-established route to terminal phosphorus dihalides.[103,278–280,44,281] As such, the syntheses of $R_3EC{\equiv}CCH_2P(NEt_2)_2$ (**21** - **22**) were attempted by generation of the respective Grignard reagents followed by filtration into cold $ClP(NEt_2)_2$ (Scheme 60).



Scheme 60. Attempted syntheses of $R_3EC{\equiv}CCH_2P(NEt_2)_2$ (**21** - **22**)

$^{n}Bu_3SnC{\equiv}CCH_2Cl$

The attempted synthesis of $^{n}Bu_3SnC{\equiv}CCH_2P(NEt_2)_2$ (**21**) afforded a yellow oil that was determined by NMR spectroscopy to consist of a mixture of three phosphorus-containing products, none of which are consistent with **21**. The ^{31}P NMR spectrum shows two multiplets at 51.2 (ca. 5 %) and 51.3 ppm (ca. 10 %), and a broad signal at 60.9 ppm (ca. 85 %, $w_{½}$ ca. 45.9 Hz). The latter resonance correlates (*via* ^{1}H-^{31}P HMBC NMR study) to protons at 3.63 ($^{2}J_{H\text{-}P}$ 3.3 Hz, 1H), 3.06 (4H), 3.18 (4H), 1.01 ($^{3}J_{H\text{-}H}$ 7.2 Hz, 9H) and 0.88 ppm ($^{3}J_{H\text{-}H}$ 7.2 Hz, 12H), in the ^{1}H NMR spectrum, the relative integrations of which are consistent with one CH proton, two diethylamine groups, and three ^{n}Bu groups. Of particular note is the existence of two separate resonances for the CH_2 diethylamine protons, which suggests inequivalence of the diethylamine groups, possibly *via* a chiral phosphorus centre. In the absence of ^{1}H-^{13}C HSQC and HMBC NMR spectra (due to the rapid sample degradation) confirmation of the presence of alkenyl or alkynyl units is not possible and the identity of **21** remains unknown.

The initial yellow oil rapidly degrades into a viscous red oil that exhibits seven resonances in the $^{31}P\{^{1}H\}$ NMR spectrum, including three doublet signals at 57.0 ($^{2}J_{P\text{-}P}$ 79.8 Hz), 70.5 ($^{2}J_{P\text{-}P}$ 79.8 Hz) and 70.8 ppm ($^{2}J_{P\text{-}P}$ 79.8 Hz), which integrate in a 2:2:1 ratio respectively; resolution of the ^{31}P NMR spectrum is not possible due to signal broadening. Four additional multiplets are

present in the ^{31}P NMR spectrum, all of which defy assignment. The ^{1}H NMR spectrum exhibits a significantly broadened collection of signals, and most notably, the loss of the resonance attributed to the CH_2P proton formerly found at 3.63 ppm (Figure 17).

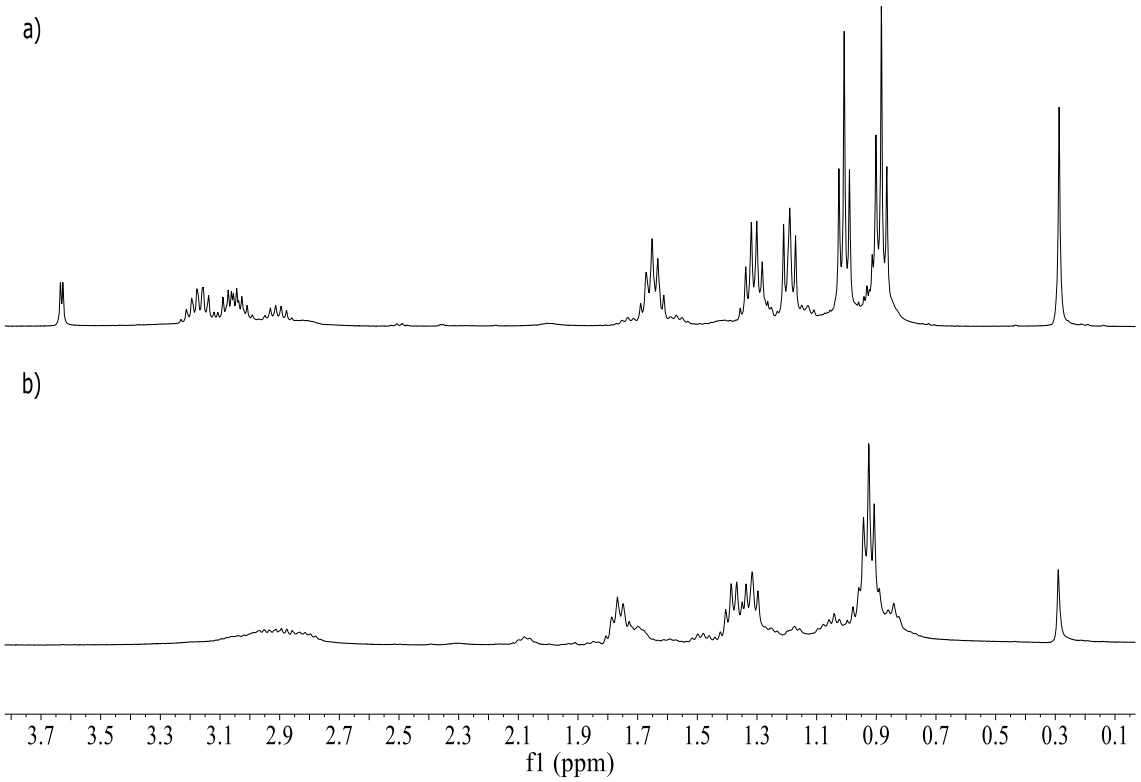


Figure 17. Selected section (0.1 - 3.7 ppm) of the ^{1}H NMR spectra of **21**; **a**) immediately, **b**) after 30 min

$^{i}Pr_3SiC{\equiv}CCH_2Cl$

The attempted synthesis of $^{i}Pr_3SiC{\equiv}CCH_2P(NEt_2)_2$ (**22**) afforded a yellow oil that was identified as a complex mixture of products. The ^{31}P NMR spectrum shows six resonances, including a broad signal at 154 ppm ($w_{½}$ ca. 70.4 Hz) that is attributed to $ClP(NEt_2)_2$.[282] An additional broad resonance at 83.6 ppm ($w_{½}$ ca. 43.5 Hz) corresponds (*via* ^{1}H-^{31}P HMBC NMR spectrum) to a doublet signal in the ^{1}H NMR spectrum at 2.55 ppm ($^{3}J_{H\text{-}P}$ 4.6 Hz), and is assigned to $^{i}Pr_3SiC{\equiv}CCH_2P(NEt_2)_2$. The chemical shift is consistent with a phosphorus centre bearing two diethylamine groups,[283] while the magnitude of coupling is comparable to the two-bond proton-phosphorus couplings of compounds **10 - 13**. The initial yellow oil rapidly (<10 min) degraded to form a pink oil, which was distilled to afford a colourless liquid. The ^{31}P NMR spectrum shows loss of the initial product mixture, and many new phosphorus-containing species in its place; significant quantities of $ClP(NEt_2)_2$ also remain. While there are fewer overlapping signals in the ^{1}H NMR spectrum than for the initial sample, no correlations to phosphorus

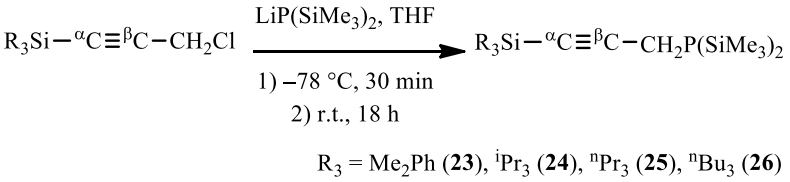
signals are exhibited in the ^{1}H-^{31}P HMBC NMR spectrum, and none of the species present can be identified.

2.5 Syntheses and reactions of $R_3SiC{\equiv}CCH_2P(SiMe_3)_2$

The syntheses of $R_3SiC{\equiv}CCH_2P(SiMe_3)_2$ (**23 - 26**) were attempted in order to gain access to propargylphosphines bearing phosphorus-silicon linkages that are prone to halodesilylation, as an alternative route to $R_3EC{\equiv}CCH_2PX_2$. Typical synthetic methodologies towards installing $P(SiMe_3)_2$ moieties include the addition of $LiP(SiMe_3)_2$,[284,62] or $P(SiMe_3)_3$ to R_3CCl.[285,286]

2.5.1 Syntheses of $R_3SiC{\equiv}CCH_2P(SiMe_3)_2$

The compounds $R_3SiC{\equiv}CCH_2P(SiMe_3)_2$ (**23 - 26**) were prepared from the reaction of $R_3SiC{\equiv}CCH_2Cl$ (**1 - 7**) with $LiP(SiMe_3)_2$ and obtained as red / brown oils that could not be further purified from a trace contaminant (Scheme 61). Attempts to isolate compounds **23 - 26** by washing (with pentane, hexane, DCM, Et_2O) and crystallisation proved ineffective, while distillation at reduced pressure afforded only $P(SiMe_3)_3$ and $HP(SiMe_3)_2$ (determined by ^{31}P NMR spectroscopy), with no evidence of **23 - 26**.



Scheme 61. Syntheses of $R_3SiC{\equiv}CCH_2P(SiMe_3)_2$ (**23 - 26**)

Compounds **23 - 26** exhibit ^{31}P NMR multiplet resonances at ca. −160 ppm; the chemical shifts are comparable with other bis(trimethylsilane)phosphine derivatives ($Cl(CH_2)_2P(SiMe_3)_2$, δ_P −175;[284] $Me_3SiCH_2P(SiMe_3)_2$, δ_P −163).[287] Each resonance is located at a significantly higher-field chemical shift than for $R_3EC{\equiv}CCH_2PPh_2$ (**8 - 13**), consistent with general trends of silyl versus alkyl phosphines (PPh_3 δ_P −6.0,[288] $P(SiMe_3)_3$ δ_P −252).[289] The ^{1}H HMR spectra show corresponding doublets at ca. 2.45 ppm ($^{2}J_{H\text{-}P}$ ca. 1.1 Hz) for the CH_2P protons (Table 14).

Compound $Me_2PhSiC{\equiv}CCH_2P(SiMe_3)_2$ (**23**) was the cleanest of the samples, which enabled a more thorough spectroscopic investigation to be performed. The $^{13}C\{^{1}H\}$ NMR spectrum exhibits a doublet resonance at 5.5 ppm ($^{1}J_{C\text{-}P}$ 23.2 Hz) that is assigned to the CH_2P carbon centre; this is shifted to significantly higher-field when compared to $R_3EC{\equiv}CCH_2PPh_2$ (**8 - 13**)

(δ_P ca. 19.9 ($^1J_{C\text{-}P}$ ca. 20 Hz)) but retains a comparable carbon-phosphorus coupling constant. The alkynic $^{\alpha}$C and $^{\beta}$C atoms are observed as a doublet resonance at 83.3 ($^3J_{C\text{-}P}$ 3.7 Hz) and a singlet signal at 109 ppm respectively, which are similar to compounds **8 - 13** (δ^{α}_C ca. 84.3 ($^3J_{C\text{-}P}$ ca. 5.7 Hz), δ^{β}_C ca. 106 ($^2J_{C\text{-}P}$ ca. 4.1 Hz)).

While isolation from the trace contaminant proved unsuccessful, alterations made to the reagent stoichiometries reduced its levels to ca. 8 % (by integration of the ^{31}P NMR spectra). This contaminant exhibits a ^{31}P NMR multiplet resonance at ca. −84.4 ppm; the chemical shift is consistent with a phosphorus centre bearing one $SiMe_3$ group (R_2PSiMe_3, δ_P −98.2 to – 53.7),[290] prompting its tentative identification as the bis-substituted product $(R_3SiC{\equiv}CH_2)_2PSiMe_3$, although correlating protons are not observed in either the ^{1}H NMR or ^{1}H-^{31}P HMBC NMR spectra.

Table 14. Selected spectroscopic data for $R_3SiC{\equiv}CCH_2P(SiMe_3)_2$ (**23 - 26**)

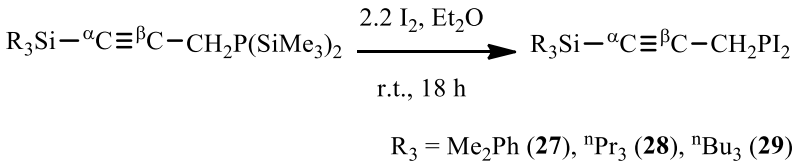
	R_3	^{31}P / ppm	^{1}H CH_2P / ppm	$^2J_{H\text{-}P}$ / Hz
23	Me_2Ph	−159	2.43	1.4
24	$^{i}Pr_3$	−161	2.45	-
25	$^{n}Pr_3$	−160	2.44	0.9
26	$^{n}Bu_3$	−160	2.46	0.9

Despite the initial success in the synthesis of compounds **23 - 26**, the reproducibility was variable; for reasons that have not been elucidated, **23 - 26** could subsequently only be produced as a minor species among vastly increased proportions (by integration) and numbers of by-products (including the tentatively identified $(R_3SiC{\equiv}CH_2)_2PSiMe_3$).

2.5.2 Reactions of $R_3SiC{\equiv}CCH_2P(SiMe_3)_2$

Syntheses and reactions of $R_3EC{\equiv}CCH_2PI_2$

The pursuit of $R_3SiC{\equiv}CCH_2PX_2$ was undertaken by the attempted double halodesilylation of $R_3SiC{\equiv}CCH_2P(SiMe_3)_2$ (**23 - 26**) to form $R_3SiC{\equiv}CCH_2PI_2$. Iodine crystals were added directly to $R_3SiC{\equiv}CCH_2P(SiMe_3)_2$ under a flow of argon to yield compounds that were identified as $R_3SiC{\equiv}CCH_2PI_2$ (**27 - 29**) (Scheme 62).



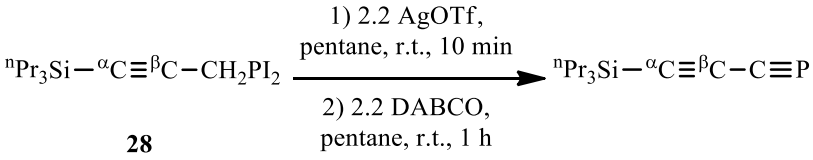
Scheme 62. Syntheses of $R_3SiC{\equiv}CCH_2PI_2$ (**27** - **29**)

Compounds **27** - **29** proved to be highly volatile and attempts to separate them from a variety of reaction solvents (Et_2O or pentane) by drying under reduced pressure result in product loss. Performing the reaction in tetraglyme was also successful, but attempts to isolate **27** - **29** by vacuum transfer afforded an unidentifiable mixture of products. Distillation at ambient pressure resulted in product degradation, as evidenced by the isolation of only iodine. Consequently, it was necessary to characterise $R_3SiC{\equiv}CCH_2PI_2$ (**27** - **29**) in solution. Triplet signals are observed in the ^{31}P NMR spectra at ca. 114 ppm ($^2J_{P\text{-}H}$ ca. 18.0 Hz) (Table 15), consistent with known compounds bearing terminal -PI_2 groups ($MePI_2$, δ_P 131;[291] $C_6H_8(PI_2)_2$, δ_P 138.3;[291] $Ph_2C(PI_2)_2$, δ_P 133.9).[291] The triplet signals correlate (by ^1H-^{31}P HMBC NMR spectroscopy) with doublet resonances in the ^1H NMR spectra at ca. 3.15 ppm ($^2J_{H\text{-}P}$ ca. 18.0 Hz); the coupling constants are typical of a two-bond proton-phosphorus separation.

Table 15. Selected data for $R_3SiC{\equiv}CCH_2PI_2$ (**27** - **29**)

	R_3	^{31}P / ppm	$^2J_{P\text{-}H}$ / Hz	^1H CH_2P / ppm
27	Me_2Ph	113.4	18.1	3.15
28	$^nPr_3$	113.8	17.7	3.12
29	$^nBu_3$	114.3	17.9	3.18

The double dehydrohalogenation of $R_3SiC{\equiv}CCH_2PI_2$ to form $R_3SiC{\equiv}CC{\equiv}P$ was attempted by addition of an excess (2.2 equivalents) of AgOTf to a pentane solution of $^nPr_3SiC{\equiv}CCH_2PI_2$ (**28**). The suspension was stirred for 10 min prior to the addition of excess (2.2 equivalents) DABCO, and the resulting suspension was stirred for 1 h (Scheme 63), after which time a pale yellow solution was isolated by filtration.

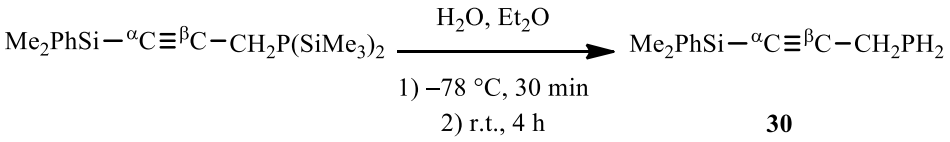


Scheme 63. Attempted double dehydrohalogenation of $^nPr_3SiC{\equiv}CCH_2PI_2$ (**28**)

No resonances are observed in the ^{31}P NMR or $^{31}P\{^{1}H\}$ spectra, while the ^{1}H NMR spectrum exhibits a singlet signal at 3.56 ppm, which is consistent with $^{n}Pr_3SiC{\equiv}CCH_2Cl$. Further pursuit of the chemistry was hindered by the lack of reagents available ($R_3SiC{\equiv}CCH_2PI_2$ (**27** - **29**)).

Synthesis of $Me_2PhSiC{\equiv}CCH_2PH_2$

In seeking more direct access to $Me_2PhSiC{\equiv}CC{\equiv}P$, the base-induced double dehydrohalogenation of $Me_2PhSiC{\equiv}CCH_2P(SiMe_3)_2$ (**23**) was attempted by the addition of NaOH. A yellow oil was afforded, in which the predominant product was identified as $Me_2PhSiC{\equiv}CCH_2PH_2$, presumably formed by the presence of trace amounts of H_2O in the NaOH. This was supported by performing additional reactions, wherein the stoichiometric addition of H_2O to $Me_2PhSiC{\equiv}CCH_2P(SiMe_3)_2$ (Scheme 64) generated a dark yellow oil in 89 % yield that was identified as $Me_2PhSiC{\equiv}CCH_2PH_2$ (**30**).



Scheme 64. Synthesis of $Me_2PhSiC{\equiv}CCH_2PH_2$ (**30**)

The ^{31}P NMR spectrum of **30** shows a triplet of triplets at −129 ppm ($^{1}J_{P\text{-}H}$ 192 Hz, $^{2}J_{P\text{-}H}$ 4.5 Hz) which is consistent with a PH_2 unit adjacent to a CH_2 group (Figure 18). Accordingly, the ^{1}H NMR spectrum exhibits two doublet of triplet signals at 1.92 ($^{3}J_{H\text{-}H}$ 7.2 Hz and $^{2}J_{H\text{-}P}$ 4.5 Hz) and 2.86 ppm ($^{1}J_{H\text{-}P}$ 192 Hz, $^{3}J_{H\text{-}H}$ 7.2 Hz) for the CH_2 and PH_2 protons in turn, correlation is confirmed by the ^{1}H-^{31}P HMBC NMR study. Each signal integrates as two protons when compared to the singlet resonance at 0.39 ppm assigned to the six methyl protons. The $^{13}C\{^{1}H\}$ NMR spectrum shows a doublet resonance at 4.26 ppm ($^{1}J_{C\text{-}P}$ 11.7 Hz) that is attributed to the CH_2 group, which is shifted significantly higher-field than $Me_2PhSiC{\equiv}CCH_2P(SiMe_3)_2$ (**23**) and exhibits a much smaller coupling constant (δ_C 5.5 ($^{1}J_{C\text{-}P}$ 23.2 Hz)). The alkynic carbon atoms are located at similar positions to **23**, as doublet and singlet resonances at 84.0 ($^{3}J_{C\text{-}P}$ 3.4 Hz) and 108 ppm, attributed to the $^{\alpha}C$ and $^{\beta}C$ alkynic carbon centres respectively.

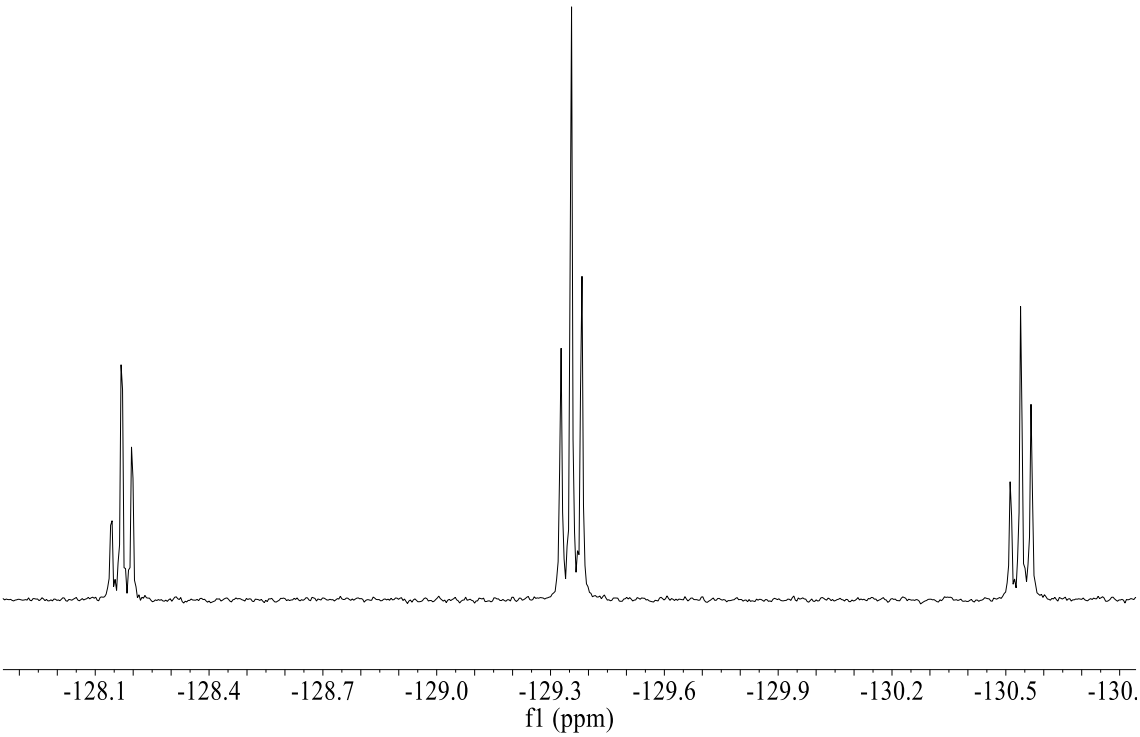
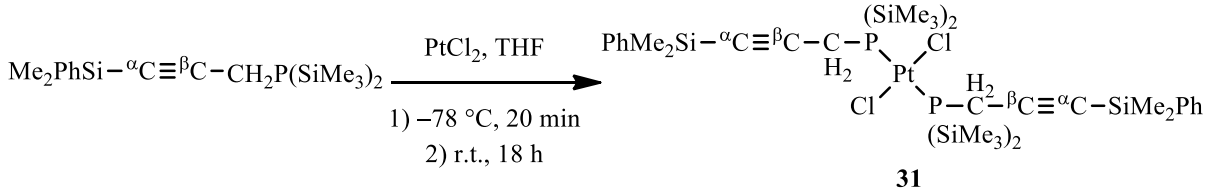


Figure 18. Selected section (−128 to −130 ppm) of the ^{31}P NMR spectrum of $Me_2PhSiC{\equiv}CCH_2PH_2$ (**30**)

Synthesis of *trans*-[$PtCl_2${$Me_2PhSiC{\equiv}CCH_2P(SiMe_3)_2$}$_2$]

While investigation of the coordination chemistry of $R_3SiC{\equiv}CCH_2P(SiMe_3)_2$ (**23**-**26**) was hindered by the lack of analytically pure reagents, it was possible to synthesise *trans*-[$PtCl_2${$Me_2PhSiC{\equiv}CCH_2P(SiMe_3)_2$}$_2$] (**31**) by addition of $PtCl_2$ to $Me_2PhSiC{\equiv}CCH_2P(SiMe_3)_2$ (Scheme 65). Complex **31** was isolated as a viscous brown oil (76 % yield), presumably indicative of the presence of impurity, although none was observed in the ^{31}P NMR spectrum. In contrast, attempts to coordinate impure samples of **24** - **26** were unsuccessful and ultimately resulted in complete degradation of compounds **24** - **26**; the ^{31}P NMR spectra exhibited in excess of 10 resonances, none of which could be assigned.



31

Scheme 65. Synthesis of *trans*-[$PtCl_2${$Me_2PhSiC{\equiv}CCH_2P(SiMe_3)_2$}$_2$] (**31**)

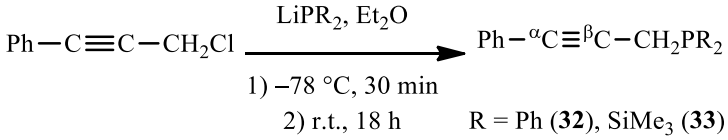
The ^{31}P NMR spectrum of **31** exhibits a broad resonance at −97.9 ppm ($^{1}J_{P\text{-}Pt}$ 1919 Hz, $w_{½}$ ca. 24.2 Hz) with satellites of a magnitude that is consistent with *trans*-coordination, and comparable to *trans*-[$PtCl_2(^{n}Pr_3SiC{\equiv}CCH_2PPh_2)_2$] (***trans*-16**). The ^{1}H NMR study shows a triplet signal at 3.00 ppm ($J_{H\text{-}P}$ = 5.9 Hz) for the CH_2P protons, which integrates as four protons when compared to the singlet resonance at 0.38 ppm attributed to the twelve methyl protons. The ^{195}Pt{^{1}H} NMR spectrum exhibits a triplet signal at −3696 ppm ($^{1}J_{Pt\text{-}P}$ 1919 Hz) which is consistent with a four-coordinate platinum centre bound to two chemically equivalent phosphorus atoms. A triplet resonance at 4.71 ppm ($^{1}J_{C\text{-}P}$ 14.1 Hz) in the ^{13}C{^{1}H} NMR spectrum is assigned to the CH_2P centre, while triplet signals due to the $^{\alpha}$C and $^{\beta}$C alkynic carbon atoms are found at 84.7 ($J_{C\text{-}P}$ 2.9 Hz) and 106 ppm ($J_{C\text{-}P}$ 6.2 Hz).

2.6 Syntheses and reactions of $PhC{\equiv}CCH_2PR_2$

Given the mixed results achieved for the attempted syntheses of main group propargylphosphines (**8 - 13** and **19 - 29**), the analogous reactions were performed with the all-carbon-containing chloropropargyl $PhC{\equiv}CCH_2Cl$ in order to probe the influence of the main group fragment on the reactions. The synthesis of $PhC{\equiv}CCH_2PPh_2$ has been previously achieved by addition of $LiPPh_2$ to $PhC{\equiv}CCH_2Br$, although characterising data were limited to a ^{31}P NMR shift at −13.1 ppm.[86]

2.6.1 Syntheses of $PhC{\equiv}CCH_2PR_2$

The compounds $PhC{\equiv}CCH_2PR_2$ (**32 - 33**) were afforded from addition of $PhC{\equiv}CCH_2Cl$ in Et_2O to an Et_2O solution of $LiPR_2$ and isolated as impure oils (Scheme 66). Small quantities of unidentified by-products remained that could not be removed by washing with pentane, crystallisation or distillation, precluding microanalysis. The products proved unstable to ESI mass spectrometry; there was no signal at the expected mass and no identifiable fragments were ascertained.



Scheme 66. Syntheses of $PhC{\equiv}CCH_2PR_2$ (**32 - 33**)

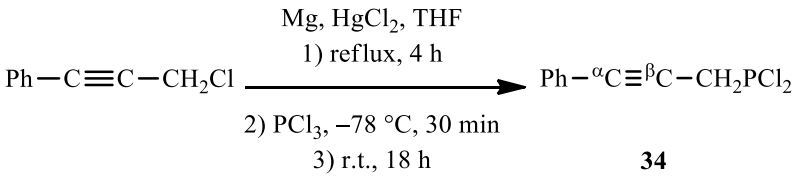
$PhC{\equiv}CCH_2PPh_2$ (**32**) exhibits a broad multiplet at −13.5 ppm ($^2J_{P\text{-}H}$ 6.8 Hz, $w_{½}$ ca. 21.9 Hz) in the ^{31}P NMR spectrum that is consistent with previous reports of **32**;[86] the multiplet splitting is attributed to coupling to the *ortho*-CH protons of the phosphine phenyl rings as determined by ^1H-^{31}P HMBC NMR studies. $PhC{\equiv}CCH_2P(SiMe_3)_2$ (**33**) shows a singlet signal at −159 ppm in the $^{31}P\{^1H\}$ NMR spectrum that is comparable to disilylphosphine $Cl(CH_2)_2P(SiMe_3)_2$,[284] in addition to compounds **23 - 26**. The ^{31}P NMR resonances of **32** and **33** correlate (by ^1H-^{31}P HMBC NMR spectra) to doublet resonances at 2.92 ($^2J_{H\text{-}P}$ 2.4 Hz) and 2.60 ppm ($^2J_{H\text{-}P}$ 1.6 Hz) respectively in the ^1H NMR spectrum, assigned to the CH_2P protons (Table 16). These signals integrate as two protons when compared to the 15 aromatic protons present in **32** (at δ_H 6.92 to 7.73) and the 18 $SiMe_3$ protons in **33** (at δ_H 0.30 ($^3J_{H\text{-}P}$ 4.6 Hz)). The $^{13}C\{^1H\}$ NMR spectrum of **32** exhibits a doublet resonance at 19.4 ppm ($^1J_{C\text{-}P}$ 19.2 Hz) for the CH_2P carbon, and two further doublet signals at 83.6 ($^3J_{C\text{-}P}$ 5.8 Hz, $^{\alpha}C$) and 86.7 ppm ($^2J_{C\text{-}P}$ 4.3 Hz, $^{\beta}C$) for the alkynic centres. The $^{13}C\{^1H\}$ NMR spectrum of **33** shows a doublet resonance at 5.08 ppm ($^1J_{C\text{-}P}$ 22.5 Hz), assigned to the CH_2P carbon centre, a doublet resonance for the $^{\alpha}C$ atom at 81.6 ($^3J_{C\text{-}P}$ 4.1 Hz) and a singlet signal at 90.7 ppm for the $^{\beta}C$ centre. The significant difference in chemical shifts between the $^{\alpha}C$ and $^{\beta}C$ alkynic carbons atoms ($\Delta\delta_C$ 3.1 for **32** and $\Delta\delta_C$ 9.1 for **33**) is consistent with **33** possessing a highly polarised triple bond due to the disparity in electron-donor/acceptor strengths of the terminal groups, which is small for **32** and large for **33**. The comparatively high-field chemical shift of the CH_2P group in the $^{13}C\{^1H\}$ and ^1H NMR spectra of **33** may also be attributed to the strongly electron-releasing $P(SiMe_3)_2$ group. Attempts to coordinate phosphines **32** and **33** to transition metal complexes were hindered by the reagent impurities; reactions with $[Pd(1,5\text{-}COD)Cl_2]$ and $PtCl_2$ both afforded a complex mixture of products, from which isolation of any species was unsuccessful.

Table 16. Selected spectroscopic data for $PhC{\equiv}CCH_2PR_2$ (**32 - 33**)

	$^{31}P\{^1H\}$ / ppm	^1H CH_2P / ppm	$^2J_{H\text{-}P}$ / Hz	$^{13}C\{^1H\}$ CH_2P / ppm	$^1J_{C\text{-}P}$ / Hz	$^{13}C\{^1H\}$ $^{\alpha}C$ / ppm	$^3J_{C\text{-}P}$ / Hz	$^{13}C\{^1H\}$ $^{\beta}C$ / ppm	$^2J_{C\text{-}P}$ / Hz
32	−13.5	2.92	2.4	19.4	19.2	83.6	5.8	86.7	4.3
33	−159	2.60	1.6	5.08	22.5	81.6	4.1	90.7	-

2.6.2 Attempted synthesis of $PhC{\equiv}CCH_2PCl_2$

$PhC{\equiv}CCH_2Cl$ was added to activated magnesium with mercuric chloride as the initiator, brought to reflux for 4 h, and filtered into PCl_3 at −78 °C (Scheme 67). An orange oil was isolated and identified as a mixture of products that included $PhC{\equiv}CCH_2PCl_2$ (**34**), although purification by washing or recrystallisation proved unsuccessful.

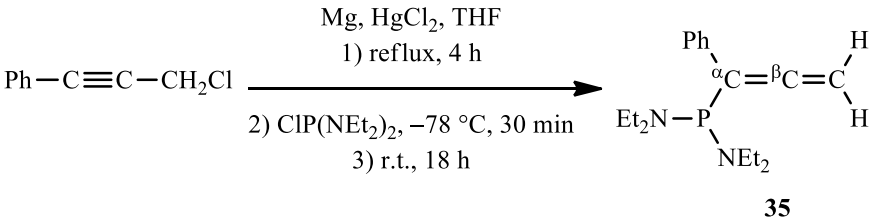


Scheme 67. Attempted synthesis of $PhC{\equiv}CCH_2PCl_2$ (**34**)

The ^{31}P NMR spectrum shows in excess of ten phosphorus-containing species, including a triplet signal at 171 ppm ($^2J_{P\text{-}H}$ 14.5 Hz) which is attributed to $PhC{\equiv}CCH_2PCl_2$ (**34**) and is consistent with comparable species ($PhCH_2PCl_2$, δ_P 179).[277] The ^1H-^{31}P HMBC NMR spectrum shows correlation to a doublet resonance at 2.74 ppm ($^2J_{H\text{-}P}$ 14.5 Hz) in the ^1H NMR spectrum for the CH_2P protons. The proton-phosphorus coupling constant is consistent with $PhCH_2PCl_2$ (δ_H 3.51 ($^2J_{P\text{-}H}$ 15.7 Hz)), while the ^1H NMR chemical shift is comparable to chloropropargyls **1** - **7** (δ_H ca. 3.57).

2.6.3 Synthesis of $Ph\{(NEt_2)_2P\}C{=}C{=}CH_2$

The synthesis of $PhC{\equiv}CCH_2P(NEt_2)_2$ was attempted *via* reaction of the Grignard reagent $PhC{\equiv}CCH_2MgCl$ with $ClP(NEt_2)_2$. The product was isolated as a dark red oil in 76 % yield; although analytical purity was not obtained, the predominant species was present in >70 % by integration of the ^{31}P NMR spectrum, identified as $Ph\{(NEt_2)_2P\}C{=}C{=}CH_2$ (**35**, Scheme 68).



Scheme 68. Synthesis of $Ph\{(NEt_2)_2P\}C{=}C{=}CH_2$ (**35**)

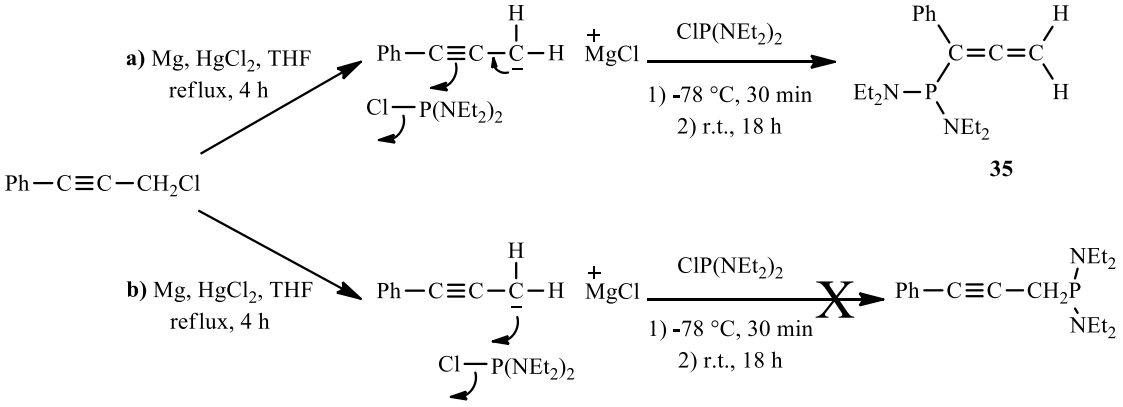
Compound **35** exhibits a broad resonance at 90.9 ppm ($w_{½}$ ca. 42.7 Hz) in the ^{31}P NMR spectrum which is consistent with a phosphorus atom bound to two diethylamine groups ($H_2C{=}C(H)P(NEt_2)_2$ δ_P 89.9, $PhP(NEt_2)_2$ δ_P 97.2).[283,292] Further minor resonances are observed at 18.8, 83.2, 118.2, 153.4 ppm, the latter of which is attributed to $ClP(NEt_2)_2$. The ^1H NMR spectrum shows resonances at 0.91 ($^3J_{H\text{-}H}$ 7.1 Hz) and 3.07 ppm for the diethylamine groups, and 4.72 ppm ($^4J_{H\text{-}P}$ 7.1 Hz) for the CH_2 protons (the ^1H-^{13}C HSQC NMR spectrum confirms the presence of a CH_2 group). Integration of these signals confirms the presence of two CH_2 protons

and two diethylamine groups when compared to the aromatic resonances, which integrate to one phenyl ring. The $^{13}C\{^{1}H\}$ NMR spectrum shows doublet signals at 106 ($^{1}J_{C\text{-}P}$ 14.1 Hz) and 210 ppm ($^{2}J_{C\text{-}P}$ 11.3 Hz) that are attributed to the $^{\alpha}C$ and $^{\beta}C$ centres in turn, and a singlet signal at 75.0 ppm for the CH_2 centre. The ^{1}H-^{13}C HMBC NMR spectrum confirms each of these resonances is contained within one compound. The spectroscopic characteristics of **35** are not consistent with the projected propargylic product $PhC{\equiv}CCH_2P(NEt_2)_2$; the resonance in the ^{1}H NMR spectrum attributed to the CH_2 protons is shifted significantly down-field and exhibits a larger proton-phosphorus coupling constant than known propargylphosphines, while the $^{13}C\{^{1}H\}$ NMR signals are also located at more down-field shifts. Compound **35** was identified as $Ph\{(NEt_2)_2P\}C{=}C{=}CH_2$ by comparison with allenes in the literature (Table 17).[293,256,294] The ^{1}H NMR resonance for the CH_2 protons is comparable with phosphorus-containing allenes $R(H_2P)C{=}C{=}CH_2$ (δ_H 4.51 ($^{4}J_{H\text{-}P}$ 4.1 Hz)),[295] while the extreme down-field shift of the $^{\beta}C$ and $^{\alpha}C$ centres are consistent with allenic carbon atoms.[293,256,294] Allenes bearing phosphorus substituents are extremely rare;[256,296,297] to date, only one publication has reported full spectroscopic data for a series of phosphorus-containing allenes $R(H_2P)C{=}C{=}CR'_2$.[295]

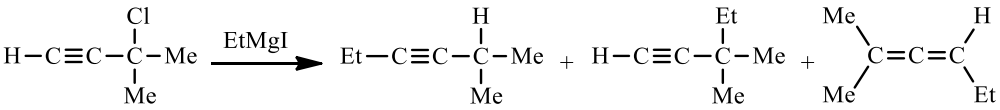
Table 17. Selected spectroscopic data for propargylphosphines (**10**, **32** - **33**) and allenes (**35**)

	Compound	**^{1}H CH_2 / ppm**	**J_{H-P} / Hz**	**$^{13}C\{^{1}H\}$ CH_2 / ppm**	**J_{C-P} / Hz**	**$^{13}C\{^{1}H\}$ $^{\alpha}C$ / ppm**	**J_{C-P} / Hz**	**$^{13}C\{^{1}H\}$ $^{\beta}C$ / ppm**	**$^{2}J_{C-P}$ / Hz**	**Source**
10	$Me_2PhSiC{\equiv}CCH_2PPh_2$	2.76	2.9	19.8	20.7	84.7	4.9	105	3.6	This work
32	$PhC{\equiv}CCH_2PPh_2$	2.92	2.4	19.4	19.2	83.6	5.8	86.7	4.3	This work
33	$PhC{\equiv}CCCH_2P(SiMe_3)_2$	2.60	1.6	5.08	22.5	81.6	4.1	90.7	-	This work
35	$Ph\{(NEt_2)_2P\}C{=}C{=}CH_2$	4.72	7.1	75.0	-	106	14.1	210	11.3	This work
	$C_6H_{10}{=}C{=}CH_2$	4.58	-	72.5	-	101	-	204	-	293
	$C_6H_{11}(Me)C{=}C{=}CH_2$	4.59	-	74.4	-	104	-	206	-	293
	$H(H_2P)C{=}C{=}CH_2$	4.60	-	71.7	6.9	72.3	11.9	213	14.6	295
	$Me(H_2P)C{=}C{=}CH_2$	4.51	4.1	70.7	8.1	83.9	9.2	210	20.4	295
	$H(H_2P)C{=}C{=}CMe_2$	-	-	92.9	9.0	71.1	7.7	210	16.0	295

The formation of **35** can be rationalised by considering the reactivity of the $[PhCCCH_2]^-$ anion in terms of hard/soft acid/base character (Scheme 69). While softer electrophiles preferentially react with softer nucleophiles like the sp^3 "$PhC{\equiv}CCH_2^-$" centre produced in pathway **b**), harder electrophiles, which include $ClP(NEt_2)_2$, are predisposed to react preferentially with harder nucleophiles, as exemplified by the *sp* "$PhC^-{=}C{=}CH_2$" centre generated *via* pathway **a**). Allenes in literature have been synthesised by the reactions of propargylhalides with Grignard reagents,[298–300] sometimes in admixture with propargylic products (Scheme 70),[299] providing precedent for the proposed route for the production of **35** from the Grignard reaction of $PhC{\equiv}CCH_2Cl$ and subsequent quenching with $ClP(NEt_2)_2$.



Scheme 69. Proposed mechanism for the synthesis of $Ph\{(NEt_2)_2P\}C{=}C{=}CH_2$ (**35**)



Scheme 70. Literature syntheses of allenes in admixture with propargylic species [299]

As previously described, the CH_2 protons exhibit an apparent doublet resonance in the ^1H NMR spectrum at ambient temperature, which is unexpected given the asymmetry of **35**; the lack of free rotation about the double bond would render the protons inequivalent. It is possible that the doublet resonance is in fact two overlapping doublets which cannot be appropriately resolved, although the doublet resonance possesses a relatively narrow half-height width ($w_{½}$) of 1.85 Hz. Nevertheless, a variable temperature (−80 to 30 °C) ^1H NMR study successfully demonstrates the inequivalence of the CH_2 protons between −10 and 0 °C (Figure 19), which further supports the identity of **35**. At temperatures lower than −10 °C the signals broaden, most likely due to

chemical shift anisotropy effects (due to reduced molecular tumbling at low temperature), although the existence of a further unrelated dynamic process cannot be ruled out.

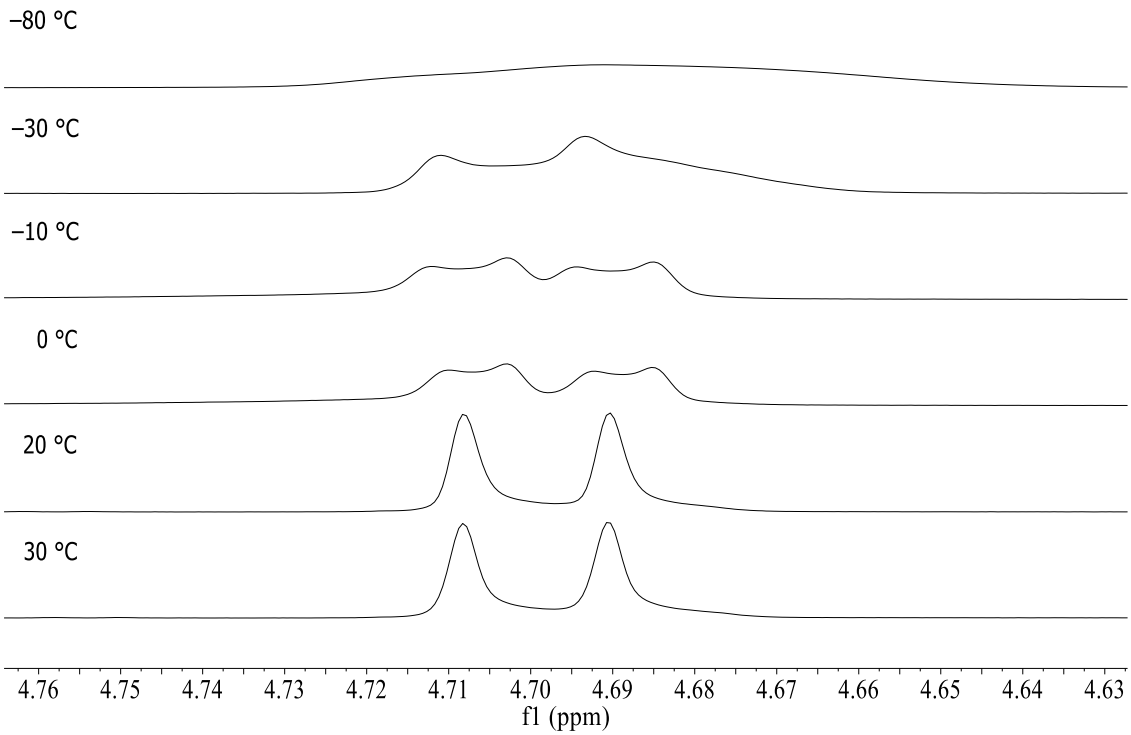


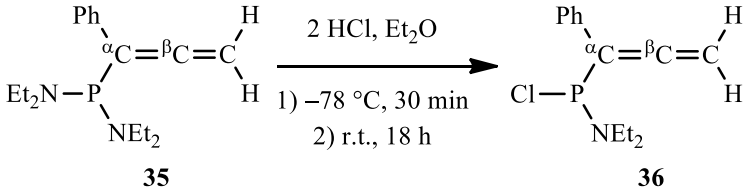
Figure 19. A selection (4.63 - 4.76 ppm) of the variable temperature ^{1}H NMR study of **35**

2.6.4 Reactions of Ph{(NEt$_2$)$_2$P}C=C=CH$_2$

Given the scarcity of phosphorus-containing allenes in the literature, reactivity studies have been rare. As such, the reactivity of **35** was probed by reaction with HCl and MeI in an attempt to install halogen centres in place of the diethylamine groups. Aminophosphines ($R_2PNR'_2$) in literature react characteristically with exactly two equivalents of HCl to generate the chlorinated species (R_2PCl).[301,44] In contrast, the addition of MeI to traditional phosphines (R_3P) reportedly generates phosphonium salts $[R_3MeP]^+[I]^-$,[302–304] or five-coordinate phosphoranes R_3MePI.[305,306] Reactions of MeI with aminophosphines are undocumented, although the propensity of diethylamine to behave as a leaving group may well achieve replacement of a diethylamine group with an iodine centre.

Reactions with HCl

The addition of exactly two equivalents of HCl to **35** afforded an orange oil that was identified as the anticipated product, Ph{(NEt_2)(Cl)P}C=C=CH_2 (**36**) (Scheme 71).



35 **36**

Scheme 71. Synthesis of Ph{(NEt_2)(Cl)P}C=C=CH_2 (**36**)

Compound **36** exhibits a broad signal at 122 ppm ($w_{½}$ ca. 40.6 Hz) in the ^{31}P NMR spectrum that is consistent with a phosphorus centre bound to one diethylamine group and one chlorine atom (MeP(Cl)NEt_2 δ_P 143).[282] This resonances correlates to two overlapping doublet of doublet signals at 4.90 ppm ($^4J_{H\text{-}P}$ 5.6 Hz) and 4.91 ppm ($^4J_{H\text{-}P}$ 6.3 Hz) in the ^{1}H NMR spectrum (Figure 20), each of which integrates as one proton when compared to a triplet resonance at 0.81 ppm ($^3J_{H\text{-}H}$ 7.1 Hz) and a multiplet signal at 2.94 ppm, assigned to one diethylamine group. The aromatic signals at 7.00, 7.11 and 7.50 ppm also integrate to one phenyl ring compared to the rest of the compound. The ^{13}C{^{1}H} NMR spectrum shows a singlet resonance at 77.6 ppm that is attributed to the CH_2 carbon, and doublet signals at 105 ($^1J_{C\text{-}P}$ 39.3 Hz) and 211 ppm ($^2J_{C\text{-}P}$ 8.3 Hz) that are assigned to the $^{\alpha}$C and $^{\beta}$C atoms; all of the spectroscopic data of **36** are comparable with those of **35**, evidencing retention of the allene unit.

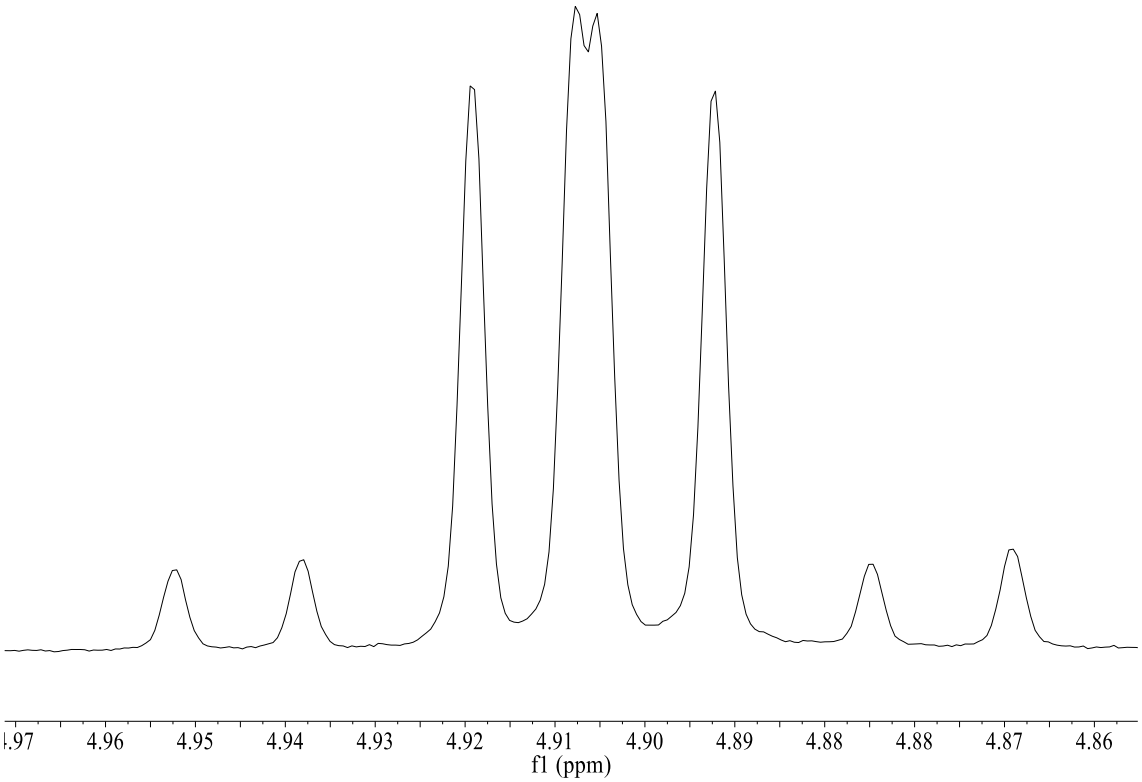
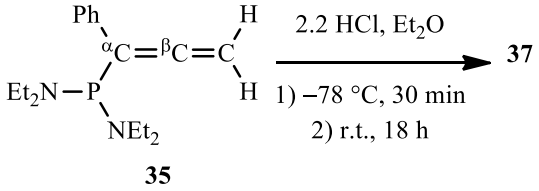


Figure 20. Selected section (4.86 - 4.97 ppm) of the ^{1}H NMR spectrum of **36**

The reaction of **35** with an excess (2.2 equivalents) of HCl was performed in an attempt to install chlorine atoms in place of both diethylamine groups. However, the yellow oil (**37**) isolated from the reaction has thus far eluded identification (Scheme 72).



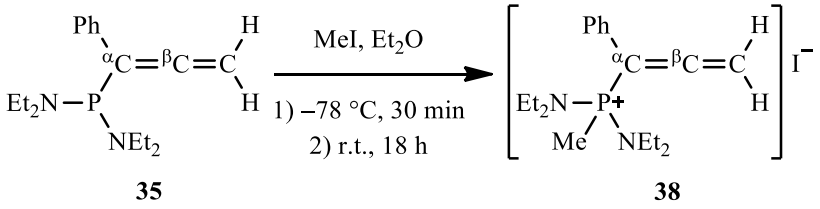
Scheme 72. The reaction of **35** with 2.2 HCl affords **37**

The ^{31}P NMR spectrum shows a multiplet resonance at 58.7 ppm that is most comparable in chemical shift with a phosphorus centre bound to one chlorine atom (Ph_2PCl, δ_P 82.3, ^{t}BuP(C≡CPh)Cl δ_P 71.9).[274,275] A doublet signal at 4.64 ppm ($^{2}J_{H\text{-}P}$ 2.2 Hz) in the ^{1}H NMR spectrum is assigned to a CH group, confirmed by ^{1}H-^{13}C HSQC NMR spectroscopy, which integrates to one proton when compared to the aromatic resonances at 7.05, 7.47 and 7.63 that integrate to five phenyl protons. No further significant resonances are observed in the ^{1}H NMR

spectrum, which is consistent with the loss of both diethylamine groups. The $^{13}C\{^{1}H\}$ NMR spectrum exhibits a doublet signal at 79.3 ppm ($J_{C\text{-}P}$ 9.2 Hz) that is assigned to the CH carbon centre, while singlet and doublet resonances at 110 and 210 ppm ($^{1}J_{C\text{-}P}$ 30.0 Hz) are attributed to the $^{\alpha}C$ and $^{\beta}C$ allenic carbon atoms in turn. The $^{13}C\{^{1}H\}$ NMR data is consistent with retention of the allene, and comparable to **35 - 36**.

Synthesis of $[Ph\{(NEt_2)_2MeP\}C{=}C{=}CH_2]^+[I]^-$

The reaction of $Ph\{(NEt_2)_2P\}C{=}C{=}CH_2$ (**35**) with MeI afforded a viscous orange oil that was tentatively identified as $[Ph\{(NEt_2)_2MeP\}C{=}C{=}CH_2]^+[I]^-$ (**38**) (Scheme 73).



35 **38**

Scheme 73. Synthesis of $[Ph\{(NEt_2)_2MeP\}C{=}C{=}CH_2]^+[I]^-$ (**38**)

The ^{31}P NMR spectrum of **38** exhibits a multiplet signal at 57.4 ppm that correlates to a doublet resonance at 5.48 ppm ($^{2}J_{H\text{-}P}$ 12.1 Hz) in the ^{1}H NMR spectrum, and is assigned to the CH_2 protons. This signal integrates to two protons when compared to a doublet resonance at 2.85 ppm ($^{2}J_{H\text{-}P}$ 13.2 Hz) that is attributed to the methyl group; both coupling constants are consistent with a two-bond proton-phosphorus separation ($PhCH_2PCl_2$ δ_P 179 (t, $^{2}J_{P\text{-}H}$ 15.7 Hz)),[277] supporting the presence of a CH_2PMe unit. Triplet and multiplet resonances at 0.85 ($^{3}J_{H\text{-}H}$ 7.1 Hz) and 2.99 ppm are assigned to two diethylamine groups by integration, and signals at 7.05, 7.23 and 7.44 ppm integrate consistently for one phenyl ring. The $^{13}C\{^{1}H\}$ NMR spectrum exhibits a multiplet signal at 96.2 ppm that is assigned to the CH_2 centre, and singlet and multiplet signals (that could not be fully resolved) at 131 and 216 ppm that are attributed to the allenic carbon atoms.

Vinylphosphonium salts in the literature exhibit comparable ^{31}P NMR resonances to **38** (Table 18),[307–309] and typically feature extremely large one-bond-separation carbon-phosphorus coupling constants in the $^{13}C\{^{1}H\}$ NMR spectra.[308]

Table 18. Selected spectroscopic data for **38** and phosphonium salts in literature [307–309]

Compound	**^{31}P / ppm**	**^{13}C{^{1}H} $^{\alpha}$C / ppm**	**$^{1}J_{C-P}$ / Hz**	**^{13}C{^{1}H} $^{\beta}$C / ppm**	**$^{2}J_{C-P}$ / Hz**	**Source**
$[Ph\{(NEt_2)_2MeP\}C{=}C{=}CH_2]^+[I]^-$ (**38**)	57.4	131	-	216	-	This work
$[(Me_2N)_3PC(H){=}C(H)C_6H_4(4\text{-}Me)]^+[Cl]^-$	48.3	106	161	152	6.0	307
$[(Me_2N)_3PMe]^+[Cl]^-$	59.2	7.2	113	-	-	307
$[(Me_2N)_3PC(H){=}C(H)C_6H_4(4\text{-}Cl)]^+[BPh_4]^-$	51.6	109	162	150	6.6	307
$[(Me_2N)_3PC(H){=}C(H)C_6H_4(4\text{-}NO_2)]^+[BPh_4]^-$	50.7	113	161	149	6.6	307
$[Ph_3P(Me)C{=}CMe_2]^+[C_6H_9\text{-}OTf]^-$	23.8	119	78.0	156	7.8	308
$[Ph_3P(Me)C{=}CMe_2]^+[Me_2C{=}CH\text{-}OTf]^-$	11.7	103	90.0	172	1.4	308
$[C_{10}H_7(1,2\text{-}OH)_2(4\text{-}P(NEt_2)_3)]^+[Cl]^-$	50.5	105	155	129	14.3	309
$[C_{10}H_7(1,2\text{-}OH)_2(3\text{-}Br)(4\text{-}P(NEt_2)_3)]^+[Br]^-$	48.2	109	157	126	5.5	309

2.7 Summary

A series of main group chloropropargyls ($R_3EC{\equiv}CCH_2Cl$, E = Si, Sn) has been successfully synthesised and characterised fully by spectroscopic and microanalytical methods. The Grignard reactions of $R_3EC{\equiv}CCH_2Cl$ followed by addition of chlorophosphines proved ineffective for the syntheses of $R_3EC{\equiv}CCH_2PX_2$ (X = Cl, NEt_2); while several examples did provide some evidence of successful synthesis of $R_3EC{\equiv}CCH_2PX_2$ (X = Cl, I, NEt_2), full conversion to the desired product, or indeed isolation of $R_3EC{\equiv}CCH_2PX_2$, ultimately proved unsuccessful. Attempts to convert crude samples of $R_3EC{\equiv}CCH_2PI_2$ to $R_3EC{\equiv}CC{\equiv}P$ by the double dehydrohalogenation method (addition of AgOTf and DABCO) were futile; no evidence for successful conversion was found, as the ^{31}P NMR spectra of the products did not exhibit any resonances whatsoever.

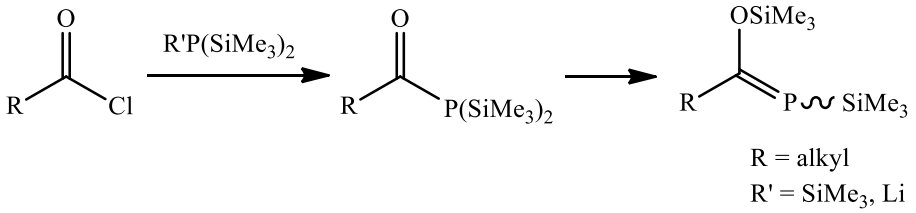
In contrast, the conversion of $R_3EC{\equiv}CCH_2Cl$ to main group propargylphosphines by addition of lithiated phosphines was successful; $R_3EC{\equiv}CCH_2PR_2$ (R = Ph, $SiMe_3$) were afforded in high yields, and with analytical purity for $R_3EC{\equiv}CCH_2PPh_2$. Coordination studies showed that $R_3EC{\equiv}CCH_2PR_2$ (R = Ph, $SiMe_3$) essentially behaved as typical phosphines upon reaction with late transition metal species, allowing the isolation and full characterisation of novel coordination complexes. Initial reactivity studies of $R_3EC{\equiv}CCH_2P(SiMe_3)_2$ towards I_2 were explored, with strong evidence for the successful conversion to $R_3EC{\equiv}CCH_2PI_2$ found; however, a thorough investigation was hindered by the lack of analytically pure $R_3EC{\equiv}CCH_2P(SiMe_3)_2$. Further exploration may yet show that $R_3EC{\equiv}CCH_2P(SiMe_3)_2$ and $R_3EC{\equiv}CCH_2PI_2$ are viable intermediates *en route* to phosphadiynes.

A brief foray into the analogous reactions of the all-carbon-containing chloropropargyl $PhC{\equiv}CCH_2Cl$ provided intriguing results; similar to $R_3EC{\equiv}CCH_2Cl$, the isolation of $PhC{\equiv}CCH_2PR_2$ (R = Ph, $SiMe_3$) was successful, albeit that analytical purity was not obtained. Further, the Grignard reaction of $PhC{\equiv}CCH_2Cl$ and subsequent addition to PCl_3 afforded a mixture of products, including $PhC{\equiv}CCH_2PCl_2$, which could not be isolated or further improved upon. In contrast, the Grignard reaction followed by addition to $ClP(NEt_2)_2$ yielded a rare example of a phosphorus-containing allene, $Ph\{(NEt_2)_2P\}C{=}C{=}CH_2$ (**35**). Reactivity studies of **35** with HCl and MeI demonstrated reaction solely at the phosphorus centre, with retention of the allene moiety evidenced by NMR spectroscopy. These reactions suggested that incorporation of the main group fragment in chloropropargyls ($R_3EC{\equiv}CCH_2Cl$) had a more profound effect on the reactivity pathway than anticipated, particularly with regard to the Grignard/$ClP(NEt_2)_2$ reaction.

3. In pursuit of conjugated phosphaalkenes and phosphaalkynes

3.1 Introduction

Since the first reported synthesis of stable phosphaalkenes,[94] many compounds of the general formula $RC(OSiMe_3)=PSiMe_3$ have been documented.[95,310,311] The Becker synthesis of phosphaalkenes is one of the most well-established synthetic routes,[310,311] and requires the addition of a silylated phosphine or phosphide ($P(SiMe_3)_3$ or $LiP(SiMe_3)_2$) to an acyl chloride to form an intermediate acyl phosphine $RC(O)P(SiMe_3)_2$ with elimination of $SiMe_3Cl$ or LiCl. The acyl phosphine undergoes a spontaneous [1,3]-silatropic rearrangement to produce the phosphaalkene $RC(OSiMe_3)=PSiMe_3$ (Scheme 74), reportedly driven by the oxophilicity of the silicon centre.

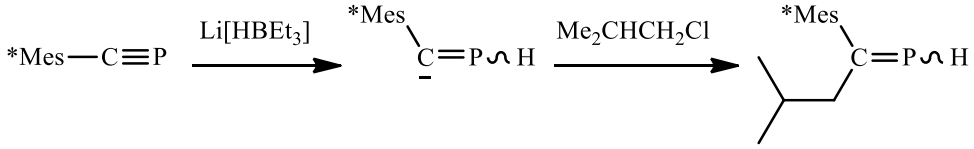


Scheme 74. Becker synthesis of phosphaalkenes [94]

Due to hindered rotation about the double bond, phosphaalkenes can exist as either *E*- or *Z*-isomers, which are easily distinguishable from one another by NMR spectroscopy when present as a mixture; the *Z*-isomer exhibits a higher-field chemical shift in both the ^{31}P and $^{13}C\{^1H\}$ NMR spectra, and the C=P carbon centre shows a greater magnitude of carbon-phosphorus coupling.[103] However, when only a single isomer is present, spectroscopic identification can be extremely challenging. While interconversion between the isomers has rarely been reported,[107] preferential synthesis of a single isomer can be achieved by careful selection of the reaction conditions,[108] although such conditions do not apply to all systems.

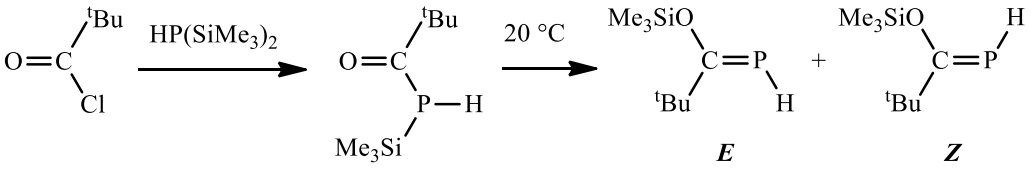
In contrast to the silyl phosphaalkenes $RC(OSiMe_3)=PSiMe_3$, those of the general formula $RC(OSiMe_3)=PH$ are extremely rare, with only two examples in the literature.[225,312] Arif generated the carbanionic phosphaalkene $Mes^*C^-=PH$ and reported very limited spectroscopic data, its identity being inferred from the addition of Me_2CHCH_2Cl, which afforded the phosphaalkene $Mes^*(Me_2CHCH_2)C=PH$, thus providing support for the existence of

Mes*C^{-}=PH (Scheme 75). Phosphaalkene Mes*(Me_2CHCH_2)C=PH was isolated as a single isomer, the stereochemistry of which was unassigned.



Scheme 75. Synthesis of Mes*(Me_2CHCH_2)C=PH [225]

The second example, *E*/*Z*-^{t}Bu(Me_3SiO)C=PH, was obtained by the thermally-induced rearrangement of the acyl phosphine ^{t}BuC(O)P($SiMe_3$)H (Scheme 76);[312] the [1,3]-silatropic rearrangement was not spontaneous at low temperature, which allowed the acyl phosphine to be detected spectroscopically. The aforementioned trend whereby the *E*-isomer of phosphaalkenes exhibit a lower-field chemical shift in the ^{31}P NMR spectrum and smaller phosphorus-carbon coupling constant is not adhered to in this case. Given the lack of comparable reports, it is not clear whether ^{t}BuC($OSiMe_3$)=PH is a one-off occurrence, or whether the chemical shift trend does not extend to RC($OSiMe_3$)=PH type phosphaalkenes; moreover, no reasoning was provided for the respective assignments of ^{31}P NMR doublet signals at 38.0 ($^{1}J_{P\text{-}H}$ 161.0 Hz, *E*-^{t}Bu(Me_3SiO)C=PH) and 53.5 ppm ($^{1}J_{P\text{-}H}$ 144.0 Hz, *Z*-^{t}Bu(Me_3SiO)C=PH).



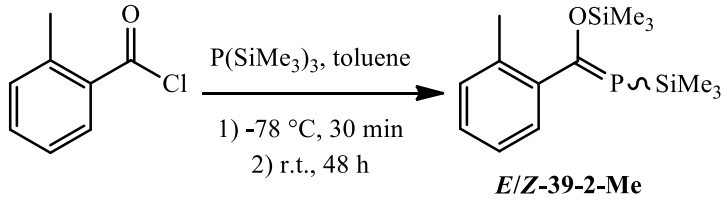
Scheme 76. Synthesis of *E*/*Z*-^{t}Bu(Me_3SiO)C=P~H [312]

The importance of conjugated phosphaalkenes with aromatic substituents has been highlighted by a recent flurry of research, most notably by Gates and Ott. The increased π-conjugation these compounds exhibit in comparison to the all-carbon containing analogues demonstrates promising potential for applications in molecular electronic devices.[130,131] Literature studies to date have largely focused upon polymeric systems stabilised by bulky Mes and Mes* groups, with a notable absence in the development of new 'building block' phosphaalkenes. The pursuit of monomeric phosphaalkenes that are conjugated with aromatic systems, particularly those that may be tolerant of further R-group functionalisation, such as C_6H_4(1-COCl)(R), would provide valuable tools for the continued development of π-conjugated materials.

3.2 Reactions of C_6H_4(1-COCl)(2-Me) with silylphosphines

3.2.1 Synthesis of *E*/*Z*-C_6H_4(1-C(OSiMe$_3$)=PSiMe$_3$)(2-Me)

The reaction of C_6H_4(1-COCl)(2-Me) and P(SiMe$_3$)$_3$ afforded a yellow oil that was identified as a mixture of products, with the two predominant species (95 % of the product mixture by integration of the $^{31}P\{^1H\}$ NMR spectrum) identified as *E*/*Z*-C_6H_4(1-C(OSiMe$_3$)=PSiMe$_3$)(2-Me) (***E*/*Z*-39-2-Me**) in a 57:43 ratio (Scheme 77). Analytical purity was obtained by extraction in pentane, affording ***E*/*Z*-39-2-Me** in 64 % yield, and leaving behind a yellow solid that was identified as {C_6H_4(1-CO)(2-Me)}$_3$P=O (**40-2-Me**) (see section **3.2.2**). Despite attempts by washing, crystallisation and fractional distillation, the separation of ***E*-39-2-Me** and ***Z*-39-2-Me** was not achieved.



Scheme 77. Synthesis of *E*/*Z*-C_6H_4(1-C(OSiMe$_3$)=P(SiMe$_3$)(2-Me) (***E*/*Z*-39-2-Me**)

The $^{31}P\{^1H\}$ NMR spectrum shows singlet resonances at 128 and 131 ppm that are assigned to ***Z*-39-2-Me** and ***E*-39-2-Me** respectively, while the $^{29}Si\{^1H\}$ NMR spectrum shows two resonances for each isomer as expected (Table 19). The protons assigned to the 2-Me and P(SiMe$_3$) groups of ***Z*-39-2-Me** both possess lower-field chemical shifts than ***E*-39-2-Me**, while those of the O(SiMe$_3$) group exhibit a higher-field chemical shift than for ***E*-39-2-Me**. The $^{13}C\{^1H\}$ NMR spectrum exhibits doublet resonances at 213 ($^1J_{C\text{-}P}$ 63.5 Hz) and 145 ppm ($^2J_{C\text{-}P}$ 25.2 Hz) for ***Z*-39-2-Me**, and 220 ($^1J_{C\text{-}P}$ 55.5 Hz) and 146 ppm ($^2J_{C\text{-}P}$ 9.3 Hz) for ***E*-39-2-Me**; the signals are attributed to the phosphaalkenic and *ipso*-aromatic carbon centres in turn, and are consistent with similar phosphaalkenes in literature (Mes*C(OSiMe$_3$)=PSiMe$_3$, δ_C 215 ($^1J_{C\text{-}P}$ 49.9 Hz), 146 ($^2J_{C\text{-}P}$ 5.9 Hz)).[313] The isomeric assignments of ***Z*-39-2-Me** and ***E*-39-2-Me** are made by comparison with previously reported examples, in which the *Z*-isomers of phosphaalkenes exhibit higher-field chemical shifts in both the ^{31}P and $^{13}C\{^1H\}$ NMR spectra and possess a larger carbon-phosphorus coupling constant.[103]

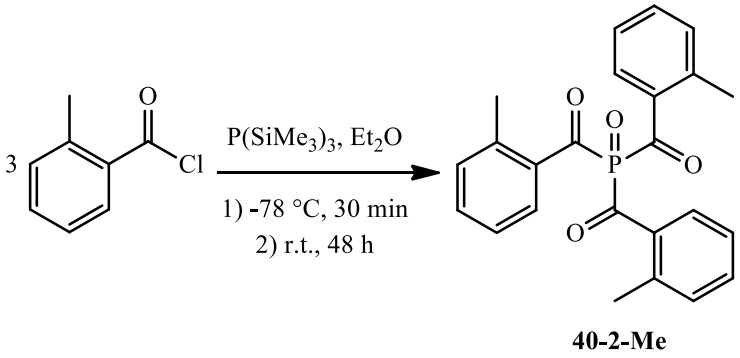
Table 19. Selected spectroscopic data for *E*/*Z*-C_6H_4(1-C($OSiMe_3$)=P($SiMe_3$)(2-Me) (***E*/*Z*-39-2-Me**)

	^{31}P {^{1}H} / ppm	^{29}Si{^{1}H} / ppm	^{1}H Me / ppm	^{1}H P($SiCH_3$)$_3$ / ppm	$^3J_{H\text{-}P}$ / Hz	^{1}H O($SiCH_3$)$_3$ / ppm	^{13}C{^{1}H} / ppm	$^1J_{C\text{-}P}$ / Hz
***E*-39-2-Me**	132	−1.6, 19.5	2.32	0.00	4.5	0.41	220	55.5
***Z*-39-2-Me**	128	−2.4, 21.7	2.35	0.46	3.4	−0.08	213	63.5

Isomeric distribution is commonly, although not universally, governed by the reaction temperature; *E*-^{t}BuC($OSiMe_3$)=P$SiMe_3$ was produced with isomeric purity upon addition of ^{t}BuCOCl to Li$P(SiMe_3)_2$ at −78 °C, while repeating the same reaction at 20 °C generated only *Z*-^{t}BuC($OSiMe_3$)=P$SiMe_3$.[108] With this in mind, the synthesis of ***E*/*Z*-39-2-Me** was attempted at both ambient temperature and at 66 °C. However, phosphaalkenes ***E*/*Z*-39-2-Me** (57:43) were isolated with no change in isomeric distribution from the low temperature reaction performed previously. Similarly, reducing the reaction duration to 4 h or increasing it to seven days failed to prompt any alteration to the isomeric distribution of the product.

3.2.2 Synthesis of {C_6H_4(1-CO)(2-Me)}$_3$P=O

The trace impurity isolated from *E*/*Z*-C_6H_4(1-C($OSiMe_3$)=P($SiMe_3$)(2-Me) (***E*/*Z*-39-2-Me**) was identified spectroscopically and crystallographically as {C_6H_4(1-CO)(2-Me)}$_3$P=O (**40-2-Me**), and a targeted synthesis using 3:1 stoichiometries (of C_6H_4(1-COCl)(2-Me) : P($SiMe_3$)$_3$) was performed (Scheme 78). Acyl phosphine oxide **40-2-Me** was isolated by washing the crude product mixture with pentane; the precipitate was dried *in vacuo* as a yellow solid in 69 % yield.



Scheme 78. Synthesis of {C_6H_4(1-CO)(2-Me)}$_3$P=O (**40-2-Me**)

The ^{31}P NMR spectrum of **40-2-Me** shows a multiplet resonance at 67.2 ppm ($^4J_{P\text{-}H}$ 3.4 Hz) with long-range coupling to the *ortho*-CH protons of the aromatic ring (confirmed by ^{1}H-^{31}P HMBC

NMR spectroscopy). The chemical shift is down-field compared to known phosphine oxides ($Me_3P{=}O$, δ_P 32.7; $^tBu_3P{=}O$, δ_P 43.7;[314] (C_6H_4(1-C(O)P(O)Ph_2)(4-Cl), δ_P 33.0),[315] although this is to be anticipated given the three adjacent carbonyl groups present in **40-2-Me**. The $^{13}C\{^1H\}$ NMR spectrum exhibits doublet signals at 209 ($^1J_{C\text{-}P}$ 34.5 Hz) and 141 ppm ($^2J_{C\text{-}P}$ 33.3 Hz), assigned to the acyl phosphine and *ipso*-carbon centres respectively. The carbon-phosphorus coupling constant is typical of a one-bond separation, while the chemical shift is consistent with known acyl phosphines (C_6H_4(1-C(O)PPh_2)(4-Cl), δ_C 213 ($^1J_{C\text{-}P}$ 38.6 Hz).[315] The isolation of **40-2-Me** has been previously described,[316] characterised on the basis of a singlet resonance at 26.9 ppm in the ^{31}P NMR spectrum and no further supporting data. While the authors used a different NMR solvent ($CDCl_3$), it is unlikely to induce such a significant difference in chemical shift ($\Delta\delta_P$ 40.3); literature studies regarding the effect of the NMR solvent (between C_6D_6 and $CDCl_3$) on the chemical shift of phosphine oxides showed a much smaller difference is typical ($\Delta\delta_P$ 4.23).[5] One might tentatively suggest that the compound previously isolated by the authors was, in fact, the acyl phosphine rather than the acyl phosphine oxide.

Yellow crystals suitable for X-ray diffraction were grown from Et_2O at −20 °C in 72 h (Figure 21); this represents the first crystallographic study of a tri-acyl phosphine oxide. The P=O bond length of 1.474(2) Å is significantly shorter than those of typical phosphine oxides ($Bu_3P{=}O$; 1.489(2) Å, $Cy_3P{=}O$; 1.504(10) Å),[5] but is similar to that of di-acyl phosphine oxide {MesC(O)}$_2$PhP=O; (1.475(2) Å), reported by Grützmacher.[317] Further similarities can be drawn between **40-2-Me** and {MesC(O)}$_2$PhP=O, including C=O and C-P bond lengths, and the adoption of pyramidal geometries (Table 20). Acyl phosphine oxide **40-2-Me** possesses C-P-C angles of less than 109.5 ° and a significantly larger O-P-C angle, attributed to the greater electronic repulsion of the phosphine oxide oxygen as compared to the carbonyl groups. The effect is less pronounced for asymmetric {MesC(O)}$_2$PhP=O.

Table 20. Selected bond lengths and angles for **40-2-Me** and $\{MesC(O)\}_2PhP{=}O$ [317]

Bond lengths (Å) and angles (deg)	***d* P=O / Å**	***d* C=O / Å**	***d* C-P / Å**	**O=P-C / deg**	**C-P-C / deg**
$\{C_6H_4(1\text{-}CO)(2\text{-}Me)\}_3P{=}O$ (**40-2-Me**)	1.474(2)	1.213(3)	1.897(2)	117.25(9)	100.09(9)
				120.08(10)	97.92(10)
				118.11(9)	99.41(10)
$\{MesC(O)\}_2PhP{=}O$	1.475(2)	1.210(3)	1.891(3)	114.67(12)	110.10(12)
				111.88(11)	105.92(12)
				116.33(12)	96.35(13)

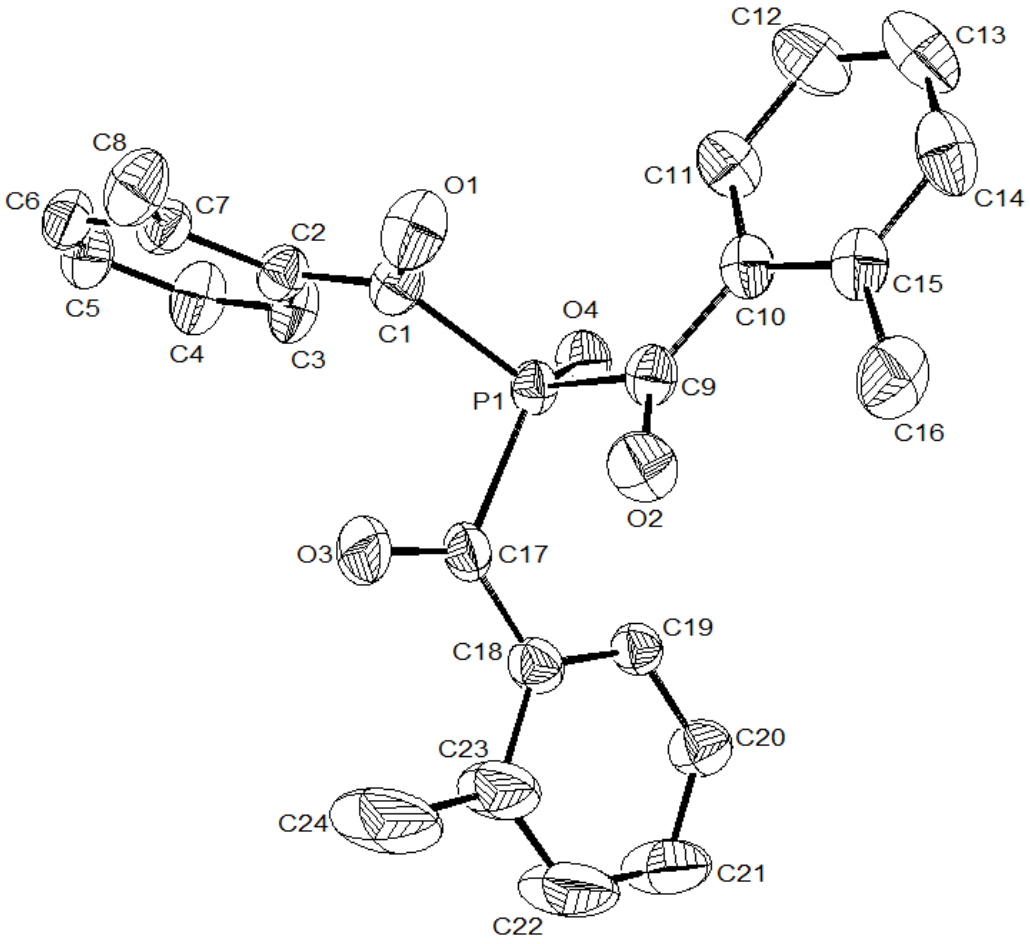
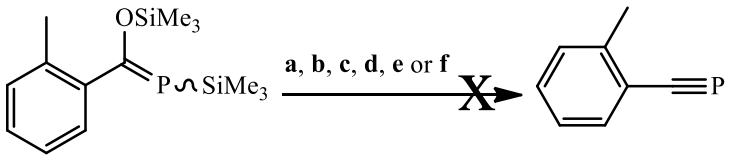


Figure 21. Molecular structure of $\{C_6H_4(1\text{-}CO)(2\text{-}Me)\}_3P{=}O$ (**40-2-Me**), with thermal ellipsoids at the 50 % probability level. Selected bond distances (Å) and angles (deg): C1-O1 1.213(3), C1-P1 1.897(2), C9-O2 1.213(3), C9-P1 1.892(2), C17-O3 1.216(3), C17-P1 1.896(2), O4-P1 1.4742(15). O1-C1-P1 114.05(16), O2-C9-P1 113.68(16), O3-C17-P1 112.90(18), O4-P1-C9 117.25(9), O4-P1-C17 120.08(10), C9-P1-C17 97.92(10), O4-P1-C1 118.11(9), C9-P1-C1 100.09(9), C17-P1-C1 99.41(10).

3.2.3 Attempted synthesis of C_6H_4(1-C≡P)(2-Me)

The base-initiated conversion of *E*/*Z*-C_6H_4(1-C(OSiMe$_3$)=P(SiMe$_3$)(2-Me) (***E*/*Z*-39-2-Me**) to C_6H_4(1-C≡P)(2-Me) was attempted by drop-wise addition of a series of suspended bases, including NaOH, DABCO and DBU, to a solution of ***E*/*Z*-39-2-Me** (Scheme 79).



***E*/*Z*-39-2-Me**

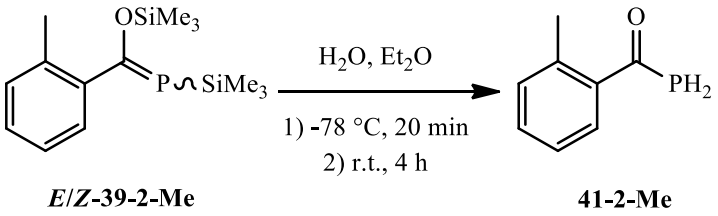
a) 1) DABCO, −78 °C, 20 min, pentane, 2) r.t., 30 min, 3) 18 h
b) 1) 0.1 NaOH, −78 °C, dme, 2) r.t., 4 h
c) 1) 0.1 NaOH, 0 °C, dme, 2) r.t., 4 h
d) 1) 0.5 NaOH, 0 °C, dme, 2) r.t., 4 h
e) 1) NaOH, 0 °C, dme, 2) r.t., 4 h
f) 1) DBU, −78 °C, 20 min, THF, 2) r.t. 4 h

Scheme 79. Attempted synthesis of C_6H_4(1-C≡P)(2-Me)

The addition of DABCO afforded a complex product mixture that included ***E*/*Z*-39-2-Me**. Attempts to separate the species by washing or recrystallisation were unsuccessful, while extending the reaction time, or heating the reaction mixture, afforded a more complex mixture of products. The addition of catalytic or stoichiometric NaOH to ***E*/*Z*-39-2-Me** afforded C_6H_4(1-C(O)PH_2)(2-Me) (**41-2-Me**), identified by a triplet in the ^{31}P NMR spectrum at −99.7 ppm ($^1J_{H\text{-}P}$ 218 Hz) that is similar to those reported for ^{t}BuC(O)PH_2 (δ_P −122 ($^1J_{P\text{-}H}$ 214 Hz)) and MeC(O)PH_2 (δ_P −106 ($^1J_{P\text{-}H}$ 217 Hz)).[318] Trace contaminants were also apparent, and the corresponding resonance in the ^{1}H NMR spectrum cannot be fully resolved due to high levels of impurities that overlap in the region (δ_H 3.60 - 3.90 ppm). The addition of DBU to ***E*/*Z*-39-2-Me** affords a colourless oil which exhibits no resonances in the ^{31}P NMR spectrum.

3.2.4 Synthesis of C_6H_4(1-C(O)PH_2)(2-Me)

Given the apparent formation of the primary acyl phosphine **41-2-Me** (vide supra), deliberate synthesis was pursued by the reaction of ***E*/*Z*-39-2-Me** with excess deionised water; compound **41-2-Me** was isolated as an impure yellow oil that degraded over 24 h to an unidentifiable mixture of products (Scheme 80).

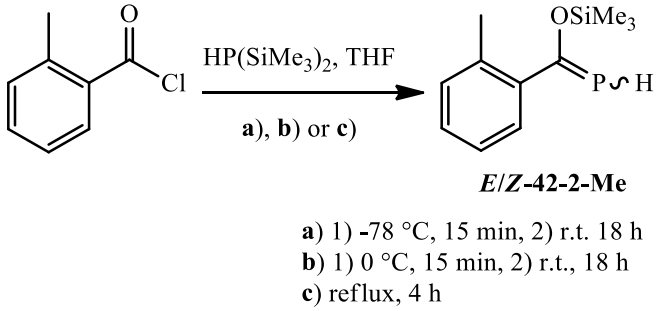


Scheme 80. Synthesis of C_6H_4(1-C(O)PH_2)(2-Me) (**41-2-Me**)

The ^{31}P NMR spectrum of primary acyl phosphine **41-2-Me** shows a triplet resonance at −99.7 ppm ($^1J_{H\text{-}P}$ 218 Hz) with a phosphorus-proton coupling constant consistent with a PH_2 group (^{t}BuC(O)PH_2; δ_P −122 ($^1J_{P\text{-}H}$ 214 Hz), MeC(O)PH_2; δ_P −106 ($^1J_{P\text{-}H}$ 217 Hz)).[318] This signal corresponds (by ^{1}H-^{31}P HMBC NMR spectrum) to a ^{1}H NMR doublet resonance at 3.87 ppm ($^1J_{H\text{-}P}$ 218 Hz). Further singlet and multiplet resonances at 2.40 and 6.84 - 6.95 ppm are assigned to the 2-Me and aromatic groups respectively. Given the potential for decomposition of **41-2-Me** to {C_6H_4(1-C(O)(2-Me)}$_2$PH and PH_3,[319] microanalysis and mass spectrometry were not performed.

3.2.5 Reactions of C_6H_4(1-COCl)(2-Me) with $HP(SiMe_3)_2$

The synthesis of *E*/*Z*-C_6H_4(1-C($OSiMe_3$)=PH)(2-Me) (***E*/*Z*-42-2-Me**) was attempted by the addition of C_6H_4(1-COCl)(2-Me) to $HP(SiMe_3)_2$ under a variety of conditions (Scheme 81). In all cases, the reaction mixtures after 18 h were complex mixtures of products, the identities of which are tentatively assigned in Table 21, and include the previously identified compounds ***E*/*Z*-39-2-Me**, **40-2-Me** and **41-2-Me**.



Scheme 81. Attempted synthesis of *E*/*Z*-C_6H_4(1-C($OSiMe_3$)=PH)(2-Me) (***E*/*Z*-42-2-Me**)

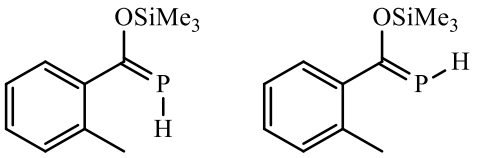
Table 21. Selected spectroscopic data for Ar(1-COCl) and $HP(SiMe_3)_2$ reactions

	^{31}**P NMR / ppm**	**Multiplicity**	$^{1}J_{P-H}$ **/ Hz**	**Assignment**
41-2-Me	−99.7	t	218	$Ar(1\text{-}C(O)PH_2)$
43-2-Me	−13.6	d	691	H-phosphonate
40-2-Me	67.2	s	-	$\{Ar(1\text{-}CO)\}_3P{=}O$
***Z*-42-2-Me**	73.3	d	143	*Z*-$Ar(1\text{-}C(OSiMe_3){=}PH)$
***E*-42-2-Me**	90.6	d	163	*E*-$Ar(1\text{-}C(OSiMe_3){=}PH)$
***Z*-39-2-Me**	127	s	-	*Z*-$Ar(1\text{-}C(OSiMe_3){=}PSiMe_3)$
***E*-39-2-Me**	131	s	-	*E*-$Ar(1\text{-}C(OSiMe_3){=}PSiMe_3)$

Phosphaalkenes ***E*/*Z*-42-2-Me** (ca. 67:33) are identified as the predominant species in the reaction mixtures regardless of temperature. The ^{31}P NMR spectra show doublet resonances at 90.6 ($^{1}J_{P-H}$ 163 Hz, ***E*-42-2-Me**) and 73.3 ppm ($^{1}J_{P-H}$ 143 Hz, ***Z*-42-2-Me**), with corresponding ^{1}H NMR doublets at 4.69 ($^{1}J_{H-P}$ 163 Hz) and 5.00 ppm ($^{1}J_{H-P}$ 143 Hz) (confirmed by ^{1}H-^{31}P HMBC NMR spectroscopy). The isomeric assignments are made in accordance with the general trend of increased coupling constants for *E*-phosphaalkenes compared to the *Z*-isomers. While the phosphorus-proton coupling constants are consistent with *E*/*Z*-^{t}Bu$(OSiMe_3)$C=PH,[312] the ^{31}P NMR resonance of ***E*-42-2-Me** is lower-field than expected when compared to *E*-^{t}Bu$(OSiMe_3)$C=PH. This might be attributed to the interaction between the *ortho*-methyl group and PH proton of ***E*-42-2-Me** (Figure 22), or else the disparity in R groups; Becker's example incorporates the electron-donating ^{t}Bu group, while ***E*/*Z*-42-2-Me** possesses a slightly electron-withdrawing aromatic system. Compounds ***E*/*Z*-42-2-Me** demonstrate that the stereochemistry of phosphaalkenes of the type $R(OSiMe_3)$C=PH cannot be assigned solely on the basis of chemical shift. The isomeric distribution of ***E*/*Z*-42-2-Me** (69:31) remains invariant over time for the low temperature reaction; in contrast, the ambient and elevated temperature reactions both exhibit increased proportions of ***E*-42-2-Me** after 18 h (Table 22).

Significant levels of phosphaalkenes ***E*/*Z*-39-2-Me** are also apparent during the reactions of C_6H_4(1-COCl)(2-Me) with $HP(SiMe_3)_2$, irrespective of temperature; for the low temperature reactions the relative proportion of ***E*/*Z*-39-2-Me** decreases after 18 h (47.0 % at 1 h, 22.9 % after 18 h), while at ambient temperature, the reverse is true (13.9 % at 5 min, 33.0 % after 18 h). While the isomeric distribution varies according to reaction temperature (Table 22), it remains unchanged over time in either case; however, during the high temperature reaction increased quantities of ***E*-39-2-Me** (to 71:29) are detected after 18 h. Low levels of acyl phosphine **41-2-Me** (ca. 1.21 %) and significant quantities of acyl phosphine oxide **40-2-Me** (ca. 10.7 %) are also present during all of the reaction variations performed, while a doublet

resonance at −13.6 ppm ($^{1}J_{P\text{-}H}$ 691 Hz), assigned to H-phosphonate **43-2-Me** (for more detail see section **3.3.2**), constitutes ca. 2.71% of the reaction mixtures.



***E*-42-2-Me** ***Z*-42-2-Me**

Figure 22. *E*/*Z*-C_6H_4(1-C(OSiMe$_3$)=PH)(2-Me) (***E*/*Z*-42-2-Me**)

Table 22. Isomeric distribution of ***E*/*Z*-42-2-Me** and ***E*/*Z*-39-2-Me** in the initial and final aliquots

Temperature	**Initial *E*/*Z*-42-2-Me ratio**	**Final *E*/*Z*-42-2-Me ratio**	**Initial *E*/*Z*-39-2-Me ratio**	**Final *E*/*Z*-39-2-Me ratio**
−78 °C	69:31	69:31	72:28	72:28
Ambient	66:34	75:25	65:35	65:35
Reflux	67:33	71:29	66:33	71:29

Quantitative studies

For the reaction of C_6H_4(1-COCl)(2-Me) with HP(SiMe$_3$)$_2$ at 66 °C, PPh_3 was used as an internal standard to enable the quantification of the products present in each aliquot (Figure 23, Table 23). Phosphaalkenes ***E*/*Z*-42-2-Me** are the major products, increasing in quantity over the first 300 min, while phosphaalkenes ***E*/*Z*-39-2-Me** are a relatively minor species in each sample, diminishing as time increases. Although acyl phosphine **41-2-Me** is not present in the initial aliquot, significant levels are observed after 300 min, in contrast to acyl phosphine oxide **40-2-Me**, which is present in low levels after 60 min and increases in proportion after 300 min.

Table 23. Species present in aliquots from the reaction of Ar(1-COCl) and HP(SiMe$_3$)$_2$ at 66 °C

Time / min	**41-2-Me / mol**	**40-2-Me / mol**	***Z*-42-2-Me / mol**	***E*-42-2-Me / mol**	***Z*-39-2-Me / mol**	***E*-39-2-Me / mol**
60	0.00	9.91×10^{-3}	1.09×10^{-2}	2.18×10^{-2}	3.17×10^{-3}	6.54×10^{-3}
300	5.47×10^{-3}	1.74×10^{-2}	1.81×10^{-2}	4.19×10^{-2}	9.38×10^{-4}	2.66×10^{-3}
1440	3.60×10^{-3}	2.06×10^{-3}	4.81×10^{-3}	1.18×10^{-2}	0.00	0.00

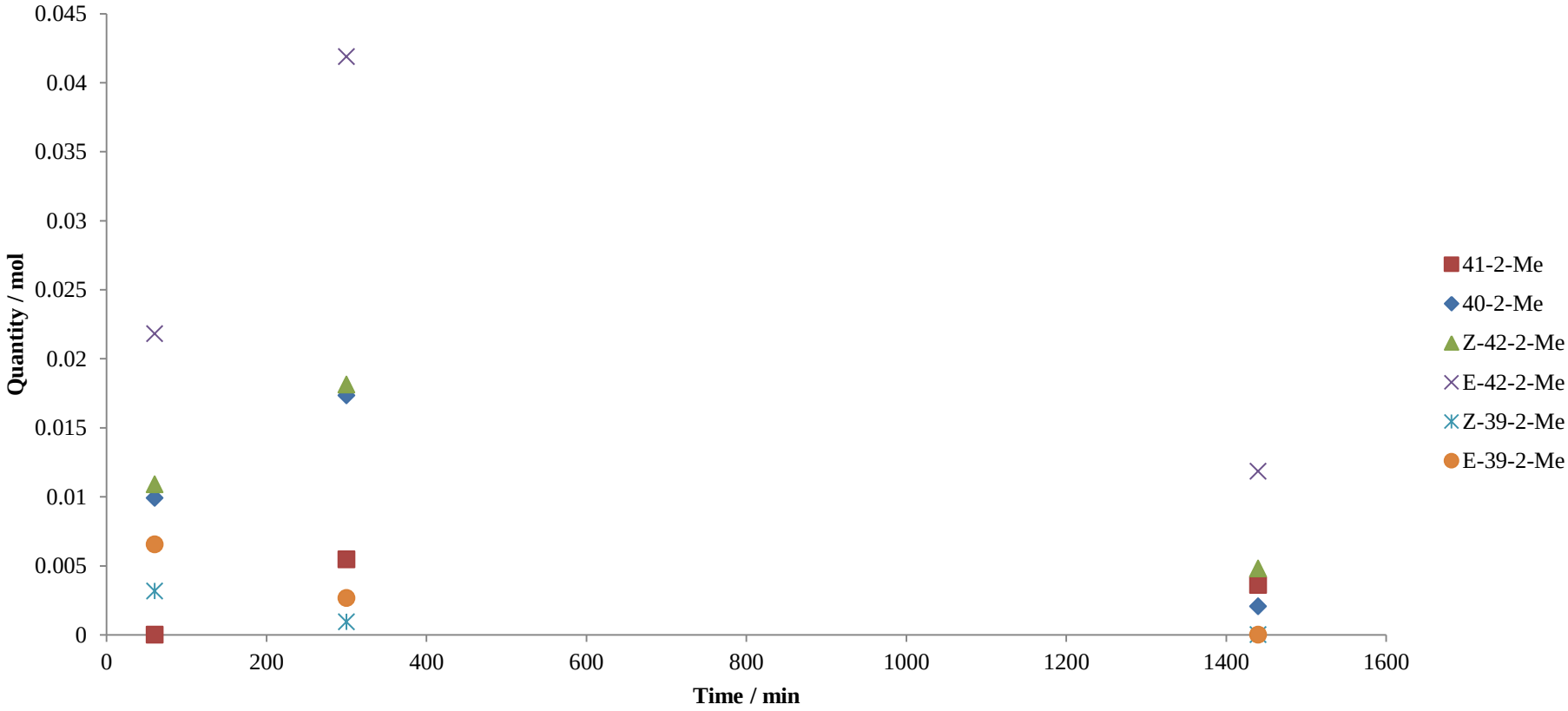


Figure 23. The reaction of Ar(1-COCl) and $HP(SiMe_3)_2$ at 66 °C (Ar = C_6H_4(2-Me))

3.3 Reactions of C_6H_4(1-COCl)(R) with silylphosphines

3.3.1 Reaction conditions

Following from the studies of C_6H_4(1-COCl)(2-Me), the C_6H_4(1-COCl)(3-R) and C_6H_4(1-COCl)(4-R) systems were investigated under a similar series of conditions (Scheme 82). In all cases, a THF solution of C_6H_4(1-COCl)(R) was added to R'P($SiMe_3$)$_2$ (R' = $SiMe_3$, H) in THF, but different contact times and temperatures were applied.

Method a

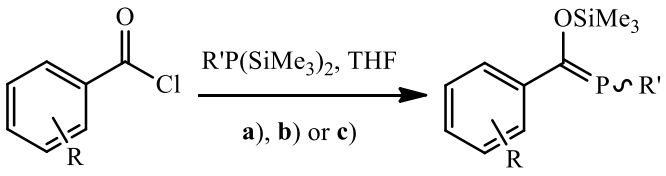
For conditions **a**, the reagents were combined at −78 °C and the resulting solutions were stirred for 15 min prior to being allowed to warm to ambient temperature over 45 min, whereupon an aliquot was isolated and dried *in vacuo*.

Method b

In the case of conditions **b**, the reagents were combined at ambient temperature and the solutions were stirred for 5 min prior to the isolation of an aliquot.

Method c

For conditions **c**, the reagents were combined at 60 °C and the solutions were immediately brought to reflux; aliquots were isolated at 80 min intervals.



R' = H, $SiMe_3$
R =3-Me, 3-CN, 4-CN, 4-CO_2Me, 4-COCl

a) 1) -78 °C, 15 min, 2) r.t. 18 h
b) r.t., 18 h
c) reflux, 18 h

Scheme 82. Reactions of C_6H_4(1-COCl)(R) with R'P($SiMe_3$)$_2$

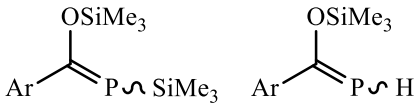
3.3.2 Reaction outcomes

With a small number of exceptions, which will be discussed individually later, the reactions of C_6H_4(1-COCl)(R) with R'P($SiMe_3$)$_2$ afford complex product mixtures. Notwithstanding, these predominantly comprise a series of characteristic components, the identities of which can be inferred from spectroscopic data *viz.* phosphaalkenes (Figure 24, types **i** and **ii**), diphosphacyclobutanes (Figure 25, types **iii** - **viii**), acyl phosphines (Figure 27, types **ix** - **xii**) and an acyl phosphine oxide (Figure 27, type **xiii**). Additionally, species that incorporate $(RO)_2(R)_2PH$ and $(RO)_2(O)PH$ units are observed (Figure 28), though precise identities cannot be established.

Phosphaalkenes (types i - ii)

The ^{31}P NMR spectra obtained for the reactions of C_6H_4(1-COCl)(R) with P($SiMe_3$)$_3$, and on rare occasions from those of C_6H_4(1-COCl)(R) with HP($SiMe_3$)$_2$, show singlet resonances in the region of 127 - 143 (*Z*-) and 131 - 147 ppm (*E*-), attributable to type **i** phosphaalkenes *E*/*Z*-C_6H_4(1-C($OSiMe_3$)=P$SiMe_3$)(R) (Figure 24, Table 24) on the basis of comparison with related species in the literature. Although the chemical shifts vary considerably with the substituents at the phosphorus and carbon centres, type **i** phosphaalkenes in literature typically exhibit ^{31}P NMR singlet resonances in the range of 100 to 140 ppm; examples include ^{t}BuC($OSiMe_3$)=P$SiMe_3$) (δ_P 120, *Z*-isomer; δ_P 124, *E*-isomer),[108] ^{i}PrC($OSiMe_3$)=P$SiMe_3$) (δ_P 102, *E*-isomer) and ^{t}BuCH$_2$C($OSiMe_3$)=P$SiMe_3$) (δ_P 123, *E*-isomer).[105]

Phosphaalkenes of the general formula *E*/*Z*-C_6H_4(1-C($OSiMe_3$)=PH)(R) (type **ii**) are frequently identified as products from the reactions of C_6H_4(1-COCl)(R) with HP($SiMe_3$)$_2$, and occasionally from the reactions of C_6H_4(1-COCl)(R) with P($SiMe_3$)$_3$. Type **ii** phosphaalkenes exhibit resonances between 65.8 - 90.6 ($^1J_{P-H}$ 159 - 163 Hz, *E*-isomer) and 67.4 - 85.6 ppm ($^1J_{P-H}$ 143 - 156 Hz, *Z*-isomer) in the ^{31}P NMR spectra, and in the region of 4.88 to 5.24 ($^1J_{P-H}$ 143 - 156 Hz, *Z*-isomer) and 4.69 to 4.75 ppm ($^1J_{P-H}$ 159 - 163 Hz, *E*-isomer) in the ^{1}H NMR spectra. The spectroscopic data are similar to *E*/*Z*-^{t}Bu($OSiMe_3$)C=PH,[312] for which ^{31}P NMR doublet resonances at 38.0 ($^1J_{P-H}$ 161 Hz, *E*-isomer) and 53.5 ppm ($^1J_{P-H}$ 144 Hz, *Z*-isomer) are reported, with corresponding doublet signals at 4.09 ($^1J_{P-H}$ 144 Hz, *Z*-isomer) and 4.51 ppm ($^1J_{P-H}$ 161 Hz, *E*-isomer) in the ^{1}H NMR spectrum. The disparity in chemical shifts is attributed to the electron-donating ability of the ^{t}Bu group compared to the electron-withdrawing characteristics of the aromatic substituents; the one-bond phosphorus-proton coupling constants are comparable.



i **ii**

Ar = C_6H_4(2-Me), C_6H_4(3-Me), C_6H_4(3-CN), C_6H_4(4-CN), C_6H_4(4-CO_2Me), C_6H_4(4-COCl)

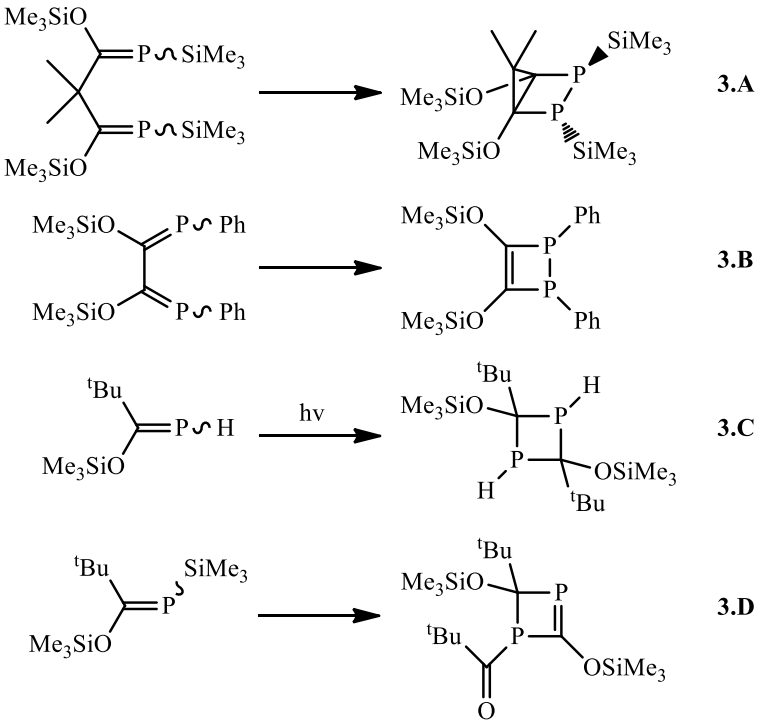
Figure 24. Phosphaalkene products from the reactions of C_6H_4(1-COCl)(R) with R'P($SiMe_3$)$_2$

Table 24. Spectroscopic data ranges for phosphaalkenes types **i** - **ii**

Type	^{31}P NMR / ppm	^{1}H NMR / ppm	$^{1}J_{P\text{-}H}$ / Hz
***Z*-i**	127 - 143	-	-
***E*-i**	131 - 147	-	-
***E*-ii**	65.8 - 90.6	4.88 - 5.24	159 - 163
***Z*-ii**	67.4 - 85.6	4.69 - 4.75	143 - 156

Diphosphacyclobutanes (types iii - viii)

The ^{31}P NMR spectra also show resonances that are tentatively assigned to six distinct diphosphacyclobutane motifs; comparable compounds are sparsely reported in literature and typically result from phosphaalkene dimerisations. Examples include compounds **3.A** and **3.B**, which both result from intramolecular head-to-head dimerisations,[320,115] as well as **3.C** and **3.D**, which are generated by intermolecular head-to-tail dimerisations (Scheme 83).[312,115] The variable spectroscopic characteristics are rationalised by the identity of the substituents (Table 25); *viz.* for diphosphacyclobutanes with both [1,2]- and [1,3]-orientation of the phosphorus atoms, those that contain electron-withdrawing $OSiMe_3$ groups exhibit high-field signals in the ^{31}P NMR spectra, while those that incorporate electron-donating ^{t}Bu groups exhibit low-field resonances.



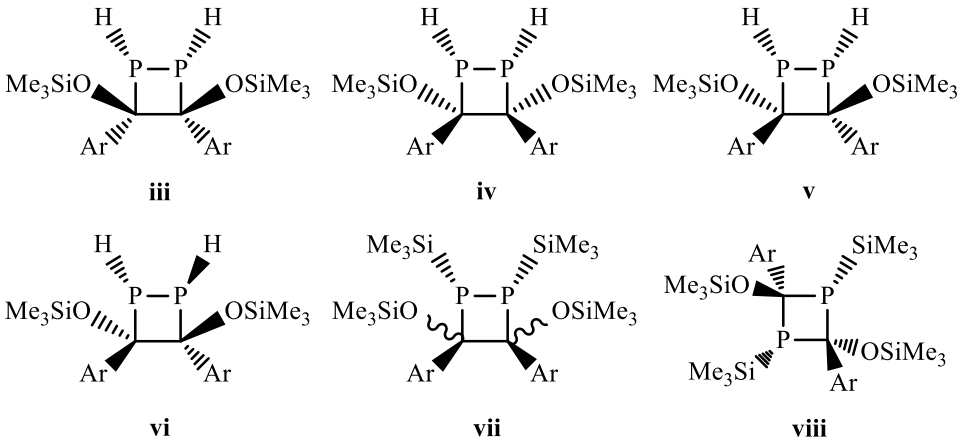
Scheme 83. Syntheses of *EZ*-[1,2]-diphosphacyclopentane (**3.A**),[320] [1,2]-diphosphacyclobutene (**3.B**),[115] [1,3]-diphosphacyclobutane (**3.C**),[312] [1,3]-diphosphacyclobutene (**3.D**) [115]

Table 25. Selected spectroscopic data for *EZ*-[1,2]-diphosphacyclopentane (**3.A**),[320] [1,2]-diphosphacyclobutene (**3.B**),[115] [1,3]-diphosphacyclobutane (**3.C**),[312] [1,3]-diphosphacyclobutene (**3.D**)[115]

Compound	^{31}P NMR / ppm	$J_{P\text{-}P}$ / Hz	$^{1}J_{P\text{-}H}$ / Hz
3.A	−104, −84.7	48.2	-
3.B	−31.5	-	-
3.C	34.5	-	195
3.D	104, 279	221	-

Two of the species generated herein, attributed to types **iii** and **iv** diphosphacyclobutanes, each exhibit a singlet resonance in the region of −108 to −103 (*ZZ*-) and −98.0 to −96.2 ppm (*EE*-) in the ^{31}P{^{1}H} NMR spectra (Figure 25, Table 26), which suggests internal symmetry similar to [1,2]-diphosphacyclobutene (Scheme 83 **3.B**). However, in the absence of proton decoupling, the signals exhibit complexity ascribed to magnetic inequivalence of the phosphorus centres with respect to the protons (Figure 26), which is further complicated by the presence of multiple coupling pathways between each phosphorus centre and the proton on the adjacent phosphorus centre. The chemical shifts are comparable to *EZ*-[1,2]-diphosphacyclopentane (**3.A**: Scheme 83, Table 25) due to the presence of strongly electron-withdrawing substituents. During the reactions of C_6H_4(1-COCl)(R) (R = 3-CN, 4-CN, 4-COCl) with R'P(SiMe$_3$)$_2$ (R' = H, SiMe$_3$),

corresponding ^{1}H NMR multiplets can be located between 2.75 to 3.03 (*EE*-isomer) and 4.54 to 4.69 ppm (*ZZ*-isomer), confirmed by ^{1}H-^{31}P HMBC NMR experiments. The isomeric assignments are speculatively based on the trend of larger phosphorus-proton coupling constants for the *E*-isomers of phosphaalkenes; although it is realised that constraint of the C_2P_2 ring may cause a reversal in the relative chemical shifts of the isomers, a logical method by which to refer to each species is necessary for discussion that will be applied throughout.



Ar = C_6H_4(2-Me), C_6H_4(3-Me), C_6H_4(3-CN), C_6H_4(4-CN), C_6H_4(4-CO_2Me), C_6H_4(4-COCl)

Figure 25. Tentative product assignments of reactions of C_6H_4(1-COCl)(R) and R'P($SiMe_3$)$_2$

Table 26. Spectroscopic data ranges for diphosphacyclobutanes types **iii-viii**

Type	^{31}P NMR / ppm	Multiplicity	$^{1}J_{P\text{-}H}$ / Hz	$^{3}J_{P\text{-}H}$ / Hz	$J_{P\text{-}P}$ / Hz
iii	−98.0 - −96.2	2nd order	-	-	-
iv	−108 - −103	2nd order	-	-	-
v	−116 - −114	ddd	172 - 175	9.9 - 11.4	70.5 - 72.1
	−86.1 - −83.9	ddd	181 - 186	11.2 - 13.7	
vi	−120 - −119	dd	162 - 165	-	89.0 - 90.5
	−83.0 - −81.9	ddd	168 - 171	7.5 - 10.2	
vii	−81.2 - −74.2	s	-	-	-
viii	−124 - −123	d	-	-	190 - 193
	−82.4 - −81.5	d	-	-	

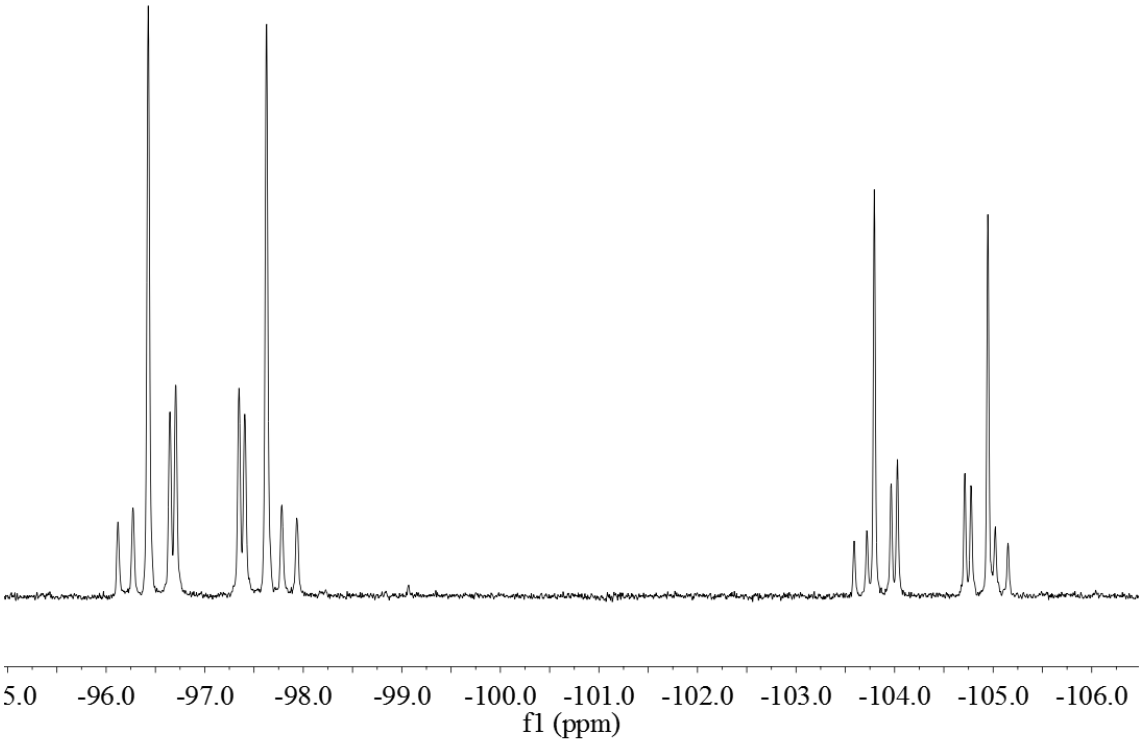


Figure 26. Selected section (δ_P −106 to −95.0) of the ^{31}P NMR spectrum of reaction of C_6H_4(1-COCl)(4-CO_2Me) and $HP(SiMe_3)_2$ (method **a**) after 18 h

Type **v** diphosphacyclobutanes are inferred from multiplet resonances in the region of −116 to −114 ($^1J_{P\text{-}H}$ 172 - 175 Hz, $^1J_{P\text{-}P}$ 70.5 - 72.1 Hz, $^3J_{P\text{-}H}$ 9.9 - 11.4 Hz) and −86.1 to −83.9 ppm ($^1J_{P\text{-}H}$ 181 - 186 Hz, $^1J_{P\text{-}P}$ 70.5 - 72.1 Hz, $^3J_{P\text{-}H}$ 11.2 - 13.7 Hz) in the ^{31}P NMR spectra, while diphosphacyclobutanes of the type **vi** exhibit similar signals between −120 to −119 ($^1J_{P\text{-}H}$ 162 - 165 Hz, $^1J_{P\text{-}P}$ 89.0 - 90.5 Hz) and −83.0 to −81.9 ppm ($^1J_{P\text{-}H}$ 168 - 171 Hz, $^1J_{P\text{-}P}$ 89.0 - 90.5 Hz, $^3J_{P\text{-}H}$ 7.5 - 10.2 Hz). Both sets of resonances are frequently observed during all of the reactions of C_6H_4(1-COCl)(R) with R'$P(SiMe_3)_2$. The spectroscopic data are comparable to *EZ*-[1,2]-diphosphacyclopentane (Scheme 83, Table 25 **3.A**), which also exhibits unusually small 'one-bond' phosphorus-phosphorus coupling constants, resulting from the presence of multiple coupling pathways. While diphosphacyclobutanes of the type **v** and **vi** differ from each other in the orientation of one of the protons bound to phosphorus, isomeric assignment is entirely arbitrary and used only as a practical means of differentiation in lieu of definite data indicative of stereochemistry, as for diphosphacyclobutanes of the types **iii** and **iv**.

Additional ^{31}P NMR signals observed during the reactions of C_6H_4(1-COCl)(R) with $P(SiMe_3)_3$, but not with $HP(SiMe_3)_2$, include doublet resonances in the range of −124 to −123 ($^2J_{P\text{-}P}$ 190 - 193 Hz) and −81.5 to −82.4 ppm ($^2J_{P\text{-}P}$ 190 - 193 Hz), assigned to diphosphacyclobutanes of the

type **viii**. The chemical shifts are similar to those of compound **3.A** (Scheme 83, Table 25) due to the presence of the strongly electron-withdrawing $OSiMe_3$ substituents, while the magnitude of phosphorus-phosphorus coupling is consistent with [1,3]-diphosphacyclobutane **3.C** ($^2J_{P\text{-}P}$ 195 Hz) and [1,3]-diphosphacyclobutene **3.D** ($^2J_{P\text{-}P}$ 221 Hz) (Scheme 83, Table 25). Further resonances between −74.2 and −81.2 ppm are tentatively assigned to diphosphacyclobutanes of the type **vii**. The definitive isomeric assignment of the type **vii** diphosphacyclobutane is not possible as *EE*- or *ZZ*-conformations are equally plausible.

The formation of diphosphacyclobutanes (types **iii – vi**) is proposed to result from the intramolecular dimerisation of type **ii** phosphaalkenes, while types **vii** and **viii** diphosphacyclobutanes are proposed from intramolecular dimerisation of phosphaalkenes of the type **i**.

Acyl phosphines and phosphine oxides (types ix - xiii)

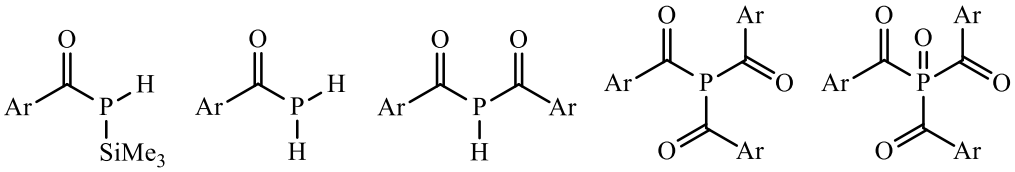
The reactions of C_6H_4(1-COCl)(R) with R'$P(SiMe_3)_2$ (R' = H, $SiMe_3$) produce complex product mixtures that are determined to contain acyl phosphines of the types **ix - xii** and acyl phosphine oxides of the type **xiii** (Figure 27, Table 27). Doublet resonances in the region of −98.6 to −97.9 ppm ($^1J_{P\text{-}H}$ 178 - 180 Hz) in the ^{31}P NMR spectra of many of the product mixtures are assigned to type **ix** acyl phosphines, ArC(O)P(H)$SiMe_3$, by comparison with the ^{31}P NMR doublet signals of ^{t}BuC(O)P(H)$SiMe_3$ (δ_P −119 $^1J_{P\text{-}H}$ 205 Hz) and C_6H_5P(H)$SiMe_3$ (δ_P −121 $^1J_{P\text{-}H}$ 199 Hz).[318] The corresponding protons are not observed *via* ^{1}H or ^{1}H-^{31}P HMBC NMR spectroscopy.

Acyl phosphines of the general formula $ArC(O)PH_2$ (type **x**) typically exhibit high-field triplet resonances in the ^{31}P NMR spectra at ca. −107 ppm ($^1J_{P\text{-}H}$ ca. 218 Hz), with larger phosphorus-proton coupling constants than those of type **ix**. Literature examples include ^{t}BuC(O)PH_2 (δ_P −107 ($^1J_{P\text{-}H}$ 218 Hz)) and MeC(O)PH_2 (δ_P −106 ($^1J_{P\text{-}H}$ 217 Hz)).[318] Type **x** acyl phosphines were duly identified by triplet resonances in the region of −110 to −99.7 ppm ($^1J_{P\text{-}H}$ 217 - 220 Hz). In all reactions, excluding that of C_6H_4(1-COCl)(4-CO_2Me) with R'$P(SiMe_3)_2$ (R' = H, $SiMe_3$), the corresponding protons can also be observed at ca. 3.79 ppm ($^1J_{H\text{-}P}$ ca. 219 Hz) in the ^{1}H NMR spectra, confirmed by ^{1}H-^{31}P HMBC NMR spectra.

Acyl phosphines of the type **x**, $ArC(O)PH_2$, are documented to undergo spontaneous co-condensations to form type **xi** acyl phosphines, $\{ArC(O)\}_2PH$, which typically exhibit doublet signals at ca. −20.0 ppm ($^1J_{P\text{-}H}$ ca. 234 Hz) in the ^{31}P NMR spectra ($\{^t$BuC(O)$\}_2$PH; δ_P −37.0 ($^1J_{P\text{-}H}$ 223 Hz), $\{$MeC(O)$\}_2$PH; δ_P −2.0 ($^1J_{P\text{-}H}$ 245 Hz));[318] PH_3 is generated as a by-product of formation.[319] Of particular note is the significantly larger one-bond phosphorus-proton coupling constants exhibited by $\{ArC(O)\}_2PH$ compared to the parent phosphines, $ArC(O)PH_2$. The reactions of C_6H_4(1-COCl)(R) with R'$P(SiMe_3)_2$ on occasion result in doublet resonances in the

region of −12.9 to −10.5 ppm ($^{1}J_{P\text{-}H}$ 214 - 219 Hz) in the ^{31}P NMR spectra, which are duly assigned to the type **xi** acyl phosphines.

Phosphines of the general formula {ArC(O)}$_3$P (**xii**) are extremely well-documented, typically exhibiting ^{31}P NMR singlet resonances at ca. 53.6 ppm {PhC(O)}$_3$P; δ_P 53.9), {C$_6$H$_4$(1-C(O))(3-Me)}$_3$P; δ_P 53.7, {C$_6$H$_4$(1-C(O))(4-Me)}$_3$P; δ_P 53.2).[321] Singlet resonances in the region of 53.4 - 57.8 ppm are observed in the ^{31}P NMR spectra in almost every reaction of C$_6$H$_4$(1-COCl)(R) with R'P(SiMe$_3$)$_2$, and are duly assigned to the type **xii** acyl phosphines. In contrast with the prevalence of type **xii** acyl phosphines in the literature, reports of phosphine oxides of the general formula {ArC(O)}$_3$P=O (**xiii**) are sparse; {C$_6$H$_4$(1-CO)(2-Me)}$_3$P=O was reported to possess a singlet resonance at 26.9 ppm in the ^{31}P NMR spectrum,[316] while traditional phosphine oxides (R$_3$P=O) such as Me$_3$P=O and ^{t}Bu$_3$P=O exhibit singlets at ca. 38.2 ppm,[314] and di-acyl phosphine oxide C$_6$H$_4$(1-C(O)P(O)Ph$_2$)(4-Cl) exhibits a singlet at 33.0 ppm.[315] Other literature examples of di- and tri-acyl phosphine oxides do not provide accompanying NMR spectra.[316] As for acyl phosphines of the type **xii**, singlet resonances in the region of 59.7 to 73.0 ppm in the ^{31}P NMR spectra, attributed to acyl phosphine oxides, are extremely prevalent during the reactions of C$_6$H$_4$(1-COCl)(R) with R'P(SiMe$_3$)$_2$.



ix **x** **xi** **xii** **xiii**

Ar = C$_6$H$_4$(2-Me), C$_6$H$_4$(3-Me), C$_6$H$_4$(3-CN), C$_6$H$_4$(4-CN), C$_6$H$_4$(4-CO$_2$Me), C$_6$H$_4$(4-COCl)

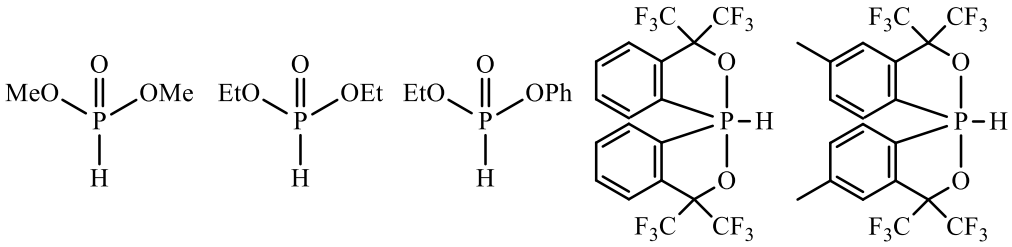
Figure 27. Tentative product assignments of reactions of C$_6$H$_4$(1-COCl)(R) and R'P(SiMe$_3$)$_2$

Table 27. Spectroscopic data ranges for acyl phosphines and acyl phosphine oxide types **ix - xiii**

Type	^{31}P NMR / ppm	Multiplicity	$^{1}J_{P\text{-}H}$ / Hz
ix	−98.6 - −97.9	d	178 - 180
x	−110 - −99.7	t	217 - 220
xi	−12.9 - −10.5	d	214 - 219
xii	53.4 - 57.8	s	-
xiii	59.7 - 73.0	s	-

H-phosphonates

Among the many reaction products of C_6H_4(1-COCl)(R) with R'P($SiMe_3$)$_2$ are species that exhibit spectroscopic data comparable with that reported for H-phosphonates $(RO)_2(R)_2PH$ and $(RO)_2(O)PH$; the H-phosphonates typically exhibit doublet resonances in the region of −48.2 to 10.7 ppm in the ^{31}P NMR spectra, with characteristically large magnitudes of phosphorus-proton coupling ($^1J_{P\text{-}H}$ ca. 718 Hz). Examples include phosphonic acids such as **3.E**) 10.7 ppm ($^1J_{P\text{-}H}$ 696 Hz),[322] **3.F**) 8.4 ppm ($^1J_{P\text{-}H}$ 692 Hz, $^3J_{P\text{-}H}$ 8.3 Hz,),[323] **3.G**) 2.1 ppm ($^1J_{P\text{-}H}$ 741 Hz),[323] and H-phosphonates such as **3.H**) −48.2 ppm ($^1J_{P\text{-}H}$ 733 Hz),[324] and **3.I**) −47.6 ppm ($^1J_{P\text{-}H}$ 730 Hz),[324] (Figure 28). As such, characteristic doublet resonances in the region of −30.3 to −2.7 ppm ($^1J_{P\text{-}H}$ 691 - 745 Hz) in the ^{31}P NMR spectra, which are lost upon proton decoupling, are tentatively identified as H-phosphonate species. The corresponding proton resonances are lost in the ^{1}H NMR baseline, while their low intensity also precludes observation by ^{1}H-^{31}P HMBC NMR experiments. Identification of any of the H-phosphonates remains elusive.



3.E **3.F** **3.G** **3.H** **3.I**

Figure 28. Literature examples of H-phosphonates [322–324]

3.4 Reactions of C_6H_4(1-COCl)(3-R) with silylphosphines

The reactions of C_6H_4(1-COCl)(3-R) with R'P($SiMe_3$)$_2$ afforded a complex mixture of products in most cases, including phosphaalkenes of the types **i - ii**, diphosphacyclobutanes of the types **iii - viii**, acyl phosphines and phosphine oxides of the types **x - xiii** and H-phosphonates, that were tentatively assigned as shown in Figure 29, and as described in section **3.3.2**.

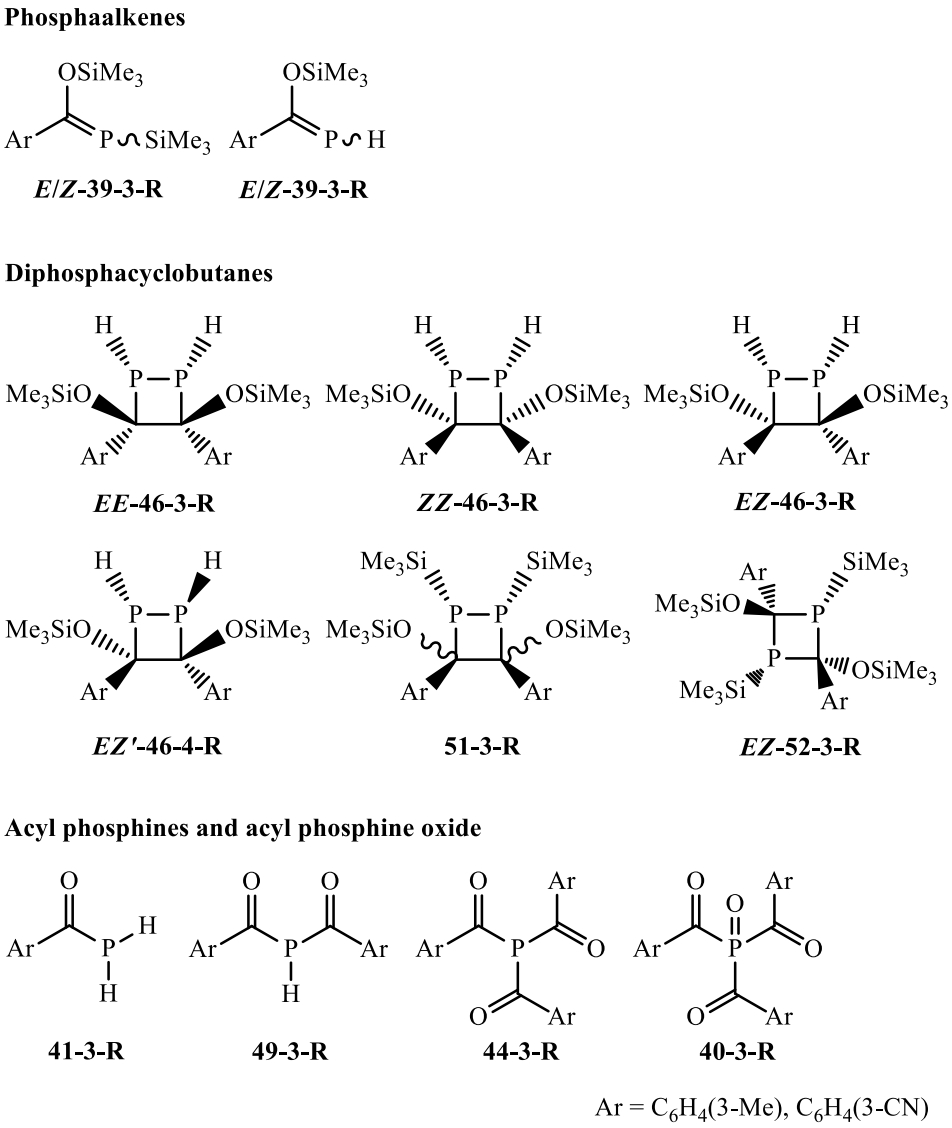
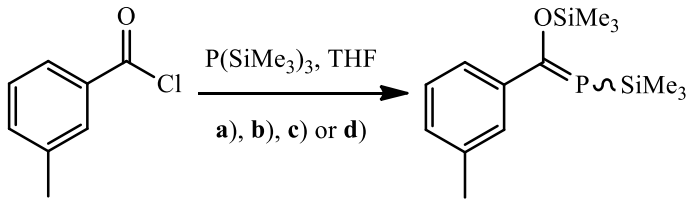


Figure 29. Tentative product assignments of reactions of C_6H_4(1-COCl)(3-R) and R'P($SiMe_3$)$_2$

3.4.1 Synthesis of *E*/*Z*-C_6H_4(1-C($OSiMe_3$)=P$SiMe_3$)(3-Me)

As for phosphaalkenes ***E*/*Z*-39-2-Me**, compounds ***E*/*Z*-39-3-Me** were identified as the predominant products irrespective of reaction conditions (Scheme 84). Complete removal of minor impurities *via* washing with a variety of solvents (pentane, hexane, toluene, THF) and distillation proved ineffective, although variations in reaction temperature and duration reduced the level of trace contaminants notably; the ambient temperature reaction (conditions **c**) afforded the cleanest sample of ***E*/*Z*-39-3-Me**.



***E*/*Z*-39-3-Me**

a) 1) -78 °C, 15 min, 2) r.t. 18 h
b) 1) 0 °C, 15 min, 2) r.t., 18 h
c) r.t., 1 h
d) reflux, 4 h

Scheme 84. Synthesis of C_6H_4(1-C(OSiMe$_3$)=PSiMe$_3$)(3-Me) (***E*/*Z*-39-3-Me**)

Phosphaalkenes ***E*/*Z*-39-3-Me** (37:63) exhibit singlet resonances at 134 (***E*-39-3-Me**) and 131 ppm (***Z*-39-3-Me**) in the $^{31}P\{^1H\}$ NMR spectra, slightly down-field from ***E*/*Z*-39-2-Me** (δ_P 131, 127). The $^{13}C\{^1H\}$ NMR spectra show doublet resonances at 213 ($^1J_{C\text{-}P}$ 65.9 Hz, ***Z*-39-3-Me**) and 219 ppm ($^1J_{C\text{-}P}$ 57.1 Hz, ***E*-39-3-Me**), attributed to the phosphaalkenic carbon centres (Table 28). The singlet signals attributed to the methyl groups (δ_H 2.03 for ***Z*-39-3-Me**, 2.06 for ***E*-39-3-Me**) are shifted significantly higher-field than for ***E*/*Z*-39-2-Me** (δ_H 2.32, 2.35), while the order in which they appear is reversed. As for ***E*/*Z*-39-2-Me**, the difference in chemical shifts in the ^1H NMR spectrum between ***E*-39-3-Me** and ***Z*-39-3-Me** is $\Delta\delta_H$ 0.03 ppm. The isomeric distribution of ***E*/*Z*-39-3-Me** (37:63) is invariant regardless of temperature, although in contrast to ***E*/*Z*-39-2-Me** (ca. 69:31), ***Z*-39-3-Me** is the preferred isomer.

Table 28. Selected spectroscopic data for *E*/*Z*-C_6H_4(1-C(OSiMe$_3$)=PSiMe$_3$)(3-Me) (***E*/*Z*-39-3-Me**)

	$^{31}P\{^1H\}$ / ppm	**$^{29}Si\{^1H\}$ / ppm**	**^1H Me / ppm**	**^1H P(SiCH_3)$_3$ / ppm**	**$^3J_{H\text{-}P}$ / Hz**	**^1H O(SiCH_3)$_3$ / ppm**	**$^{13}C\{^1H\}$ / ppm**	**$^1J_{C\text{-}P}$ / Hz**
***E*-39-3-Me**	134	−2.1, 20.9	2.06	0.08	4.3	0.45	219	57.1
***Z*-39-3-Me**	131	−3.7, 18.9	2.03	0.47	3.7	0.05	213	65.9

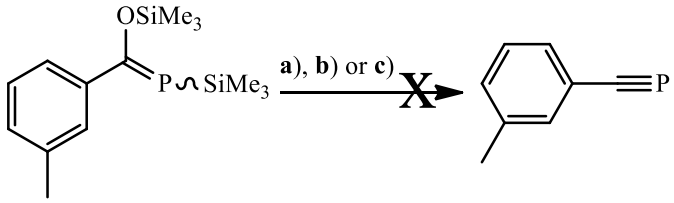
Influence of temperature

The addition of C_6H_4(1-COCl)(3-Me) to P(SiMe$_3$)$_3$ at low temperatures affords ***E*/*Z*-39-3-Me** as the initial major product with significant levels of contaminants that increase with time (9.41 % at 1 h, 46.2 % after 18 h at – 78 °C; 10.6 % at 1 h, 78.8 % at 18 h at 0 °C). In contrast, the ambient temperature reaction affords ***E*/*Z*-39-3-Me** with the lowest levels of contaminants, although analytical purity is not obtained. Spectroscopic analysis of the reaction prior to 1 h demonstrates an incomplete reaction, as determined by the observation of P(SiMe$_3$)$_3$ in the ^{31}P

NMR spectrum, while reaction for longer than 1 h affords a marginal increase in trace contaminants (ca. 5 % at 1 h, ca. 8 % at 4 h). The combination of C_6H_4(1-COCl)(3-Me) with $P(SiMe_3)_3$ at ambient temperature followed by heating at reflux for 4 h also generates a relatively pure sample of ***E*/*Z*-39-3-Me**, the phosphaalkenes representing approximately 90 % of the product mixture (by integration of the ^{31}P NMR spectrum, in the absence of an internal standard); fewer impurities are produced than for the low temperature reactions, and the trace contaminants consist primarily of $P(SiMe_3)_3$.

3.4.2 Attempted synthesis of C_6H_4(1-C≡P)(3-Me)

The conversion of ***E*/*Z*-39-3-Me** to C_6H_4(1-C≡P)(3-Me) was attempted *via* reaction with either DABCO, $[Fe_2(CO)_9]$, or $LiN(SiMe_3)_2$ in accordance with literature precedent (Scheme 85).[163,108] Aliquots were isolated and dried *in vacuo* after 1 h, and the remaining solutions were stirred for 18 h prior to solvent removal.



***E*/*Z*-39-3-Me**

a) r.t., THF, DABCO, 18 h
b) r.t., THF, $[Fe_2(CO)_9]$, 18 h
c) 1) $LiN(SiMe_3)_2$, -78 °C, 30 min, 2) r.t., 18 h

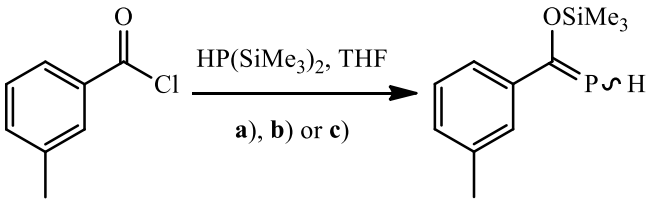
Scheme 85. Attempted synthesis of C_6H_4(1-C≡P)(3-Me)

The addition of DABCO to ***E*/*Z*-39-3-Me** affords a yellow suspension after being stirred for 1 h; solvent removal yields a yellow oil which is identified to consist primarily of unreacted ***E*/*Z*-39-3-Me** on the basis of resonances at 134 and 131 ppm in the $^{31}P\{^1H\}$ NMR spectrum. The number of unidentified trace contaminants double from six in the initial sample to twelve after 18 h, while the isomeric ratio of ***E*/*Z*-39-3-Me** is unchanged. The reaction of ***E*/*Z*-39-3-Me** with $[Fe_2(CO)_9]$ affords a mixture of compounds that defies separation by washing, crystallisation or distillation. The $^{31}P\{^1H\}$ NMR spectrum shows seven singlet resonances after 1 h that range from −212 to 218 ppm, and a more complex product mixture after 18 h. The addition of $LiN(SiMe_3)_2$ to ***E*/*Z*-39-3-Me** produces an orange oil upon solvent removal, which consists primarily of unreacted ***E*/*Z*-39-3-Me**. Trace amounts of $P(SiMe_3)_3$ are also detected at −252 ppm

in the $^{31}P\{^{1}H\}$ NMR spectrum, in addition to minor levels (ca. 3.0 % by integration of the $^{31}P\{^{1}H\}$ NMR spectrum signals) of two mutually coupled doublet resonances at −83.8 ($J_{P\text{-}P}$ 51.8 Hz) and −55.4 ppm ($J_{P\text{-}P}$ 51.8 Hz) that remain unassigned. The suspension shows no change by ^{31}P NMR spectroscopy after 18 h of stirring.

3.4.3 Reactions of C_6H_4(1-COCl)(3-Me) with $HP(SiMe_3)_2$

Similar to ***E*/*Z*-42-2-Me**, phosphaalkenes ***E*/*Z*-42-3-Me** were identified as the predominant species present in the complex product mixtures (Scheme 86); tentative assignments of the products are shown in Table 29.



***E*/*Z*-42-3-Me**

a) 1) -78 °C, 15 min, 2) r.t., 18 h
b) r.t., 18 h
c) 1) 60 °C, 2) reflux, 18 h

Scheme 86. Attempted synthesis of *E*/*Z*-C_6H_4(1-C($OSiMe_3$)=PH)(3-Me) (***E*/*Z*-42-3-Me**)

Table 29. Selected spectroscopic data for reactions of Ar(1-COCl) and $HP(SiMe_3)_2$

	^{31}P NMR / ppm	**Multiplicity**	**$J_{P\text{-}P}$ / Hz**	**$J_{P\text{-}H}$ / Hz**	**Assignment**
***EZ*-46-3-Me**	–116	d	71.3	-	**v**) *EZ*-[1,2]-{Ar(1-C($OSiMe_3$)PH)}$_2$
41-3-Me	–109	t	-	218	**x**) Ar(1-C(O)PH_2)
***ZZ*-46-3-Me**	−104	2nd order	-	-	**iv**) *ZZ*-[1,2]-{Ar(1-C($OSiMe_3$)PH)}$_2$
***EE*-46-3-Me**	−97.1	2nd order	-	-	**iii**) *EE*-[1,2]-{Ar(1-C($OSiMe_3$)PH)}$_2$
***EZ*-46-3-Me**	–86.1	d	71.3	-	**v**) *EZ*-[1,2]-{Ar(1-C($OSiMe_3$)PH)}$_2$
45-3-Me	–15.9	d	-	697	H-phosphonate
44-3-Me	53.4	s	-		**xii**) {Ar(1-CO)}$_3$P
40-3-Me	59.7	s	-	-	**xiii**) {Ar(1-CO)}$_3$P=O
***E*-42-3-Me**	65.9	d	-	161	**ii**) *E*-Ar(1-C($OSiMe_3$)=PH)
***Z*-42-3-Me**	67.4	d	-	152	**ii**) *Z*-Ar(1-C($OSiMe_3$)=PH)
***Z*-39-3-Me**	131	s	-	-	**i**) *Z*-Ar(1-C($OSiMe_3$)=P$SiMe_3$)
***E*-39-3-Me**	133	s	-	-	**i**) *E*-Ar(1-C($OSiMe_3$)=P$SiMe_3$)

Phosphaalkenes ***E*/*Z*-42-3-Me** are the most prominent species in the reaction mixtures irrespective of temperature or reaction duration. The ^{31}P NMR spectra exhibit doublet resonances at 65.8 ($^{1}J_{P\text{-}H}$ 161 Hz, ***E*-42-3-Me**) and 67.4 ppm ($^{1}J_{P\text{-}H}$ 152 Hz, ***Z*-42-3-Me**), while corresponding (by ^{1}H-^{31}P HMBC NMR spectra) doublet signals are observed at 4.75 ($^{1}J_{H\text{-}P}$ 152 Hz) and 5.24 ppm ($^{1}J_{H\text{-}P}$ 161 Hz) in the ^{1}H NMR spectra, attributed to the PH protons. Unlike ***E*/*Z*-42-2-Me**, phosphaalkene ***E*-42-3-Me** exhibits a higher-field chemical shift than ***Z*-42-3-Me**. Trace amounts (0.72 %) of phosphaalkenes ***E*/*Z*-39-3-Me** (55:45) are also apparent during the low temperature reaction, although not the ambient or high temperature variations.

Acyl phosphine **44-3-Me** is also produced from the reaction of C_6H_4(1-COCl)(3-Me) with $HP(SiMe_3)_2$, regardless of temperature, and is initially present as a prominent species that diminishes significantly after 18 h (ca. 33.4 % initially, ca. 9.46 % after 18 h). In contrast, acyl phosphine **40-3-Me** is initially apparent in trace levels that increase after 18 h (ca. 3.05 % initially, ca. 8.07 % after 18 h). Low levels of acyl phosphine **41-3-Me** are apparent in the high temperature reaction of C_6H_4(1-COCl)(3-Me) with $HP(SiMe_3)_2$, but not the −78 °C variation. The H-phosphonate **45-3-Me** constitutes a significant proportion (8.91 %) of the ambient temperature reaction mixture after 18 h, but is not detected in the initial aliquot or during any of the alternative reaction variations. Trace levels of diphosphacyclobutanes **46-3-Me** result from the reaction of C_6H_4(1-COCl)(3-Me) with $HP(SiMe_3)_2$ at −78 °C and 66 °C, but not from the ambient temperature reaction.

Isolation attempts

A crude sample from the ambient temperature reaction of C_6H_4(1-COCl)(3-Me) with $HP(SiMe_3)_2$ was washed with pentane; removal of solvent under reduced pressure affords a spectroscopically pure sample of acyl phosphine **44-3-Me**, identified by a singlet resonance at 53.4 ppm in the ^{31}P NMR spectrum. The ^{1}H NMR spectrum exhibits resonances for the methyl group at 1.90 ppm and the aromatic protons at 6.92 - 7.90 ppm; signal integration confirms the existence of four aromatic protons and three methyl protons. Doublet resonances at 206 ($^{1}J_{C\text{-}P}$ 32.6 Hz) and 141 ppm ($^{2}J_{C\text{-}P}$ 34.4 Hz) in the ^{13}C{^{1}H} NMR spectrum are assigned to the C(O)P and *ipso*-carbon centres respectively, and a singlet resonance at 20.9 ppm for the methyl carbon atom. *In vacuo* drying of the pentane filtrate affords a yellow oil that is identified as a complex mixture of products, including phosphaalkenes ***E*/*Z*-42-3-Me** (55:45), acyl phosphine oxide **40-3-Me** and diphosphacyclobutanes **46-3-Me** (*EE*-, *ZZ*- and *EZ*-isomers).

Quantitative studies

In order to further examine the wide array of products generated from the reaction of C_6H_4(1-COCl)(3-Me) with $HP(SiMe_3)_2$, the reaction was performed at reflux with PPh_3 added to the NMR samples as an internal standard (Table 30, Figure 30). Phosphaalkenes ***E/Z*-42-3-Me** are the major species in each aliquot, with quantities rising steadily for the first 400 min, but falling after 1440 min, as previously noted for the quantitative study of the reaction of C_6H_4(1-COCl)(2-Me) with $HP(SiMe_3)_2$ (section **3.2.5**). The quantities of diphosphacyclobutanes ***ZZ*-46-3-Me** and ***EE*-46-3-Me** remain extremely low throughout, while ***EZ*-46-3-Me** is not detected until 320 min, after which it remains present at a static level. Although acyl phosphine **41-3-Me** is initially present as a very minor product, the quantity increases after 1440 min; similarly, the quantities of acyl phosphine **44-3-Me** and acyl phosphine oxide **40-3-Me** increase steadily for 400 min, after which time the amount of **44-3-Me** falls significantly, while that of **40-3-Me** continues to rise.

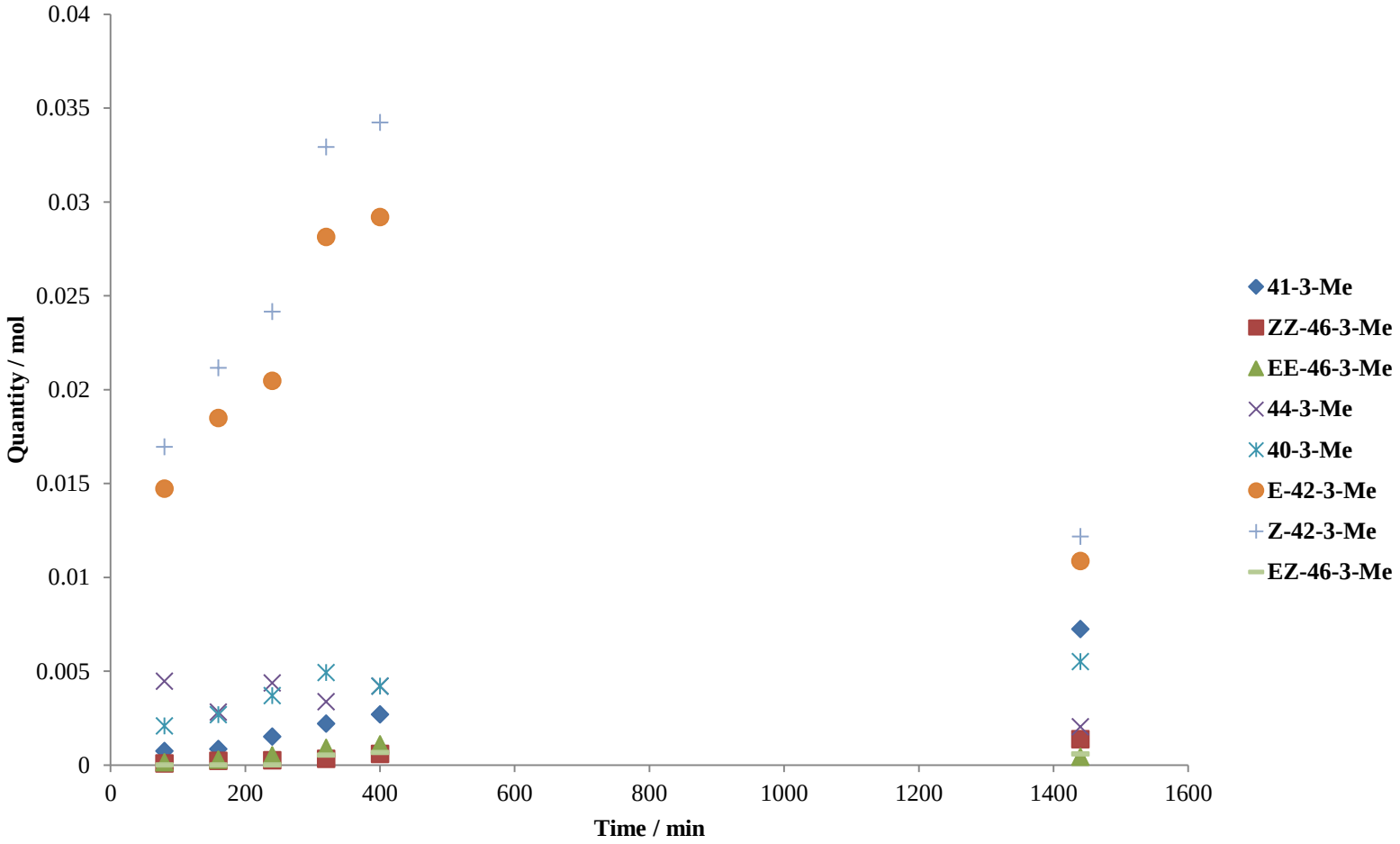


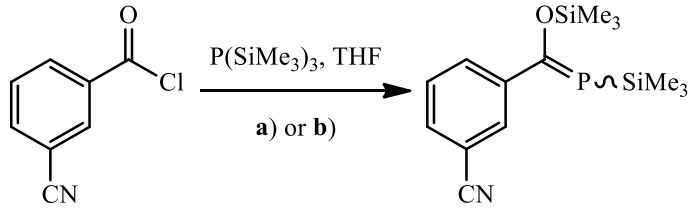
Figure 30. The reaction of Ar(1-COCl) and $HP(SiMe_3)_2$ at 66 °C (Ar = C_6H_4(3-Me))

Table 30. Quantity of species present in aliquots isolated from reflux reaction of C_6H_4(1-COCl)(3-Me) and $HP(SiMe_3)_2$

Time / min	***EZ*-46-3-Me / mol**	***ZZ*-46-3-Me / mol**	***EE*-46-3-Me / mol**	**41-3-Me / mol**	**44-3-Me / mol**	**40-3-Me / mol**	***E*-42-3-Me / mol**	***Z*-42-3-Me / mol**
80	0.00	1.49×10^{-4}	2.97×10^{-4}	7.43×10^{-4}	4.46×10^{-3}	2.08×10^{-3}	1.47×10^{-2}	1.69×10^{-2}
160	0.00	4.23×10^{-4}	5.64×10^{-4}	8.46×10^{-4}	2.82×10^{-3}	2.68×10^{-3}	1.85×10^{-2}	2.12×10^{-2}
240	0.00	5.03×10^{-4}	1.01×10^{-3}	1.51×10^{-3}	4.36×10^{-3}	3.69×10^{-3}	2.05×10^{-2}	2.42×10^{-2}
320	1.04×10^{-3}	6.48×10^{-4}	1.82×10^{-3}	2.20×10^{-3}	3.37×10^{-3}	4.93×10^{-3}	2.81×10^{-2}	3.29×10^{-2}
400	1.34×10^{-3}	1.17×10^{-3}	2.18×10^{-3}	2.68×10^{-3}	4.19×10^{-3}	4.19×10^{-3}	2.92×10^{-2}	3.42×10^{-2}
1440	1.16×10^{-3}	2.75×10^{-3}	8.69×10^{-4}	7.24×10^{-3}	2.03×10^{-3}	5.51×10^{-3}	1.09×10^{-2}	1.21×10^{-2}

3.4.4 Reactions of C_6H_4(1-COCl)(3-CN) with $P(SiMe_3)_3$

In contrast to ***E*/*Z*-39-3-Me** and ***E*/*Z*-39-2-Me**, complex product mixtures were isolated regardless of reaction conditions; the most predominant species were H-phosphonates, while phosphaalkenes ***E*/*Z*-39-3-CN** were present in low levels (Scheme 87, Table 31).



***E*/*Z*-39-3-CN**

a) 1) -78 °C, 15 min, 2) r.t., 18 h
b) r.t., 18 h

Scheme 87. Attempted synthesis of C_6H_4(1-C(OSiMe$_3$)=PSiMe$_3$)(3-CN) (**39-3-CN**)

Table 31. Selected spectroscopic data for reactions of Ar(1-COCl) and $P(SiMe_3)_3$

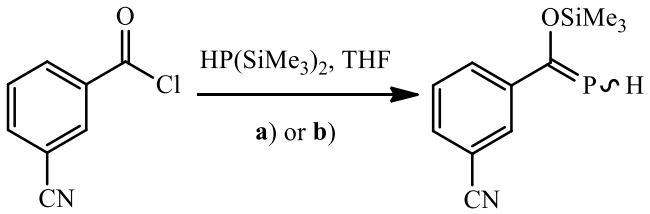
	^{31}**P NMR / ppm**	**Multiplicity**	$J_{P\text{-}P}$ **/ Hz**	$J_{P\text{-}H}$ **/ Hz**	**Assignment**
***EZ*-52-3-CN**	–123	d	193	-	**viii**) *EZ*-[1,3]-{Ar(1-C(OSiMe$_3$)PSiMe$_3$)}$_2$
***EZ*-46-3-CN**	–116	d	71.9	-	**v**) *EZ*-[1,2]-{Ar(1-C(OSiMe$_3$)PH)}$_2$
***ZZ*-46-3-CN**	–104	2nd order	-	-	**iv**) *ZZ*-[1,2]-{Ar(1-C(OSiMe$_3$)PH)}$_2$
***EE*-46-3-CN**	–97.3	2nd order	-	-	**iii**) *EE*-[1,2]-{Ar(1-C(OSiMe$_3$)PH)}$_2$
***EZ*-46-3-CN**	–84.9	ddd	71.9	186, 13.7	**v**) *EZ*-[1,2]-{Ar(1-C(OSiMe$_3$)PH)}$_2$
52-3-CN	–81.5	d	193	-	**viii**) *EZ*-[1,3]-{Ar(1-C(OSiMe$_3$)PSiMe$_3$)}$_2$
51-3-CN	–75.7	s	-	-	**vii**) [1,2]-{Ar(1-C(OSiMe$_3$)PSiMe$_3$)}$_2$
48-3-CN	–30.4	d	15.3	-	H-phosphonate
48-3-CN	–14.7	dd	15.3	737	H-phosphonate
47-3-CN	–13.9	d	-	218	**xi**) {Ar(1-CO)}$_2$PH
43-3-CN	–13.5	d	-	692	H-phosphonate
49-3-CN	–13.2	d	-	705	H-phosphonate
50-3-CN	–2.7	dt	-	701, 8.6	H-phosphonate
44-3-CN	54.6	s	-	-	**xii**) {Ar(1-CO)}$_3$P
40-3-CN	65.6	s	-	-	**xiii**) {Ar(1-CO)}$_3$P=O
***E*-42-3-CN**	73.4	d	-	160	**ii**) *E*-Ar(1-C(OSiMe$_3$)=PH)
***Z*-42-3-CN**	74.0	d	-	153	**ii**) *Z*-Ar(1-C(OSiMe$_3$)=PH)
***Z*-39-3-CN**	136	s	-	-	**i**) *Z*-Ar(1-C(OSiMe$_3$)=PSiMe$_3$)
***E*-39-3-CN**	138	s	-	-	**i**) *E*-Ar(1-C(OSiMe$_3$)=PSiMe$_3$)

The predominant species present in the reactions of C_6H_4(1-COCl)(3-CN) with $P(SiMe_3)_3$, irrespective of temperature, are H-phosphonates **43-3-CN** and **49-3-CN**. Additional H-phosphonate species **48-3-CN** and **50-3-CN** are also present, although in less significant quantities. In contrast, phosphaalkenes ***E*/*Z*-39-3-CN** (44:56) are detected as a relatively minor proportion of the low temperature reaction mixtures (11.4 % after 18 h), and are not apparent in the ambient temperature variation. The resonances are shifted somewhat down-field compared to ***E*/*Z*-39-3-Me** (δ_P 131, 127) and ***E*/*Z*-39-2-Me** (δ_P 133, 131) due to the increased electron-withdrawing ability of the CN group compared with electron-donating Me substituent. Trace levels of phosphaalkenes ***E*/*Z*-42-3-CN** (55:45) are also observed, and exhibit resonances in the ^{31}P NMR spectra that are shifted significantly down-field from ***E*/*Z*-42-3-CN** (δ_P 65.8 ($^1J_{P\text{-}H}$ 161 Hz), 67.4 ($^1J_{P\text{-}H}$ 152 Hz)).

The reaction of C_6H_4(1-COCl)(3-CN) with $P(SiMe_3)_3$ at −78 °C affords a significant quantity of acyl phosphine **47-3-CN** (8.79 %) in the initial aliquot, although the compound diminishes to undetectable levels after 18 h, and is not apparent in the ambient temperature reaction. In contrast, acyl phosphine **44-3-CN** (8.98 %) and acyl phosphine oxide **40-3-CN** (9.32 %) constitute a significant quantity of the ambient temperature reaction mixture, but are not present in the −78 °C variation. Significant proportions of diphosphacyclobutanes ***EZ*-52-3-CN** (6.46 %) and **51-3-CN** (14.5 %) result from the −78 °C reaction of C_6H_4(1-COCl)(3-CN) with $P(SiMe_3)_3$; levels of both compounds diminish to undetectable amounts after 18 h. In contrast, low levels of diphosphacyclobutanes **46-3-CN** (3.59 % combined) are observed during the comparable ambient temperature reaction, and as for ***EZ*-52-3-CN** and **51-3-CN**, are not detected after 18 h. Four H-phosphonates are also produced during the reactions.

3.4.5 Reactions of C_6H_4(1-COCl)(3-CN) with $HP(SiMe_3)_2$

Complex product mixtures that defied separation were afforded irrespective of temperature, in which phosphaalkenes ***E*/*Z*-42-3-CN** were identified in relatively minor proportions (Scheme 88, Table 32).



***E*/*Z*-42-3-CN**

a) 1) -78 °C, 15 min, 2) r.t., 18 h
b) r.t., 18 h

Scheme 88. Attempted synthesis of *E*/*Z*-C_6H_4(1-C(OSiMe$_3$)=PH)(3-CN) (***E*/*Z*-42-3-CN**)

Table 32. Selected spectroscopic data for reactions of Ar(1-COCl) and $HP(SiMe_3)_2$

	^{31}P NMR / ppm	**Multiplicity**	**$J_{P\text{-}P}$ / Hz**	**$J_{P\text{-}H}$ / Hz**	**Assignment**
***EZ*-46-3-CN**	–116	ddd	70.7	175, 10.7	**v**) *EZ*-[1,2]-{Ar(1-C(OSiMe$_3$)PH)}$_2$
41-3-CN	–110	t	-	217	**x**) Ar(1-C(O)PH_2)
***ZZ*-46-3-CN**	–103	2nd order	-	-	**iv**) *ZZ*-[1,2]-{Ar(1-C(OSiMe$_3$)PH)}$_2$
***EE*-46-3-CN**	–97.3	2nd order	-	-	**iii**) *EE*-[1,2]-{Ar(1-C(OSiMe$_3$)PH)}$_2$
***EZ*-46-3-CN**	–84.9	ddd	70.7	186, 13.7	**v**) *EZ*-[1,2]-{Ar(1-C(OSiMe$_3$)PH)}$_2$
49-3-CN	–13.3	d	-	701	H-phosphonate
53-3-CN	–10.9	d	-	745	H-phosphonate
44-3-CN	54.7	s	-	-	**xii**) {Ar(1-CO)}$_3$P
40-3-CN	65.7	s	-	-	**xiii**) {Ar(1-CO)}$_3$P=O
***E*-42-3-CN**	73.4	d	-	160	**ii**) *E*-Ar(1-C(OSiMe$_3$)=PH)
***Z*-42-3-CN**	74.1	d	-	154	**ii**) *Z*-Ar(1-C(OSiMe$_3$)=PH)

The predominant product, regardless of temperature, is primary acyl phosphine **41-3-CN**, which comprises ca. 39.9 % of the product mixture in the initial samples and ca. 25.6 % after 18 h. Identified by a ^{31}P NMR triplet resonance at –110 ppm ($^1J_{P\text{-}H}$ 220 Hz), the corresponding PH_2 protons are observed as a doublet signal at 3.67 ppm ($^1J_{H\text{-}P}$ 220 Hz) in the ^{1}H NMR spectra (confirmed by ^{1}H-^{31}P HMBC NMR spectroscopy). High levels of acyl phosphine **44-3-CN** and acyl phosphine oxide **40-3-CN** are also detected irrespective of temperature, while significant proportions of phosphaalkenes ***E*/*Z*-42-3-CN** (ca. 54:46), that remain constant over time (ca. 11.6 %), are observed during the low temperature reaction, but are not present in the ambient temperature variation. The product mixtures comprise a significant proportion of H-phosphonates **49-3-CN** and **53-3-CN**, while diphosphacyclobutanes ***ZZ*-46-3-CN**, ***EE*-46-3-CN** and ***EZ*-46-3-CN** are present in relatively minor quantities.

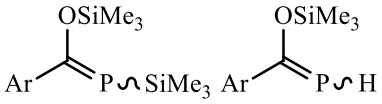
Isolation attempts

Washing the crude mixture (method **b**) affords an orange solid that is insoluble in pentane and is identified as a mixture of acyl phosphines **41-3-CN** and **44-3-CN** and the acyl phosphine oxide **40-3-CN** by ^{31}P NMR spectroscopy. Reduced pressure solvent removal from the pentane filtrate affords a yellow solid that is identified as a mixture of acyl phosphine **41-3-CN** and the reagent, C_6H_4(1-COCl)(3-CN); the latter is identified by ^{1}H NMR signals at 6.39, 6.81, 7.47 and 7.69.

3.5 Reactions of C_6H_4(1-COCl)(4-R) with silylphosphines

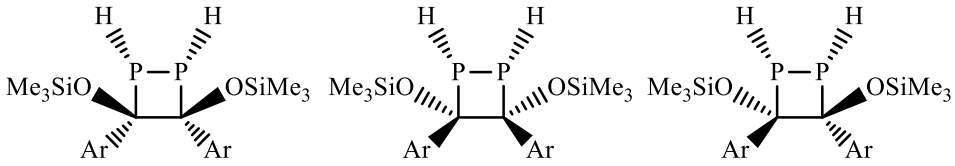
The reactions of C_6H_4(1-COCl)(4-R) with R'P($SiMe_3$)$_2$ afforded a complex mixture of products that included phosphaalkenes of the types **i - ii**, diphosphacyclobutanes of the types **iii - viii**, acyl phosphines and phosphine oxides of the types **ix - xiii**, and H-phosphonates, that were tentatively assigned as shown in Figure 31, and as described in section **3.3.2**.

Phosphaalkenes

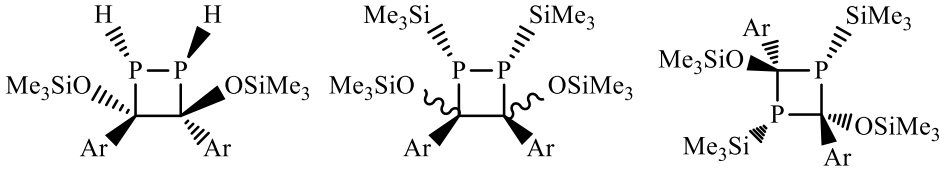


***E*/*Z*-39-4-R** ***E*/*Z*-39-4-R**

Diphosphacyclobutanes

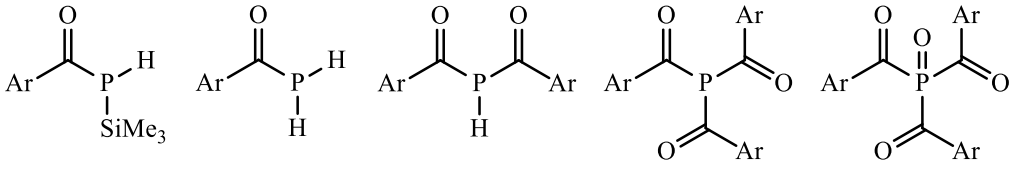


***EE*-46-4-R** ***ZZ*-46-4-R** ***EZ*-46-4-R**



***EZ'*-46-4-R** **51-4-R** ***EZ*-52-4-R**

Acyl phosphines and acyl phosphine oxide



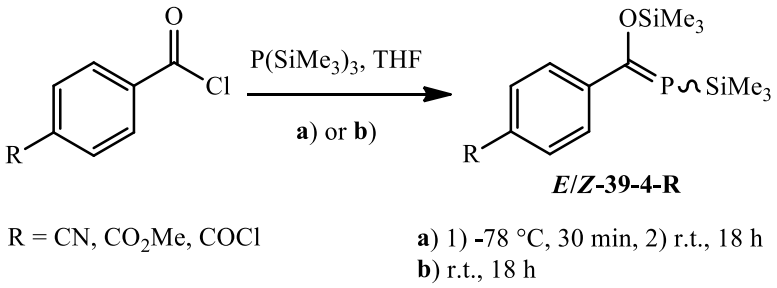
54-4-R **41-4-R** **47-4-R** **44-4-R** **40-4-R**

Ar = C_6H_4(4-CN), C_6H_4(4-CO_2Me), C_6H_4(4-COCl)

Figure 31. Tentative product assignments of reactions of C_6H_4(1-COCl)(4-R) with R'P($SiMe_3$)$_2$

3.5.1 Reactions of C_6H_4(1-COCl)(4-R) with P($SiMe_3$)$_3$

In contrast to the attempted syntheses of phosphaalkenes ***E*/*Z*-39-2-Me** and ***E*/*Z*-39-3-R**, complex product mixtures were afforded from this reaction, regardless of conditions, wherein no predominant species could be identified (Scheme 89, Table 33).



Scheme 89. Attempted syntheses of *E*/*Z*-C_6H_4(1-C($OSiMe_3$)=$PSiMe_3$)(4-R) (***E*/*Z*-39-4-R**)

Table 33. Selected spectroscopic data for reactions of Ar(1-COCl) and $P(SiMe_3)_3$

	^{31}**P NMR / ppm**	**Multiplicity**	$J_{P\text{-}P}$ **/ Hz**	$J_{P\text{-}H}$ **/ Hz**	**Assignment**
***EZ*-52-4-R**	–124	d	190	-	**viii**) *EZ*-[1,3]-{Ar(1-C($OSiMe_3$)$PSiMe_3$)}$_2$
***EZ'*-46-4-R**	–120	d	90.5	-	**vi**) *EZ'*-[1,2]-{Ar(1-C($OSiMe_3$)PH)}$_2$
***EZ*-46-4-R**	–115	ddd	71.0	172, 10.6	**v**) *EZ*-[1,2]-{Ar(1-C($OSiMe_3$)PH)}$_2$
***ZZ*-46-4-R**	–106	2nd order	-	-	**iv**) *ZZ*-[1,2]-{Ar(1-C($OSiMe_3$)PH)}$_2$
54-4-R	–98.6	d	-	180	**ix**) Ar(1-C(O)P(H)$SiMe_3$)
***EE*-46-4-R**	–97.6	2nd order	-	-	**iii**) *EE*-[1,2]-{Ar(1-C($OSiMe_3$)PH)}$_2$
***EZ*-46-4-R**	–84.2	ddd	71.0	184, 11.2	**v**) *EZ*-[1,2]-{Ar(1-C($OSiMe_3$)PH)}$_2$
***EZ'*-46-4-R**	–83.1	d	90.5	-	**vi**) *EZ'*-[1,2]-{Ar(1-C($OSiMe_3$)PH)}$_2$
***EZ*-52-4-R**	–82.4	d	190	-	**viii**) *EZ*-[1,3]-{Ar(1-C($OSiMe_3$)$PSiMe_3$)}$_2$
51-4-R	–77.7	s	-	-	**vii**) [1,2]-{Ar(1-C($OSiMe_3$)$PSiMe_3$)}$_2$
48-4-R	–30.2	d	14.9	-	H-phosphonate
48-4-R	–14.9	dd	14.9	731	H-phosphonate
53-4-R	–11.2	d	-	734	H-phosphonate
47-4-R	–10.5	d	-	214	**xi**) {Ar(1-CO)}$_2$PH
44-4-R	56.4	s	-	-	**xii**) {Ar(1-CO)}$_3$P
40-4-R	68.3	s	-	-	**xiii**) {Ar(1-CO)}$_3$P=O
***E*-42-4-R**	78.4	d	-	161	**ii**) *E*-Ar(1-C($OSiMe_3$)=PH)
***Z*-42-4-R**	81.1	d	-	156	**ii**) *Z*-Ar(1-C($OSiMe_3$)=PH)
***Z*-39-4-R**	143	s	-	-	**i**) *Z*-Ar(1-C($OSiMe_3$)=$PSiMe_3$)
***E*-39-4-R**	147	s	-	-	**i**) *E*-Ar(1-C($OSiMe_3$)=$PSiMe_3$)

Phosphaalkenes ***E*/*Z*-39-4-R** (72:28) are generated from the reaction of C_6H_4(1-COCl)(4-CO_2Me) with $P(SiMe_3)_3$, but not for the reactions of C_6H_4(1-COCl)(4-R) (R = CN, COCl) with $P(SiMe_3)_3$, irrespective of temperature. The predominance of ***E*-39-4-CO_2Me** is consistent with the case of ***E*/*Z*-39-2-Me**, for which the *E*-isomer is also favoured; in contrast, the *Z*-isomer is always the preferred form of ***E*/*Z*-39-3-R**. The relative proportion of phosphaalkenes ***E*/*Z*-39-4-**

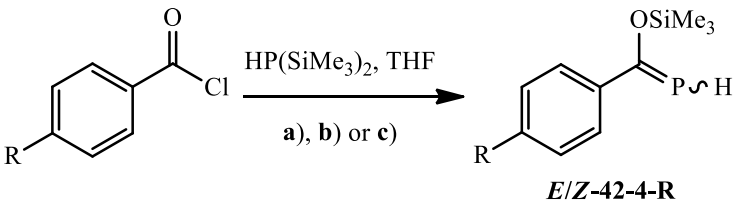
CO_2Me is high in the initial samples but diminishes with time. Low levels (4.65 %) of phosphaalkenes ***E*/*Z*-42-4-R** (41:59) are detected during the reaction of C_6H_4(1-COCl)(4-CN) with $P(SiMe_3)_3$ at −78 °C after 18 h, but not for any other reaction variation. The prevalence of ***Z*-42-4-CN** is noted again, as for phosphaalkenes ***E*/*Z*-42-3-R** (44:56 for R = Me, 46:54 for R = CN).

Significant levels (ca. 14.3 % combined) of all of the [1,2]-diphosphacyclobutanes (**46-4-R**) are apparent during the reactions of C_6H_4(1-COCl)(4-R) (R = CN, COCl) with $P(SiMe_3)_3$ after 18 h, but not in the initial aliquots, and not when R = CO_2Me. High levels of diphosphacyclobutane **51-4-R** that diminish with time (from ca. 12.4 % to ca. 6.97 % after 18 h) are detected universally except for when R = CN. Compound ***EZ*-52-4-R** constitutes ca. 2.71 % of the product mixture that results from the reactions of C_6H_4(1-COCl)(4-CO_2Me) with $P(SiMe_3)_3$, but for no other substrates; levels diminish only marginally after 18 h.

Only trace levels of acyl phosphine **44-4-R** (0.32 %) and acyl phosphine oxide **40-4-R** (0.40 %) are detected during the reactions. Significant levels of acyl phosphine **47-4-R** are apparent from the reactions of C_6H_4(1-COCl)(4-CO_2Me) with $P(SiMe_3)_3$ at both −78 °C and ambient temperature, constituting ca. 7.45 % of the mixture in the initial aliquots and ca. 5.64 % after 18 h. Low levels of acyl phosphine **54-4-R** are produced from the reactions of C_6H_4(1-COCl)(4-CN) with $P(SiMe_3)_3$ irrespective of temperature, but **54-4-R** is not detected during the reactions of C_6H_4(1-COCl)(4-R) (R = COCl, CO_2Me) with $P(SiMe_3)_3$. Two H-phosphonates are also generated in significant quantities during all reaction variations.

3.5.2 Reactions of C_6H_4(1-COCl)(4-R) with $HP(SiMe_3)_2$

As noted in pursuit of phosphaalkenes ***E*/*Z*-39-4-R**, complex product mixtures were observed during all of the reactions irrespective of temperature, in which no predominant species was detected (Scheme 90, Table 34).



***E*/*Z*-42-4-R**

R = CN, CO_2Me, COCl

a) 1) -78 °C, 30 min, 2) r.t., 18 h
b) r.t., 18 h
c) 1) 60 °C, 2) reflux, 18 h

Scheme 90. Attempted syntheses of C_6H_4(1-C(OSiMe$_3$)=PH)(4-R)

Table 34. Selected spectroscopic data for reactions of Ar(1-COCl) and $HP(SiMe_3)_2$

	^{31}**P NMR / ppm**	**Multiplicity**	$J_{P\text{-}P}$ **/ Hz**	$J_{P\text{-}H}$ **/ Hz**	**Assignment**
***EZ'*-46-4-R**	–119	dd	89.9	165	**vi**) *EZ*'-[1,2]-{Ar(1-C(OSiMe$_3$)PH)}$_2$
***EZ*-46-4-R**	–115	ddd	71.1	173, 10.7	**v**) *EZ*-[1,2]-{Ar(1-C(OSiMe$_3$)PH)}$_2$
41-4-R	–108	t	-	219	**x**) Ar(1-C(O)PH$_2$)
***ZZ*-46-4-R**	–104	2nd order	-	-	**iv**) *ZZ*-[1,2]-{Ar(1-C(OSiMe$_3$)PH)(4-R)}$_2$
54-4-R	–98.2	d	-	179	**ix**) C$_6$H$_4$(1-C(O)P(H)SiMe$_3$)
***EE*-46-4-R**	–96.7	2nd order	-	-	**iii**) *EE*-[1,2]-{Ar(1-C(OSiMe$_3$)PH)}$_2$
***EZ*-46-4-R**	–84.4	ddd	71.1	184, 12.1	**v**) *EZ*-[1,2]-{Ar(1-C(OSiMe$_3$)PH)}$_2$
***EZ'*-46-4-R**	–82.3	ddd	89.9	170, 8.9	**vi**) *EZ*'-[1,2]-{Ar(1-C(OSiMe$_3$)PH)}$_2$
48-4-R	–30.4	d	14.7	-	H-phosphonate
48-4-R	–14.9	dd	14.7	735	H-phosphonate
49-4-R	–13.3	d	-	701	H-phosphonate
47-4-R	–12.9	d	-	219	**xi**) {Ar(1-CO)}$_2$PH
53-4-R	–10.9	d	-	742	H-phosphonate
55-4-R	–10.8	d	-	737	H-phosphonate
56-4-R	–10.6	d	-	739	H-phosphonate
44-4-R	56.8	s	-	-	**xii**) {Ar(1-CO)}$_3$P
40-4-R	70.5	s	-	-	**xiii**) {Ar(1-CO)}$_3$P=O
***E*-42-4-R**	78.8	d	-	159	**ii**) *E*-Ar(1-C(OSiMe$_3$)=PH)
***Z*-42-4-R**	81.6	d	-	154	**ii**) *Z*-Ar(1-C(OSiMe$_3$)=PH)

The ^{31}P NMR spectra of the samples isolated from the reactions of C$_6$H$_4$(1-COCl)(4-R) with $HP(SiMe_3)_2$ exhibit doublets at ca. 78.8 ($^1J_{P\text{-}H}$ ca. 159 Hz) and ca. 81.6 ppm ($^1J_{P\text{-}H}$ ca. 154 Hz), assigned to phosphaalkenes ***E*/*Z*-42-4-R**. Corresponding ^{1}H NMR doublet signals at ca. 5.08 ($^1J_{P\text{-}H}$ ca. 159 Hz) and ca. 4.77 ppm ($^1J_{P\text{-}H}$ ca. 154 Hz) are assigned to the PH protons, confirmed by ^{1}H-^{31}P HMBC NMR spectroscopy. The isomeric distribution remains almost uniform at ca. 45:55 (*E*:*Z*) regardless of temperature or R group. While ***E*/*Z*-42-4-R** are detected as major species in each reaction (ca. 10.0 % in the initial aliquots), in all cases the relative proportions of ***E*/*Z*-42-4-R** diminish with time; in several examples, including when R = CN, COCl, phosphaalkenes ***E*/*Z*-42-4-R** are not apparent after 18 h. In contrast with the reactions of C$_6$H$_4$(1-COCl)(R) (R = 2-Me, 3-Me) with $HP(SiMe_3)_2$, phosphaalkenes ***E*/*Z*-39-4-R** are not detected in any of the reactions.

As for the reactions of C$_6$H$_4$(1-COCl)(4-R) with $P(SiMe_3)_3$, all of the [1,2]-diphosphacyclobutanes (**46-4-R**) are apparent during the reactions of C$_6$H$_4$(1-COCl)(4-R) with $HP(SiMe_3)_2$. In most of the reactions diphosphacyclobutanes ***EE*-46-4-R** and ***ZZ*-46-4-R** are the

predominant species in the product mixtures, levels of which increase after 18 h. The preference for the *EE*- isomer is consistent with general trends for **46-3-R**. Diphosphacyclobutanes ***EZ*-46-4-R** and ***EZ'*-46-4-R** are apparent in relatively low levels in most of the samples isolated; general trends throughout the reactions show that the relative proportion of ***EZ*-46-4-R** increases after 18 h, while that of ***EZ'*-46-4-R** diminishes.

With the exception of acyl phosphine **47-4-R**, which is only generated in low levels from the ambient temperature reaction of C_6H_4(1-COCl)(4-R) with $HP(SiMe_3)_2$, each acyl phosphine and the acyl phosphine oxide is apparent in every reaction, irrespective of temperature, reaction duration or R group. High levels of five distinct H-phosphonates are also detected during the reactivity studies of C_6H_4(1-COCl)(4-R) with $HP(SiMe_3)_2$.

Quantitative study

As in previous examples, the reaction of C_6H_4(1-COCl)(4-CO_2Me) with $HP(SiMe_3)_2$ was probed at reflux with the addition of PPh_3 as an internal standard (Figure 32, Table 35). Phosphaalkenes ***E*/*Z*-42-4-CO_2Me** are present in relatively low levels which diminish over time. Diphosphacyclobutanes **46-4-CO_2Me** are the most prominent species, present in increasing quantities within each subsequent aliquot until 1440 min, at which time the amount of ***EE*-46-4-CO_2Me** falls significantly, the quantity of ***ZZ*-46-4-CO_2Me** increases, and levels of ***EZ*-46-4-CO_2Me** remain relatively unchanged. In contrast, diphosphacyclobutane ***EZ'*-46-4-CO_2Me** is detected in trace levels that diminish with time. Similar to trends observed in the non-quantitative reactions, the amount of H-phosphonate **49-4-CO_2Me** increases steadily with time. The quantities of acyl phosphine oxide **40-4-CO_2Me** and acyl phosphine **44-4-CO_2Me** remain extremely low for the entire reaction duration, while levels of acyl phosphine **41-4-CO_2Me** increase steadily. In contrast, the initial quantity of acyl phosphine **54-4-CO_2Me** is substantial, but diminishes to undetectable levels after 160 min.

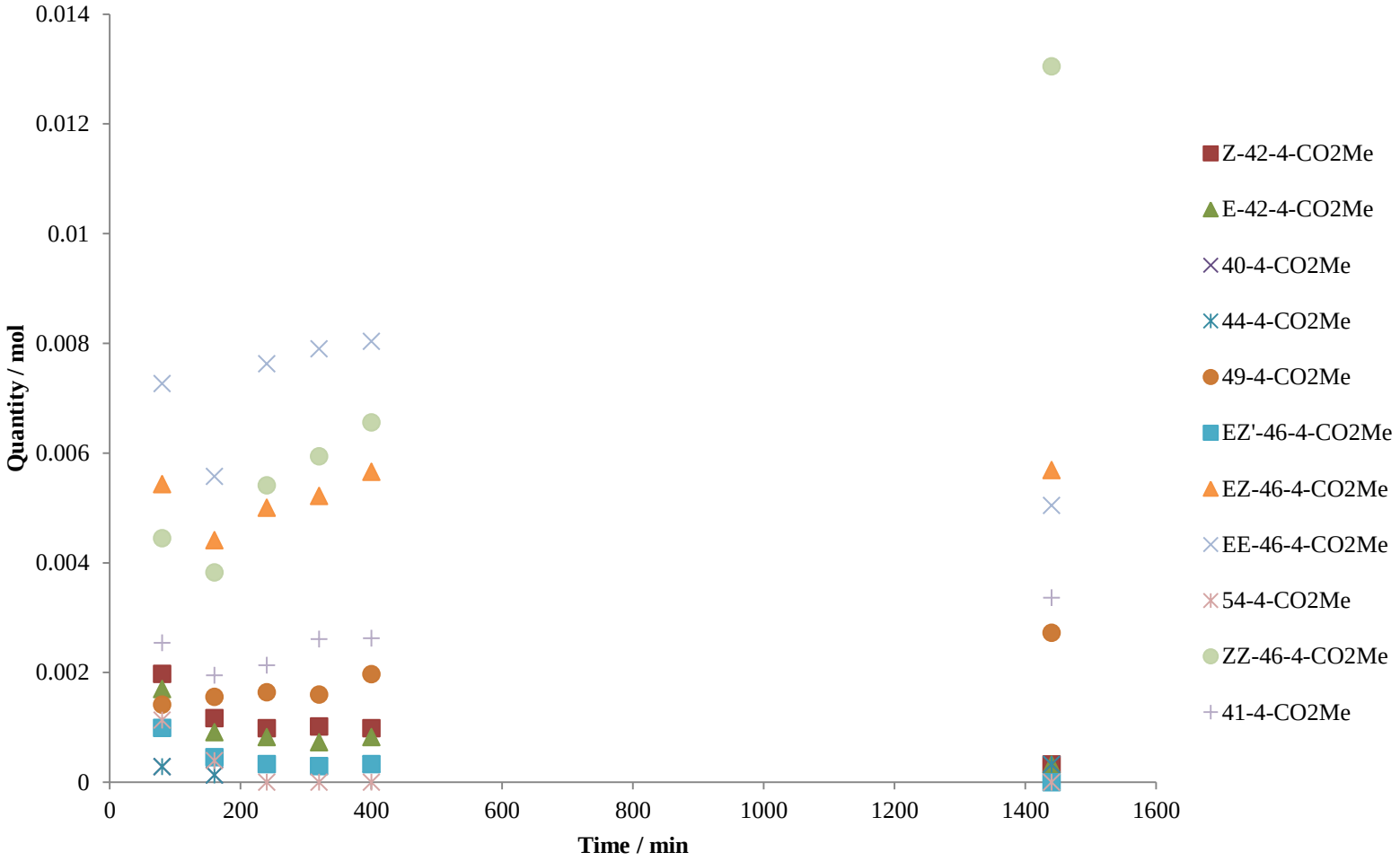


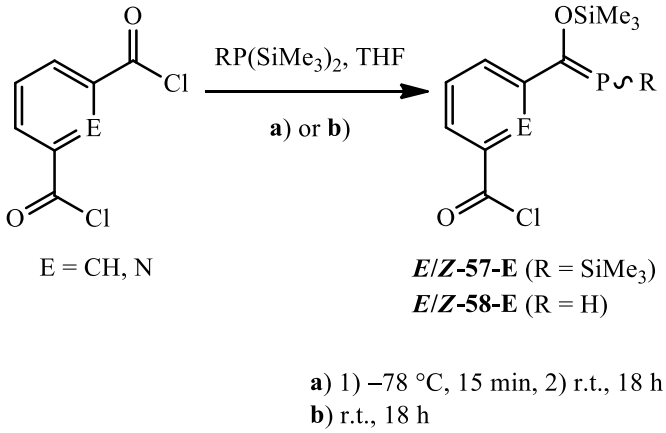
Figure 32. The reaction of Ar(1-COCl) and $HP(SiMe_3)_2$ at 66 °C (Ar = $C_6H_4(4\text{-}CO_2Me)$)

Table 35. Quantity of species present in aliquots isolated from reflux reaction of C_6H_4(1-COCl)(4-CO_2Me) and $HP(SiMe_3)_2$

Time / min	***EZ'*-46-R / mol**	***EZ*-46-R / mol**	**41-R / mol**	***ZZ*-46-R / mol**	**54-R / mol**	***EE*-46-R / mol**	**44-R / mol**	**40-R / mol**	**49-R / mol**	***E*-42-R / mol**	***Z*-42-R / mol**
80	9.87×10^{-4}	5.43×10^{-3}	2.54×10^{-3}	4.44×10^{-3}	1.13×10^{-3}	7.23×10^{-3}	4.09×10^{-3}	2.82×10^{-4}	1.41×10^{-3}	1.69×10^{-4}	1.98×10^{-3}
160	4.54×10^{-4}	4.41×10^{-3}	1.94×10^{-3}	3.82×10^{-3}	3.89×10^{-4}	5.57×10^{-3}	2.59×10^{-3}	1.30×10^{-4}	1.56×10^{-3}	9.07×10^{-4}	1.17×10^{-3}
240	3.28×10^{-4}	5.00×10^{-3}	2.13×10^{-3}	5.41×10^{-3}	0.00	7.62×10^{-3}	3.61×10^{-3}	3.28×10^{-4}	1.64×10^{-3}	8.20×10^{-4}	9.84×10^{-4}
320	2.89×10^{-4}	5.23×10^{-3}	2.61×10^{-3}	5.94×10^{-3}	0.00	7.89×10^{-3}	3.04×10^{-3}	2.90×10^{-4}	1.59×10^{-3}	7.24×10^{-4}	1.01×10^{-3}
400	3.28×10^{-4}	5.66×10^{-3}	2.62×10^{-3}	6.56×10^{-3}	0.00	8.03×10^{-3}	3.12×10^{-3}	3.28×10^{-4}	1.97×10^{-3}	8.20×10^{-4}	9.84×10^{-4}
1440	0.00	5.68×10^{-3}	3.36×10^{-3}	1.31×10^{-2}	0.00	5.04×10^{-3}	1.92×10^{-3}	3.20×10^{-4}	2.72×10^{-3}	3.20×10^{-4}	3.20×10^{-3}

3.6 Reactions of $C_5H_3E(2,6\text{-}COCl)_2$ with silylphosphines

The syntheses of *E*/*Z*-$C_5H_3E(2\text{-}C(OSiMe_3)=PSiMe_3)(6\text{-}COCl)$ (***E*/*Z*-57-E**) and *E*/*Z*-$C_5H_3E(2\text{-}C(OSiMe_3)=PH)(6\text{-}COCl)$ (***E*/*Z*-58-E**) were attempted *via* addition of the respective $C_5H_3E(2,6\text{-}COCl)_2$ (E = CH, N) to $RP(SiMe_3)_2$ (R = $SiMe_3$, H) (Scheme 91). The reactions were performed under two sets of conditions; for method **a**, additions took place at −78 °C and the resulting solutions were stirred for 15 min before being allowed to warm to ambient temperature over 45 min, whereupon an aliquot was isolated, while for method **b** the additions were performed at ambient temperature. In both cases the solutions were dried *in vacuo* after 18 h.



Scheme 91. Attempted syntheses of *E*/*Z*-$C_5H_3E(2\text{-}C(OSiMe_3)=PR)(6\text{-}COCl)$ (***E*/*Z*-57-E**, ***E*/*Z*-58-E**)

3.6.1 Reactions of $C_5H_3E(2,6\text{-}COCl)_2$ with $P(SiMe_3)_3$

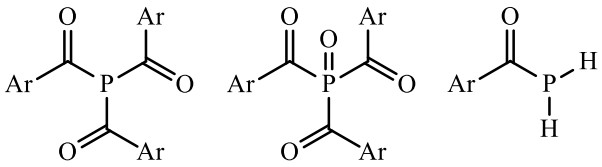
The reaction of $C_5H_3CH(2,6\text{-}COCl)_2$ with $P(SiMe_3)_3$ (method **a**) affords after 1 h a largely intractable mixture with $^{31}P\{^1H\}$ NMR resonances at −136, −55.6, −24.7, 107 and 136 ppm. After 18 h the mixture is markedly simpler, with three major species present in the ^{31}P NMR spectrum, including a singlet at −24.7 ppm which remains unidentified, and two doublet resonances at −13.2 ($^1J_{P\text{-}H}$ ca. 694 Hz) and −10.7 ppm ($^1J_{P\text{-}H}$ 735 Hz), attributed to H-phosphonates by comparison with **43-3-R** and **53-3-R**. In contrast, the reaction of $C_5H_3N(2,6\text{-}COCl)_2$ with $P(SiMe_3)_3$ (method **a**) produces a single phosphorus-containing product after 1 h with a singlet signal at −24.8 ppm in the ^{31}P NMR spectrum. The ^1H NMR spectrum shows triplet and doublet resonances for the aromatic protons at 6.97 ($^3J_{H\text{-}H}$ 7.9 Hz) and 7.95 ppm ($^3J_{H\text{-}H}$ 7.9 Hz) which are shifted significantly down-field compared to $C_5H_3N(2,6\text{-}COCl)_2$ (δ_H 6.49 ($^3J_{H\text{-}H}$ 7.6 Hz), 7.24 ($^3J_{H\text{-}H}$ 8.0 Hz)). After 18 h a more complex mixture of products is apparent; the ^{31}P NMR spectrum shows a singlet at −24.8 ppm, in addition to a doublet resonance at −13.5 ($^1J_{P\text{-}H}$ 688 Hz), attributed to a H-phosphonate compound.

The method **b** reactions of $C_5H_3E(2,6\text{-}COCl)_2$ (E = CH, N) both produce a single phosphorus-containing product with a singlet resonance at ca. −24.8 ppm in the ^{31}P NMR spectra, identical to that produced during method **a**. The ^{1}H NMR and ^{1}H-^{13}C HMBC NMR spectra enable the full assignment of the aromatic protons for each variation in E, and show that in both examples the product features aromatic resonances that are shifted down-field compared to the reagents $C_5H_3E(2,6\text{-}COCl)$. The $^{13}C\{^{1}H\}$ NMR spectra show signals for all of the aromatic resonances and for one COCl centre at ca. 166 ppm. However, none of the signals exhibit carbon-phosphorus coupling and no additional signals that might be attributed to a second carbonyl group are observed in either the $^{13}C\{^{1}H\}$ or ^{1}H-^{13}C HMBC NMR spectra. As such, the products remain unidentified.

3.6.2 Reactions of $C_5H_3E(2,6\text{-}COCl)_2$ with $HP(SiMe_3)_2$

The reactions of $C_5H_3CH(2,6\text{-}COCl)_2$ with $HP(SiMe_3)_2$ afford complex product mixtures that are almost identical irrespective of temperature or reaction duration. The ^{31}P NMR spectra show in excess of twenty resonances, including five triplet signals between –134 and –109 ppm ($^{1}J_{P\text{-}H}$ ca. 214 Hz), two of which correlate with ^{1}H NMR doublet signals at 3.79 ($^{1}J_{H\text{-}P}$ 219 Hz) and 3.89 ppm ($^{1}J_{H\text{-}P}$ 219 Hz); while the signals are consistent with known primary acyl phosphines like $^{t}BuC(O)PH_2$ (δ_P −122 ($^{1}J_{P\text{-}H}$ 214 Hz), δ_H 3.77 ppm ($^{1}J_{P\text{-}H}$ 214 Hz)),[318] identification of the compounds is not possible in lieu of additional data.

A yellow solid is extracted from the crude mixture with pentane and identified as a far simpler mixture that contains just three phosphorus-containing compounds; singlet resonances at 54.3 and 64.9 ppm in the ^{31}P NMR spectrum for acyl phosphine **59** and acyl phosphine oxide **60** (Figure 33) are assigned by comparison to acyl phosphine **44-3-Me** (δ_P 53.4) and acyl phosphine oxide **40-3-Me** (δ_P 59.7). A ^{31}P NMR triplet signal at –110 ppm ($^{1}J_{P\text{-}H}$ 219 Hz) with a corresponding doublet resonance at 3.75 ppm ($^{1}J_{H\text{-}P}$ 219 Hz) in the ^{1}H NMR spectrum, confirmed by ^{1}H-^{31}P HMBC NMR experiments, is assigned to primary acyl phosphine **61** (Figure 33) by comparison to **41-3-Me** (δ_P –109 ($^{1}J_{P\text{-}H}$ 218 Hz)). Significant quantities of $C_5H_3CH(2,6\text{-}COCl)_2$ are also present, identified by ^{1}H NMR resonances at 6.56 ($^{3}J_{H\text{-}H}$ 7.7 Hz), 7.63 ($^{3}J_{H\text{-}H}$ 7.9 Hz) and 8.45 ppm.



59 **60** **61**

Ar = $C_5H_3CH(6\text{-}COCl)$

Figure 33. Tentative product assignments from reactions of $C_5H_3CH(2,6\text{-}COCl)_2$ and $HP(SiMe_3)_2$

As for $C_5H_3CH(2,6\text{-}COCl)_2$, the reactions of $C_5H_3N(2,6\text{-}COCl)_2$ with $HP(SiMe_3)_2$ afford the same mixture of products regardless of temperature or reaction duration. A mixture of white and red solids that do not exhibit any resonances in the $^{31}P\{^1H\}$ NMR spectra are produced, in which unreacted $C_5H_3N(2,6\text{-}COCl)_2$, is identified as the predominant species by signals at 6.58 ($^3J_{H\text{-}H}$ 8.2 Hz) and 7.30 ppm ($^3J_{H\text{-}H}$ 7.8 Hz) in the ^1H NMR spectra.

3.7 Summary

The successful syntheses of phosphaalkenes *E*/*Z*-C_6H_4(1-C($OSiMe_3$)=$PSiMe_3$)(2-Me) (***E*/*Z*-39-2-Me**) and *E*/Z-C_6H_4(1-C($OSiMe_3$)=$PSiMe_3$)(3-Me) (***E*/*Z*-39-3-Me**) have been reported, both of which were isolated as isomeric mixtures (57:43 and 37:63 respectively) that defied separation. Interestingly, the reaction that produced ***E*/*Z*-39-2-Me** reached completion within 48 h, while ***E*/*Z*-39-3-Me** required only 1 h for total conversion; the *ortho*-methyl group of ***E*/*Z*-39-2-Me** may have induced a slower reaction due to steric hindrance at the reaction site. For ***E*/*Z*-39-3-R** the *E*-isomer is the favoured form, while for ***E*/*Z*-39-2-Me** the reverse is true. While Regitz asserted that *E*-RC($OSiMe_3$)=$PSiMe_3$ is favoured when R is a primary or secondary substituent, and *Z*-RC($OSiMe_3$)=$PSiMe_3$ is preferred when R is a tertiary group,[105] Kostitsyn noted exceptions to this rule (RC($OSiMe_3$)=$PSiMe_3$ (R = 2,2-dichloro-l-methylcyclopropyl)).[106] Given that a comprehensive collection of phosphaalkenes bound to substituted aromatic rings has not been previously synthesised, and that relative isomeric preferences are disputed within established systems, it has not been possible to speculate upon the reasons for the isomeric preferences of ***E*/*Z*-39-R**. Multiple attempts to convert ***E*/*Z*-39-2-Me** and ***E*/*Z*-39-3-Me** to C_6H_4(1-C≡P)(Me) were unsuccessful; this was attributed to the mixture of isomers present in each sample, an effect that has been previously noted.[108]

In contrast with ***E*/*Z*-39-2-Me** and ***E*/*Z*-39-3-Me**, the attempted syntheses of *E*/*Z*-C_6H_4(1-C($OSiMe_3$)=$PSiMe_3$)(R) (R = 3-CN, 4-CO_2Me) met with limited success; the target phosphaalkenes were detected as part of complex product mixtures that could not be isolated. Additionally, the reactions of C_6H_4(1-COCl)(R) (R = 4-CN, 4-COCl) and C_5H_3E(2,6-$COCl)_2$ (E = CH, N) with P($SiMe_3$)$_3$ provided no evidence of even trace levels of the target phosphaalkenes, demonstrating the sensitivity of the Becker synthesis toward arene substitution.

The reactions of C_6H_4(1-COCl)(R) with HP($SiMe_3$)$_2$ afforded highly complex product mixtures in all cases. While the identities of many of the products were tentatively assigned, alterations to the reaction conditions to favour one product and attempts to isolate of any of the species proved unsuccessful. Phosphaalkenes ***E*/*Z*-42-R** were identified as the predominant species in most of the product mixtures by comparison with known species,[312] and the unambiguous isomeric assignments of ***E*-42-R** and ***Z*-42-R** were achieved. With the exception of ***E*/*Z*-42-2-Me**, the *Z*-isomers were predominant in all examples. Literature precedent for the head-to-head and head-to-tail dimerisation of phosphaalkenes enabled the tentative assignments of [1,2]- and [1,3]-diphosphacyclobutanes **46-R**, **51-R** and **52-R,**[325–327] and the spectroscopic data are comparable with known species.[320,115] Although the isomeric assignments of diphosphacyclobutanes ***EE*-46-R** and ***ZZ*-46-R** remain highly speculative, the presence of such

a large isomeric variety of diphosphacyclobutane products is not unexpected given the lack of isomeric purity in the phosphaalkene precursors ***E*/*Z*-39-R** and ***E*/*Z*-42-R**.

The use of PPh_3 as an internal standard for several reactions enabled a more accurate assessment of the quantities of each species present in the reaction mixtures, although complete accuracy cannot be assured as the technique relies upon perfect homogeneity of the reaction mixture. Further, several reactions generated compounds (such as acyl phosphine oxide **40-R** and acyl phosphine **44-R**) that were present in the initial aliquot but diminished to undetectable levels after 18 h; it is likely that such compounds became indistinguishable from baseline noise in the ^{31}P NMR spectra.

4. The development of novel phosphomide derivatives

4.1 Introduction

Acyl phosphines are a well-documented class of compounds,[315,40,10,328] whose use has been limited to sporadic examples of fundamental inorganic chemistry,[329,328] and catalysis.[11,10] Clarke postulated that this may be due to "concerns regarding the stability of the P-C bond, which has been shown to undergo degradation reactions in the presence of water or oxygen".[11] Many acyl phosphines have been shown to oxidise to mixtures of phosphine oxides and phosphines upon exposure to air;[330] however, recent studies have shown that this does not necessarily extend to all acyl phosphines.[11]

Those acyl phosphines that contain aromatic groups (benzene, pyridine, naphthalene) may alternatively be described as "phosphomides" on the basis of the resonance structure postulated by Kostyanovsky (Figure 34).[39] The delocalisation of the phosphorus lone pair is comparable to that of the nitrogen lone pair in amides, resulting in reduction of the double bond character of the carbonyl, which can be measured by the IR stretching frequency.[11] It can be reasonably postulated that phosphomides may be defined as species that exhibit carbonyl stretches of similar frequencies to amides i.e. $\nu_{(C=O)}$ 1630 - 1650 cm^{-1}.[331] Given the stretching frequencies of aliphatic acyl phosphines ($\nu_{(C=O)}$ ca. 1670 cm^{-1}),[332,333] such species are not considered to possess phosphomide character.

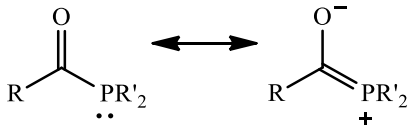


Figure 34. Resonance forms of acyl phosphines [39]

Many acyl phosphines/phosphomides have been reported in literature that might reasonably be divided into the following categories **i**) aryl,[10,334,335] **ii**) aliphatic,[329,330,315,11] **iii**) *ortho*-substituted aryl,[315,40,10,336,11,337] **iv**) *meta*-substituted aryl,[338] **v**) *para*- substituted aryl,[315,40,11,334] **vi**) poly-substituted aryl,[315,40] **vii**) pyridine,[10,315] **viii**) naphthalene,[10] **ix**) di-phosphomides,[40,328,337] (Figure 35). A representative selection (although by no means exhaustive) of acyl phosphines and phosphomides is displayed in Table 36, which serves to highlight the abundance of *ortho*- and *para*-substituted aryl phosphomides in literature, and the significant lack of *meta*-substituted aryl phosphomides and di-phosphomides.

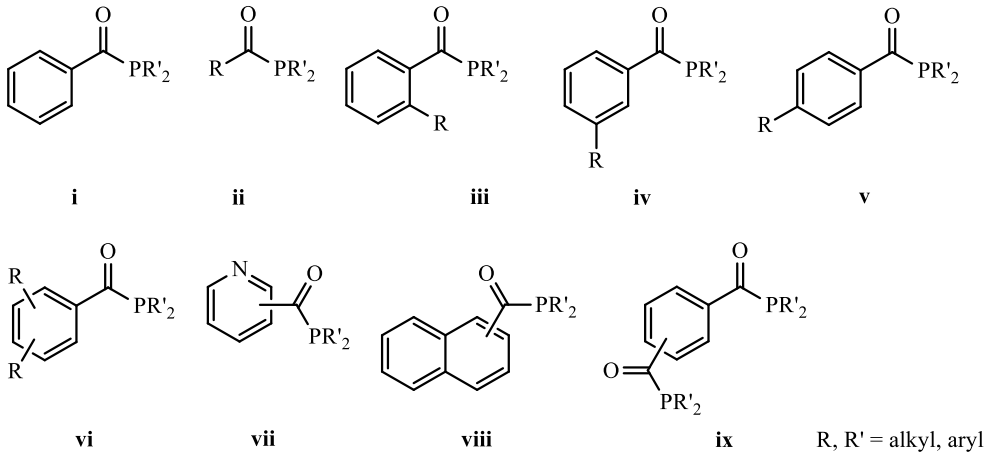


Figure 35. Categories of acyl phosphines and phosphomides

Herein the development of novel phosphomides (*meta*-, *para*- and di-substituted) is reported, allowing for the first thorough comparison of the structure and reactivities of all aryl phosphomides of the type $C_6H_4(1\text{-}C(O)PR'_2)(R)$.

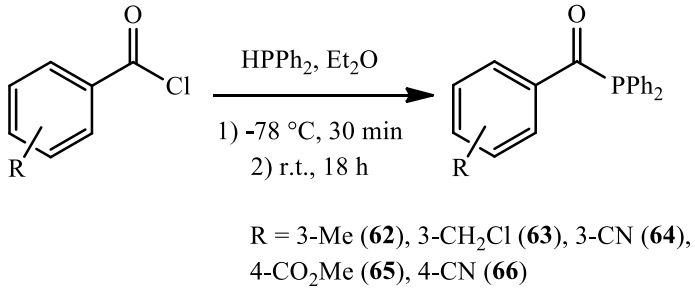
Table 36. Acyl phosphines and phosphomides in literature

Class	Category	Formula	Source	Class	Category	Formula	Source
i	aryl	$PhC(O)PAd_2$	10	**v**	*para*-substituted aryl	$C_6H_4(1\text{-}C(O)PPh_2)(4\text{-}Br)$	40
		$PhC(O)PPh_2$	334			$C_6H_4(1\text{-}C(O)PPh_2)(4\text{-}NO_2)$	40
		$F_5C_6C(O)PPh_2$	335			$C_6H_4(1\text{-}C(O)PPh_2)(4\text{-}CN)$	334
ii	aliphatic	$MeC(O)PPh_2$	329			$C_6H_4(1\text{-}C(O)PPh_2)(4\text{-}CO_2Me)$	40
		$F_3CC(O)PPh_2$	330			$C_6H_4(1\text{-}C(O)PPh_2)(4\text{-}COCl)$	11
		$^nC_9H_{19}C(O)PPh_2$	315			$C_6H_4(1\text{-}C(O)PCy_2)(4\text{-}OMe)$	40
		$C_2H_5OC(O)PPh_2$	315	**vi**	poly-substituted aryl	$C_6H_3(1\text{-}C(O)PPh_2)(3,4\text{-}Cl)_2$	315
		$CF_3(CF_2)_6C(O)PPh_2$	315			$C_6H_3(1\text{-}C(O)PPh_2)(3,5\text{-}Cl)_2$	315
		$H_2C{=}CH(CH_2)_8C(O)PPh_2$	11			$C_6H_3(1\text{-}C(O)PPh_2)(2,4\text{-}NO_2)_2$	40
iii	*ortho*-substituted aryl	$C_6H_4(1\text{-}C(O)PPh_2)(2\text{-}CH_2Cl)$	315			$C_6H_3(1\text{-}C(O)PPh_2)(3,5\text{-}NO_2)_2$	40
		$C_6H_4(1\text{-}C(O)PPh_2)(2\text{-}NO_2)$	40	**vii**	pyridine	$C_5H_4N(2\text{-}C(O)PAd_2)$	10
		$C_6H_4(1\text{-}C(O)PPh_2)(2\text{-}Br)$	336			$C_5H_4N(3\text{-}C(O)PPh_2)$	315
		$C_6H_4(1\text{-}C(O)PAd_2)(2\text{-}OMe)$	10	**viii**	naphthalene	$C_{10}H_7(1\text{-}C(O)PPh_2)$	10
		$C_6H_4(1\text{-}C(O)PAd_2)(2\text{-}CF_3)$	10			$C_{10}H_7(1\text{-}C(O)PAd_2)$	10
		$C_6H_4(1\text{-}C(O)PCy_2)(2\text{-}OMe)$	11			$C_{10}H_7(1\text{-}C(O)PCy_2)$	10
		$C_6H_4(1\text{-}C(O)PPh_2)(2\text{-}SMe)$	339			$C_{10}H_7(1\text{-}C(O)P^tBu_2)$	10
		$C_6H_4(1\text{-}C(O)PPh_2)(2\text{-}OPh)$	337			$C_{10}H_7(2\text{-}C(O)PAd_2)$	10
iv	*meta*-substituted aryl	$C_6H_4(1\text{-}C(O)PPh_2)(3\text{-}Me)$	338	**ix**	di-phosphomides	$C_6H_4(1,4\text{-}C(O)PPh_2)_2$	40
		$C_6H_4(1\text{-}C(O)PEt_2)(3\text{-}Me)$	338			$C_6H_4(1,2\text{-}C(O)PPh_2)_2$	328
v	*para*-substituted aryl	$C_6H_4(1\text{-}C(O)PPh_2)(4\text{-}Cl)$	315			$Ph_2PC(O)C(O)PPh_2$	328
		$C_6H_4(1\text{-}C(O)PPh_2)(4\text{-}Me)$	40			$\{C_6H_4(2\text{-}C(O)PPh_2)\}_2$	337

4.2. Syntheses and reactions of aryl phosphomides

4.2.1 Syntheses of $C_6H_4(1\text{-}C(O)PPh_2)(R)$

The reactions of the respective $C_6H_4(1\text{-}COCl)(R)$ with $HPPh_2$ afforded $C_6H_4(1\text{-}C(O)PPh_2)(R)$ (**62** - **66**) as bright yellow solids (yellow oil for $C_6H_4(1\text{-}COCl)(3\text{-}CN)$) in >60 % yield (Scheme 92). Significantly, the reactions proceed without the requirement of additional base or pre-generation of $NaPPh_2$, in contrast with previous reports.[11,329] Compounds **62** - **64** were characterised by NMR spectroscopy and their purity confirmed by microanalysis, while **65** and **66**, which have been previously reported (*via* alternate synthetic routes),[40,334] were identified by comparison with literature data and by mass spectrometry.



Scheme 92. Syntheses of $C_6H_4(1\text{-}C(O)PPh_2)(R)$ (**62** - **66**)

Compounds **62** - **66** exhibit similar spectroscopic data despite significant variation in the electronegativities and ring positions of the substituents (Table 37). Notwithstanding, the *para*-substituted aryl phosphomides **65** and **66** exhibit more downfield shifts than **62** - **64** for all nuclei. The ^{31}P NMR spectra exhibit multiplet resonances at ca. 12.9 ppm ($^3J_{P\text{-}H}$ ca. 8.1 Hz) for **62** - **64** and ca. 14.5 ppm ($^3J_{P\text{-}H}$ ca. 7.9 Hz) for **65** and **66**, with coupling to the *ortho*-CH protons of the phenyl rings confirmed by ^1H-^{31}P and ^1H-^{13}C HMBC NMR spectra; these chemical shifts are consistent with comparable phosphomides in the literature ($C_6H_4(1\text{-}C(O)PPh_2)(4\text{-}OMe)$ δ_P 11.8).[334] The $^{13}C\{^1H\}$ NMR spectra show doublet resonances at ca. 211 ppm ($^1J_{C\text{-}P}$ ca. 38.1 Hz) that are assigned to the carbonyl centres, and exhibit characteristic one-bond coupling to phosphorus, comparable to the case of $C_6H_4(1\text{-}C(O)PPh_2)(4\text{-}Cl)$ (δ_P 213 ($^1J_{C\text{-}P}$ 38.6 Hz)).[315] Substituent effects are evident in the $^{13}C\{^1H\}$ NMR spectra of phosphomides **62** - **66**, most notably for the strongly electron-withdrawing CN groups that results in a lower-field shift than the electron-donating substituent Me, reflective of previously reported trends.[334,340] Meanwhile, the *ipso*-carbons of the phosphomide rings are located as doublet signals at ca. 140 ppm ($^2J_{C\text{-}P}$ ca. 36.0 Hz); as before, the *meta*-substituted aryl phosphomides **62** - **64** exhibit significantly higher-field chemical shifts than the *para*-substituted analogues **65** - **66**.

Table 37. Selected spectroscopic data for C_6H_4(1-C(O)PPh_2)(R) (**62** - **66**)

	R	^{31}P / ppm	^{13}C{^{1}H} C(O)P / ppm	$^1J_{C\text{-}P}$ / Hz	^{13}C{^{1}H} *i*-C / ppm	$^2J_{C\text{-}P}$ / Hz
62	3-Me	12.4	212	36.9	140	35.7
63	3-CH_2Cl	12.9	211	37.9	140	35.4
64	3-CN	13.5	211	39.6	140	35.9
65	4-CO_2Me	14.4	212	38.3	143	34.6
66	4-CN	14.5	212	38.7	142	38.4

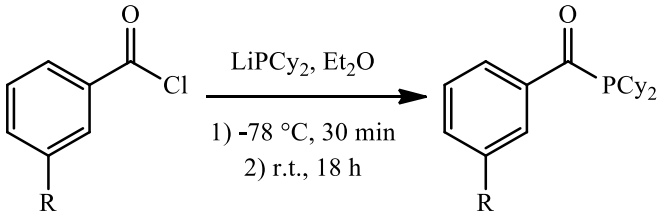
Phosphomides **62** - **66** were additionally characterised by IR spectroscopy and compared with the literature (Table 38). Literature shows that aliphatic acyl phosphines typically display carbonyl stretches at $\nu_{(C=O)}$ ca. 1672 cm^{-1}, which suggests that they do not possess any measureable phosphomide character (i.e. phosphorus pair delocalisation). This is in contrast to previously reported aryl phosphomides, which exhibit absorbances at significantly lower frequencies $\nu_{(C=O)}$ 1630 to 1650 cm^{-1}, consistent with both aromatic and aliphatic amides. The IR spectra of compounds **62** - **66** display absorbances at $\nu_{(C=O)}$ ca. 1645 cm^{-1}, showing a significant decrease in frequency from their precursors C_6H_4(1-COCl)(R) at $\nu_{(C=O)}$ ca. 1685, 1744 cm^{-1}. Baber established that the carbonyl stretching frequency could be used to determine the relative delocalisation of the phosphorus lone pair;[11] as such it is possible to conclude that while compounds **62** – **66** all possess significant phosphomide behaviour, the extent is greatest for **62** due to its very low frequency absorbance at $\nu_{(C=O)}$ 1634 cm^{-1}.

Table 38. Selected IR data for phosphomides, acyl phosphines, amides and acyl chlorides

Compound	$\nu_{(C=O)}$ / cm^{-1}	Source
$C_6H_3(1\text{-}C(O)PPh_2)(3,5\text{-}Cl)_2$	1631	315
$C_6H_4(1\text{-}C(O)PPh_2)(4\text{-}Cl)$	1652	315
$C_{10}H_7(C(O)PPh_2)$	1632	10
$MeC(O)PPh_2$	1670	332
$^tBuC(O)PPh_2$	1673	333
$MeC(O)NMe_2$	1661	341
$PhC(O)NPh_2$	1651	331
$PhC(O)NEt_2$	1627	331
$C_6H_4(1\text{-}COCl)(3\text{-}CN)$	1687, 1771	This work
$C_6H_4(1\text{-}COCl)(4\text{-}CO_2Me)$	1699, 1721	This work
$C_6H_4(1\text{-}COCl)(4\text{-}CN)$	1699, 1739	This work
(**62**) $C_6H_4(1\text{-}C(O)PPh_2)(3\text{-}Me)$	1634	This work
(**63**) $C_6H_4(1\text{-}C(O)PPh_2)(3\text{-}CH_2Cl)$	1645	This work
(**65**) $C_6H_4(1\text{-}C(O)PPh_2)(4\text{-}CO_2Me)$	1649	This work
(**66**) $C_6H_4(1\text{-}C(O)PPh_2)(4\text{-}CN)$	1650	This work

4.2.2 Syntheses of $C_6H_4(1\text{-}C(O)PCy_2)(3\text{-}R)$

Notably few examples of $RC(O)PCy_2$ (R = alkyl, aryl) have been reported previously.[329,11] However, one very recent publication detailed the use of $[Ru\{C_3H_2(2\text{-}Me)\}_2(1,5\text{-}COD)]$ / $C_6H_{10}(1\text{-}C(O)PCy_2)$ for catalysing the hydrogenation of sodium bicarbonate to sodium formate, with unprecedented TON when compared to traditional systems.[10] With applications in catalysis a possibility, the synthetic methodology derived for the production of **62** - **66** was probed for the synthesis of $C_6H_4(1\text{-}C(O)PCy_2)(3\text{-}R)$. The reaction of $C_6H_4(1\text{-}COCl)(3\text{-}Me)$ with $HPCy_2$ generated a yellow oil identified as a mixture of two major products in an 80:20 ratio; the predominant product exhibited a broad ^{31}P NMR resonance at 16.8 ppm with half-height-width ($w_{½}$) of ca. 21.6 Hz and was attributed to $C_6H_4(1\text{-}C(O)PCy_2)(3\text{-}Me)$ (**67**) (this was later confirmed by comparison with a pure sample of compound **67**). The minor product exhibited a broad resonance at 127 ppm ($w_{½}$ ca. 23.3 Hz), although identification was not possible from the data collected. Isolation of **67** proved impractical (by crystallisation, washing, or distillation), thus $HPCy_2$ was lithiated prior to reaction with $C_6H_4(1\text{-}COCl)(3\text{-}R)$, affording compounds **67** and **68** as analytically pure yellow oils in high yields (>91 %) (Scheme 93).



Scheme 93. Syntheses of $C_6H_4(1\text{-}C(O)PCy_2)(3\text{-}R)$ (**67** - **68**)

The ^{31}P NMR spectra of compounds **67** and **68** show broad resonances at ca. 17.3 ppm ($w_{½}$ ca. 24.3 Hz) (Table 39) which are shifted significantly downfield from the triplets observed for compounds **62** - **64** (δ_P ca. 12.9 ($^3J_{P\text{-}H}$ ca. 8.1 Hz)); this is attributed to decreased shielding of the phosphorus centre *via* the reduced electron-donating properties of the cyclohexyl substituent, consistent with previously reported trends ($C_6H_4(1\text{-}C(O)PR_2)(2\text{-}OMe)$; R = Ph, δ_P 25.0; R = Cy, δ_P 32.1).[11,10] The $^{13}C\{^1H\}$ NMR spectra show doublet resonances at ca. 216 ppm ($^1J_{C\text{-}P}$ 44.4 Hz) for the carbonyl carbons, that are shifted significantly downfield and exhibit increased carbon-phosphorus coupling constants when compared to compounds **62** - **64**. The *ipso*-carbon atoms are assigned to doublet resonances at 143 ppm ($^2J_{C\text{-}P}$ ca. 32.9 Hz), again featuring a small downfield shift compared to **62** - **64**, but with a reduction in the magnitude of coupling to phosphorus. The ^1H NMR spectra were largely unremarkable save to confirm a 2:1 ratio of cyclohexyl to aromatic protons by integration.

Table 39. Selected spectroscopic data for $C_6H_4(1\text{-}C(O)PCy_2)(3\text{-}R)$ (**67** - **68**)

	R	^{31}P / ppm	$^{13}C\{^1H\}$ C(O)P / ppm	$^1J_{C\text{-}P}$ / Hz	$^{13}C\{^1H\}$ *i*-C / ppm	$^2J_{C\text{-}P}$ / Hz
67	3-Me	16.7	216	44.1	143	32.6
68	3-CH_2Cl	17.8	216	44.7	143	33.2

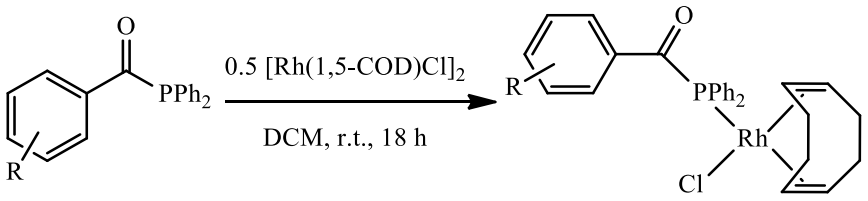
4.2.3 Coordination chemistry of $C_6H_4(1\text{-}C(O)PPh_2)(R)$

The coordination chemistry of phosphomides has been sparse throughout the literature, with reports limited to early- or mid- transition metals, including Fe,[342] Mo,[343] Mn,[315] and Ir,[344,345] and just one example each for Ru,[10] and Rh.[11] In view of this a thorough study of the reactivity profiles of compounds **62** - **66** towards late transition metal complexes featuring rhodium, palladium and platinum centres was pursued.

Coordination reactions with rhodium complexes

To date, a single report describes phosphomide complexes of rhodium, specifically [Rh(Cp*)(RC(O)PPh_2)Cl_2] and *trans*-[Rh(CO)(RC(O)PPh_2)$_2$Cl] (R = Me, $(CF_2)_6CF_3$, C_6H_4(2-OMe)).[11] Baber probed the use of [Rh(acac)$(CO)_2$] / RC(O)PPh_2 for catalysing the hydroformylation of 1-hexene, and although isolation of the active catalyst was not reported, reasonable activity was detected (60 - 85 % conversion in 3 h, linear: branched product ratios of 2.0 - 2.6:1). However, these did not compete with commercially used systems such as [Rh(acac)$(CO)_2$] / PPh_3, which exhibited 95 % conversion under the same conditions with a higher turnover frequency and an improved linear to branched ratio of 2.9:1.

Given the lack of isolated phosphomide complexes of rhodium, the syntheses of [Rh(1,5-COD){C_6H_4(1-C(O)PPh_2)(R)}Cl] (**69 - 72**) were sought by addition of C_6H_4(1-C(O)PPh_2)(R) to [Rh(1,5-COD)Cl]$_2$; yellow or orange solids were afforded in high yields (>75 %) (Scheme 94).



R = 3-Me (**69**), 3-CH_2Cl (**70**), 4-CO_2Me (**71**), 4-CN (**72**)

Scheme 94. Syntheses of [Rh(1,5-COD){C_6H_4(1-C(O)PPh_2)(R)}Cl] (**69 - 72**)

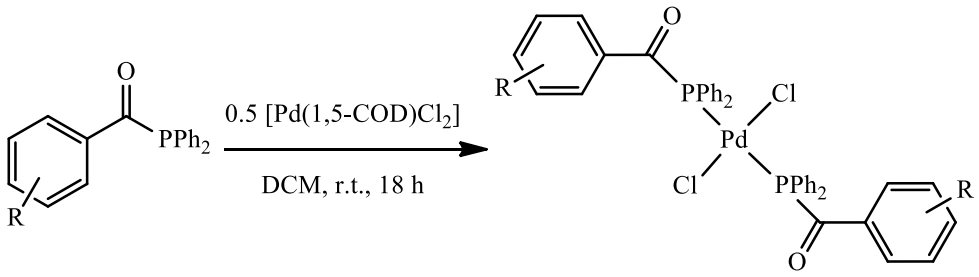
The ^{31}P NMR spectra of compounds **69 - 72** show broad doublet resonances at ca. 36.8 ppm ($^1J_{P\text{-}Rh}$ ca. 146 Hz, $w_{½}$ ca. 29.2 Hz) (Table 40), with coupling constants consistent with one-bond phosphorus-rhodium separations.[346] The ^{13}C{^{1}H} NMR data exhibit doublet (or unresolved multiplet) signals at ca. 202 ppm ($^1J_{C\text{-}P}$ ca. 17.2 Hz), attributed to the carbonyl centres; the significant upfield coordination shifts from the free phosphomides **62 - 66** (δ_C ca. 212 ($^1J_{C\text{-}P}$ ca. 38.1 Hz)) are consistent with those observed for related manganese complexes.[315] There is little change in the resonances attributed to the *ipso*-carbon atoms of the phosphomide rings, which are located at ca. 140 ppm ($^2J_{C\text{-}P}$ ca. 42.7 Hz), and the ^{1}H NMR data confirm by integration the presence of two phenyl rings, one phosphomide ring, and one 1,5-COD ligand. The IR spectra display increases in carbonyl stretching frequencies of ca. +15 cm^{-1} across all complexes, consistent with loss of delocalisation of the phosphorus lone pair.

Table 40. Selected spectroscopic data for [Rh(1,5-COD){C_6H_4(1-C(O)PPh_2)(R)}Cl] (**69** - **72**)

	R	^{31}P / ppm	$^{1}J_{P\text{-}Rh}$ / Hz	^{13}C{^{1}H} C(O)P / ppm	$^{1}J_{C\text{-}P}$ / Hz	^{13}C{^{1}H} *i*-C / ppm	$^{2}J_{C\text{-}P}$ / Hz	$\nu_{(C=O)}$ / cm^{-1}
69	3-Me	36.1	146	202	16.5	139	42.7	1657
70	3-CH_2Cl	36.4	146	202	-	139	42.9	1657
71	4-CO_2Me	36.9	147	203	17.9	142	42.5	1663
72	4-CN	37.8	147	203	-	142	42.5	1660

Coordination reactions with palladium complexes

The syntheses of *trans*-[$PdCl_2${C_6H_4(1-C(O)PPh_2)(R)}$_2$] (**73** - **76**) were achieved by addition of C_6H_4(1-C(O)PPh_2)(R) to [Pd(1,5-COD)Cl_2] (Scheme 95) and the products isolated as yellow solids in high yields (>90 %).



R = 3-Me (**73**), 3-CH_2Cl (**74**), 4-CO_2Me (**75**), 4-CN (**76**)

Scheme 95. Syntheses of *trans*-[$PdCl_2${C_6H_4(1-C(O)PPh_2)(R)}$_2$] (**73** - **76**)

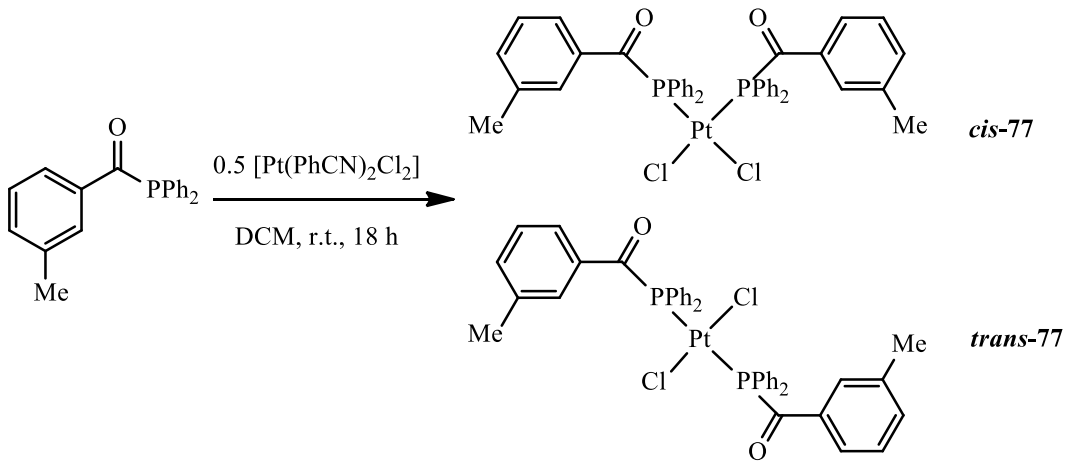
The *trans*-geometry of complexes **73** - **76** was assigned on the basis of triplet resonances in the ^{13}C{^{1}H} NMR spectra for the carbonyl and *ipso*-carbon signals. The carbonyl and *ipso*-carbon resonances all exhibit upfield coordination shifts from the free phosphomides **62** - **66** (δ_C ca. 199 ($^{1}J_{C\text{-}P}$ ca. 11.9 Hz), δ_C ca. 137 ($^{2}J_{C\text{-}P}$ ca. 22.5 Hz)). The ^{31}P NMR spectra show broad signals at ca. 25.9 ppm ($w_{½}$ ca. 24.0 Hz), the chemical shifts of which are consistent with similar complexes *trans*-[$Pd(PR_3)_2Cl_2$],[347,348] and which are observed by ^{1}H-^{31}P HMBC NMR studies to correlate to each of the phenyl protons. The carbonyl stretching frequencies ($\nu_{(C=O)}$ ca. 1656 cm^{-1}) are increased by ca. +12 cm^{-1} compared to the free phosphomides **62** - **66** (Table 41).

Table 41. Selected spectroscopic data for *trans*-$[PdCl_2\{C_6H_4(1\text{-}C(O)PPh_2)(R)\}_2]$ (**73** - **76**)

	R	^{31}P / ppm	$^{13}C\{^1H\}$ C(O)P / ppm	$^1J_{C\text{-}P}$ / Hz	$^{13}C\{^1H\}$ *i*-C / ppm	$^2J_{C\text{-}P}$ / Hz	$\nu_{(C=O)}$ / cm^{-1}
73	3-Me	25.8	199	-	131	22.8	1634
74	3-CH_2Cl	25.9	199	11.4	137	22.7	1657
75	4-CO_2Me	26.1	199	11.9	140	21.9	1669
76	4-CN	25.9	199	12.4	140	22.8	1666

Coordination reactions with platinum complexes

In contrast to the palladium complexes, syntheses of the analogous platinum species were not straight-forward. The reaction of $C_6H_4(1\text{-}C(O)PPh_2)(3\text{-}Me)$ (**62**) with $[Pt(PhCN)_2Cl_2]$ afforded $[PtCl_2\{C_6H_4(1\text{-}C(O)PPh_2)(3\text{-}Me)\}_2]$ as a mixture of *cis*- and *trans*- isomers (55:45 ratio), ***cis*-77** and ***trans*-77**, in 89 % yield (Scheme 96).

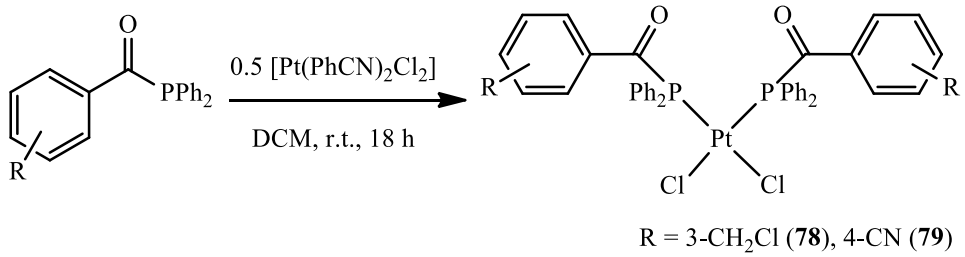


Scheme 96. Syntheses of *cis*- and *trans*-$[PtCl_2\{C_6H_4(1\text{-}C(O)PPh_2)(3\text{-}Me)\}_2]$ (***cis*/*trans*-77**)

Virtual coupling in the $^{13}C\{^1H\}$ NMR spectrum of *cis*- and *trans*-$[PtCl_2\{C_6H_4(1\text{-}C(O)PPh_2)(3\text{-}Me)\}_2]$ (***cis*/*trans*-77**) enables the unambiguous assignment of most key resonances, although signal overlap precluded full assignment. Doublet and triplet signals at 195 ($^1J_{C\text{-}P}$ 40.6 Hz) and 199 ppm ($^1J_{C\text{-}P}$ 15.0) are attributed to the carbonyl carbons of ***cis*-77** and ***trans*-77** respectively; the magnitude of the carbon-phosphorus coupling in ***trans*-77** is reduced due to virtual coupling effects (Table 42).[56] A triplet resonance at 137 ppm ($^1J_{C\text{-}P}$ 22.6 Hz) is assigned to the *ipso*-carbon of ***trans*-77**; however, the *ipso*-carbon of ***cis*-77** could not be located through $^{13}C\{^1H\}$ or $^1H\text{-}^{13}C$ HMBC NMR studies. The ^{31}P NMR spectrum shows two broad resonances at 14.8 ($^1J_{P\text{-}Pt}$ 3497 Hz, $w_{½}$ ca. 33.3 Hz) and 22.8 ppm ($^1J_{P\text{-}Pt}$ 2544 Hz, $w_{½}$ ca. 23.6 Hz) for ***cis*/*trans*-77** in a

ratio of 55:45, with chemical shifts and phosphorus-platinum coupling constants consistent with general trends for *cis*- and *trans*- platinum bisphosphine dihalide complexes.[268] The $^{195}Pt\{^{1}H\}$ NMR spectrum shows triplet resonances at −4351 and −3962 ppm for the *cis*- and *trans*-isomers respectively, while the IR spectrum exhibits a broad absorbance at $\nu_{(C=O)}$ 1661 cm^{-1}, attributed to overlapping absorbances arising from each isomer.

In contrast to ***cis*/*trans*-77**, *cis*-$[PtCl_2\{C_6H_4(1\text{-}C(O)PPh_2)(R)\}_2]$ (**78 - 79**) were isolated as analytically and isomerically pure yellow solid in good yields (>73 %) (Scheme 97).



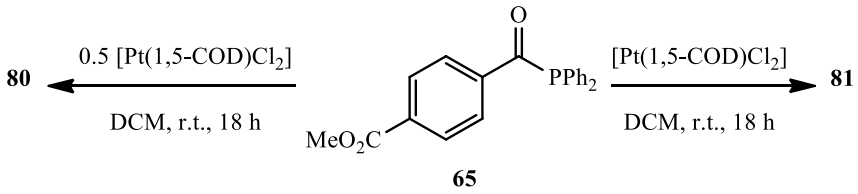
Scheme 97. Syntheses of *cis*-$[PtCl_2\{C_6H_4(1\text{-}C(O)PPh_2)(R)\}_2]$ (**78 - 79**)

Complexes *cis*-$[PtCl_2\{C_6H_4(1\text{-}C(O)PPh_2)(R)\}_2]$ (**78 - 79**) display comparable NMR characteristics to ***cis*-77**; however, due to the poor solubility of **78** in common solvents ($CDCl_3$, DCM, THF) only limited $^{13}C\{^{1}H\}$ NMR data can be directly observed. The ^{31}P NMR spectra show broad signals at 15.3 ($^{1}J_{P\text{-}Pt}$ 3503 Hz, $w_{½}$ ca. 23.5 Hz) and 16.5 ppm ($^{1}J_{P\text{-}Pt}$ 3493 Hz, $w_{½}$ ca. 23.8 Hz) for **78** and **79** respectively (Table 42), with platinum satellites typical of *cis*-coordinated complexes. A doublet resonance at 195 ppm ($^{1}J_{C\text{-}P}$ 44.8 Hz) in the $^{13}C\{^{1}H\}$ NMR spectrum of **79** is assigned to the carbonyl carbon, at a significantly higher-field shift ($\Delta\delta_C$ − 16.7) than free phosphomide **66**, while the *ipso*-carbon resonance at 140 ppm ($^{1}J_{C\text{-}P}$ 49.9 Hz) demonstrates negligible change from **66**. The IR spectra of **78 - 79** display absorbances at $\nu_{(C=O)}$ ca. 1665 cm^{-1}, a significant increase from free **63** and **66**, consistent with a reduction in electron density at the carbonyl group attributed to the loss of delocalisation of the phosphorus lone pair.

Table 42. Selected spectroscopic data for $[PtCl_2\{C_6H_4(1\text{-}C(O)PPh_2)(R)\}_2]$ (**77** - **79**)

	R	^{31}P / ppm	$^{1}J_{P\text{-}Pt}$ / Hz	^{13}C{^{1}H} C(O)P / ppm	$^{1}J_{C\text{-}P}$ / Hz	^{13}C{^{1}H} *i*-C / ppm	$^{2}J_{C\text{-}P}$ / Hz	^{195}Pt{^{1}H} / ppm	$\nu_{(C=O)}$ / cm^{-1}
***cis*-77**	3-Me	14.8	3497	195 (d)	40.6	-	-	–4351 (t)	1661
***trans*-77**	3-Me	22.8	2544	199 (t)	15.0	137 (t)	22.6	–3962 (t)	1661
78	3-CH_2Cl	15.3	3503	-	-	-	-	–4354 (t)	1668
79	4-CN	16.5	3493	195 (d)	44.8	140 (d)	49.9	–4374 (t)	1666

Interestingly, no reaction was observed upon the addition of $PtCl_2$ or $[Pt(PhCN)_2Cl_2]$ to $C_6H_4(1\text{-}C(O)PPh_2)(4\text{-}CO_2Me)$ (**65**), with only the unchanged **65** detected by NMR spectroscopy. However, reactions of **65** with $[Pt(1,5\text{-}COD)Cl_2]$ afforded yellow solids **80** or **81** dependent upon the reagent stoichiometry (Scheme 98).



Scheme 98. Syntheses of complexes **80** and **81**

Complex **80** shows a single broad ^{31}P NMR resonance at 26.1 ppm ($w_{½}$ ca. 24.3 Hz) with no visible platinum satellites, while the ^{195}Pt{^{1}H} NMR spectrum shows a singlet signal at –3340 ppm, consistent with $[Pt(1,5\text{-}COD)Cl_2]$.[349] ^{1}H NMR resonances attributed to the phosphomide ring and 1,5-COD ligand integrate as four and twelve protons respectively, consistent with one 1,5-COD ligand and one phosphomide ring; however, the 1,5-COD resonances at 2.26, 2.71 and 5.61 ppm ($J_{H\text{-}Pt}$ 66.9 Hz) are consistent with $[Pt(1,5\text{-}COD)Cl_2]$, and no other signals attributable to 1,5-COD are observed. In contrast, for $[Rh(1,5\text{-}COD)\{C_6H_4(1\text{-}C(O)PPh_2)(R)\}Cl]$ (**69** - **72**), the 1,5-COD resonances are significantly altered in both chemical shift and number of signals from $[Pt(1,5\text{-}COD)Cl_2]$. Each resonance in the ^{13}C{^{1}H} NMR spectrum is consistent with those noted for *trans*-$[PtCl_2\{C_6H_4(1\text{-}C(O)PPh_2)(R)\}_2]$ (***trans*-77**), including virtual coupling for the carbonyl and *ipso*-carbon centres. The carbonyl centre is located at 199 ppm ($^{1}J_{C\text{-}P}$ 11.7), while the IR spectrum shows a carbonyl stretch at $\nu_{(C=O)}$ 1671 cm^{-1}, both of which indicate that the carbonyl group is not coordinated to a metal centre. Further, a second carbonyl absorbance at $\nu_{(C=O)}$ 1720 cm^{-1} that is attributed to the CO_2Me group is of comparable frequency with the precursor $C_6H_4(1\text{-}COCl)(4\text{-}CO_2Me)$ ($\nu_{(C=O)}$ 1721 cm^{-1}) and the free phosphomide **65** ($\nu_{(C=O)}$ 1721

cm^{-1}). FAB mass spectrometry afforded a molecular ion peak of *m/z* = 686, consistent with $[PtCl(1,5\text{-}COD)\{C_6H_4(1\text{-}C(O)PPh_2)(4\text{-}CO_2Me)\}]^+$, while microanalysis found C (48.07 %), H (3.96 %), which is consistent with $C_{29}H_{29}O_3P_1Cl_2Pt$, or $[PtCl_2(1,5\text{-}COD)\{C_6H_4(1\text{-}C(O)PPh_2)(4\text{-}CO_2Me)\}]$. Ultimately, the product identity could not be firmly elucidated.

In contrast to **80**, complex **81** exhibits a broad ^{31}P NMR resonance at 16.1 ppm ($^1J_{P\text{-}Pt}$ 3504 Hz, $w_{½}$ ca. 30.9 Hz), consistent in both chemical shift and coupling constant with the *cis*-coordinated phosphomide complexes (***cis*-77, 78 - 79**). However, the $^{195}Pt\{^1H\}$ NMR spectrum shows only a singlet signal at –3340 ppm that is attributed to $[Pt(1,5\text{-}COD)Cl_2]$; the possibility of the signal falling outside of this window is small, as such chemical shifts are usually limited to unusual five-coordinate platinum complexes.[350] The ^1H NMR spectrum exhibits similar resonances to **80**, where the only 1,5-COD resonances can be assigned to $[Pt(1,5\text{-}COD)Cl_2]$, and small quantities of free **65** are also evident. Intriguingly, the singlet signal attributed to the CO_2Me group of **81** at 3.94 ppm exhibits platinum satellites ($J_{H\text{-}Pt}$ 31.1 Hz) that are not evident when an identical sample is dissolved in deuterated toluene. This suggests coordination to platinum through the CO_2Me group when in a neutral solvent, but no coordination when dissolved in $CDCl_3$. The $^{13}C\{^1H\}$ NMR spectrum shows doublet resonances attributed to the carbonyl and *ipso*-carbon centres at 195 ($^1J_{C\text{-}P}$ 42.9 Hz) and 140 ppm ($^1J_{C\text{-}P}$ 49.1 Hz) respectively (Table 43); the chemical shifts and coupling constants are consistent with *cis*-complexes ***cis*-77 - 79**. Variable temperature (−60 to 80°C) ^1H NMR spectroscopy shows no informative change. The IR spectrum is similar to **80**, including the phosphomide carbonyl stretch at $\nu_{(C=O)}$ 1671 cm^{-1} and the CO_2Me stretch at $\nu_{(C=O)}$ 1721 cm^{-1}. Despite multiple attempts in a variety of solvent and temperature systems, crystals suitable for X-ray diffraction remain elusive, without which the identity of **81** cannot be ascertained.

Table 43. Selected spectroscopic data for free phosphomide **65** and complexes **80** and **81**

	^{31}P / ppm	$^1J_{P\text{-}Pt}$ / Hz	$^{13}C\{^1H\}$ C(O)P / ppm	$^1J_{C\text{-}P}$ / Hz	$^{13}C\{^1H\}$ *i*-C / ppm	$^2J_{C\text{-}P}$ / Hz	$^{195}Pt\{^1H\}$ / ppm	$\nu_{(C=O)}$ / cm^{-1}
65	14.4	-	212 (d)	38.3	143 (d)	34.6	-	1649
80	26.1	-	199 (t)	11.7	140 (t)	22.8	–3340 (s)	1671
81	16.1	3504	195 (d)	42.9	140 (d)	49.1	–3340 (s)	1671

4.2.4 Comparisons of the aryl phosphomides and their complexes

The coordination chemistry of phosphomides **62 - 66** proceeded, for the most part, as anticipated; the rhodium and palladium complexes were successfully synthesised from the relevant precursors. However, coordination to platinum yielded unexpected results that could not be fully explained. Bis-phosphine *cis*-platinum complexes are common indeed,[351] as are mixtures of *cis*- and *trans*-isomers such as that encountered for ***cis*/*trans*-77**.[352,353] The isolation of **80** and **81** was not anticipated, and their identity remains unknown.

The ^{31}P NMR spectra of the phosphomide ligands and complexes display the expected characteristics, although coupling to the aromatic protons in complexes **69 - 79** was not observed due to line broadening, as evidenced by the half-height-widths reported. The free phosphomides have higher-field resonances at ca. 14.3 ppm than the complexes (Table 44), which are shifted lower-field in descending order Rh>Pd>Pt. This trend is also reflected in the resonances assigned to the carbonyl centres in the $^{13}C\{^{1}H\}$ NMR spectra. In contrast, the chemical shifts of the *ipso*-carbons are reduced only slightly in the metal complexes, although the magnitude of the carbon-phosphorus coupling is increased for the *cis*-coordinated complexes **69 - 72** and **79**. The IR spectra of **62 - 66** and **69 - 79** are particularly intriguing; the carbonyl stretches of **62 - 66** are located at $\nu_{(C=O)}$ ca. 1645 cm^{-1}, typical of phosphomide compounds, while upon coordination to metals, the stretching frequency increases in descending order Rh ($\nu_{(C=O)}$ ca. 1659 cm^{-1}) >Pd ($\nu_{(C=O)}$ ca. 1664 cm^{-1}, outlying data for **73** not included) >Pt ($\nu_{(C=O)}$ ca. 1667 cm^{-1}), consistent with the chemical shift trends in the ^{31}P and $^{13}C\{^{1}H\}$ NMR data described earlier.

Clearly, compounds **62 - 66** exhibit significant phosphorus lone pair delocalisation in view of their typical ($\nu_{(C=O)}$ 1630 - 1650 cm^{-1}) carbonyl stretching frequencies, and can be placed in order of increasing phosphomide character **66**<**65**<**64**<**63**<**62**. Notably, *meta*-substituted phosphomide **62**, which has the most electron-donating R group (Me) exhibits the most highly delocalised phosphorus lone pair, while *para*-substituted phosphomide **66**, which possesses the most electron-withdrawing R group (CN), exhibits the least delocalised lone pair. As such, it is possible to suggest that both the ring position and electronic characteristics of the R substituent play key parts in the relative phosphomide behaviour of $C_6H_4(1\text{-}C(O)PPh_2)(R)$.

While amides and phosphomides exhibit carbonyl stretches of comparable frequencies, their reactivities towards metal centres are markedly different. Complexes **69 - 79** all feature coordination modes typical of standard phosphines i.e. *via* the phosphorus lone pair, with no evidence for disruption at the carbonyl group detected by IR spectroscopy. In contrast, examples of metal amides featuring nitrogen lone pair donation are extremely rare,[354] with coordination from oxygen the usual mode.[355,356] This behaviour has been attributed to the non-basic lone pair

of nitrogen,[354] which is a direct result of its delocalisation into the π-system. Given that phosphomides **62** - **66** do not display metal coordination from oxygen, it may be suggested that the phosphorus lone pair is significantly more basic as a result of reduced overlap with the π-system.

Table 44. Selected spectroscopic data for phosphomides (**62** - **66**) and complexes (**69** - **81**)

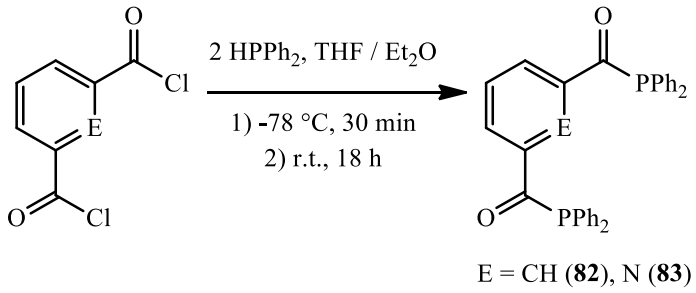
		^{31}P / ppm	^{13}C{^{1}H} C(O)P / ppm	$^{1}J_{C\text{-}P}$ / Hz	^{13}C{^{1}H} *i*-C / ppm	$^{2}J_{C\text{-}P}$ / Hz	$\nu_{(C=O)}$ / cm^{-1}
62	C_6H_4(1-C(O)PPh_2)(3-Me)	12.4	212 (d)	36.9	140 (d)	35.7	1634
63	C_6H_4(1-C(O)PPh_2)(3-CH_2Cl)	12.9	211 (d)	37.9	140 (d)	35.4	1645
64	C_6H_4(1-C(O)PPh_2)(3-CN)	13.5	211 (d)	39.6	140 (d)	35.9	-
65	C_6H_4(1-C(O)PPh_2)(4-CO_2Me)	14.4	212 (d)	38.3	143 (d)	34.6	1649
66	C_6H_4(1-C(O)PPh_2)(4-CN)	14.5	212 (d)	38.7	142 (d)	38.4	1650
69	[Rh(1,5-COD){C_6H_4(1-C(O)PPh_2)(3-Me)}Cl]	36.1	202 (d)	16.5	139 (d)	42.7	1657
70	[Rh(1,5-COD){C_6H_4(1-C(O)PPh_2)(3-CH_2Cl)}Cl]	36.4	202 (m)	-	139 (d)	42.9	1657
71	[Rh(1,5-COD){C_6H_4(1-C(O)PPh_2)(4-CO_2Me)}Cl]	36.9	203 (d)	17.9	142 (d)	42.5	1663
72	[Rh(1,5-COD){C_6H_4(1-C(O)PPh_2)(4-CN)}Cl]	37.8	203 (m)	-	142 (d)	42.5	1660
73	*trans*-[$PdCl_2${C_6H_4(1-C(O)PPh_2)(3-Me)}$_2$]	25.8	199 (m)	-	131 (t)	22.8	1634
74	*trans*-[$PdCl_2${C_6H_4(1-C(O)PPh_2)(3-CH_2Cl)}$_2$]	25.9	199 (t)	11.4	137 (t)	22.7	1657
75	*trans*-[$PdCl_2${C_6H_4(1-C(O)PPh_2)(4-CO_2Me)}$_2$]	26.1	199 (t)	11.9	140 (t)	21.9	1670
76	*trans*-[$PdCl_2${C_6H_4(1-C(O)PPh_2)(4-CN)}$_2$]	25.9	199 (t)	12.4	140 (t)	22.8	1666
***cis*-77**	*cis*-[$PtCl_2${C_6H_4(1-C(O)PPh_2)(3-Me)}$_2$]	14.8	195 (d)	40.6	-	-	1661
***trans*-77**	*trans*-[$PtCl_2${C_6H_4(1-C(O)PPh_2)(3-Me)}$_2$]	22.3	199 (t)	15.0	137 (t)	22.6	1661
78	*cis*-[$PtCl_2${C_6H_4(1-C(O)PPh_2)(3-CH_2Cl)}$_2$]	15.3	-	-	-	-	1668
79	*cis*-[$PtCl_2${C_6H_4(1-C(O)PPh_2)(4-CN)}$_2$]	16.5	195 (d)	44.8	140 (d)	49.9	1666
80	Unknown	26.1	199 (t)	11.7	140 (t)	22.8	1671
81	Unknown	16.1	195 (d)	42.9	140 (d)	49.1	1671

4.3 Syntheses and reactions of di-phosphomides

Having developed a more efficient synthetic methodology for the production of phosphomides **62 - 66**, the syntheses of di-phosphomides was considered. Previous examples of di-phosphomides in the literature are sparse, with $C_6H_4(1,4\text{-}C(O)PPh_2)_2$ and $C_6H_4(1,2\text{-}C(O)PPh_2)_2$ being the most comparable;[40,328] both were synthesised *via* addition of the relevant di-acyl chloride reagent to Me_3SiPPh_2. During the preparation of this thesis the synthesis of $C_6H_4(1,3\text{-}C(O)PPh_2)_2$ was reported in the literature, achieved by the reaction of $C_6H_4(1,3\text{-}COCl)_2$ with $HPPh_2$ in the presence of NEt_3.[357]

4.3.1 Syntheses of $C_5H_3E(2,6\text{-}C(O)PPh_2)_2$

The addition of $C_5H_3E\{2,6\text{-}(COCl)_2\}$ to two equivalents of $HPPh_2$ afforded the anticipated di-phosphomides $C_5H_3E(2,6\text{-}C(O)PPh_2)_2$ (**82 - 83**) as yellow solids in ca. 80 % yields (Scheme 99).



Scheme 99. Syntheses of $C_5H_3E(2,6\text{-}C(O)PPh_2)_2$ (**82 - 83**)

Despite the isolobal natures of CH and N in **82** and **83**, significantly different spectroscopic characteristics were recorded for each that could be ascribed to the increased electronegativity of the nitrogen atom compared to carbon (N = 3.04, C = 2.55).[358,359] Like phosphomides **62 - 64**, the di-phosphomides exhibit multiplet signals in the ^{31}P NMR spectra at 12.9 ($^3J_{P\text{-}H}$ 7.9 Hz) for **82** and 16.6 ppm ($^3J_{P\text{-}H}$ 7.4 Hz) for **83** (Table 45). The splitting arises due to coupling to the *ortho*-CH protons of the phenyl rings, as determined by ^1H-^{31}P HMBC NMR spectra. The $^{13}C\{^1H\}$ NMR spectra show the carbonyl carbons as doublet signals at ca. 212 ppm ($^1J_{C\text{-}P}$ ca. 39.3 Hz), reminiscent of phosphomides **62 - 66**. The *ipso*-carbon atoms are located at 140 ($^2J_{C\text{-}P}$ 35.7 Hz) for **82** and 153 ppm ($^2J_{C\text{-}P}$ 31.4 Hz) for **83**; while the former is consistent with **62 - 66**, the latter exhibits a significant down-field shift due to close proximity to the more electron-withdrawing nitrogen centre, similar to comparable compounds ($C_5H_3N(2,6\text{-}C(Me)PPh_2)_2$).[360] The IR spectra show carbonyl stretching frequencies at $\nu_{(C=O)}$ 1642 and 1650 cm^{-1} for **82** and **83**

respectively, similar to **62 - 66** and $C_6H_4(1,2\text{-}C(O)PPh_2)_2$ ($\nu_{(C=O)}$ ca. 1640 and 1656 cm^{-1}, respectively), consistent with significant delocalisation of the phosphorus lone pair.

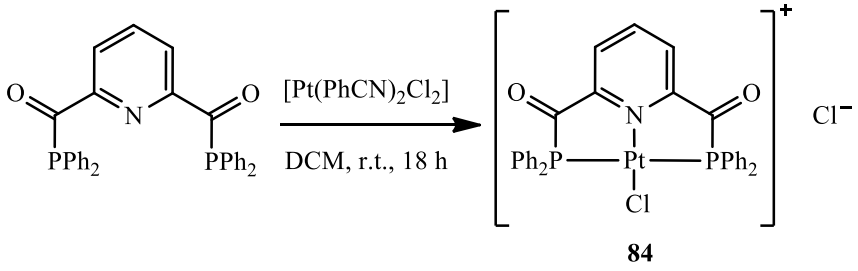
Table 45. Selected spectroscopic data for $C_5H_3E(2,6\text{-}C(O)PPh_2)_2$ (**82 - 83**)

		^{31}P / ppm	$^{13}C\{^1H\}$ C(O)P / ppm	$^1J_{C\text{-}P}$ / Hz	$^{13}C\{^1H\}$ *i*-C / ppm	$^2J_{C\text{-}P}$ / Hz	$\nu_{(C=O)}$ / cm^{-1}
82	$C_6H_4(2,6\text{-}C(O)PPh_2)_2$	12.9	211	38.1	140	35.7	1642
83	$C_5H_3N(2,6\text{-}C(O)PPh_2)_2$	16.6	214	40.4	153	31.4	1650

4.3.2 Reactions of $C_5H_3E(2,6\text{-}C(O)PPh_2)_2$

The [2,6]-substitution pattern on the central aromatic ring of **82** and **83** allows for comparison with typical pincer ligands from literature.[361,362] Such compounds have been reported to have many applications in catalysis,[12] molecular switches,[27] and as gas sensors,[22] prompting a brief exploration into the coordination chemistry of **82** and **83**. Initial attempts to react **82** with palladium or platinum complexes ([Pd(1,5-COD)Cl_2], [Pt(PhCN)$_2Cl_2$]) generated a mixture of products that could not be separated (by washing or recrystallisation) and as such was not further pursued. Similar results were obtained from the analogous reactions of **83** with palladium reagents ($PdCl_2$, [Pd(1,5-COD)Cl_2], [Pd(OAc)$_2$]).

The addition of $C_5H_3N(2,6\text{-}C(O)PPh_2)_2$ (**83**) to [Pt(PhCN)$_2Cl_2$] afforded $[PtCl\{C_5H_3N(2,6\text{-}C(O)PPh_2)_2\}]^+$ $[Cl]^-$ (**84**) as a yellow solid in high yield (70 %) (Scheme 100).



84

Scheme 100. Synthesis of $[PtCl\{C_5H_3N(2,6\text{-}C(O)PPh_2)_2\}]^+$ $[Cl]^-$ (**84**)

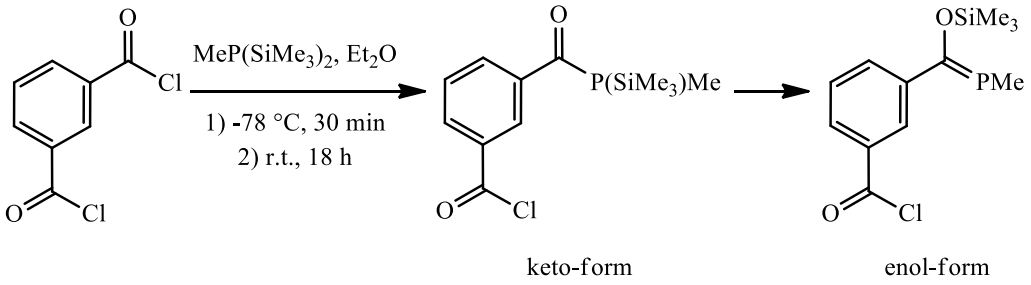
The ^{31}P NMR spectrum of **84** shows a broad resonance at 33.1 ppm ($^1J_{P\text{-}Pt}$ 2814 Hz, $w_{½}$ ca. 30.4 Hz) with platinum satellites of a magnitude consistent with a *trans*-geometry,[77] while the $^{195}Pt\{^1H\}$ NMR spectrum exhibits a triplet resonance at –3795 ppm, consistent with two equivalent phosphorus centres bound to platinum. The $^{13}C\{^1H\}$ NMR spectrum shows triplet resonances in accordance with a *trans*-coordinated complex at 202 ($^1J_{C\text{-}P}$ 16.9 Hz) and 148 ppm

($^2J_{C\text{-}P}$ 28.4 Hz), assigned to the carbonyl and *ipso*-carbon centres respectively. The high-field chemical shifts when compared to **83** (δ_C 214, 153) are consistent with trends that emerged from characterisation of the phosphomide complexes **69 - 79**. A significant increase ($\nu_{(C=O)}$ +39.7 cm^{-1}) in carbonyl stretching frequency was recorded for **84** compared to **83**, consistent with the previous assertions that **83** exhibits extensive phosphorus lone pair delocalisation, which is then vastly reduced upon coordination to platinum.

4.4 Syntheses and reactions of diphosphametacyclophanes

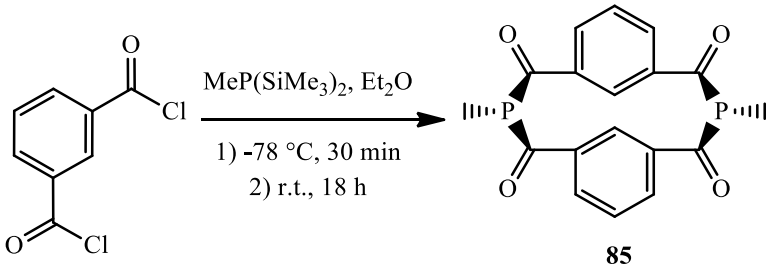
4.4.1 Synthesis of {3-CO-C_6H_4-C(O)PMe}$_2$

The development of phosphomides **62 - 68** was in part precipitated by the studies outlined in Chapter 3, in which acyl chlorides react with phosphines to afford unanticipated results. In order to further explore this reactivity, the addition of equimolar amounts of $C_6H_4(1,3\text{-}COCl)_2$ to $MeP(SiMe_3)_2$ was performed, and was envisaged to provide access to the phosphaalkene $C_6H_4(1\text{-}C(OSiMe_3)=PMe)(3\text{-}COCl)$ (Scheme 101), *via* [1,3]-silatropic rearrangement of the resulting acyl phosphine $C_6H_4(1\text{-}C(O)P(SiMe_3)Me)(3\text{-}COCl)$ i.e. the Becker condensation.[94]



Scheme 101. Proposed synthesis of $C_6H_4(1\text{-}C(OSiMe_3)=PMe)(3\text{-}COCl)$

The Becker synthesis is extremely well established in literature, and is in fact one of the primary routes towards phosphaalkenes.[363,103,105] However, the reaction of $C_6H_4(1,3\text{-}COCl)_2$ and $MeP(SiMe_3)_2$ afforded an analytically pure yellow solid in 79 % yield that was identified as the novel diphosphametacyclophane {3-CO-C_6H_4-C(O)PMe}$_2$ (**85**) (Scheme 102). As a result of the high symmetry within **85**, initial identification of the product proved non-facile; the use of mass spectrometry (*m/z* = 356) in conjunction with the NMR data enabled the postulation of **85**, which was later confirmed by an X-ray diffraction study.



85

Scheme 102. Synthesis of {3-CO-C_6H_4-C(O)PMe}$_2$ (**85**)

The $^{31}P\{^1H\}$ NMR spectrum shows a singlet resonance at 32.7 ppm that correlates (*via* ^1H-^{31}P HMBC NMR study) to a doublet signal in the ^1H NMR spectrum at 1.58 ppm ($^2J_{H\text{-}P}$ 3.1 Hz), assigned to the methyl group. This resonance integrates to six protons when compared to the remaining signals at 6.42, 7.13 and 7.14 ppm, attributed to the aromatic rings, which integrate to a total of eight protons. The $^{13}C\{^1H\}$ NMR spectrum exhibits a doublet signal at 206 ppm ($^1J_{C\text{-}P}$ 46.0 Hz), consistent with retention of the carbonyl group, which is further supported by infrared absorbances at $_{\nu(C=O)}$ 1656, 1639 cm^{-1}, corresponding to both symmetric and asymmetric modes, comparable with phosphomides **62 - 66**.

X-ray quality crystals were grown at −20 °C from THF (Figure 36); the molecular structure shows that, similar to known metacyclophanes,[364] **85** exists as a "butterfly" conformation with the methyl moieties adopting a mutually *exo* arrangement. The C1-O1 bond length is within the standard range for a typical ketone (1.21 Å for acetone) at 1.211(3) Å,[365] and is comparable with the cyclic diketophosphanyl anion $[C_6H_4(1,2\text{-}CO)_2P]^-[K\text{-}18\text{-}crown\text{-}6]^+$ (1.22(1) Å).[366] In contrast, the C1-P1 bond length (1.892(3) Å) is significantly longer than in typical phosphines (1.847(3) Å for $^nBu_3P$),[367] and phosphides $[C_6H_4(1,2\text{-}CO)_2P]^-[K\text{-}18\text{-}crown\text{-}6]^+$ (1.80(1) Å). The O1-C1-C2 and O1-C1-P1 angles (121.8(3) and 120.6(2) °) demonstrate that **85** is planar about the carbonyl, with no perturbations arising from ring strain, which is consistent with cyclic diketophosphanyls ($C_6H_4(1,2\text{-}CO)_2PPh$),[368] and $[C_6H_4(1,2\text{-}CO)_2P]^-[K\text{-}18\text{-}crown\text{-}6]^+$. The geometry about the phosphorus centre is distorted trigonal pyramidal with a C1-P1-C16 angle of 95.73(13) °, which is in contrast with the significantly smaller angle for $[C_6H_4(1,2\text{-}CO)_2P]^-[K\text{-}18\text{-}crown\text{-}6]^+$ (90.3(5) °), and much larger angle of $^nBu_3P$ (102.70(10) °).

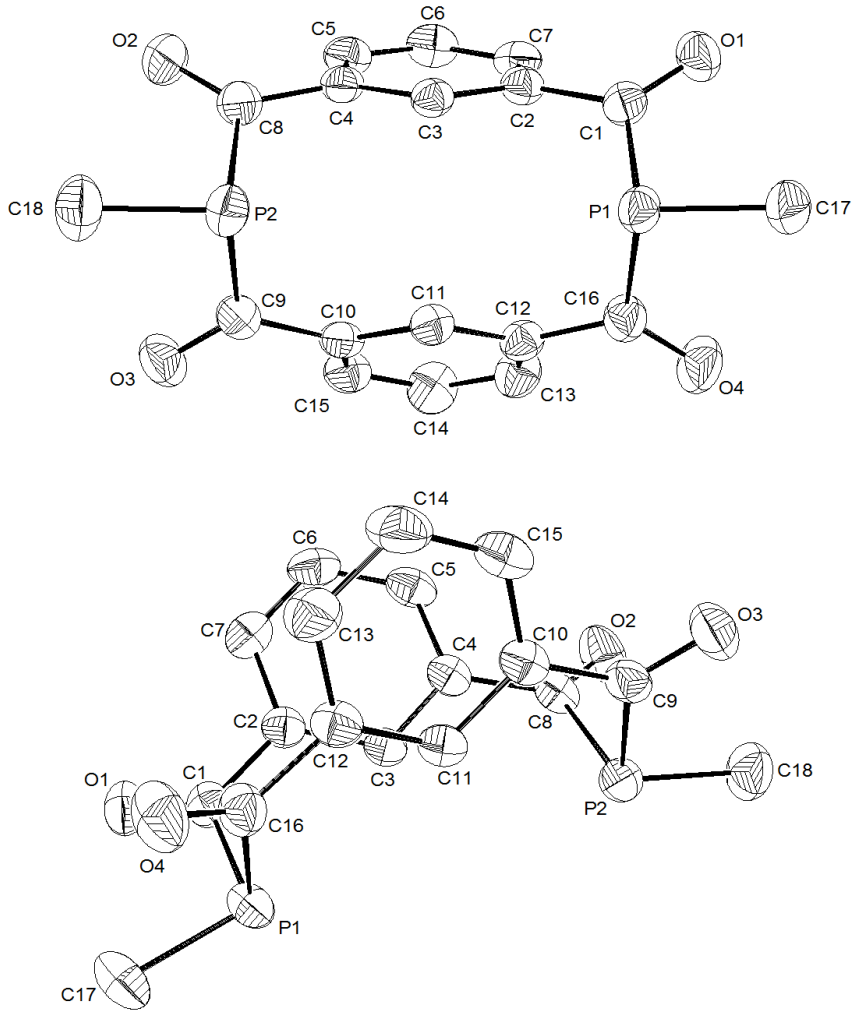


Figure 36. Molecular structure of {3-CO-C_6H_4-C(O)PMe}$_2$ (**85**), with thermal ellipsoids at the 50 % probability level, hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (deg): C1-O1 1.211(3), C8-O2 1.202(3), C9-O3 1.220(3), C16-O4 1.210(3), C1-P1 1.892(3), C16-P1 1.890(3), C17-P1 1.815(3), C8-P2 1.894(3), C9-P2 1.886(3), C18-P2 1.816(3). C1-P1-C16 95.73(13), C1-P1-C17 98.76(14), C16-P1-C17 100.06(14), C8-P2-C9 95.14(12), C8-P2-C18 99.60(14), C9-P2-C18 100.73(15), C1-C1-C2 121.8(3), O1-C1-P1 120.6(2).

Although metacyclophanes have been well documented, **85** is the first to incorporate multiple phosphorus atoms into the skeletal backbone, which is surprising given the prevalent inclusion of main group atoms into cyclophane backbones (carbon,[369–371] nitrogen,[372–375] oxygen,[376,377] sulphur,[378–380]). Unlike the facile one-pot synthesis of **85**, synthetic methodologies for known metacyclophanes entail multiple steps and afford poor yields; the "efficient" synthesis of {3-CO-C_6H_4-$(CH_2)_2$CO}$_2$ requires six steps, with an overall yield of 47 %.[369] Interestingly, **85** may also be considered a cyclic diketophosphanyl, and was recently cited amongst a very limited number of such species, "Crossley and co-workers reported another interesting example that deals with the self-assembly of diphosphametacyclophane" (Figure 37).[381] Cyclic

diketophosphanyls **4.B - 4.E** possess similar traits to **85**, including trigonal pyramidal geometry at the phosphorus centre, and comparable ^{31}P NMR spectra (δ_P −28.0 to 73.4), whereby the chemical shift is largely dependent upon ring size.[382,368] In contrast with **4.B - 4.E** and **85**, phosphide **4.A** is planar, although the ^{31}P NMR chemical shift does fall in the expected range (δ_P 43.3).[366]

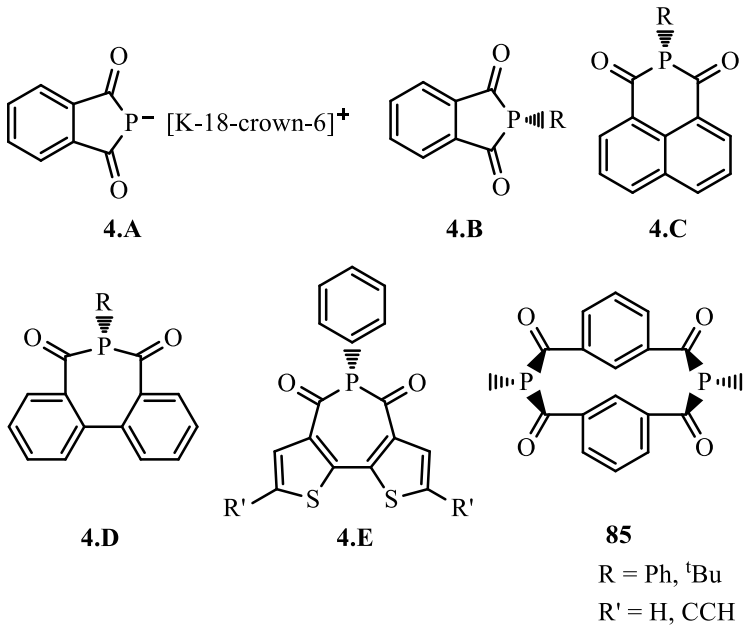
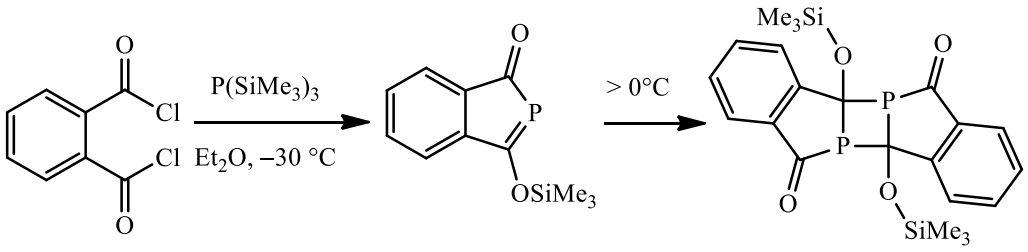


Figure 37. Cyclic diketophosphanyls in literature; **4.A**,[366] **4.B**,[382] **4.C**,[368] **4.D**,[381] compound **85**

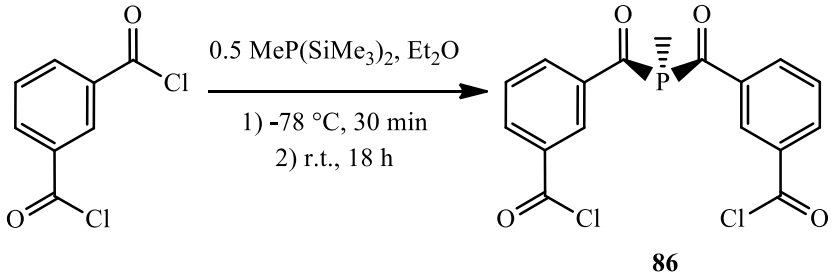
The reactivity of $C_6H_4(1,3\text{-}COCl)_2$ with $MeP(SiMe_3)_2$ is not entirely unprecedented; while in most reported cases the [1,3]-silatropic rearrangement occurs spontaneously to form the phosphaalkene, contrary examples do exist.[285] Appel reported the synthesis of $(Me_3SiO)OCP(SiMe_3)R$ by addition of $RP(SiMe_3)_2$ (R = Me, ^{t}Bu, Ph) to CO_2,[95] and showed that the acyl phosphine (keto-form) was preferred at low temperature, while at ambient temperature an equilibrium formed between $(Me_3SiO)OCP(SiMe_3)R$ and phosphaalkene $(Me_3SiO)_2C{=}PR$ (enol-form) that could be assessed by ^{31}P NMR spectroscopy. Furthermore, Markovskii reported the similar attempted synthesis of phosphaalkene $C_6H_4(1\text{-}C(OSiMe_3){=}PSiMe_3)(2\text{-}COCl)$ in the presence of a second acyl chloride moiety (Scheme 103).[383] The addition of $C_6H_4(1,2\text{-}COCl)_2$ to $P(SiMe_3)_3$ was reported to afford $C_6H_4(1\text{-}CO)(2\text{-}COSiMe_3)P$, a compound that was stable over five days in THF at −5 °C, but readily dimerised at 0 °C.



Scheme 103. Markovskii's attempted synthesis of C_6H_4(1-C(OSiMe$_3$)=PSiMe$_3$)(2-COCl)[383]

4.4.2 Synthesis of {C_6H_4(1-COCl)3-CO}$_2$PMe

In order to gain insight into the formation of **85**, further investigation *via* manipulation of the reagent stoichiometries was undertaken. The addition of C_6H_4(1,3-COCl)$_2$ to half an equivalent of MeP(SiMe$_3$)$_2$ was envisaged to either produce **85** in < 50% yield, or a non-cyclic acyl phosphine if one acyl chloride moiety reacts preferentially. A crude orange oil (71 % yield) was afforded from the reaction that was identified as {C_6H_4(1-COCl)3-CO}$_2$PMe (**86**) (Scheme 104); complete removal of small quantities of **85** was not achieved by washing, distillation or recrystallisation attempts.



86

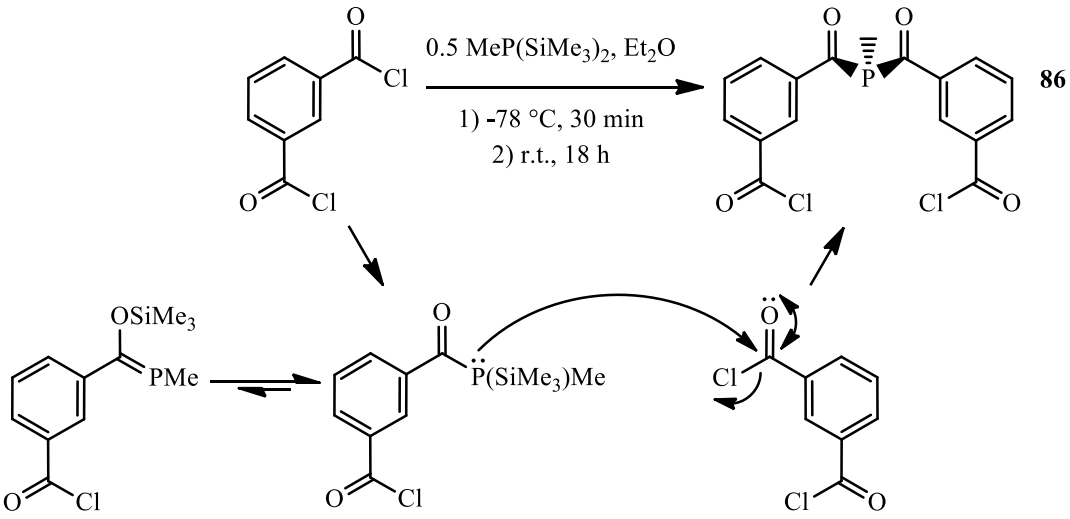
Scheme 104. Synthesis of {C_6H_4(1-COCl)3-CO}$_2$PMe (**86**)

The ^{1}H NMR spectrum shows a doublet resonance at 1.39 ppm ($^2J_{H\text{-}P}$ 3.4 Hz) that is shifted significantly up-field relative to **85**, and integrates as three protons when compared to the aromatic resonances which integrate to a total of eight protons. This is consistent with the presence of two equivalent aromatic rings and one PMe unit. The ^{31}P NMR spectrum shows a broad resonance at 20.2 ppm ($w_{½}$ ca. 12.5 Hz), which is again shifted up-field with respect to **85**. Comparison of key spectroscopic data with the related compound (C_6H_5CO)$_2$PMe lends further credence to the proposed structure of **86**;[319] the ^{31}P{^{1}H} NMR resonance was reported at 17 ppm, while the signal corresponding to the methyl protons was located as a doublet at 1.55 ppm ($^2J_{H\text{-}P}$ 6.6 Hz) in the ^{1}H NMR spectrum.

4.4.3 Mechanistic insights into the synthesis of $\{C_6H_4(1\text{-}COCl)3\text{-}CO\}_2PMe$

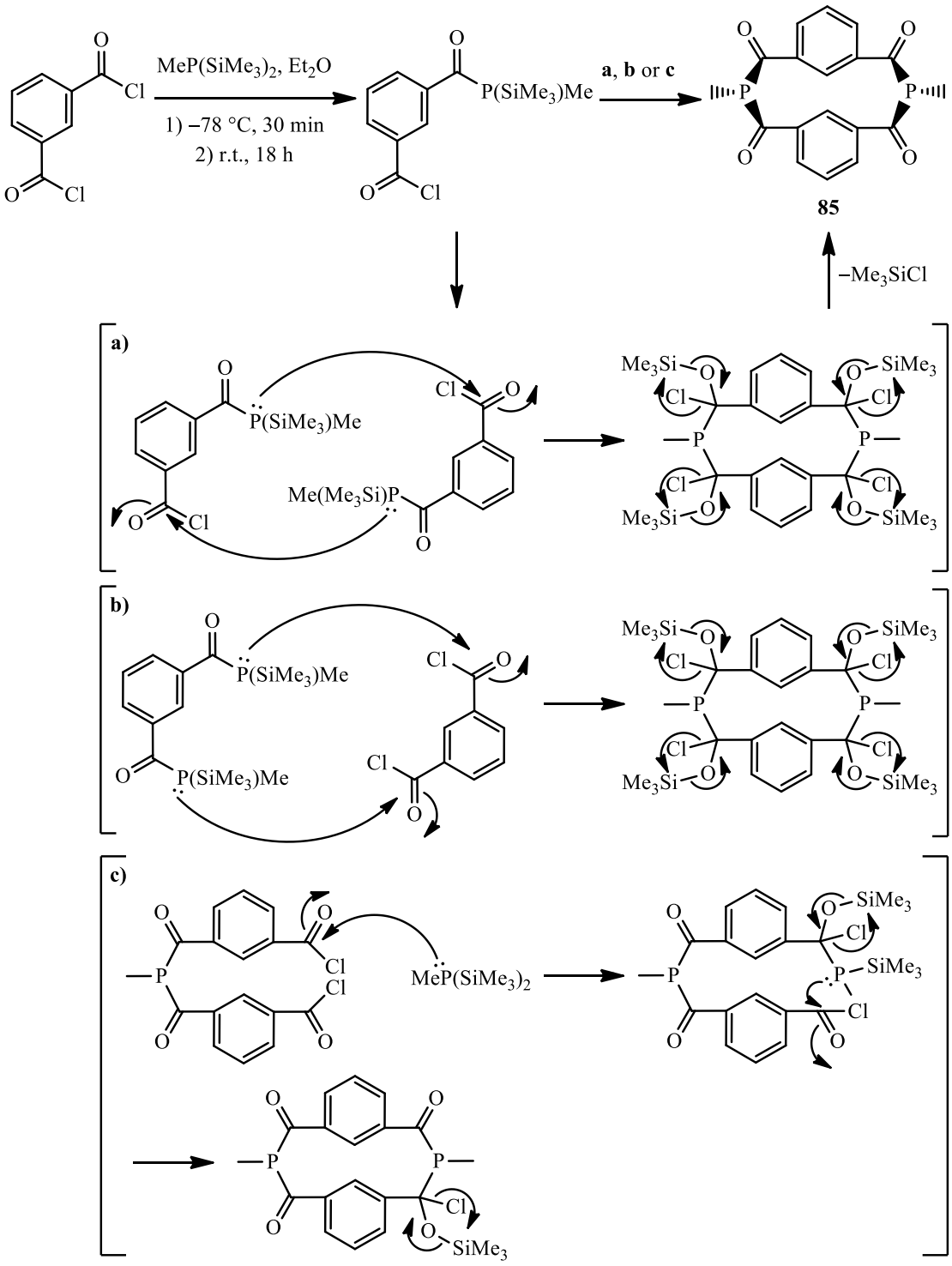
Several possible mechanisms can be postulated for the formation of **85** and **86**; however, there is no supporting evidence due to the extremely rapid rate of reaction; **85** was observed to precipitate from Et_2O at –78 °C in <5 min.

The facile and exclusive synthesis of **86** is consistent with preferential reaction at one acyl chloride moiety to form the desired acyl phosphine $C_6H_4(1\text{-}C(O)P(SiMe_3)Me)(3\text{-}COCl)$ being the initial reaction step, as non-selective reactions would result in the formation of a mixture of products, which was not found. Reaction of $C_6H_4(1\text{-}C(O)P(SiMe_3)Me)(3\text{-}COCl)$ with the remaining equivalent of $C_6H_4(1,3\text{-}COCl)_2$ to form **86** *via* loss of $ClSiMe_3$ is the logical proposal (Scheme 105). The lack of evidence for the head-to-tail combination of two units of $C_6H_4(1\text{-}C(O)P(SiMe_3)Me)(3\text{-}COCl)$, which would produce **85**, lends further support to the proposed synthetic mechanism of **86**.



Scheme 105. Proposed mechanism for formation of $\{C_6H_4(1\text{-}COCl)3\text{-}CO\}_2PMe$ (**86**)

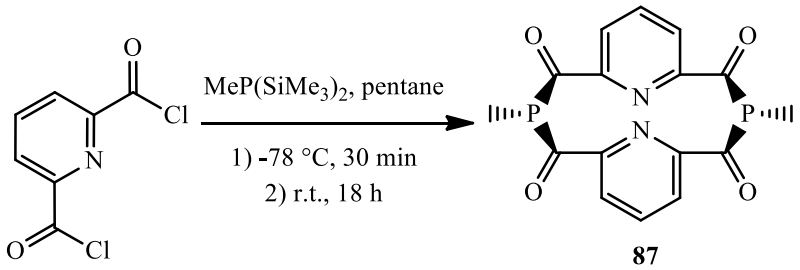
In contrast, there are several possibilities for the formation of **85**, including **a**) the condensation of two units of $C_6H_4(1\text{-}C(O)P(SiMe_3)Me)(3\text{-}COCl)$, **b**) the initial formation of $C_6H_4(1,3\text{-}C(O)PMe)_2$ followed by reaction with a second unit of $C_6H_4(1,3\text{-}COCl)_2$, or **c**) reaction of a second $MeP(SiMe_3)_2$ with **86** (Scheme 106). In each case, further reactivity is presumably driven by the favourable elimination of ClSiMe. Route **c** is the most likely pathway given that **86** can be synthesised and isolated exclusively; however, in the absence of further data, a definitive conclusion cannot be drawn.



Scheme 106. Potential mechanisms for the formation of {3-CO-C_6H_4-C(O)PMe}$_2$ (**85**)

4.4.4 Synthesis of {2-CO-C_5H_3N-C(O)PMe}$_2$

The synthesis of {2-CO-C_5H_3N-C(O)PMe}$_2$ (**87**) was considered in order to incorporate further functionality into the diphosphametacyclophane ligand. The addition of C_5H_3N{2,6-$(COCl)_2$} to $MeP(SiMe_3)_2$ afforded a crude orange solid (57 % yield) for which analytical purity could not be obtained (by washing or recrystallisation) (Scheme 107). It was thus characterised as an impure product whose identity was supported by a combination of EI mass spectrometry (*m/z* 358 $[M]^+$), NMR data, and comparison with compound **85**.



Scheme 107. Synthesis of {2-CO-C_5H_3N-C(O)PMe}$_2$ (**87**)

The ^{31}P NMR spectrum of **87** shows a broad resonance at 30.2 ppm ($w_{½}$ ca. 17.0 Hz), which is at a similar chemical shift to **85** (δ_P 32.7). The ^1H NMR spectrum exhibits a higher order multiplet at 1.63 ppm that is assigned to the CH_3 groups (Figure 38), in contrast with the doublet reported for **85**. The $^{13}C\{^1H\}$ NMR spectrum shows a doublet resonance at 3.33 ppm ($^1J_{C\text{-}P}$ 7.8 Hz) for the CH_3 carbons, while the signal attributed to the *ipso*-carbon was located as a doublet at 153 ppm ($^2J_{C\text{-}P}$ 33.2 Hz); the significant down-field shift from **85** (δ_C 138 ($^2J_{C\text{-}P}$ 37.9 Hz)) is rationalised by the increased electronegativity of nitrogen, as previously observed for di-phosphomide **83**. A doublet resonance at 209 ppm ($^1J_{C\text{-}P}$ 50.7 Hz) is assigned to the carbonyl resonance with a coupling constant consistent with a one-bond carbon-phosphorus separation.

While **87** is the second known diphosphametacyclophane, it is also a novel example of a pyridinophane.[384,385] Such pyridinophanes have been well studied, with applications in catalysis,[386–388] and metal ion sensors.[389–391]

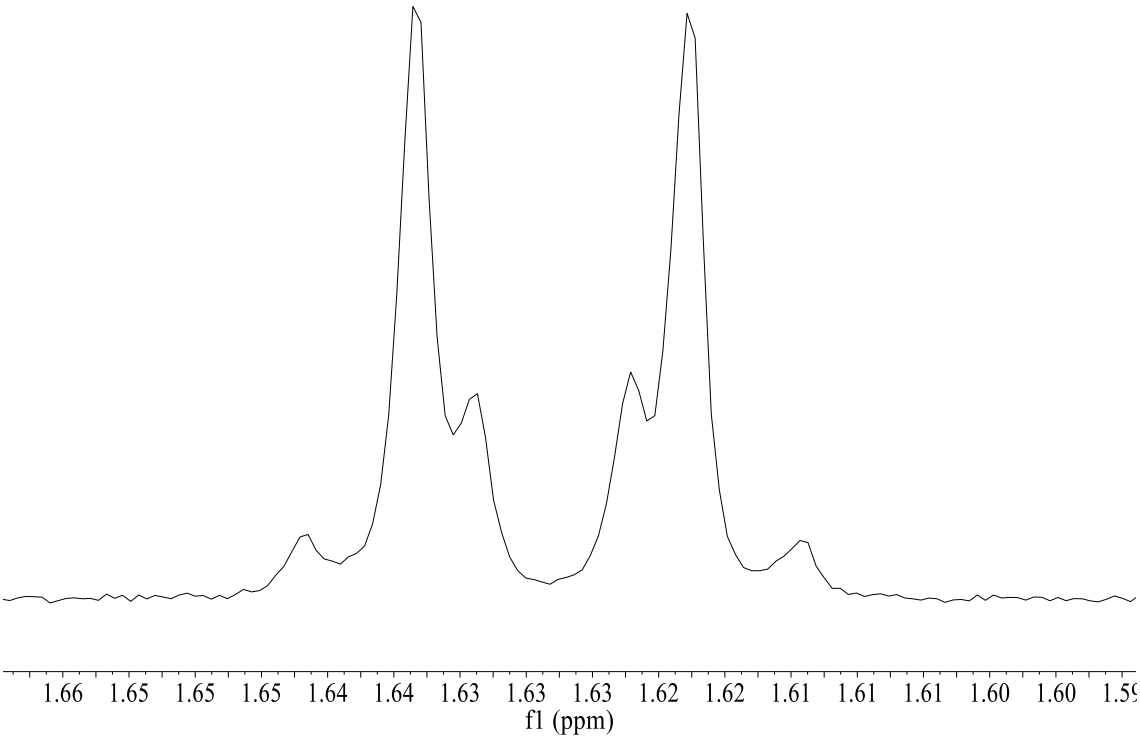
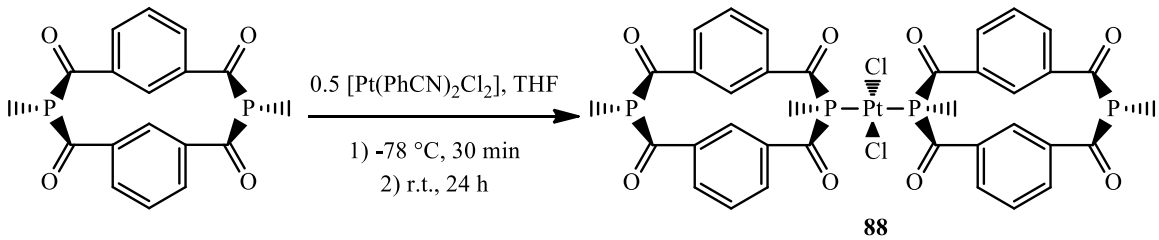


Figure 38. Selected section (1.59 – 1.66 ppm) of the ^{1}H NMR spectrum of **87**

4.4.5 Coordination reactions of diphosphametacyclophanes

Multiple attempts to coordinate {2-CO-C_5H_3N-C(O)PMe}$_2$ (**87**) to transition metals (by reaction with $PtCl_2$, [Pt(1,5-COD)Cl_2], and [Rh(1,5-COD)Cl]$_2$) were unsuccessful. However, attempts to coordinate **85** afforded two novel complexes.

The addition of equimolar amounts of **85** to *cis*-[$PtCl_2$(PhCN)$_2$] was performed in order to probe whether **85** could chelate a single metal between both phosphorus centres. However, *trans*-[$PtCl_2$({3-CO-C_6H_4-C(O)PMe}$_2$)$_2$] (**88**) was afforded as the sole product; repetition of the reaction with a 2:1 reagent stoichiometry yielded complex **88** as a yellow solid in 74 % (Scheme 108).

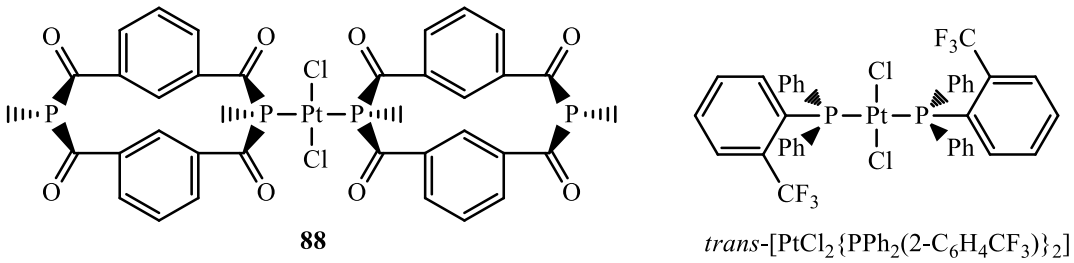


88

Scheme 108. Synthesis of *trans*-[$PtCl_2$({3-CO-C_6H_4-C(O)PMe}$_2$)$_2$] (**88**)

The $^{31}P\{^{1}H\}$ NMR spectrum shows two distinct phosphorus environments; a singlet signal at 33.2 ppm ($^{1}J_{P\text{-}Pt}$ 2296 Hz) is consistent with *trans*-coordination to platinum due to the characteristic coupling constant of the satellites (which typically range from 2200 - 2800 Hz for *trans*-isomers of bisphosphine di-halide platinum complexes),[55] and a second singlet resonance at 28.4 ppm, that displays negligible change in chemical shift from free **85**. As expected from the presence of two distinct phosphorus signals, the ^{1}H NMR spectrum displays two inequivalent methyl resonances at 1.50 (d, $^{2}J_{H\text{-}P}$ 3.2 Hz) and 2.39 ppm (t, $^{2}J_{H\text{-}P}$ 3.1 Hz); the latter signal is attributed to the platinum-coordinated phosphorus on the basis of ^{1}H-^{31}P HMBC NMR spectroscopy, and evidences virtual coupling phenomena. Due to the low solubility of the product (in THF, C_6D_6, $CDCl_3$, *etc*.) the $^{13}C\{^{1}H\}$ NMR spectrum recorded did not allow for resolution of phosphorus couplings; it was, however, possible to identify the chemical shift of each carbon environment, including two distinct signals at 196 and 205 ppm, assigned to the acyl phosphine carbons of the free and coordinated ends of **85** respectively.

Yellow crystals of **88** suitable for X-ray diffraction were grown from THF over three days at −20 °C (Figure 40). The internal ligand geometry was retained upon coordination to platinum, demonstrated by the mutually *exo* methyl groups and butterfly conformation, although the P1-C1 bond length (1.793(3) Å) was notably shortened compared to both free **85** (1.815 (3) Å) and the uncoordinated PMe group of **88** (P2-C10 1.823(4) Å). The C1-P1-C2 and C1-P1-C18 angles (101.81(16) and 102.03(16) °) of the coordinated PMe group show a significant distortion from the uncoordinated PMe group (99.22(19) and 98.74(18) °). Notably, the P2…Pt separation of 4.56 Å is too large to achieve chelation (the sum of the Van der Waals radii is 3.52 Å).[392] All of the bond lengths and angles are comparable within the bounds of statistical significance (Table 46) to Stuart's *trans*-$[PtCl_2\{PPh_2(2\text{-}C_6H_4CF_3)\}_2]$ (Figure 39),[54] including the Pt-Cl and Pt-P bond lengths, and P1-Pt-Cl angles. Indeed, both complexes exhibit almost square planar geometries about the platinum centres, with inter-ligand angles of 91.05(3) and 92.93(8) ° for **88** and *trans*-$[PtCl_2\{PPh_2(2\text{-}C_6H_4CF_3)\}_2]$ respectively. The P1-C2 bond length of **88** (1.896(3) Å) is slightly longer than that reported by Stuart (1.835(4) Å), which is attributed to the different natures of the carbon atoms in question; the carbonyl centre of **88** is very electron-withdrawing, while Stuart's is the *ipso*-carbon of a benzene ring.



88 *trans*-[$PtCl_2\{PPh_2(2\text{-}C_6H_4CF_3)\}_2$]

Figure 39. Complex **88** and *trans*-[$PtCl_2\{PPh_2(2\text{-}C_6H_4CF_3)\}_2$] [54]

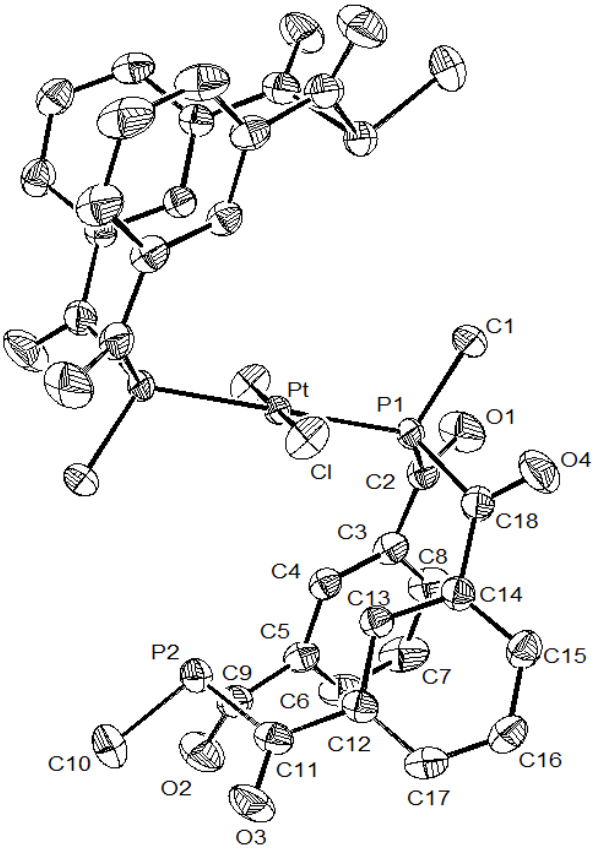
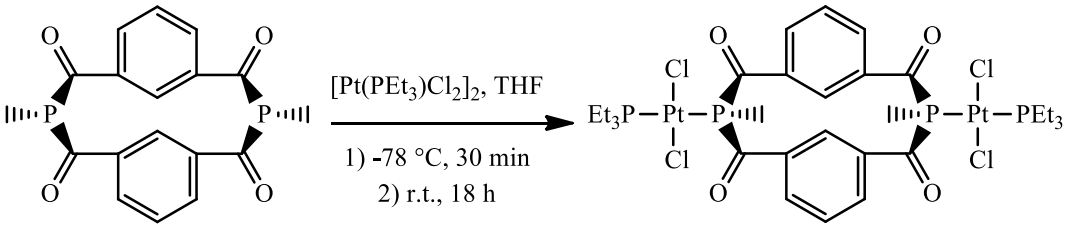


Figure 40. Molecular structure of *trans*-[$PtCl_2(\{3\text{-}CO\text{-}C_6H_4\text{-}C(O)PMe\}_2)_2$] (**88**), with thermal ellipsoids at the 50 % probability level, hydrogen atoms omitted for clarity The molecule lies on an inversion centre and equivalent atoms are generated by symmetry transformation (-x, -y+1, -z+1). Selected bond distances (Å) and angles (deg): Pt-P1 2.2940(7), Pt-Cl 2.3106(7), P1-C1 1.793(3), P1-C2 1.896(3), O1-C2 1.208(4), P2-C10 1.823(4), O2-C9 1.215(4), O3-C11 1.214(4), O4-C18 1.201(4). P1-Pt-Cl 91.05(3), C1-P1-C2 101.81(16), C1-P1-C18 102.03(16), C2-P1-C18 104.56(16), C9-P1-C10 99.22(19), C10-P2-C9 99.22(19), C10-P2-C11 98.74(18), C9-P2-C11 97.65(15).

Table 46. Selected bond lengths and angles for **88** and *trans*-[$PtCl_2\{PPh_2(2\text{-}C_6H_4CF_3)\}_2$] [54]

Bond lengths (Å) and angles (deg)	*d* Pt-Cl / Å	*d* Pt-P / Å	*d* P1-C2 / Å	P1-Pt-Cl / deg
Complex **88**	2.310(8)	2.294(7)	1.896(3)	91.05(3)
trans-[$PtCl_2\{PPh_2(2\text{-}C_6H_4CF_3)\}_2$]	2.307(2)	2.312(2)	1.835(4)	92.93(8)

The reaction of **85** with $[PtCl_2(PEt_3)]_2$ was also investigated, resulting in *trans*-[$\{Pt(PEt_3)Cl_2\}_2\{3\text{-}CO\text{-}C_6H_4\text{-}C(O)PMe\}_2$] (**89**) as a yellow solid in 88 % yield (Scheme 109).



89

Scheme 109. Synthesis of *trans*-[$\{Pt(PEt_3)Cl_2\}_2\{3\text{-}CO\text{-}C_6H_4\text{-}C(O)PMe\}_2$] (**89**)

The ^1H NMR spectrum of **89** shows a doublet signal at 2.02 ppm ($^2J_{H\text{-}P}$ 3.4 Hz) that integrates as six protons when compared to the aromatic proton resonances at 6.59, 7.89 and 9.36 ppm, which integrate to eight protons combined. The chemical shift of the methyl protons is very similar to the coordinated PMe groups of **88**, consistent with coordination of both phosphorus centres to platinum. The $^{31}P\{^1H\}$ NMR spectrum shows doublet resonances at 15.9 ($^2J_{P\text{-}P}$ 441 Hz, $^1J_{P\text{-}Pt}$ 2813 Hz) and 51.3 ppm ($^2J_{P\text{-}P}$ 441 Hz, $^1J_{P\text{-}Pt}$ 1951 Hz), indicative of two inequivalent phosphorus atoms that couple to each other across a platinum centre in a *trans*-configuration. The $^{195}Pt\{^1H\}$ NMR spectrum shows a doublet of doublets at −3934 ppm ($^1J_{Pt\text{-}P}$ 1951 Hz, $^1J_{Pt\text{-}P}$ 2813 Hz) that supports the proposed identity of **89**. The poor product solubility in common deuterated solvents (in THF, C_6D_6, $CDCl_3$) meant that signal splitting due to phosphorus could not be resolved in the $^{13}C\{^1H\}$ NMR spectrum, although each carbon environment was successfully assigned. The methyl group carbon atoms of PMe resonate at 4.68 ppm, reminiscent of **85**, while the carbonyl carbon environment is located at 203 ppm, consistent with the comparable resonance displayed by **88**. Multiple attempts to grow crystals using a variety of solvent systems and temperatures remain unsuccessful to date.

4.5 Summary

A series of *meta*- and *para*- substituted phosphomides $C_6H_4(1\text{-}C(O)PPh_2)(R)$ (**62 - 66**) has been synthesised without the requirement for additional base or prior lithiation of $HPPh_2$. Compounds **62 - 66** exhibit carbonyl stretches typical of phosphomides ($\nu_{(C=O)}$ 1630 to 1650 cm^{-1}), **62** possesses the most low frequency absorbance ($\nu_{(C=O)}$ 1634 cm^{-1}), indicative of extensive phosphorus lone pair delocalisation. Complexes of these ligands were synthesised, most of which adhered to typical phosphine coordination chemistry behaviour. Synthesis of the analogous phosphomides $C_6H_4(1\text{-}C(O)PCy_2)(R)$ (**67 - 68**) was successful, although investigations proved that prior lithiation of $HPCy_2$ was necessary to obtain them in purity.

The improved methodology for the syntheses of phosphomides **62 - 66** was applied to the production of di-phosphomides, affording $C_5H_3E(1,3\text{-}C(O)PPh_2)_2$ (**82 - 83**), which possess the [1,3]-substitution pattern typical of pincer ligands. Incorporation of carbonyl groups into the backbone induced significantly different NMR characteristics and reactivity profiles compared to known pincer ligands, hindering attempts to synthesise novel pincer complexes.

The syntheses of unprecedented diphosphametacyclophanes $\{3\text{-}CO\text{-}C_6H_4\text{-}C(O)PMe\}_2$ (**85**) and $\{2\text{-}CO\text{-}C_5H_3N\text{-}C(O)PMe\}_2$ (**87**) have been described, and three possible mechanisms of formation considered, assisted by development of the related compound $\{C_6H_4(1\text{-}COCl)3\text{-}CO\}_2PMe$ (**86**). Although definitive identification of the mechanism was not possible, it was concluded that the initial step must involve formation of acyl phosphine $C_6H_4(1\text{-}C(O)P(SiMe_3)Me)(3\text{-}COCl)$.

5. Conclusions and outlook

The primary aim of this research was to develop synthetic routes to compounds that might act as precursors to phosphaalkynes bearing extended conjugation, such as $R_3EC{\equiv}CC{\equiv}P$ and C_6H_4(1-C≡P)(2/3/4-R), which are expected to possess novel electronic properties. Though still to be achieved, significant progress has been made and valuable insights into the complexities of phosphaalkene and phosphaalkyne syntheses have resulted. Furthermore, many of the species developed *en route* provide opportunities for future investigations in low coordinate phosphorus chemistry and the development of new catalysts.

A collection of new chloropropargyls $R_3EC{\equiv}CCH_2Cl$ and their unprecedented conversion to main group propargylphosphines $R_3EC{\equiv}CCH_2PPh_2$ and $R_3EC{\equiv}CCH_2P(SiMe_3)_2$ was reported. While compounds $R_3EC{\equiv}CCH_2PPh_2$ were isolated in good yields and coordinated to platinum and palladium complexes, the silylated propargylphosphines $R_3EC{\equiv}CCH_2P(SiMe_3)_2$ could not be produced reliably. Despite this, initial investigations showed that $R_3EC{\equiv}CCH_2P(SiMe_3)_2$ could be converted to $R_3EC{\equiv}CCH_2PI_2$ *via* the addition of neat I_2, although isolation of the products was not achieved. However, given the successful synthesis of $R_3EC{\equiv}CCH_2PI_2$, the development of a reliable synthetic methodology for $R_3EC{\equiv}CCH_2P(SiMe_3)_2$ might ultimately provide a new synthetic route to phosphaalkynes of the type $R_3EC{\equiv}CC{\equiv}P$ *via* the double dehydrohalogenation of $R_3EC{\equiv}CCH_2PI_2$.

The attempted synthesis of $PhC{\equiv}CCH_2P(NEt_2)_2$ *via* the Grignard reaction of '$PhC{\equiv}CCH_2MgCl$' with $ClP(NEt_2)_2$ afforded a rare example of a phosphorus-containing allene: $Ph\{(NEt_2)_2P\}C{=}C{=}CH_2$. This synthetic methodology could prove useful in the synthesis of new phosphorus-containing allenes. Furthermore, its production provided insight into the alternative mechanistic pathways that may have hindered attempts to convert $R_3EC{\equiv}CCH_2Cl$ to $R_3EC{\equiv}CCH_2P(NEt_2)_2$ and $R_3EC{\equiv}CCH_2PCl_2$ using the same synthetic route. This information may prove useful in the design of new routes towards propargylphosphines.

The production of two new phosphaalkenes C_6H_4(1-C($OSiMe_3$)=P$SiMe_3$)(2-Me) and C_6H_4(1-C($OSiMe_3$)=P$SiMe_3$)(3-Me) was achieved, although isomeric purity was not obtained through either purification attempts or alterations to the reaction conditions. Attempts to convert the phosphaalkenes to the corresponding phosphaalkynes were unsuccessful. The synthesis of a collection of analogous phosphaalkenes C_6H_4(1-C($OSiMe_3$)=P$SiMe_3$)(R) bearing a variety of substituents at the 3- and 4-position was also unsuccessful, highlighting the sensitivity of the

Becker synthesis toward arene substitution. Future investigations into the synthesis of phosphaalkenes bearing substituted arene rings could prove more successful *via* an alternative route.

The production of a series of *meta*- and *para*-substituted phosphomides $C_6H_4(1\text{-}C(O)PPh_2)(R)$ was achieved *via* a facile one-pot synthetic route and their platinum, palladium and rhodium complexes $[MCl_2\{C_6H_4(1\text{-}C(O)PPh_2)(R)\}_2]$ (M = Pt, Pd) and $[Rh(1,5\text{-}COD)\{C_6H_4(1\text{-}C(O)PPh_2)(R)\}Cl]$ were reported. Sporadic literature studies on the use of phosphomide complexes for catalytic applications have shown promise, particularly for the hydroformylation of 4-vinylanisole. As such, testing the catalytic activity of the new phosphomide complexes reported in this thesis may provide valuable insight in the continued development of new catalysts.

Two new di-phosphomides $C_5H_3E(1,3\text{-}C(O)PPh_2)_2$ (E = N, CH) were synthesised, providing access to novel pincer ligands; at the time of writing, pincer ligands with carbonyl moieties incorporated into the skeleton are unreported in the literature. Such compounds would be expected to possess significantly different electronic characteristics to currently-established pincer ligands, which typically feature electron-donating groups in the backbone. Although initial attempts at coordination reactions resulted in the production of just one new pincer complex $[PtCl\{C_5H_3N(2,6\text{-}C(O)PPh_2)_2\}]^+ [Cl]^-$, the facile generation of the di-phosphomides suggests that the synthesis of similar compounds would be straight-forward. Pincer complexes are currently used to catalyse a wide variety of reactions, including the Heck reaction and the dehydrogenation of ammonia-borane, often providing improved results over traditional catalytic systems. As such, further research in the potential applications of pincer ligands of the type $C_5H_3E(1,3\text{-}C(O)PPh_2)_2$ and their complexes might provide industrially-valuable results.

Two novel diphosphametacyclophanes $\{3\text{-}CO\text{-}C_6H_4\text{-}C(O)PMe\}_2$ and $\{2\text{-}CO\text{-}C_5H_3N\text{-}C(O)PMe\}_2$ and a brief exploration of their coordination chemistry was also reported in this thesis. While metacyclophanes have been well-documented in the literature, the incorporation of two phosphorus units into the skeleton is unprecedented, and the facile one-pot synthesis used here is vastly improved upon typical methodologies, which usually feature a minimum of six steps. The use of such compounds is relatively unexplored, although Baumgartner cited $\{3\text{-}CO\text{-}C_6H_4\text{-}C(O)PMe\}_2$ as a rare example of a diketophosphanyl in his recent publication on the development of π-conjugated materials,[381] highlighting potential future avenues of research. The use of diphosphametacyclophanes as chelating materials also remains to be explored.

6. Experimental

6.1 General experimental procedures

6.1.1 General methods

All manipulations were performed under a dry nitrogen atmosphere in a glove box, or using standard Schlenk line techniques with an atmosphere of argon.

6.1.2 Spectroscopy

NMR spectra were obtained at 303 K unless otherwise stated using a Varian VNMRS 400 MHz spectrometer. The spectra were referenced to external $SiMe_4$ for ^{1}H (I = ½, 99.9 %, 399.50 MHz), ^{13}C (I = ½, 1.11 %, 100.46 MHz) and ^{29}Si (I = ½, 4.67 %, 79.37 MHz), to H_3PO_4 for ^{31}P (I = ½, 100 %, 161.71 MHz), $SnMe_4$ for ^{119}Sn (I = ½, 8.59 %, 148.97 MHz), and K_2PtCl_6 for ^{195}Pt (I = ½, 33.83 %, 85.53 MHz). ^{1}H-^{13}C HMBC and HSQC NMR spectra were obtained at 303 K using a Varian VNMRS 500 MHz spectrometer with external reference to $SiMe_4$ for ^{1}H (499.91 MHz) and ^{13}C (125.71 MHz). Several ^{195}Pt NMR spectra were obtained at 303 K using a Varian VNMRS 600 MHz with reference to external K_2PtCl_6 for ^{195}Pt (128.3 MHz). All chemical shifts are quoted in ppm. $^{13}C\{^{1}H\}$ NMR spectra were assigned by recourse to the ^{1}H-^{13}C HMBC and HSQC NMR spectra, while ^{1}H-^{31}P, ^{1}H-^{29}Si and ^{1}H-^{119}Sn HMBC NMR spectra were also used to aid assignment and confirm connectivity. When performing quantitative NMR studies with PPh_3 as an internal standard the relaxation delay was increased to 5 s.

Elemental analyses were performed by Mr Stephen Boyer of the London Metropolitan University elemental analysis service. Mass spectra were recorded by Dr. A. Abdul-Sada (University of Sussex departmental service) on a VG Autospec Fisons instrument (70 eV electron ionisation) or KratosMS25 spectrometer. IR spectra were recorded neat on a Perkin-Elmer Spectrum One instrument.

6.1.3 Solvents and reagents

Deuterated NMR grade solvents were obtained from Goss Scientific and purified by repeated freeze-thaws followed by reflux over calcium hydride (for $CDCl_3$, CD_2Cl_2) or potassium (for C_6D_6, THF, $C_6D_5CD_3$) for 72 h and then vacuum transferred into an ampule and stored under a nitrogen atmosphere. Other solvents were distilled for a minimum of 72 h over sodium (toluene), calcium hydride (DCM), potassium (THF, DME) or sodium potassium alloy (pentane,

hexane, Et_2O), or in the case of DME, brought to reflux over 4 Å molecular sieves for 72 h Hydrocarbons were stored over potassium mirrors, while THF and DCM were stored over 4 Å molecular sieves.

The following reagents were procured from Sigma-Aldrich and used as supplied unless otherwise stated; ^{n}BuLi (2.5 M in hexanes), C_6H_4(1-COCl)(2-Me), C_6H_4(1-COCl)(3-Me), C_6H_4(1-COCl)(3-CN), C_6H_4(1-COCl)(3-CH_2Cl), C_6H_4(1-COCl)(4-CN), C_6H_4(1-COCl)(4-CO_2Me), P($SiMe_3$)$_3$, C_5H_3N(2,6-COCl)$_2$, Ph_3SnCl, Ph_3SiCl, MeLi, MeI, PCl_3, $^{n}Bu_3$SnCl, $HgCl_2$, I_2, Mg. The following reagents were procured from Sigma-Aldrich and freeze-thawed prior to use; HC≡CCH_2Cl, $^{n}Pr_3$SiCl, $^{i}Pr_3$SiCl, $^{n}Bu_3$SiCl, Me_2PhSiCl, ClP(NEt_2)$_2$, $HPPh_2$,$HPCy_2$. The following reagents were obtained from Sigma-Aldrich and recrystallized from hot toluene prior to use; C_6H_4(1,3-COCl)$_2$, C_6H_3(1,3,5-COCl)$_3$. The following reagents were procured from Sigma-Alrich and Strem Chemicals; $PtCl_2$, $PdCl_2$ and used as supplied.

[$PtCl_2$($PhCN$)$_2$],[393] MeP($SiMe_3$)$_2$,[394] [$PtCl_2$(PEt_3)]$_2$,[395] were prepared in accordance with standard literature procedures. With thanks to John Spencer for generous donation of [$PdCl_2$], and Ben Day for [Pd(1,5-COD)Cl_2] and [Pt(1,5-COD)Cl_2].

HP($SiMe_3$)$_2$, [Rh(1,5-COD)Cl]$_2$ and [Fe_2(CO)$_9$] were available within the laboratory from previous workers.

Magnesium was pre-dried at 100 °C for 72 h and activated by stirring for 72 h under argon.

6.1.4 Crystallographic details

Single crystal X-ray diffraction data were obtained by Dr S. M. Roe and Dr. M. P. Coles using an Enraf-Nonius CAD4 system with κ CCD area detector. Data were solved using ShelX, while visualisations were performed using ORTEP,[396] or Mercury.[397] Copies of all tables and cif files are available on the supplementary data CD.

6.2 Chapter 2: The development of chloropropargyls and propargylphosphines

Synthesis of $^{n}Bu_3SnC{\equiv}CCH_2Cl$ (1)

To a THF solution of propargyl chloride (2.24 g, 3.0 x 10^{-2} mol) at −78 °C was added ^{n}BuLi (2.5 M, 6.01 cm^3, 1.5 x 10^{-2} mol) and the mixture was stirred for 30 min. $^{n}Bu_3SnCl$ (4.40 cm^3, 1.5 x 10^{-2} mol) in THF was added, producing a yellow solution that was stirred for 30 min at −78 °C and was then allowed to warm to ambient temperature. After stirring for 18 h the solvent was removed under reduced pressure; the product was extracted with pentane and dried *in vacuo* to afford a yellow oil. Yield: 5.09 g, 93.7 %.

^{1}H NMR (C_6D_6): δ_H 0.91 (t, 9H, $^{3}J_{H\text{-}H}$ 7.24 Hz, C**H**$_3$), 0.97 (t, 6H, $^{3}J_{H\text{-}H}$ 7.97 Hz, C**H**$_2$Sn), 1.34 (q, 6H, $^{3}J_{H\text{-}H}$ 7.45 Hz, C**H**$_2$CH$_2$Sn), 1.61 (quin, 6H, $^{3}J_{H\text{-}H}$ 7.85 Hz, CH$_3$C**H**$_2$), 3.70 (s, 2H, $^{4}J_{H\text{-}Sn}$ 9.21 Hz, C**H**$_2$Cl).

^{13}C{^{1}H} NMR (C_6D_6): δ_C 11.3 (s, **C**H$_2$Sn, $^{1}J_{C\text{-}Sn\ (117)}$ 364.9 Hz, $^{1}J_{C\text{-}Sn\ (119)}$ 382.1 Hz), 13.9 (s, **C**H$_3$), 27.3 (s, CH$_3$**C**H$_2$, $^{3}J_{C\text{-}Sn\ (117)}$ 57.7 Hz, $^{3}J_{C\text{-}Sn\ (119)}$ 60.2 Hz), 29.3 (s, **C**H$_2$CH$_2$Sn, $^{2}J_{C\text{-}Sn\ (119)}$ 23.6 Hz), 31.2 (s, **C**H$_2$Cl), 91.1 (s, **C**≡CCH$_2$Cl), 105.0 (s, C≡**C**CH$_2$Cl).

^{119}Sn{^{1}H} NMR (C_6D_6): δ_{Sn} −65.1.

Elem. Anal.: Calcd for $C_{15}H_{29}SnCl$: C, 49.56 %; H, 7.98 %. Found; C, 49.44 %; H, 7.86 %.

Synthesis of $Ph_3SnC{\equiv}CCH_2Cl$ (2)

Prepared as for **1** using ^{n}BuLi (2.5 M, 5.4 cm^3, 1.3 x 10^{-2} mol), propargyl chloride (2.03 g, 2.7 x 10^{-2} mol) and Ph_3SnCl (5.25 g, 1.3 x 10^{-2} mol). Isolated as a yellow oil. Yield: 3.96 g, 72.0 %.

^{1}H NMR (C_6D_6): δ_H 3.67 (s, 2H, $^{4}J_{H\text{-}Sn}$ 10.5 Hz, C**H**$_2$Cl), 7.1-7.7 (15H, C$_6$**H**$_5$).

^{13}C{^{1}H} NMR (C_6D_6): δ_C 30.3 (s, **C**H$_2$Cl), 88.1 (s, **C**≡CCH$_2$), 106.4 (s, C≡**C**CH$_2$), 128.8 (s, *p*-**C**), 129.5 (s, *m*-**C**), 130.1 (s, *i*-**C**), 136.7 (s, *o*-**C**).

^{119}Sn{^{1}H} NMR (C_6D_6): δ_{Sn} −169.4.

Elem. Anal.: Calcd for $C_{21}H_{17}SnCl$: C, 59.50 %; H, 4.01 %. Found; C, 59.63 %; H, 4.12 %.

Synthesis of $Me_2PhSiC{\equiv}CCH_2Cl$ (3)

Prepared as for **1** using ^{n}BuLi (2.5 M, 10.01 cm^3, 2.5 x 10^{-2} mol), propargyl chloride (3.73 g, 5.0 x 10^{-2} mol) and $Me_2PhSiCl$ (4.26 g, 2.5 x 10^{-2} mol). The crude product was isolated as a pale

yellow oil, which was distilled at 66 °C, 8.1 x 10^{-1} mbar, affording a colourless oil. Yield: 4.98 g, 95.9 %.

^{1}H NMR (C_6D_6): δ_H 0.32 (s, 6H, C**H**$_3$), 3.51 (s, 2H, C**H**$_2$Cl), 7.19-7.21 (m, 3H, C**H**), 7.59-7.61 (m, 2H, C**H**).

^{13}C{^{1}H} NMR (C_6D_6): δ_C -1.55 (s, **C**H$_3$), 30.1 (s, **C**H$_2$Cl), 89.7 (s, **C**≡CCH$_2$Cl), 101.8 (s, C≡**C**CH$_2$Cl), 129.5 (s, *m*-**C**), 130.1 (s, *p*-**C**), 133.6 (s, *o*-**C**), 136.0 (s, *i*-**C**).

^{29}Si{^{1}H} NMR (C_6D_6): δ_{Si} −21.6.

Elem. Anal.: Calcd for $C_{11}H_{13}SiCl$: C, 63.31 %; H, 6.23 %. Found; C, 63.18 %; H, 6.14 %.

Synthesis of ^{i}Pr$_3$SiC≡CCH$_2$Cl (4)

Prepared as for **1** using ^{n}BuLi (2.5 M, 16.8 cm^3, 4.2 x 10^{-2} mol), propargyl chloride (6.24 g, 8.4 x 10^{-2} mol) and ^{i}Pr$_3$SiCl (8.06 g, 4.2 x 10^{-2} mol). The crude product was isolated as pale yellow oil, which was distilled at 52 °C, 3.0 x 10^{-1} mbar, affording a colourless oil. Yield: 5.76 g, 60.3 %.

^{1}H NMR (C_6D_6): δ_H 1.03 (m, 3H, C**H**), 1.10 (d, 18H, $^{3}J_{H\text{-}H}$ 6.51 Hz, C**H**$_3$), 3.53 (s, 2H, C**H**$_2$Cl).

^{13}C{^{1}H} NMR (C_6D_6): δ_C 11.1 (s, **C**H), 18.3 (s, **C**H$_3$), 30.2 (s, **C**H$_2$Cl), 88.0 (s, **C**≡CCH$_2$Cl), 102.2 (s, C≡**C**CH$_2$Cl).

^{29}Si{^{1}H} NMR (C_6D_6): δ_{Si} −1.68.

Elem. Anal.: Calcd for $C_{12}H_{23}SiCl$: C, 62.47 %; H, 9.98 %. Found; C, 62.38 %; H, 9.85 %.

Synthesis of ^{n}Pr$_3$SiC≡CCH$_2$Cl (5)

Prepared as for **1** using ^{n}BuLi (2.5 M, 4.35 cm^3, 1.09 x 10^{-2} mol), propargyl chloride (1.62 g, 2.17 x 10^{-2} mol) and ^{n}Pr$_3$SiCl (2.09 g, 1.09 x 10^{-2} mol). Isolated as an orange oil. Yield: 2.33 g, 92.7 %.

^{1}H NMR (C_6D_6): δ_H 0.60 (m, 6H, SiC**H**$_2$), 0.99 (t, 9H, $^{3}J_{H\text{-}H}$ 7.16 Hz, C**H**$_3$), 1.47 (m, 6H, C**H**$_2$), 3.55 (s, 2H, C**H**$_2$Cl).

^{13}C{^{1}H} NMR (C_6D_6): δ_C 16.2 (s, Si**C**H$_2$), 17.9 (s, **C**H$_3$), 18.4 (s, **C**H$_2$), 30.7 (s, **C**H$_2$Cl), 90.2 (s, **C**≡CCH$_2$Cl), 101.8 (s, C≡**C**CH$_2$Cl).

^{29}Si{^{1}H} NMR (C_6D_6): δ_{Si} −13.0.

Elem. Anal.: Calcd for $C_{12}H_{23}SiCl$: C, 63.01 %; H, 9.98 %. Found; C, 62.87 %; H, 9.79 %.

Synthesis of $^{n}Bu_3SiC{\equiv}CCH_2Cl$ (6)

Prepared as for **1** using ^{n}BuLi (2.5 M, 5.15 cm^3, 1.29 x 10^{-2} mol), propargyl chloride (1.92 g, 2.5 x 10^{-2} mol) and $^{n}Bu_3SiCl$ (3.02 g, 1.29 x 10^{-2} mol). Isolated as an orange oil. Yield: 3.08 g, 87.8 %.

^{1}H NMR (C_6D_6): δ_H 0.67 (m, 6H, SiC**H**$_2$), 0.92 (t, 9H, $^3J_{H\text{-}H}$ 7.28 Hz, C**H**$_3$), 1.38 (m, 6H, $^3J_{H\text{-}H}$ 7.82 Hz, CH_3C**H**$_2$), 1.46 (quin, 6H, C**H**$_2$$CH_2$Si), 3.56 (s, 2H, C**H**$_2$Cl).

^{13}C{^{1}H} NMR (C_6D_6): δ_C 13.3 (s, Si**C**H_2), 14.0 (s, **C**H_3), 26.6 (s, CH_3**C**H_2), 26.8 (s, **C**H_2CH_2Si), 30.7 (s, **C**H_2Cl), 90.3 (s, **C**≡CCH_2Cl), 101.8 (s, C≡**C**CH_2Cl).

^{29}Si{^{1}H} NMR (C_6D_6): δ_{Si} −11.3.

Elem. Anal.: Calcd for $C_{15}H_{27}SiCl$: C, 66.54 %; H, 9.98 %. Found; C, 66.39 %; H, 10.02 %.

Synthesis of $Ph_3SiC{\equiv}CCH_2Cl$ (7)

Prepared as for **1** using ^{n}BuLi (2.5 M, 2.68 cm^3, 6.70 x 10^{-3} mol), propargyl chloride (1.00 g, 1.03 x 10^{-2} mol) and Ph_3SiCl (3.83 g, 1.30 x 10^{-3} mol). Isolated as a brown solid. Yield: 3.04 g, 88.5 %.

^{1}H NMR (C_6D_6): δ_H 3.49 (s, 2H, C**H**$_2$Cl), 7.16 (m, 9H, C**H**), 7.76 (m, 6H, C**H**).

^{13}C{^{1}H} NMR (C_6D_6): δ_C 30.4 (s, **C**H_2Cl), 87.6 (s, **C**≡CCH_2Cl), 104.9 (s, C≡**C**CH_2Cl), 128.4 (s, *m*-**C**), 130.4 (s, *p*-**C**), 133.4 (s, *o*-**C**), 136.0 (s, *i*-**C**).

^{29}Si{^{1}H} NMR (C_6D_6): δ_{Si} −28.8.

Elem. Anal.: Calcd for $C_{21}H_{17}SiCl$: C, 75.79 %; H, 5.11 %. Found; C, 75.68 %; H, 5.14 %.

Synthesis of $^{n}Bu_3SnC{\equiv}CCH_2PPh_2$ (8)

To an Et_2O solution of Ph_2PH (0.375 g, 2.02 x 10^{-3} mol) at −78 °C was added ^{n}BuLi (2.5 M, 0.808 cm^3, 2.02 x 10^{-3} mol) and the mixture was stirred for 30 min. $^{n}Bu_3SnC{\equiv}CCH_2Cl$ (0.733 g, 2.02 x 10^{-3} mol) in Et_2O was added, resulting in a brown solution that was stirred for 30 min at −78 °C and was then allowed to warm to ambient temperature. After stirring for 18 h the solvent was removed under reduced pressure; the product was extracted with pentane and dried *in vacuo* to afford a yellow oil. Yield: 0.800 g, 77.2 %.

^{1}H NMR (C_6D_6): δ_H 0.88(m, $^{n}BuPh_3Sn$), 0.93 (m, 15H, C**H**$_3$ and C**H**$_2$Sn), 1.32(m, $^{n}BuPh_3Sn$), 1.35 (m, 6H, CH_3C**H**$_2$), 1.55(m, $^{n}BuPh_3Sn$), 1.59 (quin, 6H, $^3J_{H\text{-}H}$ 7.83 Hz, C**H**$_2$$CH_2$Sn), 2.87 (d, 2H, $^2J_{H\text{-}P}$ 1.71 Hz, C**H**$_2$P), 7.09 (m, 6H, *m*- and *p*-C**H**), 7.47 (t, 4H, $^3J_{H\text{-}H}$ 7.07 Hz, *o*-C**H**).

$^{13}C\{^{1}H\}$ NMR (C_6D_6): δ_C 11.3 (s, **C**H_2Sn), 13.9 (s, **C**H_3), 20.4 (d, $^{1}J_{C\text{-}P}$ 18.5 Hz, **C**H_2P), 27.4 (s, CH_3**C**H_2), 29.3 (s, **C**H_2CH_2Sn), 85.0 (d, $^{3}J_{C\text{-}P}$ 6.68 Hz, **C**≡CCH_2P), 106.8 (d, $^{2}J_{C\text{-}P}$ 4.89 Hz, C≡**C**CH_2P), 128.6 (d, $^{3}J_{C\text{-}P}$ 6.37 Hz, *m*-**C**H), 128.9 (s, *p*-**C**H), 133.2 (d, $^{2}J_{C\text{-}P}$ 18.7 Hz, *o*-**C**H), 138.8 (d, $^{1}J_{C\text{-}P}$ 16.9 Hz, *i*-**C**).

$^{31}P\{^{1}H\}$ NMR (C_6D_6): δ_P −13.4 (br, $^{4}J_{P\text{-}Sn}$ 14.5 Hz).

$^{119}Sn\{^{1}H\}$ NMR (C_6D_6): δ_{Sn} −68.4 (d, $^{4}J_{Sn\text{-}P}$ 14.5 Hz),), −12.0 ($^{n}Bu_4$Sn).

Synthesis of $Ph_3SnC{\equiv}CCH_2PPh_2$ (9)

Prepared as for **8** using ^{n}BuLi (2.1 M, 0.792 cm^3, 1.66 x 10^{-3} mol), Ph_2PH (0.309 g, 1.66 x 10^{-3} mol) and $Ph_3SnC{\equiv}CCH_2Cl$ (0.876 g, 1.66 x 10^{-3} mol). Isolated as a pale yellow oil. Yield: 0.734 g, 65.4 %.

^{1}H NMR (C_6D_6): δ_H 0.91 (m, 3H, $^{n}BuPh_3Sn$), 1.44 (m, 2H, $^{n}BuPh_3Sn$), 1.60 (m, 2H, $^{n}BuPh_3Sn$), 1.70 (m, 2H, $^{n}BuPh_3Sn$), 2.87 (d, 2H, $^{2}J_{H\text{-}P}$ 3.01 Hz, $^{4}J_{H\text{-}Sn}$ 9.10 Hz, $^{4}J_{H\text{-}Sn}$ 15.0 Hz, C**H**$_2$P), 7.02 (m, 2H, *p*-C**H**), 7.04 (m, 3H, *p*-C**H**), 7.14 (m, 10H, *m*-C**H**), 7.28 (m, 9H, $^{n}BuPh_3Sn$), 7.46(m, 6H, $^{n}BuPh_3Sn$), 7.58 (m, 6H, *o*-C**H**), 7.61 (m, 4H, *o*-C**H**).

$^{13}C\{^{1}H\}$ NMR (C_6D_6): δ_C 20.2 (m, $^{1}J_{C\text{-}P}$ 20.5 Hz, **C**H_2P), 82.8 (d, $^{3}J_{C\text{-}P}$ 5.98 Hz, **C**≡CCH_2P), 109.3 (d, $^{2}J_{C\text{-}P}$ 3.40 Hz, C≡**C**CH_2P), 128.6 - 137.5 (**C**H).

^{31}P NMR (C_6D_6): δ_P −13.2 (br, $^{4}J_{P\text{-}Sn}$ 13.9 Hz).

$^{119}Sn\{^{1}H\}$ NMR (C_6D_6): δ_{Sn} −168.4 (d, $^{4}J_{Sn\text{-}P}$ 13.9 Hz), −99.3 ($^{n}BuPh_3Sn$).

Synthesis of $Me_2PhSiC{\equiv}CCH_2PPh_2$ (10)

Prepared as for **8** using ^{n}BuLi (12.5 M, 1.69 cm^3, 4.24 x 10^{-3} mol), Ph_2PH (0.780 g, 4.24 x 10^{-3} mol) and $Me_2PhSiC{\equiv}CCH_2Cl$ (0.884 g, 4.24 x 10^{-3} mol). Isolated as a brown oil. Yield: 1.19 g, 78.4 %.

^{1}H NMR (C_6D_6): δ_H 0.30 (s, 6H, C**H**$_3$), 2.76 (d, 2H, $^{2}J_{H\text{-}P}$ 2.91 Hz, C**H**$_2$P), 7.06 (m, 6H, *m*- and *p*-C**H**), 7.20 (m, 4H, *o*-C**H**), 7.43 (m, 3H, *m*- and *p*-C**H**), 7.55 (m, 2H, *o*-C**H**).

$^{13}C\{^{1}H\}$ NMR (C_6D_6): δ_C –0.59 (s, **C**H_3), 19.8 (d, $^{1}J_{C\text{-}P}$ 20.7 Hz, **C**H_2P), 85.7 (d, $^{3}J_{C\text{-}P}$ 4.99 Hz, **C**≡CCH_2P), 104.9 (d, $^{2}J_{C\text{-}P}$ 3.59 Hz, C≡**C**CH_2P), 128.1 (m, *m*-**C**H), 128.7 (d, $^{3}J_{C\text{-}P}$ 6.50 Hz, *m*-**C**H), 129.0 (s, *p*-**C**H), 129.5 (s, *p*-**C**H), 133.2 (d, $^{2}J_{C\text{-}P}$ 19.5 Hz, *o*-**C**H), 134.2 (s, *o*-**C**H), 137.7 (s, *i*-**C**), 138.1 (d, $^{1}J_{C\text{-}P}$ 15.8 Hz, *i*-**C**).

^{31}P NMR (C_6D_6): δ_P −13.5 (br).

$^{29}Si\{^{1}H\}$ NMR (C_6D_6): δ_{Si} −22.9.

Elem. Anal.: Calcd for $C_{23}H_{23}SiP$: C, 77.09 %; H, 6.42 %. Found; C, 76.89 %; H, 6.34 %.

Synthesis of $^{i}Pr_3SiC{\equiv}CCH_2PPh_2$ (11)

Prepared as for **8** using ^{n}BuLi (2.5 M, 1.68 cm^3, 4.19 x 10^{-3} mol), Ph_2PH (0.779 g, 4.19 x 10^{-3} mol) and $^{i}Pr_3SiC{\equiv}CCH_2Cl$ (0.965 g, 4.19 x 10^{-3} mol). Isolated as an orange oil. Yield: 1.58 g, 99.2 %.

^{1}H NMR (C_6D_6): δ_H 1.01 (m, 3H, C**H**), 1.09 (d, 18H, $^{3}J_{H\text{-}H}$ 6.78 Hz, C**H**$_3$), 2.75 (d, 2H, $^{2}J_{H\text{-}P}$ 2.06 Hz C**H**$_2$P), 7.07 (m, 6H, *m*- and *p*-C**H**), 7.43 (t, 4H, *o*-C**H**).

$^{13}C\{^{1}H\}$ NMR (C_6D_6): δ_C 11.7 (s, **C**H), 18.9 (s, **C**H$_3$), 19.9 (d, $^{1}J_{C\text{-}P}$ 19.3 Hz, **C**H$_2$P), 83.3 (d, $^{3}J_{C\text{-}P}$ 5.19 Hz, **C**≡CCH$_2$P), 104.7 (d, $^{2}J_{C\text{-}P}$ 4.24 Hz, C≡**C**CH$_2$P), 128.7 (d, $^{3}J_{C\text{-}P}$ 6.54 Hz, *m*-**C**H), 129.0 (s, *p*-**C**H), 133.1 (d, $^{2}J_{C\text{-}P}$ 19.1 Hz, *o*-**C**H), 138.3 (d, $^{1}J_{C\text{-}P}$ 15.8 Hz, *i*-**C**).

^{31}P NMR (C_6D_6): δ_P −13.5 (br).

$^{29}Si\{^{1}H\}$ NMR (C_6D_6): δ_{Si} −3.03.

Elem. Anal.: Calcd for $C_{24}H_{33}SiP$: C, 75.79 %; H, 8.68 %. Found; C, 75.77 %; H, 8.64 %.

Synthesis of $^{n}Pr_3SiC{\equiv}CCH_2PPh_2$ (12)

Prepared as for **8** using ^{n}BuLi (2.5 M, 1.39 cm^3, 3.49 x 10^{-3} mol), Ph_2PH (0.650 g, 3.49 x 10^{-3} mol) and $^{n}Pr_3SiC{\equiv}CCH_2Cl$ (0.805 g, 3.49 x 10^{-3} mol). Isolated as a brown oil. Yield: 1.25 g, 94.3 %.

^{1}H NMR (C_6D_6): δ_H 0.58 (m, 6H, SiC**H**$_2$), 0.99 (t, 9H, $^{3}J_{H\text{-}H}$ 7.62 Hz, C**H**$_3$), 1.42 (m, 6H, C**H**$_2$), 2.76 (d, 2H, $^{2}J_{H\text{-}P}$ 2.52 Hz, C**H**$_2$P), 7.09 (m, 6H, *m*- and *p*-C**H**), 7.44 (m, 4H, *o*-C**H**).

$^{13}C\{^{1}H\}$ NMR (C_6D_6): δ_C 16.7 (s, Si**C**H$_2$), 17.9 (s, **C**H$_3$), 18.5 (s, **C**H$_2$), 19.9 (d, $^{1}J_{C\text{-}P}$ 19.9 Hz, **C**H$_2$P), 85.4 (d, $^{3}J_{C\text{-}P}$ 5.18 Hz, **C**≡CCH$_2$P), 103.0 (d, $^{2}J_{C\text{-}P}$ 4.00 Hz, C≡**C**CH$_2$P), 128.5 (d, $^{3}J_{C\text{-}P}$ 6.56 Hz, *m*-**C**H), 129.0 (s, *p*-**C**H), 133.2 (d, $^{2}J_{C\text{-}P}$ 19.0 Hz, *o*-**C**H), 138.3 (d, $^{1}J_{C\text{-}P}$ 16.5 Hz, *i*-**C**).

^{31}P NMR (C_6D_6): δ_P −13.6 (br).

$^{29}Si\{^{1}H\}$ NMR (C_6D_6): δ_{Si} −14.5.

Elem. Anal.: Calcd for $C_{24}H_{33}SiP$: C, 75.79 %; H, 8.68 %. Found; C, 75.77 %; H, 8.59 %.

Synthesis of $^{n}Bu_3SiC{\equiv}CCH_2PPh_2$ (13)

Prepared as for **8** using ^{n}BuLi (2.5 M, 1.15 cm^3, 2.87 x 10^{-3} mol), Ph_2PH (0.535 g, 2.87 x 10^{-3} mol) and $^{n}Bu_3SiC{\equiv}CCH_2Cl$ (0.784 g, 2.87 x 10^{-3} mol). Isolated as a brown oil. Yield: 1.12 g, 92.5 %.

^{1}H NMR (C_6D_6): δ_H 0.63 (m, 6H, SiC**H**$_2$), 0.93 (t, 9H, $^3J_{H\text{-}H}$ 7.19 Hz, C**H**$_3$), 1.37 (quin, 6H, C**H**$_2$CH$_2$Si), 1.40 (m, 6H, CH$_3$C**H**$_2$), 2.76 (d, 2H, $^2J_{H\text{-}P}$ 2.36 Hz, C**H**$_2$P), 7.10 (br, 6H, *m*- and *p*-C**H**), 7.44 (t, 4H, $^3J_{H\text{-}H}$ 7.30 Hz, *o*-C**H**).

^{13}C{^{1}H} NMR (C_6D_6): δ_C 13.7 (s, Si**C**H$_2$), 14.1 (s, **C**H$_3$), 19.9 (d, $^1J_{C\text{-}P}$ 19.8 Hz, **C**H$_2$P), 26.7 (s, CH$_3$**C**H$_2$), 26.9 (s, **C**H$_2$CH$_2$Si), 85.5 (d, $^3J_{C\text{-}P}$ 4.83 Hz, **C**≡CCH$_2$P), 104.0 (d, $^2J_{C\text{-}P}$ 4.09 Hz, C≡**C**CH$_2$P), 128.6 (d, $^3J_{C\text{-}P}$ 6.39 Hz, *m*-**C**H), 129.0 (s, *p*-**C**), 133.2 (d, $^2J_{C\text{-}P}$ 19.0 Hz, *o*-**C**H), 138.3 (d, $^1J_{C\text{-}P}$ 15.5 Hz, *i*-**C**).

^{31}P NMR (C_6D_6): δ_P −13.5 (br).

^{29}Si{^{1}H} NMR (C_6D_6): δ_{Si} −12.9.

Elem. Anal.: Calcd for $C_{27}H_{39}SiP$: C, 76.78 %; H, 9.24 %. Found; C, 76.85 %; H, 9.32 %.

Synthesis of *cis*-$[PtCl_2(^{n}Bu_3SnC{\equiv}CCH_2PPh_2)_2]$ (14)

To a DCM solution of $^{n}Bu_3SnC{\equiv}CCH_2PPh_2$ (0.515 g, 1.00 x 10^{-3} mol) at −78 °C was added $PtCl_2$(0.134 g, 5.02 x 10^{-4} mol) in DCM resulting in a suspended orange solid that was stirred for 30 min. The suspension was allowed to warm to ambient temperature and was stirred for 18 h then the solvent was removed under reduced pressure; the product was washed with pentane and dried *in vacuo* to afford a dark orange solid. Yield: 0.507 g, 78.2 %.

^{1}H NMR (C_6D_6): δ_H 0.88 (m, 30H, C**H**$_3$ and C**H**$_2$Sn), 1.27 (m, 12H, $^3J_{H\text{-}H}$ 7.38 Hz, CH$_3$C**H**$_2$), 1.44 (quin, 12H, $^3J_{H\text{-}H}$ 7.61 Hz, C**H**$_2$CH$_2$Sn), 3.78 (m, 4H, $^2J_{H\text{-}P}$ 10.9 Hz, C**H**$_2$P), 6.95 (m, 12H, *m*- and *p*-C**H**), 7.70 (m, 8H, *o*-C**H**).

^{13}C{^{1}H} NMR (C_6D_6): δ_C 11.2 (s, $^1J_{C\text{-}Sn}$ 366.3 Hz, $^1J_{C\text{-}Sn}$ 381.9 Hz, **C**H$_2$Sn), 13.9 (s, **C**H$_3$), 23.8 (m, $^1J_{C\text{-}P}$ 42.1 Hz, **C**H$_2$P), 27.4 (s, $^3J_{C\text{-}Sn}$ 58.3 Hz, $^3J_{C\text{-}Sn}$ 60.9 Hz, CH$_3$**C**H$_2$), 29.2 (s, $J_{C\text{-}Sn}$ 23.3 Hz, **C**H$_2$CH$_2$Sn), 88.7 (m, $^3J_{C\text{-}P}$ 7.77 Hz, **C**≡CCH$_2$P), 104.0 (m, $^2J_{C\text{-}P}$ 12.2 Hz, C≡**C**CH$_2$P), 127.9 (br, *m*-**C**H), 129.1 (br, *i*-**C**), 131.1 (s, *p*-**C**H), 134.4 (m, $^2J_{C\text{-}P}$ 10.4 Hz, *o*-**C**H).

^{31}P NMR (C_6D_6): δ_P 6.02 (br, $^1J_{P\text{-}Pt}$ 3611 Hz).

^{119}Sn{^{1}H} NMR (C_6D_6): δ_{Sn} −68.16 (m, $^4J_{Sn\text{-}P}$ 9.51 Hz).

^{195}Pt{^{1}H} NMR (C_6D_6): δ_{Pt} −4407 (t, $^1J_{Pt\text{-}P}$ 3611 Hz).

Elem. Anal.: Calcd for $C_{54}H_{78}Sn_2P_2Cl_2Pt$: C, 50.15 %; H, 6.04 %. Found; C, 50.23 %; H, 5.95 %.

Synthesis of *cis*-[$PtCl_2(^iPr_3SiC{\equiv}CCH_2PPh_2)_2$] (15)

Method A

Prepared as for **14** using $PtCl_2$ (0.136 g, 5.11 x 10^{-4} mol) and $^iPr_3SiC{\equiv}CCH_2PPh_2$ (0.388 g, 1.02 x 10^{-3} mol). Isolated as a yellow solid. Yield: 0.529 g, 86.4 %.

Method B

Prepared as for **14** using [Pt(1,5-COD)Cl_2] (0.182 g, 4.88 x 10^{-4} mol) and $^iPr_3SiC{\equiv}CCH_2PPh_2$ (0.371 g, 9.76 x 10^{-4} mol). Isolated as a yellow solid. Yield: 0.422 g, 84.2 %.

^{1}H NMR (C_6D_6): δ_H 0.84 (m, 6H, C**H**), 0.95 (d, 36H, $^3J_{H\text{-}H}$ 6.81 Hz, C**H**$_3$), 3.87 (d, 4H, $^2J_{H\text{-}P}$ 10.0 Hz, C**H**$_2$P), 6.85 (t, 8H, $^3J_{H\text{-}H}$ 7.71 Hz, *m*-C**H**), 6.92 (d, 4H, $^3J_{H\text{-}H}$ 7.21 Hz, *p*-C**H**), 7.54 (t, 8H, $^3J_{H\text{-}H}$ 8.90 Hz, *o*-C**H**).

^{13}C{^{1}H} NMR (C_6D_6): δ_C 11.6 (s, **C**H), 18.8 (s, C**H**$_3$), 23.9 (m, $^1J_{C\text{-}P}$ 42.3 Hz, **C**H$_2$P), 85.8 (m, $^3J_{C\text{-}P}$ 3.07 Hz, **C**≡CCH$_2$P), 101.9 (m, $^2J_{C\text{-}P}$ 6.34 Hz, C≡**C**CH$_2$P), 127.9 (m, *m*-**C**H), 131.1 (s, *p*-**C**H), 134.2 (m, $^2J_{C\text{-}P}$ 4.97 Hz, *o*-**C**H), 134.6 (m, $^1J_{C\text{-}P}$ 5.77 Hz, *i*-**C**).

^{31}P NMR (C_6D_6): δ_P 5.83 (br, $J_{P\text{-}Pt}$ 3618 Hz).

^{29}Si{^{1}H} NMR (C_6D_6): δ_{Si} −2.98.

^{195}Pt{^{1}H} NMR (C_6D_6): δ_{Pt} −4399 (t, $J_{Pt\text{-}P}$ 3618Hz).

Elem. Anal.: Calcd for $C_{48}H_{66}Si_2P_2Cl_2Pt$: C, 56.14 %; H, 6.43 %. Found; C, 56.03 %; H, 6.39 %.

Synthesis of *cis*-[$PtCl_2(^nPr_3SiC{\equiv}CCH_2PPh_2)_2$] (*cis*-16)

Method A

Prepared as for **14** using $PtCl_2$ (0.135 g, 5.07 x 10^{-4} mol) and $^nPr_3SiC{\equiv}CCH_2PPh_2$ (0.386 g, 1.02 x 10^{-3} mol). Isolated as a white solid. Yield: 0.407 g, 78.2 %.

Method B

Prepared as for **14** using [Pt(1,5-COD)Cl_2] (0.228 g, 6.11 x 10^{-4} mol) and $^nPr_3SiC{\equiv}CCH_2PPh_2$ (0.464 g, 1.22 x 10^{-3} mol). Isolated as a white solid. Yield: 0.475 g, 75.8 %.

^{1}H NMR (C_6D_6): δ_H 0.41 (m, 12H, SiC**H**$_2$), 0.93 (t, 18H, $^{3}J_{H\text{-}H}$ 7.31 Hz, C**H**$_3$), 1.23 (m, 12H, C**H**$_2$), 3.82 (d, 4H, $^{2}J_{H\text{-}P}$ 9.55 Hz, C**H**$_2$P), 6.90 (t, 8H, $^{3}J_{H\text{-}H}$ 7.00 Hz, *m*-C**H**), 6.97 (m, 4H, *p*-C**H**), 7.58 (t, 8H, $^{3}J_{H\text{-}H}$ 8.92 Hz, *o*-C**H**).

^{13}C{^{1}H} NMR (C_6D_6): δ_C 16.3 (s, Si**C**H$_2$), 17.8 (s, **C**H$_3$), 18.5 (s, **C**H$_2$), 23.9 (m, $^{1}J_{C\text{-}P}$ 46.1 Hz, **C**H$_2$P), 88.0 (m, $^{3}J_{C\text{-}P}$ 3.26 Hz, **C**≡CCH$_2$P), 101.4 (m, $^{2}J_{C\text{-}P}$ 6.04 Hz, C≡**C**CH$_2$P), 128.2 (m, $^{3}J_{C\text{-}P}$ 5.25 Hz, *m*-**C**H), 129.0 (s, *p*-**C**H), 131.1 (s, *o*-**C**H), 134.3 (m, $^{1}J_{C\text{-}P}$ 5.28 Hz, *i*-**C**).

^{31}P NMR (C_6D_6): δ_P 5.95 (br, $J_{P\text{-}Pt}$ 3608 Hz).

^{29}Si{^{1}H} NMR (C_6D_6): δ_{Si} −13.8.

^{195}Pt{^{1}H} NMR (C_6D_6): δ_{Pt} −4403 (t, $J_{Pt\text{-}P}$ 3608 Hz).

Elem. Anal.: Calcd for $C_{48}H_{66}Si_2P_2Cl_2Pt$: C, 56.14 %; H, 6.43 %. Found; C, 56.13 %; H, 6.45 %.

Synthesis of *trans*-[PtCl$_2$(^{n}Pr$_3$SiC≡CCH$_2$PPh$_2$)$_2$] (*trans*-16)

An NMR sample (borosilicate glass) of *cis*-[PtCl$_2$(^{n}Pr$_3$SiC≡CCH$_2$PPh$_2$)$_2$] in C_6D_6 was placed before a 500 MW full spectrum mercury lamp for 30 min; a dark orange precipitate separated from the solution, which could be re-dissolved upon agitation. Yield: 57.5 % by ^{1}H NMR resonance integration.

^{1}H NMR (C_6D_6): δ_H 0.46 (m, 12H, SiC**H**$_2$), 0.92 (t, 18H, $^{3}J_{H\text{-}H}$ 7.29 Hz, C**H**$_3$), 1.25 (m, 12H, C**H**$_2$), 3.77 (t, 4H, $^{2}J_{H\text{-}P}$ 4.55 Hz, C**H**$_2$P), 6.09 (m, 12H, *m*- and *p*-C**H**), 7.99 (m, 8H, *o*-C**H**).

^{13}C{^{1}H} NMR (C_6D_6): δ_C 16.4 (s, Si**C**H$_2$), 17.8 (s, **C**H$_3$), 18.5 (s, **C**H$_2$), 23.8 (t, $^{1}J_{C\text{-}P}$ 23.8 Hz, **C**H$_2$P), 88.1 (m, **C**≡CCH$_2$P), 100.7 (t, $^{2}J_{C\text{-}P}$ 4.86 Hz, C≡**C**CH$_2$P), 128.2 (d, $^{3}J_{C\text{-}P}$ 2.31 Hz, *m*-**C**H), 128.8 (s, *p*-**C**H), 130.9 (s, *o*-**C**H), 134.7 (t, $^{1}J_{C\text{-}P}$ 5.96 Hz, *i*-**C**).

^{31}P NMR (C_6D_6): δ_P 11.49 (br, $J_{P\text{-}Pt}$ 2217 Hz).

^{29}Si{^{1}H} NMR (C_6D_6): δ_{Si} −13.3.

^{195}Pt{^{1}H} NMR (C_6D_6): δ_{Pt} −3993 (t, $^{1}J_{Pt\text{-}P}$ 2217 Hz).

cis-[PtCl$_2$(^{n}Pr$_3$SiC≡CCH$_2$PPh$_2$)$_2$] was present in 42.5 % abundance.

Synthesis of *trans*-[PdCl$_2$(^{i}Pr$_3$SiC≡CCH$_2$PPh$_2$)$_2$] (17)

Method A

Prepared as for **14** using $PdCl_2$ (0.113 g, 6.41^{-4} mol) and ^{i}Pr$_3$SiC≡CCH$_2$PPh$_2$ (0.487 g, 1.28 x 10^{-3} mol). Isolated as a yellow solid. Yield: 0.526 g, 87.6 %.

Method B

Prepared as for **14** using [Pd(1,5-COD)Cl_2] (0.202 g, 7.09 x 10^{-4} mol) and $^{i}Pr_3SiC{\equiv}CCH_2PPh_2$ (0.539 g, 1.42 x 10^{-3} mol). Isolated as a yellow solid. Yield: 0.670 g, 85.1 %.

^{1}H NMR (C_6D_6): δ_H 0.91 (m, 6H, C**H**), 0.97 (d, 36H, $^3J_{H\text{-}H}$ 6.48 Hz, C**H**$_3$), 3.74 (t, 4H, $^2J_{H\text{-}P}$ 3.95 Hz, C**H**$_2$), 7.07 (br, 12H, *m*- and *p*-C**H**), 7.96 (br, 8H, *o*-C**H**).

^{13}C{^{1}H} NMR (C_6D_6): δ_C 11.2 (s, **C**H), 18.4 (m, **C**H_2P and **C**H_3), 85.3 (t, $^3J_{C\text{-}P}$ 3.00 Hz, **C**≡CCH_2P), 100.9 (t, $^2J_{C\text{-}P}$ 5.56 Hz, C≡**C**CH_2P), 128.0 (d, $^3J_{C\text{-}P}$ 4.99 Hz, *m*-**C**H), 128.9 (t, $^1J_{C\text{-}P}$ 23.8 Hz, *i*-**C**), 130.4 (s, *p*-**C**H), 134.2 (t, $^2J_{C\text{-}P}$ 6.10 Hz, *o*-**C**H).

^{31}P NMR (C_6D_6): δ_P 15.9 (br).

^{29}Si{^{1}H} NMR (C_6D_6): δ_{Si} −2.75.

Elem. Anal.: Calcd for $C_{48}H_{66}Si_2P_2Cl_2Pd$: C, 61.14 %; H, 7.04 %. Found; C, 61.07 %; H, 6.94 %.

Synthesis of *trans*-[$PdCl_2$($^{n}Pr_3SiC{\equiv}CCH_2PPh_2$)$_2$] (18)

Method A

Prepared as for **14** using $PdCl_2$ (0.137 g, 7.71 x 10^{-4} mol) and $^{n}Pr_3SiC{\equiv}CCH_2PPh_2$ (0.586 g, 1.54 x 10^{-3} mol). Isolated as an orange solid. Yield: 0.701 g, 88.6 %.

Method B

Prepared as for **14** using [Pd(1,5-COD)Cl_2] (0.195 g, 6.84 x 10^{-4} mol) and $^{n}Pr_3SiC{\equiv}CCH_2PPh_2$ (0.520 g, 1.37 x 10^{-3} mol). Isolated as an orange solid. Yield: 0.850 g, 91.3 %.

^{1}H NMR (C_6D_6): δ_H 0.45 (m, 12H, SiC**H**$_2$), 0.91 (t, 18H, $J_{H\text{-}H}$ 7.22 Hz, C**H**$_3$), 1.24 (m, 12H, C**H**$_2$), 3.75 (t, 4H, $^2J_{H\text{-}P}$ 3.87 Hz, C**H**$_2$P), 7.08 (br, 12H, *m*- and *p*-C**H**), 7.94 (br, 8H, *o*-C**H**).

^{13}C{^{1}H} NMR (C_6D_6): δ_C 16.4 (s, Si**C**H_2), 17.8 (s, **C**H_3), 18.5 (s, **C**H_2), 18.8 (t, $^1J_{C\text{-}P}$ 13.1 Hz, **C**H_2P), 87.9 (t, $^3J_{C\text{-}P}$ 2.99 Hz, **C**≡CCH_2P), 100.8 (t, $^2J_{C\text{-}P}$ 4.71 Hz, C≡**C**CH_2P), 128.2 (m, *m*-**C**H), 129.2 (t, $^1J_{C\text{-}P}$ 24.3 Hz, *i*-**C**), 130.9 (s, *p*-**C**H), 134.7 (t, $^2J_{C\text{-}P}$ 6.00 Hz, *o*-**C**H).

^{31}P NMR (C_6D_6): δ_P 15.9 (br).

^{29}Si{^{1}H} NMR (C_6D_6): δ_{Si} −13.8.

Elem. Anal.: Calcd for $C_{48}H_{66}Si_2P_2Cl_2Pd$: C, 61.14 %; H, 7.04 %. Found; C, 61.08 %; H, 7.00 %.

Attempted synthesis of $^{n}Bu_3SnC{\equiv}CCH_2PCl_2$

To a THF suspension of activated magnesium and $HgCl_2$ (0.100 g, 3.68 x 10^{-4} mol) was added drop-wise $^{n}Bu_3SnC{\equiv}CCH_2Cl$ (1.48 g, 4.07 x 10^{-3} mol) in THF and the mixture was brought to reflux for 4 h. After allowing to cool to ambient temperature the mixture was filtered into a THF solution of PCl_3 (0.36 cm^3, 4.07 x 10^{-3} mol) at −78 °C, resulting in a yellow solution that was stirred for 30 min. The solution was then allowed to warm to ambient temperature and stirred for 18 h, resulting in a suspended brown solid from which the solvent was removed under reduced pressure; the product was extracted with pentane and the filtrate was dried *in vacuo* to afford a crude brown oil, which was distilled at 98 °C, 3.8 x 10^{-1} mbar.

^{1}H NMR (C_6D_6): δ_H 0.86 (t, 9H, $^{3}J_{H\text{-}H}$ 7.44Hz, C**H**$_3$), 1.10 (t, 6H, $^{3}J_{H\text{-}H}$ 7.64 Hz, C**H**$_2$Sn), 1.27 (q, 6H, $^{3}J_{H\text{-}H}$ 7.33 Hz, CH_3C**H**$_2$), 1.58 (quin, 6H, $^{3}J_{H\text{-}H}$ 8.15Hz, C**H**$_2$$CH_2$Sn), 3.45 (m, 0.18H), 3.70 (s, 0.5H, $^{4}J_{H\text{-}Sn}$ 9.21Hz, C**H**$_2$Cl).

^{13}C{^{1}H} NMR (C_6D_6): δ_C 11.3 (**C**H_2Sn of $^{n}Bu_3SnC{\equiv}CCH_2Cl$), 13.8 (**C**$H_2$Sn of $^{n}Bu_3SnCl$), 13.9 (**C**H_3 of $^{n}Bu_3SnC{\equiv}CCH_2Cl$), 17.3 (**C**$H_3$ of $^{n}Bu_3SnCl$), 27.1 (CH_3**C**H_2 of $^{n}Bu_3SnCl$), 27.3 (CH_3**C**H_2 of $^{n}Bu_3SnC{\equiv}CCH_2Cl$), 28.2 (**C**$H_2CH_2Sn$ of $^{n}Bu_3SnCl$), 29.3 (**C**H_2CH_2Sn of $^{n}Bu_3SnC{\equiv}CCH_2Cl$), 31.2 (**C**$H_2Cl$ of $^{n}Bu_3SnC{\equiv}CCH_2Cl$), 91.1 (**C**$\equiv CCH_2Cl$ of $^{n}Bu_3SnC{\equiv}CCH_2Cl$), 105.0 (C$\equiv$**C**$CH_2Cl$ of $^{n}Bu_3SnC{\equiv}CCH_2Cl$).

^{31}P NMR (C_6D_6): δ_P 48.9 (m).

^{119}Sn{^{1}H} NMR (C_6D_6): δ_{Sn} −65.1 ($^{n}Bu_3$**Sn**C$\equiv CCH_2Cl$), 146.3 ($^{n}Bu_3$**Sn**Cl).

Attempted synthesis of $Me_2PhSiC{\equiv}CCH_2PCl_2$ (19)

To an Et_2O suspension of activated magnesium and $HgCl_2$ (0.100 g, 3.68 x 10^{-4} mol) was added drop-wise $Me_2PhSiC{\equiv}CCH_2Cl$ (0.81 g, 3.88 x 10^{-3} mol) in Et_2O and the mixture was brought to reflux for 4 h. After allowing to cool to ambient temperature the mixture was filtered into a THF solution of PCl_3 (0.33 cm^3, 3.88 x 10^{-3} mol) at −78 °C, resulting in a yellow solution that was stirred for 30 min. The solution was then allowed to warm to ambient temperature and stirred for 18 h, resulting in a suspended yellow solid from which the solvent was removed under reduced pressure; the product was extracted with pentane and the filtrate was dried *in vacuo* to afford an orange solid.

^{1}H NMR (C_6D_6): δ_H 0.27 (s, 9H), 0.35 (s, 8H), 0.36 (s, 6H, C**H**$_3$), 0.40 (s, 8H), 1.50 (s, 1.3H), 1.66 (s, 3.6H), 2.50 (d, $^{2}J_{H\text{-}P}$ 4.52 Hz), 2.57 (d, 2H, $^{2}J_{H\text{-}P}$ 14.6 Hz, C**H**$_2$P), 2.65 (m, 5H), 7.21-7.25 (m, 9H, C**H**), 7.66-7.22 (m, 6.5H, C**H**).

^{31}P NMR (C_6D_6): δ_P 170.4 (t, $^{2}J_{P\text{-}H}$ 14.6 Hz, CH_2**P**Cl_2), 81.8 (m), -27.4 (br).

Attempted synthesis of $^{i}Pr_3SiC{\equiv}CCH_2PCl_2$ (20)

Synthesis attempted as for **19** using $^{i}Pr_3SiC{\equiv}CCH_2Cl$ (1.29 g, 5.59 x 10^{-3} mol), PCl_3 (0.48 cm^3, 5.59 x 10^{-3} mol) and THF. The crude product was isolated as a yellow oil.

^{1}H NMR (C_6D_6): δ_H 1.03 (m, 3H, C**H**), 1.11 (d, 18H, $^3J_{H\text{-}P}$ 6.05 Hz, SiC**H**$_3$), 2.54 (d, 0.5H, $^2J_{H\text{-}P}$ 14.8 Hz, C**H**$_2$P), 3.53 (s, 0.20H, C**H**$_2$Cl), 4.39 (d, 2H, $^2J_{H\text{-}P}$ 8.75 Hz).

^{31}P NMR (C_6D_6): δ_P 78.8 (br), 81.4 (br), 170.2 (br), 170.8 (t, $^2J_{P\text{-}H}$ 14.8 Hz, **P**Cl_2), 179.1 (br).

The crude product was distilled at 90 °C, 6.4 x 10^{-1} mbar.

^{1}H NMR (C_6D_6): δ_H 1.03 (m, 7H, C**H**), 1.11 (d, 28H, $^3J_{H\text{-}P}$ 6.05 Hz, SiC**H**$_3$), 1.18 (t, 5H, *J* 6.86 Hz), 2.54 (d, 0.2H, $^2J_{H\text{-}P}$ 14.8 Hz, C**H**$_2$P), 3.53 (s, 0.8H, C**H**$_2$Cl), 4.39 (d, 2H, $^2J_{H\text{-}P}$ 8.75 Hz).

^{31}P NMR (C_6D_6): δ_P –2.89 (br), 33.9 (br), 170.2 (br), 170.8 (t, $^2J_{P\text{-}H}$ 14.8 Hz), 179.1 (br, **P**Cl_2).

Attempted synthesis of $^{n}Bu_3SnC{\equiv}CCH_2P(NEt_2)_2$ (21)

To an Et_2O suspension of activated magnesium and I_2 (0.100 g, 3.68 x 10^{-4} mol) was added drop-wise $^{n}Bu_3SnC{\equiv}CCH_2Cl$ (1.84 g, 5.09 x 10^{-3} mol) in Et_2O and the mixture was brought to reflux for 4 h. After allowing to cool to ambient temperature the mixture was filtered into an Et_2O solution of $(NEt_2)_2PCl$ (1.07 g, 5.09 x 10^{-3} mol) at −78 °C, resulting in a yellow solution with a suspended white solid that was stirred for 30 min. The suspension was then allowed to warm to ambient temperature and stirred for 18 h. The suspension was filtered and the filtrate was dried *in vacuo* to afford a yellow oil.

^{1}H NMR (C_6D_6): δ_H 0.88 (t, 12H, $^3J_{H\text{-}H}$ 7.15 Hz, NCH$_2$C**H**$_3$), 1.01 (t, 9H, $^3J_{H\text{-}H}$ 7.23 Hz, C**H**$_3$), 1.19 (t, 6H, $^3J_{H\text{-}H}$ 8.26Hz, C**H**$_2$Sn), 1.31 (q, 6H, $^3J_{H\text{-}H}$ 7.67 Hz, CH$_3$C**H**$_2$), 1.65 (quin, 6H, $^3J_{H\text{-}H}$ 8.11 Hz, C**H**$_2$CH$_2$Sn), 2.91 (m, 2H, $^3J_{H\text{-}H}$ 7.35Hz, NC**H**$_2$), 3.06 (m, 4H, NC**H**$_2$), 3.18 (m, 4H, NC**H**$_2$), 3.63 (d, 1H, $^2J_{H\text{-}P}$ 3.27 Hz, C**H**$_2$P).

^{31}P NMR (C_6D_6): δ_P 51.2 (m), 51.3 (m), 60.9 (br, CH$_2$**P**$(NEt_2)_2$).

^{119}Sn{^{1}H} NMR (C_6D_6): δ_{Sn} 128.8.

Standing for 30 min at ambient temperature afforded a viscous red oil.

^{1}H NMR (C_6D_6): δ_H 0.93 (t, 9H, $^3J_{H\text{-}H}$ 7.14 Hz), 1.32 (m, 3H), 1.38 (m, 3H), 1.77 (m, 3H), 2.89 (m, 5H).

^{31}P NMR (C_6D_6): δ_P 26.2 (m), 51.3 (m), 51.4 (m) 57.0 (dm, $^2J_{P\text{-}P}$ 79.8 Hz), 64.9 (m), 70.5 (dm, $^2J_{P\text{-}P}$ 79.8 Hz), 70.8 (dm, $^2J_{P\text{-}P}$ 79.8 Hz).

Attempted synthesis of $^{i}Pr_3SiC{\equiv}CCH_2P(NEt_2)_2$ (22)

Synthesis was attempted as for **21** using $^{i}Pr_3SiC{\equiv}CCH_2Cl$ (1.28 g, 5.55 x 10^{-3} mol) and $(NEt_2)_2PCl$ (1.17 g, 5.55 x 10^{-3} mol). The crude product was isolated as a yellow oil.

^{1}H NMR (C_6D_6): δ_H 0.94 (m, 26H), 1.05 (m, 18H), 1.18 (m, 18H), 1.25 (m, 25H), 2.55 (d, 1.2H, $^3J_{H\text{-}P}$ 4.61 Hz), 2.92 (m, 17H), 3.18 (m, 17H), 4.16 (br, 2H).

^{31}P NMR (C_6D_6): δ_P 83.6 (br), 85.3 (br), 118.2 (br), 126.3 (br), 130.0 (br), 153.5 (br, $ClP(NEt_2)_2$).

The yellow oil rapidly turned pink, and was distilled at 41 °C, 1.3 x 10^{-1} mbar to afford a colourless oil which turned pink again over 2 days.

^{1}H NMR (C_6D_6): δ_H 0.94 (t, 38H, $^3J_{H\text{-}H}$ 7.05 Hz), 1.05 (t, 14H, $^3J_{H\text{-}H}$ 7.05 Hz), 1.16 (m, 9H), 1.66 (s, 1H), 2.35 (q, 2H, *J* 7.12 Hz), 3.00 (m, 42H).

^{31}P NMR (C_6D_6): δ_P 3.24 (br), 18.6 (br), 26.3 (br), 118.2 (br), 153.4 (br, $ClP(NEt_2)_2$).

Synthesis of $Me_2PhSiC{\equiv}CCH_2P(SiMe_3)_2$ (23)

To a THF solution of $HP(SiMe_3)_2$ (1.04 g, 5.84 x 10^{-3} mol) at −78 °C was added ^{n}BuLi (2.5 M, 2.34 cm^3, 5.84 x 10^{-3} mol) and the mixture was stirred for 30 min. $Me_2PhSiC{\equiv}CCH_2Cl$ (1.25 g, 6.00 x 10^{-3} mol) in THF was added at −78 °C and stirred for 30 min then allowed to warm to ambient temperature. After stirring for 18 h the solvent was removed under reduced pressure; the product was extracted with pentane and dried *in vacuo* to afford a brown oil. Yield: 1.84 g, 90.0 %.

^{1}H NMR (C_6D_6): δ_H 0.25 (d, 18H, $^3J_{H\text{-}P}$ 4.61 Hz, $P(Si(C\underline{\mathbf{H}}_3)_2)$, 0.44 (s, 6H, $Si(C\underline{\mathbf{H}}_3)_2$), 2.43 (d, 2H, $^2J_{H\text{-}P}$ 1.36 Hz, $C\underline{\mathbf{H}}_2P$), 2.52 (m, 0.44H), 7.24 (br, 3H, *o*-, *p*-C**H**), 7.72 (m, 2H, *m*-C**H**).

^{13}C{^{1}H} NMR (C_6D_6): δ_C −0.56 (s, $Si(\underline{\mathbf{C}}H_3)_2$), 1.07 (d, $^2J_{C\text{-}P}$ 11.9 Hz, $(P(Si(\underline{\mathbf{C}}H_3)_3)_2)$, 5.51 (d, $^1J_{C\text{-}P}$ 23.2 Hz, $\underline{\mathbf{C}}H_2P$), 83.3 (d, $^3J_{C\text{-}P}$ 3.74 Hz, $\underline{\mathbf{C}}{\equiv}CCH_2P$), 109.3 (s, $C{\equiv}\underline{\mathbf{C}}CH_2P$), 128.2 (s, *m*-**C**H), 129.6 (s, *p*-**C**H), 134.2 (s, *o*-**C**H), 137.7 (s, *i*-**C**).

^{31}P NMR (C_6D_6): δ_P −158.9 (m, $\underline{\mathbf{P}}(Si(CH_3)_2)$, −84.1 (m, $\underline{\mathbf{P}}SiCH_3$).

^{29}Si{^{1}H} NMR (C_6D_6): δ_{Si} −22.8 ($P(\underline{\mathbf{Si}}(CH_3)_3)_2$), 3.47 ($\underline{\mathbf{Si}}(CH_3)_2$).

Elem. Anal.: Calcd for $C_{17}H_{31}Si_3P$: C, 58.29 %; H, 8.86 %. Found; C, 58.18 %; H, 8.71 %.

Synthesis of $^{i}Pr_3SiC{\equiv}CCH_2P(SiMe_3)_2$ (24)

Prepared as for **23** using ^{n}BuLi (2.5 M, 1.64 cm^3, 4.10 x 10^{-3} mol), $HP(SiMe_3)_2$ (0.73 g, 4.10 x 10^{-3} mol) and $^{i}Pr_3SiC{\equiv}CCH_2Cl$ (1.00 g, 4.35 x 10^{-3} mol). Isolated as a red oil.

^{1}H NMR (C_6D_6): δ_H 0.24 (d, 18H, $^3J_{H\text{-}P}$ 4.56 Hz, P(Si(C**H**$_3$)$_2$), 1.13 (br, 3H, C**H**), 1.20 (br, 21H, C**H**$_3$), 2.45 (s, 2H, C**H**$_2$P).

^{31}P NMR (C_6D_6): δ_P −161.4 (m, **P**(Si(CH$_3$)$_2$), −84.5 (m, **P**SiCH$_3$).

Synthesis of $^{n}Pr_3SiC{\equiv}CCH_2P(SiMe_3)_2$ (25)

Prepared as for **23** using ^{n}BuLi (2.5 M, 1.26 cm^3, 3.15 x 10^{-3} mol), $HP(SiMe_3)_2$ (0.56 g, 3.15 x 10^{-3} mol) and $^{n}Pr_3SiC{\equiv}CCH_2Cl$ (0.76 g, 3.31 x 10^{-3} mol). Isolated as a brown oil.

^{1}H NMR (C_6D_6): δ_H 0.27 (d, 18H, $^3J_{H\text{-}P}$ 4.48 Hz, P (Si(C**H**$_3$)$_2$), 0.31 (d, 1.3H, $^3J_{H\text{-}P}$ 4.46 Hz, P(Si(C**H**$_3$)$_2$), 0.69 (m, 6H, SiC**H**$_2$), 0.82 (t, 4H, $J_{H\text{-}P}$ 7.09 Hz), 0.99 (t, 5H, $J_{H\text{-}P}$ 7.20 Hz), 1.06 (t, 9H, $^3J_{H\text{-}H}$ 7.21 Hz, C**H**$_3$), 1.56 (br m, 25H, C**H**$_2$), 2.07 (t, 2.3H, $J_{H\text{-}P}$ 7.08 Hz), 2.17 (s, 1.5H), 2.44 (d, 2H, $^2J_{H\text{-}P}$ 0.89 Hz, C**H**$_2$P), 2.55 (m, 1.2H), 3.56 (s, 0.6H, C**H**$_2$ of $^{n}Pr_3SiC{\equiv}CCH_2Cl$).

^{31}P NMR (C_6D_6): δ_P −159.9 (m, **P**(Si(CH$_3$)$_2$), −84.3 (m, **P**SiCH$_3$).

Synthesis of $^{n}Bu_3SiC{\equiv}CCH_2P(SiMe_3)_2$ (26)

Prepared as for **23** using ^{n}BuLi (2.5 M, 1.32 cm^3, 3.31 x 10^{-3} mol), $HP(SiMe_3)_2$ (0.59 g, 3.31 x 10^{-3} mol) and $^{n}Bu_3SiC{\equiv}CCH_2Cl$ (0.95 g, 3.48 x 10^{-3} mol). Isolated as a brown oil.

^{1}H NMR (C_6D_6): δ_H 0.28 (d, 18H, $^3J_{H\text{-}P}$ 4.46 Hz, P(Si(C**H**$_3$)$_2$), 0.76 (m, 6H, SiC**H**$_2$), 0.97 (t, 9H, $^3J_{H\text{-}H}$ 7.17 Hz, C**H**$_3$), 1.44 (br, 6H, C**H**$_2$), 1.54 (br, 6H, C**H**$_2$), 2.46 (d, 2H, $^2J_{H\text{-}P}$ 0.95 Hz, C**H**$_2$P), 2.57 (m, 1.2H).

^{31}P NMR (C_6D_6): δ_P −159.9 (m, **P**(Si(CH$_3$)$_2$), − 84.8 (m, **P**SiCH$_3$).

Synthesis of $Me_2PhSiC{\equiv}CCH_2PI_2$ (27)

To an Et_2O solution of $Me_2PhSiC{\equiv}CCH_2P(SiMe_3)_2$ (0.29 g, 8.49 x 10^{-4} mol) at −78 °C was added neat I_2 (0.47 g, 1.86 x 10^{-3} mol) under a flow of argon and the mixture was stirred for 20 min, resulting in an orange solution that was allowed to warm to ambient temperature then stirred for 18 h. The resulting red mixture was filtered and stored as a red solution at ambient temperature under argon.

^{1}H NMR (C_6D_6): δ_H 0.25 (s, 6H, C**H**$_3$), 1.10 (t, Et_2O), 3.15 (d, 2H, $^{2}J_{H\text{-}P}$ 18.1 Hz, C**H**$_2$P), 3.27 (q, Et_2O), 7.22 (br, 2H, C**H**), 7.67 (br, 3H, C**H**).

^{31}P NMR (C_6D_6): δ_P 113.4 (t, $^{2}J_{P\text{-}H}$ 18.1 Hz).

^{29}Si{^{1}H} NMR (C_6D_6): δ_{Si} −21.2.

Synthesis of ^{n}Pr$_3$SiC≡CCH$_2$PI$_2$ (28)

Prepared as for **27** using I_2 (1.76 g, 6.93 x 10^{-3} mol) and $^{n}Pr_3SiC{\equiv}CCH_2P(SiMe_3)_2$ (1.17 g, 3.15 x 10^{-3} mol). Isolated as a red solution and stored at ambient temperature under argon.

^{1}H NMR (C_6D_6): δ_H 0.88 (t, pentane), 1.06 (br, SiC**H**$_2$), 1.26 (m, pentane), 1.41 (m, C**H**$_3$), 1.54 (br, C**H**$_2$), 3.12 (d, 2H, $^{2}J_{H\text{-}P}$ 17.7 Hz, C**H**$_2$P).

^{31}P NMR (C_6D_6): δ_P 113.8 (t, $^{2}J_{P\text{-}H}$ 17.7 Hz).

Synthesis of ^{n}Bu$_3$SiC≡CCH$_2$PI$_2$ (29)

Prepared as for **27** using I_2 (0.31 g, 1.24 x 10^{-3} mol) and $^{n}Bu_3SiC{\equiv}CCH_2P(SiMe_3)_2$ (0.23 g, 5.65 x 10^{-4} mol). Isolated as a red solution and stored at ambient temperature under argon.

^{1}H NMR (C_6D_6): δ_H 0.67 (br, C**H**$_2$), 1.10 (t, Et_2O), 1.42 (br, C**H**$_2$), 3.27 (q, Et_2O), 3.18 (d, 2H, $^{2}J_{H\text{-}P}$ 17.9 Hz, C**H**$_2$P).

^{31}P NMR (C_6D_6): δ_P 114.3 (t, $^{2}J_{P\text{-}H}$ 17.9 Hz).

Attempted synthesis of ^{n}Pr$_3$SiC≡CC≡P

To a pentane solution of $^{n}Pr_3SiC{\equiv}CCH_2PI_2$ (1.17 g, 3.15 x 10^{-3} mol) at ambient temperature was added AgOTf (1.78 g, 6.93 x 10^{-3} mol) and the mixture was stirred for 10 min, resulting in a pale yellow solution with a suspended off-white solid. A pentane suspension of DABCO (0.78 g, 6.93 x 10^{-3} mol) was added drop-wise, resulting in a pale yellow solution with a suspended off-white solid that was stirred for 1 h; the mixture was filtered to afford a pale yellow solution.

^{1}H NMR (C_6D_6): δ_H 0.12 (s, 12H), 0.15 (s, 8H), 0.88 (t, pentane), 1.26 (m, pentane), 2.08 (t, 10H, *J* 6.88 Hz), 2.18 (s, 5H), 2.24 (br, 30H), 3.56 (s, 2H, C**H**$_2$Cl of $^{n}Pr_3SiC{\equiv}CCH_2Cl$).

^{31}P{^{1}H} NMR (C_6D_6): None observed.

Synthesis of $Me_2PhSiC{\equiv}CCH_2PH_2$ (30)

To an Et_2O solution of $Me_2PhSiC{\equiv}CCH_2P(SiMe_3)_2$ (0.29 g, 8.17 x 10^{-4} mol) at −78 °C was added H_2O (excess), resulting in an orange solution that was stirred for 20 min. The solution was allowed to warm to ambient temperature then stirred for 4 h; the solvent was removed under reduced pressure to afford a dark yellow oil. Yield: 0.150 g, 89.2 %.

^{1}H NMR (C_6D_6): δ_H 0.39 (s, 6H, C**H**$_3$), 1.92 (dt, 2H, $^3J_{H\text{-}H}$ 7.15Hz, $^2J_{H\text{-}P}$ 4.49 Hz, C**H**$_2$P), 2.86 (dt, 2H, $^1J_{H\text{-}P}$ 191.6 Hz, $^3J_{H\text{-}H}$ 7.15 Hz, P**H**$_2$), 7.22 (m, 3H, C**H**), 7.70 (m, 2H, *m*-C**H**).

^{13}C{^{1}H} NMR (C_6D_6): δ_C −0.50 (s, **C**H$_3$), 4.31 (d, $^1J_{C\text{-}P}$ 11.7 Hz, **C**H$_2$P), 84.0 (d, $^3J_{C\text{-}P}$ 3.44 Hz, **C**≡CCH$_2$P), 108.3 (s, C≡**C**CH$_2$P), 128.2 (s, *p*-**C**H), 129.7 (s, *o*-**C**H), 134.1 (s, *m*-**C**H), 137.7 (s, *i*-**C**).

^{31}P NMR (C_6D_6): δ_P −129.4 (tt, $^1J_{P\text{-}H}$ 191.6 Hz, $^2J_{P\text{-}H}$ 4.49 Hz, **P**H$_2$).

^{29}Si{^{1}H} NMR (C_6D_6): δ_{Si} −22.8.

Synthesis of *trans*-$[PtCl_2\{Me_2PhSiC{\equiv}CCH_2P(SiMe_3)_2\}_2]$ (31)

To a THF solution of $Me_2PhSiC{\equiv}CCH_2P(SiMe_3)_2$ (0.54 g, 1.55 x 10^{-3} mol) at −78 °C was added $PtCl_2$ (0.20 g, 7.75 x 10^{-4} mol) in THF and the mixture was stirred for 20 min. The resulting brown mixture was allowed to warm to ambient temperature then stirred for 18 h. The solvent was removed under reduced pressure; the product was extracted with pentane and dried *in vacuo* as a brown oil. Yield: 0.560 g, 75.6 %.

^{1}H NMR ($CDCl_3$): δ_H 0.38 (s, 12H, C**H**$_3$), 0.49 (t, 36H, $^3J_{H\text{-}P}$ 5.67 Hz, Si(C**H**$_3$)$_3$), 3.00 (t, 4H, $J_{H\text{-}P}$ 5.88 Hz, C**H**$_2$), 7.34 (m, 6H, C**H**), 7.61 (m, 4H, C**H**).

^{13}C{^{1}H} NMR ($CDCl_3$): δ_C 1.19 (s, **C**H$_3$), 1.71 (t, $^2J_{C\text{-}P}$ 9.15 Hz, Si(**C**H$_3$)$_3$), 4.71 (t, $^1J_{C\text{-}P}$ 14.1 Hz, **C**H$_2$P), 84.7 (t, $^3J_{C\text{-}P}$ 2.94 Hz, **C**≡CCH$_2$P), 105.8 (t, $^2J_{C\text{-}P}$ 6.16 Hz, C≡**C**CH$_2$P), 127.9 (s, *m*-**C**H), 129.4 (s, *p*-**C**H), 133.2 (s, *o*-**C**H), 134.0 (s, *i*-**C**).

^{31}P NMR ($CDCl_3$): δ_P −97.9 (s, $^1J_{P\text{-}Pt}$ 1919 Hz, **P**(SiMe$_3$)$_2$).

^{29}Si{^{1}H} NMR ($CDCl_3$): δ_{Si} −23.1 (s, Me$_2$Ph**Si**), 7.80 (s, P(**Si**Me$_3$)$_2$).

^{195}Pt{^{1}H} NMR ($CDCl_3$): δ_{Pt} −3696 (t, $^1J_{Pt\text{-}P}$ 1919 Hz).

Synthesis of $PhC{\equiv}CCH_2PPh_2$ (32)

To an Et_2O solution of Ph_2PH (0.400 g, 2.15 x 10^{-3} mol) at −78 °C was added ^{n}BuLi (2.5 M, 1.02 cm^3, 2.15 x 10^{-3} mol) then the mixture was allowed to warm to ambient temperature. An

Et_2O solution of $PhC{\equiv}CCH_2Cl$ (0.324 g, 2.15 x 10^{-3} mol) was added at −78 °C, resulting in a red-brown solution that was stirred for 30 min then allowed to warm to ambient temperature. After stirring for 18 h the solvent was removed under reduced pressure; the product was extracted with pentane and dried *in vacuo* to afford a dark red oil. Yield: 0.290 g, 44.9 %.

^{1}H NMR (C_6D_6): δ_H 2.92 (d, 2H, $^2J_{H\text{-}P}$ 2.44 Hz, C**H**$_2$P), 6.92 - 7.73 (m, aromatic C**H**).

^{13}C{^{1}H} NMR (C_6D_6): δ_C 19.4 (d, $^1J_{C\text{-}P}$ 19.2 Hz, **C**H$_2$P), 83.6 (d, $^2J_{C\text{-}P}$ 5.82 Hz, C≡**C**CH$_2$P), 86.7 (d, $^3J_{C\text{-}P}$ 4.34 Hz, **C**≡CCH$_2$P), 124.4-138.4 (m, aromatic **C**).

^{31}P NMR (C_6D_6): δ_P −13.5 (br m, $^2J_{P\text{-}H}$ 6.77 Hz).

Synthesis of PhC≡CCH$_2$P(SiMe$_3$)$_2$ (33)

Prepared as for **32** using ^{n}BuLi (2.5 M, 2.27 cm^3, 5.67 x 10^{-3} mol), HP(SiMe$_3$)$_2$ (1.01 g, 5.67 x 10^{-3} mol) and $PhC{\equiv}CCH_2Cl$ (0.850 g, 5.67 x 10^{-3} mol). Isolated as a dark brown oil. Yield: 1.45 g, 87.6 %.

^{1}H NMR (C_6D_6): δ_H 0.30 (d, 18H, $^3J_{H\text{-}P}$ 4.55 Hz, Si(C**H**$_3$)$_2$), 2.60 (d, 2H, $^2J_{H\text{-}P}$ 1.56 Hz, C**H**$_2$P), 7.00 (m, 3H, *m*- and *p*-C**H**), 7.48 (m, 2H, *o*-C**H**).

^{13}C{^{1}H} NMR (C_6D_6): δ_C 1.09 (d, $^2J_{C\text{-}P}$ 11.7 Hz, Si(**C**H$_3$)$_2$), 5.08 (d, $^1J_{C\text{-}P}$ 22.5 Hz, **C**H$_2$P), 81.6 (d, $^2J_{C\text{-}P}$ 4.14 Hz, C≡**C**CH$_2$P), 90.7 (s, **C**≡CCH$_2$P), 127.9 (m, *m*-**C**H), 128.6 (s, *p*-**C**H), 131.72 (s, *o*-**C**H), 131.9 (d, $^4J_{C\text{-}P}$ 10.43 Hz, *i*-**C**).

^{31}P NMR (C_6D_6): δ_P −158.8 (br).

^{29}Si{^{1}H} NMR (C_6D_6): δ_{Si} 3.65.

Attempted synthesis of PhC≡CCH$_2$PCl$_2$ (34)

To a THF suspension of activated magnesium and $HgCl_2$ (0.100 g, 3.68 x 10^{-4} mol) was added drop-wise $PhC{\equiv}CCH_2Cl$ (0.552 g, 3.67 x 10^{-3} mol) in THF and the mixture was brought to reflux for 4 h. After allowing to cool to ambient temperature the mixture was filtered into a THF solution of PCl_3 (0.320 cm^3, 3.67 x 10^{-3} mol) at −78 °C, resulting in an orange solution that was stirred for 30 min. The solution was allowed to warm to ambient temperature then stirred for 18 h, resulting in a dark red solution from which the solvent was removed under reduced pressure; the product was extracted with pentane and the filtrate was dried *in vacuo* to afford a dark orange oil.

^{1}H NMR (C_6D_6): δ_H 1.66 (s, 4H), 1.78 (s, 1H), 2.43 (s, 2H), 2.74 (d, 2H, $^2J_{H\text{-}P}$ 14.5 Hz, C**H**$_2$P), 3.07 (d, 3H, $J_{H\text{-}P}$ 12.6 Hz), 3.22 (s, 2H), 4.60 (d, 4H, $J_{H\text{-}P}$ 8.31 Hz), 6.98-7.77 (m, 113H).

^{31}P NMR (C_6D_6): δ_P −37.19 (br), −19.1 (br), −13.4 (br), 58.7 (t, J_{P-H} 4.88 Hz), 72.9 (m), 83.6 (t, J_{P-H} 8.60 Hz), 170.8 (t, $^2J_{P-H}$ 14.5 Hz, CH_2**P**), 178.2 (q, J_{P-H} 12.6 Hz), 178.6 (br), 179.0 (m), 199.5 (t, J_{P-H} 17.2 Hz).

Synthesis of Ph{$(NEt_2)_2$P}C=C=CH_2 (35)

To a THF suspension of activated magnesium and $HgCl_2$ (0.100 g, 3.68 x 10^{-4} mol) was added drop-wise PhC≡CCH_2Cl (1.00 g, 6.65 x 10^{-3} mol) in THF and the mixture was brought to reflux for 4 h. After allowing to cool to ambient temperature the mixture was filtered into a THF solution of $ClP(NEt_2)_2$ (1.39 cm^3, 6.65 x 10^{-3} mol) at −78 °C, resulting in a red solution that was stirred for 30 min. The solution was allowed to warm to ambient temperature then stirred for 18 h, resulting in an orange solution from which the solvent was removed under reduced pressure; the product was extracted with pentane and the filtrate was dried *in vacuo* to afford a dark red oil. Yield: 1.46 g, 75.7 %.

^{1}H NMR (C_6D_6): δ_H 0.91 (t, 12H, $^3J_{H-H}$ 7.08 Hz, C**H**$_3$), 3.07 (m, 8H, C**H**$_2$), 4.72 (d, 2H, $^2J_{H-P}$ 7.13 Hz, C**H**$_2$P), 7.03 (t, 1H, $^3J_{H-H}$ 7.59 Hz, *p*-C**H**), 7.17 (m, 2H, *m*-C**H**), 7.64 (d, 2H, $^3J_{H-H}$ 8.51 Hz, *o*-C**H**).

^{13}C{^{1}H} NMR (C_6D_6): δ_C 14.7 (d, $^3J_{C-P}$ 3.42 Hz, **C**H_3), 43.4 (d, $^2J_{C-P}$ 17.6 Hz, **C**H_2), 75.0 (s, **C**H_2P), 105.9 (d, $^3J_{C-P}$ 14.1 Hz, **C**≡CCH_2P), 126.7 (d, J_{C-P} 1.35 Hz, *p*-**C**H), 128.2 (s, *m*-**C**H and *o*-**C**H), 137.4 (d, $^4J_{C-P}$ 16.8 Hz, *i*-**C**), 209.9 (d, $^2J_{C-P}$ 11.3 Hz, C≡**C**CH_2P).

^{31}P NMR (C_6D_6): δ_P 153.4 (m, Cl**P**$(NEt_2)_2$), 118.2 (m), 90.9 (br, **P**$(NEt_2)_2$), 83.2 (br), 18.8 (br).

Synthesis of Ph{(NEt_2)ClP}C=C=CH_2 (36)

To an Et_2O solution of Ph{$(NEt_2)_2$P}C=C=CH_2 (**35**) (0.545 g, 1.87 x 10^{-3} mol at −78 °C was added drop-wise HCl (1.0M, 3.75 cm^3, 3.75 x 10^{-3} mol) and the mixture was stirred for 20 min. The solution was allowed to warm to ambient temperature, resulting in a yellow solution with a suspended solid that was stirred for 18 h then filtered; the solvent was removed under reduced pressure to afford an orange oil.

^{1}H NMR (C_6D_6): δ_H 0.81 (t, 6H, $^3J_{H-H}$ 7.08 Hz, C**H**$_3$), 2.93 (m, 4H, C**H**$_2$), 4.90 (dd, 1H, $^4J_{H-P}$ 5.61 Hz), 4.91 (dd, 1H, $^4J_{H-P}$ 6.26 Hz), 4.91 (m, 2H, $^4J_{H-P}$ 5.61 Hz, $^4J_{H-P}$ 6.26 Hz, C**H**$_2$P), 7.00 (t, 1H, $^3J_{H-H}$ 7.38 Hz, *p*-C**H**), 7.11 (t, 2H, $^3J_{H-H}$ 7.38 Hz, *m*-C**H**), 7.50 (d, 2H, $^3J_{H-H}$ 8.21 Hz, *o*-C**H**).

$^{13}C\{^{1}H\}$ NMR (C_6D_6): δ_C 13.9 (d, $^{3}J_{C\text{-}P}$ 6.27 Hz, **C**H_3), 43.9 (d, $^{2}J_{C\text{-}P}$ 14.0 Hz, **C**H_2), 77.6 (s, **C**H_2P), 105.3 (d, $J_{C\text{-}P}$ 39.3 Hz, **C**≡CCH_2P), 127.5 (d, $J_{C\text{-}P}$ 1.52 Hz, *p*-**C**H), 127.9 (s, *o*-**C**H), 128.9 (s, *m*-**C**H), 135.4 (d, $J_{C\text{-}P}$ 25.7 Hz, *i*-**C**), 210.5 (d, $J_{C\text{-}P}$ 8.25 Hz, C≡**C**CH_2P).

^{31}P NMR (C_6D_6): δ_P 121.9 (br).

Attempted synthesis of $Ph(Cl)_2PC=C=CH_2$ (37)

Synthesis attempted as for **36** using HCl (1.0M, 2.27 cm^3, 2.27 x 10^{-3} mol) and Ph{$(NEt_2)_2$P}C=C=CH_2 (**35**) (0.300 g, 1.03 x 10^{-3} mol). Isolated as a yellow oil.

^{1}H NMR (C_6D_6): δ_H 4.64 (d, 1H, $^{2}J_{H\text{-}P}$ 2.17 Hz, C**H**$_2$P), 7.05 (m, 2H, *m*-C**H**), 7.47 (d, 1H, $^{3}J_{H\text{-}H}$ 7.44 Hz, *p*-C**H**), 7.63 (d, 1H, $^{3}J_{H\text{-}H}$ 7.31 Hz, *o*-C**H**).

$^{13}C\{^{1}H\}$ NMR (C_6D_6): δ_C 39.0 (d, $J_{C\text{-}P}$ 13.1 Hz), 79.3 (d, $J_{C\text{-}P}$ 9.22 Hz, **C**H_2P), 110.4 (s, **C**≡CCH_2P), 127.2 (d, $J_{C\text{-}P}$ 5.32 Hz, *o*-**C**H), 128.5 (d, $J_{C\text{-}P}$ 4.83 Hz), 129.0 (s, *p*-**C**H), 129.7 (s), 131.1 (d, $J_{C\text{-}P}$ 11.2 Hz, *m*-C**H**), 147.8 (d, $J_{C\text{-}P}$ 31.2 Hz, *i*-**C**), 210.1 (d, $J_{C\text{-}P}$ 30.0 Hz, C≡**C**CH_2P).

^{31}P NMR (C_6D_6): δ_P 58.7 (m).

Synthesis of $[Ph\{(NEt_2)_2MeP\}C=C=CH_2]^+[I]^-$ (38)

To a solution of Ph{$(NEt_2)_2$P}C=C=CH_2 (**35**) (0.372 g, 1.28 x 10^{-3} mol) at −78 °C was added drop-wise MeI (0.079 cm^3, 1.28 x 10^{-3} mol) and the mixture was stirred for 20 min. The solution was allowed to warm to ambient temperature, resulting in an orange solution with a suspended solid that was stirred for 18 h then filtered; the solvent was removed under reduced pressure to afford a viscous dark orange oil.

^{1}H NMR (C_6D_6): δ_H 0.85 (t, 12H, $^{3}J_{H\text{-}H}$ 7.07 Hz, C**H**$_3$ of NEt), 1.12 (t, 12H, $^{3}J_{H\text{-}H}$ 7.07 Hz, C**H**$_3$ of Et_2O), 2.85 (d, 3H, $J_{H\text{-}P}$ 13.2 Hz, C**H**$_3$), 2.99 (m, 8H, C**H**$_2$ of NEt), 3.27 (q, 8H, $^{3}J_{H\text{-}H}$ 6.96 Hz, C**H**$_2$ of Et_2O), 5.48 (br d, 2H, $^{2}J_{H\text{-}P}$ 12.1 Hz, C**H**$_2$P), 7.05 (d, 1H, $^{3}J_{H\text{-}H}$ 6.97 Hz, *p*-C**H**), 7.23 (t, 2H, $^{3}J_{H\text{-}H}$ 7.52 Hz, *m*-C**H**), 7.44 (d, 2H, $^{3}J_{H\text{-}H}$ 7.56 Hz, *o*-C**H**).

$^{13}C\{^{1}H\}$ NMR (C_6D_6): δ_C 14.1 (d, $^{3}J_{C\text{-}P}$ 3.37 Hz, **C**H_3 of NEt_2), 15.6 (s, **C**H_3 of Et_2O), 41.4 (d, $^{2}J_{C\text{-}P}$ 3.65 Hz, **C**H_2 of NEt_2), 41.9 (s, **C**H_3), 65.9 (s, **C**H_3 of Et_2O), 96.2 (m, C**H**$_2$P), 128.2 (s, *p*-**C**H), 128.8 (d, $J_{C\text{-}P}$ 4.69 Hz, *o*-**C**H), 129.6 (s, *m*-**C**H), 130.6 (s, **C**≡CCH_2P), 216.1 (m, C≡**C**CH_2P).

^{31}P NMR (C_6D_6): δ_P 57.4 (m).

6.3 Chapter 3: In pursuit of conjugated phosphaalkenes and phosphaalkynes

Synthesis of *E*/*Z*-C_6H_4(1-CO($SiMe_3$)=P$SiMe_3$)(2-Me) (*E*/*Z*-39-2-Me)

To a toluene solution of $P(SiMe_3)_3$ (1.91 g, 7.64 x 10^{-3} mol) at −78 °C was added C_6H_4(1-COCl)(2-Me) (1.18 g, 7.64 x 10^{-3} mol) in toluene and the mixture was stirred for 30 min. The resulting colourless solution was allowed to warm to ambient temperature, producing a bright yellow solution after 48 h. The solvent was concentrated under reduced pressure and cooled to −78 °C; a yellow solid precipitated and was removed by filtration (later identified as **41-2-Me**). The yellow filtrate was dried *in vacuo* as a yellow oil. Yield: 2.33 g, 64.1 %.

^{1}H NMR (C_6D_6): δ_H −0.08 (s, 9H, *Z*- O(SiC**H**$_3$)$_3$), 0.00 (d, 9H, $^3J_{H\text{-}P}$ 4.45 Hz, *E*- P(SiC**H**$_3$)$_3$), 0.41 (s, 9H, *E*- O(SiC**H**$_3$)$_3$), 0.46 (d, 9H, $^3J_{H\text{-}P}$ 3.44 Hz, *Z*- P(SiC**H**$_3$)$_3$), 2.32 (s, 3H, *E*- C**H**$_3$), 2.35 (s, 3H, *Z*- C**H**$_3$), 6.89 (m, 4H, *E*- and Z, *m*-C**H**), 6.96 (m, 2H, *E*- and *Z*- *p*-C**H**), 7.24 (d, 1H, $^3J_{H\text{-}H}$ 7.48 Hz, *E*- *o*-C**H**), 7.37 (d, 1H, $^3J_{H\text{-}H}$ 7.87 Hz, *Z*- *o*-C**H**).

^{13}C{^{1}H} NMR (C_6D_6): δ_C 0.32 (d, $^5J_{H\text{-}P}$ 5.96 Hz, *E*- OSi(**C**H$_3$)$_3$), 0.51 (s, *Z*- OSi(**C**H$_3$)$_3$), 1.00 (d, $^3J_{H\text{-}P}$ 8.12 Hz, *Z*- PSi(**C**H$_3$)$_3$), 1.16 (d, $^3J_{H\text{-}P}$ 11.1 Hz, *E*- PSi(**C**H$_3$)$_3$), 19.5 (s, *E*- **C**H$_3$), 19.8 (s, *Z*- **C**H$_3$), 125.4 (s, *m*-**C**H), 125.6 (s, *m*-**C**H), 128.7 (s, *Z*- *o*-**C**H), 128.9 (s, *p*-**C**H), 128.9 (s, *p*-**C**H), 129.5 (*E*- *o*-**C**H), 133.9 (d, $^3J_{C\text{-}P}$ 4.22 Hz, *E*- *o*-**C**CH$_3$), 135.4 (d, $^3J_{C\text{-}P}$ 6.23 Hz, *Z*- *o*-**C**CH$_3$), 144.7 (d, $^2J_{C\text{-}P}$ 25.2 Hz, *Z*- *i*-**C**), 146.1 (d, $^2J_{C\text{-}P}$ 9.30 Hz, *E*- *i*-**C**), 213.3 (d, $^1J_{C\text{-}P}$ 63.5 Hz, *Z*- **C**=P), 220.3 (d, $^1J_{C\text{-}P}$ 55.5 Hz, *E*- **C**=P).

^{31}P{^{1}H} NMR (C_6D_6): δ_P 127.5 (s, *Z*- C=**P**), 131.1 (s, *E*- C=**P**).

^{29}Si{^{1}H} NMR (C_6D_6): δ_{Si} −2.37 (*Z*- P**Si**Me$_3$), −1.64 (*E*- P**Si**Me$_3$), 19.5 (*Z*- O**Si**Me$_3$), 21.7 (*E*- O**Si**Me$_3$).

Elem. Anal.: Calcd for $C_{14}H_{25}Si_2OP$: C, 56.76 %; H, 8.45 %. Found; C, 56.56 %; H, 8.39 %.

Synthesis of {C_6H_4(1-CO)(2-Me)}$_3$P=O (40-2-Me)

To an Et_2O solution of $P(SiMe_3)_3$ (1.21 g, 4.84 x 10^{-3} mol) at −78 °C was added C_6H_4(1-COCl)(2-Me) (2.24 g, 1.45 x 10^{-2} mol) in Et_2O and the mixture was stirred for 30 min. The resulting colourless solution was allowed to warm to ambient temperature, resulting in a suspended yellow solid after 48 h from which the solvent was removed under reduced pressure; the product was washed with pentane and dried *in vacuo* as a yellow solid. Yield: 1.33 g, 68.5 %.

^{1}H NMR (C_6D_6): δ_H 2.51 (s, 9H, C**H**$_3$), 6.84 (m, 3H, *p*-C**H**), 6.93 (m, 6H, *m*-C**H**), 8.04 (m, 3H, *o*-C**H**).

$^{13}C\{^{1}H\}$ NMR (C_6D_6): δ_C 21.1 (s, **C**H_3), 125.7 (s, *p*-**C**H), 131.5 (d, $^{4}J_{C\text{-}P}$ 15.8 Hz, *o*-**C**H), 132.1 (d, $^{5}J_{C\text{-}P}$ 1.26 Hz, *m*-**C**H), 132.4 (d, $^{5}J_{C\text{-}P}$ 2.70 Hz, *m*-**C**H), 138.8 (d, $^{4}J_{C\text{-}P}$ 3.62 Hz, *o*-**C**), 140.8 (d, $^{2}J_{C\text{-}P}$ 33.3 Hz, *i*-**C**), 208.9 (d, $^{1}J_{C\text{-}P}$ 34.5 Hz, **C**=O).

$^{31}P\{^{1}H\}$ NMR (C_6D_6): δ_P 67.2 (m, $^{4}J_{P\text{-}H}$ 3.44 Hz).

Elem. Anal.: Calcd for $C_{24}H_{21}O_4P$: C, 71.29 %; H, 5.19 %. Found; C, 71.42 %; H, 5.19 %.

Colourless crystals were grown over 3 days from Et_2O at -20 °C. Crystal data: $C_{26}H_{26}O_{4.5}P$, M_w = 441.46, Triclinic, *P-1*(no. 2), *a* = 8.6463(4), *b* = 12.0839(5), *c* = 12.5443(4) Å, α = 106.344(2), β = 100.317(2), γ = 110.101(2) °,V = 1166.29(8) Å^3, Z = 2, D_c = 1.257 Mg/m^3, μ (Mo-Ka) = 0.149 mm^{-1}, T = 173(2) K, 14520 independent reflections, full-matrix F^2 refinement R_1 = 0.0599, wR_2 = 0.1765 on 5249 independent absorption corrected reflections [$I > 2\sigma(I)$; $2\theta_{max}$ = 55 °], 289 parameters.

Attempted synthesis of C_6H_4(1-C≡P)(2-Me)

Method A

To a pentane solution of C_6H_4(1-CO($SiMe_3$)=P$SiMe_3$)(2-Me) (0.112 g, 2.35 x 10^{-4} mol) at −78 °C was added DABCO (0.057 g, 5.17 x 10^{-4} mol) in pentane, resulting in a suspended yellow solid that was stirred for 20 min. The suspension was allowed to warm to ambient temperature and an aliquot was extracted after 30 min and dried *in vacuo* as a yellow oil.

^{1}H NMR (C_6D_6): δ_H −0.08 (s, 9H), 0.00 (d, 13H, $^{3}J_{H\text{-}P}$ 4.45 Hz), 0.28 (s, 7.5H), 0.31 (s, 5.5H), 0.41 (s, 13H), 0.46 (d, 10H, $^{3}J_{H\text{-}P}$ 3.44 Hz), 2.32 (s, 6.5H), 2.35 (s, 4.5H), 6.89 (m, 7H), 6.96 (m, 11H), 7.24 (d, 4H, $^{3}J_{H\text{-}H}$ 7.48 Hz), 7.37 (d, 6H, $^{3}J_{H\text{-}H}$ 7.87 Hz).

^{31}P NMR (C_6D_6): δ_P 73.6 (s), 90.5 (s), 127.7 (s, *Z*- C=**P**), 131.1 (s, *E*- C=**P**).

The suspension was stirred for 18 h and an aliquot was dried *in vacuo* as a yellow oil.

^{1}H NMR (C_6D_6): δ_H −0.08 (s, 9H), 0.00 (d, 13H, $^{3}J_{H\text{-}P}$ 4.45 Hz), 0.28 (s, 22H), 0.31 (s, 8H), 0.41 (s, 13H), 0.46 (d, 10H, $^{3}J_{H\text{-}P}$ 3.44 Hz), 2.32 (s, 6.5H), 2.35 (s, 4.5H), 6.89 (m, 7H), 6.96 (m, 11H), 7.24 (d, 4H, $^{3}J_{H\text{-}H}$ 7.48 Hz), 7.37 (d, 6H, $^{3}J_{H\text{-}H}$ 7.87 Hz).

$^{31}P\{^{1}H\}$ NMR (C_6D_6): δ_P 73.6 (s), 90.5 (s), 127.7 (s, *Z*- C=**P**), 131.1 (s, *E*- C=**P**).

The suspension was brought to reflux for 4 h and the solvent was removed under reduced pressure to afford a yellow oil.

$^{31}P\{^{1}H\}$ NMR (C_6D_6): δ_P −13.5 (s), 73.5 (s), 90.5 (s), 127.7 (s, *Z*- C=**P**), 131.1 (s, *E*- C=**P**).

Method B – 0.1 equivalents NaOH

To a DME solution of C_6H_4(1-CO($SiMe_3$)=P$SiMe_3$)(2-Me) (0.052 g, 1.76 x 10^{-4} mol) at −78 °C was added NaOH (0.0007 g, 1.76 x 10^{-5} mol) in DME, resulting in a suspended yellow solid that turned orange upon being allowed to warm to ambient temperature. The suspension was stirred for 4 h then the solvent was removed under reduced pressure; the product was washed with pentane to afford a yellow solid that was dried *in vacuo*, while solvent removal from the filtrate afforded a yellow oil.

Yellow solid:

^{1}H NMR (C_6D_6): None observed.

^{31}P{^{1}H} NMR (C_6D_6): None observed.

Yellow oil:

^{1}H NMR (C_6D_6): δ_H 0.07 (s, 0.5H), 0.09 (s, 0.5H), 0.17 (s, 1H), 0.18 (d, 1H, $^3J_{H\text{-}P}$ 1.51 Hz), 0.25 (s, 1H), 0.26 (s, 0.5H), 2.40 (s, 3.5H), 2.47 (s, 1.5H), 3.87 (d, 2H, $^1J_{H\text{-}P}$ 218.0 Hz, P**H**$_2$), 6.83 (m, 3H), 6.86 (m, 2H), 7.37 (d, 0.25H, $^3J_{H\text{-}H}$ 7.87 Hz), 7.45 (d, 1H, $^3J_{H\text{-}H}$ 7.86 Hz), 7.94 (d, 0.5H, $^3J_{H\text{-}H}$ 8.05 Hz).

^{31}P NMR (C_6D_6): δ_P −99.7 (t, $^1J_{P\text{-}H}$ 218.0 Hz, **P**H$_2$), 73.7 (br).

Method C - 0.1 equivalents NaOH

To a DME solution of C_6H_4(1-CO($SiMe_3$)=P$SiMe_3$)(2-Me) (0.052 g, 1.76 x 10^{-4} mol) at 0 °C was added NaOH (0.0007 g, 1.76 x 10^{-5} mol) in DME, resulting in a suspended yellow solid that turned orange when allowed to warm to ambient temperature. The suspension was stirred for 4 h then the solvent was removed under reduced pressure; the product was washed with pentane to afford a yellow solid that was dried *in vacuo*, while solvent removal from the filtrate afforded a yellow oil.

^{1}H NMR (C_6D_6): δ_H 0.07 (s, 0.5H), 0.09 (s, 0.5H), 0.17 (s, 1H), 0.18 (d, 1H, $^3J_{H\text{-}P}$ 1.51 Hz), 0.25 (s, 1H), 0.26 (s, 0.5H), 2.40 (s, 3.5H), 2.47 (s, 2H), 3.87 (d, 2H, $^1J_{H\text{-}P}$ 218.0 Hz, P**H**$_2$), 6.83 (m, 3H), 6.86 (m, 2H), 7.37 (d, 0.25H, $^3J_{H\text{-}H}$ 7.87 Hz), 7.45 (d, 1H, $^3J_{H\text{-}H}$ 7.86 Hz), 7.94 (d, 0.5H, $^3J_{H\text{-}H}$ 8.05 Hz).

^{31}P NMR (C_6D_6): δ_P −99.7 (t, $^1J_{P\text{-}H}$ 218.0 Hz, **P**H$_2$), −32.8 (dt, $^1J_{P\text{-}H}$ 220.3 Hz, $J_{P\text{-}H}$ 7.20 Hz), 73.7 (br), 168.9 (s).

Method D – 0.5 equivalents NaOH

Synthesis attempted as for **method C** using NaOH (0.23 g, 7.72 x 10^{-4} mol) and C_6H_4(1-CO($SiMe_3$)=P$SiMe_3$)(2-Me) (0.154 g, 3.86 x 10^{-4} mol). Isolated as an orange oil.

^{1}H NMR (C_6D_6): δ_H 0.12 (s, 7H), 2.56 (s, 22H), 7.00 (m, 33H), 7.37 (br, 1.5H), 7.58 (br, 4H), 7.84 (br, 8H).

^{31}P NMR (C_6D_6): δ_P −31.9 (s), 76.9 (br).

Method E – 1 equivalent NaOH

Synthesis attempted as for **method C** using NaOH (0.044 g, 1.48 x 10^{-4} mol) and C_6H_4(1-CO($SiMe_3$)=P$SiMe_3$)(2-Me) (0.0059 g, 1.48 x 10^{-4} mol). Isolated as a yellow oil.

^{1}H NMR (C_6D_6): δ_H 2.08 (s, 0.4H), 2.10 (s, 0.6H), 2.38 (s, 0.6H), 2.40 (s, 3.5H), 2.44 (s, 0.8H), 2.47 (s, 0.8H), 3.87 (d, 2H, $^1J_{H\text{-}P}$ 218.0 Hz, P**H**$_2$), 6.83 (m, 2H), 6.86 (m, 2H), 7.35 (br, 0.2H), 7.46 (d, 0.8H, $^3J_{H\text{-}H}$ 7.86 Hz), 7.94 (d, 0.3H, $^3J_{H\text{-}H}$ 8.05 Hz).

^{31}P NMR (C_6D_6): δ_P −99.7 (t, $^1J_{P\text{-}H}$ 218.0 Hz, **P**H$_2$), −32.8 (dt, $^1J_{P\text{-}H}$ 220.3 Hz, $J_{P\text{-}H}$ 7.20 Hz).

Method F

To a THF solution of C_6H_4(1-CO($SiMe_3$)=P$SiMe_3$)(2-Me) (0.0583 g, 1.96 x 10^{-4} mol) at −78 °C was added DBU (0.036 g, 2.36 x 10^{-4} mol) in THF, resulting in a suspended dark yellow solid that was stirred for 20 min. An unidentified gas was also produced. The suspension was allowed to warm to ambient temperature and was stirred for 4 h then cooled to −78 °C and filtered; the solvent was removed from the filtrate under reduced pressure to afford a colourless oil.

^{1}H NMR (C_6D_6): δ_H 1.17 (m, 1H), 1.29 (m, 1H), 1.53 (m, 2H), 2.44 (m, 1H), 2.66 (m, 1H), 2.74 (t, 1H, $J_{H\text{-}H}$ 5.30 Hz), 3.44 (t, 1H, $J_{H\text{-}H}$ 5.30 Hz).

^{31}P{^{1}H} NMR (C_6D_6): None observed.

Synthesis of C_6H_4(1-C(O)PH_2)(2-Me) (41-2-Me)

To an Et_2O solution of (C_6H_4(1-CO($SiMe_3$)=P$SiMe_3$)(2-Me) (0.43 g, 2.84 x 10^{-3} mol) at −78 °C was added H_2O (1.00 cm^3) and the mixture was stirred for 20 min. The solution was allowed to warm to ambient temperature then stirred for 4 h; the solvent was removed under reduced pressure to afford a yellow oil.

^{1}H NMR (C_6D_6): δ_H 2.40 (s, 3H, C**H**$_3$), 3.87 (d, 2H, $^{1}J_{H\text{-}P}$ 218.4 Hz, P**H**$_2$), 6.84-6.95 (br, 4H, C**H**).

^{31}P NMR (C_6D_6): δ_P −99.7 (t, $^{1}J_{P\text{-}H}$ 218.4 Hz, **P**H$_2$).

Attempted synthesis of *E*/*Z*-C$_6$H$_4$(1-CO(SiMe$_3$)=PH)(2-Me) (*E*/*Z*-42-2-Me)

Method A

To a THF solution of HP(SiMe$_3$)$_2$ (0.440 g, 2.47 x 10^{-3} mol) at −78 °C was added C$_6$H$_4$(1-COCl)(2-Me) (0.382 g, 2.47 x 10^{-3} mol) in THF and the mixture was stirred for 15 min. The resulting colourless solution was allowed to warm to ambient temperature over 45 min, resulting in a yellow solution; an aliquot was dried *in vacuo* as a yellow oil.

^{1}H NMR (C_6D_6): δ_H −0.21 (s, 5H), −0.08 (s, 11H), −0.01 (d, 27H, $^{3}J_{H\text{-}P}$ 4.05 Hz), 0.14 (s, 7H), 0.18 (s, 6H), 0.19 (s, 9H), 0.23 (s, 8H), 0.27 (s, 13H), 0.31 (s, 5H), 0.41 (s, 25H), 0.46 (d, 11H, $^{3}J_{H\text{-}P}$ 3.60 Hz), 2.08 (s, 1H), 2.14 (s, 2H), 2.18 (s, 2H), 2.24 (s, 89H), 2.31 (s, 15H), 2.34 (s, 5H), 2.36 (s, 3H), 2.46 (s, 3H), 2.49 (s, 5H), 2.55 (s, 3H), 2.61 (s, 2H), 2.66 (s, 2.5H), 3.87 (d, 0.1H, $^{1}J_{H\text{-}P}$ 218.4 Hz, P**H**$_2$), 4.69 (d, 3H, $^{1}J_{H\text{-}P}$ 162.6 Hz, *E*- C=P**H**), 5.00 (d, 2H, $^{1}J_{H\text{-}P}$ 143.3 Hz, *Z*- C=P**H**), 6.69 (d, 24H, $^{3}J_{H\text{-}H}$ 7.57 Hz), 6.80 (t, 25H, $^{3}J_{H\text{-}H}$ 7.57 Hz), 6.93 (t, 36H, $^{3}J_{H\text{-}H}$ 7.57 Hz), 7.23 (d, 3.5H, $^{3}J_{H\text{-}H}$ 7.13 Hz), 7.36 (m, 4.5H), 7.97 (d, 21H, $^{3}J_{H\text{-}H}$ 8.06 Hz).

^{31}P NMR (C_6D_6): δ_P −181.6 (t, $^{1}J_{P\text{-}H}$ 184.6 Hz), −180.5 (t, $^{1}J_{P\text{-}H}$ 186.6 Hz), −177.6 (s), −176.6 (s), −99.7 (t, $^{1}J_{P\text{-}H}$ 218.4 Hz, **P**H$_2$), −53.2 (s), −51.9 (s), −24.6 (s), −17.3 (s), −15.1 (s), −13.6 (br d, $^{1}J_{P\text{-}H}$ 690.9 Hz), −9.19 (s), −0.58 (s), 11.4 (d, $^{1}J_{P\text{-}H}$ 246.0 Hz), 67.2 (m, $^{4}J_{P\text{-}H}$ 3.44 Hz), 73.3 (d, $^{1}J_{P\text{-}H}$ 143.3 Hz, *Z*- C=**P**H), 73.7 (s), 90.6 (d, $^{1}J_{P\text{-}H}$ 162.6 Hz, *E*- C=**P**H), 116.3, 117.9 (s), 118.9 (s), 127.4 (s, *E*- C=**P**), 131.1 (s, *Z*- C=**P**), 151.1 (s), 159.1 (s), 164.3 (s).

The solution was stirred for 18 h and dried *in vacuo* to afford a yellow oil.

^{1}H NMR (C_6D_6): δ_H −0.20 (s, 1H), −0.08 (s, 5H), 0.00 (d, 12H, $^{3}J_{H\text{-}P}$ 4.05 Hz), 0.13 (s, 9H), 0.18 (s, 8H), 0.19 (s, 9H), 0.23 (s, 7H), 0.27 (s, 21H), 0.31 (s, 8H), 0.42 (s, 11H), 0.46 (d, 6H, $^{3}J_{H\text{-}P}$ 3.60 Hz), 0.49 (s, 4H), 2.16 (s, 1.5H), 2.23 (s, 48H), 2.32 (s, 10H), 2.35 (s, 2.5H), 2.37 (s, 4H), 2.40 (s, 2H), 2.47 (s, 5.5H), 2.51 (s, 11.5H), 2.56 (s, 2H), 2.63 (s, 3H), 4.69 (d, 3H, $^{1}J_{H\text{-}P}$ 162.6 Hz, *E*- C=P**H**), 5.00 (d, 2H, $^{1}J_{H\text{-}P}$ 143.3 Hz, *Z*- C=P**H**), 6.66 (d, 13H, $^{3}J_{H\text{-}H}$ 7.43 Hz), 6.77 (t, 14H, $^{3}J_{H\text{-}H}$ 7.74 Hz), 6.91 (m, 46H), 7.24 (d, 2H, $^{3}J_{H\text{-}H}$ 7.80 Hz), 7.36 (s, 1H), 7.40 (d, 2.5H, $^{3}J_{H\text{-}H}$ 7.30 Hz), 7.67 (d, 1.5H, $^{3}J_{H\text{-}H}$ 8.30 Hz), 7.89 (d, 1.5H, $^{3}J_{H\text{-}H}$ 7.80 Hz), 7.97 (d, 11H, $^{3}J_{H\text{-}H}$ 8.07 Hz), 8.05 (br, 4H), 8.12 (d, 1H, $^{3}J_{H\text{-}H}$ 7.42 Hz).

^{31}P NMR (C_6D_6): δ_P −181.7 (t, $^{1}J_{P\text{-}H}$ 184.6 Hz), −180.6 (t, $^{1}J_{P\text{-}H}$ 186.6 Hz), −99.7 (t, $^{1}J_{P\text{-}H}$ 218.4 Hz, **P**H$_2$), −24.6 (s), −17.2 (s), −13.5 (d, $^{1}J_{P\text{-}H}$ 690.9 Hz), −0.48 (s), 11.7 (d, $^{1}J_{P\text{-}H}$ 246.0 Hz), 43.5

(s), 67.2 (s), 73.3 (d, $^{1}J_{P\text{-}H}$ 143.3 Hz, *Z*- C=**P**H), 73.7 (s), 90.5 (d, $^{1}J_{P\text{-}H}$ 162.6 Hz, *E*- C=***P***H), 116.3, 127.4 (s, *E*- C=**P**), 131.1 (s, *Z*- C=**P**), 151.6 (s).

Method B

To a THF solution of $HP(SiMe_3)_2$ (0.300 g, 1.69 x 10^{-3} mol) at ambient temperature was added C_6H_4(1-COCl)(2-Me) (0.260 g, 1.69 x 10^{-3} mol) in THF and the mixture was stirred for 5 min, resulting in a yellow solution; an aliquot was dried *in vacuo* as a yellow oil.

^{1}H NMR (C_6D_6): δ_H −0.20 (s, 2H), −0.08 (s, 2H), 0.00 (d, 5H, $^{3}J_{H\text{-}P}$ 4.46 Hz), 0.13 (s, 5.5H), 0.18 (s, 5H), 0.23 (s, 4.5H), 0.26 (s, 13H), 0.29 (s, 5H), 0.41 (s, 4H), 0.46 (d, 2H, $^{3}J_{H\text{-}P}$ 3.20 Hz), 2.16 (s, 1H), 2.20 (s, 1H), 2.23 (s, 32H), 2.32 (s, 5.5H), 2.35 (s, 1H), 2.37 (s, 2H), 2.47 (s, 1H), 2.51 (s, 13H), 2.56 (s, 2.5H), 2.67 (s, 1H), 4.72 (d, 1H, $^{1}J_{H\text{-}P}$ 162.6 Hz, *E*- C=P**H**), 5.02 (d, 1H, $^{1}J_{H\text{-}P}$ 143.3 Hz, *Z*- C=P**H**), 6.67 (d, 9H, $^{3}J_{H\text{-}H}$ 7.47 Hz), 6.77 (t, 9H, $^{3}J_{H\text{-}H}$ 7.78 Hz), 6.85 (t, 9H, $^{3}J_{H\text{-}H}$ 6.86 Hz), 6.89 (t, 15H, $^{3}J_{H\text{-}H}$ 7.78 Hz), 6.93 (t, 14H, $^{3}J_{H\text{-}H}$ 7.17 Hz), 7.24 (d, 1H, $^{3}J_{H\text{-}H}$ 8.06 Hz), 7.39 (d, 1.5H, $^{3}J_{H\text{-}H}$ 7.10 Hz), 7.67 (d, 1H, $^{3}J_{H\text{-}H}$ 7.10 Hz), 7.89 (d, 1H, $^{3}J_{H\text{-}H}$ 8.06 Hz), 7.97 (d, 7H, $^{3}J_{H\text{-}H}$ 8.06 Hz), 8.04 (br, 4H).

^{31}P NMR (C_6D_6): δ_P −24.6 (s), −17.2 (s), 67.2 (s), 73.2 (d, $^{1}J_{P\text{-}H}$ 143.3 Hz, *E*- C=**P**H), 90.5 (d, $^{1}J_{P\text{-}H}$ 162.6 Hz, *Z*- C=**P**H), 127.4 (s, *Z*- C=**P**), 131.1 (s, *E*- C=**P**), 151.6 (s), 159.1 (s), 164.4 (s).

The solution was stirred for 18 h and dried *in vacuo* to afford a yellow oil.

^{1}H NMR (C_6D_6): δ_H −0.20 (s, 1H), −0.08 (s, 8.5H), 0.00 (d, 15H, $^{3}J_{H\text{-}P}$ 4.46 Hz), 0.14 (s, 8H), 0.18 (s, 11H), 0.23 (s, 7H), 0.27 (s, 16H), 0.29 (s, 6H), 0.31 (s, 5H), 0.34 (s, 1.5H), 0.42 (s, 15H), 0.46 (d, 9H, $^{3}J_{H\text{-}P}$ 3.20 Hz), 0.49 (s, 1H), 2.15 (s, 1.5H), 2.24 (s, 61H), 2.32 (s, 10H), 2.35 (s, 4H), 2.37 (s, 3H), 2.40 (s, 2H), 2.47 (s, 4.5H), 2.51 (s, 10H), 2.56 (s, 3H), 2.63 (s, 2H), 4.72 (d, 3H, $^{1}J_{H\text{-}P}$ 162.6 Hz, *E*- C=P**H**), 5.02 (d, 3H, $^{1}J_{H\text{-}P}$ 143.3 Hz, *Z*- C=P**H**), 6.66 (d, 17H, $^{3}J_{H\text{-}H}$ 7.32 Hz), 6.77 (t, 17H, $^{3}J_{H\text{-}H}$ 7.32 Hz), 6.85 (t, 6.5H, $^{3}J_{H\text{-}H}$ 6.71 Hz), 6.87 (d, 1H, $^{1}J_{H\text{-}P}$ 690.9 Hz), 6.89 (t, 21H, $^{3}J_{H\text{-}H}$ 7.23 Hz), 6.93 (t, 16H, $^{3}J_{H\text{-}H}$ 7.94 Hz), 7.24 (d, 2.5H, $^{3}J_{H\text{-}H}$ 7.34 Hz), 7.36 (s, 1H), 7.40 (d, 3H, $^{3}J_{H\text{-}H}$ 8.03 Hz), 7.97 (d, 15H, $^{3}J_{H\text{-}H}$ 8.54 Hz), 8.04 (br, 3.5H).

^{31}P NMR (C_6D_6): δ_P −99.7 (s), −24.6 (s), −17.2 (s), −13.5 (d, $^{1}J_{P\text{-}H}$ 690.9 Hz), −0.48 (s), 11.7 (s), 67.2 (s), 73.3 (d, $^{1}J_{P\text{-}H}$ 143.3 Hz, *Z*- C=**P**H), 73.7 (s), 90.6 (d, $^{1}J_{P\text{-}H}$ 162.6 Hz, *E*- C=**P**H), 116.3, 127.4 (s, *E*- C=**P**), 131.1 (s, *Z*- C=**P**), 151.6 (s).

Method C

To a THF solution of $HP(SiMe_3)_2$ (0.780 g, 4.38 x 10^{-3} mol) at 60 °C was added C_6H_4(1-COCl)(2-Me) (0.677 g, 4.38 x 10^{-3} mol) in THF and the mixture was brought to reflux for 1 h; an aliquot was dried *in vacuo* as a yellow oil and 5.2 mg of PPh_3 was added to the NMR sample.

^{1}H NMR (C_6D_6): δ_H −0.20 (s, 0.5H), −0.08 (s, 1.5H), 0.00 (d, 4H, $^3J_{H\text{-}P}$ 4.41 Hz), 0.14 (s, 5.5H, *Z*- $SiMe_3$), 0.18 (s, 2H), 0.23 (s, 1H), 0.27 (s, 11.5H, *E*- $SiMe_3$), 0.29 (s, 14H), 0.41 (s, 4H), 0.46 (d, 2H, $^3J_{H\text{-}P}$ 3.48 Hz), 2.24 (s, 16.5H), 2.32 (s, 5H, *E*- C**H**$_3$), 2.35 (s, 1H), 2.37 (s, 2H, *Z*- C**H**$_3$), 2.51 (s, 6H), 2.56 (s, 0.5H), 4.72 (d, 1.5H, $^1J_{H\text{-}P}$ 162.6 Hz, *E*- C=P**H**), 5.02 (d, 1H, $^1J_{H\text{-}P}$ 143.3 Hz, *Z*- C=P**H**), 6.67 (d, 4.5H, $^3J_{H\text{-}H}$ 7.69 Hz), 6.77 (t, 4.5H, $^3J_{H\text{-}H}$ 7.37 Hz), 6.85 (d, 2.5H, $^3J_{H\text{-}H}$ 7.58 Hz), 6.90 (t, 6.5H, $^3J_{H\text{-}H}$ 7.69 Hz), 6.93 (t, 7H, $^3J_{H\text{-}H}$ 7.69 Hz), 7.05 (br, 9H, PPh_3), 7.24 (d, 1H, $^3J_{H\text{-}H}$ 7.41 Hz), 7.38 (br, 9H, PPh_3), 7.67 (d, 1H, $^3J_{H\text{-}H}$ 7.41 Hz), 7.89 (d, 0.5H, $^3J_{H\text{-}H}$ 7.80 Hz), 7.97 (d, 3.5H, $^3J_{H\text{-}H}$ 8.09 Hz), 8.04 (br, 2H).

^{31}P NMR (C_6D_6): δ_P −5.29 (br, **P**Ph_3), 67.2 (s), 73.2 (d, $^1J_{P\text{-}H}$ 143.3 Hz, *Z*- C=**P**H), 90.5 (d, $^1J_{P\text{-}H}$ 162.6 Hz, *E*- C=**P**H), 116.3 (s), 127.3 (s, *E*- C=**P**), 131.0 (s, *Z*- C=**P**), 151.5 (s), 164.3 (s).

After 5 h at reflux an aliquot was extracted and dried *in vacuo* as a yellow oil; 4.1 mg of PPh_3 was added to the NMR sample.

^{1}H NMR (C_6D_6): δ_H −0.08 (s, 1H), 0.00 (d, 3H, $^3J_{H\text{-}P}$ 4.47 Hz), 0.14 (s, 9.5H, *Z*- $SiMe_3$), 0.18 (s, 2H), 0.23 (s, 1.5H), 0.27 (s, 19H, *E*- $SiMe_3$), 0.29 (s, 44H), 0.41 (s, 2.5H), 0.46 (d, 1H, $^3J_{H\text{-}P}$ 3.89 Hz), 0.48 (s, 0.5H), 2.15 (s, 0.5H), 2.24 (s, 16.5H), 2.31 (s, 7H, *E*- C**H**$_3$), 2.37 (s, 3.5H, *Z*- C**H**$_3$), 2.40 (s, 1.5H), 2.46 (s, 1.5H), 2.50 (s, 9H), 2.56 (s, 1H), 3.88 (d, 1H, $^1J_{H\text{-}P}$ 217.9 Hz, P**H**$_2$), 4.72 (d, 2.5H, $^1J_{H\text{-}P}$ 162.6 Hz, *E*- C=P**H**), 5.01 (d, 1.5H, $^1J_{H\text{-}P}$ 143.3 Hz, *Z*- C=P**H**), 6.67 (d, 4.5H, $^3J_{H\text{-}H}$ 7.69 Hz), 6.78 (t, 5H, $^3J_{H\text{-}H}$ 7.37 Hz), 6.85 (d, 3.5H, $^3J_{H\text{-}H}$ 7.58 Hz), 6.90 (t, 9H, $^3J_{H\text{-}H}$ 7.69 Hz), 6.93 (t, 9H, $^3J_{H\text{-}H}$ 7.69 Hz), 6.97 (m, 3H), 7.05 (br, 7.5H, PPh_3), 7.24 (d, 1H, $^3J_{H\text{-}H}$ 7.41 Hz), 7.39 (br, 8H, PPh_3), 7.46 (d, 1H, $^3J_{H\text{-}H}$ 7.85 Hz), 7.67 (d, 1H, $^3J_{H\text{-}H}$ 7.41 Hz), 7.89 (d, 1H, $^3J_{H\text{-}H}$ 7.80 Hz), 7.97 (d, 4H, $^3J_{H\text{-}H}$ 8.09 Hz), 8.04 (br, 3H).

^{31}P NMR (C_6D_6): δ_P −99.7 (t, $^1J_{P\text{-}H}$ 217.8 Hz, **P**H_2), −5.27 (br, **P**Ph_3), 11.6 (s), 67.2 (s), 73.2 (d, $^1J_{P\text{-}H}$ 143.3 Hz, *Z*- C=**P**H), 73.7 (s), 90.5 (d, $^1J_{P\text{-}H}$ 162.6 Hz, *E*- C=**P**H), 116.3 (s), 127.6 (s, *E*- C=**P**), 131.0 (s, *Z*- C=**P**), 151.5 (s), 164.3 (s).

After 18h at reflux the solution was cooled to ambient temperature and the solvent was removed under reduced pressure to afford a yellow oil; 4.5 mg of PPh_3 was added to the NMR sample.

^{1}H NMR (C_6D_6): δ_H 0.14 (s, 9H, *Z*- $SiMe_3$), 0.18 (s, 1.5H), 0.23 (s, 1H), 0.27 (s, 13.5H, *E*- $SiMe_3$), 0.31 (s, 2H), 0.49 (s, 0.5H), 2.16 (s, 0.5H), 2.24 (s, 19H), 2.32 (s, 5H, *E*- C**H**$_3$), 2.35 (s, 0.5), 2.37 (s, 3H, *Z*- C**H**$_3$), 2.40 (s, 2H), 2.47 (s, 3.5H), 2.51 (s, 3H), 2.56 (s, 0.5H), 2.61 (s, 0.5H), 2.63 (s, 1H), 3.88 (d, 1.2H, $^1J_{H\text{-}P}$ 217.9 Hz, P**H**$_2$), 4.72 (d, 2H, $^1J_{H\text{-}P}$ 162.6 Hz, *E*- C=P**H**),

5.01 (d, 1H, $^{1}J_{H\text{-}P}$ 143.3 Hz, *Z*- C=P**H**), 6.66 (d, 5H, $^{3}J_{H\text{-}H}$ 7.69 Hz), 6.77 (t, 5.5H, $^{3}J_{H\text{-}H}$ 7.37 Hz), 6.84 (d, 2H, $^{3}J_{H\text{-}H}$ 7.58 Hz), 6.89 (t, 7H, $^{3}J_{H\text{-}H}$ 7.69 Hz), 6.93 (t, 7H, $^{3}J_{H\text{-}H}$ 7.69 Hz), 6.99 (m, 3.5H), 7.05 (br, 19H, PPh_3), 7.39 (br, 15H, PPh_3), 7.46 (d, 1H, $^{3}J_{H\text{-}H}$ 7.85 Hz), 7.68 (d, 1H, $^{3}J_{H\text{-}H}$ 7.41 Hz), 7.89 (d, 0.5H, $^{3}J_{H\text{-}H}$ 7.80 Hz), 7.97 (d, 4.5H, $^{3}J_{H\text{-}H}$ 8.09 Hz), 8.04 (br, 1H).

^{31}P NMR (C_6D_6): δ_P −99.7 (t, $^{1}J_{P\text{-}H}$ 217.8 Hz, **P**H_2), −17.2 (s), −5.27 (br, **P**Ph_3), 11.7 (s), 67.2 (s), 73.3 (d, $^{1}J_{P\text{-}H}$ 143.3 Hz, *Z*- C=**P**H), 73.7 (s), 90.5 (d, $^{1}J_{P\text{-}H}$ 162.6 Hz, *E*- C=**P**H), 116.3 (s).

Synthesis of *E*/*Z*-C_6H_4(1-CO($SiMe_3$)=P$SiMe_3$)(3-Me) (*E*/*Z*-39-3-Me)

Method A

To a THF solution of $P(SiMe_3)_3$ (0.046 g, 1.84 x 10^{-4} mol) at −78 °C was added C_6H_4(1-COCl)(3-Me) (0.0284 g, 1.84 x 10^{-4} mol) in THF and the mixture was stirred for 15 min, resulting in a colourless solution that was warmed to ambient temperature and turned yellow; an aliquot was dried *in vacuo* to afford a yellow oil.

^{1}H NMR (C_6D_6): δ_H –0.01 (s, 5H), 0.05 (s, 44H), 0.09 (d, 25H, $^{3}J_{H\text{-}P}$ 4.32 Hz), 0.25 (s, 6H), 0.28 (s, 10H), 0.31 (d, 12.5H, $^{3}J_{H\text{-}P}$ 4.32 Hz), 0.32 (s, 10H), 0.44 (s, 22H), 0.46 (d, 47H, $^{3}J_{H\text{-}P}$ 3.84 Hz), 0.57 (d, 3H, $^{3}J_{H\text{-}P}$ 4.81 Hz), 0.65 (s, 3H), 2.03 (s, 18H), 2.06 (s, 9H), 4.73 (d, 0.1H, $^{1}J_{H\text{-}P}$ 153.1 Hz, *Z*- C=P**H**), 5.22 (d, 0.1H, $^{1}J_{H\text{-}P}$ 159.1 Hz, *E*- C=P**H**), 6.87 (t, 9H, $^{3}J_{H\text{-}H}$ 7.37 Hz), 6.94 (t, 9H, $^{3}J_{H\text{-}H}$ 7.31 Hz), 7.00 (m, 5H), 7.04 (t, 3H, $^{3}J_{H\text{-}H}$ 7.55 Hz), 7.23 (d, 3.5H, $^{3}J_{H\text{-}H}$ 7.54 Hz), 7.26 (s, 3H), 7.44 (s, 7H), 7.46 (s, 3H), 8.03 (s, 1H), 8.05 (s, 2H).

^{31}P{^{1}H} NMR (C_6D_6): δ_P –252.1, (s, $P(SiMe_3)_3$), –236.8 (s, $HP(SiMe_3)_2$), –86.6 (s), –83.8 (d, $J_{P\text{-}P}$ 52.3 Hz), –55.4 (d, $J_{P\text{-}P}$ 52.3 Hz), –24.6 (s), –17.5 (s), –13.5 (s), –9.17 (s), –1.23 (s), 65.9 (s, *E*-C=**P**H), 67.4 (s, *Z*- C=**P**H), 131.2 (s, *Z*- C=**P**), 133.4 (s, *E*- C=**P**), 227.2 (s).

The solution was stirred for 18 h and dried *in vacuo* to afford a yellow oil.

^{1}H NMR (C_6D_6): δ_H 0.05 (s, 13H), 0.08 (d, 9H, $^{3}J_{H\text{-}P}$ 4.80 Hz), 0.18 (s, 13H), 0.25 (s, 14H), 0.28 (s, 26H), 0.32 (s, 38H), 0.44 (s, 7H), 0.46 (d, 14H, $^{3}J_{H\text{-}P}$ 3.62 Hz), 1.99 (s, 1.5H), 2.02 (s, 12H), 2.03 (s, 4H), 2.05 (s, 1H), 2.06 (s, 3H), 6.85 (d, 1H, $^{1}J_{H\text{-}P}$ 689.5 Hz), 6.87 (t, 4H, $^{3}J_{H\text{-}H}$ 7.68 Hz), 6.94 (t, 5H, $^{3}J_{H\text{-}H}$ 7.31 Hz), 7.01 (t, 5H, $^{3}J_{H\text{-}H}$ 7.03 Hz), 7.04 (t, 4H, $^{3}J_{H\text{-}H}$ 7.31 Hz), 7.22 (s, 1.5H), 7.25 (d, 1H, $^{3}J_{H\text{-}H}$ 6.16 Hz), 7.43 (s, 2.5H), 7.46 (s, 1H), 7.71 (s, 1H), 8.03 (s, 2H), 8.05 (s, 5H).

^{31}P NMR (C_6D_6): δ_P –30.5 (d, $J_{P\text{-}P}$ 17.5 Hz), –30.2 (s), –29.9 (d, $J_{P\text{-}P}$ 17.5 Hz), –24.6 (s), –17.5 (s), –15.1 (dd, $J_{P\text{-}P}$ 14.8 Hz, $^{1}J_{P\text{-}H}$ 729.7 Hz), –13.5 (d, $^{1}J_{P\text{-}H}$ 689.5 Hz), –9.17 (s), –1.23 (s), –0.89 (d, $J_{P\text{-}P}$ 14.8 Hz), 65.9 ($^{1}J_{P\text{-}H}$ 159.3 Hz, *E*- C=**P**H), 67.4 (d, $^{1}J_{P\text{-}H}$ 150.9 Hz, *Z*- C=**P**H), 131.1 (s, *Z*- C=**P**), 133.5 (s, *E*- C=**P**), 161.5 (s), 227.2 (s).

Method B

To a THF solution of $P(SiMe_3)_3$ (0.0420 g, 1.68 x 10^{-4} mol) at 0 °C was added C_6H_4(1-COCl)(3-Me) (0.0259 g, 1.68 x 10^{-4} mol) in THF and the mixture was stirred for 15 min, resulting in a colourless solution that was warmed to ambient temperature and turned yellow; an aliquot was dried *in vacuo* to afford a yellow oil.

^{1}H NMR (C_6D_6): δ_H –0.01 (s, 5H), 0.05 (s, 47H), 0.09 (d, 25H, $^3J_{H\text{-}P}$ 4.32 Hz), 0.25 (s, 6H), 0.28 (s, 6H), 0.32 (s, 11H), 0.44 (s, 23H), 0.46 (d, 47H, $^3J_{H\text{-}P}$ 4.01 Hz), 0.56 (d, 3H, $^3J_{H\text{-}P}$ 5.09 Hz), 0.65 (s, 2.5H), 1.97 (s, 1H), 2.03 (s, 20H), 2.06 (s, 10H), 2.25 (s, 2H), 6.87 (t, 9H, $^3J_{H\text{-}H}$ 7.04 Hz), 6.94 (t, 8H, $^3J_{H\text{-}H}$ 7.50 Hz), 6.98 (t, 6H, $^3J_{H\text{-}H}$ 7.68 Hz), 7.04 (t, 3H, $^3J_{H\text{-}H}$ 7.50 Hz), 7.23 (d, 2H, $^3J_{H\text{-}H}$ 8.00 Hz), 7.26 (s, 3H), 7.44 (s, 8H), 7.46 (s, 3H), 8.03 (br, 1H), 8.05 (br, 1.5H).

^{31}P{^{1}H} NMR (C_6D_6): δ_P –86.6 (s), –83.8 (d, $J_{P\text{-}P}$ 52.3 Hz), –55.4 (d, $J_{P\text{-}P}$ 52.3 Hz), –24.7 (s), –17.5 (s), –13.5 (d, $^1J_{P\text{-}H}$ 689.5 Hz), –9.17 (s), 65.9 (s, *E*- C=**P**H), 67.4 (s, *Z*- C=**P**H), 131.2 (s, *Z*- C=**P**), 133.4 (s, *E*- C=**P**).

The solution was stirred for 18 h and dried *in vacuo* to afford a yellow oil.

^{1}H NMR (C_6D_6): δ_H 0.17 (s, 16H), 0.25 (s, 13H), 0.27 (s, 51H), 0.32 (s, 72H), 2.02 (s, 24H), 6.85 (d, 2H, $^1J_{H\text{-}P}$ 689.5 Hz), 7.01 (t, 8H, $^3J_{H\text{-}H}$ 7.41 Hz), 7.04 (t, 7H, $^3J_{H\text{-}H}$ 7.41 Hz), 8.02 (s, 3.5H), 8.04 (s, 8.5H).

^{31}P NMR (C_6D_6): δ_P –30.3 (s), –29.9 (d, $J_{P\text{-}P}$ 14.7 Hz), –24.7 (s), –15.1 (dd, $J_{P\text{-}P}$ 14.7 Hz, $^1J_{P\text{-}H}$ 730.7 Hz), –13.5 (d, $^1J_{P\text{-}H}$ 689.5 Hz), –11.2 (d, $^1J_{P\text{-}H}$ 725.3 Hz), –9.18 (s), –1.23 (s), 121.3 (s), 131.2 (s, *Z*- C=**P**), 133.4 (s, *E*- C=**P**).

Method C

To a THF solution of $P(SiMe_3)_3$ (0.0950 g, 3.80 x 10^{-4} mol) at ambient temperature was added C_6H_4(1-COCl)(3-Me) (0.587 g, 3.80 x 10^{-4} mol) in THF and the mixture was stirred for 1 h, resulting in a yellow solution that was dried *in vacuo* to afford a yellow oil. Yield: 0.093 g, 82.7 %.

^{1}H NMR (C_6D_6): δ_H 0.05 (s, 9H, *Z*- O(SiC**H**$_3$)$_3$), 0.08 (d, 9H, $^3J_{H\text{-}P}$ 4.33 Hz, *E*- P(SiC**H**$_3$)$_3$), 0.45 (s, 9H, *E*- O(SiC**H**$_3$)$_3$), 0.47 (d, 9H, $^3J_{H\text{-}P}$ 3.69 Hz, *Z*- P(SiC**H**$_3$)$_3$), 2.03 (s, 3H, *Z*- C**H**$_3$), 2.06 (s, 3H, *E*- C**H**$_3$), 6.87 (t, 2H, $^3J_{H\text{-}H}$ 8.44 Hz, *E*- and *Z*- *m*-C**H**), 6.94 (t, 1H, $^3J_{H\text{-}H}$ 7.39 Hz, *Z*- *p*-C**H**), 6.98 (t, 1H, $^3J_{H\text{-}H}$ 7.55 Hz, *E*- *p*-C**H**), 7.22 (d, 1H, $^3J_{H\text{-}H}$ 7.63 Hz, *E*- middle-C**H**), 7.25 (br, 1H, *E*- *o*-C**H**), 7.43 (br, 1H, *Z*- *o*-C**H**), 7.45 (d, 1H, $^3J_{H\text{-}H}$ 8.56 Hz, *Z*- middle-C**H**).

$^{13}C\{^{1}H\}$ NMR (C_6D_6): δ_C 0.48 (d, $^{4}J_{C\text{-}P}$ 6.13 Hz, *E*- O(Si**C**H_3)$_3$), 1.15 (d, $^{2}J_{C\text{-}P}$ 8.67 Hz, *Z*- P(Si**C**H_3)$_3$), 1.28 (s, *Z*- O(Si**C**H_3)$_3$), 1.85 (d, $^{2}J_{C\text{-}P}$ 11.6 Hz, *E*- P(Si**C**H_3)$_3$), 21.1 (s, *E*- **C**H_3), 21.2 (s, *Z*- **C**H_3), 124.8 (d, $^{3}J_{C\text{-}P}$ 11.9 Hz, *Z*- middle-**C**H), 124.8 (d, $^{3}J_{C\text{-}P}$ 4.33 Hz, *E*- middle-**C**H), 127.9 (m, *Z*- *p*-C**H**), 128.2 (m, *Z*- *o*-C**H**), 128.8 (d, $^{4}J_{C\text{-}P}$ 4.20 Hz, *E*- *o*-**C**H), 129.9 (s, *E*- *p*-**C**H), 130.2 (d, $^{5}J_{C\text{-}P}$ 2.75 Hz, *m*-**C**H), 137.4 (s, *E*- **C**CH_3), 137.5 (s, *Z*- **C**CH_3), 145.5 (d, $^{2}J_{C\text{-}P}$ 26.4 Hz, *Z*- *i*-**C**), 146.8 (d, $^{2}J_{C\text{-}P}$ 9.99 Hz, *E*- *i*-**C**), 213.1 (d, $^{1}J_{C\text{-}P}$ 65.9 Hz, *Z*- **C**=P), 219.2 (d, $^{1}J_{C\text{-}P}$ 57.1 Hz, *E*- **C**=P).

^{31}P NMR (C_6D_6): δ_P 131.1 (s, *Z*- C=**P**), 133.5 (s, *E*- C=**P**).

$^{29}Si\{^{1}H\}$ NMR (C_6D_6): δ_{Si} −3.67 (*Z*- P**Si**Me_3), −2.13 (*E*- P**Si**Me_3), 18.9 (*Z*- O**Si**Me_3), 20.9 (*E*- O**Si**Me_3).

Method D

To a THF solution of $P(SiMe_3)_3$ (0.0.058 g, 2.32 x 10^{-4} mol) at ambient temperature was added C_6H_4(1-COCl)(3-Me) (0.0358 g, 2.32 x 10^{-4} mol) in THF and the mixture was brought to reflux for 4 h, resulting in a bright yellow solution that was cooled to ambient temperature and dried *in vacuo* to afford a yellow oil.

^{1}H NMR (C_6D_6): δ_H –0.03 (s, 1H), –0.02 (s, 3H), 0.05 (s, 21H), 0.08 (d, 11H, $^{3}J_{H\text{-}P}$ 4.80 Hz), 0.25 (s, 4.5H), 0.27 (s, 88H), 0.31 (d, 12H, $^{3}J_{H\text{-}P}$ 4.31 Hz), 0.32 (s, 4H), 0.44 (s, 9.5H), 0.46 (d, 21H, $^{3}J_{H\text{-}P}$ 3.62 Hz), 0.56 (d, 1.5H, $^{3}J_{H\text{-}P}$ 4.75 Hz), 0.64 (s, 1.5H), 1.96 (s, 1H), 2.03 (s, 8H), 2.06 (s, 4H), 2.24 (s, 1H), 5.23 (d, 1H, $^{1}J_{H\text{-}P}$ 159.3 Hz, *E*- C=P**H**), 6.68 (t, 1H, $^{3}J_{H\text{-}H}$ 7.21 Hz), 6.79 (t, 1H, $^{3}J_{H\text{-}H}$ 7.21 Hz), 6.87 (t, 4H, $^{3}J_{H\text{-}H}$ 7.43 Hz), 6.94 (t, 3H, $^{3}J_{H\text{-}H}$ 7.21 Hz), 6.98 (t, 2H, $^{3}J_{H\text{-}H}$ 7.43 Hz), 7.22 (d, 1.5H, $^{3}J_{H\text{-}H}$ 7.43 Hz), 7.25 (s, 1H), 7.43 (s, 3.5H), 7.45 (s, 1H), 7.58 (s, 1H), 8.02 (s, 0.5H), 8.04 (s, 0.5H).

$^{31}P\{^{1}H\}$ NMR (C_6D_6): δ_P –252.1 (s, $P(SiMe_3)_3$), –86.7 (s), –83.8 (d, $J_{P\text{-}P}$ 52.4 Hz), –55.4 (d, $J_{P\text{-}P}$ 52.4 Hz), –24.7 (s), –17.5 (s), 65.9 (s, *E*- C=**P**H), 67.4 (s, *Z*- C=**P**H), 131.1 (s, *Z*- C=**P**), 133.5 (s, *E*- C=**P**), 227.2 (s).

Attempted synthesis of C_6H_4(1-C≡P)(3-Me)

Method A

To a THF solution of C_6H_4(1-CO($SiMe_3$)=P$SiMe_3$)(3-Me) (0.093 g, 3.12 x 10^{-4} mol) at ambient temperature was added DABCO (0.045 g, 4.02 x 10^{-4} mol) in THF, resulting in a suspended off-white solid that was stirred for 60 min; an aliquot was dried *in vacuo* as a yellow oil.

^{1}H NMR (C_6D_6): δ_H 0.05 (s, 21H), 0.08 (d, 11H, $^3J_{H\text{-}P}$ 4.80 Hz), 0.31 (d, 5H, $^3J_{H\text{-}P}$ 4.31 Hz), 0.32 (s, 9H), 0.44 (s, 10H), 0.46 (d, 21H, $^3J_{H\text{-}P}$ 3.62 Hz), 2.03 (s, 9H), 2.06 (s, 4H), 4.33 (br, 16H), 6.87 (t, 3.5H, $^3J_{H\text{-}H}$ 7.43 Hz), 6.94 (t, 4H, $^3J_{H\text{-}H}$ 7.21 Hz), 6.98 (t, 2H, $^3J_{H\text{-}H}$ 7.43 Hz), 7.22 (d, 1.5H, $^3J_{H\text{-}H}$ 7.43 Hz), 7.25 (s, 1H), 7.43 (s, 3.5H), 7.45 (s, 1H), 8.02 (s, 0.5H), 8.04 (s, 0.5H).

^{31}P NMR (C_6D_6): δ_P –83.8 (d, $J_{P\text{-}P}$ 52.4 Hz), –55.4 (d, $J_{P\text{-}P}$ 52.4 Hz), –24.7 (s), 65.9 (s, *E*-C=**P**H), 67.4 (s, *Z*- C=**P**H), 131.1 (s, *Z*- C=**P**), 133.5 (s, *E*- C=**P**).

The solution was stirred for 18 h and dried *in vacuo* to afford a yellow oil.

^{1}H NMR (C_6D_6): δ_H 0.05 (s, 21H), 0.08 (d, 11H, $^3J_{H\text{-}P}$ 4.80 Hz), 0.31 (d, 5H, $^3J_{H\text{-}P}$ 4.31 Hz), 0.32 (s, 9H), 0.44 (s, 10H), 0.46 (d, 21H, $^3J_{H\text{-}P}$ 3.62 Hz), 2.03 (s, 9H), 2.06 (s, 4H), 4.33 (br, 16H), 6.87 (t, 3.5H, $^3J_{H\text{-}H}$ 7.43 Hz), 6.94 (t, 4H, $^3J_{H\text{-}H}$ 7.21 Hz), 6.98 (t, 2H, $^3J_{H\text{-}H}$ 7.43 Hz), 7.22 (d, 1.5H, $^3J_{H\text{-}H}$ 7.43 Hz), 7.25 (s, 1H), 7.43 (s, 3.5H), 7.45 (s, 1H), 8.02 (s, 0.5H), 8.04 (s, 0.5H).

^{31}P{^{1}H} NMR (C_6D_6): δ_P –86.7 (s), –83.8 (d, $J_{P\text{-}P}$ 52.4 Hz), –55.4 (d, $J_{P\text{-}P}$ 52.4 Hz), –24.7 (s), –17.5 (s), 65.9 (s, *E*- C=**P**H), 67.4 (s, *Z*- C=**P**H), 131.1 (s, *Z*- C=**P**), 133.5 (s, *E*- C=**P**), 227.2 (s).

Method B

To a THF solution of C_6H_4(1-CO($SiMe_3$)=P$SiMe_3$)(3-Me) (0.0426 g, 1.44 x 10^{-4} mol) at ambient temperature was added [$Fe_2(CO)_9$] (0.052 g, 1.44 x 10^{-4} mol) in THF, resulting in an orange solution that turned red after being stirred for 10 min; an aliquot was taken after 1 h and dried *in vacuo* to afford a red solid.

^{31}P NMR{^{1}H} (C_6D_6): δ_P −212.4 (s), −155.5 (s), −102.7 (s), −14.1 (s), 124.2 (s), 149.2 (s), 218.4 (s).

The solution was stirred for 18 h and dried *in vacuo* to afford a dark red solid.

^{1}H NMR (C_6D_6): δ_H −0.16 (s, 4.5H), 0.07 (s, 189H), 0.31 (s, 7H), 0.35 (s, 5H), 0.40 (s, 13H), 0.93 (m, 5H), 1.32 (br, 5H), 2.21 (s, 4H), 2.32 (s, 2H), 2.37 (s, 4.5H), 2.40 (s, 6H), 2.45 (br, 3H), 3.60 (br, 4H), 4.22 (t, 3H, *J* 5.66 Hz), 6.91 (t, 4H, $^3J_{H\text{-}H}$ 7.71 Hz), 6.96 (d, 2H, $^3J_{H\text{-}H}$ 7.56 Hz), 7.04 (s, 2H), 7.34 (m, 6H), 7.59 (br, 1H), 7.77 (br, 1H), 7.83 (br, 1.5H), 7.85 (s, 2.5H).

$^{31}P\{^{1}H\}$ NMR (C_6D_6): δ_P −14.1 (d, $^{1}J_{P\text{-}P}$ 334.7 Hz), 14.5 (s), 22.2 (m), 124.2 (s), 157.7 (s), 213.6 (s), 218.4 (s).

Method C

To a pentane solution of C_6H_4(1-CO($SiMe_3$)=P$SiMe_3$)(3-Me) (0.392 g, 8.24 x 10^{-4} mol) at −78 °C was added Li$N(SiMe_3)_2$ (0.300 g, 1.81 x 10^{-3} mol) in pentane, resulting in a suspended yellow solid that was stirred for 30 min and was allowed to warm to ambient temperature then stirred for 1 h; an aliquot was dried *in vacuo* to afford an orange oil.

^{1}H NMR (C_6D_6): δ_H 0.05 (s, 21H), 0.08 (d, 10H, $^{3}J_{H\text{-}P}$ 4.80 Hz), 0.09 (s, 8H), 0.31 (d, 13H, $^{3}J_{H\text{-}P}$ 4.31 Hz), 0.32 (s, 15H), 0.35 (s, 63H), 0.44 (s, 11H), 0.46 (d, 21H, $^{3}J_{H\text{-}P}$ 3.62 Hz), 2.03 (s, 12H), 2.06 (s, 4H), 4.33 (br, 18H), 6.87 (t, 4.5H, $^{3}J_{H\text{-}H}$ 7.43 Hz), 6.94 (t, 4H, $^{3}J_{H\text{-}H}$ 7.21 Hz), 6.98 (t, 3.5H, $^{3}J_{H\text{-}H}$ 7.43 Hz), 7.22 (d, 2H, $^{3}J_{H\text{-}H}$ 7.43 Hz), 7.25 (s, 1H), 7.43 (s, 3.5H), 7.45 (s, 1.5H), 8.02 (s, 1H), 8.04 (s, 2.5H).

$^{31}P\{^{1}H\}$ NMR (C_6D_6): δ_P −252.1 (s, **P**$(SiMe_3)_3$), −86.7 (s), −83.8 (d, $J_{P\text{-}P}$ 51.8 Hz), −55.4 (d, $J_{P\text{-}P}$ 51.8 Hz), 131.1 (s, *Z*- C=**P**), 133.5 (s, *E*- C=**P**).

The suspension was stirred for 18 h then solvent was removed under reduced pressure to afford an orange oil. No change was noted from the previous NMR spectra.

Attempted synthesis of *E*/*Z*-C_6H_4(1-CO($SiMe_3$)=PH)(3-Me) (*E*/*Z*-42-3-Me)

Method A

To a THF solution of $HP(SiMe_3)_2$ (0.610 g, 3.43 x 10^{-3} mol) at –78 °C was added C_6H_4(1-COCl)(3-Me) (0.529 g, 3.43 x 10^{-3} mol) in THF and the mixture was stirred for 15 min, resulting in a colourless solution that was warmed to ambient temperature over 45 min and turned yellow; an aliquot was dried *in vacuo* to afford a yellow oil.

^{1}H NMR (C_6D_6): δ_H −0.18 (s, 4.5H), 0.05 (s, 6.5H), 0.20 (d, 12H, $^{3}J_{H\text{-}P}$ 12.9 Hz), 0.34 (s, 4.5H), 1.84 (s, 13H), 1.90 (s, 11H), 1.92 (s, 2H), 1.99 (s, 2.5H), 2.02 (s, 5.5H), 2.05 (s, 2.5H), 2.07 (s, 2H), 2.18 (s, 2H), 4.75 (d, 1H, $^{1}J_{H\text{-}P}$ 151.5 Hz, *Z*- C=P**H**), 5.24 (d, 1H, $^{1}J_{H\text{-}P}$ 160.7Hz, *E*- C=P**H**), 6.80 (t, 4H, $^{3}J_{H\text{-}H}$ 7.64 Hz), 6.84 (t, 5H, $^{3}J_{H\text{-}H}$ 7.64 Hz), 6.93 (t, 7H, $^{3}J_{H\text{-}H}$ 7.53 Hz), 6.96 (t, 7H, $^{3}J_{H\text{-}H}$ 7.64 Hz), 7.69 (s, 3H), 7.71 (d, 3H, $^{3}J_{H\text{-}H}$ 7.82 Hz), 7.90 (s, 3.5H), 7.93 (d, 3.5H, $^{3}J_{H\text{-}H}$ 7.82 Hz).

$^{13}C\{^{1}H\}$ NMR (C_6D_6): δ_C −0.12 (d, $J_{C\text{-}P}$ 6.29 Hz), 0.04 (s), 0.46 (s), 0.93 (s), 1.88 (s), 2.25 (s), 2.37 (s), 2.77 (s), 3.04 (s), 12.7 (m), 20.8 (s), 20.8 (s), 20.9 (s), 21.2 (s), 21.3 (s), 21.4 (s), 23.8 (d, $J_{C\text{-}P}$ 84.2 Hz), 30.1 (d, $J_{C\text{-}P}$ 153.5 Hz), 39.3 (s), 121.9 (d, $J_{C\text{-}P}$ 18.9 Hz), 123.6 (d, $J_{C\text{-}P}$ 3.70 Hz),

125.6 (d, $J_{C\text{-}P}$ 20.2 Hz), 126.8 (d, $J_{C\text{-}P}$ 9.02 Hz), 127.0 (d, $J_{C\text{-}P}$ 3.91 Hz), 128.9 (d, $J_{C\text{-}P}$ 10.9 Hz), 128.9 (s), 129.2 (d, $J_{C\text{-}P}$ 7.11 Hz), 130.8 (s), 131.5 (d, $J_{C\text{-}P}$ 5.40 Hz), 131.9 (s), 133.4 (s), 133.6 (s), 134.4 (s), 134.8 (d, $J_{C\text{-}P}$ 1.14 Hz), 135.9 (s), 138.9 (s), 141.2 (d, $J_{C\text{-}P}$ 35.6 Hz), 168.9 (d, $J_{C\text{-}P}$ 62.8 Hz), 205.9 (d, $J_{C\text{-}P}$ 32.9 Hz).

^{31}P NMR (C_6D_6): δ_P –52.7 (d, $^1J_{P\text{-}H}$ 171.3 Hz), –52.3 (d, $^1J_{P\text{-}H}$ 174.2 Hz), 53.4 (s), 65.8 (d, $^1J_{P\text{-}H}$ 160.7 Hz, *E*- C=**P**H), 67.4 (d, $^1J_{P\text{-}H}$ 151.5 Hz, *Z*- C=**P**H), 145.6 (s).

^{29}Si{^{1}H} NMR (C_6D_6): δ_{Si} 12.3, 21.2, 22.5, 22.7.

The solution was stirred for 18 h and dried *in vacuo* to afford a yellow oil.

^{1}H NMR (C_6D_6): δ_H 0.18 (s, 3H), 0.22 (s, 7H), 0.24 (s, 1.5H), 0.28 (s, 1H), 0.32 (s, 2.5H), 0.34 (s, 6H), 1.84 (s, 7H), 1.90 (s, 7H), 1.92 (s, 2H), 1.99 (s, 2.5H), 2.02 (s, 1H), 2.05 (s, 3H), 2.07 (s, 2.5H), 4.75 (d, 1H, $^1J_{H\text{-}P}$ 153.1 Hz, *Z*- C=P**H**), 5.24 (d, 1H, $^1J_{H\text{-}P}$ 159.1 Hz, *E*- C=P**H**), 6.81 (t, 2H, $^3J_{H\text{-}H}$ 7.61 Hz), 6.84 (t, 3H, $^3J_{H\text{-}H}$ 7.01 Hz), 6.93 (t, 4.5H, $^3J_{H\text{-}H}$ 7.61 Hz), 6.97 (t, 3H, $^3J_{H\text{-}H}$ 7.54 Hz), 7.02 (t, 3H, $^3J_{H\text{-}H}$ 8.14 Hz), 7.55 (s, 0.6H), 7.57 (s, 1H), 7.63 (m, 0.6H), 7.69 (s, 2H), 7.71 (d, 2H, $^3J_{H\text{-}H}$ 7.81 Hz), 7.89 (s, 2.5H), 7.92 (d, 2H, $^3J_{H\text{-}H}$ 7.81 Hz), 8.04 (m, 1.5H).

^{31}P NMR (C_6D_6): δ_P –115.6 (d, $^1J_{P\text{-}P}$ 71.5 Hz), –109.4 (t, $^1J_{P\text{-}H}$ 217.9 Hz, **P**H$_2$), –104.2 (2nd order), –97.1 (2nd order), –86.1 (d, $^1J_{P\text{-}P}$ 71.5 Hz), –52.7 (d, $^1J_{P\text{-}H}$ 171.3 Hz), –52.3 (d, $^1J_{P\text{-}H}$ 174.2 Hz), –49.4 (s), –47.9 (s), –24.7 (s), –17.5 (s), –0.24 (s), 29.0 (s), 53.4 (s), 59.7 (s), 65.8 (d, $^1J_{P\text{-}H}$ 160.7 Hz, *E*- C=**P**H), 67.4 (d, $^1J_{P\text{-}H}$ 151.5 Hz, *Z*- C=**P**H), 112.5 (s), 130.3 (s), 131.8 (s, *Z*- C=**P**), 133.3 (s, *E*- C=**P**).

^{29}Si{^{1}H} NMR (C_6D_6): δ_{Si} 19.8, 21.3.

The crude product was washed with pentane and filtered; a yellow solid was dried *in vacuo*, and reduced pressure solvent removal from the filtrate afforded a yellow oil.

Yellow solid:

^{1}H NMR (C_6D_6): δ_H 1.90 (s, 3H, C**H**$_3$), 6.92 (t, 1H, $^3J_{H\text{-}H}$ 7.58 Hz), 6.96 (t, 1H, $^3J_{H\text{-}H}$ 7.58 Hz), 7.90 (s, 1H, middle-C**H**), 7.93 (d, 1H, $^3J_{H\text{-}H}$ 7.79 Hz, *p*-C**H**).

^{13}C{^{1}H} NMR (C_6D_6): δ_C 20.9 (s, **C**H$_3$), 126.9 (d, $^3J_{C\text{-}P}$ 8.79 Hz, *o*-**C**H), 128.9 (s, *m*-**C**H), 129.2 (d, $^3J_{C\text{-}P}$ 7.24 Hz, middle-**C**H), 134.8 (s, *p*-**C**H), 138.9 (s, **C**CH$_3$), 141.2 (d, $^2J_{C\text{-}P}$ 34.4 Hz, *i*-**C**), 206.0 (d, $^1J_{C\text{-}P}$ 32.6 Hz, **C**P).

^{31}P NMR (C_6D_6): δ_P 53.4 (s).

Yellow oil:

^{1}H NMR (C_6D_6): δ_H –0.18 (s, 1.5H), 0.21 (s, 5H), 0.24 (s, 2.5H), 0.28 (s, 1H), 0.32 (s, 2.5H), 0.34 (s, 4H), 1.84 (s, 2H), 1.87 (s, 1H), 1.99 (s, 3H), 2.02 (s, 1H), 2.05 (s, 2H), 2.07 (s, 2H),

2.26 (s, 1H), 4.75 (d, 1H, $^{1}J_{H\text{-}P}$ 151.5 Hz, *Z*- C=P**H**), 5.22 ((d, $^{1}J_{H\text{-}P}$ 160.7 Hz, *E*- C=P**H**), 6.80-8.03 (m, 28H).

^{31}P NMR (C_6D_6): δ_P –115.6 (d, $^{1}J_{P\text{-}P}$ 71.3 Hz), –109.4 (t, $^{1}J_{P\text{-}H}$ 218.0 Hz, **P**H$_2$), –104.2 (2nd order), –97.1 (2nd order), –86.1 (d, $^{1}J_{P\text{-}P}$ 71.3 Hz), –52.7 (d, $^{1}J_{P\text{-}H}$ 171.3 Hz), –52.3 (d, $^{1}J_{P\text{-}H}$ 174.2 Hz), –17.5 (s), 29.0 (s), 59.7 (s), 65.9 (d, $^{1}J_{P\text{-}H}$ 160.7 Hz, *E*- C=**P**H), 67.4 (d, $^{1}J_{P\text{-}H}$ 151.5 Hz, *Z*- C=**P**H), 112.5 (s).

^{29}Si{^{1}H} NMR (C_6D_6): δ_{Si} 13.5, 20.9, 23.1.

Method B

To a THF solution of HP(SiMe$_3$)$_2$ (0.320 g, 1.79 x 10^{-3} mol) at ambient temperature was added C_6H_4(1-COCl)(3-Me) (0.278 g, 1.79 x 10^{-3} mol) in THF and the mixture was stirred for 5 min, resulting in a yellow solution; an aliquot was dried *in vacuo* to afford a yellow oil.

^{1}H NMR (C_6D_6): δ_H 0.18 (s, 2.5H), 0.20 (s, 8H), 0.22 (s, 4.6H), 0.24 (s, 6H), 0.34 (s, 4H), 1.87 (s, 30H, C**H**$_3$), 1.92 (s, 15H, C**H**$_3$), 2.00 (s, 1H, C**H**$_3$), 2.01 (s, 1H, C**H**$_3$), 2.05 (s, 2H, C**H**$_3$), 2.08 (s, 2H, C**H**$_3$), 4.73 (d, 1H, $^{1}J_{H\text{-}P}$ 153.1 Hz, *Z*- C=P**H**), 5.22 (d, 1H, $^{1}J_{H\text{-}P}$ 159.1 Hz, *E*- C=P**H**), 6.83 (t, 6H, $^{3}J_{H\text{-}H}$ 7.51 Hz), 6.87 (t, 9H, $^{3}J_{H\text{-}H}$ 7.37 Hz), 6.94 (t, 6H, $^{3}J_{H\text{-}H}$ 7.37 Hz), 6.98 (t, 5H, $^{3}J_{H\text{-}H}$ 7.70 Hz), 7.69 (s, 5H), 7.71 (d, 6H, $^{3}J_{H\text{-}H}$ 7.98 Hz), 7.88 (s, 4.6H), 7.92 (d, 5H, $^{3}J_{H\text{-}H}$ 7.41 Hz).

^{13}C{^{1}H} NMR (C_6D_6): δ_C −0.11 (d, $J_{C\text{-}P}$ 6.09 Hz), 0.05 (s), 0.74 (s), 0.94 (s), 1.42 (s), 3.06 (s), 11.2 (s), 14.2 (s), 20.8 (s), 21.0 (s), 21.1 (s), 21.3 (s), 21.4 (s), 23.4 (s), 24.2 (s), 29.4 (s), 30.9 (s), 39.3 (s), 126.8 (d, $J_{C\text{-}P}$ 9.14 Hz), 128.9 (s), 128.9 (s), 129.2 (d, $J_{C\text{-}P}$ 7.20 Hz), 131.9 (s), 133.6 (s), 134.8 (s), 136.0 (s), 138.9 (s), 139.0 (s), 141.1 (d, $J_{C\text{-}P}$ 35.1 Hz), 167.6 (s), 168.2 (s), 205.9 (d, $J_{C\text{-}P}$ 32.7 Hz), 211.3 (d, $^{1}J_{C\text{-}P}$ 59.6 Hz, *Z*- **C**=PH), 215.9 (d, $^{1}J_{C\text{-}P}$ 42.7 Hz, *E*- **C**=PH), 228.6 (d, $J_{C\text{-}P}$ 85.8 Hz).

^{31}P NMR (C_6D_6): δ_P −24.7 (s), −17.5 (s), 53.4 (s), 59.7 (s), 65.7 (d, $^{1}J_{P\text{-}H}$ 159.1 Hz, *E*- C=**P**H), 67.3 (d, $^{1}J_{P\text{-}H}$ 153.1 Hz, *Z*- C=**P**H), 145.2 (s).

^{29}Si{^{1}H} NMR (C_6D_6): δ_{Si} 22.3, 22.6, 30.8.

The solution was stirred for 18 h and dried *in vacuo* to afford a yellow oil.

^{1}H NMR (C_6D_6): δ_H 0.18 (s, 4H), 0.21 (s, 5H), 0.25 (d, 5H, $^{3}J_{H\text{-}P}$ 3.79 Hz), 0.32 (s, 8H), 0.34 (d, 4.5H, $^{3}J_{H\text{-}P}$ 1.02 Hz), 1.84 (s, 21H), 1.99 (s, 2H), 2.00 (s, 1H), 2.02 (s, 3H), 2.05 (s, 2H), 2.07 (s, 2H), 4.75 (d, 1H, $^{1}J_{H\text{-}P}$ 153.1 Hz, *Z*- C=P**H**), 5.24 (d, 1H, $^{1}J_{H\text{-}P}$ 159.1 Hz, *E*- C=P**H**), 6.80 (t, 6.5H, $^{3}J_{H\text{-}H}$ 7.63 Hz), 6.84 (m, 3.8H), 6.85 (m, 2H), 6.91-7.06 (m, 10H), 7.69 (m, 5H), 7.71 (dm, 5.5H, $^{3}J_{H\text{-}H}$ 7.71 Hz), 8.03 (br, 1H), 8.05 (br, 1.5H).

^{31}P NMR (C_6D_6): δ_P −111.9 (s), −27.3 (s), −20.0 (s), −15.9 (d, $^1J_{P\text{-}H}$ 696.9 Hz), 50.9 (m), 59.7 (s), 65.7 (d, $^1J_{P\text{-}H}$ 159.1 Hz, *E*- C=**P**H), 67.3 (d, $^1J_{P\text{-}H}$ 153.1 Hz, *Z*- C=**P**H), 110.0 (s).

Method C

To a THF solution of $HP(SiMe_3)_2$ (0.800 g, 4.49 x 10^{-3} mol) at 60 °C was added C_6H_4(1-COCl)(3-Me) (0.694 g, 4.49 x 10^{-3} mol) in THF, resulting in a bright yellow solution that was brought to reflux for 80 min; an aliquot was dried *in vacuo* to afford a yellow oil and 3.9 mg of PPh_3 was added to the NMR sample.

^{1}H NMR (C_6D_6): δ_H –0.17 (s, 3H), –0.10 (s, 1.5H), –0.02 (s, 1.5H), 0.05 (s, 5H), 0.18 (s, 3.5H), 0.21 (s, 10H), 0.29 (s, 18H), 0.34 (s, 38H), 1.83 (s, 18.5H), 1.89 (s, 3H), 1.92 (s, 1H), 1.98 (s, 2.5H), 2.02 (s, 4H), 2.04 (s, 4H), 2.07 (s, 3H), 2.16 (s, 0.5H), 2.17 (s, 1H), 2.21 (s, 0.5H), 3.90 (d, $^1J_{H\text{-}P}$ 217.6 Hz, PH_2, 0.4H), 4.77 (d, $^1J_{H\text{-}P}$ 153.1 Hz, *Z*- C=P**H**, 1.5H), 5.24 (d, $^1J_{H\text{-}P}$ 159.1 Hz, *E*- C=P**H**, 1.4H), 6.79 (t, $^3J_{H\text{-}H}$ 7.30 Hz, 5H), 6.83 (t, $^3J_{H\text{-}H}$ 7.60 Hz, 6H), 6.94 (m, 6H), 7.00 (m, 3.5H), 7.04 (br, 8H), 7.38 (br, 6H), 7.56 (s, 1H), 7.58 (s, 2H), 7.69 (s, 4H), 7.71 (d, $^3J_{H\text{-}H}$ 7.70 Hz, 4.5H), 7.83 (br, 2H), 7.90 (s, 2H), 7.93 (d, $^3J_{H\text{-}H}$ 7.70 Hz, 1H), 8.04 (br, 1H), 8.05 (br, 0.5H).

^{31}P NMR (C_6D_6): δ_P –109.4 (t, $^1J_{P\text{-}H}$ 217.6 Hz, **P**H_2), –104.2 (2nd order), –97.1 (2nd order), –90.7 (d, $^1J_{P\text{-}H}$ 172.9 Hz), –89.8 (d, $^1J_{P\text{-}H}$ 170.7 Hz), –52.7 (d, $^1J_{P\text{-}H}$ 172.3 Hz), –52.3 (d, $^1J_{P\text{-}H}$ 171.6 Hz), –17.5 (s), –5.26 (s), 53.4 (s), 59.8 (s), 65.9 (d, $^1J_{P\text{-}H}$ 160.7 Hz, *E*- C=**P**H), 67.5 (d, $^1J_{P\text{-}H}$ 151.5 Hz, *Z*- C=**P**H), 145.6 (s).

After 160 min at reflux an aliquot was dried *in vacuo* to afford a yellow oil; 3.7 mg of PPh_3 was added to the NMR sample.

^{1}H NMR (C_6D_6): δ_H –0.17 (s, 1.5H), –0.10 (s, 1H), –0.02 (s, 1H), 0.05 (s, 3.5H), 0.18 (s, 2.5H), 0.22 (s, 12H), 0.29 (s, 15.5H), 0.34 (s, 9.5H), 1.83 (s, 15H), 1.89 (s, 2H), 1.99 (s, 2H), 2.02 (s, 2.5H), 2.04 (s, 4H), 2.07 (s, 3.5H), 3.90 (d, $^1J_{H\text{-}P}$ 217.6 Hz, PH_2, 0.5H), 4.77 (d, $^1J_{H\text{-}P}$ 153.1 Hz, *Z*- C=P**H**, 2H), 5.24 (d, $^1J_{H\text{-}P}$ 159.1 Hz, *E*- C=P**H**, 1.6H), 6.79 (t, $^3J_{H\text{-}H}$ 7.30 Hz, 4H), 6.83 (t, $^3J_{H\text{-}H}$ 7.60 Hz, 5H), 6.94 (m, 5H), 7.00 (m, 3H), 7.04 (br, 8H), 7.38 (br, 6H), 7.56 (s, 1H), 7.58 (s, 2H), 7.69 (s, 3.5H), 7.71 (d, $^3J_{H\text{-}H}$ 7.70 Hz, 3.5H), 7.84 (br, 2H), 7.90 (s, 2H), 7.93 (d, $^3J_{H\text{-}H}$ 7.70 Hz, 1H), 8.04 (br, 1H), 8.05 (br, 0.5H).

^{31}P NMR (C_6D_6): δ_P –109.4 (t, $^1J_{P\text{-}H}$ 217.6 Hz, **P**H_2), –104.2 (2nd order), –97.1 (2nd order), –90.7 (d, $^1J_{P\text{-}H}$ 172.9 Hz), –89.9 (d, $^1J_{P\text{-}H}$ 170.7 Hz), –52.7 (d, $^1J_{P\text{-}H}$ 172.3 Hz), –52.3 (d, $^1J_{P\text{-}H}$ 171.6 Hz), –17.5 (s), –5.26 (s), 53.4 (s), 59.8 (s), 65.9 (d, $^1J_{P\text{-}H}$ 160.7 Hz, *E*- C=**P**H), 67.5 (d, $^1J_{P\text{-}H}$ 151.5 Hz, *Z*- C=**P**H), 145.6 (s).

After 240 min at reflux an aliquot was dried *in vacuo* to afford a yellow oil; 4.4 mg of PPh_3 was added to the NMR sample.

^{1}H NMR (C_6D_6): δ_H –0.18 (s, 1H), –0.10 (s, 1H), –0.06 (s, 0.5H), –0.02 (s, 1H), 0.05 (s, 2H), 0.18 (s, 2H), 0.22 (s, 11H), 0.29 (s, 15H), 0.34 (s, 9H), 1.83 (s, 14H), 1.89 (s, 2H), 1.94 (s, 0.5H), 1.98 (s, 2H), 2.02 (s, 1H), 2.04 (s, 4H), 2.07 (s, 3H), 3.90 (d, $^{1}J_{H\text{-}P}$ 217.6 Hz, P**H**$_2$, 0.6H), 4.77 (d, $^{1}J_{H\text{-}P}$ 153.1 Hz, *Z*- C=P**H**, 2H), 5.24 (d, $^{1}J_{H\text{-}P}$ 159.1 Hz, *E*- C=P**H**, 1.6H), 6.79 (t, $^{3}J_{H\text{-}H}$ 7.30 Hz, 3.5H), 6.83 (t, $^{3}J_{H\text{-}H}$ 7.60 Hz, 5H), 6.94 (m, 4H), 7.00 (m, 2.5H), 7.04 (br, 8H), 7.38 (br, 6H), 7.56 (s, 1H), 7.58 (s, 2H), 7.69 (s, 3H), 7.71 (d, $^{3}J_{H\text{-}H}$ 7.70 Hz, 3.5H), 7.84 (br, 1.5H), 7.90 (s, 2H), 7.93 (d, $^{3}J_{H\text{-}H}$ 7.70 Hz, 1H), 8.04 (br, 1H).

^{31}P NMR (C_6D_6): δ_P –109.4 (t, $^{1}J_{P\text{-}H}$ 217.6 Hz, **P**H$_2$), –104.2 (2nd order), –97.1 (2nd order), –52.7 (d, $^{1}J_{P\text{-}H}$ 172.3 Hz), –52.3 (d, $^{1}J_{P\text{-}H}$ 171.6 Hz), –17.5 (s), –5.26 (s), 53.4 (s), 59.8 (s), 65.9 (d, $^{1}J_{P\text{-}H}$ 160.7 Hz, *E*- C=**P**H), 67.5 (d, $^{1}J_{P\text{-}H}$ 151.5 Hz, *Z*- C=**P**H), 145.6 (s).

After 320 min at reflux an aliquot was dried *in vacuo* to afford a yellow oil; 3.4 mg of PPh_3 was added to the NMR sample.

^{1}H NMR (C_6D_6): δ_H –0.18 (s, 1H), –0.10 (s, 1H), –0.06 (s, 1H), –0.02 (s, 1H), 0.06 (s, 2H), 0.22 (s, 16H), 0.29 (s, 18H), 0.34 (s, 13H), 1.83 (s, 19H), 1.89 (s, 2H), 1.94 (s, 1H), 1.98 (s, 2H), 2.04 (s, 5.5H), 2.07 (s, 4.5H), 3.90 (d, $^{1}J_{H\text{-}P}$ 217.6 Hz, P**H**$_2$, 0.8H), 4.77 (d, $^{1}J_{H\text{-}P}$ 153.1 Hz, *Z*- C=P**H**, 2.6H), 5.24 (d, $^{1}J_{H\text{-}P}$ 159.1 Hz, *E*- C=P**H**, 2.4H), 6.79 (t, $^{3}J_{H\text{-}H}$ 7.30 Hz, 5H), 6.83 (t, $^{3}J_{H\text{-}H}$ 7.60 Hz, 6H), 6.94 (m, 5H), 7.00 (m, 3.5H), 7.04 (br, 8H), 7.38 (br, 6H), 7.56 (s, 1H), 7.58 (s, 2H), 7.69 (s, 4H), 7.71 (d, $^{3}J_{H\text{-}H}$ 7.70 Hz, 5H), 7.84 (br, 2H), 7.90 (s, 2H), 7.93 (d, $^{3}J_{H\text{-}H}$ 7.70 Hz, 1H), 8.04 (br, 1.5H).

^{31}P NMR (C_6D_6): δ_P –115.5 (d, $^{1}J_{P\text{-}P}$ 72.1 Hz), –109.4 (t, $^{1}J_{P\text{-}H}$ 217.6 Hz, **P**H$_2$), –104.2 (2nd order), –97.1 (2nd order), –86.1 (d, $^{1}J_{P\text{-}P}$ 72.1 Hz), –52.7 (d, $^{1}J_{P\text{-}H}$ 172.3 Hz), –52.3 (d, $^{1}J_{P\text{-}H}$ 171.6 Hz), –17.5 (s), –5.26 (s), 53.4 (s), 59.8 (s), 65.9 (d, $^{1}J_{P\text{-}H}$ 160.7 Hz, *E*- C=**P**H), 67.5 (d, $^{1}J_{P\text{-}H}$ 151.5 Hz, *Z*- C=**P**H), 145.6 (s).

After 400 min at reflux an aliquot was dried *in vacuo* to afford a yellow oil; 4.4 mg of PPh_3 was added to the NMR sample.

^{1}H NMR (C_6D_6): δ_H –0.18 (s, 1H), –0.10 (s, 0.5H), –0.06 (s, 1H), –0.02 (s, 0.5H), 0.06 (s, 1H), 0.18 (s, 2H), 0.22 (s, 15.5H), 0.24 (s, 2H), 0.29 (s, 18H), 0.34 (s, 12H), 1.83 (s, 17.5H), 1.89 (s, 2H), 1.94 (s, 1H), 1.98 (s, 2H), 2.04 (s, 5.5H), 2.07 (s, 4.5H), 3.90 (d, $^{1}J_{H\text{-}P}$ 217.6 Hz, P**H**$_2$, 0.7H), 4.77 (d, $^{1}J_{H\text{-}P}$ 153.1 Hz, *Z*- C=P**H**, 2.4H), 5.24 (d, $^{1}J_{H\text{-}P}$ 159.1 Hz, *E*- C=P**H**, 2H), 6.79 (t, $^{3}J_{H\text{-}H}$ 7.30 Hz, 4H), 6.83 (t, $^{3}J_{H\text{-}H}$ 7.60 Hz, 6H), 6.94 (m, 5H), 7.00 (m, 3H), 7.04 (br, 8H), 7.38 (br, 6H), 7.56 (s, 0.5H), 7.58 (s, 2H), 7.69 (s, 4H), 7.71 (d, $^{3}J_{H\text{-}H}$ 7.70 Hz, 4H), 7.84 (br, 1.5H), 7.90 (s, 2H), 7.93 (d, $^{3}J_{H\text{-}H}$ 7.70 Hz, 1H), 8.04 (br, 1H).

^{31}P NMR (C_6D_6): δ_P –115.5 (d, $^{1}J_{P\text{-}P}$ 72.1 Hz), –109.4 (t, $^{1}J_{P\text{-}H}$ 217.6 Hz, **P**H$_2$), –104.2 (2nd order), –97.1 (2nd order), –86.1 (d, $^{1}J_{P\text{-}P}$ 72.1 Hz), –52.7 (d, $^{1}J_{P\text{-}H}$ 172.3 Hz), –52.3 (d, $^{1}J_{P\text{-}H}$ 171.6

Hz), –17.5 (s), –5.26 (s), 53.4 (s), 59.8 (s), 65.9 (d, $^{1}J_{P\text{-}H}$ 160.7 Hz, *E*- C=**P**H), 67.5 (d, $^{1}J_{P\text{-}H}$ 151.5 Hz, *Z*- C=**P**H).

After 1440 min at reflux the solvent was removed under reduced pressure to afford a yellow oil; 3.8 mg of PPh_3 was added to the NMR sample.

^{1}H NMR (C_6D_6): δ_H –0.18 (s, 1H), –0.06 (s, 2.5H), 0.06 (s, 2.5H), 0.18 (s, 2H), 0.22 (s, 9H), 0.24 (s, 2H), 0.29 (s, 7H), 0.34 (s, 5.5H), 1.83 (s, 14H), 1.89 (s, 1.5H), 1.94 (s, 2.5H), 1.98 (s, 3H), 2.01 (s, 2H), 2.04 (s, 3H), 2.07 (s, 2.5H), 2.17 (s, 1H), 2.22 (s, 1H), 3.90 (d, $^{1}J_{H\text{-}P}$ 217.6 Hz, P**H**$_2$, 1.2H), 4.77 (d, $^{1}J_{H\text{-}P}$ 153.1 Hz, *Z*- C=P**H**, 1.4H), 5.24 (d, $^{1}J_{H\text{-}P}$ 159.1 Hz, *E*- C=P**H**, 1.2H), 6.79 (t, $^{3}J_{H\text{-}H}$ 7.30 Hz, 4H), 6.83 (t, $^{3}J_{H\text{-}H}$ 7.60 Hz, 5.5H), 6.94 (m, 7H), 7.00 (m, 3H), 7.04 (br, 8H), 7.38 (br, 6H), 7.56 (s, 1H), 7.58 (s, 1.5H), 7.69 (s, 3.5H), 7.71 (d, $^{3}J_{H\text{-}H}$ 7.70 Hz, 3.5H), 7.84 (br, 2H), 7.90 (s, 1.5H), 7.93 (d, $^{3}J_{H\text{-}H}$ 7.70 Hz, 1H), 8.04 (br, 2.5H).

^{31}P NMR (C_6D_6): δ_P –115.5 (d, $^{1}J_{P\text{-}P}$ 72.1 Hz), –109.4 (t, $^{1}J_{P\text{-}H}$ 217.6 Hz, **P**H$_2$), –104.2 (2nd order), –97.1 (2nd order), –86.1 (d, $^{1}J_{P\text{-}P}$ 72.1 Hz), –17.5 (s), –5.26 (s), 53.4 (s), 59.8 (s), 65.9 (d, $^{1}J_{P\text{-}H}$ 160.7 Hz, *E*- C=**P**H), 67.5 (d, $^{1}J_{P\text{-}H}$ 151.5 Hz, *Z*- C=**P**H).

Attempted synthesis of *E*/*Z*-C$_6$H$_4$(1-CO(SiMe$_3$)=PSiMe$_3$)(3-CN) (*E*/*Z*-39-3-CN)

Method A

To a THF solution of P(SiMe$_3$)$_3$ (0.0740 g, 2.96 x 10^{-4} mol) at −78 °C was added C$_6$H$_4$(1-COCl)(3-CN) (0.0489 g, 2.96 x 10^{-4} mol) in THF and the mixture was stirred for 15 min, resulting in a colourless solution that was allowed to warm to ambient temperature and turned yellow; an aliquot was *dried in vacuo* to afford an orange oil.

^{1}H NMR (C_6D_6): δ_H −0.32 (s, 3H), −0.22 (s, 2H), −0.21 (s, 2H), −0.14 (s, 2H), 0.02 (s, 2H), 0.11 (s, 3.5H), 0.14 (s, 2H), 0.18 (s, 2H), 0.25 (s, 10.5H), 0.28 (s, 4H), 0.42 (br, 2.5H), 0.49 (s, 1.5H), 6.76 (m, 1H), 6.82 (br, 1H), 6.90 (br, 1.5H), 6.92 (d, 3H, $^{3}J_{H\text{-}H}$ 7.86 Hz), 7.08 (d, 2H, $^{3}J_{H\text{-}H}$ 8.59 Hz), 7.46 (d, 1H, $^{3}J_{H\text{-}H}$ 8.04 Hz), 7.55 (d, 1.5H, $^{3}J_{H\text{-}H}$ 7.82 Hz), 7.64 (br, 1H), 7.54 (d, 2H, $^{3}J_{H\text{-}H}$ 8.04 Hz).

^{31}P NMR (C_6D_6): δ_P −236.8 (br), −236.2 (br), −123.1 (d, $^{2}J_{P\text{-}P}$ 192.8 Hz), −82.6 (d, $J_{P\text{-}P}$ 53.1 Hz), −81.5 (d, $^{2}J_{P\text{-}P}$ 192.8 Hz), −75.7 (s), −52.1 (d, $J_{P\text{-}P}$ 53.1 Hz), −24.7 (s), −15.4 (s), −13.9 (d, $^{1}J_{P\text{-}H}$ 218.1 Hz), −9.19 (s), −3.90 (s), −2.54 (s), 64.3 (d, $^{1}J_{P\text{-}H}$ 200.4 Hz), 142.9 (s), 153.1 (s), 154.0 (s), 158.6 (s), 160.3 (s), 172.2 (s), 178.2 (s).

The solution was stirred for 18 h and dried *in vacuo* to afford a yellow oil.

^{1}H NMR (C_6D_6): δ_H −0.29 (s, 6.5H), 0.01 (s, 5H), 0.18 (s, 12H), 0.25 (s, 90H), 0.28 (s, 50H), 6.47 (t, 2H, $^{3}J_{H\text{-}H}$ 7.92 Hz), 6.61 (t, 9.5H, $^{3}J_{H\text{-}H}$ 7.44 Hz), 6.80 (t, 4H, $^{3}J_{H\text{-}H}$ 7.92 Hz), 6.98 (d, 9H,

$^{3}J_{H\text{-}H}$ 7.92 Hz), 7.69 (s, 1H), 7.72 (d, 1.5H, $^{3}J_{H\text{-}H}$ 6.36 Hz), 7.87 (d, 1.5H, $^{3}J_{H\text{-}H}$ 7.52 Hz), 7.92 (d, 7H, $^{3}J_{H\text{-}H}$ 8.29 Hz), 8.09 (s, 5H), 8.16 (d, 1.5H, $^{3}J_{H\text{-}H}$ 7.52 Hz), 8.69 (s, 1H).

^{31}P NMR (C_6D_6): δ_P −236.8 (br), −236.2 (br), −24.7 (s), −13.5 (d, $^{1}J_{P\text{-}H}$ 692.2 Hz), −9.14 (s), −2.45 (s), 2.50 (s), 88.5 (s), 89.6 (s), 114.7 (s), 136.3 (s, *Z*- C=**P**), 137.8 (s, *E*- C=**P**), 176.3 (s).

Method B

To a THF solution of $P(SiMe_3)_3$ (0.064 g, 2.56 x 10^{-4} mol) at ambient temperature was added C_6H_4(1-COCl)(3-CN) (0.0423 g, 2.56 x 10^{-4} mol) in THF, resulting in the rapid formation of a yellow solution within 5 min; an aliquot was dried *in vacuo* to afford a yellow oil.

^{1}H NMR (C_6D_6): δ_H −0.45 (s, 3.5H), −0.39 (s, 3.5H), 0.11 (s, 7H), 0.17 (s, 6H), 0.24 (s, 18H), 0.25 (s, 18H), 0.28 (s, 10H), 0.30 (s, 10H), 6.62 (m, 9H), 6.95 (m, 13H), 7.65 (d, 5H, $^{3}J_{H\text{-}H}$ 8.19 Hz), 7.84 (m, 5H), 7.91 (s, 1.5H), 7.93 (s, 3H), 8.04 (s, 2.5H), 8.09 (s, 2H), 8.52 (s, 2H), 8.68 (s, 1H).

^{31}P NMR (C_6D_6): δ_P –134.3 (m), –129.8 (s), –128.9 (s), –130.9 (m), –116.1 (d, $^{1}J_{P\text{-}P}$ 71.9 Hz), –109.9 (m), –103.5 (2nd order), –97.3 (2nd order), –89.9 (m), –84.9 (ddd, $^{1}J_{P\text{-}P}$ 71.9Hz, $^{1}J_{P\text{-}H}$ 186.0 Hz, $J_{P\text{-}H}$ 13.7 Hz), –83.7 (m), –68.2 (dd, $J_{P\text{-}P}$ 106.6, $^{1}J_{P\text{-}H}$ 188.7 Hz), –47.3 (d, $^{1}J_{P\text{-}H}$ 177.7 Hz), –46.8 (d, $^{1}J_{P\text{-}H}$ 180.5 Hz), –24.8 (br), –24.5 (s), –21.7 (d, $^{1}J_{P\text{-}H}$ 219.9 Hz), –18.1 (dd, $J_{P\text{-}P}$ 106.6 Hz, $J_{P\text{-}H}$ 16.6 Hz), –13.2 (s), –12.8 (s), –2.47 (s), 54.6 (s), 63.2 (d, $^{1}J_{P\text{-}H}$ 195.9 Hz), 65.6 (s), 73.4 (d, $^{1}J_{P\text{-}H}$ 160.4 Hz, *E*- C=**P**H), 74.0 (d, $^{1}J_{P\text{-}H}$ 153.4 Hz, *Z*- C=**P**H).

The yellow solution turned colourless after stirring for 18 h and was dried *in vacuo* to afford a colourless oil.

^{1}H NMR (C_6D_6): δ_H 0.17 (s, 15H), 0.25 (s, 25H), 0.28 (s, 27H), 5.95 (s, 1H), 6.41 (t, 1.5H, $^{3}J_{H\text{-}H}$ 8.36 Hz), 6.62 (t, 6H, $^{3}J_{H\text{-}H}$ 7.96 Hz), 6.81 (d, 2H, $^{3}J_{H\text{-}H}$ 7.96 Hz), 6.95 (m, 6H), 7.65 (m, 2H), 7.92 (m, 2.5H), 8.03 (d, 3H, $^{3}J_{H\text{-}H}$ 8.47 Hz), 8.10 (s, 1.5H), 8.23 (br, 2.5H), 12.5 (br, 4H).

^{31}P NMR (C_6D_6): δ_P –30.8 (s), –30.4 (d, $J_{P\text{-}P}$ 15.3 Hz), –26.9 (s), –26.2 (s), –19.1 (s), –14.7 (dd, $J_{P\text{-}P}$ 15.3 Hz, $^{1}J_{P\text{-}H}$ 737.4 Hz), –13.2 (d, $^{1}J_{P\text{-}H}$ 704.6 Hz), –10.7 (s), –10.0 (s), –2.73 (dt, $^{1}J_{P\text{-}H}$ 700.9 Hz, $J_{P\text{-}H}$ 8.61 Hz), 54.6 (s).

Attempted synthesis of *E*/*Z*-C_6H_4(1-CO($SiMe_3$)=PH)(3-CN) (*E*/*Z*-42-3-CN)

Method A

To a THF solution of $HP(SiMe_3)_2$ (0.350 g, 1.97 x 10^{-3}) at −78 °C was added C_6H_4(1-COCl)(3-CN) (0.325 g, 1.97 x 10^{-3}) in THF and the mixture was stirred for 15 min, resulting in a

colourless solution that was warmed to ambient temperature over 45 min; an aliquot was dried *in vacuo* to afford a yellow oil.

^{1}H NMR (C_6D_6): δ_H –0.39 (s, 3H), –0.29 (s, 1H), –0.09 (s, 1.5H), 0.01 (s, 1H), 0.08 (d, 1H, $^{3}J_{H\text{-}P}$ 3.99 Hz), 0.12 (s, 1H), 0.19 (d, 5.5H, $^{3}J_{H\text{-}P}$ 5.11 Hz), 0.21 (s, 1H), 0.26 (s, 15.5H), 0.31 (s, 2H), 3.67 (d, 2H, $^{1}J_{H\text{-}P}$ 219.5 Hz, P**H**$_2$), 6.44 (t, 11H, $^{3}J_{H\text{-}H}$ 7.33 Hz), 6.57 (t, 2H, $^{3}J_{H\text{-}H}$ 7.33 Hz), 6.65 (t, 5H, $^{3}J_{H\text{-}H}$ 8.33 Hz), 6.85 (d, 11H, $^{3}J_{H\text{-}H}$ 7.00 Hz), 6.95 (m, 3H), 6.99 (m, 4H), 7.41 (d, 1.5H, $^{3}J_{H\text{-}H}$ 7.33 Hz), 7.49 (d, 11H, $^{3}J_{H\text{-}H}$ 8.03 Hz), 7.62 (s, 1H), 7.66 (d, 2.5H, $^{3}J_{H\text{-}H}$ 8.17 Hz), 7.84 (d, 1H, $^{3}J_{H\text{-}H}$ 8.03 Hz), 7.92 (d, 2H, $^{3}J_{H\text{-}H}$ 8.03 Hz), 7.97 (s, 1.5H), 8.05 (s, 1H), 8.10 (s, 1H).

^{31}P NMR (C_6D_6): δ_P –186.2 (d, $J_{P\text{-}P}$ 209.7 Hz), –133.5 (dt, $J_{P\text{-}P}$ 209.7 Hz, $J_{P\text{-}H}$ 15.8 Hz), –116.1 (ddd, $^{1}J_{P\text{-}P}$ 70.7 Hz, $^{1}J_{P\text{-}H}$ 175.4 Hz, $J_{P\text{-}H}$ 10.7 Hz), –109.8 (t, $^{1}J_{P\text{-}H}$ 219.5 Hz, **P**H$_2$), –103.4 (2nd order), –97.3 (2nd order), –84.9 (ddd, $^{1}J_{P\text{-}P}$ 70.7 Hz, $^{1}J_{P\text{-}H}$ 186.0 Hz, $J_{P\text{-}H}$ 13.7 Hz), –65.3 (m), –62.8 (m), –21.7 (s), 14.3 (m), 47.6 (s), 54.3 (s), 54.8 (s), 65.7 (s), 73.4 (d, $^{1}J_{P\text{-}H}$ 160.3 Hz, *E*- C=**P**H), 74.1 (d, $^{1}J_{P\text{-}H}$ 153.8 Hz, *Z*- C=**P**H).

The solution was stirred for 18 h and dried *in vacuo* to afford a yellow oil.

^{1}H NMR (C_6D_6): δ_H –0.39 (s, 4H), –0.09 (s, 3.5H), 0.01 (s, 3H), 0.08 (s, 2.5H), 0.12 (s, 3H), 0.18 (s, 6H), 0.19 (s, 4H), 0.26 (s, 27H), 0.28 (s, 39H), 2.75 (2nd order, 1H), 3.67 (d, 2H, $^{1}J_{H\text{-}P}$ 219.5 Hz, P**H**$_2$), 4.55 (2nd order, 1H), 4.68 (d, 1H, $^{1}J_{H\text{-}P}$ 153.8 Hz, *Z*- C=P**H**), 4.88 (d, 1H, $^{1}J_{H\text{-}P}$ 160.3 Hz, *E*- C=P**H**), 6.45 (t, 15H, $^{3}J_{H\text{-}H}$ 7.82 Hz), 6.57 (t, 2H, $^{3}J_{H\text{-}H}$ 7.69 Hz), 6.66 (t, 10H, $^{3}J_{H\text{-}H}$ 8.76 Hz), 6.86 (d, 13H, $^{3}J_{H\text{-}H}$ 7.82 Hz), 6.98 (m, 10H), 7.13 (d, 1H, $^{3}J_{H\text{-}H}$ 7.82 Hz), 7.34 (s, 1H), 7.41 (d, 2H, $^{3}J_{H\text{-}H}$ 8.29 Hz), 7.49 (d, 13H, $^{3}J_{H\text{-}H}$ 8.29Hz), 7.62 (s, 1H), 7.66 (d, 4H, $^{3}J_{H\text{-}H}$ 7.85 Hz), 7.70 (s, 9H), 7.84 (d, 2H, $^{3}J_{H\text{-}H}$ 8.87 Hz), 7.92 (d, 3H, $^{3}J_{H\text{-}H}$ 8.87 Hz), 7.97 (s, 3H), 8.05 (s, 1H), 8.08 (s, 1H), 8.10 (s, 2H), 8.15 (s, 1H).

^{31}P NMR (C_6D_6): δ_P –197.0 (m), –186.2 (d, $J_{P\text{-}P}$ 209.7 Hz), –133.5 (dt, $J_{P\text{-}P}$ 209.7 Hz, $J_{P\text{-}H}$ 15.8 Hz), –118.9 (d, $J_{P\text{-}P}$ 93.4 Hz), –116.1 (ddd, $^{1}J_{P\text{-}P}$ 70.7 Hz, $^{1}J_{P\text{-}H}$ 175.4 Hz, $J_{P\text{-}H}$ 10.7 Hz), –109.8 (t, $^{1}J_{P\text{-}H}$ 219.5 Hz, **P**H$_2$), –103.4 (2nd order), –97.3 (2nd order), –88.2 (m), –84.9 (ddd, $^{1}J_{P\text{-}P}$ 70.7 Hz, $^{1}J_{P\text{-}H}$ 186.0 Hz, $J_{P\text{-}H}$ 13.7 Hz), –83.6 (d, $J_{P\text{-}P}$ 93.4 Hz),–65.3 (m), –26.3 (s), –21.7 (s), –19.2 (s), –13.3 (d, $^{1}J_{P\text{-}H}$ 702.9 Hz), 47.6 (s), 54.3 (s), 54.8 (s), 65.7 (s), 73.4 (d, $^{1}J_{P\text{-}H}$ 160.3 Hz, *E*- C=**P**H), 74.1 (d, $^{1}J_{P\text{-}H}$ 153.8 Hz, *Z*- C=**P**H).

Method B

To a THF solution of HP(SiMe$_3$)$_2$ (0.400 g, 2.47 x 10^{-3} mol) at ambient temperature was added C_6H_4(1-COCl)(3-CN) (0.372 g, 2.47 x 10^{-3} mol) in THF, resulting in the rapid formation of a yellow solution within 5 min; an aliquot was dried *in vacuo* to afford a yellow oil.

^{1}H NMR (C_6D_6): δ_H 0.11 (s, 1H), 0.18 (s, 10H), 0.25 (s, 3H), 0.26 (s, 15H), 3.67 (d, 2H, $^{1}J_{H\text{-}P}$ 219.5 Hz, PH_2), 6.47 (t, 11H, $^{3}J_{H\text{-}H}$ 8.02 Hz), 6.67 (m, 4H), 6.87 (d, 10H, $^{3}J_{H\text{-}H}$ 8.12 Hz), 7.00 (m, 4H), 7.43 (d, 1H, $^{3}J_{H\text{-}H}$ 8.09 Hz), 7.51 (d, 10H, $^{3}J_{H\text{-}H}$ 8.09Hz), 7.66 (d, 1H, $^{3}J_{H\text{-}H}$ 8.09 Hz), 7.72 (s, 7H), 7.85 (d, 1H, $^{3}J_{H\text{-}H}$ 8.51 Hz), 7.92 (d, 1.5H, $^{3}J_{H\text{-}H}$ 8.09 Hz), 7.97 (s, 0.5H), 8.03 (d, 1.2H, $^{3}J_{H\text{-}H}$ 8.09 Hz), 8.05 (s, 0.5H), 8.10 (s, 1H), 8.21 (s, 1H).

^{31}P NMR (C_6D_6): δ_P −109.8 (t, $^{1}J_{P\text{-}H}$ 216.6 Hz, **P**H_2), −26.0 (s), −19.0 (s), −13.3 (d, $^{1}J_{P\text{-}H}$ 700.8 Hz), −10.9 (d, $^{1}J_{P\text{-}H}$ 744.5 Hz), −9.91 (s), 54.8 (s), 65.7 (s).

The solution was stirred for 18 h and was dried *in vacuo* to afford a yellow oil.

^{1}H NMR (C_6D_6): δ_H 0.18 (s, 9H), 0.25 (s, 3H), 0.26 (s, 18H), 3.67 (d, 2H, $^{1}J_{H\text{-}P}$ 219.5 Hz, PH_2), 6.46 (t, 18H, $^{3}J_{H\text{-}H}$ 8.05 Hz), 6.59 (t, 2H, $^{3}J_{H\text{-}H}$ 8.15 Hz), 6.67 (t, 6H, $^{3}J_{H\text{-}H}$ 8.05 Hz), 6.87 (d, 16H, $^{3}J_{H\text{-}H}$ 7.75 Hz), 7.00 (m, 7H), 7.42 (d, 1.5H, $^{3}J_{H\text{-}H}$ 7.89 Hz), 7.51 (d, 16H, $^{3}J_{H\text{-}H}$ 7.89 Hz), 7.66 (d, 2H, $^{3}J_{H\text{-}H}$ 8.29 Hz), 7.72 (s, 12H), 7.85 (d, 2H, $^{3}J_{H\text{-}H}$ 8.29 Hz), 7.92 (d, 2H, $^{3}J_{H\text{-}H}$ 8.08 Hz), 7.97 (s, 1H), 8.02 (d, 1.5H, $^{3}J_{H\text{-}H}$ 7.89 Hz), 8.05 (s, 1H), 8.10 (s, 1H), 8.20 (s, 1.2H).

^{31}P NMR (C_6D_6): δ_P −109.8 (t, $^{1}J_{P\text{-}H}$ 216.6 Hz, **P**H_2), −13.3 (d, $^{1}J_{P\text{-}H}$ 700.8 Hz), −10.9 (d, $^{1}J_{P\text{-}H}$ 744.5 Hz), 54.8 (s), 65.7 (s).

The crude product was washed with pentane and filtered; an orange solid was dried *in vacuo*, and a yellow solid was afforded from reduced pressure solvent removal of the filtrate.

Orange solid:

^{1}H NMR (C_6D_6): δ_H 6.39 (t, 3.5H, $^{3}J_{H\text{-}H}$ 8.19 Hz), 6.61 (t, 3.5H, $^{3}J_{H\text{-}H}$ 7.94 Hz), 6.80 (d, 3H, $^{3}J_{H\text{-}H}$ 7.81 Hz), 6.93 (m, 3.5H), 7.46 (d, 3H, $^{3}J_{H\text{-}H}$ 8.17 Hz), 7.62 (m, 3H), 7.68 (2H), 7.81 (br), 7.91 (s, 1H), 7.99 (d, 1.5H, $^{3}J_{H\text{-}H}$ 7.63 Hz), 8.05 (br, 1H), 8.18 (s, 1H).

^{31}P NMR (C_6D_6): δ_P –109.9 (t, $^{1}J_{P\text{-}H}$ 219.8 Hz, **P**H_2), 54.5 (s), 65.6 (s).

Yellow solid:

^{1}H NMR (C_6D_6): δ_H 6.39 (t, 1H, $^{3}J_{H\text{-}H}$ 7.93 Hz, C_6H_4(1-COCl)(3-CN)), 6.81 (d, 1H, $^{3}J_{H\text{-}H}$ 8.03 Hz, C_6H_4(1-COCl)(3-CN)), 7.47 (d, 1H, $^{3}J_{H\text{-}H}$ 8.24 Hz, C_6H_4(1-COCl)(3-CN)), 7.69 (s, 1H, C_6H_4(1-COCl)(3-CN)).

^{31}P NMR (C_6D_6): δ_P –109.9 (t, $^{1}J_{P\text{-}H}$ 219.8 Hz, **P**H_2).

Attempted synthesis of *E*/*Z*-C_6H_4(1-CO($SiMe_3$)=P$SiMe_3$)(4-CN) (*E*/*Z*-39-4-CN)

Method A

To a THF solution of $P(SiMe_3)_3$ (0.0660 g, 2.64 x 10^{-4} mol) at −78 °C was added C_6H_4(1-COCl)(4-CN) (0.0437 g, 2.64 x 10^{-4} mol) in THF and the mixture was stirred for 15 min,

resulting in a colourless solution that turned yellow when it was allowed to warm to ambient temperature over 45 min; an aliquot was *dried in vacuo* to afford an orange oil.

^{1}H NMR (C_6D_6): δ_H –0.29 (s, 5.5H), –0.03 (s, 5.5H), 0.12 (br, 8H), 0.20 (s, 6.5H), 0.23 (s, 6.5H), 0.25 (s, 36H), 0.28 (s, 9.5H), 0.30 (br, 20H), 0.31 (s, 13.5H), 6.48 (d, 2H, $^{3}J_{H\text{-}H}$ 8.06 Hz), 6.81 (t, 5H, $^{3}J_{H\text{-}H}$ 7.23 Hz), 6.98 (d, 6.5H, $^{3}J_{H\text{-}H}$ 7.71 Hz), 7.63 (m, 2H), 7.71 (m, 3H), 7.87 (d, 2.5H, $^{3}J_{H\text{-}H}$ 8.28 Hz), 7.92 (d, 4H, $^{3}J_{H\text{-}H}$ 7.36 Hz), 8.07 (s, 1H), 8.10 (s, 2H), 8.15 (d, 2H, $^{3}J_{H\text{-}H}$ 7.36 Hz), 8.68 (s, 1H).

^{31}P NMR (C_6D_6): δ_P –252.1 (m, **P**$(SiMe_3)_3$), –236.8 (dm, $^{1}J_{P\text{-}H}$ 190.7 Hz, H**P**$(SiMe_3)_2$), –24.7 (s), –9.19 (s), –2.47 (s), 63.2 (d, $^{1}J_{P\text{-}H}$ 190.9 Hz), 73.7 (m), 143.9 (s), 145.6 (s), 151.5 (s), 153.2 (s), 167.9 (s), 170.8 (s), 176.4 (s), 203.6 (s), 233.2 (s).

The solution was stirred for 18 h and dried *in vacuo* to afford a yellow oil.

^{1}H NMR (C_6D_6): δ_H –0.41 (s, 1H), –0.31 (s, 2H), –0.02 (s, 3H), 0.11 (d, 3.5H, $^{3}J_{H\text{-}P}$ 5.12 Hz), 0.17 (s, 10H), 0.25 (s, 52H), 0.28 (s, 15H), 0.32 (s, 2H), 6.77 (t, 2H, $^{3}J_{H\text{-}H}$ 6.55 Hz), 6.82 (br, 1H), 6.90 (d, 2H, $^{3}J_{H\text{-}H}$ 8.35 Hz), 6.94 (d, 11H, $^{3}J_{H\text{-}H}$ 8.01 Hz), 7.07 (t, 3H, $^{3}J_{H\text{-}H}$ 7.75 Hz), 7.47 (d, 1H, $^{3}J_{H\text{-}H}$ 8.31 Hz), 7.55 (d, 1H, $^{3}J_{H\text{-}H}$ 8.69 Hz), 7.73 (d, 10H, $^{3}J_{H\text{-}H}$ 8.2 Hz), 7.87 (d, 1.5H, $^{3}J_{H\text{-}H}$ 8.02 Hz).

^{31}P NMR (C_6D_6): δ_P –119.8 (d, $^{1}J_{P\text{-}P}$ 90.5 Hz), –115.9 (d, $^{1}J_{P\text{-}P}$ 71.2 Hz), –108.9 (m), –108.2 (s), –104.5 (2nd order), –98.6 (d, $^{1}J_{P\text{-}H}$ 180.1 Hz), –97.1 (2nd order), –84.4 (d, $^{1}J_{P\text{-}P}$ 71.2 Hz), –83.1 (d, $^{1}J_{P\text{-}P}$ 90.5 Hz), –25.4 (s), –13.4 (d, $^{1}J_{P\text{-}H}$ 695.6 Hz), –11.1 (d, $^{1}J_{P\text{-}H}$ 734.5 Hz), –9.45 (s), –2.66 (s), 2.40 (s), 6.93 (s), 56.1 (s), 70.0 (s), 78.4 (d, $^{1}J_{P\text{-}H}$ 160.6 Hz, *E*- C=**P**H), 81.1 (d, $^{1}J_{P\text{-}H}$ 155.5 Hz, *Z*- C=**P**H), 114.2 (s), 177.3 (s), 239.5 (s).

Method B

To a THF solution of $P(SiMe_3)_3$ (0.0420 g, 1.68 x 10^{-4} mol) at ambient temperature was added C_6H_4(1-COCl)(4-CN) (0.0278 g, 1.68 x 10^{-4} mol) in THF, resulting in a bright yellow solution within 5 min; an aliquot was dried *in vacuo* to afford an orange oil.

^{1}H NMR (C_6D_6): δ_H –0.31 (s, 7H), –0.19 (s, 2H), 0.02 (s, 4.5H), 0.04 (s, 3H), 0.12 (s, 2.5H), 0.14 (s, 7H), 0.18 (s, 5H), 0.25 (s, 30H), 0.29 (s, 9H), 0.32 (d, 9H, $^{3}J_{H\text{-}H}$ 3.57 Hz), 0.33 (s, 5H), 0.35 (s, 3H), 6.81 (s, 1.5H), 6.87 (d, 1.5H, $^{3}J_{H\text{-}H}$ 7.95 Hz), 6.92 (d, 3H, $^{3}J_{H\text{-}H}$ 7.65 Hz), 6.97 (d, 2H, $^{3}J_{H\text{-}H}$ 8.96 Hz), 7.03 (d, 3.5H, $^{3}J_{H\text{-}H}$ 8.25Hz), 7.38 (d, 1H, $^{3}J_{H\text{-}H}$ 8.81 Hz), 7.45 (d, 1H, $^{3}J_{H\text{-}H}$ 7.37 Hz), 7.54 (d, 2.5H, $^{3}J_{H\text{-}H}$ 7.80 Hz), 7.60 (d, 1.5H, $^{3}J_{H\text{-}H}$ 7.80 Hz), 7.73 (d, 2H, $^{3}J_{H\text{-}H}$ 7.80 Hz), 8.02 (d, 1H, $^{3}J_{H\text{-}H}$ 8.81 Hz).

^{31}P NMR (C_6D_6): δ_P –252.1 (m, **P**($SiMe_3$)$_3$), –236.8 (dm, $^1J_{P-H}$ 190.7 Hz, H**P**($SiMe_3$)$_2$), –30.2 (s), –24.6 (s), –16.7 (d, J_{P-P} 34.9 Hz), –13.5 (d, $^1J_{P-H}$ 694.3 Hz), –9.11 (s), –2.52 (s), –0.89 (d, J_{P-P} 34.9 Hz), 64.2 (d, $^1J_{P-H}$ 190.9 Hz), 109.8 (s), 114.7 (s), 172.2 (s), 178.1 (s).

The solution was stirred for 18 h and dried *in vacuo* to afford a yellow oil.

^{1}H NMR (C_6D_6): δ_H –0.31 (s, 1.5H), 0.02 (s, 2.5H), 0.17 (s, 17H), 0.24 (s, 51H), 0.33 (s, 7H), 6.81 (s, 1H), 6.88 (d, 4.5H, $^3J_{H-H}$ 8.09 Hz), 6.92 (d, 7H, $^3J_{H-H}$ 8.27 Hz), 7.54 (d, 1.5H, $^3J_{H-H}$ 7.97 Hz), 7.73 (d, 7H, $^3J_{H-H}$ 7.87 Hz), 7.88 (d, 4H, $^3J_{H-H}$ 7.87 Hz).

^{31}P NMR (C_6D_6): δ_P –115.9 (d, $^1J_{P-P}$ 70.9 Hz), –108.3 (t, $^1J_{P-H}$ 218.2 Hz, **P**H_2) –104.5 (2nd order), –98.6 (m), –97.1 (s), –95.5 (s), –84.4 (d, $^1J_{P-P}$ 70.9 Hz), –30.7 (s), –25.9 (s), –13.2 (d, $^1J_{P-H}$ 694.3 Hz), –10.9 (s), –9.75 (s), –2.83 (s), 2.36 (s), 6.88 (s).

Attempted synthesis of *E*/*Z*-C_6H_4(1-COSiMe_3)=PSiMe_3)(4-CO_2Me) (*E*/*Z*-39-4-CO_2Me)

Method A

To a THF solution of P($SiMe_3$)$_3$ (0.058 g, 2.32 x 10^{-4} mol) at −78 °C was added C_6H_4(1-COCl)(4-CO_2Me) (0.0461 g, 0.0660 g, 2.32 x 10^{-4} mol) in THF and the mixture was stirred for 15 min, resulting in a colourless solution that turned yellow when it was allowed to warm to ambient temperature over 45 min; an aliquot was dried *in vacuo* to afford a yellow oil.

^{1}H NMR (C_6D_6): δ_H –0.19 (s, 4H), –0.12 (s, 8H), –0.10 (s, 19H), –0.07 (s, 14H), –0.02 (s, 4H), 0.12 (d, 6.5H, $^3J_{H-P}$ 5.24 Hz), 0.18 (s, 5.5H), 0.21 (br, 15H), 0.23 (s, 4H), 0.25 (s, 5H), 0.28 (s, 25H), 0.41 (d, 7H, $^3J_{H-P}$ 3.90 Hz), 0.49 (d, 14.5H, $^3J_{H-P}$ 4.84 Hz), 0.57 (s, 14H), 3.30 (s, 5H), 3.33 (s, 4.5H), 3.38 (s, 2H), 3.42 (s, 3.5H), 3.45 (s, 5H), 3.46 (s, 2.5H), 3.47 (s, 2.5H), 3.50 (s, 5.5H), 4.71 (t, 2H, *J* 6.73 Hz), 6.70 (d, 1.5H, $^3J_{H-H}$ 6.86 Hz), 6.96 (br, 1.5H), 7.29 (d, 5H, $^3J_{H-H}$ 7.98 Hz), 7.35 (d, 1.5H, $^3J_{H-H}$ 8.80 Hz), 7.43 (d, 2H, $^3J_{H-H}$ 7.98 Hz), 7.55 (d, 2H, $^3J_{H-H}$ 7.98 Hz), 7.63 (br, 2H), 7.70 (d, 2.5H, $^3J_{H-H}$ 8.14 Hz), 7.78 (d, 2H, $^3J_{H-H}$ 8.58 Hz), 7.80 (d, 5H, $^3J_{H-H}$ 8.14 Hz), 7.85 (d, 5.5H, $^3J_{H-H}$ 7.82 Hz), 7.91 (br, 6H), 7.95 (d, 2H, $^3J_{H-H}$ 7.82 Hz), 8.03 (d, 4H, $^3J_{H-H}$ 7.82 Hz), 8.10 (d, 4H, $^3J_{H-H}$ 7.82 Hz), 8.15 (s, 2H), 8.20 (d, 4.5H, $^3J_{H-H}$ 8.14 Hz), 8.51 (d, 1H, $^3J_{H-H}$ 8.05 Hz).

^{31}P NMR (C_6D_6): δ_P –124.4 (d, $^2J_{P-P}$ 189.9 Hz), –95.9 (d, J_{P-P} 59.1 Hz), –82.9 (d, J_{P-P} 52.8 Hz), –82.4 (d, $^2J_{P-P}$ 189.9 Hz), –81.2 (s), –58.1 (d, J_{P-P} 89.6 Hz), –52.9 (d, J_{P-P} 52.8 Hz), –44.1 (dd, J_{P-P} 59.1 Hz, $^1J_{P-H}$ 174.8 Hz), –28.7 (d, J_{P-P} 91.7 Hz), –24.7 (s), –18.3 (s), –13.5 (d, $^1J_{P-H}$ 692.8 Hz), –10.5 (d, $^1J_{P-H}$ 213.7 Hz), –9.17 (s), –5.46 (d, $^1J_{P-P}$ 91.7 Hz), 19.3 (d, J_{P-P} 89.6 Hz), 56.4 (s), 68.3 (s), 142.5 (s, *Z*- C=**P**), 146.5 (s, *E*- C=**P**), 175.2 (s).

The solution was stirred for 18 h and dried *in vacuo* to afford a yellow oil.

^{1}H NMR (C_6D_6): δ_H –0.10 (s, 11H), –0.06 (s, 12.5H), 0.18 (s, 21H), 0.25 (s, 28H), 0.28 (s, 204H), 0.33 (s, 21H), 3.25 (s, 2.5H), 3.29 (s, 3.5H), 3.33 (s, 4H), 3.36 (s, 3.5H), 6.87 (d, $^{1}J_{H\text{-}P}$ 692.8 Hz), 8.03 (d, 41H, $^{3}J_{H\text{-}H}$ 8.32 Hz), 8.10 (d, 41H, $^{3}J_{H\text{-}H}$ 8.32 Hz).

^{31}P NMR (C_6D_6): δ_P –124.4 (d, $^{2}J_{P\text{-}P}$ 189.9 Hz), –82.9 (d, $J_{P\text{-}P}$ 52.8 Hz), –82.4 (d, $^{2}J_{P\text{-}P}$ 189.9 Hz), –81.2 (s), –57.7 (s), –56.4 (s), –52.9 (d, $J_{P\text{-}P}$ 52.8 Hz), 24.6 (s), –18.3 (s), –13.5 (d, $^{1}J_{P\text{-}H}$ 692.8 Hz), –11.3 (m), –10.5 (d, $^{1}J_{P\text{-}H}$ 213.7 Hz), –9.11 (s), –2.04 (s), 56.4 (s), 64.2 (s), 75.8 (s), 78.2 (s), 121.6 (s), 146.5 (s), 175.2 (s), 236.9 (s).

Method B

To a THF solution of $P(SiMe_3)_3$ (0.0450 g, 1.80 x 10^{-4}) at ambient temperature was added C_6H_4(1-COCl)(4-CO_2Me) (0.0357 g, 1.80 x 10^{-4}) in THF, resulting in the formation of a yellow solution within 5 min; an aliquot was dried *in vacuo* to afford a yellow oil.

^{1}H NMR (C_6D_6): δ_H –0.19 (s, 2.5H), –0.12 (s, 6H), –0.10 (s, 12H), –0.07 (s, 9H), 0.11 (s, 2H), 0.13 (s, 2H), 0.18 (br, 3.5H), 0.21 (br, 10.5H), 0.23 (s, 3H), 0.25 (s, 6H), 0.28 (s, 9H), 0.49 (d, 9H, $^{3}J_{H\text{-}P}$ 4.79 Hz), 0.57 (s, 9H), 0.58 (s, 3H), 3.30 (s, 3H), 3.33 (s, 3H), 3.38 (s, 1H), 3.44 (s, 1.5H), 3.47 (br, 2.5H), 3.50 (s, 3.5H), 6.70 (d, 1H, $^{3}J_{H\text{-}H}$ 6.90 Hz), 6.95 (br, 1H), 7.30 (d, 3H, $^{3}J_{H\text{-}H}$ 7.79 Hz), 7.43 (d, 1H, $^{3}J_{H\text{-}H}$ 8.89 Hz), 7.55 (d, 1H, $^{3}J_{H\text{-}H}$ 8.31 Hz), 7.63 (br, 1H), 7.81 (d, 2.5H, $^{3}J_{H\text{-}H}$ 7.96 Hz), 7.85 (d, 3H, $^{3}J_{H\text{-}H}$ 7.96 Hz), 7.91 (br, 4H), 8.04 (s, 1H), 8.09 (s, 1H), 8.11 (s, 1H), 8.15 (s, 2H), 8.20 (d, 3H, $^{3}J_{H\text{-}H}$ 8.22 Hz), 8.51 (d, 1H, $^{3}J_{H\text{-}H}$ 7.97 Hz).

^{31}P NMR (C_6D_6): δ_P –124.4 (d, $^{2}J_{P\text{-}P}$ 190.5 Hz), –98.3 (m), –96.4 (d, $J_{P\text{-}P}$ 58.7 Hz), –82.9 (d, $J_{P\text{-}P}$ 53.4 Hz), –82.4 (d, $^{2}J_{P\text{-}P}$ 190.5 Hz), –81.3 (s), –52.9 (d, $J_{P\text{-}P}$ 53.4 Hz), –44.1 (dd, $J_{P\text{-}P}$ 58.7 Hz, $J_{P\text{-}H}$ 174.9 Hz), –24.6 (s), –18.3 (s), –13.5 (d, $^{1}J_{P\text{-}H}$ 689.6 Hz), –10.5 (d, $^{1}J_{P\text{-}H}$ 212.7 Hz), –2.06 (s), 142.5 (s, *Z*- C=**P**), 146.5 (s, *E*- C=**P**).

The yellow solution was stirred for 18 h and dried *in vacuo* to afford a yellow oil.

^{1}H NMR (C_6D_6): δ_H –0.19 (s, 2.5H), –0.11 (s, 5H), –0.07 (s, 4.5H), 0.11 (br, 8H), 0.18 (br, 7H), 0.21 (br, 10.5H), 0.25 (s, 8H), 0.32 (s, 6H), 0.49 (d, 4.5H, $^{3}J_{H\text{-}P}$ 4.79 Hz), 0.56 (s, 3H), 0.58 (s, 1.5H), 3.31 (s, 1H), 3.34 (s, 1H), 3.38 (s, 1H), 3.45 (s, 15H), 3.47 (br, 2.5H), 3.49 (s, 2H), 3.50 (s, 2.5H), 6.96 (m, 1H), 7.29 (d, 1H, $^{3}J_{H\text{-}H}$ 7.79 Hz), 7.63 (br, 1.5H), 7.81 (d, 2H, $^{3}J_{H\text{-}H}$ 7.96 Hz), 7.85 (d, 2H, $^{3}J_{H\text{-}H}$ 7.96 Hz), 8.01 (d, 9H, $^{3}J_{H\text{-}H}$ 8.45 Hz), 8.10 (d, 9H, $^{3}J_{H\text{-}H}$ 8.45 Hz), 8.15 (s, 1H), 8.19 (s, 1H).

^{31}P NMR (C_6D_6): δ_P –124.4 (d, $^{2}J_{P\text{-}P}$ 190.5 Hz), –98.3 (m), –82.9 (d, $J_{P\text{-}P}$ 53.4 Hz), –82.4 (d, $^{2}J_{P\text{-}P}$ 190.5 Hz), –81.3 (s), –52.9 (d, $J_{P\text{-}P}$ 53.4 Hz), –24.7 (s), –13.5 (d, $^{1}J_{P\text{-}H}$ 689.6 Hz), –10.5 (s), –9.18 (s), –2.06 (s), 98.2 (s), 121.5 (s), 146.5 (s), 175.2 (s), 236.9 (s).

Attempted synthesis of *E*/*Z*-C_6H_4(1-CO($SiMe_3$)=P$SiMe_3$)(4-COCl) (*E*/*Z*-39-4-COCl)

Method A

To a THF solution of $P(SiMe_3)_3$ (0.129 g, 5.16 x 10^{-4} mol) at −78 °C was added C_6H_4(1,4-$COCl)_2$ (0.105 g, 5.16 x 10^{-4} mol) in THF and the mixture was stirred for 15 min, resulting in a bright yellow solution that turned brown when it was allowed to warm to ambient temperature over 45 min; an aliquot was dried *in vacuo* to afford a brown oil.

^{1}H NMR (C_6D_6): δ_H −0.27 (s, 2.5H), −0.19 (s, 3H), −0.18 (s, 9H), −0.08 (s, 7H), 0.07 (d, 6H, $^3J_{H\text{-}P}$ 4.92 Hz), 0.11 (s, 9H), 0.18 (s, 13H), 0.25 (s, 9H), 0.28 (s, 21H), 0.46 (d, 9H, $^3J_{H\text{-}P}$ 4.75 Hz), 0.54 (s, 6H), 6.96 (br, 2.5H), 7.46 (s, 1.5H), 7.59 (d, 3H, $^3J_{H\text{-}H}$ 8.14 Hz), 7.63 (m, 3H), 7.73 (d, 5H, $^3J_{H\text{-}H}$ 8.04 Hz), 7.87 (d, 6H, $^3J_{H\text{-}H}$ 8.14 Hz), 7.96 (d, 3H, $^3J_{H\text{-}H}$ 8.04 Hz), 8.06 (d, 3H, $^3J_{H\text{-}H}$ 8.04 Hz), 8.13 (s, 2H).

^{31}P{^{1}H} NMR (C_6D_6): δ_P −82.1 (d, $J_{P\text{-}P}$ 53.4 Hz), −74.2 (s), −50.6 (d, $J_{P\text{-}P}$ 53.4 Hz), −24.7 (s), −3.90 (s).

The solution was stirred for 18 h and dried *in vacuo* to afford a brown solid.

^{1}H NMR (C_6D_6): δ_H −0.27 (s, 5H), −0.19 (d, 5H, $^3J_{H\text{-}P}$ 3.96 Hz), 0.06 (s, 4H), 0.11 (s, 5.5H), 0.17 (br, 4.5H), 0.21 (s, 4.5H), 0.24 (s, 8.5H), 0.27 (s, 26H), 7.03 (d, 1H, $^3J_{H\text{-}H}$ 7.94 Hz), 7.08 (d, 1H, $^3J_{H\text{-}H}$ 8.82 Hz), 7.57 (br, 2.5H), 7.67 (d, 2.5H, $^3J_{H\text{-}H}$ 8.36 Hz), 7.73 (d, 5H, $^3J_{H\text{-}H}$ 7.39 Hz), 7.87 (d, 3H, $^3J_{H\text{-}H}$ 8.24 Hz), 7.96 (d, 3H, $^3J_{H\text{-}H}$ 8.24 Hz), 8.12 (s, 2H), 8.28 (d, 1H, $^3J_{H\text{-}H}$ 7.75 Hz).

^{31}P NMR (C_6D_6): δ_P −114.5 (ddd, $^1J_{P\text{-}P}$ 70.9 Hz, $^1J_{P\text{-}H}$ 172.1 Hz, $J_{P\text{-}H}$ 10.6 Hz), −111.4 (d, $J_{P\text{-}P}$ 154.0 Hz), −107.6 (2nd order), −98.0 (2nd order), −95.4 (d, $J_{P\text{-}P}$ 59.5 Hz), −83.9 (ddd, $^1J_{P\text{-}P}$ 70.9 Hz, $^1J_{P\text{-}H}$ 183.8 Hz, $J_{P\text{-}H}$ 11.2 Hz), −82.1 (d, $J_{P\text{-}P}$ 53.4 Hz), −69.3 (d, $J_{P\text{-}P}$ 154.0 Hz), −50.6 (d, $J_{P\text{-}P}$ 53.4 Hz), −43.0 (dd, $J_{P\text{-}P}$ 59.5 Hz, $^1J_{P\text{-}H}$ 176.4 Hz), −30.3 (s), −26.5 (s), −24.8 (s), −18.8 (s), −18.3 (s), −13.5 (d, $^1J_{P\text{-}H}$ 690.7 Hz), −11.2 (d, $^1J_{P\text{-}H}$ 733.0 Hz), −9.20 (s).

Method B

To a THF solution of $P(SiMe_3)_3$ (0.050 g, 2.00 x 10^{-4} mol) at ambient temperature was added C_6H_4(1,4-$COCl)_2$ (0.041 g, 2.00 x 10^{-4} mol) in THF, resulting in a brown solution within 5 min; an aliquot was dried *in vacuo* to afford a brown oil.

^{1}H NMR (C_6D_6): δ_H −0.27 (s, 1.5H), −0.18 (s, 4.5H), −0.08 (s, 3.5H), 0.07 (d, 3H, $^3J_{H\text{-}P}$ 4.44 Hz), 0.12 (s, 8H), 0.18 (s, 9H), 0.25 (s, 4H), 0.28 (s, 9H), 0.46 (d, 5H, $^3J_{H\text{-}P}$ 4.73 Hz), 0.54 (s, 4H), 6.96-8.13 (m, 28H).

^{31}P NMR (C_6D_6): δ_P −95.4 (d, $J_{P\text{-}P}$ 59.5 Hz), −82.2 (d, $J_{P\text{-}P}$ 53.9 Hz), −74.2 (s), −50.7 (d, $J_{P\text{-}P}$ 53.9 Hz), −42.6 (d, $J_{P\text{-}P}$ 59.5 Hz), −24.7 (s), −12.9 (s).

The solution turned orange after it was stirred for 18 h and was dried *in vacuo* to afford an orange solid.

^{1}H NMR (C_6D_6): δ_H −0.27 (s, 5.5H), 0.06 (s, 5.5H), 0.11 (s, 4H), 0.17 (s, 9.5H), 0.18 (s, 3.5H), 0.21 (s, 4H), 0.24 (s, 9H), 0.28 (s, 40H), 7.03 (d, 2H, $^{3}J_{H\text{-}H}$ 7.80 Hz), 7.48 (s, 2H), 7.74 (d, 8H, $^{3}J_{H\text{-}H}$ 8.77 Hz), 7.87 (d, 6H, $^{3}J_{H\text{-}H}$ 7.80 Hz), 7.96 (d, 3.5H, $^{3}J_{H\text{-}H}$ 8.77 Hz), 8.01 (d, 3H, $^{3}J_{H\text{-}H}$ 8.04 Hz), 8.12 (s, 2H).

^{31}P NMR (C_6D_6): δ_P −114.5 (d, $^{1}J_{P\text{-}P}$ 70.8 Hz), −96.3 (s), −83.9 (d, $^{1}J_{P\text{-}P}$ 70.8 Hz), −30.6 (s), −30.2 ($J_{P\text{-}P}$ 14.9 Hz) −26.7 (s), −25.7 (s), −18.9 (s), −18.5 (s), −14.9 (dd, $^{1}J_{P\text{-}H}$ 731.3 Hz, $J_{P\text{-}P}$ 14.9 Hz), −13.3 (d, $^{1}J_{P\text{-}H}$ 694.7 Hz), −10.9 (s), −11.0 (s), −9.63 (s), −8.29 (s), −4.66 (s).

Attempted synthesis of *E*/*Z*-C_6H_4(1-CO(SiMe$_3$)=PH)(4-CN) (*E*/*Z*-42-4-CN)

Method A

To a THF solution of $HP(SiMe_3)_2$ (0.400 g, 2.25 x 10^{-3}) at −78 °C was added C_6H_4(1-COCl)(4-CN) (0.372 g, 2.25 x 10^{-3}) in THF and the mixture was stirred for 15 min, resulting in a pale yellow solution that turned bright yellow when it was allowed to warm to ambient temperature over 45 min; an aliquot was dried *in vacuo* to afford a yellow solid.

^{1}H NMR (C_6D_6): δ_H –0.40 (s, 7H), –0.13 (s, 3H), –0.10 (s, 6H), 0.03 (s, 4H), 0.08 (s, 3H), 0.13 (s, 4H), 0.17 (s, 5.5H), 0.19 (s, 8H), 0.26 (s, 36H), 0.28 (s, 4H), 2.87 (2nd order, 1H), 3.69 (d, 2H, $^{1}J_{H\text{-}P}$ 218.6 Hz, P**H**$_2$), 4.59 (2nd order, 1H), 4.75 (d, 1H, $^{1}J_{H\text{-}P}$ 153.6 Hz, *Z*- C=P**H**), 4.99 (d, 1H, $^{1}J_{H\text{-}P}$ 159.4 Hz, *E*- C=P**H**), 6.73 (d, 41H, $^{3}J_{H\text{-}H}$ 8.15 Hz), 6.79 (d, 3H, $^{3}J_{H\text{-}H}$ 7.62 Hz), 6.79 (t, 8H, $^{3}J_{H\text{-}H}$ 7.62 Hz), 6.97 (d, 9H, $^{3}J_{H\text{-}H}$ 7.62 Hz), 7.09 (d, 4.5H, $^{3}J_{H\text{-}H}$ 8.15 Hz), 7.22 (d, 4H, $^{3}J_{H\text{-}H}$ 8.32 Hz), 7.34 (d, 41H, $^{3}J_{H\text{-}H}$ 8.32 Hz), 7.49 (d, 4H, $^{3}J_{H\text{-}H}$ 7.62 Hz), 7.66 (d, 3H, $^{3}J_{H\text{-}H}$ 8.32 Hz), 7.75 (t, 10H, $^{3}J_{H\text{-}H}$ 8.15 Hz).

^{31}P NMR (C_6D_6): δ_P –131.4 (s), –131.3 (s), –130.1 (s), –129.9 (s), –129.8 (s), –129.5 (s), –128.7 (s), –128.4 (s), –128.2 (s), –119.8 (dd, $^{1}J_{P\text{-}P}$ 90.3 Hz, $^{1}J_{P\text{-}H}$ 167.2 Hz), –115.8 (ddd, $^{1}J_{P\text{-}P}$ 72.1 Hz, $^{1}J_{P\text{-}H}$ 173.3 Hz, $J_{P\text{-}H}$ 9.88 Hz), –108.9 (s), –108.2 (t, $^{1}J_{P\text{-}H}$ 218.6 Hz, **P**H$_2$), –104.4 (2nd order), –98.5 (m), –97.1 (2nd order), –91.1 (d, $^{1}J_{P\text{-}H}$ 170.5 Hz), –90.3 (d, $^{1}J_{P\text{-}H}$ 169.5 Hz), –84.4 (ddd, $^{1}J_{P\text{-}P}$ 72.1 Hz, $^{1}J_{P\text{-}H}$ 184.8 Hz, $J_{P\text{-}H}$ 11.9 Hz), –83.0 (d, $^{1}J_{P\text{-}P}$ 90.3 Hz), –81.2 (d, $J_{P\text{-}P}$ 85.3 Hz), –33.5 (s), –30.4 (s), –26.4 (s), –25.8 (s), –23.9 (d, $J_{P\text{-}P}$ 85.3 Hz), –22.1 (s), –16.5 (s), –16.3 (s), –13.6 (s), –12.6 (s), –9.35 (s), –9.20 (s), –8.67 (s), 21.3 (s), 25.0 (s), 26.6 (s), 48.2 (s), 48.8 (s), 49.5 (s), 51.2 (s), 51.9 (s), 55.7 (s), 56.1 (s), 70.1 (s), 78.5 (d, $^{1}J_{P\text{-}H}$ 159.4 Hz, *E*- C=**P**H), 81.2 (d, $^{1}J_{P\text{-}H}$ 153.6 Hz, *Z*- C=**P**H), 113.7 (s), 153.6 (s).

The solution was stirred for 18 h and dried *in vacuo* to afford an orange solid.

^{1}H NMR (C_6D_6): δ_H –0.44 (s, 12H), –0.32 (s, 1H), –0.27 (d, 2H, $^{3}J_{H\text{-}H}$ 4.39 Hz), –0.14 (s, 9H), –0.09 (s, 2H), –0.01 (s, 5.5H), 0.04 (s, 4H), 0.08 (s, 3H), 0.13 (s, 4H), 0.15 (s, 3H), 0.21 (s, 15H), 0.23 (s, 7H), 0.46 (s, 1H), 2.83 (2nd order, 1.5H), 3.65 (d, 1H, $^{1}J_{H\text{-}P}$ 218.6 Hz, P**H**$_2$), 4.54 (2nd order, 1.2H), 6.69 (d, 22H, $^{3}J_{H\text{-}H}$ 7.77 Hz), 6.76 (d, 4H, $^{3}J_{H\text{-}H}$ 7.77 Hz), 6.86 (d, 4H, $^{3}J_{H\text{-}H}$ 78.42 Hz), 6.92 (t, 7H, $^{3}J_{H\text{-}H}$ 8.64 Hz), 7.05 (d, 3.5H, $^{3}J_{H\text{-}H}$ 7.77 Hz), 7.17 (d, 4H, $^{3}J_{H\text{-}H}$ 7.77 Hz), 7.30 (d, 22H, $^{3}J_{H\text{-}H}$ 7.77 Hz), 7.45 (t, 6H, $^{3}J_{H\text{-}H}$ 8.64 Hz), 7.71 (m, 5H).

^{31}P NMR (C_6D_6): δ_P –197.4 (m), –193.0 (s), –191.7 (s), –119.8 (dd, $^{1}J_{P\text{-}P}$ 90.3 Hz, $^{1}J_{P\text{-}H}$ 167.2 Hz), –115.8 (ddd, $^{1}J_{P\text{-}P}$ 72.1 Hz, $^{1}J_{P\text{-}H}$ 173.3 Hz, $J_{P\text{-}H}$ 9.88 Hz), –108.9 (s), –108.2 (t, $^{1}J_{P\text{-}H}$ 218.6 Hz, **P**H$_2$), –104.4 (2nd order), –98.5 (m), –97.1 (2nd order), –91.1 (d, $^{1}J_{P\text{-}H}$ 170.5 Hz), –90.3 (d, $^{1}J_{P\text{-}H}$ 169.5 Hz), –87.1 (s), –86.1 (s), –84.4 (ddd, $^{1}J_{P\text{-}P}$ 72.1 Hz, $^{1}J_{P\text{-}H}$ 184.8 Hz, $J_{P\text{-}H}$ 11.9 Hz), –83.0 (ddd, $^{1}J_{P\text{-}P}$ 90.3 Hz, $^{1}J_{P\text{-}H}$ 171.4 Hz, $J_{P\text{-}H}$ 7.53 Hz), –81.2 (dd, $J_{P\text{-}P}$ 85.3 Hz, $^{1}J_{P\text{-}H}$ 179.3 Hz), –60.7 (d, $^{1}J_{P\text{-}H}$ 194.1 Hz), –60.2 (d, $^{1}J_{P\text{-}H}$ 194.1 Hz), –59.4 (d, $^{1}J_{P\text{-}H}$ 179.8 Hz), –58.8 (d, $^{1}J_{P\text{-}H}$ 178.8 Hz), –42.2 (s), –41.7 (s), –26.5 (s), –13.1 (d, $^{1}J_{P\text{-}H}$ 704.5 Hz), –8.92 (dd, $J_{P\text{-}P}$ 85.3 Hz, $J_{P\text{-}H}$ 19.2 Hz), 56.1 (s), 70.1 (s), 78.5 (d, $^{1}J_{P\text{-}H}$ 159.4 Hz, *E*- C=**P**H), 81.2 (d, $^{1}J_{P\text{-}H}$ 153.6 Hz, *Z*- C=**P**H), 113.7 (s).

Method B

To a THF solution of $HP(SiMe_3)_2$ (0.530 g, 2.98 x 10^{-3}) at ambient temperature was added C_6H_4(1-COCl)(4-CN) (0.493 g, 2.98 x 10^{-3}) in THF, resulting in the formation of a bright yellow solution within 5 min; an aliquot was dried *in vacuo* to afford a yellow solid.

^{1}H NMR (C_6D_6): δ_H –0.39 (s, 2H), –0.09 (s, 1.5H), 0.04 (s, 1H), 0.09 (d, 2H, $^{3}J_{H\text{-}P}$ 8.45 Hz), 0.18 (s, 2H), 0.20 (s, 3H), 0.27 (s, 9H), 2.89 (2nd order, 1H), 3.73 (d, 0.5H, $^{1}J_{H\text{-}P}$ 219.5 Hz, P**H**$_2$), 4.61 (2nd order, 1H), 6.83 (d, 10.5H, $^{3}J_{H\text{-}H}$ 7.81 Hz), 6.99 (d, 1H, $^{3}J_{H\text{-}H}$ 7.86 Hz), 7.03 (d, 2.5H, $^{3}J_{H\text{-}H}$ 8.45 Hz), 7.26 (d, 1H, $^{3}J_{H\text{-}H}$ 8.09 Hz), 7.40 (d, 10.5H, $^{3}J_{H\text{-}H}$ 7.98 Hz), 7.52 (d, 1H, $^{3}J_{H\text{-}H}$ 8.41 Hz), 7.56 (d, 1H, $^{3}J_{H\text{-}H}$ 8.41 Hz), 7.76 (d, 2H, $^{3}J_{H\text{-}H}$ 7.98 Hz), 7.85 (d, 1H, $^{3}J_{H\text{-}H}$ 8.09 Hz).

^{31}P NMR (C_6D_6): δ_P –119.7 (dd, $^{1}J_{P\text{-}P}$ 91.6 Hz, $^{1}J_{P\text{-}H}$ 164.9 Hz), –115.8 (ddd, $^{1}J_{P\text{-}P}$ 70.6 Hz, $^{1}J_{P\text{-}H}$ 173.1 Hz, $J_{P\text{-}H}$ 10.2 Hz), –108.1 (t, $^{1}J_{P\text{-}H}$ 219.5 Hz, **P**H$_2$), –104.4 (2nd order), –97.0 (2nd order), –84.4 (ddd, $^{1}J_{P\text{-}P}$ 70.6 Hz, $^{1}J_{P\text{-}H}$ 184.6 Hz, $J_{P\text{-}H}$ 11.3 Hz), –82.9 (ddd, $^{1}J_{P\text{-}P}$ 91.6 Hz, $^{1}J_{P\text{-}H}$ 163.1 Hz, $J_{P\text{-}H}$ 8.11 Hz), –26.6 (s), –19.4 (s), –13.2 (d, $^{1}J_{P\text{-}H}$ 706.0 Hz), –12.6 (d, $J_{P\text{-}P}$ 84.3 Hz), –10.5 (d, $^{1}J_{P\text{-}H}$ 742.9 Hz), –8.60 (dd, $J_{P\text{-}P}$ 84.3 Hz, $J_{P\text{-}H}$ 19.5 Hz), 49.6 (d, $J_{P\text{-}P}$ 25.3 Hz), 51.3 (s), 51.9 (s), 56.3 (s), 70.3 (s), 78.4 (d, $^{1}J_{P\text{-}H}$ 159.7 Hz, *E*- C=**P**H), 81.2 (d, $^{1}J_{P\text{-}H}$ 154.1 Hz, *Z*- C=**P**H), 113.7 (s).

^{29}Si{^{1}H} NMR (C_6D_6): δ_{Si} 15.6, 16.2, 19.3, 22.6, 25.8.

The solution turned orange after it was stirred for 18 h and was dried *in vacuo* to afford an orange solid.

^{1}H NMR (C_6D_6): δ_H –0.39 (s, 5H), –0.09 (s, 4H), 0.04 (s, 2H), 0.08 (s, 2H), 0.17 (s, 4H), 0.20 (s, 2H), 0.27 (s, 7H), 2.89 (2nd order, 1H), 3.73 (d, 0.5H, $^{1}J_{H\text{-}P}$ 219.5 Hz, P**H**$_2$), 4.61 (2nd order, 1H), 6.83 (d, 12H, $^{3}J_{H\text{-}H}$ 7.81 Hz), 6.97 (d, 3H, $^{3}J_{H\text{-}H}$ 7.86 Hz), 7.01 (d, 3H, $^{3}J_{H\text{-}H}$ 8.37 Hz), 7.26 (d, 2H, $^{3}J_{H\text{-}H}$ 8.09 Hz), 7.41 (d, 11H, $^{3}J_{H\text{-}H}$ 7.98 Hz), 7.52 (d, 2H, $^{3}J_{H\text{-}H}$ 8.41 Hz), 7.56 (d, 1.5H, $^{3}J_{H\text{-}H}$ 8.41 Hz), 7.76 (d, 2H, $^{3}J_{H\text{-}H}$ 7.98 Hz), 7.85 (d, 2H, $^{3}J_{H\text{-}H}$ 8.09 Hz).

^{31}P NMR (C_6D_6): δ_P –119.7 (dd, $^{1}J_{P\text{-}P}$ 91.6 Hz, $^{1}J_{P\text{-}H}$ 164.9 Hz), –115.8 (ddd, $^{1}J_{P\text{-}P}$ 70.6 Hz, $^{1}J_{P\text{-}H}$ 173.1 Hz, $J_{P\text{-}H}$ 10.2 Hz), –108.1 (t, $^{1}J_{P\text{-}H}$ 219.5 Hz, **P**H$_2$), –104.4 (2nd order), –97.0 (2nd order), –84.4 (ddd, $^{1}J_{P\text{-}P}$ 70.6 Hz, $^{1}J_{P\text{-}H}$ 184.6 Hz, $J_{P\text{-}H}$ 11.3 Hz), –82.9 (ddd, $^{1}J_{P\text{-}P}$ 91.6 Hz, $^{1}J_{P\text{-}H}$ 163.1 Hz, $J_{P\text{-}H}$ 8.11 Hz), –26.6 (s), –19.4 (s), –13.2 (d, $^{1}J_{P\text{-}H}$ 706.0 Hz), –12.6 (d, $J_{P\text{-}P}$ 84.3 Hz), –10.5 (d, $^{1}J_{P\text{-}H}$ 742.9 Hz), –8.60 (dd, $J_{P\text{-}P}$ 84.3 Hz, $J_{P\text{-}H}$ 19.5 Hz), 56.3 (s), 70.3 (s), 78.4 (d, $^{1}J_{P\text{-}H}$ 159.7 Hz, *E*- C=**P**H), 81.2 (d, $^{1}J_{P\text{-}H}$ 154.1 Hz, *Z*- C=**P**H), 113.8 (s).

The crude product was washed with pentane; a peach solid was dried *in vacuo*, while removal of solvent at reduced pressure afforded an off-white solid.

Peach solid:

^{1}H NMR (C_6D_6): δ_H –0.31 (s, 3.5H), –0.11 (s, 1H), 0.25 (s, 1H), 0.28 (s, 2H), 6.68 (d, 1H, $^{3}J_{H\text{-}H}$ 7.85 Hz), 6.89 (d, 3H, $^{3}J_{H\text{-}H}$ 7.85 Hz), 7.07 (d, 1.5H, $^{3}J_{H\text{-}H}$ 7.65 Hz), 7.32 (d, 1H, $^{3}J_{H\text{-}H}$ 7.85 Hz), 7.47 (d, 1H, $^{3}J_{H\text{-}H}$ 7.97 Hz), 7.65 (d, 1H, $^{3}J_{H\text{-}H}$ 8.33 Hz), 7.81 (d, 2H, $^{3}J_{H\text{-}H}$ 8.06 Hz).

^{31}P NMR (C_6D_6): δ_P –108.2 (t, $^{1}J_{P\text{-}H}$ 218.9 Hz, **P**H$_2$), –109.5 (2nd order), –97.1 (2nd order), –13.2 (d, $^{1}J_{P\text{-}H}$ 707.6 Hz), 56.0 (s), 69.9 (s).

Off-white solid:

^{1}H NMR (C_6D_6): δ_H –0.31 (s, 3H), 0.28 (s, 3.5H), 6.67 (d, 12H, $^{3}J_{H\text{-}H}$ 8.18 Hz), 6.90 (d, 2H, $^{3}J_{H\text{-}H}$ 7.50 Hz), 6.96 (br, 1H), 7.08 (d, 1.5H, $^{3}J_{H\text{-}H}$ 8.34 Hz), 7.32 (d, 12H, $^{3}J_{H\text{-}H}$ 8.18 Hz), 7.55 (d, 1H, $^{3}J_{H\text{-}H}$ 8.22 Hz), 7.63 (br, 1H), 7.83 (d, 1H, $^{3}J_{H\text{-}H}$ 8.22 Hz).

^{31}P{^{1}H} NMR (C_6D_6): None observed.

Attempted synthesis of *E*/*Z*-C$_6$H$_4$(1-CO(SiMe$_3$)=PH)(4-CO$_2$Me) (*E*/*Z*-42-4-CO$_2$Me)

Method A

To a THF solution of HP(SiMe$_3$)$_2$ (0.430 g, 2.42 x 10^{-3}) at −78 °C was added C$_6$H$_4$(1-COCl)(4-CO$_2$Me) (0.479 g, 2.42 x 10^{-3}) in THF and the mixture was stirred for 15 min, resulting in a pale

yellow solution that turned orange when it was allowed to warm to ambient temperature over 45 min; an aliquot was dried *in vacuo* to afford an orange solid.

^{1}H NMR (C_6D_6): δ_H –0.31 (s, 1H), –0.16 (s, 1H), 0.18 (s, 7.5H), 0.22 (s, 5H), 0.25 (s, 3H), 0.27 (s, 2.5H), 0.29 (s, 14H), 0.33 (s, 2H), 0.51 (s, 1H), 3.42 (s, 1H), 3.44 (s, 1.5H), 3.45 (s, 66H), 3.48 (s, 6H), 3.49 (s, 1.5H), 3.51 (s, 2H), 3.54 (s, 1.5H), 3.56 (s, 1H), 3.64 (s, 1H), 7.70 (d, 35H, $^{3}J_{H\text{-}H}$ 8.20 Hz), 7.78 (d, 35H, $^{3}J_{H\text{-}H}$ 8.20 Hz), 7.91 (d, 2H, $^{3}J_{H\text{-}H}$ 7.93 Hz), 7.96 (d, 2H, $^{3}J_{H\text{-}H}$ 7.93 Hz), 8.00 (d, 4.5H, $^{3}J_{H\text{-}H}$ 7.93 Hz), 8.08 (d, 4.5H, $^{3}J_{H\text{-}H}$ 7.93 Hz), 8.15 (d, 1.5H, $^{3}J_{H\text{-}H}$ 7.93 Hz), 8.49 (d, 1H, $^{3}J_{H\text{-}H}$ 7.93 Hz).

^{31}P NMR (C_6D_6): δ_P –186.5 (t, $^{1}J_{P\text{-}H}$ 191.9 Hz), –185.2 (t, $^{1}J_{P\text{-}H}$ 191.9 Hz), –129.8 (s), –128.5 (s), –115.3 (d, $^{1}J_{P\text{-}P}$ 70.5 Hz), –108.6 (s), –108.4 (t, $^{1}J_{P\text{-}H}$ 218.2 Hz, **P**H$_2$), –104.2 (2nd order), –96.9 (2nd order), –84.9 (d, $^{1}J_{P\text{-}P}$ 70.5 Hz), –58.9 (s), –57.7 (s), –30.5 (s), –30.1 (s), –25.5 (s), –18.5 (s), –17.2 (s), –13.3 (d, $^{1}J_{P\text{-}H}$ 695.3 Hz), –10.9 (d, $^{1}J_{P\text{-}H}$ 742.7 Hz), –9.56 (s), –1.65 (s), 26.9 (s), 32.3 (s), 42.4 (s), 46.5 (s), 50.9 (s), 56.5 (s), 68.3 (s), 75.6 (d, $^{1}J_{P\text{-}H}$ 159.9 Hz, *E*- C=**P**H), 78.1 (d, $^{1}J_{P\text{-}H}$ 152.8 Hz, *Z*- C=**P**H), 114.2 (s).

The solution was stirred for 18 h and dried *in vacuo* to afford an orange solid.

^{1}H NMR (C_6D_6): δ_H –0.32 (s, 5H), –0.04 (s, 3.5H), 0.09 (s, 3H), 0.14 (s, 2.5H), 0.18 (s, 12H), 0.20 (s, 3H), 0.23 (s, 6H), 0.25 (s, 5H), 0.26 (s, 13.5H), 0.30 (s, 25H), 0.32 (s, 3H), 3.29 (s, 1H), 3.37 (s, 1H), 3.41 (s, 1H), 3.48 (s, 94H), 3.50 (s, 12.5H), 3.53 (s, 4H), 3.56 (s, 4H), 3.66 (s, 1H), 7.05 (d, 1H, $^{3}J_{H\text{-}H}$ 7.70 Hz), 7.12 (d, 1.5H, $^{3}J_{H\text{-}H}$ 7.24 Hz), 7.22 (d, 1.5H, $^{3}J_{H\text{-}H}$ 8.32 Hz), 7.44 (d, 1.5H, $^{3}J_{H\text{-}H}$ 7.86 Hz), 7.51 (d, 2H, $^{3}J_{H\text{-}H}$ 8.32 Hz), 7.57 (d, 2H, $^{3}J_{H\text{-}H}$ 7.86 Hz), 7.72 (d, 51H, $^{3}J_{H\text{-}H}$ 8.45 Hz), 7.78 (d, 51H, $^{3}J_{H\text{-}H}$ 8.45 Hz), 7.99 (d, 9H, $^{3}J_{H\text{-}H}$ 8.58 Hz), 8.04 (d, 7H, $^{3}J_{H\text{-}H}$ 8.58 Hz), 8.15 (d, 3H, $^{3}J_{H\text{-}H}$ 8.58 Hz), 8.18 (d, 2H, $^{3}J_{H\text{-}H}$ 8.58 Hz), 8.46 (d, 1.5H, $^{3}J_{H\text{-}H}$ 8.05 Hz).

^{31}P NMR (C_6D_6): δ_P –197.5 (d, $J_{P\text{-}P}$ 152.4 Hz), –186.5 (t, $^{1}J_{P\text{-}H}$ 191.9 Hz), –185.2 (t, $^{1}J_{P\text{-}H}$ 191.9 Hz), –161.6 (s), –160.4 (s), –128.8 (s), –127.4 (s), –115.3 (ddd, $^{1}J_{P\text{-}P}$ 70.5 Hz, $^{1}J_{P\text{-}H}$ 172.0 Hz, $J_{P\text{-}H}$ 13.5 Hz), –108.4 (t, $^{1}J_{P\text{-}H}$ 218.2 Hz, **P**H$_2$), –104.1 (2nd order), –96.9 (2nd order), –87.2 (d, $J_{P\text{-}P}$ 152.4Hz), –84.9 (ddd, $^{1}J_{P\text{-}P}$ 70.5 Hz, $^{1}J_{P\text{-}H}$ 180.4 Hz, $J_{P\text{-}H}$ 11.7 Hz), –82.1 (s), –81.6 (s), –30.7 (s), –26.8 (s), –25.7 (s), –18.6 (s), –13.3 (d, $^{1}J_{P\text{-}H}$ 695.3 Hz), –10.8 (d, $^{1}J_{P\text{-}H}$ 742.7 Hz), –9.70 (s), 32.2 (s), 40.7 (s), 42.4 (s), 46.9 (s), 50.0 (s), 56.5 (s), 57.0 (s), 68.3 (s), 75.5 (d, $^{1}J_{P\text{-}H}$ 159.9 Hz, *E*- C=**P**H), 78.1 (d, $^{1}J_{P\text{-}H}$ 152.8 Hz, *Z*- C=**P**H), 114.2 (s), 172.8 (s).

Method B

To a THF solution of HP(SiMe$_3$)$_2$ (0.430 g, 2.42 x 10^{-3}) at ambient temperature was added C_6H_4(1-COCl)(4-CO$_2$Me) (0.479 g, 2.42 x 10^{-3}) in THF, resulting in the formation of a bright yellow solution within 5 min; an aliquot was dried *in vacuo* to afford a yellow solid.

^{1}H NMR (C_6D_6): δ_H –0.30 (s, 2H), –0.15 (s, 2H), 0.18 (s, 5.5H), 0.22 (s, 5H), 0.29 (s, 11.5H), 0.51 (s, 1H), 3.43 (s, 67H), 3.46 (s, 5H), 4.79 (d, 0.5H, $^{1}J_{P\text{-}H}$ 152.8 Hz, *Z*- C=P**H**), 5.16 (d, 0.5H, $^{1}J_{P\text{-}H}$ 159.9 Hz, *E*- C=P**H**), 7.49 (d, 1.5H, $^{3}J_{H\text{-}H}$ 8.82 Hz), 7.56 (d, 1.5H, $^{3}J_{H\text{-}H}$ 8.47 Hz), 7.69 (d, 34H, $^{3}J_{H\text{-}H}$ 8.20 Hz), 7.78 (d, 34H, $^{3}J_{H\text{-}H}$ 8.20 Hz), 7.89 (t, 4H, $^{3}J_{H\text{-}H}$ 8.75 Hz), 7.96 (d, 2H, $^{3}J_{H\text{-}H}$ 7.90 Hz), 8.02 (d, 3.5H, $^{3}J_{H\text{-}H}$ 7.41 Hz), 8.09 (d, 3H, $^{3}J_{H\text{-}H}$ 7.90 Hz), 8.50 (d, 1H, $^{3}J_{H\text{-}H}$ 8.26 Hz).

^{31}P NMR (C_6D_6): δ_P –129.8 (s), –128.5 (s), –115.3 (d, $^{1}J_{P\text{-}P}$ 70.5 Hz), –108.6 (s), –108.4 (t, $^{1}J_{P\text{-}H}$ 218.2 Hz, **P**H_2), –104.2 (2nd order), –98.3 (m), –96.9 (2nd order), –84.9 (d, $^{1}J_{P\text{-}P}$ 70.5 Hz), –58.9 (s), –57.7 (s), –54.3 (s), –52.7 (s), –25.2 (s), –18.8 (s), –18.4 (s), –17.2 (d, $J_{P\text{-}H}$ 23.4 Hz), –13.3 (s), 26.9 (s), 29.7 (s), 32.3 (s), 46.5 (s), 50.9 (s), 56.4 (s), 68.4 (s), 75.7 (d, $^{1}J_{P\text{-}H}$ 159.9 Hz, *E*- C=**P**H), 78.1 (d, $^{1}J_{P\text{-}H}$ 152.8 Hz, *Z*- C=**P**H), 114.3 (s).

The solution turned orange after it has been stirred for 18 h and was dried *in vacuo* to afford an orange solid.

^{1}H NMR (C_6D_6): δ_H –0.31 (s, 4H), –0.04 (s, 4H), 0.10 (s, 3H), 0.14 (s, 4H), 0.18 (s, 4.5H), 0.22 (s, 2H), 0.25 (s, 1H), 0.29 (s, 5.5H), 0.31 (s, 6.5H), 0.33 (d, 2H, $^{3}J_{H\text{-}H}$ 4.45 Hz), 0.47 (s, 1H), 0.61 (s, 1H), 3.35 (s, 1.5H), 3.40 (s, 1H), 3.47 (s, 7.5H), 3.51 (s, 3H), 3.54 (s, 3H), 7.08 (d, 1H, $^{3}J_{H\text{-}H}$ 8.22 Hz), 7.12 (d, 1H, $^{3}J_{H\text{-}H}$ 8.22 Hz), 7.44 (d, 1H, $^{3}J_{H\text{-}H}$ 8.36 Hz), 7.55 (d, 1H, $^{3}J_{H\text{-}H}$ 8.54 Hz), 7.70 (d, 24H, $^{3}J_{H\text{-}H}$ 8.54 Hz), 7.78 (d, 24H, $^{3}J_{H\text{-}H}$ 8.54 Hz), 7.83 (t, 3.5H, $^{3}J_{H\text{-}H}$ 8.54 Hz), 7.90 (t, 4H, $^{3}J_{H\text{-}H}$ 7.81 Hz), 7.96 (d, 3.5H, $^{3}J_{H\text{-}H}$ 7.99 Hz), 8.01 (d, 3H, $^{3}J_{H\text{-}H}$ 7.499 Hz), 8.07 (m, 3H), 8.13 (d, 1.5H, $^{3}J_{H\text{-}H}$ 7.99 Hz), 8.20 (d, 2H, $^{3}J_{H\text{-}H}$ 7.81 Hz), 8.49 (d, 0.5H, $^{3}J_{H\text{-}H}$ 8.54 Hz).

^{31}P NMR (C_6D_6): δ_P –197.9 (s), –196.9 (s), –186.5 (s), –185.2 (s), –128.7 (m), –119.6 (dd, $^{1}J_{P\text{-}P}$ 89.0 Hz, $^{1}J_{P\text{-}H}$ 162.2 Hz), –115.3 (ddd, $^{1}J_{P\text{-}P}$ 70.5 Hz, $^{1}J_{P\text{-}H}$ 172.6 Hz, $J_{P\text{-}H}$ 11.4 Hz), –108.6 (s), –108.4 (t, $^{1}J_{P\text{-}H}$ 218.2 Hz, **P**H_2), –104.2 (2nd order), –98.3 (m), –96.9 (2nd order), –90.6 (d, $^{1}J_{P\text{-}H}$ 171.1 Hz), –89.8 (d, $^{1}J_{P\text{-}H}$ 172.4 Hz), –87.6 (s), –86.7 (s), –84.9 (ddd, $^{1}J_{P\text{-}P}$ 70.5 Hz, $^{1}J_{P\text{-}H}$ 180.9 Hz, $J_{P\text{-}H}$ 11.9 Hz), –81.9 (ddd, $^{1}J_{P\text{-}P}$ 89.0 Hz, $^{1}J_{P\text{-}H}$ 168.3 Hz, $J_{P\text{-}H}$ 9.03 Hz), –59.9 (d, $^{1}J_{P\text{-}H}$ 191.7 Hz), –59.5 (d, $^{1}J_{P\text{-}H}$ 189.2 Hz), –56.3 (s), –55.9 (s), –55.7 (s), –54.6 (s), –45.6 (s), –43.8 (s), –40.3 (dd, $J_{P\text{-}P}$ 79.2 Hz, $^{1}J_{P\text{-}H}$ 175.8 Hz), –33.7 (d, $^{1}J_{P\text{-}H}$ 217.9 Hz), –25.6 (s), –18.5 (s), –18.5 (s), –13.3 (d, $^{1}J_{P\text{-}H}$ 698.9 Hz), –11.9 (d, $J_{P\text{-}P}$ 79.2 Hz), –9.62 (s), –4.69 (dd, $J_{P\text{-}P}$ 77.9 Hz, $J_{P\text{-}H}$ 20.2 Hz), –1.49 (s), –0.70 (s), 1.11 (d, $J_{P\text{-}P}$ 77.9 Hz), 2.47 (s), 2.57 (s), 46.9 (s), 49.9 (s), 56.5 (s), 56.9 (s), 68.4 (s), 75.6 (d, $^{1}J_{P\text{-}H}$ 159.9 Hz, *E*- C=**P**H), 78.1 (d, $^{1}J_{P\text{-}H}$ 152.8 Hz, *Z*- C=**P**H), 114.3 (s).

Method C

To a THF solution of $HP(SiMe_3)_2$ (0.960 g, 5.39 x 10^{-3}) at 60 °C was added C_6H_4(1-COCl)(4-CO_2Me) (1.071 g, 5.39 x 10^{-3}) in THF, resulting in an orange solution that was brought to

reflux for 80 min; an aliquot was dried *in vacuo* to afford an orange solid and 3.7 mg of PPh_3 was added to the NMR sample.

^{1}H NMR (C_6D_6): δ_H –0.31 (s, 8H), –0.04 (s, 5H), 0.10 (s, 4.5H), 0.15 (s, 4.5H), 0.18 (s, 4H), 0.22 (s, 1.5H), 0.25 (s, 1H), 0.28 (s, 34H), 3.32 (s, 1H), 3.38 (s, 1.5H), 3.42 (s, 13H), 3.44 (s, 3H), 3.45 (s, 3H), 3.47 (s, 1H), 3.50 (s, 2.5H), 3.52 (s, 3.5H), 7.06 (m, 7H), 7.08 (s, 1H), 7.11 (s, 1H), 7.13 (s, 1H), 7.37 (m, 5H), 7.44 (d, 1.5H, $^3J_{H\text{-}H}$ 7.50 Hz), 7.63 (m, 2H), 7.69 (d, 7.5H, $^3J_{H\text{-}H}$ 8.27 Hz), 7.78 (d, 7.5H, $^3J_{H\text{-}H}$ 8.27 Hz), 7.83 (d, 3.5H, $^3J_{H\text{-}H}$ 7.90 Hz), 7.88 (d, 3.5H, $^3J_{H\text{-}H}$ 7.91 Hz), 7.91 (d, 1.5H, $^3J_{H\text{-}H}$ 8.26 Hz), 7.96 (d, 3.5H, $^3J_{H\text{-}H}$ 8.60 Hz), 8.01 (m, 2.5H), 8.07 (d, 2H, $^3J_{H\text{-}H}$ 7.57 Hz), 8.11 (d, 2H, $^3J_{H\text{-}H}$ 7.14 Hz), 8.21 (d, 2.5H, $^3J_{H\text{-}H}$ 8.26Hz).

^{31}P NMR (C_6D_6): δ_P –119.6 (dd, $^1J_{P\text{-}P}$ 89.2 Hz, $^1J_{P\text{-}H}$ 164.9 Hz), –115.4 (ddd, $^1J_{P\text{-}P}$ 70.1 Hz, $^1J_{P\text{-}H}$ 173.8 Hz, $J_{P\text{-}H}$ 11.3 Hz), –108.3 (t, $^1J_{P\text{-}H}$ 219.1 Hz, **P**H_2), –104.2 (2nd order), –98.3 (s), –96.9 (2nd order), –84.9 (ddd, $^1J_{P\text{-}P}$ 70.1 Hz, $^1J_{P\text{-}H}$ 183.5 Hz, $J_{P\text{-}H}$ 11.2 Hz), –81.9 (ddd, $^1J_{P\text{-}P}$ 89.2 Hz, $^1J_{P\text{-}H}$ 169.8 Hz, $J_{P\text{-}H}$ 9.02 Hz), –56.6 (d, $^1J_{P\text{-}H}$ 177.1 Hz), –56.1 (d, $^1J_{P\text{-}H}$ 176.4 Hz), –25.5 (s), –18.5 (s), –13.2 (d, $^1J_{P\text{-}H}$ 701.1 Hz), –5.27 (br, **P**Ph_3), 56.4 (s), 68.4 (s), 75.7 (d, $^1J_{P\text{-}H}$ 159.6 Hz, *E*- C=**P**H), 78.2 (d, $^1J_{P\text{-}H}$ 154.0 Hz, *Z*- C=**P**H), 114.3 (s).

After 160 min at reflux an aliquot was dried *in vacuo* to afford an orange solid; 3.4 mg of PPh_3 was added to the NMR sample.

^{1}H NMR (C_6D_6): δ_H –0.31 (s, 5H), –0.04 (s, 3.5H), 0.10 (s, 2.5H), 0.15 (s, 3H), 0.18 (s, 2.5H), 0.22 (s, 1H), 0.25 (s, 1H), 0.28 (s, 23H), 3.32 (s, 1H), 3.38 (s, 1H), 3.42 (s, 8H), 3.44 (s, 1.5H), 3.45 (s, 2H), 3.50 (s, 2H), 3.52 (s, 2H), 7.06 (m, 4.5H), 7.08 (s, 1H), 7.11 (s, 1H), 7.13 (s, 1H), 7.37 (m, 3H), 7.44 (d, 1H, $^3J_{H\text{-}H}$ 7.50 Hz), 7.69 (d, 4H, $^3J_{H\text{-}H}$ 8.27 Hz), 7.78 (d, 4H, $^3J_{H\text{-}H}$ 8.27 Hz), 7.85 (d, 2H, $^3J_{H\text{-}H}$ 7.90 Hz), 7.88 (d, 2H, $^3J_{H\text{-}H}$ 7.91 Hz), 7.91 (d, 1H, $^3J_{H\text{-}H}$ 8.26 Hz), 7.96 (d, 2H, $^3J_{H\text{-}H}$ 8.60 Hz), 8.01 (m, 1H), 8.08 (d, 1H, $^3J_{H\text{-}H}$ 7.57 Hz), 8.12 (d, 1H, $^3J_{H\text{-}H}$ 7.14 Hz), 8.21 (d, 1H, $^3J_{H\text{-}H}$ 8.26Hz).

^{31}P NMR (C_6D_6): δ_P –119.6 (dd, $^1J_{P\text{-}P}$ 89.2 Hz, $^1J_{P\text{-}H}$ 164.9 Hz), –115.4 (ddd, $^1J_{P\text{-}P}$ 70.1 Hz, $^1J_{P\text{-}H}$ 173.8 Hz, $J_{P\text{-}H}$ 11.3 Hz), –108.3 (t, $^1J_{P\text{-}H}$ 219.1 Hz, **P**H_2), –104.2 (2nd order), –98.3 (s), –96.9 (2nd order), –84.9 (ddd, $^1J_{P\text{-}P}$ 70.1 Hz, $^1J_{P\text{-}H}$ 183.5 Hz, $J_{P\text{-}H}$ 11.2 Hz), –81.9 (ddd, $^1J_{P\text{-}P}$ 89.2 Hz, $^1J_{P\text{-}H}$ 169.8 Hz, $J_{P\text{-}H}$ 9.02 Hz), –56.6 (d, $^1J_{P\text{-}H}$ 177.1 Hz), –56.1 (d, $^1J_{P\text{-}H}$ 176.4 Hz), –25.5 (s), –18.5 (s), –13.2 (d, $^1J_{P\text{-}H}$ 701.1 Hz), –5.27 (br, **P**Ph_3), 56.4 (s), 68.4 (s), 75.7 (d, $^1J_{P\text{-}H}$ 159.6 Hz, *E*- C=**P**H), 78.2 (d, $^1J_{P\text{-}H}$ 154.0 Hz, *Z*- C=**P**H), 114.3 (s).

After 240 min at reflux an aliquot was dried *in vacuo* to afford an orange solid; 4.3 mg of PPh_3 was added to the NMR sample.

^{1}H NMR (C_6D_6): δ_H –0.31 (s, 5.5H), –0.04 (s, 5H), 0.10 (s, 3H), 0.15 (s, 3H), 0.18 (s, 2.5H), 0.22 (s, 1H), 0.25 (s, 1H), 0.28 (s, 22H), 3.32 (s, 1H), 3.38 (s, 1H), 3.42 (s, 8.5H), 3.44 (s, 2H),

3.45 (s, 2H), 3.50 (s, 2H), 3.52 (s, 2.5H), 7.06 (m, 4.5H), 7.08 (s, 1H), 7.11 (s, 1H), 7.13 (s, 1H), 7.37 (m, 4.5H), 7.44 (d, 1H, $^{3}J_{H\text{-}H}$ 7.50 Hz), 7.69 (d, 5H, $^{3}J_{H\text{-}H}$ 8.27 Hz), 7.78 (d, 5H, $^{3}J_{H\text{-}H}$ 8.27 Hz), 7.85 (d, 2.5H, $^{3}J_{H\text{-}H}$ 7.90 Hz), 7.88 (d, 2H, $^{3}J_{H\text{-}H}$ 7.91 Hz), 7.91 (d, 1H, $^{3}J_{H\text{-}H}$ 8.26 Hz), 7.96 (d, 2H, $^{3}J_{H\text{-}H}$ 8.60 Hz), 8.01 (m, 1H), 8.08 (d, 1H, $^{3}J_{H\text{-}H}$ 7.57 Hz), 8.12 (d, 1H, $^{3}J_{H\text{-}H}$ 7.14 Hz), 8.21 (d, 2H, $^{3}J_{H\text{-}H}$ 8.26Hz).

^{31}P NMR (C_6D_6): δ_P –119.6 (dd, $^{1}J_{P\text{-}P}$ 89.2 Hz, $^{1}J_{P\text{-}H}$ 164.9 Hz), –115.4 (ddd, $^{1}J_{P\text{-}P}$ 70.1 Hz, $^{1}J_{P\text{-}H}$ 173.8 Hz, $J_{P\text{-}H}$ 11.3 Hz), –108.3 (t, $^{1}J_{P\text{-}H}$ 219.1 Hz, **P**H_2), –104.2 (2nd order), –96.9 (2nd order), –84.9 (ddd, $^{1}J_{P\text{-}P}$ 70.1 Hz, $^{1}J_{P\text{-}H}$ 183.5 Hz, $J_{P\text{-}H}$ 11.2 Hz), –81.9 (ddd, $^{1}J_{P\text{-}P}$ 89.2 Hz, $^{1}J_{P\text{-}H}$ 169.8 Hz, $J_{P\text{-}H}$ 9.02 Hz), –56.6 (d, $^{1}J_{P\text{-}H}$ 177.1 Hz), –56.1 (d, $^{1}J_{P\text{-}H}$ 176.4 Hz), –18.5 (s), –13.2 (d, $^{1}J_{P\text{-}H}$ 701.1 Hz), –5.27 (br, **P**Ph_3), 56.4 (s), 68.4 (s), 75.7 (d, $^{1}J_{P\text{-}H}$ 159.6 Hz, *E*- C=**P**H), 78.2 (d, $^{1}J_{P\text{-}H}$ 154.0 Hz, *Z*- C=**P**H), 114.3 (s).

After 320 min at reflux an aliquot was dried *in vacuo* to afford an orange solid; 3.8 mg of PPh_3 was added to the NMR sample.

^{1}H NMR (C_6D_6): δ_H –0.31 (s, 7H), –0.04 (s, 6H), 0.10 (s, 3.5H), 0.15 (s, 4H), 0.18 (s, 3H), 0.22 (s, 1.5H), 0.25 (s, 1.5H), 0.28 (s, 31H), 3.32 (s, 1H), 3.38 (s, 1H), 3.42 (s, 10H), 3.44 (s, 3H), 3.45 (s, 2H), 3.50 (s, 3H), 3.52 (s, 3.5H), 7.06 (m, 5H), 7.08 (s, 1H), 7.11 (s, 1H), 7.13 (s, 1H), 7.37 (m, 4H), 7.44 (d, 1H, $^{3}J_{H\text{-}H}$ 7.50 Hz), 7.69 (d, 6H, $^{3}J_{H\text{-}H}$ 8.27 Hz), 7.78 (d, 6H, $^{3}J_{H\text{-}H}$ 8.27 Hz), 7.85 (d, 2.5H, $^{3}J_{H\text{-}H}$ 7.90 Hz), 7.88 (d, 2.5H, $^{3}J_{H\text{-}H}$ 7.91 Hz), 7.91 (d, 1H, $^{3}J_{H\text{-}H}$ 8.26 Hz), 7.96 (d, 2H, $^{3}J_{H\text{-}H}$ 8.60 Hz), 8.01 (m, 1.5H), 8.08 (d, 2H, $^{3}J_{H\text{-}H}$ 7.57 Hz), 8.12 (d, 1H, $^{3}J_{H\text{-}H}$ 7.14 Hz), 8.21 (d, 2H, $^{3}J_{H\text{-}H}$ 8.26Hz).

^{31}P NMR (C_6D_6): δ_P –119.6 (dd, $^{1}J_{P\text{-}P}$ 89.2 Hz, $^{1}J_{P\text{-}H}$ 164.9 Hz), –115.4 (ddd, $^{1}J_{P\text{-}P}$ 70.1 Hz, $^{1}J_{P\text{-}H}$ 173.8 Hz, $J_{P\text{-}H}$ 11.3 Hz), –108.3 (t, $^{1}J_{P\text{-}H}$ 219.1 Hz, **P**H_2), –104.2 (2nd order), –96.9 (2nd order), –84.9 (ddd, $^{1}J_{P\text{-}P}$ 70.1 Hz, $^{1}J_{P\text{-}H}$ 183.5 Hz, $J_{P\text{-}H}$ 11.2 Hz), –81.9 (ddd, $^{1}J_{P\text{-}P}$ 89.2 Hz, $^{1}J_{P\text{-}H}$ 169.8 Hz, $J_{P\text{-}H}$ 9.02 Hz), –56.6 (d, $^{1}J_{P\text{-}H}$ 177.1 Hz), –56.1 (d, $^{1}J_{P\text{-}H}$ 176.4 Hz), –25.5 (s), –18.5 (s), –13.2 (d, $^{1}J_{P\text{-}H}$ 701.1 Hz), –5.27 (br, **P**Ph_3), 56.4 (s), 68.4 (s), 75.7 (d, $^{1}J_{P\text{-}H}$ 159.6 Hz, *E*- C=**P**H), 78.2 (d, $^{1}J_{P\text{-}H}$ 154.0 Hz, *Z*- C=**P**H), 114.3 (s).

After 400 min at reflux an aliquot was dried *in vacuo* to afford an orange solid; 4.3 mg of PPh_3 was added to the NMR sample.

^{1}H NMR (C_6D_6): δ_H –0.31 (s, 8H), –0.04 (s, 7H), 0.10 (s, 3.5H), 0.15 (s, 4H), 0.18 (s, 3.5H), 0.22 (s, 1.5H), 0.25 (s, 1.5H), 0.28 (s, 37H), 3.32 (s, 1H), 3.38 (s, 1H), 3.42 (s, 12H), 3.44 (s, 2.5H), 3.45 (s, 3H), 3.50 (s, 3H), 3.52 (s, 3H), 7.06 (m, 6H), 7.08 (s, 1H), 7.11 (s, 1H), 7.13 (s, 1H), 7.37 (m, 5.5H), 7.44 (d, 1H, $^{3}J_{H\text{-}H}$ 7.50 Hz), 7.69 (d, 7H, $^{3}J_{H\text{-}H}$ 8.27 Hz), 7.78 (d, 7H, $^{3}J_{H\text{-}H}$ 8.27 Hz), 7.85 (d, 3.5H, $^{3}J_{H\text{-}H}$ 7.90 Hz), 7.88 (d, 3H, $^{3}J_{H\text{-}H}$ 7.91 Hz), 7.91 (d, 1H, $^{3}J_{H\text{-}H}$ 8.26 Hz), 7.96 (d, 2.5H, $^{3}J_{H\text{-}H}$ 8.60 Hz), 8.01 (m, 1.5H), 8.08 (d, 2.5H, $^{3}J_{H\text{-}H}$ 7.57 Hz), 8.12 (d, 1H, $^{3}J_{H\text{-}H}$ 7.14 Hz), 8.21 (d, 2H, $^{3}J_{H\text{-}H}$ 8.26Hz).

^{31}P NMR (C_6D_6): δ_P –119.6 (dd, $^1J_{P\text{-}P}$ 89.2 Hz, $^1J_{P\text{-}H}$ 164.9 Hz), –115.4 (ddd, $^1J_{P\text{-}P}$ 70.1 Hz, $^1J_{P\text{-}H}$ 173.8 Hz, $J_{P\text{-}H}$ 11.3 Hz), –108.3 (t, $^1J_{P\text{-}H}$ 219.1 Hz, **P**H_2), –104.2 (2nd order), –96.9 (2nd order), –84.9 (ddd, $^1J_{P\text{-}P}$ 70.1 Hz, $^1J_{P\text{-}H}$ 183.5 Hz, $J_{P\text{-}H}$ 11.2 Hz), –81.9 (ddd, $^1J_{P\text{-}P}$ 89.2 Hz, $^1J_{P\text{-}H}$ 169.8 Hz, $J_{P\text{-}H}$ 9.02 Hz), –56.6 (d, $^1J_{P\text{-}H}$ 177.1 Hz), –56.1 (d, $^1J_{P\text{-}H}$ 176.4 Hz), –25.5 (s), –18.5 (s), –13.2 (d, $^1J_{P\text{-}H}$ 701.1 Hz), –5.27 (br, **P**Ph_3), 56.4 (s), 68.4 (s), 75.7 (d, $^1J_{P\text{-}H}$ 159.6 Hz, *E*- C=**P**H), 78.2 (d, $^1J_{P\text{-}H}$ 154.0 Hz, *Z*- C=**P**H), 114.3 (s).

After 1440 min at reflux the solvent was removed under reduced pressure to afford an orange solid; 4.2 mg of PPh_3 was added to the NMR sample.

^{1}H NMR (C_6D_6): δ_H –0.31 (s, 3H), –0.20 (s, 3H), –0.04 (s, 8H), 0.10 (s, 4.5H), 0.15 (s, 4.5H), 0.18 (s, 1H), 0.22 (s, 1.5H), 0.25 (s, 1H), 0.28 (s, 17H), 3.34 (s, 1H), 3.38 (s, 1H), 3.42 (s, 12H), 3.44 (s, 2H), 3.45 (s, 3.5H), 3.50 (s, 4H), 3.52 (s, 2.5H), 7.06 (m, 3.5H), 7.08 (s, 1H), 7.11 (s, 1H), 7.13 (s, 1H), 7.37 (m, 3.5H), 7.44 (d, 1H, $^3J_{H\text{-}H}$ 7.50 Hz), 7.69 (d, 7H, $^3J_{H\text{-}H}$ 8.27 Hz), 7.78 (d, 7H, $^3J_{H\text{-}H}$ 8.27 Hz), 7.85 (d, 2H, $^3J_{H\text{-}H}$ 7.90 Hz), 7.88 (d, 4 H, $^3J_{H\text{-}H}$ 7.91 Hz), 7.91 (d, 1H, $^3J_{H\text{-}H}$ 8.26 Hz), 7.96 (d, 2H, $^3J_{H\text{-}H}$ 8.60 Hz), 8.01 (m, 1.5H), 8.08 (d, 2H, $^3J_{H\text{-}H}$ 7.57 Hz), 8.12 (d, 1H, $^3J_{H\text{-}H}$ 7.14 Hz), 8.21 (d, 2H, $^3J_{H\text{-}H}$ 8.26Hz).

^{31}P NMR (C_6D_6): δ_P –115.4 (ddd, $^1J_{P\text{-}P}$ 70.1 Hz, $^1J_{P\text{-}H}$ 173.8 Hz, $J_{P\text{-}H}$ 11.3 Hz), –108.3 (t, $^1J_{P\text{-}H}$ 219.1 Hz, **P**H_2), –104.2 (2nd order), –96.9 (2nd order), –84.9 (ddd, $^1J_{P\text{-}P}$ 70.1 Hz, $^1J_{P\text{-}H}$ 183.5 Hz, $J_{P\text{-}H}$ 11.2 Hz), –56.6 (d, $^1J_{P\text{-}H}$ 177.1 Hz), –56.1 (d, $^1J_{P\text{-}H}$ 176.4 Hz), –25.8 (s), –18.5 (s), –13.2 (d, $^1J_{P\text{-}H}$ 701.1 Hz), –5.27 (br, **P**Ph_3), 56.4 (s), 68.4 (s), 75.7 (d, $^1J_{P\text{-}H}$ 159.6 Hz, *E*- C=**P**H), 78.2 (d, $^1J_{P\text{-}H}$ 154.0 Hz, *Z*- C=**P**H), 114.3 (s), 172.8 (s).

Attempted synthesis of *E*/*Z*-C_6H_4(1-CO($SiMe_3$)=PH)(4-COCl) (*E*/*Z*-42-4-COCl)

Method A

To a THF solution of $HP(SiMe_3)_2$ (0.440 g, 2.47 x 10^{-3} mol) at –78 °C was added C_6H_4(1,4-$COCl)_2$ (0.502 g, 2.47 x 10^{-3} mol) in THF, resulting in a yellow solution that was stirred for 15 min then turned brown when it was allowed to warm to ambient temperature over 45 min; an aliquot was dried *in vacuo* to afford a brown solid.

^{1}H NMR (C_6D_6): δ_H –0.34 (s, 3.5H), –0.24 (s, 1.5H), –0.05 (s, 3H), 0.10 (s, 3H), 0.13 (s, 2.5H), 0.18 (s, 19H), 0.20 (s, 6H), 0.24 (s, 5H), 0.27 (s, 5H), 0.30 (s, 22H), 3.78 (d, 1H, $^1J_{H\text{-}P}$ 220.3 Hz, PH_2), 6.93 (d, 1H, $^3J_{H\text{-}H}$ 7.65 Hz), 6.97 (d, 1.5H, $^3J_{H\text{-}H}$ 8.06 Hz), 7.30 (d, 2H, $^3J_{H\text{-}H}$ 8.36 Hz), 7.36 (d, 1.5H, $^3J_{H\text{-}H}$ 7.75 Hz), 7.73 (t, 9H, $^3J_{H\text{-}H}$ 7.82 Hz), 7.82 (d, 3H, $^3J_{H\text{-}H}$ 8.45 Hz), 7.88 (d, 6H, $^3J_{H\text{-}H}$ 8.18 Hz), 7.99 (t, 4.5H, $^3J_{H\text{-}H}$ 7.18 Hz), 8.09 (s, 1H).

^{31}P NMR (C_6D_6): δ_P –118.7 (dd, $^1J_{P-P}$ 90.4 Hz, $^1J_{P-H}$ 164.9 Hz), –114.4 (ddd, $^1J_{P-P}$ 70.7 Hz, $^1J_{P-H}$ 172.7 Hz, J_{P-H} 10.8 Hz), –107.4 (t, $^1J_{P-H}$ 220.3 Hz, **P**H_2), –103.5 (2nd order), –97.9 (d, $^1J_{P-H}$ 181.2 Hz), –96.2 (2nd order d), –83.9 (ddd, $^1J_{P-P}$ 70.7 Hz, $^1J_{P-H}$ 185.4 Hz, J_{P-H} 12.6 Hz), –81.9 (ddd, $^1J_{P-P}$ 90.4 Hz, $^1J_{P-H}$ 171.4 Hz, J_{P-H} 10.2 Hz), –30.8 (s), –30.4 (d, J_{P-P} 14.7 Hz), –26.0 (s), –19.0 (s), –14.9 (dd, J_{P-P} 14.7 Hz, $^1J_{P-H}$ 734.8 Hz), –13.4 (d, $^1J_{P-H}$ 704.1 Hz), –10.9 (d, $^1J_{P-H}$ 741.5 Hz), –10.8 (d, $^1J_{P-H}$ 736.8 Hz), –9.90 (s), 57.8 (s), 73.0 (s), 82.3 (d, $^1J_{P-H}$ 158.5 Hz, *E*- C=**P**H), 85.6 (d, $^1J_{P-H}$ 154.6 Hz, *Z*- C=**P**H), 115.0 (s), 182.6 (s).

The orange solution was stirred for 18 h and was dried *in vacuo* to afford an orange solid.

^{1}H NMR (C_6D_6): δ_H –0.27 (s, 3H), –0.24 (s, 1H), 0.16 (s, 9H), 0.22 (s, 6H), 0.28 (s, 10H), 0.29 (s, 12H), 7.23 (d, 1H, $^3J_{H-H}$ 8.42 Hz), 7.66 (d, 5H, $^3J_{H-H}$ 8.42 Hz), 7.72 (m, 6H), 7.87 (d, 6H, $^3J_{H-H}$ 8.42 Hz), 7.96 (d, 2H, $^3J_{H-H}$ 8.42 Hz), 8.31 (d, 1H, $^3J_{H-H}$ 8.42 Hz).

^{31}P NMR (C_6D_6): δ_P –26.9 (s), –26.4 (s), –19.1 (s), –13.1 (d, $^1J_{P-H}$ 704.1 Hz), –10.9 (d, $^1J_{P-H}$ 741.5 Hz), –10.6 (d, $^1J_{P-H}$ 739.3Hz), –6.33 (s), 118.8 (s).

Method B

To a THF solution of $HP(SiMe_3)_2$ (0.36 g, 2.02 x 10^{-3}) at ambient temperature was added C_6H_4(1-COCl)(4-COCl) (0.416 g, 2.02 x 10^{-3}) in THF, resulting in a pale yellow solution that turned brown within 5 min; an aliquot was dried *in vacuo* to afford a brown solid.

^{1}H NMR (C_6D_6): δ_H –0.36 (s, 2H), –0.21 (s, 1.5H), –0.19 (br, 4.5H), 0.08 (s, 5.5H), 0.12 (br, 7H), 0.17 (s, 4H), 0.19 (s, 7H), 0.21 (s, 4H), 0.24 (s, 3H), 0.27 (s, 2H), 3.03 (2nd order, 1H), 4.69 (2nd order, 1H), 7.22 (br, 7.5H), 7.86 (br, 6H), 7.98 (m, 3H), 8.11 (s, 1H), 8.32 (d, 1H, $^3J_{H-H}$ 7.96 Hz).

^{31}P NMR (C_6D_6): δ_P –126.9 (m), –121.8 (br d, $^2J_{P-P}$ 196.8Hz), –118.8 (m), –114.5 (ddd, $^1J_{P-P}$ 70.7 Hz, $^1J_{P-H}$ 172.7 Hz, J_{P-H} 10.8 Hz), –107.6 (d, $^1J_{P-H}$ 167.5 Hz), –107.4 (t, $^1J_{P-H}$ 219.8 Hz, **P**H_2), –103.6 (2nd order), –97.9 (d, $^1J_{P-H}$ 181.2 Hz), –96.3 (2nd order), –83.9 (ddd, $^1J_{P-P}$ 70.7 Hz, $^1J_{P-H}$ 185.4 Hz, J_{P-H} 12.6 Hz), –81.9 (ddd, J_{P-P} 89.9 Hz, J_{P-H} 171.4 Hz, J_{P-H} 10.2 Hz), –79.8 (d, $^2J_{P-P}$ 196.8 Hz), –56.1 (s), –54.7 (d, J_{P-H} 98.5 Hz), –56.9 (d, J_{P-P} 89.9 Hz), –54.7 (dd, J_{P-P} 77.3 Hz, $^1J_{P-H}$ 176.5 Hz), –43.0 (m), –13.8 (d, $^1J_{P-H}$ 213.8 Hz), –12.9 (d, $^1J_{P-H}$ 218.5 Hz), –5.80 (d, J_{P-P} 77.3 Hz), 57.6 (s), 72.8 (s), 82.3 (d, $^1J_{P-H}$ 158.5 Hz, *E*- C=**P**H), 85.5 (d, $^1J_{P-H}$ 153.1 Hz, *Z*- C=**P**H).

The solution turned orange after it was stirred for 18 h and was dried *in vacuo* to afford a red solid.

^{1}H NMR (C_6D_6): δ_H –0.36 (s, 4H), –0.26 (s, 1H), –0.07 (s, 5H), 0.08 (s, 3H), 0.12 (s, 3H), 0.15 (s, 3.5H), 0.19 (s, 2.5H), 0.27 (s, 5H), 3.03 (2nd order, 1H), 4.69 (2nd order, 1H), 6.91 (d, 1H, $^{3}J_{H-H}$ 7.96 Hz), 6.95 (d, 1.5H, $^{3}J_{H-H}$ 8.35 Hz), 7.25 (d, 1.5H, $^{3}J_{H-H}$ 9.01 Hz), 7.35 (d, 1H, $^{3}J_{H-H}$ 7.32 Hz), 7.53 (d, 1H, $^{3}J_{H-H}$ 8.27 Hz), 7.61 (d, 2H, $^{3}J_{H-H}$ 7.68 Hz), 7.65 (d, 3H, $^{3}J_{H-H}$ 9.30 Hz), 7.71 (br, 5H), 7.81 (br, 2H), 7.87 (d, 2H, $^{3}J_{H-H}$ 8.19 Hz), 7.98 (br, 3H).

^{31}P NMR (C_6D_6): δ_P –114.5 (ddd, $^{1}J_{P-P}$ 70.7 Hz, $^{1}J_{P-H}$ 172.7 Hz, J_{P-H} 10.8 Hz), –107.4 (t, $^{1}J_{P-H}$ 219.8 Hz, **P**H$_2$), –103.6 (2nd order), –96.3 (2nd order), –83.9 (ddd, $^{1}J_{P-P}$ 70.7 Hz, $^{1}J_{P-H}$ 185.4 Hz, J_{P-H} 12.6 Hz), –54.7 (dd, J_{P-P} 77.3 Hz, $^{1}J_{P-H}$ 176.5 Hz), –25.9 (s), –13.5 (d, $^{1}J_{P-H}$ 700.9 Hz), –5.80 (d, J_{P-P} 77.3 Hz), 57.6 (s), 72.8 (s).

The crude solid was washed with pentane; a brown solid was dried *in vacuo*, while reduced pressure solvent removal from the filtrate afforded an orange solid.

Brown solid:

^{1}H NMR (C_6D_6): δ_H –0.37 (s, 1H), –0.30 (s, 1H), –0.27 (s, 1.5H), –0.20 (s, 2H), –0.09 (s, 2H), –0.08 (s, 2H), 0.06 (br, 4.5H), 0.12 (s, 3H), 0.15 (s, 3H), 0.18 (s, 3H), 0.21 (br, 2.5H), 0.23 (br, 2H), 0.28 (s, 4H), 6.94 (br, 4H), 7.69 (br, 19H), 7.97 (d, 5H, $^{3}J_{H-H}$ 8.17 Hz).

^{31}P{^{1}H} NMR (C_6D_6): δ_P –107.4 (t, $^{1}J_{P-H}$ 221.1 Hz, **P**H$_2$), –103.6 (2nd order), –96.3 (2nd order), –54.7 (dd, J_{P-P} 77.3 Hz, $^{1}J_{P-H}$ 175.7 Hz), –5.72 (dd, J_{P-P} 77.3 Hz, J_{P-H} 20.7 Hz), –3.90 (s), 57.6 (s), 72.8 (s).

Orange solid:

^{1}H NMR (C_6D_6): δ_H –0.37 (s, 2H), –0.27 (s, 5H), –0.20 (s, 1.5H), –0.09 (s, 1H), –0.08 (s, 2H), 0.06 (s, 1.5H), 0.08 (s, 1.5H), 0.12 (s, 2H), 0.17 (s, 2H), 0.28 (s, 7H), 6.96 (br, 2H), 7.64 (d, 3H, $^{3}J_{H-H}$ 7.53 Hz), 7.70 (m, 3H), 7.74 (d, 2H, $^{3}J_{H-H}$ 8.57 Hz), 7.97 (d, 3H, $^{3}J_{H-H}$ 7.57 Hz).

^{31}P NMR (C_6D_6): δ_P –114.5 (ddd, $^{1}J_{P-P}$ 70.7 Hz, $^{1}J_{P-H}$ 172.7 Hz, J_{P-H} 10.8 Hz), –107.5 (t, $^{1}J_{P-H}$ 219.8 Hz, **P**H$_2$), –103.6 (2nd order), –96.3 (2nd order), –83.9 (ddd, $^{1}J_{P-P}$ 70.7 Hz, $^{1}J_{P-H}$ 185.4 Hz, J_{P-H} 12.6 Hz),–54.7 (dd, J_{P-P} 77.3 Hz, $^{1}J_{P-H}$ 175.7 Hz), –13.5 (d, $^{1}J_{P-H}$ 700.9 Hz), –5.80 (d, J_{P-P} 77.3 Hz), 57.6 (s), 72.8 (s).

Attempted synthesis of *E*/*Z*-C$_6$H$_4$(1-CO(SiMe$_3$)=PSiMe$_3$)(3-COCl) (*E*/*Z*-57-CH)

Method A

To a THF solution of P(SiMe$_3$)$_3$ (0.049 g, 1.96 x 10^{-4} mol) at –78 °C was added C$_6$H$_4$(1,3-COCl)$_2$ (0.039 g, 1.96 x 10^{-4} mol) in THF and the mixture was stirred for 15 min, resulting in a colourless solution that turned red when allowed to warm to ambient temperature over 45 min; an aliquot was dried *in vacuo* to afford a red oil.

^{1}H NMR (C_6D_6): δ_H 0.11 (s, 9H), 0.18 (s, 11H), 0.25 (s, 8H), 0.28 (s, 25H), 7.00 (t, 2H, $^{3}J_{H\text{-}H}$ 7.33 Hz, *p*-C**H**), 8.20 (d, 2H, $^{3}J_{H\text{-}H}$ 7.71 Hz, *o*-C**H**), 9.07 (br, 1H, middle-C**H**).

^{31}P{^{1}H} NMR (C_6D_6): δ_P −136.1 (s), −55.6 (m), −24.7 (s), 107.3 (br), 135.7 (br).

The solution was stirred for 18 h and dried *in vacuo* to afford an orange solid.

^{1}H NMR (C_6D_6): δ_H 0.11 (s, 21H), 0.17 (s, 17H), 0.25 (s, 12.5H), 0.28 (s, 70H), 6.78 (t, 3H, $^{3}J_{H\text{-}H}$ 7.90 Hz), 7.01 (t, 5H, $^{3}J_{H\text{-}H}$ 7.90 Hz), 8.19 (d, 5H, $^{3}J_{H\text{-}H}$ 7.81 Hz), 9.06 (s, 1.5H), 9.14 (s, 1H).

^{31}P NMR (C_6D_6): δ_P −26.0 (s), −25.5 (s), −13.2 (d, $^{1}J_{P\text{-}H}$ 693.8 Hz), −10.7 (d, $^{1}J_{P\text{-}H}$ 735.1 Hz).

^{29}Si{^{1}H} NMR (C_6D_6): δ_{Si} −22.9, 5.00, 23.9.

Method B

To a THF solution of $P(SiMe_3)_3$ (0.263 g, 1.05 x 10^{-3} mol) at ambient temperature was added $C_6H_4(1,3\text{-}COCl)_2$ (0.214 g, 1.05 x 10^{-3} mol) in THF, resulting in the rapid formation of a red solution that was stirred for 18 h. The solvent was removed under reduced pressure; the product was extracted with pentane and dried *in vacuo* to afford a red oil.

^{1}H NMR (C_6D_6): δ_H 0.25 (s, 4H), 7.00 (t, 1H, $^{3}J_{H\text{-}H}$ 7.80 Hz, *p*-C**H**), 8.19 (d, 2H, $^{3}J_{H\text{-}H}$ 7.77 Hz, *o*-C**H**), 9.07 (br, 1H, middle-C**H**).

^{13}C{^{1}H} NMR (C_6D_6): δ_C −0.31 (s), 128.7 (s, *p*-**C**H), 132.3 (s, middle-**C**H), 132.4 (s, *i*-**C**), 134.5 (s, *o*-**C**H), 165.8 (s, **C**OCl).

^{31}P NMR (C_6D_6): δ_P −24.9 (s).

^{29}Si{^{1}H} NMR (C_6D_6): δ_{Si} 23.1.

Attempted synthesis of *E*/*Z*-$C_5H_3N(2\text{-}CO(SiMe_3)\text{=}PSiMe_3)(6\text{-}COCl)$ (*E*/*Z*-57-N)

Method A

To a THF solution of $P(SiMe_3)_3$ (0.069 g, 2.76 x 10^{-4} mol) at –78 °C was added $C_5H_3N(2,6\text{-}COCl)_2$ (0.056 g, 2.76 x 10^{-4} mol) in THF, resulting in the rapid formation of a yellow solution that was stirred for 15 min. The solution turned dark red when allowed to warm to ambient temperature over 45 min; an aliquot was dried *in vacuo* to afford a dark red oil.

^{1}H NMR (C_6D_6): δ_H 0.18 (s, 4H), 0.25 (s, 3H), 0.28 (s, 3H), 0.31 (s, 8H), 6.97 (t, 1H, $^{3}J_{H\text{-}H}$ 7.89 Hz, *p*-C**H**), 7.95 (d, 2H, $^{3}J_{H\text{-}H}$ 7.87 Hz, *m*-C**H**).

^{31}P NMR (C_6D_6): δ_P −24.7 (s).

The solution was stirred for 18 h and dried *in vacuo* to afford a brown solid.

^{1}H NMR (C_6D_6): δ_H 0.11 (s, 3H), 0.18 (s, 5H), 0.25 (s, 5.5H), 0.28 (s, 17H), 0.31 (s, 9H), 6.98 (t, 1H, $^{3}J_{H\text{-}H}$ 8.00 Hz), 7.96 (d, 2H, $^{3}J_{H\text{-}H}$ 7.71 Hz).

^{31}P NMR (C_6D_6): δ_P −30.2 (s), −26.1 (s), −24.8 (s), −13.5 (d, $^{1}J_{P\text{-}H}$ 688.4 Hz), −9.22 (s).
^{29}Si{^{1}H} NMR (C_6D_6): δ_{Si} −22.1, 5.27, 20.1, 25.2.

Method B

To a THF solution of $P(SiMe_3)_3$ (0.210 g, 8.40 x 10^{-4} mol) at ambient temperature was added $C_5H_3N(2,6\text{-}COCl)_2$ (0.172 g, 8.40 x 10^{-4} mol) in THF, resulting in a dark red solution that was stirred for 18 h. The solvent was removed under reduced pressure; the product was extracted with pentane and dried *in vacuo* to afford an off-white solid.

^{1}H NMR (C_6D_6): δ_H 0.31 (s, 20H), 6.98 (t, 1H, $^{3}J_{H\text{-}H}$ 7.90 Hz, *p*-C**H**), 7.96 (d, 2H, $^{3}J_{H\text{-}H}$ 7.84 Hz, *m*-C**H**).

^{13}C{^{1}H} NMR (C_6D_6): δ_C −0.24 (s), 127.9 (s, *m*-**C**H), 137.4 (s, *p*-**C**H), 149.8 (s, *i*-**C**), 165.1 (s, **C**=O).

^{31}P NMR (C_6D_6): δ_P −24.7 (s).

Attempted synthesis of *E*/*Z*-C_6H_4(1-CO(SiMe$_3$)=PH)(3-COCl) (*E*/*Z*-58-CH)

Method A

To a THF solution of $HP(SiMe_3)_2$ (0.580 g, 2.98 x 10^{-3}) at −78 °C was added $C_6H_4(1,3\text{-}COCl)_2$ (0.604 g, 2.98 x 10^{-3}) in THF and the mixture was stirred for 15 min, resulting in a pale yellow solution that turned bright red when it was allowed to warm to ambient temperature over 45 min; an aliquot was dried *in vacuo* to afford a mixture of red and white solids (the white solid was identified as $C_6H_4(1,3\text{-}COCl)_2$).

^{1}H NMR (C_6D_6): δ_H 0.07 (br, 7.5H), 0.18 (s, 2.5H), 0.20 (s, 3.5H), 0.24 (s, 1.5H), 0.27 (s, 1.5H), 0.30 (s, 5H), 3.79 (d, 1H, $^{1}J_{H\text{-}P}$ 219.1 Hz, P**H**$_2$), 3.89 (d, 0.8H, $^{1}J_{H\text{-}P}$ 219.1 Hz, P**H**$_2$), 6.66 (t, 7H, $^{3}J_{H\text{-}H}$ 7.82 Hz), 6.85 (t, 2.5H, $^{3}J_{H\text{-}H}$ 7.82 Hz), 7.69 (d, 11H, $^{3}J_{H\text{-}H}$ 7.29 Hz), 7.80 (t, 2.5H, $^{3}J_{H\text{-}H}$ 8.62 Hz), 8.00 (d, 1H, $^{3}J_{H\text{-}H}$ 7.96 Hz), 8.45 (s, 4H), 8.74 (s, 1H).

^{31}P NMR (C_6D_6): δ_P –133.8 (t, $^{1}J_{P\text{-}H}$ 206.6 Hz, **P**H$_2$), –133.7 (t, $^{1}J_{P\text{-}H}$ 205.1 Hz, **P**H$_2$), –109.7 (t, $^{1}J_{P\text{-}H}$ 219.1 Hz, **P**H$_2$), –109.6 (t, $^{1}J_{P\text{-}H}$ 219.1 Hz, **P**H$_2$), –109.4 (t, $^{1}J_{P\text{-}H}$ 219.1 Hz, **P**H$_2$), –32.5 (m), –31.7 (s), –31.3 (m), –30.2 (m), –16.4 (s), –15.3 (s), –14.9 (s), –14.4 (s), –13.3 (s), –12.9 (s), –

12.0 (s), 54.5 (s), 64.6 (s), 64.8 (s), 65.2 (s), 70.1 (s), 70.7 (s), 72.1 (s), 72.4 (s), 73.2 (s), 74.2 (d, $J_{P\text{-}H}$ 154.6 Hz), 101.7 (s), 103.7 (s), 105.1 (s), 107.1 (s), 109.4 (s), 111.5 (s), 111.9 (s), 113.4 (s).

$^{29}Si\{^{1}H\}$ NMR (C_6D_6): δ_{Si} –22.2, 16.3, 17.9, 22.2, 25.1, 31.3.

The solution turned orange after being stirred for 18 h and was dried *in vacuo* to afford a red solid.

^{1}H NMR (C_6D_6): δ_H 0.11 (s, 2H), 0.18 (s, 5.5H), 0.20 (s, 8H), 0.24 (s, 2.5H), 0.27 (s, 7H), 3.78 (d, 2H, $^{1}J_{H\text{-}P}$ 219.1 Hz, P**H**$_2$), 3.89 (d, 0.8H, $^{1}J_{H\text{-}P}$ 219.1 Hz, P**H**$_2$),6.63 (t, 14H, $^{3}J_{H\text{-}H}$ 7.85 Hz), 6.82 (t, 9H, $^{3}J_{H\text{-}H}$ 7.19 Hz), 7.67 (d, 22H, $^{3}J_{H\text{-}H}$ 8.21 Hz), 7.76 (d, 6H, $^{3}J_{H\text{-}H}$ 7.92 Hz), 7.80 (d, 4.5H, $^{3}J_{H\text{-}H}$ 7.92 Hz), 7.85 (d, 4.5H, $^{3}J_{H\text{-}H}$ 8.21 Hz), 8.31 (s, 1H), 8.45 (s, 7H), 8.65 (s, 2.5H), 8.75 (s, 2.5H).

^{31}P NMR (C_6D_6): δ_P –109.7 (t, $^{1}J_{P\text{-}H}$ 219.1 Hz, **P**H$_2$), –109.6 (t, $^{1}J_{P\text{-}H}$ 219.1 Hz, **P**H$_2$), –109.4 (t, $^{1}J_{P\text{-}H}$ 219.1 Hz, **P**H$_2$), –109.3 (t, $^{1}J_{P\text{-}H}$ 219.1 Hz, **P**H$_2$), 54.4 (s), 64.5 (s), 64.8 (s), 65.1 (s), 113.4 (s).

The crude solid was washed with pentane; an orange solid was dried *in vacuo*, while reduced pressure solvent removal from the filtrate afforded a yellow solid.

Orange solid:

^{1}H NMR (C_6D_6): δ_H 0.12 (s, 4H), 0.17 (s, 5H), 0.18 (s, 3H), 0.24 (s, 2.5H), 0.25 (s, 1.5H), 0.28 (s, 9H), 0.31 (s, 2.5H), 6.55 (t, 4.5H, $^{3}J_{H\text{-}H}$ 7.90 Hz), 6.76 (m, 15.5H), 6.95 (br, 7H), 7.63 (d, 6H, $^{3}J_{H\text{-}H}$ 7.84 Hz), 7.73 (d, 8H, $^{3}J_{H\text{-}H}$ 7.84 Hz), 7.76 (d, 7.5H, $^{3}J_{H\text{-}H}$ 7.84 Hz), 7.82 (d, 6H, $^{3}J_{H\text{-}H}$ 7.97 Hz), 7.97 (br, 5H), 8.15 (d, 3H, $^{3}J_{H\text{-}H}$ 7.60 Hz), 8.44 (s, 1.5H), 8.67 (s, 3H), 8.72 (s, 2.5H), 8.77 (s, 2.5H), 8.79 (s, 2H), 8.89 (s, 1.5H).

^{31}P NMR (C_6D_6): δ_P –109.8 (t, $^{1}J_{P\text{-}H}$ 219.2 Hz, **P**H$_2$), –109.5 (t, $^{1}J_{P\text{-}H}$ 220.8 Hz, **P**H$_2$), –109.4 (t, $^{1}J_{P\text{-}H}$ 220.8 Hz, **P**H$_2$), –13.3 (d, $^{1}J_{P\text{-}H}$ 700.9 Hz), 54.2 (s), 54.3 (s), 54.3 (s), 64.4 (s), 64.6 (s), 64.9 (s), 65.0 (s).

Yellow solid:

^{1}H NMR (C_6D_6): δ_H 0.12 (s, 4H), 0.28 (s, 16H), 3.75 (d, 2H, $^{1}J_{H\text{-}P}$ 219.2 Hz, P**H**$_2$), 6.56 (t, 21H, $^{3}J_{H\text{-}H}$ 7.68 Hz), 6.77 (t, 4H, $^{3}J_{H\text{-}H}$ 7.86 Hz), 6.96 (br, 3H), 7.63 (d, 35H, $^{3}J_{H\text{-}H}$ 7.90 Hz), 7.76 (d, 3H, $^{3}J_{H\text{-}H}$ 7.57 Hz), 8.15 (d, 2.5H, $^{3}J_{H\text{-}H}$ 7.65 Hz), 8.45 (s, 9.5H), 8.88 (s, 2H).

^{31}P NMR (C_6D_6): δ_P –109.8 (t, $^{1}J_{P\text{-}H}$ 219.2 Hz, **P**H$_2$), 54.3 (s), 64.9 (s).

Method B

To a THF solution of $HP(SiMe_3)_2$ (0.520 g, 2.92 x 10^{-3} mol) at ambient temperature was added $C_6H_4(1,3\text{-}COCl)_2$ (0.593 g, 2.92 x 10^{-3} mol) in THF, resulting in a red solution that was stirred for 5 min; an aliquot was dried *in vacuo* to afford an orange oil.

^{1}H NMR (C_6D_6): δ_H 0.18 (s, 6H), 0.19 (s, 8H), 0.28 (br, 15H), 3.76 (d, 2H, $^1J_{H\text{-}P}$ 220.0 Hz, PH_2), 3.81 (d, 1H, $^1J_{H\text{-}P}$ 219.2 Hz, P**H**$_2$), 3.87 (d, 2H, $^1J_{H\text{-}P}$ 220.0 Hz, P**H**$_2$), 6.58 (t, 12H, $^3J_{H\text{-}H}$ 7.75 Hz), 6.79 (t, 6H, $^3J_{H\text{-}H}$ 7.54 Hz), 7.65 (d, 20 H, $^3J_{H\text{-}H}$ 7.96 Hz), 7.98 (d, 3H, $^3J_{H\text{-}H}$ 7.52 Hz), 8.19 (d, 2H, $^3J_{H\text{-}H}$ 8.29 Hz), 8.45 (s, 6H), 8.66 (s, 1H), 8.76 (s, 2H).

^{31}P NMR (C_6D_6): δ_P −109.8 (t, $^1J_{P\text{-}H}$ 220.0 Hz, **P**H$_2$), −109.7 (t $^1J_{P\text{-}H}$ 219.2 Hz, **P**H$_2$), −109.5 (t $^1J_{P\text{-}H}$ 220.0 Hz, **P**H$_2$), −109.4 (s), 54.3 (s), 54.4 (s), 64.4 (s), 64.7 (s), 65.0 (s).

The solution was stirred for 18 h and the solvent was removed under reduced pressure to afford an orange oil; no change was noted from the previous NMR spectra.

Attempted synthesis of *E*/*Z*-$C_5H_3N(2\text{-}CO(SiMe_3)\text{=}PH)(6\text{-}COCl)$ (*E*/*Z*-58-N)

Method A

To a THF solution of $HP(SiMe_3)_2$ (0.470 g, 2.64 x 10^{-3} mol) at −78 °C was added $C_5H_3N(2,6\text{-}COCl)_2$ (0.539 g, 2.64 x 10^{-3} mol) in THF and the mixture was stirred for 15 min, resulting in a bright yellow solution that turned dark red when it was allowed to warm to ambient temperature over 45 min; an aliquot was dried *in vacuo* to afford a dark red oil.

^{1}H NMR (C_6D_6): δ_H 0.19 (s, 4H), 6.59 (t, 1H, $^3J_{H\text{-}H}$ 7.59 Hz, *p*-C**H**), 7.30 (d, 2H, $^3J_{H\text{-}H}$ 7.96 Hz, *m*-C**H**).

^{31}P{^{1}H} NMR (C_6D_6): None observed.

The solution was stirred for 18 h and dried under reduced pressure as a dark red solid.

^{1}H NMR (C_6D_6): δ_H 0.16 (s, 1H), 0.18 (s, 2.5H), 0.28 (s, 1H), 6.59 (t, 4H, $^3J_{H\text{-}H}$ 7.59 Hz, *p*-C**H**), 7.30 (d, 8H, $^3J_{H\text{-}H}$ 7.96 Hz, *m*-C**H**).

^{31}P{^{1}H} NMR (C_6D_6): None observed.

Method B

To a THF solution of $HP(SiMe_3)_2$ (0.380 g, 2.13 x 10^{-3} mol) at ambient temperature was added $C_5H_3N(2,6\text{-}COCl)_2$ (0.436 g, 2.13 x 10^{-3} mol) in THF, resulting in a dark red solution within 5 min; an aliquot was dried *in vacuo* to afford a dark purple solid.

^{1}H NMR (C_6D_6): δ_H 0.19 (s, 1H), 6.58 (t, 1H, $^{3}J_{H-H}$ 8.20 Hz, *p*-C**H**), 7.30 (d, 2H, $^{3}J_{H-H}$ 7.84 Hz, *m*-C**H**).

^{31}P{^{1}H} NMR (C_6D_6): None observed.

The solution was stirred for 18 h then the solvent was removed under reduced pressure to afford a dark purple solid; no change was noted from the previous NMR spectra.

6.4 Chapter 4: The development of novel phosphomide derivatives

Synthesis of C_6H_4(1-C(O)PPh_2)(3-Me) (62)

To an Et_2O solution of $HPPh_2$ (1.29 g, 6.95 x 10^{-3} mol) at −78 °C was added drop-wise C_6H_4(1-COCl)(3-Me) (1.07 g, 6.95 x 10^{-3} mol) in Et_2O, resulting in a colourless solution that was stirred for 30 min. Upon warming to ambient temperature the solution turned yellow then stirred for 18 h. The solvent was removed under reduced pressure; the product was washed with pentane and dried *in vacuo* to afford a yellow solid. Yield: 1.41 g, 66.7 %.

^{1}H NMR (C_6D_6): δ_H 1.88 (s, 3H, C**H**$_3$), 6.81 (d, 1H, $^{3}J_{H-H}$ 7.43 Hz, *p*-C**H**), 6.87 (t, 1H, $^{3}J_{H-H}$ 7.68 Hz, *m*-C**H**), 7.01 (m, 6H, *m*-C**H** and *p*-C**H** of Ph), 7.50 (m, 4H, *o*-C**H** of Ph), 7.96 (s, 1H, middle-C**H**), 7.99 (d, 1H, $^{3}J_{H-H}$ 7.87 Hz, *o*-C**H**).

^{13}C{^{1}H} NMR (C_6D_6): δ_C 21.0 (s, **C**H$_3$), 126.3 (d, $^{3}J_{C-P}$ 10.9 Hz, *o*-**C**H), 128.6 (s, *m*-**C**H), 128.8 (s, middle-**C**H), 128.9 (d, $^{3}J_{C-P}$ 7.85 Hz, *m*-**C**H of Ph), 129.5 (s, *p*-**C**H of Ph), 133.9 (s, *p*-**C**H), 135.3 (d, $^{2}J_{C-P}$ 18.9 Hz, *o*-**C**H of Ph), 138.6 (s, **C**Me), 140.2 (d, $^{2}J_{C-P}$ 35.7 Hz, *i*-**C**), 211.8 (d, $^{1}J_{C-P}$ 36.9 Hz, **C**(O)P).

^{31}P NMR (C_6D_6): δ_P 12.4 (m, $^{3}J_{P-H}$ 7.94 Hz).

Elem. Anal.: Calcd for $C_{20}H_{17}OP$: C, 78.95 %; H, 5.59 %. Found; C, 78.84 %; H, 5.47 %.

IR: $\nu_{(C=O)}$ 1634 cm^{-1}.

Synthesis of C_6H_4(1-C(O)PPh_2)(3-CH_2Cl) (63)

Prepared as for **62** using C_6H_4(1-COCl)(3-CH_2Cl) (0.712 g, 3.76 x 10^{-3} mol) and $HPPh_2$ (0.701 g, 3.76 x 10^{-3} mol). Isolated as a yellow solid. Yield: 1.13 g, 88.8 %.

^{1}H NMR (C_6D_6): δ_H 3.83 (s, 2H, C**H**$_2$Cl), 6.77 (t, 1H, $^{3}J_{H-H}$ 7.61 Hz, *m*-C**H**), 6.88 (d, 1H, $^{3}J_{H-H}$ 7.55 Hz, *p*-C**H**), 7.01 (m, 6H, *m*-C**H** and *p*-C**H** of Ph), 7.47 (m, 4H, *o*-C**H** of Ph), 7.96 (dq, 1H, $^{3}J_{H-H}$ 7.74 Hz, $^{4}J_{H-H}$ 1.38 Hz, *o*-C**H**), 8.03 (q, 1H, $^{4}J_{H-H}$ 1.73 Hz, middle-C**H**).

$^{13}C\{^{1}H\}$ NMR (C_6D_6): δ_C 45.2 (s, **C**H_2Cl), 128.4 (s, middle-**C**H), 128.5 (s, *o*-**C**H), 129.0 (s, *m*-**C**H), 129.0 (d, $^{3}J_{C\text{-}P}$ 7.76 Hz, *m*-**C**H of Ph), 129.6 (s, *p*-**C**H of Ph), 132.9 (s, *p*-**C**H), 133.4 (d, $^{1}J_{C\text{-}P}$ 6.09 Hz, *i*-**C** of Ph), 135.3 (d, $^{2}J_{C\text{-}P}$ 18.5 Hz, *o*-**C**H of Ph), 138.4 (s, **C**CH_2Cl), 140.2 (d, $^{2}J_{C\text{-}P}$ 35.4 Hz, *i*-**C**), 211.4 (d, $^{1}J_{C\text{-}P}$ 37.9 Hz, **C**(O)P).

^{31}P NMR (C_6D_6): δ_P 12.9 (m, $^{3}J_{P\text{-}H}$ 8.25 Hz).

Elem. Anal.: Calcd for $C_{20}H_{16}OPCl$: C, 70.90 %; H, 4.73 %. Found; C, 70.98 %; H, 4.68 %.

IR: $\nu_{(C=O)}$ 1645 cm^{-1}.

Synthesis of C_6H_4(1-C(O)PPh_2)(3-CN) (64)

Prepared as for **62** using C_6H_4(1-COCl)(3-CN) (0.334 g, 2.02 x 10^{-3} mol) and $HPPh_2$ (0.375 g, 2.02 x 10^{-3} mol) in THF. Isolated as a viscous yellow oil. Yield: 0.663 g, 93.6 %.

^{1}H NMR (C_6D_6): δ_H 6.43 (t, $^{3}J_{H\text{-}H}$ 7.79 Hz, 1H, *m*-C**H**), 6.72 (d, $^{3}J_{H\text{-}H}$ 8.10 Hz, 1H, *p*-C**H**), 6.99 (m, 6H, *m*-C**H** and *p*-C**H** of Ph), 7.36 (t, $^{3}J_{H\text{-}H}$ 7.02 Hz, 4H, *o*-C**H** of Ph), 7.81 (d, $^{3}J_{H\text{-}H}$ 7.77 Hz, 1H, *o*-C**H**), 8.06 (s, 1H, middle-C**H**).

$^{13}C\{^{1}H\}$ NMR (C_6D_6): δ_C 113.5 (s, *i*-**C**C≡N), 117.8 (s, **C**≡N), 129.1 (d, $^{3}J_{C\text{-}P}$ 7.71 Hz, *m*-**C**H of Ph and *m*-**C**H), 129.9 (s, *p*-**C**H of Ph), 131.4 (d, $^{3}J_{C\text{-}P}$ 9.12 Hz, middle-**C**H), 131.5 (d, $^{3}J_{C\text{-}P}$ 9.12 Hz, *o*-**C**H), 132.4 (d, $^{1}J_{C\text{-}P}$ 5.90 Hz, *i*-**C** of Ph), 135.3 (d, $^{2}J_{C\text{-}P}$ 18.2 Hz, *o*-**C**H of Ph), 135.5 (s, *p*-**C**H**)** 140.1 (d, $^{2}J_{C\text{-}P}$ 35.9 Hz, *i*-**C**), 210.7 (d, $^{1}J_{C\text{-}P}$ 39.6 Hz, **C**(O)P).

^{31}P NMR (C_6D_6): δ_P 13.5 (br).

Synthesis of C_6H_4(1-C(O)PPh_2)(4-CO_2Me) (65)

Prepared as for **62** using C_6H_4(1-COCl)(4-CO_2Me) (0.610 g, 3.07 x 10^{-3} mol) and $HPPh_2$ (0.572 g, 3.07 x 10^{-3} mol). Isolated as a yellow solid. Yield: 0.853 g, 79.8 %.

^{1}H NMR (C_6D_6): δ_H 3.35 (s, 3H, C**H**$_3$), 7.00 (m, 6H, *m*-C**H** and *p*-C**H** of Ph), 7.42 (m, 4H, $^{3}J_{H\text{-}H}$ 8.00 Hz, *o*-C**H** of Ph), 7.84 (d, 2H, $^{3}J_{H\text{-}H}$ 8.35 Hz, *m*-C**H**), 7.97 (dd, 2H, $^{3}J_{H\text{-}H}$ 6.80 Hz, $^{4}J_{H\text{-}P}$ 1.76 Hz, *o*-C**H**).

$^{13}C\{^{1}H\}$ NMR (C_6D_6): δ_C 51.7 (s, **C**H_3), 128.2 (m, *o*-**C**H), 129.0 (d, $^{3}J_{C\text{-}P}$ 7.69 Hz, *m*-**C**H of Ph), 129.7 (s, *m*-**C**H), 130.0 (s, *p*-**C**H of Ph), 134.2 (s, **C**CO_2Me), 135.3 (d, $^{2}J_{C\text{-}P}$ 19.1 Hz, *o*-**C**H of Ph), 142.9 (d, $^{2}J_{C\text{-}P}$ 34.6 Hz, *i*-**C**), 165.6 (s, **C**O_2Me), 212.1 (d, $^{1}J_{C\text{-}P}$ 38.3 Hz, **C**(O)P).

^{31}P NMR (C_6D_6): δ_P 14.4 (m, $^{3}J_{P\text{-}H}$ 7.61 Hz).

IR: $\nu_{(C=O)}$ 1721 cm^{-1}, $\nu_{(C=O)}$ 1649 cm^{-1}.

FAB-MS *m/z* 349 $[MH]^+$. No other fragments were identified.

Synthesis of C_6H_4(1-C(O)PPh_2)(4-CN) (66)

Prepared as for **62** using C_6H_4(1-COCl)(4-CN) (0.659 g, 3.98 x 10^{-3} mol) and $HPPh_2$ (0.741 g, 3.98 x 10^{-3} mol). Isolated as a yellow solid. Yield: 1.00 g, 79.9 %.

^{1}H NMR (C_6D_6): δ_H 6.71 (br d, 2H $^3J_{H\text{-}H}$ 8.20 Hz, *m*-C**H**), 7.01 (m, 4H, *m*-C**H** of Ph), 7.02 (m, 2H, *p*-C**H** of Ph), 7.35 (m, 4H, *o*-C**H** of Ph), 7.63 (br d, 2H, $^3J_{H\text{-}H}$ 8.46 Hz, *o*-C**H**).

^{13}C{^{1}H} NMR (C_6D_6): δ_C 116.5 (d, $J_{C\text{-}P}$ 1.96 Hz, *i*-**C**C≡N), 117.9 (s, **C**≡N), 128.2 (s, *o*-**C**H), 129.1 (d, $^3J_{C\text{-}P}$ 7.78 Hz, *m*-**C**H of Ph), 129.9 (s, *p*-**C**H of Ph), 132.3 (s, *m*-**C**H), 135.3 (d, $^2J_{C\text{-}P}$ 18.9 Hz, *o*-**C**H of Ph), 141.9 (d, $^2J_{C\text{-}P}$ 38.4 Hz, *i*-**C**), 211.5 (d, $^1J_{C\text{-}P}$ 38.7 Hz, **C**(O)P).

^{31}P NMR (C_6D_6): δ_P 14.5 (m, $^3J_{P\text{-}H}$ 8.12 Hz).

IR: $\nu_{(C\equiv N)}$ 2229 cm^{-1}, $\nu_{(C=O)}$ 1650 cm^{-1}.

FAB-MS *m/z* 316 $[MH]^+$. No other fragments were identified.

Synthesis of C_6H_4(1-C(O)PCy_2)(3-Me) (67)

To an Et_2O solution of $HPCy_2$ (0.269 g, 1.36 x 10^{-3} mol) at −78 °C was added ^{n}BuLi (2.5 M, 0.54 cm^3, 1.36 x 10^{-3} mol) and the mixture was allowed to warm to ambient temperature over 30 min. An Et_2O solution of C_6H_4(1-C(O)PPh_2)(3-Me) (0.209 g, 1.36 x 10^{-3} mol) was added at −78 °C, resulting in a pale yellow solution that was stirred for 30 min and was then allowed to warm to ambient temperature. After stirring for 18 h the solvent was removed under reduced pressure; the product was extracted with pentane and dried *in vacuo* to afford a yellow oil. Yield: 0.395 g, 91.2 %.

^{1}H NMR (C_6D_6): δ_H 1.03 (m, 2H, C**H**$_2$, *p*-C**H** of Cy), 1.22 (m, 8H, C**H**$_2$ of Cy), 1.50 (m, 2H, C**H**$_2$, *p*-C**H** of Cy), 1.61 (m, 4H, C**H**$_2$ of Cy), 1.85 (m, 2H, C**H**$_2$ of Cy), 1.97 (m, 2H, C**H**$_2$ of Cy), 2.02 (s, 3H, C**H**$_3$), 2.20 (m, 2H, C**H** of Cy), 6.96 (d, 1H, $^3J_{H\text{-}H}$ 7.51 Hz, *p*-C**H**), 7.05 (t, $^3J_{H\text{-}H}$ 7.51 Hz, *m*-C**H**), 8.08 (s, 1H, middle-C**H**), 8.13 (d, 1H, $^3J_{H\text{-}H}$ 8.35 Hz, *o*-C**H**).

^{13}C{^{1}H} NMR (C_6D_6): δ_C 21.1 (s, **C**H$_3$), 26.7 (s, **C**H$_2$, *p*-**C**H of Cy), 27.5 (d, $J_{C\text{-}P}$ 9.80 Hz, **C**H$_2$ of Cy), 27.7 (d, $J_{C\text{-}P}$ 9.94 Hz, **C**H$_2$ of Cy), 30.3 (d, $J_{C\text{-}P}$ 10.9 Hz, **C**H$_2$ of Cy), 31.3 (d, $J_{C\text{-}P}$ 10.5 Hz, **C**H$_2$ of Cy), 33.0 (d, $^1J_{C\text{-}P}$ 13.3 Hz, **C**H of Cy), 126.2 (d, $^3J_{C\text{-}P}$ 11.7 Hz, *o*-**C**H), 128.7 (s, *m*-C**H**), 128.8 (d, $^3J_{C\text{-}P}$ 10.0 Hz, middle-**C**H), 134.0 (s, *p*-**C**H), 138.6 (s, **C**CH$_3$), 143.1 (d, $^2J_{C\text{-}P}$ 32.6 Hz, *i*-**C**), 216.4 (d, $^1J_{C\text{-}P}$ 44.1 Hz, **C**(O)P).

^{31}P NMR (C_6D_6): δ_P 16.7 (br).

EI-MS *m/z* 316 $[MH]^+$. No other fragments were identified.

Synthesis of $C_6H_4(1\text{-}C(O)PCy_2)(3\text{-}CH_2Cl)$ (68)

Prepared as for **67** using ^{n}BuLi (2.5 M, 0.657 cm^3, 1.64 x 10^{-3} mol), $HPCy_2$ (0.325 g, 1.64 x 10^{-3} mol) and $C_6H_4(1\text{-}C(O)PPh_2)(3\text{-}CH_2Cl)$ (0.310 g, 1.64 x 10^{-3} mol). Isolated as a yellow oil. Yield: 0.562 g, 97.8 %.

^{1}H NMR (C_6D_6): δ_H 1.02 (m, 2H, *p*-C**H**$_2$ of Cy), 1.23 (m, 8H, C**H**$_2$ of Cy), 1.50 (m, 2H, *p*-C**H**$_2$ of Cy), 1.60 (m, 4H, C**H**$_2$ of Cy), 1.82 (m, 2H, C**H**$_2$ of Cy), 1.96 (m, 2H, C**H**$_2$ of Cy), 2.17 (m, 2H, C**H** of Cy), 3.97 (s, 2H, C**H**$_2$Cl), 6.96 (t, 1H, $^3J_{H\text{-}H}$ 7.70 Hz, *m*-C**H**), 7.04 (d, 1H, $^3J_{H\text{-}H}$ 7.80 Hz, *p*-C**H**), 8.09 (d, 1H, $^3J_{H\text{-}H}$ 7.60 Hz, C**H**, *o*-C**H**), 8.17 (s, 1H, C**H**, middle-C**H**).

^{13}C{^{1}H} NMR (C_6D_6): δ_C 26.6 (s, **C**H$_2$, *p*-**C**H of Cy), 27.5 (d, $J_{C\text{-}P}$ 9.53 Hz, **C**H$_2$ of Cy), 27.7 (d, $J_{C\text{-}P}$ 10.0 Hz, **C**H$_2$ of Cy), 30.2 (d, $J_{C\text{-}P}$ 10.8 Hz, **C**H$_2$ of Cy), 31.3 (d, $J_{C\text{-}P}$ 10.0 Hz, **C**H$_2$ of Cy), 32.9 (d, $^1J_{C\text{-}P}$ 13.7 Hz, **C**H of Cy), 45.4 (s, **C**H$_2$Cl), 128.4 (s, *o*-**C**H), 128.5 (s, middle-**C**H), 129.1 (s, *m*-**C**H), 133.1 (s, *p*-**C**H), 138.6 (s, **C**CH_2Cl), 143.1 (d, $^2J_{C\text{-}P}$ 33.2 Hz, *i*-**C**), 216.3 (d, $^1J_{C\text{-}P}$ 44.7 Hz, **C**(O)P).

^{31}P NMR (C_6D_6): δ_P 17.8 (br).

EI-MS *m/z* 349 $[M - H]^+$. No other fragments were identified.

Synthesis of $[Rh(1,5\text{-}COD)\{C_6H_4(1\text{-}C(O)PPh_2)(3\text{-}Me)\}Cl]$ (69)

To a DCM solution of $[Rh(1,5\text{-}COD)Cl]_2$ (0.184 g, 3.73 x 10^{-4} mol) at ambient temperature was added $C_6H_4(1\text{-}C(O)PPh_2)(3\text{-}Me)$ (0.227 g, 7.47 x 10^{-4} mol), resulting in an orange solution that was stirred for 18 h. The solvent was removed under reduced pressure; the product was washed with pentane and dried *in vacuo* to afford a dark yellow solid. Yield: 0.155 g, 75.5 %.

^{1}H NMR ($CDCl_3$): δ_H 2.04-2.17 (m, 4H, C**H**$_2$ of COD), 2.47 (br, 7H, C**H**$_2$ of COD and C**H**$_3$), 3.42 (br, 2H, C**H** of COD), 5.61 (br, 2H, C**H** of COD), 7.35 (t, 4H, $^3J_{H\text{-}H}$ 7.54 Hz, *m*-C**H** of Ph), 7.43 (m, 4H, *p*-C**H** of Ph, *m*-C**H** and *p*-C**H**), 7.66 (t, 4H, $^3J_{H\text{-}H}$ 9.13 Hz, *o*-C**H** of Ph), 8.51 (s, 1H, middle-C**H**), 8.71 (br, 1H, *o*-C**H**).

^{13}C{^{1}H} NMR ($CDCl_3$): δ_C 21.7 (s, **C**H$_3$), 29.2 (s, **C**H$_2$ of COD), 33.2 (d, $^3J_{C\text{-}Rh}$ 2.51 Hz, **C**H$_2$ of COD), 71.0 (d, $^1J_{C\text{-}Rh}$ 13.2 Hz, **C**H of COD), 105.4 (dd, $^1J_{C\text{-}Rh}$ 11.5 Hz, $^2J_{C\text{-}P}$ 7.41 Hz, **C**H of COD), 128.4 (d, $^3J_{C\text{-}P}$ 9.70 Hz, *m*-**C**H of Ph), 128.4 (s, *m*-**C**H), 128.5 (d, $^3J_{C\text{-}P}$ 3.51 Hz, *o*-**C**H), 129.8 (d, $^1J_{C\text{-}P}$ 39.9 Hz, *i*-**C** of Ph), 130.7 (d, $^4J_{C\text{-}P}$ 2.26 Hz, *p*-**C**H of Ph), 131.2 (d, $^3J_{C\text{-}P}$ 3.67 Hz,

middle-**C**H), 134.9 (s, *p*-**C**H), 135.6 (d, $^{2}J_{C\text{-}P}$ 11.1 Hz, *o*-**C**H of Ph), 138.6 (d, $^{2}J_{C\text{-}P}$ 42.7 Hz, *i*-**C**), 138.5 (s, **C**CH_3), 202.2 (d, $^{1}J_{C\text{-}P}$ 16.5 Hz, **C**(O)P).

^{31}P NMR ($CDCl_3$): δ_P 36.1 (d, $^{1}J_{P\text{-}Rh}$ 145.8 Hz).

Elem. Anal.: Calcd for $C_{28}H_{29}OPRhCl$: C, 61.04 %; H, 5.27 %. Found; C, 60.93 %; H, 5.18 %.

IR: $\nu_{(C=O)}$ 1657 cm^{-1}.

Synthesis of [Rh(1,5-COD){C_6H_4(1-C(O)PPh_2)(3-CH_2Cl)}Cl] (70)

Prepared as for **69** using C_6H_4(1-C(O)PPh_2)(3-CH_2Cl) (0.189 g, 5.58 x 10^{-4} mol) and [Rh(1,5-COD)Cl]$_2$ (0.138 g, 2.79 x 10^{-4} mol). Isolated as a dark yellow solid. Yield: 0.124 g, 75.9 %.

^{1}H NMR ($CDCl_3$): δ_H 2.05-2.16 (m, 4H, C**H**$_2$ of COD), 2.49 (br 4H, C**H**$_2$ of COD), 3.42 (br, 2H, C**H** of COD), 4.68 (s, 2H, C**H**$_2$Cl), 5.63 (br, 2H, C**H** of COD), 7.37 (t, 4H, $^{3}J_{H\text{-}H}$ 7.32 Hz, *m*-C**H** of Ph), 7.44 (t, 2H, $^{3}J_{H\text{-}H}$ 7.32 Hz, *p*-C**H** of Ph), 7.53 (t, 1H, $^{3}J_{H\text{-}H}$ 7.68 Hz, *m*-C**H**), 7.66 (t, 5H, $^{3}J_{H\text{-}H}$ 8.91 Hz, *o*-C**H** of Ph and *p*-C**H**), 8.73 (d, 1H, $^{3}J_{H\text{-}H}$ 7.83 Hz, *o*-C**H**), 8.81 (s, 1H, middle-C**H**).

^{13}C{^{1}H} NMR ($CDCl_3$): δ_C 29.2 (s, **C**H_2 of COD), 33.2 (s, **C**H_2 of COD), 45.9 (s, **C**H_2Cl), 71.4 (d, $^{1}J_{C\text{-}Rh}$ 13.8 Hz, **C**H of COD), 105.8 (dd, $^{1}J_{C\text{-}Rh}$ 11.6 Hz, $^{2}J_{C\text{-}P}$ 7.18 Hz, **C**H of COD), 128.6 (d, $^{3}J_{C\text{-}P}$ 9.52 Hz, *m*-**C**H of Ph), 128.9 (s, *m*-**C**H), 129.4 (d, $^{1}J_{C\text{-}P}$ 39.8 Hz, *i*-**C** of Ph), 130.8 (d, $^{3}J_{C\text{-}P}$ 4.19 Hz, *o*-**C**H), 130.9 (d, $^{4}J_{C\text{-}P}$ 2.67 Hz, *p*-**C**H of Ph), 131.2 (d, $^{3}J_{C\text{-}P}$ 3.43 Hz, middle-**C**H), 133.9 (s, *p*-**C**H), 135.5 (d, $^{2}J_{C\text{-}P}$ 9.93 Hz, *o*-**C**H of Ph), 138.0 (s, **C**CH_2Cl), 139.0 (d, $^{2}J_{C\text{-}P}$ 42.9 Hz, *i*-**C**), 202.1 (m, **C**(O)P).

^{31}P NMR ($CDCl_3$): δ_P 36.4 (d, $^{1}J_{P\text{-}Rh}$ 145.7 Hz).

Elem. Anal.: Calcd for $C_{28}H_{28}OPRhCl_2$: C, 57.44 %; H, 4.79 %. Found; C, 57.43 %; H, 4.75 %.

IR: $\nu_{(C=O)}$ 1657 cm^{-1}.

Synthesis of [Rh(1,5-COD){C_6H_4(1-C(O)PPh_2)(4-CO_2Me)}Cl] (71)

Prepared as for **69** using C_6H_4(1-C(O)PPh_2)(4-CO_2Me) (0.278 g, 7.99 x 10^{-4} mol) and [Rh(1,5-COD)Cl]$_2$ (0.197 g, 3.99 x 10^{-4} mol). Isolated as a yellow solid. Yield: 0.205 g, 86.4 %.

^{1}H NMR ($CDCl_3$): δ_H 2.08-2.16 (m, 4H, C**H**$_2$ of COD), 2.49 (br, 4H, C**H**$_2$ of COD), 3.43 (br, 2H, C**H** of COD), 3.97 (s, 3H, C**H**$_3$), 5.62 (br, 2H, C**H** of COD), 7.35 (m, 4H, *m*-C**H** of Ph), 7.43 (d, 2H, $^{3}J_{H\text{-}H}$ 7.27 Hz, *p*-C**H** of Ph), 7.62 (t, 4H, $^{3}J_{H\text{-}H}$ 8.85 Hz, *o*-C**H** of Ph), 8.18 (d, 2H, $^{3}J_{H\text{-}H}$ 8.26 Hz, *m*-C**H**), 8.87 (d, 2H, $^{3}J_{H\text{-}H}$ 8.26 Hz, *o*-C**H**).

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ_C 29.3 (s, **C**H_2 of COD), 33.2 (s, **C**H_2 of COD), 52.7 (s, **C**H_3), 71.4 (d, $^{1}J_{C\text{-}Rh}$ 13.9 Hz, **C**H of COD), 106.0 (dd, $^{1}J_{C\text{-}Rh}$ 11.6 Hz, $^{2}J_{C\text{-}P}$ 7.26 Hz, **C**H of COD), 128.6 (d, $^{3}J_{C\text{-}P}$ 9.73 Hz, *m*-**C**H of Ph), 129.8 (s, *m*-**C**H), 130.7 (m, *o*-**C**H), 131.0 (m, *p*-**C**H of Ph), 135.5 (d, $^{2}J_{C\text{-}P}$ 10.7 Hz, *o*-**C**H of Ph), 141.8 (d, $^{2}J_{C\text{-}P}$ 42.5 Hz, *i*-**C**), 166.3 (s, **C**O_2Me), 202.5 (d, $^{1}J_{C\text{-}P}$ 17.9 Hz, **C**(O)P).

^{31}P NMR ($CDCl_3$): δ_P 36.9 (d, $^{1}J_{P\text{-}Rh}$ 146.9 Hz).

Elem. Anal.: Calcd for $C_{29}H_{29}O_3PClRh$: C, 58.55 %; H, 4.88 %. Found; C, 58.42 %; H, 4.96 %.

IR: $\nu_{(C=O)}$ 1718 cm^{-1}, $\nu_{(C=O)}$ 1663 cm^{-1}.

Synthesis of [Rh(1,5-COD){C_6H_4(1-C(O)PPh_2)(4-CN)}Cl] (72)

Prepared as for **69** using C_6H_4(1-C(O)PPh_2)(4-CN) (0.091 g, 2.89 x 10^{-4} mol) and [Rh(1,5-COD)Cl]$_2$ (0.072 g, 1.45 x 10^{-4} mol). Isolated as an orange solid. Yield: 0.070 g, 85.9 %.

^{1}H NMR (CD_2Cl_2): δ_H 2.12 (m, 4H, C**H**$_2$ of COD), 2.48 (m, 4H, C**H**$_2$ of COD), 3.46 (br, 2H, C**H** of COD), 5.57 (br, 2H, C**H** of COD), 7.39 (m, 4H, *m*-C**H** of Ph), 7.48 (m, 2H, *p*-C**H** of Ph), 7.59 (m, 4H, *o*-C**H** of Ph), 7.85 (d, 2H, $^{3}J_{H\text{-}H}$ 8.17 Hz, *m*-C**H**), 8.86 (d, $^{3}J_{H\text{-}H}$ 8.14 Hz, 2H, *o*-C**H**).

$^{13}C\{^{1}H\}$ NMR (CD_2Cl_2): δ_C 29.6 (s, **C**H_2 of COD), 33.5 (s, **C**H_2 of COD), 72.2 (d, $^{2}J_{C\text{-}P}$ 13.5 Hz, **C**H of COD), 106.9 (dd, $^{1}J_{C\text{-}Rh}$ 12.1 Hz, $^{2}J_{C\text{-}P}$ 6.34 Hz, **C**H of COD), 117.3 (s, *i*-**C**C≡N), 118.5 (s, **C**≡N), 129.1 (d, $^{3}J_{C\text{-}P}$ 9.68 Hz, *m*-**C**H of Ph), 131.3 (d, $^{3}J_{C\text{-}P}$ 3.21 Hz, *o*-**C**H), 131.6 (d, $^{4}J_{C\text{-}P}$ 2.38 Hz, *p*-**C**H of Ph), 132.9 (s, *m*-**C**H), 135.8 (d, $^{3}J_{C\text{-}P}$ 10.7 Hz, *o*-**C**H of Ph), 142.0 (d, $^{2}J_{C\text{-}P}$ 42.5 Hz, *i*-**C**), 202.9 (m, **C**(O)P).

^{31}P NMR$\{^{1}H\}$ (CD_2Cl_2): δ_P 37.8 (d, $^{1}J_{P\text{-}Rh}$ 147.1 Hz).

Elem. Anal.: Calcd for $C_{28}H_{26}OPClNRh$: C, 59.84 %; H, 5.03 %; N, 2.49 %. Found; C, 59.85 %; H, 4.96 %; N, 2.57 %.

IR: $\nu_{(C\equiv N)}$ 2229 cm^{-1}, $\nu_{(C=O)}$ 1660 cm^{-1}.

Synthesis of *trans*-[$PdCl_2${C_6H_4(1-C(O)PPh_2)(3-Me)}$_2$] (73)

To a DCM solution of [Pd(1,5-COD)Cl_2] (0.085 g, 2.97 x 10^{-4} mol) at ambient temperature was added C_6H_4(1-C(O)PPh_2)(3-Me) (0.181 g, 5.95 x 10^{-4} mol) in DCM, resulting in a yellow solution that was stirred for 18 h. The solvent was removed under reduced pressure; the product was washed with pentane and dried *in vacuo* to afford a yellow solid. Yield: 0.217 g, 93.0 %.

^{1}H NMR ($CDCl_3$): δ_H 2.32 (s, 6H, C**H**$_3$), 7.35 (m, 12H, *m*-C**H** of Ph and *m*-C**H** and *p*-C**H**), 7.45 (t, 4H, $^{3}J_{H\text{-}H}$ 7.69 Hz, *p*-C**H** of Ph), 7.75 (m, 8H, *o*-C**H** of Ph), 8.09 (s, 2H, middle-C**H**), 8.25 (d, 2H, $^{3}J_{H\text{-}H}$ 8.31 Hz, *o*-C**H**).

^{13}C{^{1}H} NMR ($CDCl_3$): δ_C 21.5 (s, **C**H$_3$), 126.9 (t, $^{1}J_{C\text{-}P}$ 22.7 Hz, *i*-**C** of Ph), 127.9 (s, *o*-**C**H), 128.5 (s, *m*-**C**H), 128.6 (t, $^{3}J_{C\text{-}P}$ 4.93 Hz, *m*-**C**H of Ph), 130.2 (s, middle-**C**H), 131.3 (s, *p*-**C**H of Ph), 134.9 (s, *p*-**C**H), 135.9 (t, $^{2}J_{C\text{-}P}$ 6.02 Hz, *o*-**C**H of Ph), 131.2 (t, $^{2}J_{C\text{-}P}$ 22.8 Hz, *i*-**C**), 138.6 (s, **C**CH$_3$), 198.8 (m, **C**(O)P).

^{31}P NMR ($CDCl_3$): δ_P 25.8 (br).

Elem. Anal.: Calcd for $C_{40}H_{34}O_2P_2PdCl_2$: C, 61.12 %; H, 4.33 %. Found; C, 61.02 %; H, 4.45 %.

IR: $\nu_{(C=O)}$ 1634 cm^{-1}.

Synthesis of *trans*-[PdCl$_2${C$_6$H$_4$(1-C(O)PPh$_2$)(3-CH$_2$Cl)}$_2$] (74)

Prepared as for **73** using C_6H_4(1-C(O)PPh$_2$)(3-CH$_2$Cl) (0.100 g, 2.95 x 10^{-4} mol) and [Pd(1,5-COD)Cl$_2$] (0.042 g, 1.47 x 10^{-4} mol). Isolated as a yellow solid. Yield: 0.117 g, 93.2 %.

^{1}H NMR ($CDCl_3$): δ_H 4.50 (s, 4H, C**H**$_2$Cl), 7.33 (d, 2H, $^{3}J_{H\text{-}H}$ 7.66 Hz, *m*-C**H**), 7.38 (t, 8H, $^{3}J_{H\text{-}H}$ 7.51 Hz, *m*-C**H** of Ph), 7.48 (t, 4H, $^{3}J_{H\text{-}H}$ 7.15 Hz, *p*-C**H** of Ph), 7.55 (d, 2H, $^{3}J_{H\text{-}H}$ 7.71 Hz, *p*-C**H**), 7.78 (m, 8H, *o*-C**H** of Ph), 8.24 (s, 2H, middle-C**H**), 8.29 (d, 2H, $^{3}J_{H\text{-}H}$ 7.99 Hz, *o*-C**H**).

^{13}C{^{1}H} NMR ($CDCl_3$): δ_C 45.5 (s, **C**H$_2$Cl), 126.2 (t, $^{1}J_{C\text{-}P}$ 22.7 Hz, *i*-**C** of Ph), 128.8 (t, $^{3}J_{C\text{-}P}$ 5.57 Hz, *m*-**C**H of Ph), 129.0 (s, *m*-**C**H), 129.6 (s, middle-**C**H), 130.1 (s, *o*-**C**H), 131.5 (s, *p*-**C**H of Ph), 133.8 (s, *p*-**C**H), 135.8 (t, $^{2}J_{C\text{-}P}$ 5.70 Hz, *o*-**C**H of Ph), 137.3 (t, $^{2}J_{C\text{-}P}$ 22.7 Hz, *i*-**C**), 138.1 (s, **C**CH$_2$Cl), 198.8 (t, $^{1}J_{C\text{-}P}$ 11.41 Hz, **C**(O)P).

^{31}P NMR ($CDCl_3$): δ_P 25.9 (br).

Elem. Anal.: Calcd for $C_{40}H_{32}O_2P_2PdCl_4$: C, 56.18 %; H, 3.75 %. Found; C, 56.24 %; H, 3.74 %.

IR: $\nu_{(C=O)}$ 1657 cm^{-1}.

Synthesis of *trans*-[PdCl$_2${C$_6$H$_4$(1-C(O)PPh$_2$)(4-CO$_2$Me)}$_2$] (75)

Prepared as for **73** using C_6H_4(1-C(O)PPh$_2$)(4-CO$_2$Me) (0.395 g, 1.13 x 10^{-3} mol) and [Pd(1,5-COD)Cl$_2$] (0.162 g, 5.67 x 10^{-4} mol). Isolated as a yellow solid. Yield: 0.452 g, 91.3 %.

^{1}H NMR ($CDCl_3$): δ_H 3.96 (s, 6H, C**H**$_3$), 7.39 (t, 8H, $^{3}J_{H\text{-}H}$ 7.47 Hz, *m*-C**H** of Ph), 7.48 (d, 4H, $^{3}J_{H\text{-}H}$ 7.47 Hz, *p*-C**H** of Ph), 7.76 (m, 8H, *o*-C**H** of Ph), 8.01 (d, 4H, $^{3}J_{H\text{-}H}$ 8.31 Hz, *m*-C**H**), 8.31 (d, 4H, $^{3}J_{H\text{-}H}$ 8.31 Hz, *o*-C**H**).

^{13}C{^{1}H} NMR ($CDCl_3$): δ_C 52.67 (s, **C**H$_3$), 125.9 (t, $^{1}J_{C\text{-}P}$ 23.2 Hz, *i*-**C** of Ph), 128.9 (t, $^{3}J_{C\text{-}P}$ 5.34 Hz, *m*-**C**H of Ph), 129.7 (s, *m*-**C**H), 129.8 (s, *o*-**C**H), 131.7 (s, *p*-**C**H of Ph), 134.5 (s, *i*-**C**CO$_2$Me), 135.7 (t, $^{2}J_{C\text{-}P}$ 5.84 Hz, *o*-**C**H of Ph), 140.1 (t, $^{2}J_{C\text{-}P}$ 21.9 Hz, *i*-**C**), 166.1 (s, **C**O$_2$Me), 199.2 (m, **C**(O)P).

^{31}P NMR ($CDCl_3$): δ_P 26.1 (br).

Elem. Anal.: Calcd for $C_{42}H_{34}O_6P_2Cl_2Pd$: C, 57.71 %; H, 3.89 %. Found; C, 57.63 %; H, 4.03 %.

IR: $\nu_{(C=O)}$ 1720 cm^{-1}, $\nu_{(C=O)}$ 1670 cm^{-1}.

Synthesis of *trans*-[PdCl$_2${C$_6$H$_4$(1-C(O)PPh$_2$)(4-CN)}$_2$] (76)

Prepared as for **73** using C_6H_4(1-C(O)PPh$_2$)(4-CN) (0.118 g, 3.75 x 10^{-4} mol) and [Pd(1,5-COD)Cl$_2$] (0.053 g, 1.87 x 10^{-4} mol). Isolated as a dark yellow solid. Yield: 0.139 g, 92.1 %.

^{1}H NMR ($CDCl_3$): δ_H 7.43 (br t, 8H, $^{3}J_{H\text{-}H}$ 7.71 Hz, *m*-C**H** of Ph), 7.55 (br t, 4H, $^{3}J_{H\text{-}H}$ 7.39 Hz, *p*-C**H** of Ph), 7.59 (d, 4H, $^{3}J_{H\text{-}H}$ 8.34 Hz, *m*-C**H**), 7.73 (m, 8H, *o*-C**H** of Ph), 8.26 (d, 4H, $^{3}J_{H\text{-}H}$ 8.34 Hz, *o*-C**H**).

^{13}C{^{1}H} NMR ($CDCl_3$): δ_C 116.9 (s, *i*-**C**C≡N), 117.8 (s, **C**≡N), 125.3 (t, $^{1}J_{C\text{-}P}$ 23.1 Hz, *i*-**C** of Ph), 129.1 (t, $^{3}J_{C\text{-}P}$ 5.10 Hz, *m*-**C**H of Ph), 129.9 (s, *o*-**C**H), 132.1 (s, *p*-**C**H of Ph), 132.3 (s, *m*-**C**H), 135.5 (t, $^{2}J_{C\text{-}P}$ 5.90 Hz, *o*-**C**H of Ph), 139.8 (t, $^{2}J_{C\text{-}P}$ 22.8 Hz, *i*-**C**), 198.8 (t, $^{1}J_{C\text{-}P}$ 12.4 Hz, **C**(O)P).

^{31}P NMR ($CDCl_3$): δ_P 25.9 (br).

Elem. Anal.: Calcd for $C_{40}H_{28}O_2P_2Cl_2N_2Pd$: C, 59.48 %; H, 3.47 %; N, 3.47 %. Found; C, 59.58 %; H, 3.52 %; N, 3.48 %.

IR: $\nu_{(C\equiv N)}$ 2229 cm^{-1}, $\nu_{(C=O)}$ 1666 cm^{-1}.

Synthesis of *cis*- and *trans*-[PtCl$_2${C$_6$H$_4$(1-C(O)PPh$_2$)(3-Me)}$_2$] (*cis*-/*trans*-77)

To a DCM solution of [PtCl$_2$(PhCN)$_2$] (0.143 g, 3.03 x 10^{-4} mol) at ambient temperature was added C_6H_4(1-C(O)PPh$_2$)(3-Me) (0.184 g, 6.05 x 10^{-4} mol) in DCM, resulting in a light yellow solution that was stirred for 18 h. The solvent was removed under reduced pressure; the product

was washed with Et_2O and pentane and dried *in vacuo* to afford a yellow solid. Yield: 0.235 g, 88.7 %.

cis-[$PtCl_2${C_6H_4(1-C(O)PPh_2)(3-Me)}$_2$] (_cis_-77)

^{1}H NMR ($CDCl_3$): δ_H 2.33 (s, 12H, C**H**$_3$), 7.19 (t, 9H, $^3J_{H\text{-}H}$ 7.80 Hz, *m*-C**H** of Ph and *m*-C**H**), 7.27 (m, 4H, *p*-C**H** of Ph), 7.51 (t, 9H, $^3J_{H\text{-}H}$ 7.56 Hz, *o*-C**H** of Ph and *p*-C**H**), 8.06 (s, 2H, middle-C**H**), 8.18 (d, 2H, *o*-C**H**).

^{13}C{^{1}H} NMR ($CDCl_3$): δ_C 21.5 (s, **C**H$_3$), 125.4 (d, $^1J_{C\text{-}P}$ 58.4 Hz, *i*-**C** of Ph), 128.5 (m, *m*-**C**H of Ph), 128.5 (s, *m*-**C**H), 130.4 (s, *o*-**C**H), 131.3 (s, middle-**C**H), 134.6 (s, *p*-**C**H of Ph), 135.8 (d, $^2J_{C\text{-}P}$ 4.86 Hz, *o*-**C**H of Ph), 138.4 (s, **C**CH$_3$), 195.1 (d, $^1J_{C\text{-}P}$ 40.6 Hz, **C**(O)P).

^{31}P NMR ($CDCl_3$): δ_P 14.8 (br, $^1J_{P\text{-}Pt}$ 3497 Hz).

^{195}Pt{^{1}H} NMR ($CDCl_3$): δ_{Pt} –4351.2 (t, $^1J_{Pt\text{-}P}$ 3497 Hz).

trans-[$PtCl_2${C_6H_4(1-C(O)PPh_2)(3-Me)}$_2$] (_trans_-77)

^{1}H NMR ($CDCl_3$): δ_H 2.33 (s, 12H, C**H**$_3$), 7.36 (t, 12H, $^3J_{H\text{-}H}$ 7.45 Hz, *m*-C**H** of Ph, *m*-C**H** and *p*-C**H**), 7.45 (t, 4H, $^3J_{H\text{-}H}$ 7.30 Hz, *p*-C**H** of Ph), 7.77 (m, 8H, *o*-C**H** of Ph), 8.15 (s, 2H, middle-C**H**), 8.33 (d, 2H, $^3J_{H\text{-}H}$ 7.42 Hz, *o*-C**H**).

^{13}C{^{1}H} NMR ($CDCl_3$): δ_C 21.5 (s, **C**H$_3$), 126.6 (t, $^1J_{C\text{-}P}$ 26.4 Hz, *i*-**C** of Ph), 128.0 (s, *o*-**C**H), 128.5 (m, *m*-**C**H of Ph), 128.7 (s, *m*-**C**H), 131.2 (s, middle-**C**H), 131.8 (s, *p*-**C**H of Ph), 134.8 (s, *p*-**C**H), 135.9 (t, $^2J_{C\text{-}P}$ 5.54 Hz, *o*-**C**H of Ph), 137.4 (t, $^2J_{C\text{-}P}$ 22.6 Hz, *i*-**C**), 138.3 (s, **C**CH$_3$), 198.6 (t, $^1J_{C\text{-}P}$ 15.0 Hz, **C**(O)P).

^{31}P NMR ($CDCl_3$): δ_P 22.3 (s, $^1J_{P\text{-}Pt}$ 2544 Hz).

^{195}Pt{^{1}H} NMR ($CDCl_3$): δ_{Pt} –3962 (t, $^1J_{Pt\text{-}P}$ 2544 Hz).

Elem. Anal.: Calcd for $C_{40}H_{34}O_2P_2PtCl_2$: C, 54.92 %; H, 3.89 %. Found; C, 54.86 %; H, 3.78 %.

IR: $\nu_{(C=O)}$ 1661 (br) cm^{-1}.

Synthesis of _cis_-[$PtCl_2${C_6H_4(1-C(O)PPh_2)(3-CH_2Cl)}$_2$] (78)

Prepared as for **77** using C_6H_4(1-C(O)PPh_2)(3-CH_2Cl) (0.0303 g, 8.94 x 10^{-5} mol) and [$PtCl_2$(PhCN)$_2$] (0.211 g, 4.47 x 10^{-5} mol). Isolated as a yellow solid. Yield: 0.031 g, 73.5 %.

^{1}H NMR ($CDCl_3$): δ_H 4.58 (s, 4H, C**H**$_2$Cl), 7.22 (t, 8H, $^{3}J_{H\text{-}H}$ 7.35 Hz, *m*-C**H** of Ph), 7.32 (t, 2H, $^{3}J_{H\text{-}H}$ 7.35 Hz, *m*-C**H**), 7.41 (t, 4H, $^{3}J_{H\text{-}H}$ 7.45 Hz, *p*-C**H** of Ph), 7.50 (m, 10H, *o*-C**H** of Ph and *p*-C**H**), 8.22 (d, 2H, $^{3}J_{H\text{-}H}$ 8.53 Hz, *o*-C**H**), 8.32 (s, 2H, middle-C**H**).

^{13}C{^{1}H} NMR ($CDCl_3$): δ_C 45.7 (s, **C**H$_2$Cl), 124.8 (d, $^{1}J_{C\text{-}P}$ 58.3 Hz, *i*-**C** of Ph), 128.6 (m, $^{3}J_{C\text{-}P}$ 5.44 Hz, *m*-**C**H of Ph), 128.9 (s, *m*-**C**H), 130.8 (s, middle-**C**H), 130.9 (s, *o*-**C**H), 132.0 (s, *p*-**C**H of Ph), 133.6 (s, *p*-**C**H), 135.8 (m, $^{2}J_{C\text{-}P}$ 4.93 Hz, *o*-**C**H of Ph), 137.8 (s, **C**CH$_2$Cl).

^{31}P NMR ($CDCl_3$): δ_P 15.3 (br, $^{1}J_{P\text{-}Pt}$ 3503 Hz).

^{195}Pt{^{1}H} NMR ($CDCl_3$): δ_{Pt} –4354 (t, $^{1}J_{Pt\text{-}P}$ 3503 Hz).

Elem. Anal.: Calcd for $C_{40}H_{32}O_2P_2PtCl_4$: C, 50.90 %; H, 3.39 %. Found; C, 50.88 %; H, 3.33 %.

IR: $\nu_{(C=O)}$ 1668 cm^{-1}.

Synthesis of *cis*-[PtCl$_2${C$_6$H$_4$(1-C(O)PPh$_2$)(4-CN)}$_2$] (79)

Prepared as for **77** using C_6H_4(1-C(O)PPh$_2$)(4-CN) (0.267 g, 8.48 x 10^{-4} mol) and [Pt(PhCN)$_2$Cl$_2$] (0.200 g, 4.24 x 10^{-4} mol). Isolated as a yellow solid. Yield: 0.320 g, 84.2 %.

^{1}H NMR ($CDCl_3$): δ_H 7.24 (m, 4H, *p*-C**H** of Ph), 7.40 (d, 8H, $^{3}J_{H\text{-}H}$ 13.7 Hz, *m*-C**H** of Ph), 7.42 (m, 8H, *o*-C**H** of Ph), 7.60 (d, 4H, $^{3}J_{H\text{-}H}$ 8.84 Hz, *m*-C**H**), 8.22 (d, 4H, $^{3}J_{H\text{-}H}$ 8.22 Hz, *o*-C**H**).

^{13}C{^{1}H} NMR ($CDCl_3$): δ_C 116.6 (s, *i*-**C**C≡N), 117.8 (s, **C**≡N), 124.1 (d, $^{1}J_{C\text{-}P}$ 59.5 Hz, *i*-**C** of Ph), 128.8 (m, $^{5}J_{C\text{-}P}$ 5.58 Hz, *p*-**C**H of Ph), 130.8 (s, *o*-**C**H), 132.1 (s, *m*-**C**H), 132.5 (br, *o*-**C**H of Ph), 135.6 (m, $^{4}J_{C\text{-}P}$ 5.03 Hz, *m*-**C**H of Ph), 139.5 (d, $^{2}J_{C\text{-}P}$ 49.9 Hz, *i*-**C**), 194.8 (d, $^{1}J_{C\text{-}P}$ 44.8 Hz, **C**(O)P).

^{31}P NMR ($CDCl_3$): δ_P 16.5 (br, $^{1}J_{P\text{-}Pt}$ 3493 Hz).

^{195}Pt{^{1}H} NMR ($CDCl_3$): δ_{Pt} –4374 (t, $^{1}J_{Pt\text{-}P}$ 3493 Hz).

Elem. Anal.: Calcd for $C_{40}H_{28}O_2P_2Cl_2N_2Pt$: C, 53.57 %; H, 3.13 %; N, 3.13 %. Found; C, 53.65 %; H, 3.15 %; N, 3.10 %.

IR: $\nu_{(C\equiv N)}$ 2230 cm^{-1}, $\nu_{(C=O)}$ 1666 cm^{-1}.

Attempted synthesis of [PtCl$_2${C$_6$H$_4$(1-C(O)PPh$_2$)(4-CO$_2$Me)}$_2$] (80)

Synthesis attempted as for **77** using C_6H_4(1-C(O)PPh$_2$)(4-CO$_2$Me) (0.298 g, 8.56 x 10^{-4} mol) and [Pt(1,5-COD)Cl$_2$] (0.160 g, 4.28 x 10^{-4} mol). Isolated as a yellow solid. Yield: 0.269 g.

^{1}H NMR ($CDCl_3$): δ_H 2.26 (br, 4H, C**H**$_2$ of COD), 2.71 (br, 4H, C**H**$_2$ of COD), 3.95 (s, 3H, C**H**$_3$), 5.61 (br s, 4H, $^{2}J_{H\text{-}Pt}$ 66.9 Hz, C**H** of COD), 7.39 (t, 4H, $^{3}J_{H\text{-}H}$ 7.60 Hz, *m*-C**H** of Ph), 7.49 (t, 2H, $^{3}J_{H\text{-}H}$ 7.60 Hz, *p*-C**H** of Ph), 7.76 (m, 4H, *o*-C**H** of Ph), 8.01 (d, 2H, $^{3}J_{H\text{-}H}$ 8.32 Hz, *m*-C**H**), 8.31 (d, 2H, $^{3}J_{H\text{-}H}$ 8.32 Hz, *o*-C**H**).

^{13}C{^{1}H} NMR ($CDCl_3$): δ_C 31.1 (s, **C**H$_2$ of COD), 52.7 (s, **C**H$_3$), 100.2 (s, $J_{C\text{-}Pt}$ 151.9 Hz, **C**H of COD), 125.9 (t, $^{1}J_{C\text{-}P}$ 21.7 Hz, *i*-**C** of Ph), 128.9 (t, $^{3}J_{C\text{-}P}$ 5.15 Hz, *m*-**C**H of Ph), 129.8 (s, *o*-**C**H and *m*-**C**H), 131.7 (s, *p*-C**H** of Ph), 134.5 (s, **C**CO_2Me), 135.7 (t, $^{2}J_{C\text{-}P}$ 5.96 Hz, *o*-**C**H of Ph), 140.1 (t, $^{2}J_{C\text{-}P}$ 22.8 Hz, *i*-**C**), 166.1 (s, **C**O_2Me), 199.2 (t, $^{1}J_{C\text{-}P}$ 11.7 Hz, **C**(O)P).

^{31}P NMR ($CDCl_3$): δ_P 26.1 (br).

^{195}Pt{^{1}H} NMR ($CDCl_3$): δ_{Pt} –3340 (s).

Elem. Anal.: Calcd for $C_{29}H_{29}O_3P_1Cl_2Pt$: C, 48.19 %; H, 4.02 %. Found; C, 48.07 %; H, 3.96 %.

IR: $\nu_{(C=O)}$ 1720 cm^{-1}, $\nu_{(C=O)}$ 1671 cm^{-1}.

FAB-MS *m/z* 686 [M–Cl]$^{+}$. No other fragments were identified.

Attempted synthesis of [$PtCl_2${C_6H_4(1-C(O)PPh_2)(4-CO_2Me)}$_2$] (81)

Synthesis attempted as for **77** using C_6H_4(1-C(O)PPh_2)(4-CO_2Me) (0.109 g, 3.16 x 10^{-4} mol) and [Pt(1,5-COD)Cl_2] (0.118 g, 3.16 x 10^{-4} mol). Isolated as a yellow solid. Yield: 0.216 g.

^{1}H NMR ($CDCl_3$): δ_H 2.26 (br, 4H, C**H**$_2$ of COD), 2.70 (br, 4H, C**H**$_2$ of COD), 3.94 (s, 3H, $J_{H\text{-}Pt}$ 31.1 Hz, C**H**$_3$), 5.60 (br s, 4H, $^{2}J_{H\text{-}Pt}$ 66.7 Hz, C**H** of COD), 7.22 (t, 4H, $^{3}J_{H\text{-}H}$ 7.58 Hz, *m*-C**H** of Ph), 7.42 (t, 4H, $^{3}J_{H\text{-}H}$ 7.52 Hz, C_6H_4(1-C(O)PPh_2)(4-CO_2Me)), 7.47 (t, 6H, $^{3}J_{H\text{-}H}$ 7.60 Hz, *p*-C**H** of Ph, *o*-C**H** of Ph), 7.98 (d, 2H, $^{3}J_{H\text{-}H}$ 8.22 Hz, *m*-C**H**), 8.26 (d, 2H, $^{3}J_{H\text{-}H}$ 8.56 Hz, *o*-C**H**).

^{13}C{^{1}H} NMR ($CDCl_3$): δ_C 31.1 (s, **C**H$_2$ of COD), 52.7 (s, **C**H$_3$), 100.1 (s, $J_{C\text{-}Pt}$ 152.1 Hz, **C**H of COD), 124.7 (d, $^{1}J_{C\text{-}P}$ 58.5 Hz, *i*-**C** of Ph), 128.6 (d, $^{3}J_{C\text{-}P}$ 5.41 Hz, *m*-**C**H of Ph), 128.7 (m, C_6H_4(1-C(O)PPh_2)(4-CO_2Me)), 128.8 (s, C_6H_4(1-C(O)PPh_2)(4-CO_2Me)), 129.5 (s, *m*-**C**H), 130.6 (s, *o*-**C**H), 132.2 (s, *p*-**C**H of Ph), 134.1 (s, **C**CO_2Me), 135.7 (m, C_6H_4(1-C(O)PPh_2)(4-CO_2Me)), 135.7 (d, $^{2}J_{C\text{-}P}$ 4.99 Hz, *o*-**C**H of Ph), 139.7 (d, $^{2}J_{C\text{-}P}$ 49.1 Hz, *i*-**C**), 166.1 (s, **C**O_2Me), 195.1 (d, $^{1}J_{C\text{-}P}$ 42.9, **C**(O)P).

^{31}P NMR ($CDCl_3$): δ_P 16.1 (br, $^{1}J_{P\text{-}Pt}$ 3504 Hz).

^{195}Pt{^{1}H} NMR ($CDCl_3$): δ_{Pt} –3340 (s).

Elem. Anal.: Calcd for $C_{29}H_{29}O_3P_1Cl_2Pt$: C, 48.19 %; H, 4.02 %. Found; C, 43.61 %; H, 3.89 %.

IR: $\nu_{(C=O)}$ 1721 cm^{-1}, $\nu_{(C=O)}$ 1671 cm^{-1}.

Synthesis of $C_6H_4(1,3\text{-}C(O)PPh_2)_2$ (82)

To a THF solution of $HPPh_2$ (0.504 g, 2.71 x 10^{-3} mol) at −78 °C was added drop-wise $C_6H_4(1,3\text{-}COCl)_2$ (0.275 g, 1.35 x 10^{-3} mol) in THF, resulting in a yellow solution after stirring for 30 min that was allowed to warm to ambient temperature then stirred for 18 h. The solvent was removed under reduced pressure; the product was washed with pentane and dried *in vacuo* to afford a yellow solid. Yield: 0.574 g, 84.7 %.

^{1}H NMR (C_6D_6): δ_H 6.67 (t, 2H, $^3J_{H\text{-}H}$ 7.86 Hz, *m*-C**H**), 6.99 (t, 8H, $^3J_{H\text{-}H}$ 1.63 Hz, *m*-C**H** of Ph), 7.01 (m, 4H, *p*-C**H** of Ph), 7.40 (m, 8H, *o*-C**H** of Ph), 7.90 (dt, 2H, $^4J_{P\text{-}H}$ 7.85 Hz, $^3J_{H\text{-}H}$ 1.52 Hz, *o*-C**H**), 9.02 (m, 1H, middle C**H**).

^{13}C{^{1}H} NMR (C_6D_6): δ_C 128.4 (m, middle **C**H), 128.6 (m, *m*-**C**H), 129.0 (d, $^3J_{C\text{-}P}$ 7.66 Hz, *m*-**C**H of Ph), 129.7 (s, *p*-**C**H of Ph), 132.1 (d, $^3J_{C\text{-}P}$ 8.61 Hz, *o*-**C**H), 133.1 (d, $^1J_{C\text{-}P}$ 6.14 Hz, *i*-**C** of Ph), 135.3 (d, $^2J_{C\text{-}P}$ 18.3 Hz, *o*-**C**H of Ph), 139.9 (d, $^2J_{C\text{-}P}$ 35.7 Hz, *i*-**C**), 211.2 (d, $^1J_{C\text{-}P}$ 38.1 Hz, **C**(O)P).

^{31}P NMR (C_6D_6): δ_P 12.9 (m, $^3J_{P\text{-}H}$ 7.85 Hz).

Elem. Anal.: Calcd for $C_{32}H_{24}O_2P_2$: C, 76.49 %; H, 4.78 %. Found; C, 76.42 %; H, 4.80 %.

IR: $\nu_{(C=O)}$ 1642 cm^{-1}, $\nu_{(C=O)}$ 1588 cm^{-1}.

Synthesis of $C_5H_3N(2,6\text{-}C(O)PPh_2)_2$ (83)

Prepared as for **82** using $C_5H_3N(2,6\text{-}COCl)_2$ (0.338 g, 1.67 x 10^{-3} mol) and $HPPh_2$ (0.617 g, 3.32 x 10^{-3} mol) in Et_2O. Isolated as a yellow solid. Yield: 0.623 g, 74.2 %.

^{1}H NMR (C_6D_6): δ_H 6.71 (t, 1H, $^3J_{H\text{-}H}$ 7.91 Hz, *p*-C**H**), 7.03 (t, 4H, $^3J_{H\text{-}H}$ 7.47 Hz, *p*-C**H** of Ph), 7.09 (t, 8H, $^3J_{H\text{-}H}$ 7.47 Hz, *m*-C**H** of Ph), 7.42 (d, 2H, $^3J_{H\text{-}H}$ 7.62 Hz, *m*-C**H**), 7.63 (t, 8H, $^3J_{H\text{-}H}$ 7.54 Hz, *o*-C**H** of Ph).

^{13}C{^{1}H} NMR (C_6D_6): δ_C 123.2 (t, $^4J_{C\text{-}P}$ 2.06 Hz, *m*-**C**H), 128.7 (d, $^3J_{C\text{-}P}$ 7.90 Hz, *m*-**C**H of Ph), 129.3 (s, *p*-**C**H of Ph), 134.3 (d, $^1J_{C\text{-}P}$ 8.47 Hz, *i*-**C** of Ph), 135.4 (d, $^2J_{C\text{-}P}$ 20.1 Hz, *o*-**C**H of Ph), 138.1 (s, *p*-**C**H), 153.4 (d, $^2J_{C\text{-}P}$ 31.4 Hz, *i*-**C**), 213.5 (d, $^1J_{C\text{-}P}$ 40.4 Hz, **C**(O)P).

^{31}P NMR (C_6D_6): δ_P 16.6 (m, $^3J_{P\text{-}H}$ 7.37 Hz).

Elem. Anal.: Calcd for $C_{31}H_{23}O_2P_2N$: C, 73.96 %; H, 4.57 %; N, 2.78 %. Found; C, 73.82 %; H, 4.55 %; N, 2.88%.

IR: $\nu_{(C=O)}$ 1650 cm^{-1}.

Synthesis of *trans*-[PtCl{$C_5H_3N(2,6\text{-}C(O)PPh_2\}_2)$]$^+$ [Cl]$^-$ (84)

To a DCM solution of $[Pt(PhCN)_2Cl_2]$ (0.087 g, 1.85 x 10^{-4} mol) at ambient temperature was added drop-wise $C_5H_3N(2,6\text{-}C(O)PPh_2)_2$ (0.093 g, 1.85 x 10^{-4} mol) in DCM, resulting in a bright orange solution that was stirred for 18 h. The solvent was removed under reduced pressure; the product was washed with Et_2O and pentane and dried *in vacuo* to afford a dark yellow solid. Yield: 0.101 g, 70.1 %.

^{1}H NMR ($CDCl_3$): δ_H 7.53 (t, 8H, $^3J_{H\text{-}H}$ 7.30 Hz, *m*-C**H** of Ph), 7.58 (t, 4H, $^3J_{H\text{-}H}$ 7.04 Hz, *p*-C**H** of Ph), 8.15 (q, 8H, $^3J_{H\text{-}H}$ 6.55 Hz, *o*-C**H** of Ph), 8.32 (d, 2H, $^3J_{H\text{-}H}$ 7.47 Hz, *m*-C**H**), 8.55 (t, 1H, $^3J_{H\text{-}H}$ 8.28 Hz, *p*-C**H**).

^{13}C{^{1}H} NMR ($CDCl_3$): δ_C 123.0 (t, $^1J_{C\text{-}P}$ 28.4 Hz, *i*-**C** of Ph), 129.6 (t, $^3J_{C\text{-}P}$ 6.00 Hz, *m*-**C**H of Ph), 131.9 (br, *m*-**C**H), 133.1 (s, *p*-**C**H of Ph), 134.9 (t, $^2J_{C\text{-}P}$ 6.82 Hz, *o*-**C**H of Ph), 143.3 (s, *p*-**C**H), 148.1 (t, $^2J_{C\text{-}P}$ 28.4 Hz, *i*-**C**), 202.1 (t, $^1J_{C\text{-}P}$ 16.9 Hz, **C**(O)P).

^{31}P NMR ($CDCl_3$): δ_P 33.1 (br, $^1J_{P\text{-}Pt}$ 2814 Hz).

^{195}Pt{^{1}H} NMR ($CDCl_3$): δ_{Pt} –3795 (t, $^1J_{Pt\text{-}P}$ 2814 Hz).

Elem. Anal.: Calcd for $C_{31}H_{23}O_2P_2NPtCl_2$: C, 47.8 %; H, 2.95 %; N, 1.79 %. Found; C, 51.61 %; H, 3.06 %; N, 2.05 %.

IR: $\nu_{(C=O)}$ 1690 (br) cm^{-1}.

Synthesis of {3-CO-C_6H_4-C(O)PMe}$_2$ (85)

To an Et_2O solution of $MeP(SiMe_3)_2$ (0.66 g, 2.27 x 10^{-3} mol) at −78 °C was added $C_6H_4(1,3\text{-}COCl)_2$ (0.46 g, 2.27 x 10^{-3} mol) in Et_2O, resulting in a suspended yellow solid that was stirred for 30 min and was then allowed to warm to ambient temperature then stirred for 18 h. The precipitate was collected by filtration and washed with Et_2O; the product was dried *in vacuo* to afford a yellow solid. Yield: 0.320 g, 79.2 %.

^{1}H NMR (C_6D_6): δ_H 1.55 (d, 6H, $^2J_{H\text{-}P}$ 3.10 Hz, PC**H**$_3$), 6.42 (t, 2H, $^3J_{H\text{-}H}$ 7.75 Hz, *m*-C**H**), 7.13 (d, 2H, $^3J_{H\text{-}H}$ 1.67 Hz, *o*-C**H**), 7.14 (d, 2H, $^3J_{H\text{-}H}$ 1.76Hz, *o*-C**H**), 9.25 (br, 2H, middle-C**H**).

^{13}C{^{1}H} NMR (C_6D_6): δ_C 1.73 (d, $^1J_{C\text{-}P}$ 4.45 Hz, **C**H$_3$), δ130.3 (m, $^2J_{C\text{-}P}$ 1.89 Hz, *m*-**C**H), 130.6 (m, $^3J_{C\text{-}P}$ 2.32 Hz, *o*-**C**H), 134.0 (t, $^3J_{C\text{-}P}$ 13.9 Hz, middle **C**H), 137.6 (d, $^2J_{C\text{-}P}$ 37.9 Hz, *i*-**C**), 205.9 (d, $^1J_{C\text{-}P}$ 46.0 Hz, **C**=O).

^{31}P{^{1}H} NMR (C_6D_6): δ_P 32.7.

IR: $\nu_{(C=O)}$ 1656, 1639 cm^{-1}.

Elem. Anal.: Calcd for $C_{18}H_{14}O_4P_2$: C, 60.67 %; H, 3.93 %. Found; C, 60.59 %; H, 3.82 %.

X-ray quality crystals were grown at −20 °C from THF in 3 days. Crystal data: $C_{18}H_{14}Cl_2O_4P_2$, M_w = 356.23, Monoclinic, $P2_1/n$ (no. 14), a = 12.0985(9), b = 7.6709(3), c = 18.3347(13) Å, β = 100.317(2) °, V= 1674.047(18) Å^3, Z = 4, D_c = 1.413 Mg m^{-3}, μ(MoKα) = 0.279 mm^{-1}, T = 173(2) K, 3776 independent reflections, full-matrix F^2 refinement R_1 = 0.0530, wR_2 = 0.1699 on 2648 independent absorption corrected reflections [$I > 2\sigma(I)$; $2\theta_{max}$ = 55 °], 217 parameters.

Synthesis of {C$_6$H$_4$(1-COCl)3-CO}$_2$PMe (86)

To an Et_2O solution of $MeP(SiMe_3)_2$ (0.71 g, 2.44 x 10^{-3} mol) at −78 °C was added $C_6H_4(1,3\text{-}COCl)_2$ (0.99 g, 4.88 x 10^{-3} mol) in Et_2O, resulting in a suspended yellow solid that was stirred for 30 min and then allowed to warm to ambient temperature then stirred for 18 h. The suspension was filtered and the solvent removed from the filtrate under reduced pressure to afford an orange oil. Yield: 0.660 g, 70.9 %.

^{1}H NMR (C_6D_6): δ_H 1.39 (d, 3H, $^2J_{H\text{-}P}$ 3.41 Hz, PC**H**$_3$), 6.22 (t, 2H, $^3J_{H\text{-}H}$ 8.04 Hz, *m*-C**H**), 7.60 (d, 2H, $^3J_{H\text{-}H}$ 1.83 Hz, *o*-C**H**), 7.62 (d, 2H, $^3J_{H\text{-}H}$ 1.83 Hz, *o*-C**H**), 8.44 (br, 2H, middle-C**H**).

^{31}P NMR (C_6D_6): δ_P 20.2 (br, **P**CH_3).

Synthesis of {2-CO-C$_5$H$_3$N-C(O)PMe}$_2$ (87)

Prepared as for **85** using $C_5H_3N(2,6\text{-}COCl)_2$ (0.216 g, 1.06 x 10^{-3} mol) and $MeP(SiMe_3)_2$ (0.203 g, 1.06 x 10^{-3} mol) in pentane. Isolated as an orange solid. Yield: 0.215 g, 56.7 %.

^{1}H NMR (C_6D_6): δ_H 1.63 (m, 6H, C**H**$_3$), 6.57 (t, 2H, $^3J_{H\text{-}H}$ 7.74 Hz, *p*-C**H**), 7.20 (d, 4H, $^3J_{H\text{-}H}$ 7.74 Hz, *m*-C**H**).

^{13}C{^{1}H} NMR (C_6D_6): δ_C 3.33 (d, $^1J_{C\text{-}P}$ 7.80 Hz, **C**H$_3$), 124.3 (t, $^3J_{C\text{-}P}$ 1.90 Hz, *m*-**C**H), 138.0 (s, *p*-**C**H), 152.5 (d, $^2J_{C\text{-}P}$ 33.2 Hz, *i*-**C**), 208.8 (d, $^1J_{C\text{-}P}$ 50.7 Hz, **C**=O).

^{31}P NMR (C_6D_6): δ_P 30.2 (br).

EI-MS *m/z* 358 [M]$^+$. No other fragments were identified.

Synthesis of *trans*-[PtCl$_2$({3-CO-C$_6$H$_4$-C(O)PMe}$_2$)$_2$] (88)

To a THF solution of *cis*-$[PtCl_2(PhCN)_2]$ (0.079 g, 1.68 x 10^{-4} mol) at −78 °C was added {3-CO-C_6H_4-C(O)PMe}$_2$ (0.120 g, 3.36 x 10^{-4} mol) in THF, resulting in a yellow solution that was

stirred for 30 min and then allowed to warm to ambient temperature then stirred for 18 h. The solvent was removed under reduced pressure to afford a yellow solid. Yield: 0.121 g, 73.6 %.

^{1}H NMR (THF): δ_H 1.70 (d, 3H, $^{2}J_{H\text{-}P}$ 3.19 Hz, PC**H**$_3$), 2.33 (t, 3H, $^{2}J_{H\text{-}P}$ 3.14 Hz, PC**H**$_3$), 7.41 (t, 2H, $^{3}J_{H\text{-}H}$ 7.33 Hz, *m*-C**H**), 7.66 (d, 2H, $^{3}J_{H\text{-}H}$ 7.53 Hz, *o*-C**H**), 7.68 (d, 2H, $^{3}J_{H\text{-}H}$ 7.65 Hz, *o*-C**H**), 10.64 (br, 2H, middle-C**H**).

^{13}C{^{1}H} NMR (THF): δ_C 0.27 (**C**H$_3$), 25.6 (**C**H$_3$), 130.3 (**C**H), 132.3 (**C**), 133.7 (**C**H), 133.7 (**C**H), 134.9 (**C**H), 136.9 (**C**H), 196.0 (**C**=O), 204.8 (**C**=O).

^{31}P{^{1}H} NMR (C_6D_6): δ_P 28.4 (s, **P**Me), 33.2 (s, **P**Me, $^{1}J_{P\text{-}Pt}$ 2296 Hz).

Elem. Anal.: Calcd for $C_{36}H_{28}O_8P_4Cl_2Pt$: C, 44.17 %; H, 2.86 %. Found; C, 44.28 %; H, 2.80 %.

Yellow crystals grew over 3 days from THF at −20 °C. Crystal data: $C_{36}H_{28}Cl_2O_8P_4Pt$, M_w = 1122.65, Triclinic, *P-1* (no. 2), *a* = 10.4564(4), *b* = 11.3437(6), *c* = 11.5627(7) Å, α = 87.512(3), β = 69.834(3), γ = 64.064(3) °, V= 1148.36(10) Å^3, Z = 1, D_c = 1.62 Mg/m^3, μ(Mo-Ka) = 3.366 mm^{-1}, T = 173(2) K, 4843 independent reflections, full-matrix F^2 refinement R_1 = 0.026, wR_2 = 0.066 on 4812 independent absorption corrected reflections [$I > 2\sigma(I)$; $2\theta_{max}$ = 53 °], 324 parameters.

Synthesis of *trans*-[{Pt(PEt$_3$)Cl$_2$}$_2${3-CO-C$_6$H$_4$-C(O)PMe}$_2$] (89)

Prepared as for **88** using {3-CO-C$_6$H$_4$-C(O)PMe}$_2$ (0.043 g, 1.23 x 10^{-4} mol) and *trans*-[PtCl$_2$(PEt$_3$)]$_2$ (0.097 g, 1.23 x 10^{-4} mol). Isolated as a yellow solid. Yield: 0.130 g, 88.2 %.

^{1}H NMR (C_6D_6): δ_H 0.99 (dt, 18H, $^{3}J_{H\text{-}H}$ 8.98 Hz, $^{3}J_{H\text{-}P}$ 17.2 Hz, C**H**$_3$), 1.67 (m, 12H, C**H**$_3$), 2.02 (d, 6H, $^{2}J_{H\text{-}P}$ 7.19 Hz, PC**H**$_3$), 6.59 (t, 2H, $^{3}J_{H\text{-}H}$ 7.96 Hz, *m*-C**H**), 7.89 (d, 4H, $^{3}J_{H\text{-}H}$ 7.45 Hz, *o*-C**H**), 9.36 (s, 2H, middle C**H**).

^{13}C{^{1}H} NMR (C_6D_6): δ_C 4.68 (P**C**H$_3$), 7.97 (**C**H$_3$), 13.5 (**C**H$_2$), 128.9 (*m*-**C**H), 130.4 (middle **C**H), 131.0 (*o*-**C**H), 140.0 (*i*-**C**), 202.6 (**C**=O).

^{195}Pt{^{1}H} NMR 600 Hz (C_6D_6): δ_{Pt} −3934 (dd, $^{1}J_{Pt\text{-}P}$ 1951 Hz, $^{1}J_{Pt\text{-}P}$ 2813 Hz).

^{31}P{^{1}H} NMR (C_6D_6): δ_P 15.9 (d, $^{2}J_{P\text{-}P}$ 441.0 Hz, $^{1}J_{P\text{-}Pt}$ 2813 Hz, **P**Et$_3$), 51.3 (d, $^{2}J_{P\text{-}P}$ 441.0 Hz, $^{1}J_{P\text{-}Pt}$ 1951 Hz, **P**CH$_3$).

Elem. Anal.: Calcd for $C_{30}H_{44}O_4P_4Cl_4Pt_2$: C, 32.03 %; H, 3.91 %. Found; C, 32.13 %; H, 3.82 %.

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8. Appendix

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COMMUNICATION

Facile self-assembly of the first diphosphametacyclophane†

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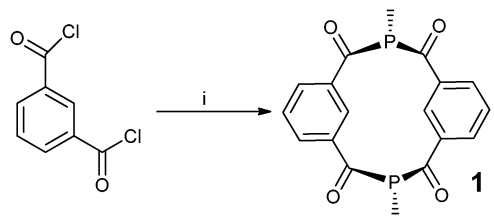
The reaction of isophthaloyl chloride and methyl-bis(trimethylsilyl)phosphane under mild conditions affords high yields of *m*-{-C(O)-C_6H_4(C(O)PMe)}$_2$ (1,10-dimethyl-1,10-diphospha-[3.3]-metacyclophane-2,9,11,18-tetraone): the first example of a diphosphametacyclophane.

Cyclophanes have long held significant importance in the fields of supramolecular chemistry and molecular recognition,[1] and have also found widespread utility in selective asymmetric synthesis and catalysis,[2] and in biomimetic applications.[3] In many of these roles it has proven desirable to include donor atoms, either as appended functionalities (*e.g.* exocyclic phosphanes, phosphates, amines)[4] or commonly as bridging units within the cyclophane motif; *viz.* poly(thia) or poly(aza) cyclophanes.[5] However, notably absent from this selection are phosphacyclophanes, despite the considerable impetus to explore the phosphorus/nitrogen and phosphorus/carbon analogies, and a prevalence of other phosphorus heterocycles that often incorporate an aromatic unit as part of the cyclic skeleton.[6] Herein, we report the facile synthesis of the first such compound, and preliminary investigation of its coordination chemistry.

The reaction (Scheme 1)[7] between equimolar amounts of isophthaloyl chloride (1,3-benzenedicarbonyl dichloride) and methyl-bis(trimethylsilyl)phosphane in diethyl ether proceeds over 12 h to afford a single product, **1**, which deposits from solution and is conveniently isolated by filtration. Spectroscopically[8] **1** is deceptively simple; ^{31}P-NMR data reveal a single phosphorus environment (δ_P 32.7) with retention of the methyl substituent, the ^{1}H-NMR signal for which (δ_H 1.58) integrates consistently for a 1 : 1 addition product with respect to the charactistic isophthaloyl aromatic resonances. Retention of the carbonyl functions is confirmed by ^{13}C{^{1}H}-NMR and infrared spectroscopic data.§



Scheme 1 *Reagents and conditions*: (i) MeP(SiMe$_3$)$_2$, Et$_2$O, −78 °C → r.t., 12 h.

The formulation of **1** as the cyclophane *m*-{-C(O)-C_6H_4(C(O)PMe)}$_2$, followed from: (i) observation of the parent ion by EI-MS (*m*/*z* 356 [M]$^+$); (ii) the absence of SiMe$_3$ functions; (iii) precedent for condensation of RP(SiMe$_3$)$_2$ with acid chlorides,[9] and was ultimately confirmed by an X-ray diffraction study (Fig. 1).[10]

In common with documented diaza[3.3]metacyclophanes[11] **1** adopts a 'butterfly' conformation enforced by the pseudo-pyramidal phosphorus centres, with the methyl substituents assuming a mutually *exo* arrangement. This displaces the skeletal benzene rings from coplanarity by 41.6°, with a centroid-centroid separation of 3.93 Å, which would seemingly dispose the aromatic scaffold to metal inclusion. However, DFT studies (B3LYP/6-311++G(3d,3p))[12,13] reveal the molecular HOMO to be predominantly associated with the phosphorus lone-pairs, though some π-antibonding character is noted for the LUMO, albeit 383.5 kJ mol^{-1} higher in energy. The aromatic bonding orbitals are associated with HOMO-4,

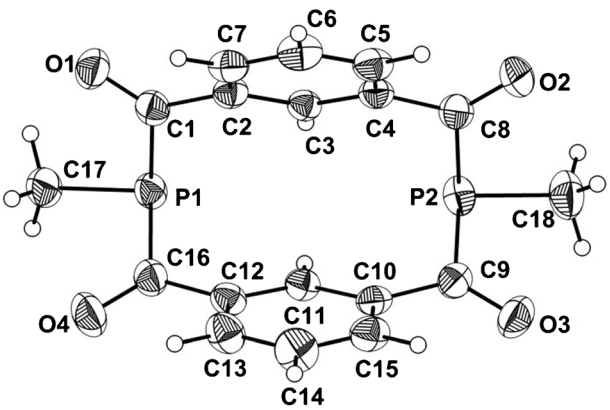


Fig. 1 Molecular structure of **1**, with thermal ellipsoids at the 50% probability level. Selected bond distances (Å) and angles (deg.):C1-O1 1.211(3), C8-O2 1.202(3), C9-O3 1.220(3), C16-O4 1.210(3), C1-P1 1.892(3), C16-P1 1.890(3), C17-P1 1.815(3), C8-P2 1.894(3), C9-P2 1.886(3), C18-P2 1.816(3). C1-P1-C16 95.73(13), C1-P1-C17 98.76(14), C16-P1-C17 100.06(14), C8-P2-C9 95.14(12), C8-P2-C18 99.60(14), C9-P2-C18 100.73(15).

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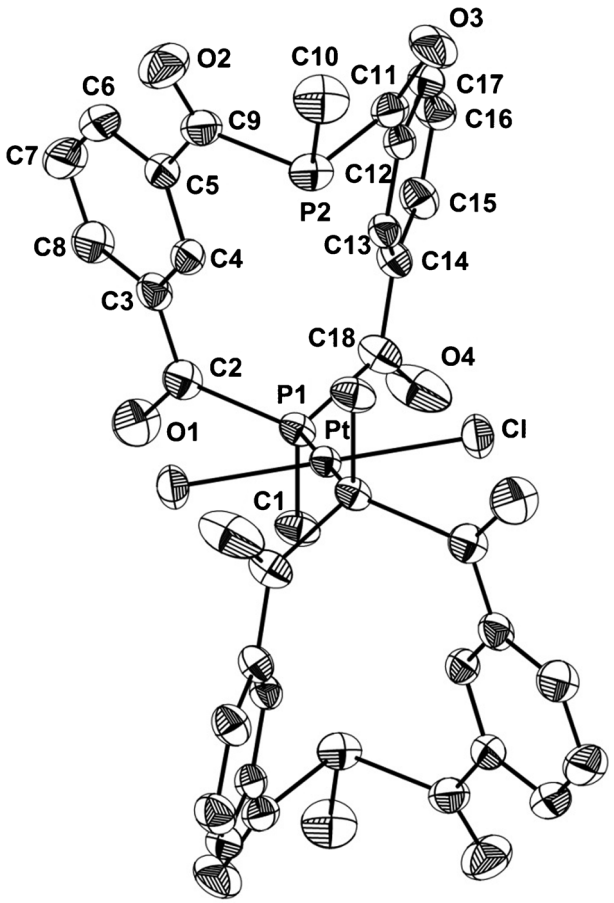
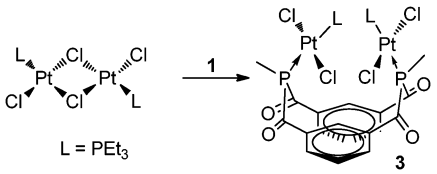


Fig. 2 Molecular structure of **2**, with thermal ellipsoids at the 50% probability level, hydrogen atoms omitted for clarity. The molecule lies on an inversion centre and equivalent atoms are generated by symmetry transformation (−x, −y + 1, −z + 1). Selected bond distances (Å) and angles (deg): Pt-P1 2.2940(7), Pt-Cl 2.3106(7), P1-C1 1.793(3), P2-C10 1.823(4), O1-C2 1.208(4), O2-C9 1.215(4), O3-C11 1.214(4), O4-C18 1.201(4), P1-Pt-Cl 91.05(3), C1-P1-C2 101.81(16), C1-P1-C18 102.03(16), C2-P1-C18 104.56(16), C9-P2-C10 99.22(19), C10-P2-C11 98.74(18), C9-P2-C11 97.65(15).

ca. 88.5 kJ mol^{-1} below the HOMO. These data would suggest that **1** should preferentially engage in metal-binding through phosphorus, rather than the aromatic skeleton. Given the rigid geometry of **1** and the significant P···P separation (5.11 Å) the likelihood of *cis*-chelation would seem low; however, this situation is not significantly removed from that of the rigid diphosphane SPANphos (P···P 4.99 Å),[14] which engages in *trans*-chelation, an area of considerable current interest.[15]

The propensity of **1** toward chelation was tested through its 1 : 1 reaction with $PtCl_2(NCPh)_2$, which afforded, in admixture with $PtCl_2(NCPh)_2$, a single product formulated as *trans*-$PtCl_2(\mathbf{1})_2$ (**2**) on the basis of (i) broken symmetry of the cyclophane fragment (indicated by two $^{31}P\{^1H\}$-NMR resonances; δ_P 28.4, 33.2); (ii) observation of ^{195}Pt satellites on a single ^{31}P-NMR resonance; (iii) the magnitude of the ^{195}Pt-^{31}P coupling constant ($|J|$ = 2296 Hz) being consistent with a *trans*-platinum bis-phosphane complex; (iv) a single-crystal X-ray diffraction study (Fig. 2).[16] Complete consumption of $PtCl_2(NCPh)_2$ is achieved through use of 2 equivalents of **1**.[17]



Scheme 2 *Reagents and conditions*: THF, −78 °C → r.t.

The internal geometry of the cyclophane ligands in **2** remains largely unchanged from uncoordinated **1**, though the P–Me linkage of the ligating centre is somewhat truncated (*d*(P1-C1) 1.793(3) Å) relative to both the free ligand and uncoordinated centre (1.816(3) and 1.823(4) Å respectively); the geometry about platinum is unremarkable other than in illustrating the influence of sterics in directing *trans* over *cis*-coordination, despite the *cis*-geometry of the platinum precursor. We have thus far been unable to identify any intermediate species or kinetic products.

The uncoordinated phosphorus centres (P2) are geometrically disposed to assume antipodal positions along the platinum *z*-axis and thus effectively shield the vacant coordination sites. However, there is no evidence for long-range Pt–P interactions, the separation of 4.56 Å far exceeding the sum of the Van der Waals radii (3.52 Å[18]). This underlines the significant rigidity within **1**, which it seems also precludes *trans*-chelation by inhibiting even marginal contraction of the P···P separation.

This inherent rigidity does, however, predispose **1** to bridging metal centres, as illustrated by its stoichiometric reaction with the dimeric $[PtCl_2(PEt_3)]_2$, to afford [μ-*P*,*P*′-(**1**){$PtCl_2(PEt_3)$}$_2$] (**3**, Scheme 2) in excess of 80% yield. While **3** has thus far defied crystallisation, its formulation follows convincingly from spectroscopic data, *viz.*: (i) two distinct $^{31}P\{^1H\}$-NMR signals (δ_P 15.9, J_{PtP} = 1936 Hz; 51.3, J_{PtP} = 2810 Hz; $^2J_{PP\text{-}trans}$ = 441 Hz¶) associated with PEt_3 and **1** respectively; (ii) characteristically symmetric ^{1}H-NMR signals for the isophthaloyl fragment; (iii) consistent microanalytical data, confirming sample purity.[20]

In conclusion, we have reported the facile synthesis of the first member of the phosphametacyclophane family and demonstrated its potential as a sterically encumbered ligand. This offers potential access to a wide range of similarly bulky phosphorus heterocycles, including asymmetric variants, with significant promise as both bridging polyphosphane ligands and supramolecular scaffolds, targets we continue to pursue.

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Notes and references

§ While we have not yet explicitly studied the hydrolytic sensitivity of **1**, we find this molecule to be relatively robust, being amenable to the acquisition of infrared spectroscopic data in air without any notable decomposition. The reactivity of the carbonyl functions is the subject of on-going investigation.

¶ A *trans* P-P coupling constant of 441 Hz is consitent with other saturated *trans* phosphanes, which typically lie in the 400–500 Hz region,[19a,b] *cf.* more common examples with one phosphite or phosphaalkene ligand (500–700 Hz).[19c,d]

1 See for example: (*a*) F. Diederich, *Cyclophanes*, The Royal Society of Chemistry, Cambridge, 1991; (*b*) C. Jones, *Chem. Soc. Rev.*, 1998, **27**, 289.

2 (*a*) U. Worsdofer, F. Votgle, M. Nieger, M. Waletzke, S. Grimme, F. Gloriusk and A. Pfalts, *Synthesis*, 1999, 597; (*b*) I. Tabushi and K. Yamanmura, *Top. Curr. Chem.*, 1983, **113**, 145.

3 J. Lahan, H. Hocker and R. Langer, *Angew. Chem., Int. Ed.*, 2001, **40**, 726.

4 See for example: M. C. Aversa, A. Barattucci, P. Bonaccorsi, C. Faggi and T. Papalia, *J. Org. Chem.*, 2007, **72**, 4486 and references therein.

5 See for example: R. Quevedo, M. Gonzalez and C. Diaz-Oviedo, *Tetrahedron Lett.*, 2012, **53**, 1595 and references therein.

6 See for example: (*a*) J. I. Bates and D. P. Gates, *Chem.–Eur. J.*, 2012, **18**, 1674; (*b*) K. Nakano, J. Oyama, Y. Nishimura, S. Nakasako and K. Nozaki, *Angew. Chem., Int. Ed.*, 2012, **51**, 695; (*c*) G. Baccolini, C. Boga and M. Galeotti, *Angew. Chem., Int. Ed.*, 2004, **43**, 3058; (*d*) M. D. McReynolds, J. M. Dougherty and P. R. Hanson, *Chem. Rev.*, 2004, **104**, 2239; (*e*) L. Nyulaszi, *Chem. Rev.*, 2001, **101**, 1229 and references therein.

7 *Typical synthesis for* **1**: Ethereal solutions of isophthaloyl chloride (0.46 g, 2.27 mmol) and $MeP(SiMe_3)_2$ (0.66 g, 2.27 mmol) were combined at −78 °C, resulting in a yellow solution and precipitate. After 30 min the mixture was allowed to attain ambient temperature and stirred for a further 12 h. The precipitate was collected by filtration, washed with Et_2O and dried *in vacuo*.

8 *Selected characterising data for* **1**: ^{1}H-NMR (C_6D_6, 30 °C, 399.5 MHz): δ_H 1.58 (d, 6H, $^{2}J_{HP}$ = 3.1 Hz) 6.45 (t, 2H, $^{3}J_{HH}$ = 1.75 Hz), 7.17 (d, 4H, $^{3}J_{HH}$ = 1.67 Hz), 9.28 (br., 2H). $^{31}P\{^{1}H\}$-NMR (C_6D_6, 30 °C, 161.73 MHz): δ_P 32.7 (s). $^{13}C\{^{1}H\}$-NMR (C_6D_6, 30 °C, 150.81 MHz): δ_C 1.7 (d, $^{1}J_{CP}$ 4.5 Hz, Me), 130.3 (J_{CP} = 1.6 Hz, C^{m}), 130.6 (dd, J_{CP} ∼ 2 Hz, $C^{o,p}$), 134.0 (t, $^{3}J_{CP}$ = 13.9 Hz, C^{o}), 137.6 (d, J_{CP} = 37.9 Hz, C^{i}), 205.9 (d, J_{CP} = 46.0 Hz, C═O). Anal. Found: C, 60.59%; H, 3.82%. Cacld for $C_{18}H_{14}O_4P_2$: C, 60.67%; H, 3.93%.

9 See for example: (*a*) V. A. Write, B. O. Patrick, C. Schneider and D. P. Gates, *J. Am. Chem. Soc.*, 2006, **128**, 8836; (*b*) V. A. Write and D. P. Gates, *Angew. Chem., Int. Ed.*, 2002, **41**, 2389; (*c*) A. R. Barron, S. W. Hall and A. H. Cowley, *J. Chem. Soc., Chem. Commun.*, 1987, 1753; (*d*) R. Appel, F. Knoch and H. Kunze, *Chem. Ber.*, 1984, **117**, 3151 and references therein.

10 *Crystal data for* **1**: $C_{18}H_{14}O_4P_2$, M_w = 356.23, Monoclinic, $P2_1/n$ (no. 14), a = 12.0985(9), b = 7.6709(3), c = 18.3347(13) Å, β = 100.317(2)°, V = 1674.047(18) Å^3, Z = 4, D_c = 1.413 Mg m^{-3}, μ(Mo-Kα) = 0.279 mm^{-1}, T = 173(2)K, 3776 independent reflections, full-matrix F^2 refinement R_1 = 0.0530, wR_2 = 0.1699 on 2648 independent absorption corrected reflections [$I > 2\sigma(I)$; $2\theta_{max}$ = 55°], 217 parameters, CCDC 873362.

11 (*a*) H. Takemura, H. Kariyazono, M. Yasutake, N. Kon, K. Tani, K. Sako, T. Shinmyozu and T. Inazu, *Eur. J. Org. Chem.*, 2000, 141; (*b*) N. Kon, H. Takemura, K. Otsuka, K. Tanoue, S. Nakashima, M. Yasutake, K. Tani, J. Kimoto, T. Shinmyozu and T. Inazu, *J. Org. Chem.*, 2000, **65**, 3708; (*c*) W. Boomgaarden, F. Vogtle, M. Nieger and H. Hupfer, *Chem.–Eur. J.*, 1999, **5**, 345; (*d*) H. Plenio and J. Hermann, *Z. Anorg. Allg. Chem.*, 1998, **624**, 792; (*e*) J. Harren, A. Sobanski, M. Nieger, C. Yamamoto, Y. Okamoto and F. Vogtle, *Tetrahedron: Asymmetry*, 1998, **9**, 1369; (*f*) S. Breidenbach, s. Ohren, M. Nieger and F. Vogtle, *Chem. Commun.*, 1995, 1237.

12 *Computational details*: Geometry optimization and frequency calculations were performed using an unrestricted B3LYP functional with the 6-311++G(3d,3p) basis set, with full NBO analysis. The calculations were performed on an Intel Core i5 with 4 GB RAM using Gaussian 03W (multi-processor).

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14 Z. Freixa, M. S. Beentjes, G. G. Batema, C. B. Dieleman, G. P. F. van Strijdonck, J. N. H. reek, P. C. J. Kamer, J. Fraanje, K. Goubitz and P. W. N. M. van Leeuwen, *Angew. Chem., Int. Ed.*, 2003, **42**, 1284.

15 Y. Canac, N. Debono, C. Lepetit, C. Duhayon and R. Chauvin, *Inorg. Chem.*, 2011, **50**, 10810.

16 *Crystal data for* **2**: $C_{36}H_{28}Cl_2O_8P_4Pt{\cdot}2C_4H_8O$, M_w = 1122.65, Triclinic, $P\bar{1}$ (no. 2), a = 10.4564(4), b = 11.3437(6), c = 11.5627(7) Å, α = 87.512(3), β = 69.834(3), γ = 64.064(3)°, V = 1148.36(10) Å^3, Z = 1, D_c = 1.62 Mg m^{-3}, μ(Mo-Kα) = 3.366 mm^{-1}, T = 173(2)K, 4843 independent reflections, full-matrix F^2 refinement R_1 = 0.026, wR_2 = 0.066 on 4812 independent absorption corrected reflections [$I > 2\sigma(I)$; $2\theta_{max}$ = 53°], 324 parameters, CCDC 873363.

17 *Synthetic details for* **2**: THF solutions of **1** (120 mg, 3.36 × 10^{-4} mol) and $PtCl_2(NCPh)_2$ (79 mg, 1.68 × 10^{-4} mol) were combined at low temperature (−78 °C) and then allowed to warm slowly to ambitent temperature while stirring over 12 h. Volatiles were removed under reduced pressure to afford crude **2** as a yellow solid, dried *in vacuo*. Recrystallisation from concentrated THF solution at −20 °C afforded analytically pure samples of **2** as X-ray quality crystals. Yield: 121 mg, 73.8%. *Selected data*: ^{1}H-NMR (d_8-THF, 30 °C, 399.5 MHz): δ_H 1.50 (d, 6H, $^{2}J_{HP}$ = 3.2 Hz, 2 × PCH_3), 2.39 (t, 6H , J_{PH} = 3.1 Hz, 2 × Pt-PCH_3) 7.41 (d, 4H, J_{HH} = 7.5 Hz), 7.67 (dm, 8H, J_{HH} = 7.5 Hz), 10.64 (br., 4H). $^{31}P\{^{1}H\}$-NMR (d_8-THF, 30 °C, 161.73 MHz): δ_P 28.4 (s), 33.2 (s, $^{1}J_{PtP}$ = 2296 Hz) Anal. Found: C, 44.28%; H, 2.80%. Cacld for $C_{18}H_{14}O_4P_2$: C, 44.17%; H, 2.86%.

18 R. S. Rowlands and R. Taylor, *J. Phys. Chem.*, 1996, **100**, 7384.

19 For representative examples see: (*a*) F. H. Allen and S. N. Sze, *J. Chem. Soc. A*, 1971, 2054; (*b*) J. Fawcett, E. G. Hope, R. D. W. Kemmitt, D. R. Paige, D. R. Russell and A. M. Stuart, *J. Chem. Soc., Dalton Trans.*, 1998, 3751; (*c*) P. B. Hitchcock, B. Jacobson and A. Pidcock, *J. Chem. Soc., Dalton Trans.*, 1977, 2038; (*d*) K. B. Dillon and H. P. Goodwin, *J. Organomet. Chem.*, 1994, **469**, 125.

20 *Synthetic details for* **3**: THF solutions of **1** (43 mg, 1.23 × 10^{-4} mol) and $[PtCl_2(PEt_3)]_2$ (97 mg, 1.23 × 10^{-4} mol) were combined at −78 °C, then allowed to warm slowly to ambient temperature while stirring overnight. Removal of volatiles under reduced pressure afforded **3** as a yellow solid. Yield: 61 mg, 88.2%. *Selected data*: ^{1}H-NMR (C_6D_6, 30 °C, 399.5 MHz): δ_H 0.99 (dt, 18H, $^{3}J_{HH}$ = 9.0 Hz, $^{2}J_{HP}$ = 17.2 Hz), 1.67 (m, 12 H), 2.02 (d, $^{2}J_{HP}$ 7.2 Hz), 6.59 (t, 2H, J = 7.9 Hz), 7.89 (d, 4H, J = 7.5 Hz), 9.36 (s., 2H). $^{31}P\{^{1}H\}$-NMR (C_6D_6, 30 °C, 161.73 MHz): δ_P 15.9 (d, $^{2}J_{PP}$ = 441 Hz, $^{1}J_{PtP}$ = 1936 Hz, 2P), 51.3 (d, $^{2}J_{PP}$ = 441 Hz, $^{1}J_{PtP}$ = 2810 Hz, 2P). $^{195}Pt\{^{1}H\}$-NMR (C_6D_6, 30 °C, 85.53 MHz): δ_{Pt} −3933 (dd, $^{1}J_{PtP}$ 1936, 2810 Hz). Anal. Found: C, 32.13%; H, 3.82%. Cacld for $C_{18}H_{14}O_4P_2$: C, 32.03%; H, 3.91%.

