Novel (N-Heterocyclic Carbene)-Palladium(0) Complexes as Catalysts in Element-Element Bond Additions to Unsaturated Moieties

Melvyn B. Ansell

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DECLARATION

I hereby declare that all work described in this thesis was carried out at the University of Sussex under the supervision of Professor John Spencer (40%), Dr Oscar Navarro (40%) and Professor F. Geoffrey N. Cloke FRS (20%) from October 2013 to January 2017. The work is my own unless otherwise stated. The thesis conforms to an 'article format' in which the Chapters 1-5 consist of discrete articles written in a style that is appropriate for publication in peer-review journals in this field. In all cases, additional unpublished content is also included.

Chapter 1 presents a synthetic overview and discussion of the field of research undertaken. It is written in the style of an article appropriate for *Coordination Chemistry Reviews*:

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The author contributions are as follows: Melvyn B. Ansell (M.B.A) was responsible for all aspects of literature reviewing and writing of the manuscript. Dr Oscar Navarro (O.N) and Prof. John Spencer (J.S) were collectively responsible for providing feedback and corrections to the manuscript.

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Chapter 6 is a miscellaneous chapter including further preliminary investigations and therefore not in an article format. The final chapter presents a summary of the preceding chapters.

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.

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ABSTRACT

Novel (N-Heterocyclic carbene)-Palladium(0) Complexes as Catalysts in Element-Element Bond Additions to Unsaturated Moieties

Melvyn B. Ansell

Ph.D Thesis

The focus of this thesis is the synthesis of novel palladium(0) complexes bearing the ligand 1,3,4,5-tetramethylimidazol-2-ylidene (ITMe), a small percentage buried volume N-heterocyclic carbene. These complexes have been assessed as mediators for the 1,2-additions of hetero element-element bonds to unsaturated organic moieties. In particular, Si-Si, Si-B and B-B bond additions to alkynes and azobenzenes were chosen as reactions of interest due to their challenging nature.

Chapter 1 introduces the concept of transition metal mediated element-element additions to alkynes and includes a thorough review on the current literature state.

Chapter 2 describes the first solution based synthesis of [Pd(ITMe)$_2$] and its *in situ* reactivity with $Me_3SiSiMe_3$ under mild conditions to form the novel complex *cis*-[Pd(ITMe)$_2$(SiMe$_3$)$_2$], the first NHC-bearing complex resulting from the oxidative addition of hexamethyldisilane to a palladium centre. The use of this complex as a pre-catalyst for the bis(silyl)ation of electronically and sterically challenging internal acetylenes using non-activated disilanes is reported. A series of novel 1,2-disilylstilbenes were synthesized in high yield and with 100% *Z*-stereoselectivity.

Chapter 3 details the use of [Pd(ITMe)$_2$(PhC≡CPh)], the first bis(N-heterocyclic carbene)Pd(0)-alkyne complex, as a highly reactive pre-catalyst in the silaboration of terminal and internal alkynes to yield a number of known and novel 1-silyl-2-boryl

alkenes. Unprecedented mild reaction temperatures for terminal alkynes, short reaction times and low catalytic loadings are reported. During mechanistic studies, *cis*-[Pd(ITMe)$_2$(SiMe$_2$Ph)(Bpin)] was directly synthesized by oxidative addition of PhMe$_2$SiBpin to [Pd(ITMe)$_2$(PhC≡CPh)]. This represents a very rare example of a (silyl)(boryl)palladium complex. A plausible catalyst decomposition route was also examined.

In **Chapter 4**, [Pd(ITMe)$_2$(PhC≡CPh)] acts as a highly reactive pre-catalyst in the unprecedented homogeneous catalyzed diboration of terminal and internal alkynes, yielding a number of novel and known *syn*-1,2-diborylalkenes in a 100% stereoselective manner. DFT calculations conducted by our collaborators suggest that a similar reaction pathway to that proposed for platinum phosphine analogues is followed, and that destabilization of key intermediates by ITMe is vital to the overall success for the palladium-catalyzed B-B addition to alkynes.

Chapter 5 reports the use of [Pd(ITMe)$_2$(PhC≡CPh)] as a highly active pre-catalyst in the diboration and silaboration of azobenzenes to synthesize a series of novel functionalized hydrazines. The reactions proceed using commercially available diboranes and silaboranes under mild reaction conditions.

Preliminary investigations into further reactivity of [Pd(ITMe)$_2$(PhC≡CPh)], [Pd(ITMe)$_2$] and *cis*-[Pd(ITMe)$_2$(SiR$_3$)$_2$] (SiR$_3$ = SiMe$_2$Ph or SiMe$_3$) are reported in **Chapter 6**. This includes the oxidative cleavage of Me$_3$GeGeMe$_3$ by [Pd(ITMe)$_2$(PhC≡CPh)] to form the novel *cis*-[Pd(ITMe)$_2$(GeMe$_3$)$_2$] and an initial study into the catalytic alkyne digermylations. The hydrogenation of diphenylacetylene to form *Z*-stilbene using an amine-borane and catalytic quantities of [Pd(ITMe)$_2$(PhC≡CPh)] was also investigated. Finally, the stoichiometric reactions of allyl bromides with *cis*-[Pd(ITMe)$_2$(SiR$_3$)$_2$] to form the novel complexes *trans*-[Pd(ITMe)$_2$(SiR$_3$)(Br)] are detailed.

LIST OF ABBREVIATION USED IN THE TEXT

General

Å	angstrom
Ac	acetate
acac	acetylacetonate
Ad	adamantyl
APCI	atomospheric-pressure chemical ionization
Ar	aryl
atm	atmosphere
Bu, ^{n}Bu, ^{t}Bu	butyl, *n*-butyl, *t*-butyl
^{o}C	degrees Celsius
cat	catecholato
cod	1,5-cyclooctadiene
Cy	cyclohexyl
d	day
^{o}	degrees (angles)
dan	naphthalene-1,8-diaminato
dba	dibenzylideneacetone
DCE	1,2-dichloroethane
DCM	dichloromethane
dcpe	1,2-bis(dicyclohexylphosphino)ethane
DFT	density functional theory
DIBALH	diisobutylaluminum hydride
DMF	dimethylformamide
DMSO	dimethylsulfoxide

DNA	deoxyribonucleic acid
dppb	1,4-bis(diphenylphosphino)butane
dppf	1,1’-bis(diphenylphosphino)ferrocene
E, E’	hetero-element (not hydrogen)
E	*trans* or *anti*
e^-	electron
epto	4-ethyl-2,6,7-troxa-1-phosphabicyclo[2.2.2]octane
ESI	electrospray ionization
Et	ethyl
g	grams
h	hour
n-Hex	*n*-hexyl
HMRS	high resolution mass spectrometry
HOMO	highest occupied molecular orbital
i	ipso
IPr	1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene
ITMe	1,3,4,5-tetramethylimidazol-2-ylidene
K	Kelvin
kcal	kilocalorie
L	generic ligand
LUMO	lowest occupied molecular orbital
m	meta
M	generic platinum group transition metal
M	molarity
ma	maleic anhydride

mbar	milli-bar
Me	methyl
MeCN	acetonitrile
Mes	mesityl
MIDA	*N*-methylimidiacetic acid
min	minute
µL	micro-litre
µmol	micro-mole
mg	milli-gram
mL	milli-litre
mmol	milli-mole
M_r	molecular weight
µwave	microwave
NA	napthyl
nbd	norbornadiene
nep	neopentyl glycolato
NHC	N-heterocyclic carbene
NPore	nanoporous
nq	1,4-naphthaquinone
o	ortho
^{n}Oc/t, ^{t}Oc/t	*n*-octyl, *t*-octyl
p	para
Ph	phenyl
pin	pinacolato
ppm	parts per million

^{i}Pr	isopropyl
PTSA	*p*-toluenesulfonic acid
r.t.	room temperature
SOMO	singularly occupied molecular orbital
SIPr	1,3-bis(2,6-diisopropylphenylimidazolidine
S_N2	two component nucleophilic substitution reaction
S_N2'	two component conjugate nucleophilic substitution reaction
Σ	sum of
T	temperature
TBAF	*tetra*-*n*-butylammonium fluoride
TBDPS	*t*-butyldiphenylsilyl
TBS	*t*-butyldimethylsilyl
Tf	triflate
THF	tetrahydrofuran
TM	transition metal
W	Watts
X	halide
Z	*cis* or *syn*

Nuclear Magnetic Resonance spectroscopic data

br	broad
d	doublet
dd	doublet of doublets
δ	chemical shift in ppm
DQF	double quantum filter

Hz	hertz
^{x}J	coupling constant over x bonds
m	multiplet
MHz	megahertz
NMR	nuclear magnetic resonance
NOESY	nuclear Overhauser effect spectroscopy
q	quartet
s	singlet
sept	septet
t	triplet

TABLE OF CONTENTS

Chapter 1

General Introduction

1.1 Alkenes

Alkenes are defined as either branched or unbranched hydrocarbons that possess at least one carbon-carbon double bond (C=C).[1] Each carbon atom in a C=C bond is sp^2-hybridized, forming σ-bonds to three other atoms. An unhybridized $2p_z$ orbital, perpendicular to the σ-bonding plane, overlaps with a symmetrically equivalent orbital on an adjacent carbon to form a π-bond (Scheme 1). The C=C bond is effectively described as a combination of a σ and π-bond between two carbon centres. The geometry around each carbon atom is trigonal planar with bond angles of approximately 120 °.[2] If the alkene has more than one substituent around the C=C bond then two geometric configurations are possible, *E* or *Z* (often termed *trans* or *cis*, although this older terminology can sometimes be ambiguous and is frequently interchanged with *anti* or *syn*, respectively). These labels originate from the German words 'entgegen' meaning opposite and 'zusammen' meaning together (Figure 1.1).

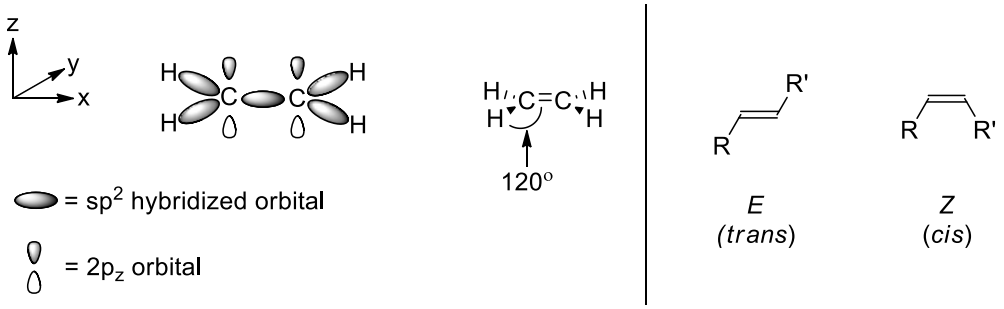


Figure 1.1 Alkene orbitals, shape and configurations for simple alkenes (olefins)

The importance of alkene stereochemistry is reflected in biologically relevant molecules and is often the difference between an active or inactive compound.[3] Furthermore, highly

functionalized and stereodefined multi-substituted alkenes are found in many industrially important compounds including pharmaceuticals (Scheme 1.2),[4–8] dipeptide mimetics,[9] and polymeric materials.[10] The stereoselective synthesis of, or precursors to these alkenes has therefore attracted substantial attention from both academia and industry. Stereoselective syntheses include Peterson olefination,[11,12] the Ramberg-Bäcklund reaction,[13] the Wittig reaction (as well as the Wittig-Horner variation),[14,15] olefin metathesis,[16] Julia-Lythgoe olefination,[17,18] and the McMurry reaction (Figure 1.2).[19,20]

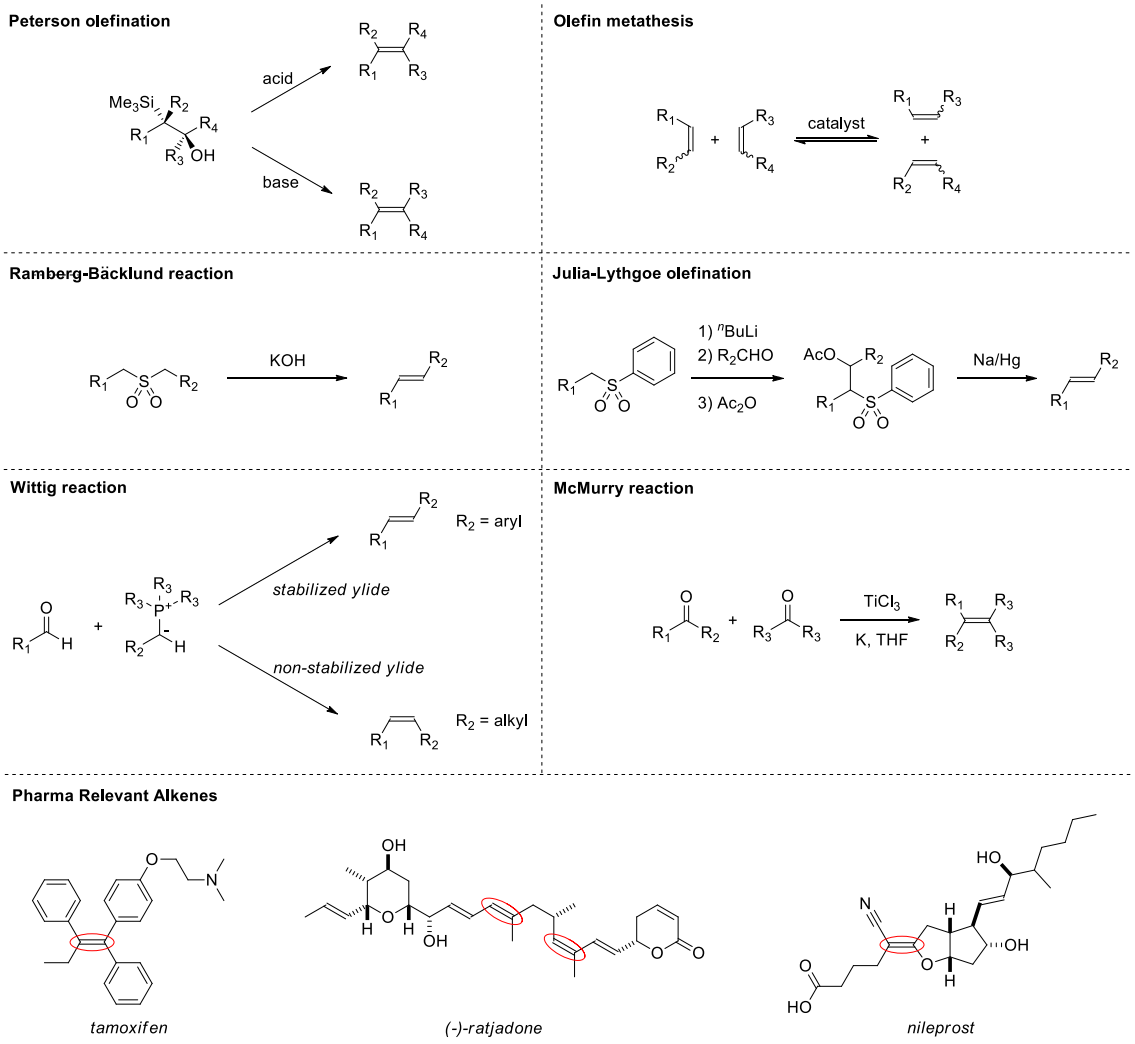
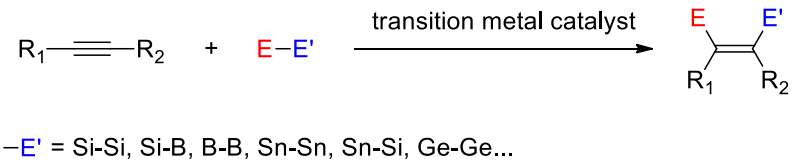


Figure 1.2 Selected examples of multi-substituted alkene synthesis and pharma-relevant alkenes

Arguably, one of the most atom economical routes (maximum number of atoms of reactants appearing in the product/s)[21] to the stereoselective synthesis of *syn/cis*-configured multi-substituted alkenes is alkyne reduction by its π-insertion into hetero element-element' (E-E') bonds.[22] The following sections will focus on the transition metal catalysed additions of E-E' bonds (where E and E' ≠ H) to alkynes and the proposed mechanistic pathways.

1.2 Transition Metal Mediated E-E' Additions to Alkynes

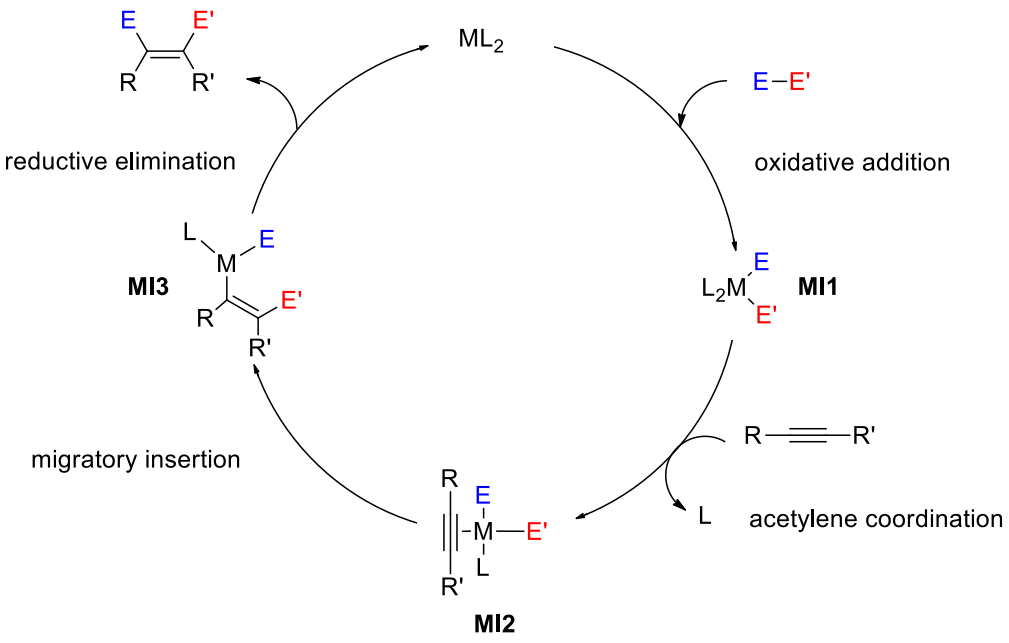
The π-insertion of alkynes into a E-E' bond results in the regio- and stereoselective synthesis of *syn/cis*-1-element-2-element'-alkenes in a single step (Scheme 1.1). A range of E-E' bonds are accessible including Si-Si, Si-B, B-B, Sn-Sn, Sn-Si, Ge-Ge etc, and are mediated either stoichiometrically or catalytically by a variety of low-valent transition metal complexes.



Scheme 1.1 General scheme for transition metal mediated E-E' additions to alkynes

The main mediators in the E-E' additions to alkynes are low valent platinum group transition metal complexes coordinated by either phosphine or isocyanide ligand sets. The mechanism is well established, both computationally and experimentally, and consists of three major steps: oxidative addition, insertion and reductive elimination.[23,24] The first step in this catalytic cycle is the oxidative cleavage of an E-E' bond by a $M(0)L_2$ (M = platinum group metal, L = phosphine/isocyanide) species to form *cis*-(E)(E')$M(II)L_2$

(**MI1**). **MI1** is often kinetically stable and is isolated experimentally for many of the E-E' bonds discussed above (the relevant E-E' oxidative additions will be discussed in the appropriate chapters).[25–29] A ligand exchange then occurs with decoordination of a single L ligand and coordination of the alkyne in its place to yield **MI2**. This is swiftly followed by an insertion of the alkyne into a M-E or M-E' bond (**MI3**).[30,31] The regioselectivity of the E-E' addition is usually defined by this step and dictating factors include: the energetics of the bonds broken *vs.* the bonds formed, the sterics of the system and electronic stabilization effects within the resulting intermediates.[32,33] Experimental studies suggest that the insertion is often the rate-limiting step in these reaction pathways.[30] An isomerization and re-coordination of the L ligand results in the E and (E') vinyl groups adjacent to one another. This positioning is then ideally suited for stereoselective reductive elimination to yield the corresponding *Z*-1,2-disubstituted alkenes and consequent reformation of $M(0)L_2$ (Scheme 1.2).



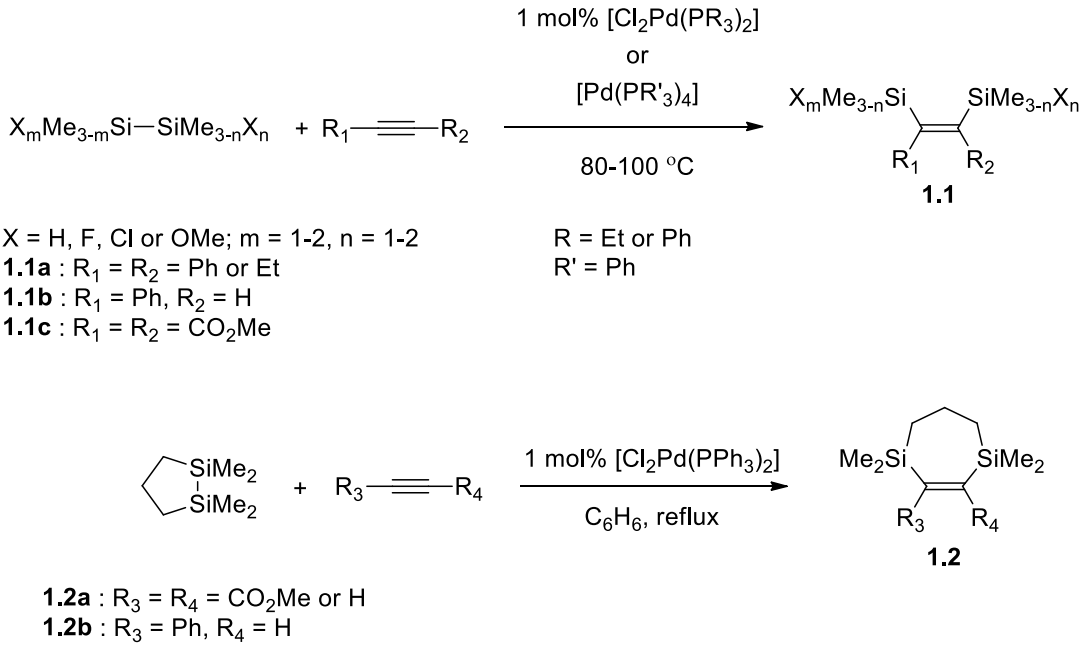
Scheme 1.2 General mechanism for platinum group transition metal mediated addition of E-E' bonds to alkynes

The subsequent sections will overview the history, state-of-the-art and scope of this field, arranged by heteroatom bonds activated and metals used.

1.2.1 Silicon-Silicon (Si-Si)

Palladium

The π-insertion of unsaturated moieties into Si-Si bonds is often called bis(silyl)ation. Palladium mediated bis(silyl)ation of alkynes is one of the most investigated reactions within this area of chemistry.[34] The first examples were reported by Kumada and Sakurai utilizing activated and strained disilanes, respectively. Kumada and co-workers demonstrated that activated disilanes, of the form $X_{3-m}Me_mSiSiMe_nX_{3-n}$ (X = H, F, Cl or OMe; m = 1-2, n = 1-2), added to various alkynes when catalytic quantities of $[Cl_2Pd(PR_3)_2]$ or $[Pd(PR'_3)_4]$ (R = Et or Ph and R' = Ph) were employed (Scheme 1.3).[35,36] The extension of this protocol to non-activated disilanes, such as hexamethyldisilane ($Me_3SiSiMe_3$), was unsuccessful. Elsewhere, Sakurai showed that the extent of alkyne bis(silyl)ation using the strained cyclic disilane, 1,1,2,2-tetramethyl-1,2-disilacyclopentane, was dependent upon the choice of alkyne.[37] Dimethyl acetylenedicarboxylate, phenylacetylene and ethylene all underwent bis(silyl)ation (Scheme 1.3). However, no reaction was observed with the internal alkynes diphenylacetylene and bis(trimethylsilyl)acetylene.



Scheme 1.3 Kumada's activated and Sakurai's strained disilane bis(silyl)ations

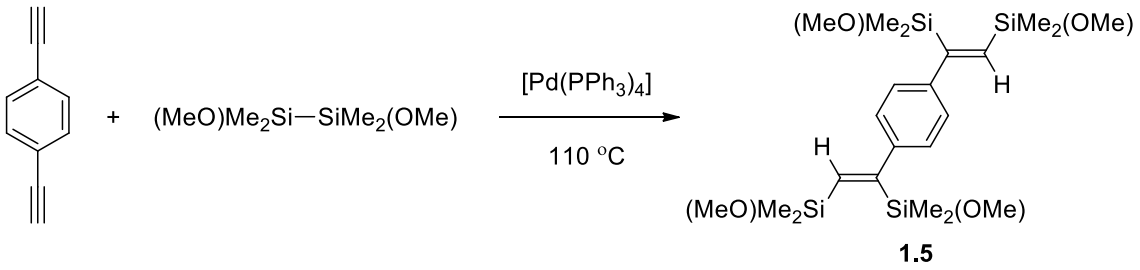
Watanabe performed the bis(silyl)ation of acetylene using chlorinated disilanes, $Me_nSi_2Cl_{6-n}$ (n = 2-5).[38] The formation of the *Z*-1,2-disilylated alkenes was favoured, although significant quantities of the *E*-isomers were noted. It was observed that upon heating, *Z* to *E* isomerization occurred in the presence of the Pd(0) complex. This work was extended to other activated disilanes such as methoxymethyldisilanes, $(MeO)_mMe_{3-m}SiSiMe_{3-n}(OMe)_n$, as well as the acetylenes 1-hexyne and trimethylsilylacetylene.[39] Bis(silyl)ation with $Me_3SiSiMe_3$ was extremely sluggish even at temperatures of 140 °C.

Hiyama and co-workers utilized these chlorinated disilanes in the palladium catalysed bis(silyl)ation of bis(trimethylsilyl)butadiyne.[40] Subsequent treatment of the reaction mixture with MeMgBr resulted in the formation of 1,1,4,4-tetrakis(trimethylsilyl)butatriene (**1.3**) and/or 1,1,2,4-tetrakis(trimethylsilyl)-1-buten-3-yne (**1.4**) (Scheme 1.4).

Scheme 1.4 Bis(silyl)ation of diynes using chlorinated disilanes

The bis(silyl)ation of a number of internal and terminal alkynes using the activated disilane Me_3SiSiF_2Ph was achieved by Ozawa.[41] The catalyst was generated *in situ* from a mixture of 1 mol% $[Pd(\eta^3\text{-allyl})Cl]_2$ and 2 mol% PMe_2Ph. Reactions were completed within several hours at room temperature giving the corresponding *Z*-alkenes. The choice of disilane was essential with no reactivity arising from the use of $Me_3SiSiMe_3$ or PhF_2SiSiF_2Ph.

Loy and co-workers employed the activated disilane, 1,2-dimethoxy-1,1,2,2-tetramethyldisilane in the bis(silyl)ation of 1,4-diethynylbenzene to form **1.5** (Scheme 1.5). **1.5** then ring closed at each alkenyl unit to form the corresponding disiloxacyclopentenes. Subsequent hydrogenation with hydrogen gas using Pd on carbon resulted in a saturated monomer that underwent ring-opening polymerization in tetrahydrofuran (THF) or in the presence of catalytic quantities of *tert*-butylammonium hydroxide (TBAH) giving rise to a crack free sol-gel in a matter of seconds.[42]

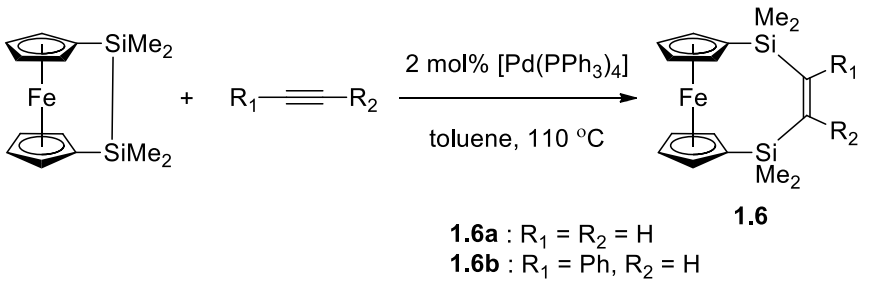


1.5

Scheme 1.5 Bis(silyl)ation of 1,4-diethynylbenzene towards crack free sol-gels

Seyferth and co-workers demonstrated that the very reactive and strained Si-Si σ-bond in octamethyl-1,2-disilacyclobutane was capable of bis(silyl)ating a number of alkynes including acetylene, phenylacetylene and dimethyl acetylenedicarboxylate when using catalytic quantities of $[Cl_2Pd(PPh_3)_2]$. However, extension of this protocol to other internal alkynes was unsuccessful, even at temperatures of 140 °C.[43]

Manners showed that the ferrocenyldisilane, $[Fe(\eta^5\text{-}C_5H_4)_2(SiMe_2)_2]$ added across acetylene or phenylacetylene to form the organometallic rings **1.6a** and **1.6b**, respectively (Scheme 1.6).[44] The reaction of alkynes such as dimethyl acetylenedicarboxylate resulted in a mixture of mono- and di-insertion products with significant quantities of the alkyne cyclotrimerization product, a common occurrence with alkynes such as dimethyl acetylenedicarboxylate and acetylene.[45] Other palladium mediated bis(silyl)ations of alkynes using strained disilanes include Ko's 'super-aromatic' *o*-carborane disilane **1.7**,[46] and Braunschweig's [2]silachromoarenophane **1.8**,[47] bis(silyl)ated terminal and internal alkynes, respectively (Figure 1.3). The cyclic nature of these disilanes pre-conditioned the formation of the *Z*-configured 1,2-disilylated alkene products.



Scheme 1.6 Palladium catalysed alkyne insertions into ferrocenyldisilane

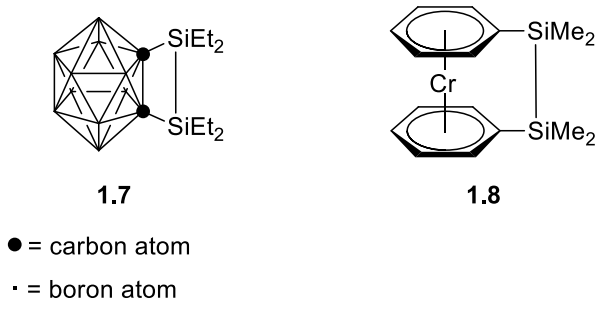
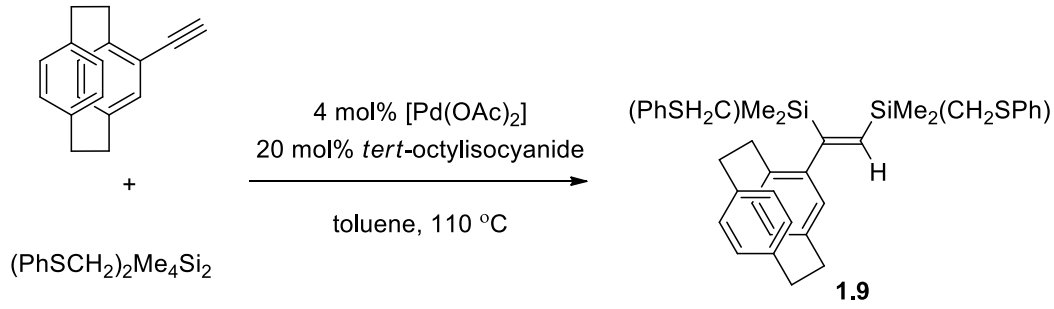


Figure 1.3 Ko's *o*-carborane disilane **1.7** and Braunschweig's [2]silachromoarenophanes **1.8**

In 1991, a communication from Ito and co-workers revolutionised the field of alkyne bis(silyl)ation by the introduction of the pre-catalytic combination of $[Pd(OAc)_2]$ (OAc = acetate) and isocyanide ligands.[48] As a result, the bis(silyl)ation of alkynes was no longer limited to activated or strained disilanes. A combination of 2 mol% $[Pd(OAc)_2]$/30 mol% *tert*-octyl isocyanide was enough to catalyse the bis(silyl)ation of terminal alkynes such as 1-phenylpropyne, 1-phenylhexyne, 1-nonyne and phenylacetylene using the non-activated disilane, $Me_3SiSiMe_3$. Reactions proceeded at 110 °C and resulted in unprecedented high stereoselectivities. Ito and co-workers extended this protocol to a range of bis(silyl)ations including the intramolecular bis(silyl)ation of alkynes in the

stereoselective synthesis of 1,2,4-triols,[49] cyclic tetrakis(organosilyl)ethenes as organic chromophores,[50] chiral allenylsilanes,[51] and enantioenriched propargyl silanes.[52]

Many authors since have utilized the [$Pd(OAc)_2$]/isocyanide combination within their own work. For example, Strohmann and co-workers used the pre-catalytic combination above in a number of alkyne bis(silyl)ations using 1,1,2,2-tetramethyl-1,2-bis(phenylthiomethyl)disilane as the disilane source.[53] In particular, the bis(silyl)ation of ethynyl[2.2]paracyclophanes resulted in the formation of **1.9** (Scheme 1.7), which have potential applications in chiral catalysis and optoelectronic materials.[54]

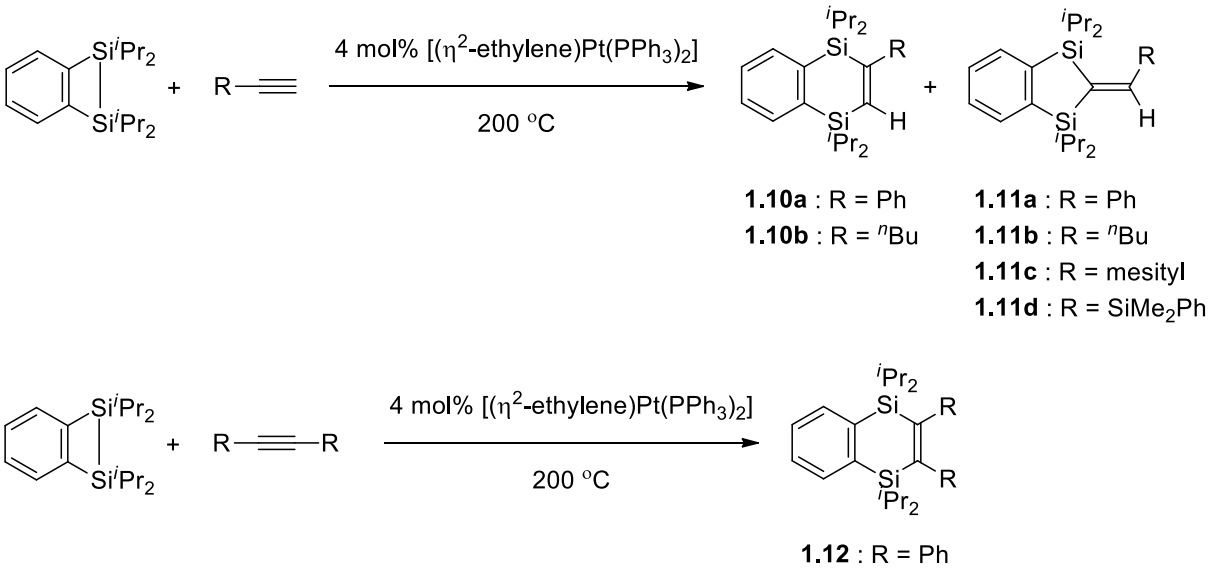


Scheme 1.7 Bis(silyl)ation of ethynyl[2.2]paracyclophanes

Platinum

In contrast, platinum catalysed bis(silyl)ation of alkynes has been investigated to a lesser extent. The most common bis(silyl)ation mediator is [(η^2-ethylene)$Pt(PPh_3)_2$]. Ishikawa detailed the bis(silyl)ation of a number of alkynes using 3,4-benzo-1,1,2,2,-tetra(isopropyl)-1,2-disilacyclobut-3-ene.[55] The reactivity and product selectivity using this platinum catalyst differed from the palladium analogues and depended on the alkyne used, notably employing extreme temperatures. Reactions with 1-hexyne and phenylacetylene resulted in a mixture of **1.10** and **1.11**. The bulky mono-substituted alkynes mesitylacetylene and (phenyldimethylsilyl)acetylene formed **1.11** as the sole

product, whereas diphenylacetylene resulted in only the 1,2-disilylated alkene **1.12** (Scheme 1.8).

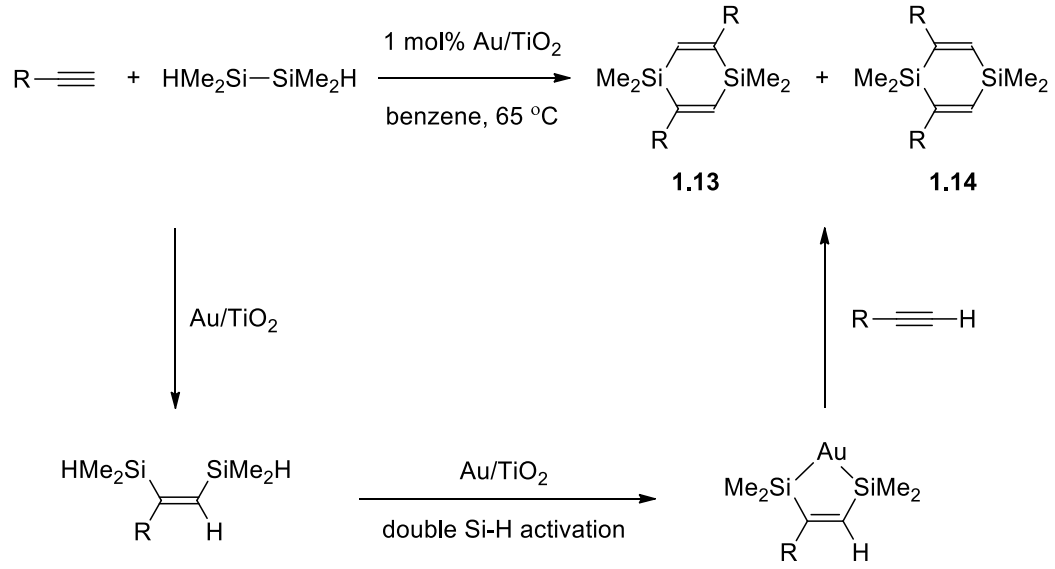


Scheme 1.8 Bis(silyl)ation of alkynes with 3,4-benzo-1,1,2,2,-tetra(isopropyl)-1,2-disilacyclobut-3-ene

Investigations into the reactivity of 1,2-bis(dimethylsilyl)carborane by Ko and co-workers were extended to the platinum catalysed bis(silyl)ation of alkynes. Normal 1,2-bis(silyl)ation was observed in the reaction with phenylacetylene, diphenylacetylene, 3-hexyne, 2-butyne and dimethyl acetylenedicarboxylate. However, the use of 1-hexyne resulted in geminal or 1,1-bis(silyl)ation and the formation of a five-membered disilyl ring.[56] A later report by Ishikawa described the bis(silyl)ation of a range of terminal and internal alkynes using *cis*- and *trans*-1,2-dimethyl-1,2-diphenyl-disilacyclopentane. The reactions proceeded with high stereospecificity and translation of the *cis* or *trans* nature of disilane in all cases.[57]

Gold

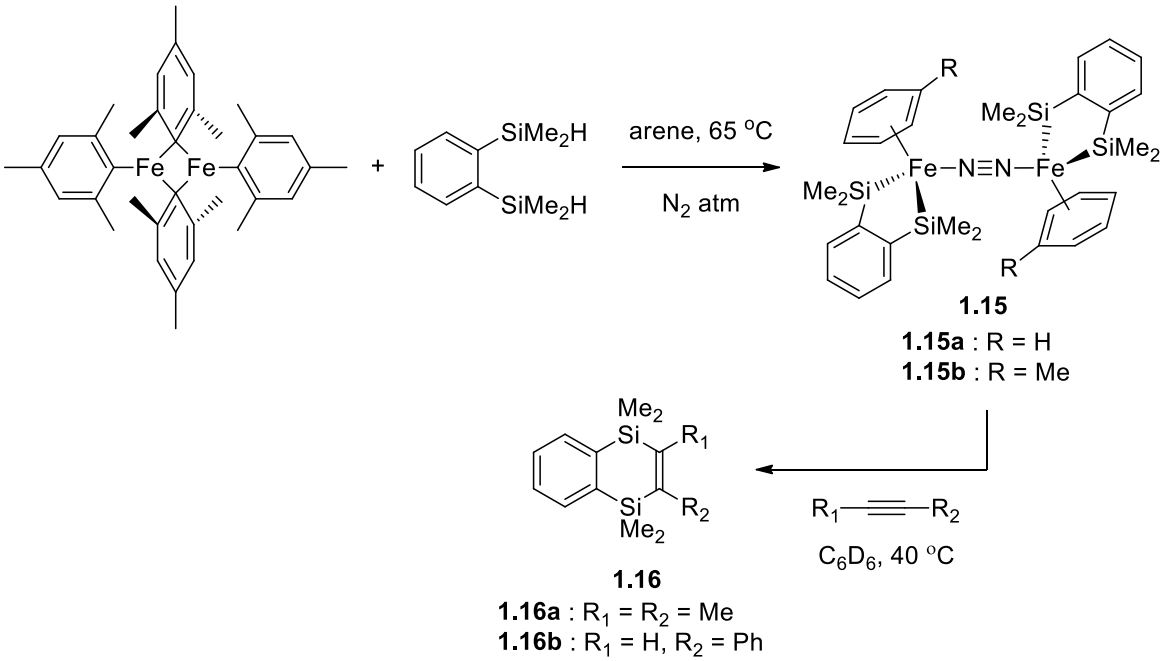
The redox chemistry between gold(I)/(III) is similar to that of palladium(0)/(II), given that they are isolobal. This has triggered substantial research into the development of gold catalysts that are as active as their palladium analogues.[58–60] Despite this effort, gold catalysis is very much in its infancy with the only reports of alkyne bis(silyl)ation in the literature being mediated by gold nanoparticles supported on titanium oxide (Au/TiO_2).[61] Stratakis and co-workers showed the bis(silyl)ation of a range of terminal alkynes using hexamethyldisilane and 1,2-diphenyl-1,1,2,2-tetramethyldisilane was possible.[62] In all cases, the *Z*-alkenes were favoured with a small percentage of the *E*-isomers formed. The heterogeneous catalyst gave comparable activities upon recycling. Stratakis extended the protocol to 1,1,2,2-tetramethydisilane ($HMe_2SiSiMe_2H$). However, the two isomers **1.13** (major) and **1.14** (minor) were isolated (Scheme 1.9). Mechanistically, this observation was explained by an initial bis(silyl)ation followed by a dehydrogenative addition to a second alkyne.[63]



Scheme 1.9 Gold catalysed bis(silyl)ation-dehydrogenative addition

Iron

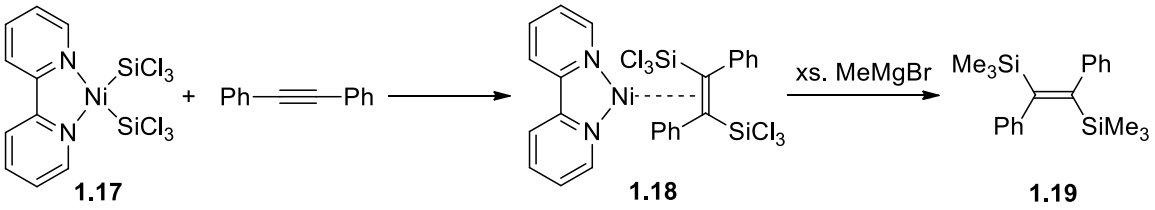
Sunada and co-workers reacted 1,2-bis(dimethylsilyl)benzene with $[Fe(mesityl)_2]_2$ (mesityl = 2,4,6-$Me_3C_6H_2$) in aromatic solvents under a nitrogen (N_2) atmosphere to form **1.15** (Scheme 1.10). Subsequent addition of 2-butyne or phenylacetylene resulted in the quantitative formation of the disilacarbocycles **1.16a** and **1.16b**, respectively (Scheme 1.10).[64] This process was made catalytic upon addition of 1,2-bis(dimethylsilyl)benzene to phenylacetylene and 20 mol% of Fe.[65] Although this is not a bis(silyl)ation in the traditional sense (it lacks a Si-Si σ-bond and it proceeds through a dehydrogenative double silylation), it is still a very rare example of an iron mediated bis(silyl)ation of alkynes.



Scheme 1.10 Formation of a bis(silyl)Fe(II) complex and resulting reactivity with alkynes

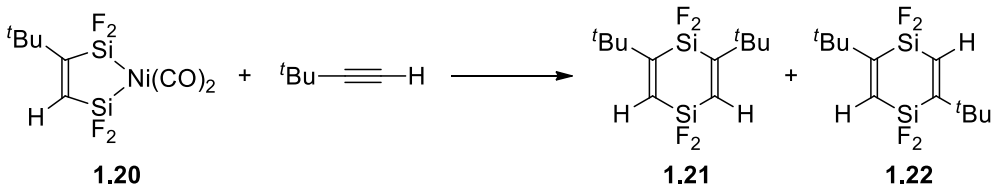
Nickel

The first examples of alkyne bis(silyl)ation were accomplished by Kumada and co-workers using a nickel mediator. It was reported that the bis(silyl)bipyridylnickel(II) complex **1.17** reacted with diphenylacetylene to form **1.18**. Treatment of the latter with MeMgBr, followed by an acidic work up resulted in the isolation of *E*-1,2-bis(trimethylsilyl)stilbene (**1.19**) (Scheme 1.11).[66] Extension to other alkynes yielded mixtures of *Z* and *E*-alkene products.



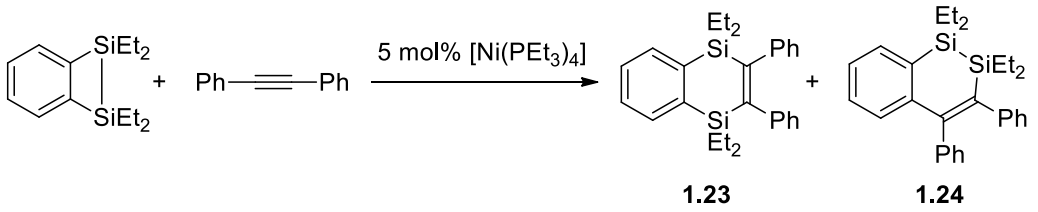
Scheme 1.11 Stoichiometric reaction of a bis(silyl)Ni(II) complex with diphenylacetylene

At the same time, Liu showed that a tetrafluorodisilacyclobutene underwent oxidative addition to $[Ni(CO)_4]$. The corresponding bis(silyl)Ni(II) complex **1.20** was reacted with *tert*-butylacetylene to form the 1,4-disilacyclohexadienes **1.21** and **1.22**, where the ^{t}Bu groups are *syn* and *anti*, respectively (Scheme 1.12).[67]



Scheme 1.12 Nickel mediated bis(silyl)ation using a strained cyclic disilane

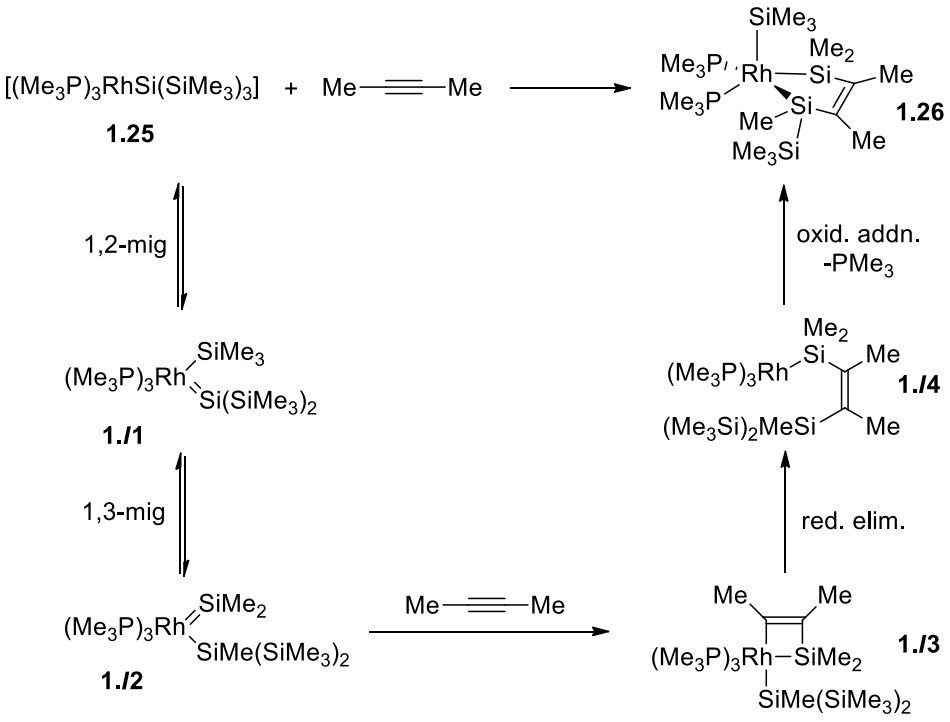
The first catalytic bis(silyl)ation of alkynes employing nickel was reported by Naka and co-workers. The reaction of 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobutene with diphenylacetylene in the presence of catalytic amounts of [$Ni(PEt_3)_4$] formed the *Z*-alkene **1.23**.[68] As well as bis(silyl)ation, an alkyne insertion into one of the phenylene-Si bonds occurred, with **1.24** isolated as a minor product (Scheme 1.13). This type of insertion was consistently observed on applying the methodology to other alkynes.[69]



Scheme 1.13 Ni(0) catalysed bis(silyl)ation and phenylene-Si insertion

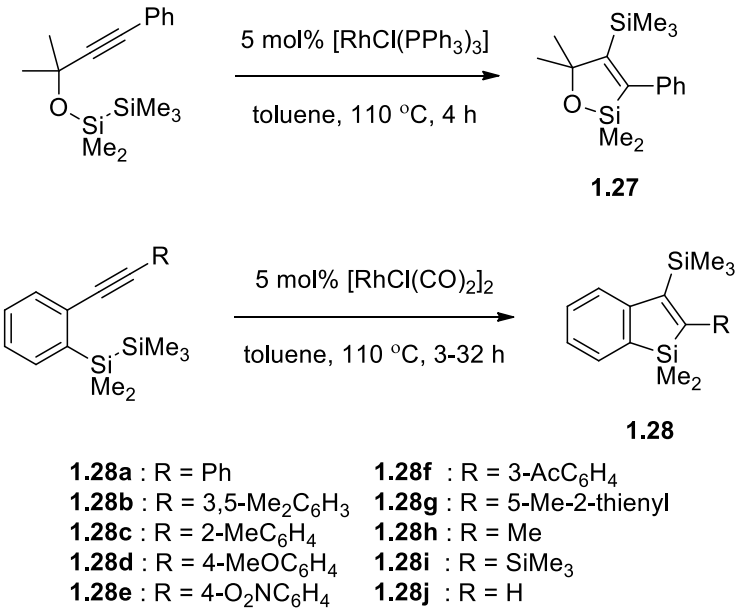
Rhodium

Examples of rhodium mediated alkyne bis(silyl)ations are rare. Tilley and co-workers carried out the stoichiometric reaction of [$(Me_3P)_3RhSi(SiMe_3)_3$] (**1.25**) with 2-butyne resulting in the isolation of the Rh(III) complex **1.26**.[70] The authors proposed that **1.25** undergoes a facile silyl 1,2- and 1,3-migration (**1.*I*1** and **1.*I*2**, respectively) process in the presence of alkyne resulting in a [2+2] cycloaddition and the formation of a transient metallasilacyclobutene **1.*I*3**. The reductive elimination of a Si-C bond in **1.*I*3** gives a Rh(I)-silyl intermediate **1.*I*4**, which then loses one PMe_3 ligand. This induces an oxidative addition of a Si-Si bond in the tethered trisilyl group and subsequent formation of **1.26** (Scheme 1.14).



Scheme 1.14 Stoichiometric bis(silyl)ation of 2-butyne mediated by Rh(I) species

Rhodium(I) catalysed intramolecular bis(silyl)ations of alkynes were reported by Matsuda and co-workers. Initial testing and optimization were executed on the disilanyl ether of a propargylic alcohol.[71] It was observed that 4-silyl-2,5-dihydro-1,2-oxasilole (**1.27**) was formed as the sole product (Scheme 1.15). This *trans*-bis(silyl)ation proceeded with the complete opposite stereoselectivity to the analogous palladium-catalysed reaction. The protocol was then extended to a variety of (2-alkynylphenyl)disilanes affording the corresponding 3-silyl-1-benzosiloles (**1.28**) (Scheme 1.15).



Scheme 1.15 Rh(I)-catalysed intramolecular *trans*-bis(silyl)ation of alkynes

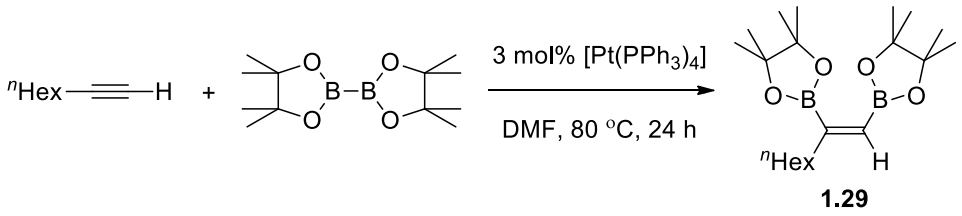
1.2.2 Boron-Boron (B-B)

Platinum

Due to their low toxicity, high stability under atmospheric conditions and versatile reactivity, the synthesis of organoboron reagents has attracted significant interest. In particular, there is substantial focus towards *Z*-1,2-diborylated alkenes as the products of alkyne diboration.[72] The resulting newly formed B-C bonds are able to participate in Suzuki-Miyaura cross-coupling reactions,[73] to build more complex and useful tri- and tetra-substituted alkenes. The first source of B-B bonds investigated was diboron tetrahalides. These contain the most reactive B-B bond available (the lack of π-donating substituents increases the Lewis acidity of the boron based p-orbitals and therefore their susceptibility towards nucleophilic attack) and often react with unsaturated organic substrates without the need for a transition metal mediator or catalyst.[74] However, the preparations of diboron tetrahalides are difficult and this therefore limits their synthetic

utility.[75,76] Tetraalkoxy- and tetraaryloxydiborons are air stable, easily handled and, despite their relatively high B-B bond strengths, are now widely utilized in the stoichiometric and catalytic addition of B-B bonds to alkynes. These diboron reagents will be the main focus of this section.

Platinum is by far the most effective and widely studied mediator of alkyne diboration. The first examples were reported by Suzuki and Miyaura in 1993.[77] Initial results indicated that 1-octyne inserted into the B-B bond of bis(pinacolato)diboron (B_2pin_2) using catalytic quantities of [$Pt(PPh_3)_4$] to form **1.29** (Scheme 1.16).

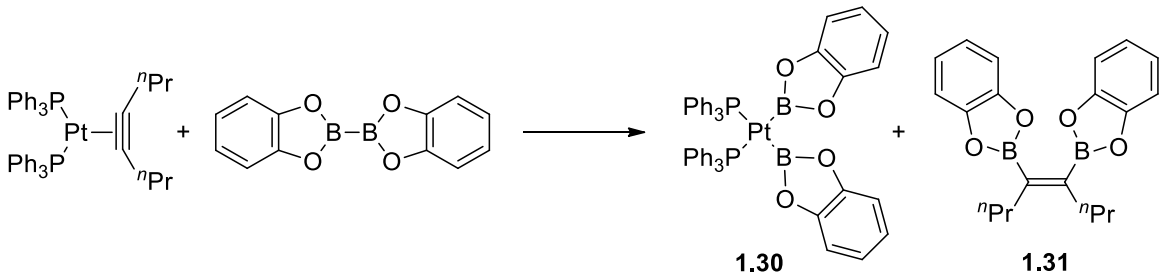


1.29

Scheme 1.16 The first diboration of alkynes catalysed by [$Pt(PPh_3)_4$]

The protocol was then extended to a range of internal and terminal alkynes with similarly high stereoselectivities obtained. The rate of diboration was drastically affected by the polarity of the solvent, with the more polar solvents (e.g. DMF) accelerating the rate. However, the authors later showed that hexane also accelerated the reaction rate and to a greater extent than most polar solvents.[78] Other transition metal complexes proved ineffective within this study e.g. [$Pd(PPh_3)_4$] and [$Pd(OAc)_2$]/isocyanide (the best catalysts in the bis(silyl)ation of alkynes). Suzuki-Miyaura coupling protocols have since been widely employed *en route* to, for example, enantiomerically enriched 1,2-diols,[79] 5-benzylidenylbenzopyridyloxepine analogues as nuclear hormone receptors,[80] *1H*-phosphindoles as chiral helicenes,[81] 10-mesitylborylsubstututed-dibenzoborepin as a photoresponsive material,[82] and the pentacyclic alkaloid, tylophorine.[83]

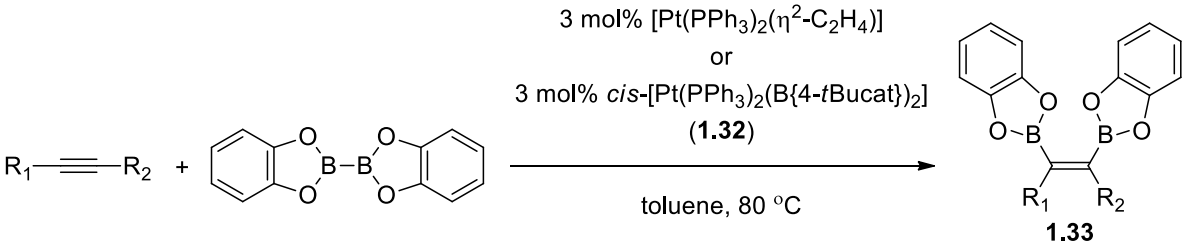
Smith and co-workers carried out a stoichiometric diboration by reaction of commercially available bis(catecholato)diboron (B_2cat_2) with [(η^2-4-octyne)Pt(PPh_3)$_2$]. This resulted in the oxidative addition bis(boryl)Pt(II) complex **1.30**, and the *Z*-1,2-diborylated alkene **1.31** (Scheme 1.17).[84]



1.30 **1.31**

Scheme 1.17 Platinum-mediated stoichiometric diboration of an alkyne

Marder and Norman extended the synthesis of bis(boryl)platinum(II) complexes to the use of other diborons including B_2pin_2 and $B_2(4\text{-}^t\text{Bucat})_2$ (4-^{t}Bucat = 1,2-O_2-^{t}BuC_6H_3). [(η^2-ethylene)Pt(PPh_3)$_2$] and **1.32** were then used as catalysts in the diboration of terminal and internal alkynes employing B_2pin_2 and B_2cat_2 as B-B bond sources (Scheme 1.18).



1.33

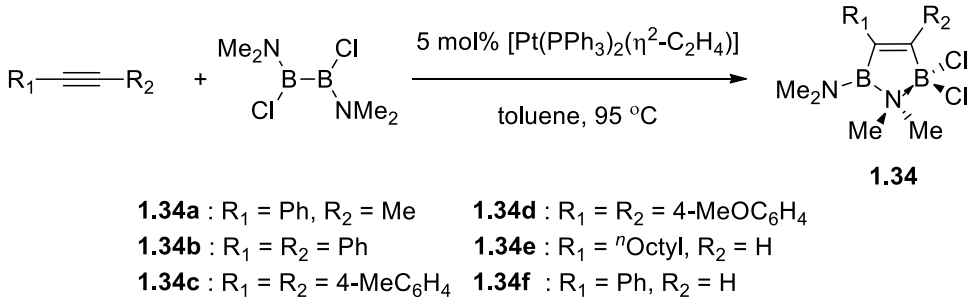
1.33a : R_1 = C_6H_{13}, R_2 = H
1.33b : R_1 = Ph, R_2 = H
1.33c : R_1 = 4-$MeOC_6H_4$, R_2 = H
1.33d : R_1 = 4-NCC_6H_4, R_2 = H
1.33e : R_1 = R_2 = Ph
1.33f : R_1 = R_2 = 4-MeC_6H_4
1.33g : R_1 = R_2 = 4-$MeOC_6H_4$

Scheme 1.18 Pt(0) and Pt(II) catalysed diboration of internal and terminal alkynes

These catalysts were more efficient in the stereoselective formation of *Z*-1,2-diborylated alkenes than [$Pt(PPh_3)_4$], with reactions proceeding smoothly using 3 mol% of either

catalyst at 80 °C. The rate and conversions were significantly affected by the choice of substituents on the alkyne and the diboron reagent. The presence of π-donating moieties on the alkyne resulted in faster reactions than π-withdrawing substituents and the fastest conversions proceeded in the order of B_2cat_2 > B_2pin_2 > $B_2(4\text{-}Bu^tcat)_2$.[85]

Norman and co-workers reported the platinum catalysed diboration of internal and terminal alkynes using the diboron 1,2-$B_2Cl_2(NMe_2)_2$, to afford cyclic 1-azonia-2-borata-5-boroles (**1.34**) (Scheme 1.19). The key feature within these structures was that the boron and nitrogen atoms exhibited both a three and four-coordinated centre. Although the mechanism for forming **1.34** was unclear, the authors proposed an initial diboration followed by a rearrangement of the B-Cl and B-NMe_2 bonds.[86]

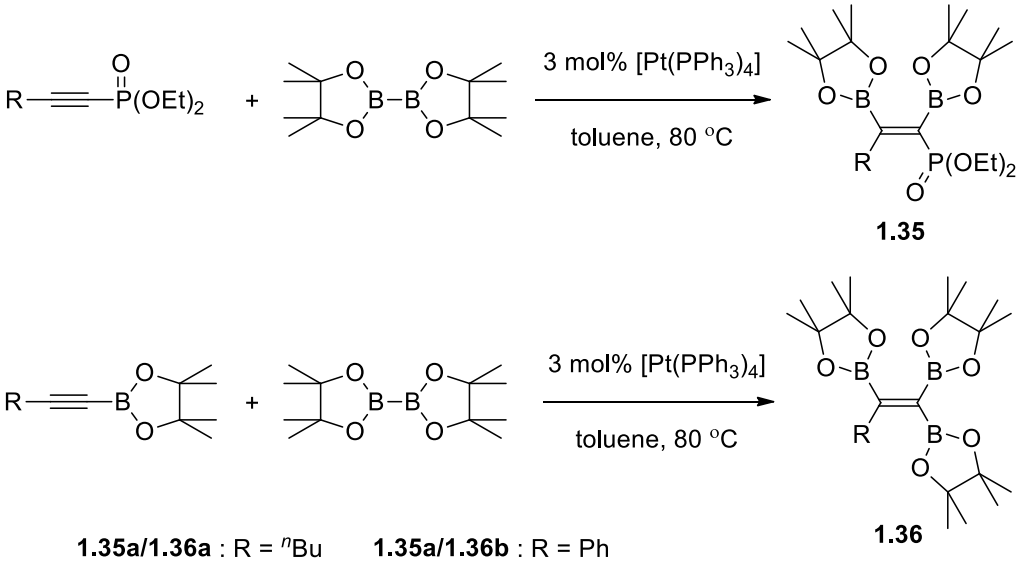


Scheme 1.19 Diboration-rearrangement of alkynes using 1,2-$B_2Cl_2(NMe_2)_2$

In 2000, Baker and co-workers developed a phosphine-free platinum catalysed diboration of 1-octyne and di-*p*-methylphenylacetylene using B_2cat_2.[87] The reactions proceeded using 5 mol% of the commercially available [$Cl_2Pt(cod)$] (cod = 1,5-cyclooctadiene) at 55 °C. This protocol was highly dependent on the choice of diboron source, with only B_2cat_2 accessible, as well as the choice of halide and diene on the platinum metal. [$Br_2Pt(cod)$] required pre-stirring for 24 h before a homogeneous catalytic mixture was obtained and even then, reaction yields were lower. The use of dicyclopentadiene instead

of cod as a ligand also resulted in the formation of the 1,2-diborylated alkenes in lower yields.

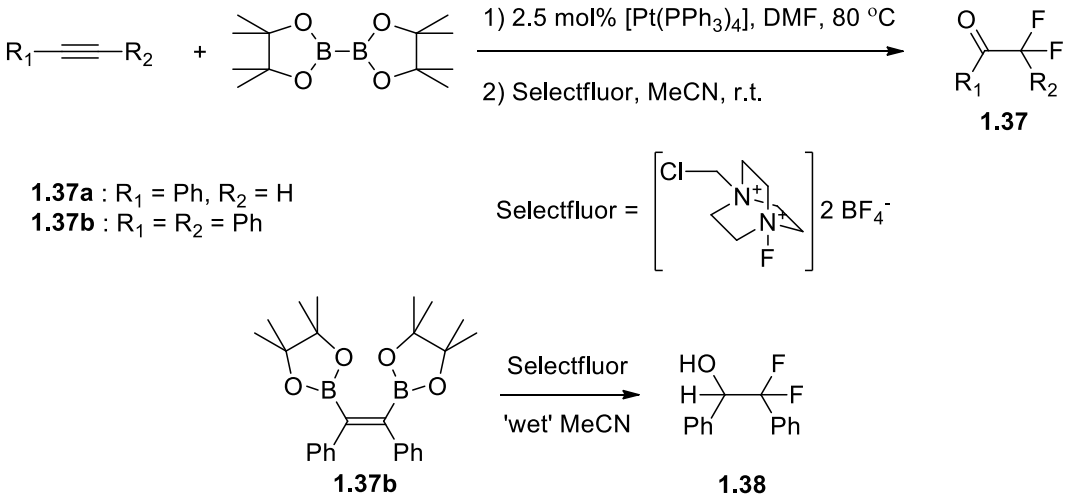
In a study into new routes for the preparation of 1,1-geminal sp^2-organo-bismetallic derivatives, Srebnik and co-workers demonstrated the platinum catalysed diboration of 1-alkynylphosphonates and 1-alkynylboronates furnished the *Z*-1,2-diborylated vinylphosphonates and trisboronated alkene products **1.35** and **1.36**, respectively (Scheme 1.20).[88] The reaction with alkynylboronates was extremely sensitive to the moisture content of the solvent with 'wet' solvents resulting in B-C bond cleavage *via* a hydrodeboronation. Elsewhere, Nishihara reported the platinum catalysed diboration of phenylethynyl MIDA (MIDA = *N*-methylimidiacetic acid) boronate with B_2pin_2 to form 1,1,2-triboryl-2-phenylethene.[89]



Scheme 1.20 Diboration of 1-alkynylphosphonates and 1-alkynylboronates

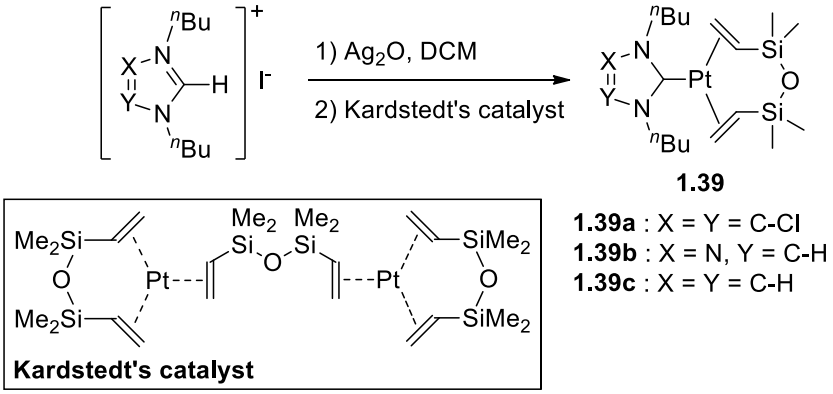
Fernandez and co-workers reported the preparation of *α,α*'-difluorinated carbonyl compounds. The reactions proceeded by an initial platinum(0) catalysed diboration of internal and terminal alkynes to form *Z*-1,2-diborylated alkenes. Subsequent work-up with the electrophilic fluoro-deboronation agent 1-(chloromethyl)-4-fluoro-1,4-

diazoniabicyclo[2.2.2]octane ditetrafluoroborate (or Selectfluor) resulted in formation of the α,α'-difluorinated carbonyl compounds **1.37** (Scheme 1.21) The stereochemistry of the diborylated alkene remained in the fluorinated carbonyls. If trace amounts of water were found within the solvent or reaction mixture the difluoromethyl alcohols **1.38** were isolated.[90] The authors later optimized this protocol to a one-pot diboration/fluoro-deboronation microwave procedure. This resulted in the shortening of reaction times to several minutes and the lowering of catalyst loadings to as little as 0.05 mol%.[91]



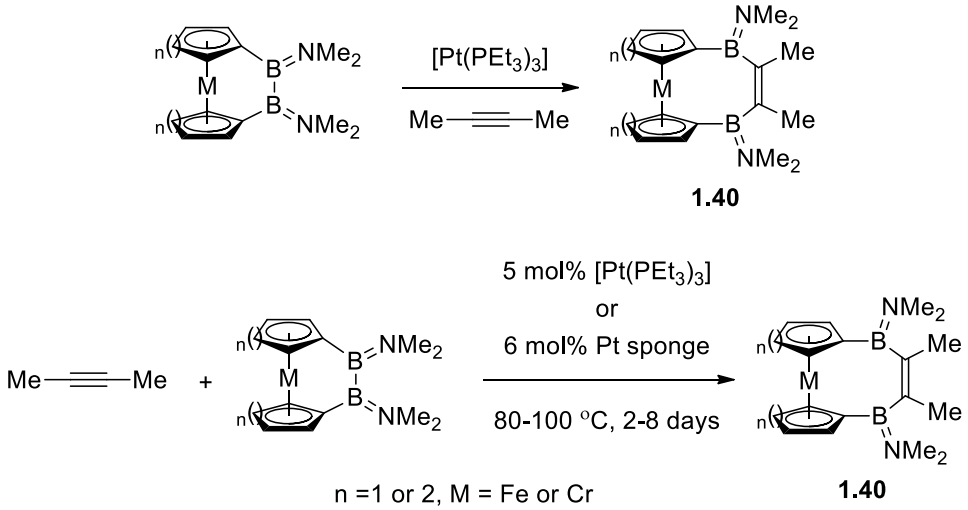
Scheme 1.21 Stepwise diboration/fluorodeboronation of alkynes

Fernandez and co-workers extended their investigations into the use of N-heterocyclic carbene (NHC) platinum complexes as catalysts. The platinum species **1.39** were formed by the transmetallation reaction between the corresponding NHC-silver compound and Karstedt's catalyst (Scheme 1.22). Initial assessment of **1.39** catalytic activity in the diboration of alkynes found that **1.39b**, with triazoylidene carbene, was the most active and suitable mediator for this reaction. A range of internal and terminal alkynes were then diborylated using B_2cat_2 and 5 mol% of **1.39b**.[92]



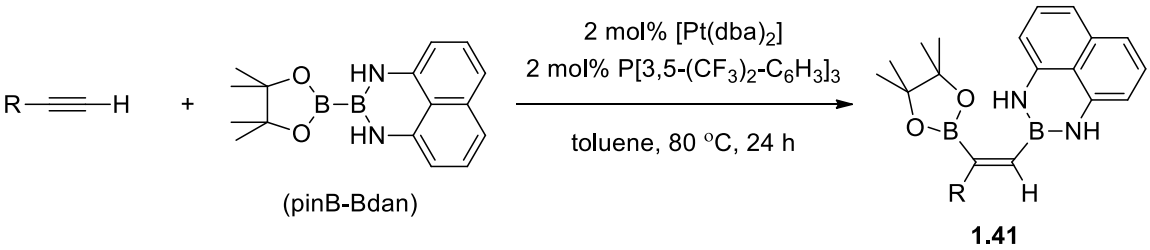
Scheme 1.22 Synthesis of NHC-platinum based complexes, catalysts in diboration of alkynes

Braunschweig and co-workers demonstrated that alkynes could insert into the B-B bond of [2]borametallarenophanes. These B-B bonds were deemed moderately strained, but thermally stable. The diboration was achieved stoichiometrically using [$Pt(PPh_3)_4$] and 10 equivalents of 2-butyne to yield the *ansa*-bis(boryl)alkenes **1.40** (Scheme 1.23).[93] The diboration was also completed catalytically under both homogeneous and heterogeneous conditions over several days.[94]



Scheme 1.23 Stoichiometric and catalytic diboration of alkynes using [2]borametallarenophanes

The selective, stepwise reactions of two non-equivalent boryl groups is highly desirable in the catalytic diboration of alkynes, as it may enable telescopic (sequential) couplings. Suginome and co-workers developed an unsymmetrical diboron, pinB-Bdan (pin = pinacolato; dan = naphthalene-1,8-diaminato) (Scheme 1.24).[95] In the presence of phosphine-platinum catalysts, the diboration of terminal alkynes resulted in the regioselective formation of **1.41** with -Bdan, a boryl protecting group, in the terminal position. The palladium-catalysed Suzuki-Miyaura cross-coupling occurred chemoselectively on the more reactive internal Bpin. This was in sharp contrast to the B_2pin_2 based diborations, where the coupling selectively proceeds initially at the more reactive terminal Bpin group.



1.41a : R = Ph
1.41b : R = 4-MeC_6H_4
1.41c : R = 2-MeC_6H_4
1.41d : R = 4-$MeOC_6H_4$
1.41e : R = 4-AcC_6H_4
1.41f : R = 4-$EtO_2CC_6H_4$
1.41g : R = 4-BrC_6H_4
1.41h : R = 2-BrC_6H_4
1.41i : R = 2-thiophenyl
1.41j : R = ^{n}Hexyl

Scheme 1.24 Diboration of alkynes using the diboron, pinB-Bdan

Escribano and co-workers showed that titania-supported platinum nanoparticles were efficient catalysts for the diboration of alkynes under solvent and ligand free conditions in air. Terminal and internal alkynes were accessible at 70 °C using 0.2 mol% of Pt/TiO_2. A range of electron-donating and withdrawing aromatic or alkyl, branched and cycloalkyl substituents were accessible. Exclusively *Z*-1,2-diborylated alkenes were observed in all

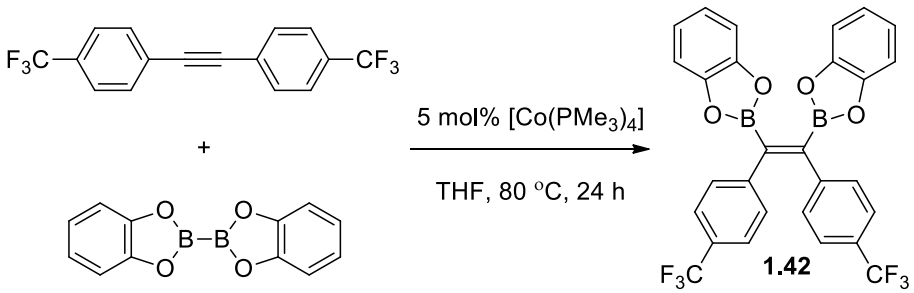
cases.[96] In contrast, when the support was magnesia (MgO), higher loadings and the use of solvent and elevated temperatures of 130 °C were required.[97]

Palladium

Palladium-catalysed diboration of alkynes are rare. The only examples use the [2]borametalloarenophanes reported in the homogeneous and heterogeneous platinum catalysed diboration of alkynes. The source of palladium catalyst was palladium on carbon and the reactions required higher temperatures and longer conversion times than their platinum analogues.[93,94] The rarity of palladium mediated alkyne diborations can be attributed to the energetics of the B-B bond oxidative addition at the Pd(0) centre. Theoretical calculations suggest that this is both a kinetically and thermodynamically unfavourable process.[98]

Cobalt

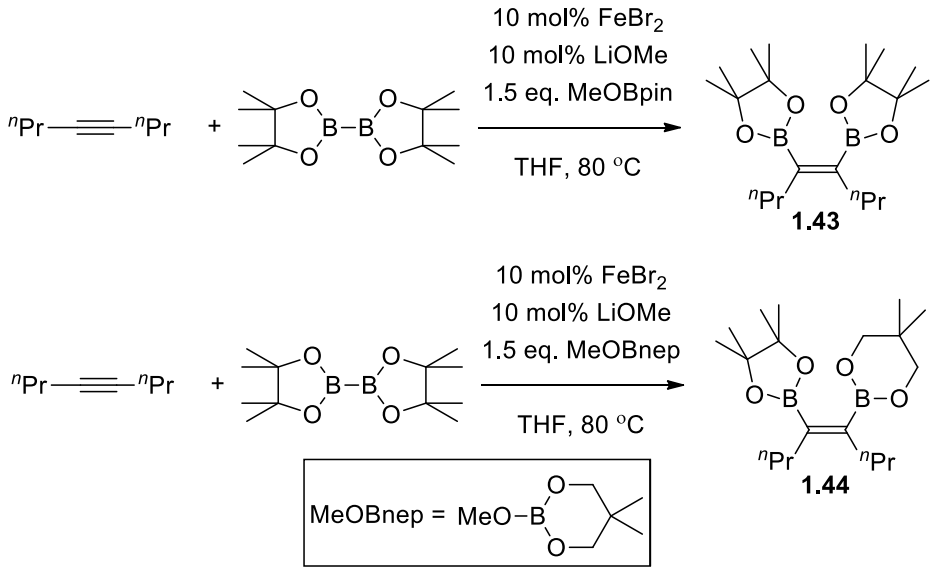
In their investigations into the diboration of alkynes, Marder and co-workers described the diboration of 1,2-bis(4-(trifluoromethyl)phenyl)ethyne with B_2cat_2 (Scheme 1.25) using a [$Co(PMe_3)_4$] catalyst. Compound **1.42** was isolated as the major product of this reaction with small quantities of the *E*-isomer detected.[99]



Scheme 1.25 Cobalt(0) catalysed diboration of an internal alkynes

Iron

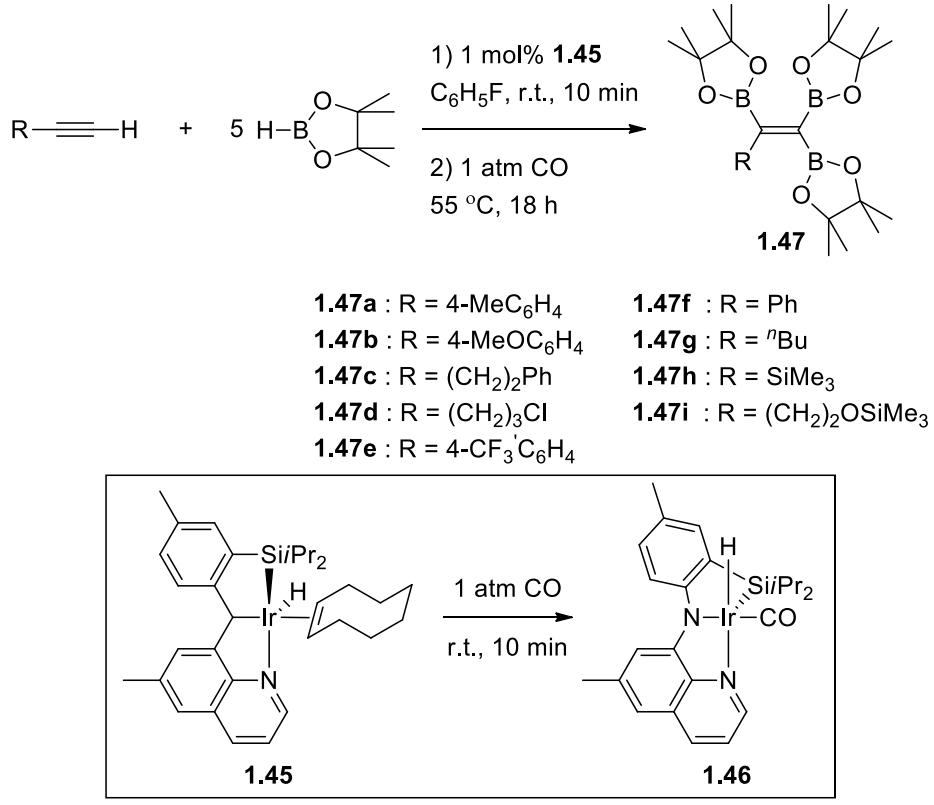
The only example of iron catalysed diboration of alkynes was detailed by Nakamura in 2015. Initial optimizations focused on the diboration of 4-octyne using B_2pin_2. The authors showed that catalytic quantities of $FeBr_2$ and LiOMe with 1.5 equivalents of MeOBpin were enough to afford **1.43** in high yields.[100] On extending to other Fe(II) and Fe(III) catalysts, yields dramatically decreased. The diboration of a variety of internal alkynes was possible; those with alkyl substituents proceeded in high yields, whereas aryl or bulky alkyl groups retarded the diboration. The role of the additional borating agent was also assessed. In the absence of MeOBpin the reactions still proceeded, but with lower conversions. When using MeOBnep (MeOBnep = 2-methoxy-5,5-dimethyl-1,3,2-dioxaborinane) the unsymmetrical diborylalkene **1.44** was isolated as the major product (Scheme 1.26). This suggested that the incorporation of the second boryl unit was introduced by an electrophilic substitution reaction with MeOBnep or MeOBpin.



Scheme 1.26 Iron(II) catalysed diboration of alkynes in a symmetric and unsymmetric manner

Iridium

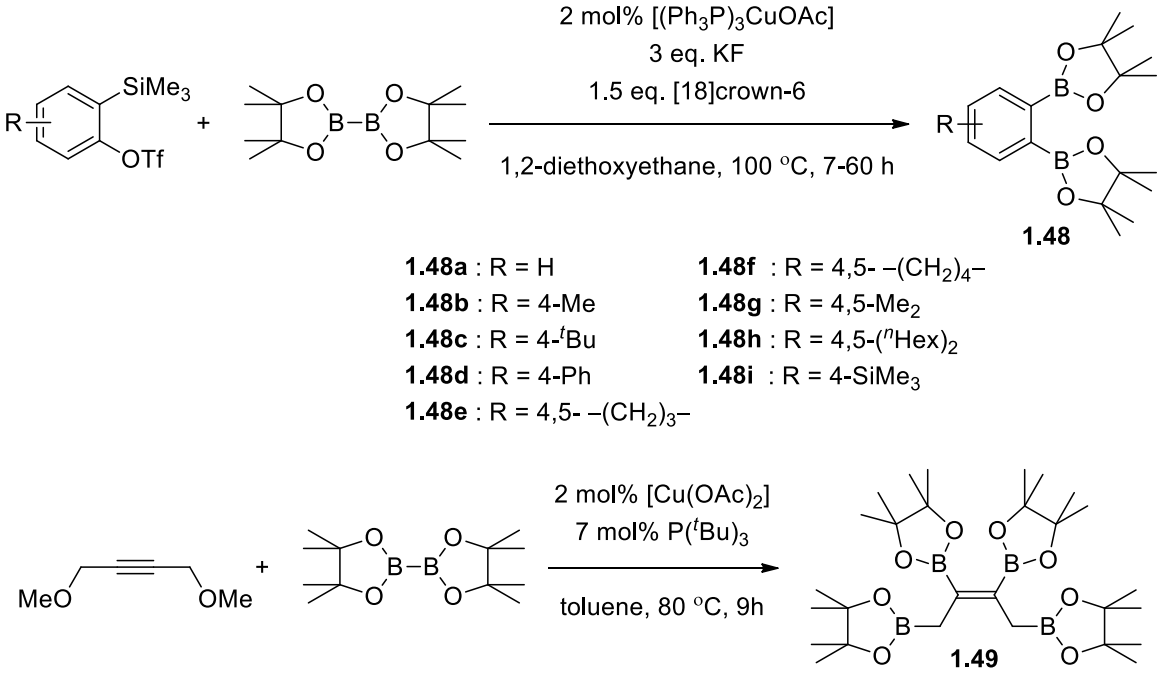
Ozerov and co-workers devised a two-step reaction to convert alkynes into trisborylalkenes. The first step transformed terminal alkynes into alkynylboronates using pinacolborane (HBpin) and iridium complex **1.45** as a catalyst. Degassing this reaction mixture followed by the introduction of a CO atmosphere generated the new catalyst **1.46**, which mediated the dehydrogenative diboration of the newly formed alkynylboronate with HBpin to form **1.47** (Scheme 1.27).[101] This reaction was extended to a range of alkyl and aryl terminal alkynes. The authors proposed the reaction to proceed *via* hydroboration intermediates or *via* B_2pin_2.



Scheme 1.27 Iridium catalysed dehydrogenative borylation/diboration of terminal alkynes

Copper

Examples of group 11 transition metal catalysed diboration of alkynes are rare, with only one example of copper and one of gold described in the literature.[102] The first diboration of alkynes employing a copper catalyst was performed by Yoshida. The diboration of alkyl and aryl internal alkynes using B_2pin_2 in the presence of [$Cu(OAc)_2$] and PCy_3 resulted in high yields of the corresponding *Z*-1,2-diborylated alkenes.[103] The authors also extended this to the diboration of benzynes to form the resulting 1,2-diborylated benzenes (**1.48**) (Scheme 1.28). Changing the phosphine to P(^{t}Bu)$_3$, P(^{n}Oc)$_3$ or PPh_3 resulted in either prolonged reaction times or lower yields. A striking feature of this copper catalysis was the diboration of propargyl ethers. In all cases the tetraborylated product **1.49** was exclusively isolated (Scheme 1.28).



Scheme 1.28 Copper-catalysed diboration of benzynes and tetraborylation of propargyl ethers

Gold

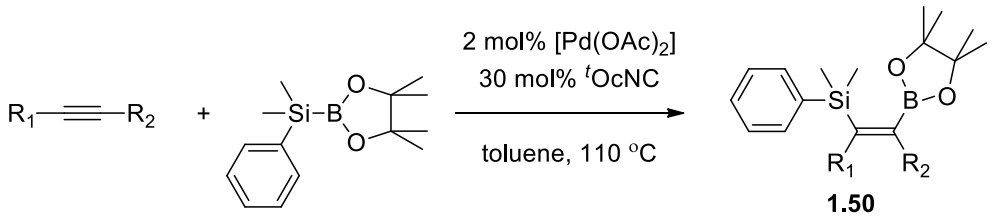
Jin and co-workers reported that nanopourous gold (AuNPore), prepared by dealloying the monolithic $Au_{30}Ag_{70}$ alloy in a 70% nitric acid electrolyte, was a highly active catalyst in the diboration of alkynes. The system was optimized using phenylacetylene and B_2pin_2 utilizing 2 mol% of AuNPore at 100 ^oC.[104] The AuNPore catalyst was recyclable with no notable decrease in catalytic activity over multiple cycles. The protocol was extended to a variety of terminal and internal alkynes, however, other diborons were ineffective. Mechanistically, the authors proposed absorption of the B_2pin_2 onto the AuNPore surface. The B-B bond is then cleaved at the low coordinate Au atoms to give an Au-Bpin species. The alkyne then adsorbs and reacts rapidly with two Au-Bpin species either through a simultaneous addition path to form the corresponding *Z*-adduct or in a stepwise manner.

1.2.3 Silicon-Boron (Si-B)

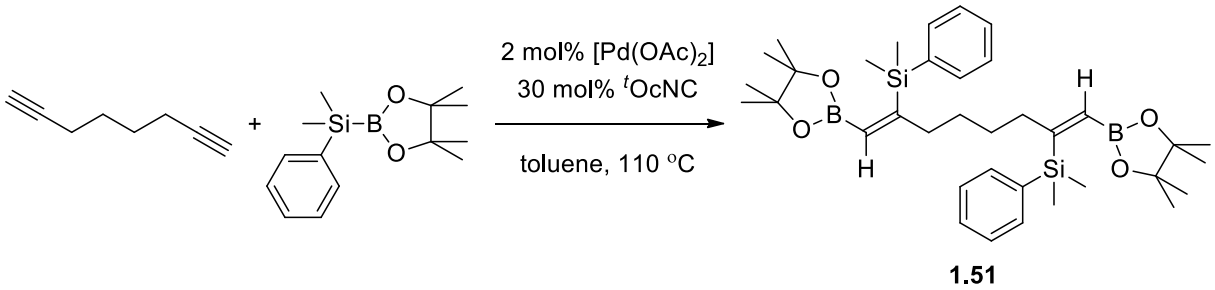
Palladium

Silaboranes are attractive precursors in the element-element additions to unsaturated substrates such as alkynes. According to the Pauling scale, the electronegativity difference between the Si (2.12) and B (1.88) atoms,[105] is such that 1-boryl-2-silyl alkenes are synthesised with chemo-, regio- and stereoselective control in a single transformation.[106,107] The boron and silicon functionalities in these alkene adducts can subsequently undergo chemoselective stepwise reactivity towards the preparation of more complex and unsymmetrical tri- and tetra substituted alkenes.[108,109] The most widely used catalysts for the silaboration of alkynes are group 10 transition metal complexes, specifically palladium-containing complexes.

One of the first Pd-mediated examples was reported by Ito and co-workers. The palladium/*tert*-alkyl isocyanide combination, previously detailed in alkyne bis(silyl)ations, was effective in the silaboration of both terminal and internal alkynes to form *syn*-1-boryl-2-silyl alkenes (**1.50**) with high regio- and stereoselectivities (Scheme 1.29).[110] The silaborane of choice was (dimethylphenylsilyl)boronic acid pinacol ester ($PhMe_2SiBpin$); this Si-B compound is thermally stable under inert conditions and the Bpin functionality improves the stability of the subsequent organo-compounds towards hydrolysis during purification. In the case of terminal alkynes, the silaboration proceeded with the addition of the boryl group at the terminal position. Silaboration attempts employing other metal complexes resulted in either lower yields and mixtures of regioisomers (*e.g.* $[Pt(PPh_3)_4]$) or no activity (*e.g.* $[RhCl(PPh_3)_3]$).



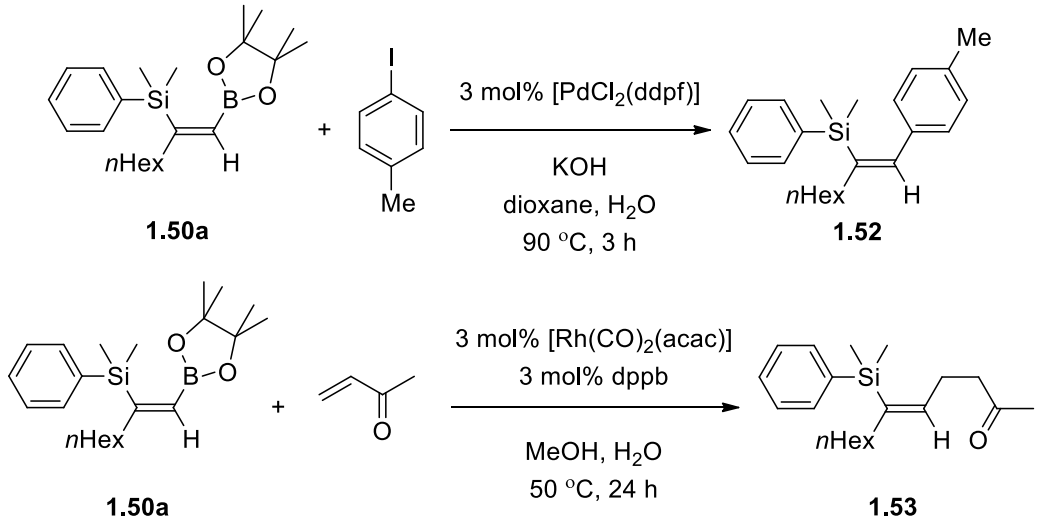
1.50a : R_1 = ^{n}Hex, R_2 = H
1.50b : R_1 = Ph, R_2 = H
1.50c : R_1 = THPO, R_2 = H
1.50d : R_1 = MEMO, R_2 = H
1.50e : R_1 = cyclohexyl, R_2 = H
1.50f : R_1 = R_2 = Ph
1.50h : R_1 = R_2 = ^{n}Bu



Scheme 1.29 Silaboration of alkynes employing a palladium/isocyanide catalyst

The authors later extended this protocol to other silaboranes (*i.e.* $PhMe_2SiB(NEt_2)_2$ and $PhMe_2SiBcat$) and to a larger array of terminal and internal alkynes, including 1,7-

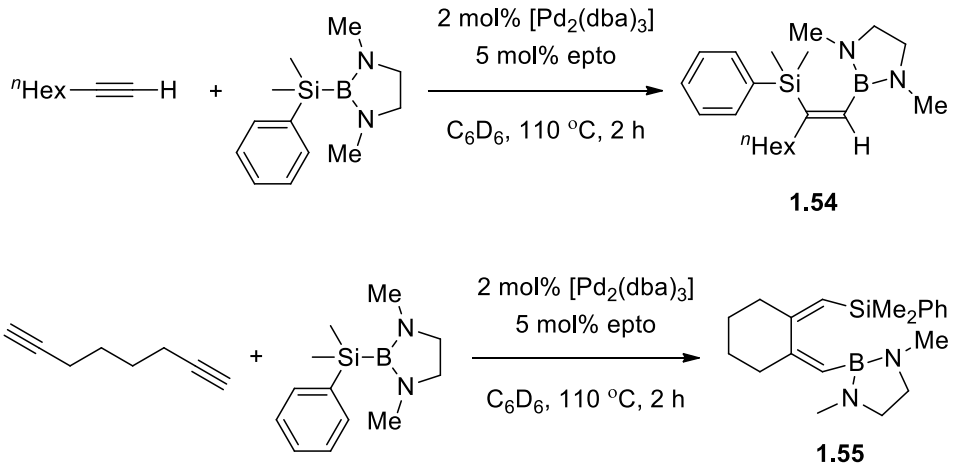
octadiyne to afford the double silaboration product **1.51** (Scheme 1.29). The reactivity of the *syn*-1-boryl-2-silyl alkenes was also assessed. It was observed that Suzuki-Miyaura cross-coupling and conjugate additions to methyl vinyl ketones at the alkenyl boryl group were possible, leading to **1.52** and **1.53**, respectively (Scheme 1.30).[111] Many authors have since utilized [$Pd(OAc)_2$]/isocyanide as a mediator in the silaboration of alkynes including in the synthesis of *syn*-homoallylic alcohols,[112] multi-arylated olefins,[113] and enamides.[114]



Scheme 1.30 Suzuki-Miyaura cross-coupling and conjugate additions at C-boryl group

Tanaka and co-workers described the silaboration of 1-octyne employing the silaborane, 1,3-dimethyl-2-dimethylphenysilyl-2-bora-1,3-diazacyclopentane. The corresponding *Z*-1-boryl-2-silyl alkene **1.54** was isolated by utilizing the pre-catalytic combination of [$Pd_2(dba)_3$] and epto (epto = 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane, $P(OCH_2)_3CEt$). Pre-heating of the pre-catalytic combination at 80 °C for 5 minutes was necessary in order to generate the active catalytic species, proposed to be [$Pd(epto)_2$]. As observed in Ito's report, the silaboration of terminal alkynes proceeded in a regioselective

manner with the boryl group inserting at the terminal position. Low to no yields were observed on applying other phosphorus containing ligands such as PMe_3 and PPh_3. The protocol was also expanded to the silaboryl carbocyclization of hepta-1,6-diyne to form **1.55** (Scheme 1.31).[115]

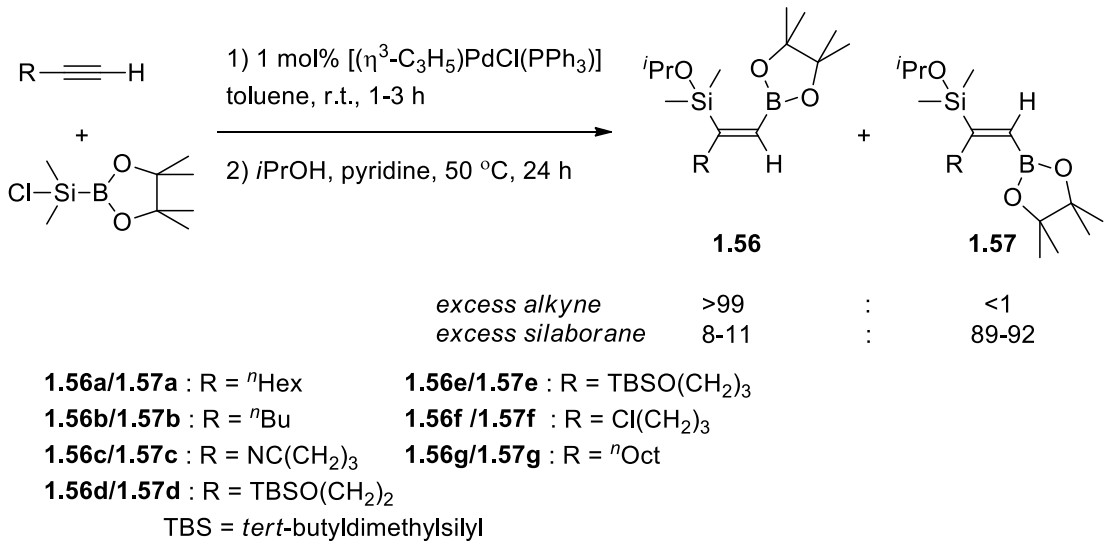


Scheme 1.31 Silaboration and silaboryl carbocyclization of terminal alkynes

Pilot and co-workers synthesized stable organosilylboranes possessing mesityl groups on the boryl atom, (diphenylmethylsilyl)dimesitylborane ($PhMe_2SiBMes_2$) and (diphenyl-*tert*-butylsilyl)dimesitylborane ($Ph_2{}^tBuSiBMes_2$). These silaboranes are not stabilized by electronegative groups on the boron atom *e.g.* oxygen or nitrogen, but instead through the steric bulk of the mesityl functionality. They were employed in the silaboration of terminal alkynes such as phenylacetylene, using the $[Pd_2(dba)_3]$/epto catalytic combination. Steric clashing between the substituents of the alkyne and the boryl moiety precluded the silaboration of internal alkynes.[116]

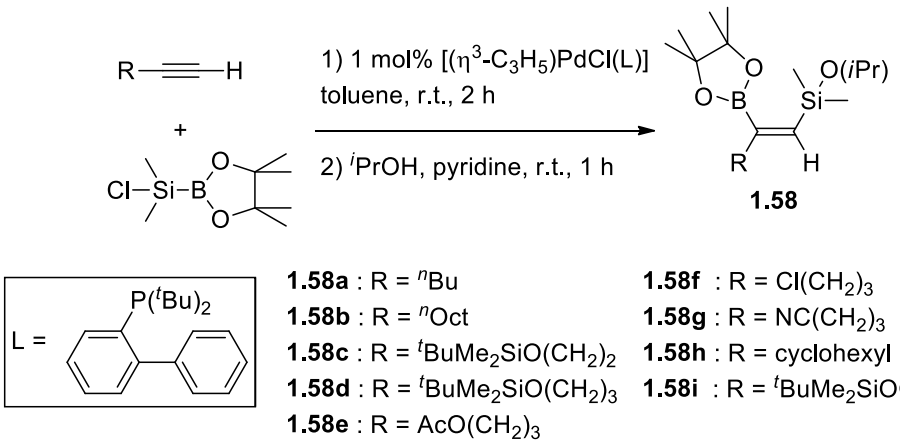
In their investigations into the silaboration of terminal alkynes, Suginome and co-workers showed that it was possible to tune the stereoselective preference of the reaction by altering the reagent stoichiometry. The reaction parameters were assessed on treating

(chlorodimethylsilyl)pinacolborane ($ClMe_2SiBpin$) with 1-octyne in the presence of 1 mol% [(η^3-C_3H_5)Pd(PPh_3)Cl], followed by subsequent addition of isopropyl alcohol (IPA) and pyridine. When excess 1-octyne was used the *Z*-isomer **1.56** was isolated as the sole product. However, excess $ClMe_2SiBpin$ results in the formation of the *E*-isomer **1.57** as the major product (Scheme 1.32). This observation was applicable to a range of terminal alkynes, although sterically hindered substituents on the alkyne restricted *E*-silaboration.[117]

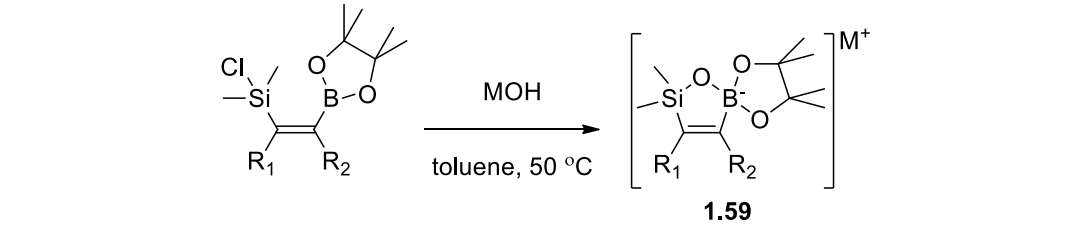


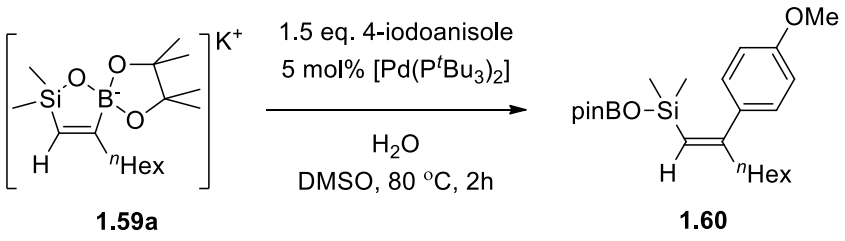
Scheme 1.32 Reagent dependent stereoselective silaboration of terminal alkynes

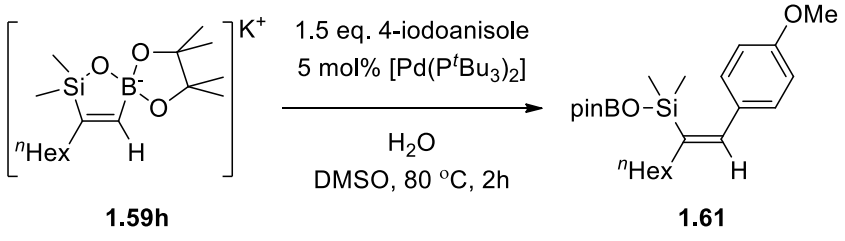
It was also possible to tune the regioselectivity in the silboration of terminal alkynes. The silaboration proceeds with 'normal' regioselectivity in the presence of catalytic quantities of [(η^3-C_3H_5)Pd(PPh_3)Cl]. However, using the more sterically hindered phosphine P(^{t}Bu)$_2$(biphenyl-2-yl) an inverse or 'abnormal' regioselectivity was observed, with *Z*-2-boryl-1-silyl-1-alkenes **1.58** isolated as the major product (Scheme 1.33).[118]



Scheme 1.33 Ligand-controlled stereoselective 'abnormal' regioselective silaboration



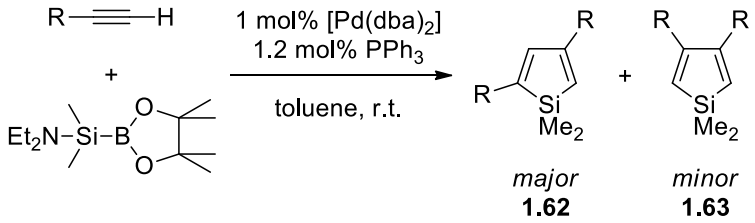




Scheme 1.34 Silylborate formation and resulting external-base free cross-coupling

Suginome and co-workers also hydrolysed the 'normal' and 'abnormal' silaborated alkenes with metal hydroxides MOH (M = Na or K) instead of the IPA/pyridine mixture. This resulted in the formation of a five-membered cyclic borate **1.59** *via* intramolecular attack of the resulting silanol oxygen with the tricoordinated boron atom. The potassium borates **1.59a** and **1.59h** were then subjected to external-base free Suzuki-Miyaura cross-coupling with 4-iodoanisole to form **1.60** and **1.61**, respectively (Scheme 1.34).[119]

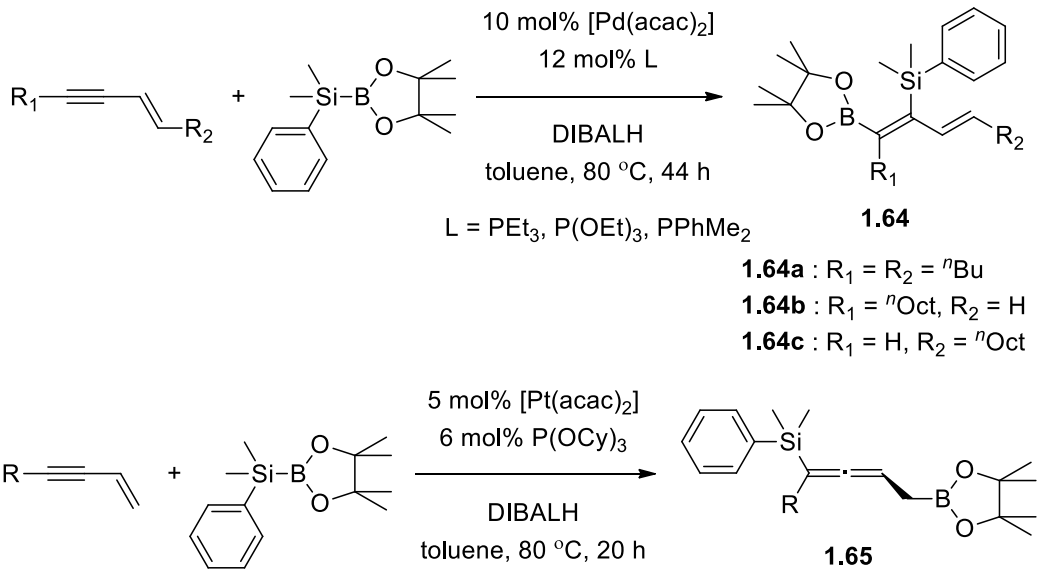
The authors achieved a different mode of reactivity by substituting one of the substituents of the silicon atom of a silaborane for an amino group. The reaction of $(Et_2N)Me_2SiBpin$ with aliphatic or aryl terminal alkynes resulted in the formation of 2,4- and 3,4-disubstituted siloles, **1.62** and **1.63** respectively (Scheme 1.35). Isomer **1.62** was favoured in most cases and this was attributed to steric clashing within intermediates in the catalytic cycle. Deviations in the electronic and steric properties of the alkyne substituents had little influence on the regioisomer formed. However, altering the phosphine ligand to the more sterically hindered $P(^tBu)_2$(2-biphenyl), resulted in a higher ratio of **1.62** *vs.* **1.63**. The synthesis of siloles was also accompanied by the formation of the corresponding aminopinacolborane, and was extended to other silaboranes including $(Me_2N)Me_2SiBpin$ and (pyrrolidino)$Me_2SiBpin$.[120]



1.62a/1.63a : R = Ph
1.62b/1.63b : R = 4-MeC_6H_4
1.62c/1.63c : R = 4-$MeOC_6H_4$
1.62d/1.63d : R = 4-$Me_2NC_6H_4$
1.62e/1.63e : R = 4-$CF_3C_6H_4$
1.62f /1.63f : R = 2-MeC_6H_4
1.62g/1.63g : R = 2,4,6-$Me_3C_6H_2$
1.62h/1.63h : R = 1-naphthyl

Scheme 1.35 Regioselective synthesis of disubstituted siloles

Moberg and co-workers subjected a number of 1,3-enynes to palladium catalysed silaboration using $PhMe_2SiBpin$. The reactions required relatively high loadings of palladium and phosphine ligand, as well as stoichiometric quantities of diisobutylaluminium hydride (DIBALH). 1,2-Silaboration led to dienes **1.64** in all cases. Alternatively, changing the transition metal catalyst to a platinum analogue and the 1,3-enynes substituent to a sterically hindering functionality resulted in 1,4-silaboration and isolation of the corresponding allene **1.65** (Scheme 1.36).[121]

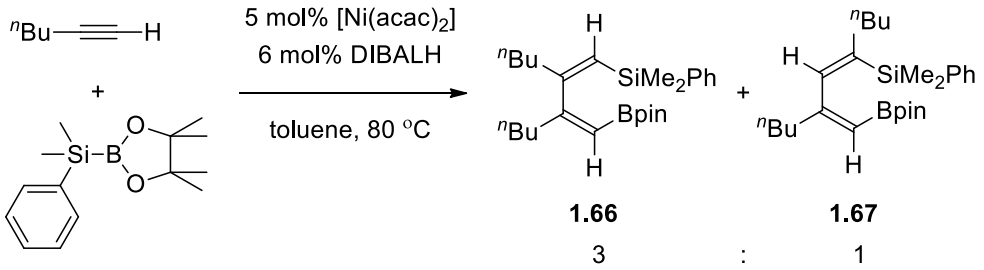


Scheme 1.36 Substrate controlled silaborations of 1,3-enynes

Nickel

Ito reported the double insertion of terminal alkynes into the Si-B bond of $PhMe_2SiBpin$ to afford *Z,Z*-1-silyl-4-boryl-1,3-butadiene derivatives in a regio- and stereoselective manner. The reactions proceeded using catalytic quantities of $[Ni(acac)_2]$ and the reductant DIBALH to afford a 3:1 mixture of **1.66** and **1.67** (Scheme 1.37). The major product **1.66** was a result of head-to-head dimerization of the alkyne, whereas head-to-tail dimerization gave **1.67**. Dimerization yields were increased by using a large excess

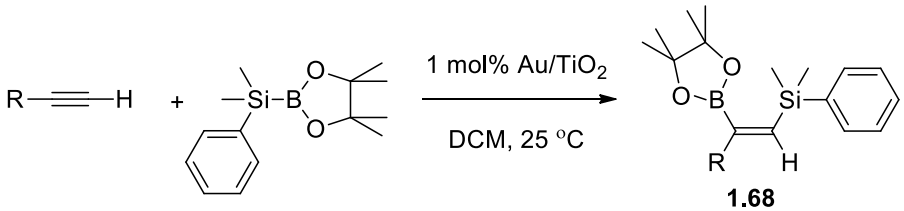
of alkyne and were retarded by the introduction of a phosphine. This protocol was also extended to internal alkynes with the exception of diphenylacetylene, which was inert under the reaction conditions. The application to diynes resulted in intramolecular cyclization and the formation of the dimethylenecyclohexane derivatives.[122]



Scheme 1.37 Silaborative dimerization of alkynes

Gold

The only other metal mediated alkyne silaboration in the literature utilized gold nanoparticles supported on titania (Au/TiO_2). Stratakis and co-workers used 1 mol% Au/TiO_2 to catalyse the silaboration of terminal alkynes at room temperature to form *syn*-2-boryl-1-silyl-1-alkenes **1.68** (Scheme 1.38). These alkenes were formed with opposite or 'abnormal' regioselectivities with respect to the analogous palladium examples, which was attributed to the steric factors imposed by the Au nanoparticles during the 1,2-addition of the silaborane to the alkynes. Side products in this reaction were the 'normal' regioselective silaborated alkenes, the bis(silyl)ated alkenes and B_2pin_2. The presence of bis(silyl)ated alkene and B_2pin_2 was explained by separately stirring $PhMe_2SiBpin$ under the catalytic conditions in the absence of alkyne. The authors observed the formation of $PhMe_2SiSiMe_2Ph$ and B_2pin_2 as a result of metal-catalysed silaborane metathesis, a competing reaction in this silaboration protocol. Extension to internal alkynes resulted in mixtures of regioisomers or no yield at all.[123]



1.68a : R = cyclopropyl
1.68b : R = cyclohexyl
1.68c : R = cyclohex-1-enyl
1.68d : R = $PhOCH_2$
1.68e : R = $4\text{-}MeOC_6H_4OC(Me)_2$
1.68f : R = tBuPh$_2$SiOCH$_2$
1.68g : R = $AcO(CH_2)_4$
1.68h : R = C(O)OEt
1.68i : R = $4\text{-}MeC_6H_4$
1.68j : R = $2\text{-}MeOC_6H_4$
1.68k : R = $4\text{-}F_3CC_6H_4$

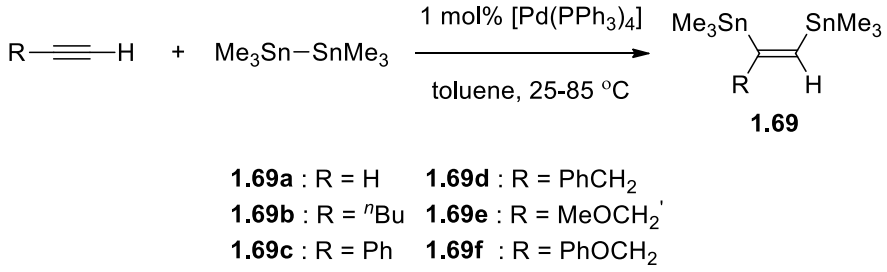
Scheme 1.38 Gold catalysed 'abnormal' silaboration of terminal alkynes

1.2.4 Tin-Tin (Sn-Sn)

Palladium

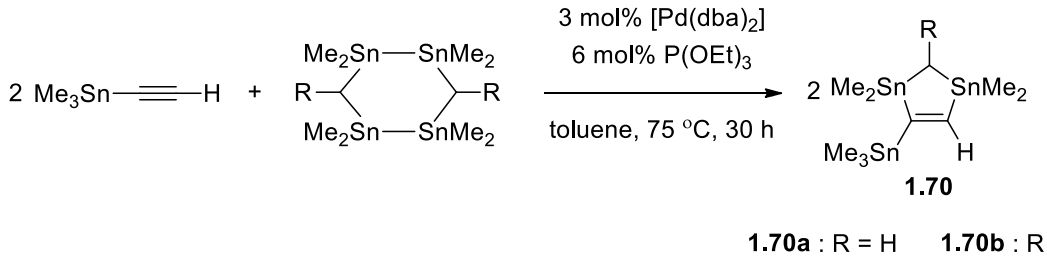
Organostannanes are often utilized in the chemoselective formation of C-C bonds through Migita-Kosugi-Stille reactions.[124] The development of new methodologies in the construction of C-Sn bonds is therefore of high interest. A particularly attractive example is the insertion of alkynes into Sn-Sn bonds, distannation. The resulting alkenes have two new C-Sn bonds and are frequently formed with high stereoselectivities. Low-valent palladium complexes are regularly used to catalyse the distannation of alkynes.

Some of the first investigations into distannation of alkynes were carried out by Mitchell and co-workers. Hexamethyldistannane ($Me_3SnSnMe_3$) and terminal alkynes were mixed in the presence of catalytic quantities of [$Pd(PPh_3)_4$] to form *Z*-1,2-distannyl alkenes **1.69** (Scheme 1.39). Aryl, alkyl and propargyl ether substituents were tolerated. Distannation of acetylene at elevated temperatures initially led to the *Z*-isomer, which quickly isomerized to the thermally stable *E*-isomer. The *Z* to *E* isomerization was also observed in the absence of catalyst under photolysing conditions.[125]



Scheme 1.39 The first palladium catalysed distannation of terminal alkynes

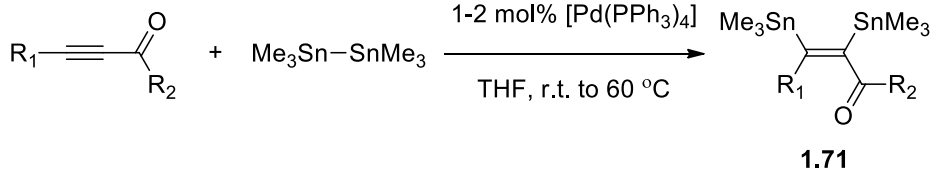
Mitchell later expanded this protocol to a wider variety of terminal alkynes including functionalities such as alcohols, amides, esters and silyl groups. The Sn-Sn bond precursor was also extended to other hexaalkyldistannes (hexaethyl and hexabutyl ditin),[126] and to 1,2,4,5-tetrastannacyclohexanes.[127] The latter were further employed in the distannation of trimethylstannylethyne to synthesise the first 1,1,2-trisstannylalkene derivatives **1.70** (Scheme 1.40).[128]



Scheme 1.40 Distannation of trimethylstannylethyne

Piers and co-workers reported the distannation of alkyl-2-alkynyloates using $Me_3SnSnMe_3$ and a $[Pd(PPh_3)_4]$ catalyst in THF at room temperature (or reflux) to form *Z*-2,3-bis(trimethylstannyl)-2-alkenoates **1.71** (Scheme 1.41). A vast array of functionality was tolerated including alkenyls, ethers, silyl ethers and primary halides.[129] Alkenoates with an ω-halogeno-alkyl group were treated with MeLi which resulted in a

transmetallation-cyclization reaction to afford 2-trimethylstannylcycloalk-1-enes **1.72** (Scheme 1.42).[130] The distannation protocol was also extended to *N*,*N*-dimethyl-2-alkynylamides and the formation of *Z*-*N*,*N*-dimethyl-2,3-bis(trimethylstannyl)-2-alkenamide **1.71q**. Compounds **1.71** were thermally labile and transformed upon heating or at room temperature to the thermodynamically stable *E*-isomers.[129]

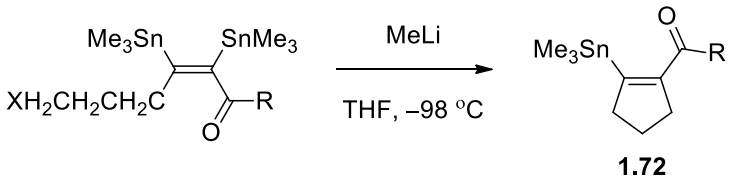


1.71

1.71a : R_1 = Me, R_2 = OEt
1.71b : R_1 = Et, R_2 = OMe
1.71c : R_1 = ^{i}Pr, R_2 = OMe
1.71d : R_1 = cyclopropyl, R_2 = OMe
1.71e : R_1 = $H_2C{=}CH(CH_2)_2$, R_2 = OMe
1.71f : R_1 = $THPO(CH_2)_3$, R_2 = OMe
1.71g : R_1 = $^{t}BuMe_2SiOCH_2$, R_2 = OMe
1.71h : R_1 = $Cl(CH_2)_2$, R_2 = OEt
1.71i : R_1 = $Br(CH_2)_2$, R_2 = OEt
THP = tetrahydropyranyl

1.71j : R_1 = $Cl(CH_2)_3$, R_2 = OMe
1.71k : R_1 = $Br(CH_2)_3$, R_2 = OMe
1.71l : R_1 = $I(CH_2)_3$, R_2 = OMe
1.71m : R_1 = $Br(CH_2)_4$', R_2 = OMe
1.71n : R_1 = $Br(CH_2)_5$, R_2 = OMe
1.71o : R_1 = $I(CH_2)_5$, R_2 = OMe
1.71p : R_1 = $H_2C{=}C(Br)(CH_2)_4$, R_2 = OMe
1.71q : R_1 = Me, R_2 NMe_2

Scheme 1.41 Distannation of alkynyloates and alkynylamides



1.72

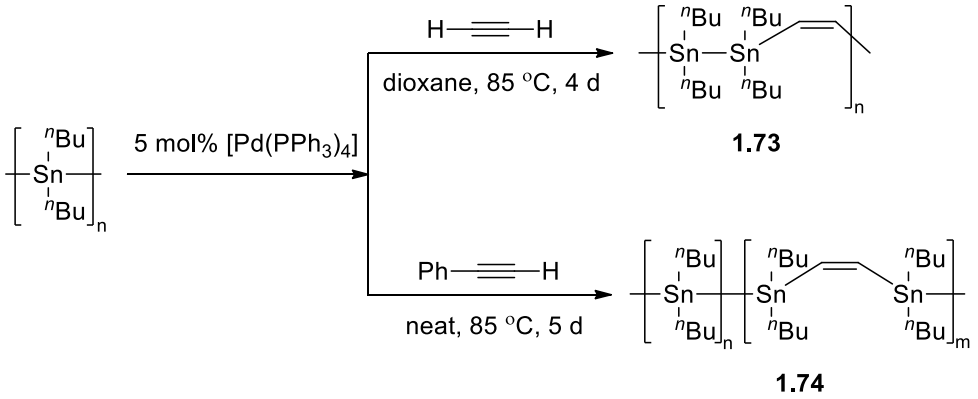
1.72a : X = Cl, R = OMe
1.72b : X = Br, R = NMe_2

Scheme 1.42 Transmetallation-cyclization of distannylated *ω*-halogeno-alkenoates

The weakness of the C-Sn bond meant that it was possible to use vinyltins in electrophilic substitution reactions. Mitchell and co-workers detailed the reactivity potential of the *Z*-1,2-bis(trimethylstannyl)-1-alkenes with the electrophiles *p*-tolylsulphonylisocyanate

(TSI), dichloromethylmethylether (DCME), trimethylsilyl chlorosulphonates and sulphur oxides.[131]

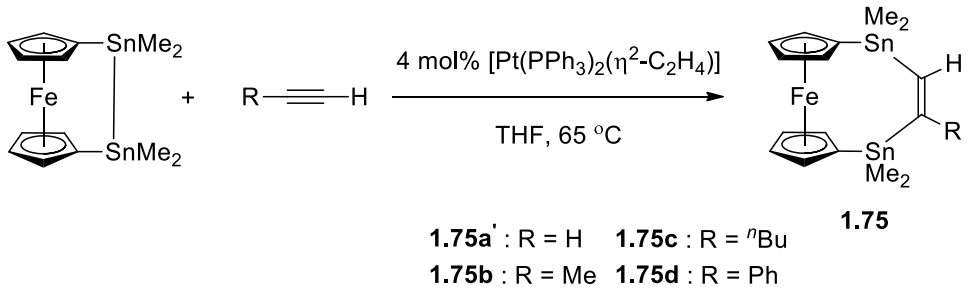
Recently, Foucher and co-workers detailed the insertion of acetylene and phenylacetylene into the backbone of poly[di(*n*butyl)]stannane. This resulted in the formation of alkene-tin polymers **1.73** and **1.74**, respectively (Scheme 1.43).[132]



Scheme 1.43 Distannation employing the backbone of poly[di(*n*butyl)]stannane

Platinum

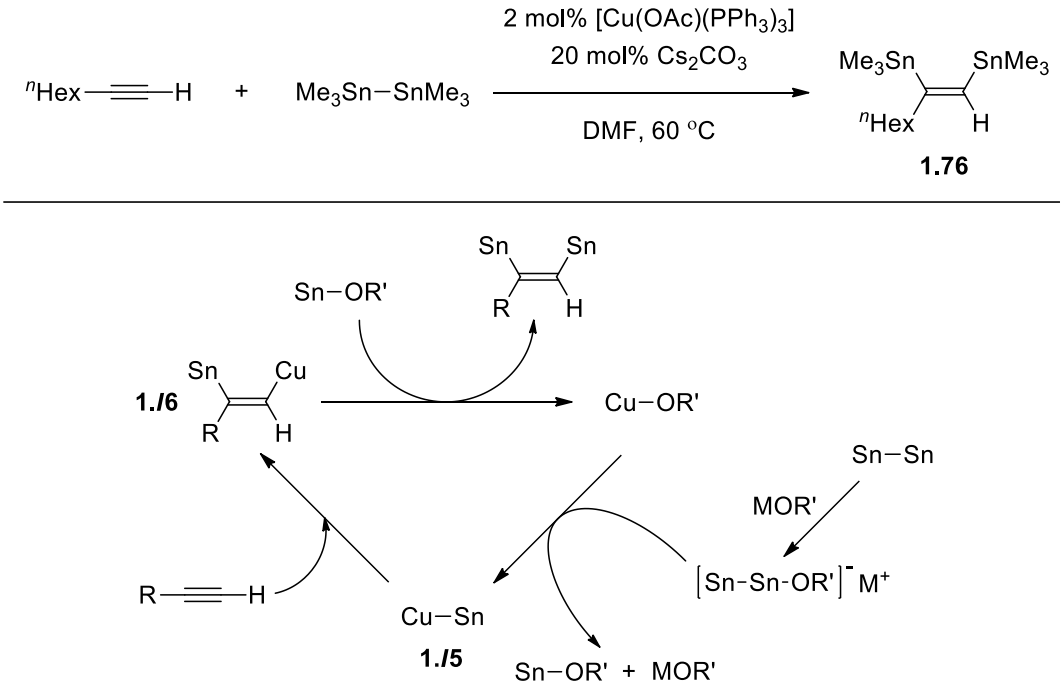
The only examples of distannation of alkynes employing a platinum catalyst were reported by Wrackmeyer and co-workers. The distannane, 1,2-distanna-[2]ferrocenophane reacted sequentially or in one pot with $[Pt(PPh_3)_2(\eta^2\text{-}C_2H_4)]$ and a range of terminal alkynes to form the corresponding 1,4-distanna-[4]ferroceophanes **1.75** (Scheme 1.44).[133] Both terminal and internal alkynes were accessible. However, dimethyl acetylenedicarboxylate gave the distannation product in a side reaction while favouring cyclotrimerization to form hexamethylbenzene hexacarboxylate. Extension to analogous palladium catalysts such as $[Pd(PPh_3)_4]$ and $[Pd(dba)_2]$ was unsuccessful.[134]



Scheme 1.44 1,2-Distanna-[2]ferrocenophane distannation of terminal alkynes

Copper

In 2013, Yoshida carried out the first catalytic distannation of alkynes using a copper catalyst. $[Cu(OAc)(PPh_3)_3]$ in the presence of Cs_2CO_3 was used to optimize the reaction between $Me_3SnSnMe_3$ and 1-octyne affording **1.76**. The authors then managed to distannylate 1-hexyne, 1-decyne and branched aliphatic terminal alkynes bearing isoamyl, isobutyl and cyclopentyl, as well as chloro, amino and cyano functionalities. Alkynes that were sterically congested resulted in sluggish reactions and low yields. It was proposed that the reaction proceeded through a Cu-Sn bonded intermediate **1.*I*5** derived from a CuOR' complex and a base-activated distannane. Subsequent addition of **1.*I*5** to a C-C triple bond afford β-stannylalkenyl copper species **1.*I*6**, which is then recaptured with Me_3SnOR' to give the 1,2-distannylated alkene with regeneration of the CuOR' complex (Scheme 1.45).[135]



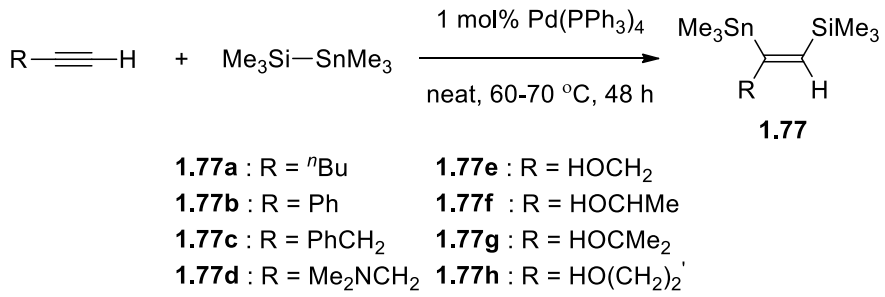
Scheme 1.45 Copper catalysed distannation of 1-octyne and proposed mechanism

1.2.5 Tin-Silicon (Sn-Si)

Palladium

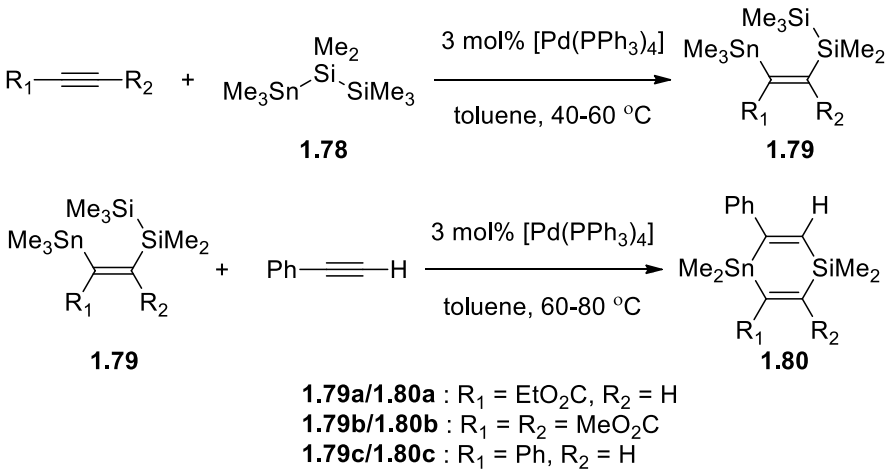
Sn-Si bond (silylstannation) addition to alkynes results in the formation of alkenes with a new C-Sn and C-Si bond, often in a regio- and stereoselective manner. Palladium catalysed silylstannation of alkynes are by far the most reported examples within the literature and have found application in the synthesis of natural products,[136,137] and pharmaceuticals.[138]

The first palladium catalysed examples of alkyne silylstannations were shown by Mitchell and co-workers. In this report the authors reacted a range of terminal alkynes with (trimethylsilyl)trimethylstannane ($Me_3SiSnMe_3$) in the presence of [$Pd(PPh_3)_4$] under solvent-free conditions to yield the corresponding *Z*-1-silyl-2-stannyl-1-alkenes (**1.77**) (Scheme 1.46). In all cases the silyl moiety added regioselectively at the terminal carbon.[139]



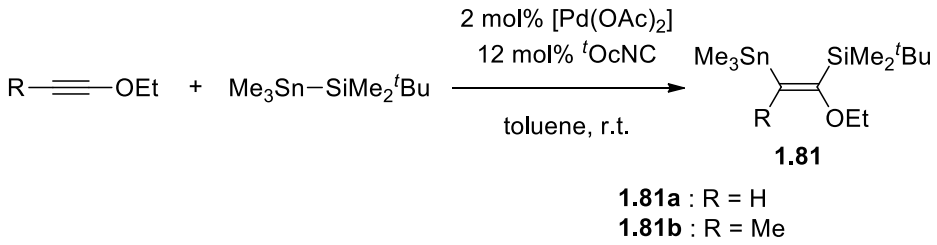
Scheme 1.46 Palladium(0)-catalysed silylstannation of terminal alkynes

Ito extended the use of [$Pd(PPh_3)_4$] as a catalyst in the reaction of the disilanylstannane **1.78** with alkynes affording the (β-disilanylalkenyl)stannanes **1.79**. The reaction proceeded with the *Z*-addition of the Si-Sn bond to the C-C triple bond. **1.79**, in the presence of phenylacetylene and further quantities of [$Pd(PPh_3)_4$], then underwent regioselective cyclization to form the silastannacyclohexadiene **1.80** as a single isomer (Scheme 1.47). [140]



Scheme 1.47 Palladium(0)-catalysed silylstannation followed by regioselective cyclization

Ito later accomplished the silylstannation of 1-alkoxyalkynes employing the combination of [$Pd(OAc)_2$]/*tert*-octylisocyanide. The reactions proceeded at room temperature and yielded the *syn*-addition products **1.81**, with the silyl group regioselectively introduced at the carbon atom bearing the alkoxy moiety (Scheme 1.48).



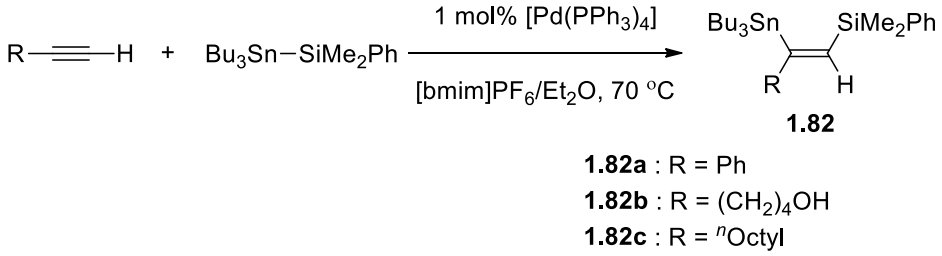
Scheme 1.48 Silylstannation of 1-alkoxyalkynes

[$Pd(PPh_3)_4$] was inactive in these transformations at both room and elevated temperatures.[141] The resulting alkene adducts were then exposed to a range of reactions including Stille cross-couplings, iodination at the C-Sn bond and the formation of acylsilanes.

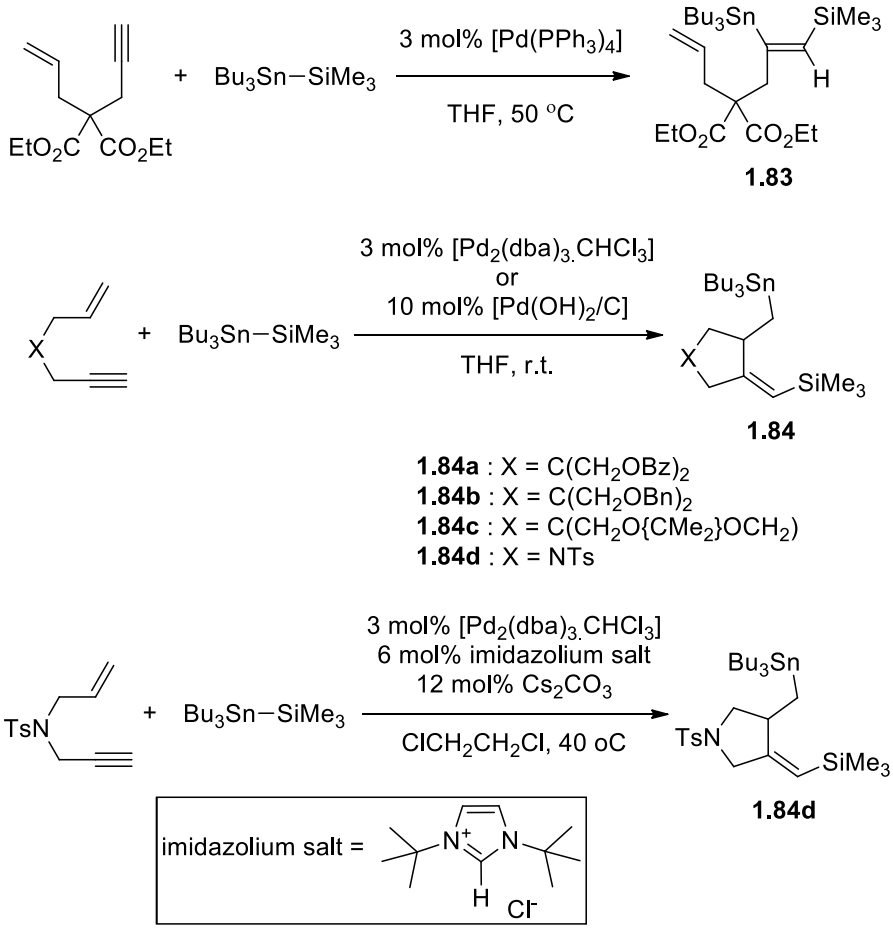
Singer reported the silylstannation of terminal alkynes with $Bu_3SnSiMe_2Ph$ using catalytic quantities of [$Pd(PPh_3)_4$] immobilised in the ionic liquid 1-^{n}butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]). High stereo- and regioselectivies were observed and simple ether extraction resulted in isolation of the *Z*-1-silyl-2-stannyl-1-alkenes **1.82** (Scheme 1.49).[142] The palladium(0)-ionic liquid combination was recyclable with no loss of activity even after 10 cycles.[143]

Mori and co-workers reported that the bismetallative cyclization of 1,3-enynes, using $Bu_3SnSiMe_3$, was dependent on the choice of ligand and palladium source. The use of [$Pd(PPh_3)_4$] results in 'normal' silylstannation of the alkyne affording **1.83**. However, upon removing the phosphine and using [$Pd_2(dba)_3{\cdot}CHCl_3$] or [$Pd(OH)_2$/C], cyclized compounds **1.84** were isolated as the major products of the reaction (Scheme 1.50). The

bismetallative cyclization can also be observed on employing nucleophilic N-heterocyclic carbenes with bulky alkyl N-substituents. [144]

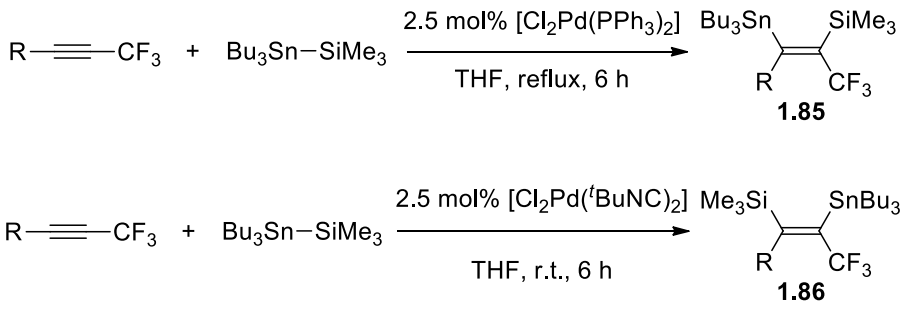


Scheme 1.49 Alkyne silylstannation using ionic liquid immobilised palladium(0)



Scheme 1.50 Silylstannation and bismetallitive cyclization of 1,3-enynes

Konno reported that it was possible to tune the regioselectivity of alkyne silylstannation by changing the ligand of a palladium(II) catalyst. Treatment of fluorine-containing internal alkynes with $Bu_3SnSiMe_3$ in the presence of 2.5 mol% $[Cl_2Pd(PPh_3)_2]$ yielded the silylstannylated adducts **1.85**. However, by switching the palladium catalyst to $[Cl_2Pd(^tBuNC)_2]$, the opposite regioselectivities **1.86** were observed (Scheme 1.51).[145]



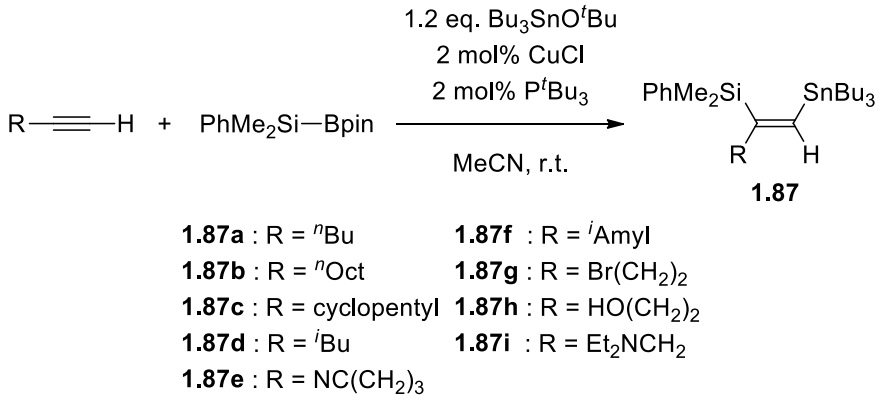
1.85a/1.86a : R = 4-MeOPh
1.85b/1.86b : R = 3-MeOPh
1.85c/1.86c : R = 2-MeOPh
1.85d/1.86d : R = 4-ClPh
1.85e/1.86e : R = 4-EtO_2CPh
1.85f /1.86f : R = CO_2Et
1.85g/1.86g : R = $P(O)(OEt)_2$
1.85h/1.86h : R = CH(OH)(4-ClPh)
1.85i /1.86i : R = CH(OH)(CH=CHPh)
1.85j /1.86j : R = CH(OH)($\{CH_2\}_5CH_3$)

Scheme 1.51 Palladium catalyst-dependent regioselective silylstannation

Copper

The only example of a copper catalysed alkyne silylstannation was reported by Yoshida and co-workers. The authors detailed a three-component coupling reaction employing terminal alkynes, a silylborane ($PhMe_2SiBpin$) and a tin alkoxide ($^nBu_3SnO^tBu$) in the presence of a Cu(I) catalyst ([CuCl-P^tBu_3]). The observed regioselectivities were inverse to those of conventional silylstannation under palladium catalysed conditions, with the stannyl moiety predominantly adding to the terminal carbon as shown in **1.87**. A range of alkyl branched and unbranched alkynes bearing cyano, bromo, hydroxyl or amino functionalities were accessible (Scheme 1.52). The authors proposed a similar mechanism to the distannation of alkynes mediated by a copper(I) catalyst. A silylcopper species,

$CuSiMe_2Ph$, is initially formed *via* a sigma-bond metathesis between a copper alkoxide and a silylborane. An alkyne would then insert into the Cu-Si bond to give a β-silylalkenylcopper intermediate, which is subsequently trapped by a tin alkoxide to furnish the silylstannation alkene adduct and the regenerated copper alkoxide.[146]

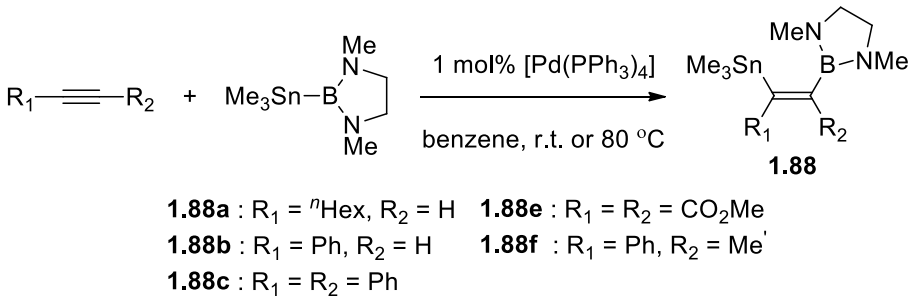


Scheme 1.52 Cu(I) catalysed 'abnormal' silylstannation of terminal alkynes

1.2.6 Tin-Boron (Sn-B)

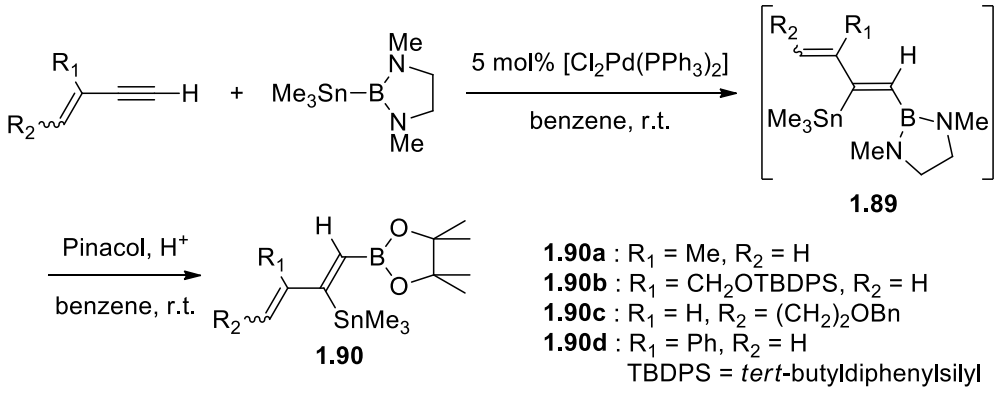
Palladium

The borylstannation of alkynes results in the formation of alkenes with a new C-Sn and C-B bond. The first palladium catalysed example was shown by Tanaka and co-workers in 1996. The borylstannane 1,3-dimethyl-2-(trimethylstannyl)-2-bora-1,3-diazacyclopentane ($Me_3SnB[NMe\{CH_2CH_2\}NMe]$) was added to alkynes using catalytic quantities of $[Pd(PPh_3)_4]$ (Scheme 1.53). The reagents were added together in benzene at 0 °C and then warmed to room temperature. Terminal alkynes yielded *syn*-1-boryl-2-stannyl-1-alkenes **1.88** as the sole product. Internal alkynes were also accessible, although a higher temperature (80 °C) was necessary.[147] Weber later extended this protocol to the more sterically hindered borylstannane, 1,3-di-tert-butyl-2-(trimethylstannyl)-2-bora-1,3-diazacyclopentane ($Me_3SnB[N^tBu\{CH_2CH_2\}N^tBu]$).[148]



Scheme 1.53 Palladium(0)-catalysed borylstannation of alkynes

RajanBabu developed Tanaka's methodology and extended it to the borylstannation of 1,3-enynes. This protocol resulted in the isolation of the *syn*-1-boryl-2-stannyl-1-alkenes (**1.89**) in chemo-, regio- and stereoselective fashions with no complications arising due to the adjacent alkene. However, the boryl group in **1.89** was hydrolytically unstable. *In situ* treatment with pinacol and *p*-toluenesulfonic acid (PTSA) yielded the hydrolytically stable **1.90** (Scheme 1.54)[149]



Scheme 1.54 Borylstannation of 1,3-enyles followed by boryl alcoholysis

Copper

Yoshida detailed the copper(II)-catalysed borylstannation of alkynes. A three-component coupling reaction employed an alkyne, a diboron (B_2pin_2) and a tin alkoxide (^{n}BuSnOMe) with the aid of a copper(II)acetate/tricyclohexylphosphine combination. A range of

internal and terminal alkynes were accessible. Internal alkynes with one aryl and one alkyl substituent resulted in perfect regioselectivities with the boryl moiety geminal to the alkyl group. In the case of terminal alkynes, the boryl group added to the terminal carbon.[150] All reactions proceeded at room temperature with catalyst loadings as low as 1 mol%. The authors proposed that these reactions proceeded through a similar mechanism to that of the silylstannation.[146]

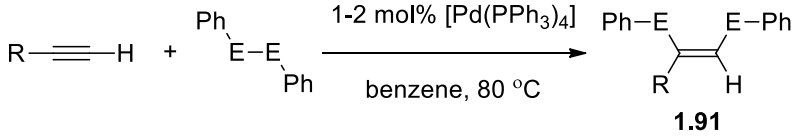
1.2.7 Sulphur-Sulphur and Selenium-Selenium (S-S and Se-Se)

Palladium

Organochalcogens are known to exhibit a range of pharmacological activity profiles including as potential anticancer,[151] anti-inflammatory,[152] and antibacterial agents.[153] The introduction of chalcogens into alkynes to form 1,2-bis(chalcogen)alkenes is challenging. The formation of 1,2-bis(chalcogen)alkenes often requires the use of heavy metals, high temperatures, and results in a mixture of stereoisomers. Such methods include the reaction vinyldichlorides with thiolate anions,[154] and radical reactivity between chalcogen species and alkynes.[155] The transition metal catalysed addition of dichalcogens to alkynes is a possible alternative to synthesizing 1,2-bis(chalcogen)alkenes in a stereoselective and atom economical manner.

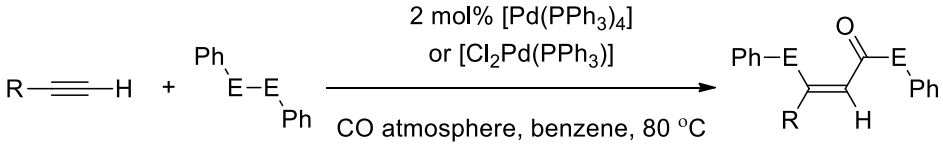
Sonoda reported the first palladium mediated addition of diaryl disulphides and diselenides to terminal alkynes to yield the corresponding *Z*-1,2-bis(arylthio) and *Z*-1,2-bis(arylseleno)-1-alkenes (**1.91**), respectively (Scheme 1.55). This protocol tolerated functionalities such as hydroxyl, trimethylsilyl and amino groups. The inclusion of a carbon monoxide (CO) atmosphere in these reactions lead instead to the isolation of the carbonylative addition adducts *Z*-1,3-bis(arylchalcogen)-2-alken-1-ones (**1.92**) (Scheme 1.55). A stepwise attempt at carbonylation of **1.91** with CO to yield **1.92** resulted in

isolation of only **1.91**, suggesting that CO insertion was part of dichalcogen additions in the first instance. [156]



1.91

1.91a : R = $(CH_2)_2CH(CH_3)_2$, E = S/Se
1.91b : R = $C(CH_3)_2OH$, E = S/Se
1.91c : R = $CH(CH_3)OH$, E = S
1.91d : R = CH_2OH, E = S
1.91e : R = $(CH_2)_2OH$, E = S/Se
1.91f : R = $SiMe_3$, E = S/Se
1.91g : R = CH_2NMe_2, E = S/Se
1.91h : R = Ph, E = S
1.91i : R = CH_2Br, E = Se



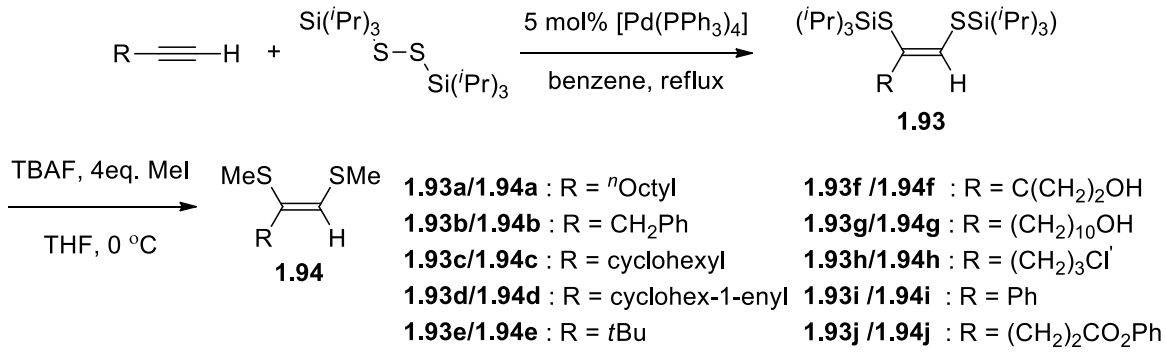
1.92

1.92a : R = ^{n}Hex, E = S
1.92b : R = $(CH_2)_2CH(CH_3)_2$, E = Se
1.92c : R = Ph, E = S/Se
1.92d : R = $(CH_2)_3OH$, E = Se

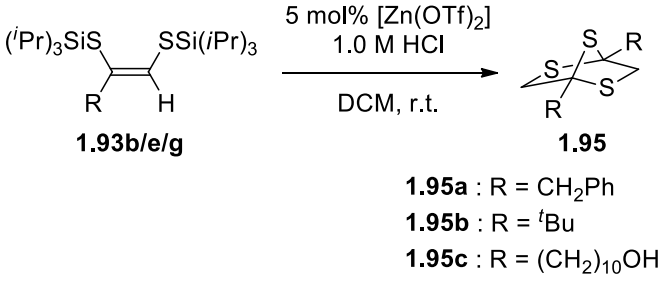
Scheme 1.55 Dichalcogen and carbonylative dichalcogen additions to alkynes

Gareau and co-workers established a procedure that effectively introduced 'dialkyl'-disulphides in the dithiolation of alkynes. Upon protecting the disulphide with a bulky silyl group, the dithiolation of terminal alkynes with bis(triisopropylsilyl)disulphide resulted in the isolation of the corresponding *Z*-1,2-bis(thio)alkenes (**1.93**). Subsequent treatment with tetra-^{n}butylammonium fluoride (TBAF) in the presence of excess methyl iodide (MeI) deprotected/alkylated the sulphur atoms affording **1.94** (Scheme 1.56).[157] Additionally, Gareau investigated the reactivity of **1.93** towards other electrophiles including halides, epoxides and acyl chlorides.[158] Furthermore, treatment of **1.93** with HCl in the presence of a Lewis acid ([Zn{OTf}$_2$]) yielded the bicyclic adducts 2,5,7-trithiabicyclo[2.2.1]heptane (**1.95**, Scheme 1.57).[159]

Beletskaya and co-workers reported an alternative methodology in the addition of S-S and Se-Se bonds to alkynes. Diphenyl disulphide (Ph_2S_2) and diphenyl diselenide



Scheme 1.56 Synthesis of *Z*-1,2-bis(methylthio)alkenes *via* silyl-protected dichalcogens



Scheme 1.57 Reactivity of **1.93** with acid/Lewis acid combination forming 2,5,7-trithiabicyclo[2.2.1]heptane adducts

(Ph_2Se_2) were reacted with a variety of terminal alkynes in the presence of catalytic quantities of [Cl_2Pd (PPh_3)$_2$], PhEH (E = S or Se) and triethylamine (NEt_3) to yield *Z*-1,2-bis(arylthio) and *Z*-1,2-bis(arylseleno)-1-alkenes. Both PhEH and NEt_3 were essential for the success of the reaction. The yields increased on the addition of excess PPh_3, which contradicts the general trend observed for other E-E additions to alkynes within the literature.[160] It was later shown that excess PPh_3 prevented the rapid polymerization to [$Pd(EAr)_2$]$_n$ and therefore the inhibition of the palladium catalyst.[161]

Beletskaya also reported the dithiolation of terminal alkynes utilizing a Pd(0) catalyst supported by a triphenylphosphine resin under conventional,[162] and microwave heating conditions.[163] Simple filtration resulted in the isolation of the *Z*-1,2-bis(thio)-1-alkenes.

This approach was not applicable to diaryl diselenides. Other palladium(0) supported mediators for the dithiolation of terminal alkynes include the MCM-41-supported bidentate phosphine Pd(0) catalyst reported by Cai. [164]

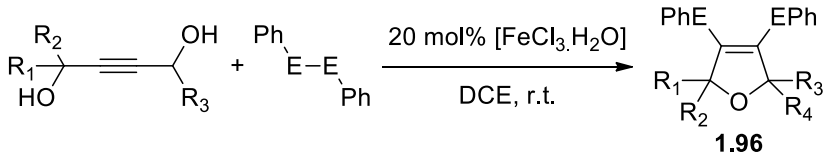
Iron

Zeni described the addition of diorganyl diselenides and disulphides to terminal alkynes in the presence of an iron(III) chloride ($FeCl_3$) catalyst. The best results were observed using diaryl diselenides bearing neutral electron-donating and withdrawing groups. The electronic nature of the terminal alkyne substituent did not have an effect on the rate or yield of the reaction.[165] Iron catalysed addition to 1,4-butyn-diols, pentyne-1,5-diol and 4-amino butynol afforded 3,4-bis(organochalcogen)-2,5-dihydrofurans (**1.96**), 4,5-bis(organochalcogen)-3,6-dihydro-2H-pyrans (**1.97**) and 2,5-dihydro 1H-pyrrole derivatives (**1.98**), respectively, under mild aerobic conditions (Scheme 1.58).[166] 1,3-Diynes in the presence of dibutyl diselenide or dimethyldisulfide and stoichiometric quantities of $FeCl_3$ yielded symmetrical and unsymmetrical 3,4-bis(butylselanyl)chalcogenophanes (**1.99**). In the synthesis of the selenophanes **1.99**, the cyclization was stereoselective providing exclusively the desired *E*-selenoenynes as intermediates. The selenophanes then formed *via* an intramolecular 5-*endo*-dig cyclization.[167]

Copper

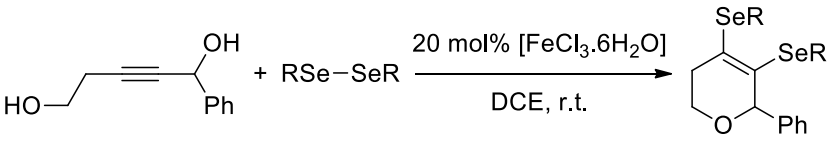
The addition of the catalytic mixture of CuI, zinc dust and glycerol resulted in the stereoselective addition of diaryl dichlcogenides to form a variety of *E*-1,2-bis-chalcogen alkenes (**1.100**) (Scheme 1.59). Zinc and glycerol were essential to the reaction; Zn

reduced Cu(I) to Cu(0) while glycerol acted as a solvent, but also as a possible reducing agent for the reduction of Zn(II) to Zn(0).[168]



1.96

1.96a : $R_1 = R_2 = R_3 = H$, R_4 = Ph, E = Se/S
1.96b : $R_1 = R_2 = R_3 = H$, R_4 = 4-MeC_6H_5, E = Se/S
1.96c : $R_1 = R_2 = R_3 = H$, R_4 = 4-ClC_6H_5, E = Se/S
1.96d : $R_1 = R_2 = R_3 = H$, R_4 = 2-naphthyl, E = Se
1.96e : $R_1 = R_2$ = Me, R_3 = Ph, $R_4 = H$, E = Se
1.96f : $R_1 = R_2 = R_3$ = Me, R_4 = Ph, E = Se
1.96g : $R_1 = R_2 = R_3 = R_4$ = Me, E = Se

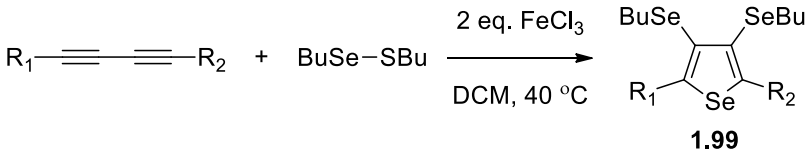


1.97

1.97a : R = Ph **1.97c** : R = 4-FC_6H_5
1.97b : R = 4-MeC_6H_5 **1.97d** : R = ^{n}Bu

1.98

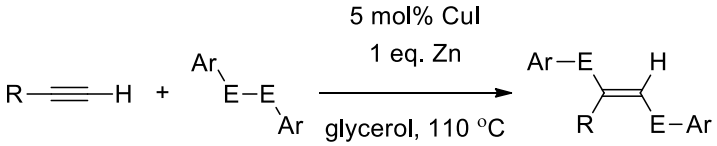
1.98a : R = Ph **1.98c** : R = 4-FC_6H_5
1.98b : R = 4-MeC_6H_5 **1.98d** : R = ^{n}Bu



1.99

1.99a : $R_1 = R_2$ = Ph
1.99b : $R_1 = R_2$ = 4-MeC_6H_5
1.99c : $R_1 = R_2$ = 4-$MeOC_6H_5$
1.99d : $R_1 = R_2$ = 4-ClC_6H_5
1.99e : $R_1 = R_2$ = 4-FC_6H_5
1.99f : $R_1 = R_2$ = 2-MeC_6H_5
1.99g : $R_1 = R_2$ = 1-naphthyl
1.99h : $R_1 = R_2$ = 2-naphthyl
1.99i : $R_1 = R_2 = {}^n$Bu
1.99j : $R_1 = {}^n$Bu, R_2 = Ph
1.99k : $R_1 = {}^n$Bu, R_2 = 4-MeC_6H_5
1.99l : $R_1 = {}^n$Bu, R_2 = 4-ClC_6H_5
1.99m : R_1 = Ph, R_2 = 4-MeC_6H_5
1.99n : R_1 = Ph, R_2 = 2-MeC_6H_5

Scheme 1.58 Synthesis of bis(organochalcogen)-dihydrofurans, dihydro-*2H*-pyrans, dihydro *1H*-pyrroles and selenophanes



1.100a : R = Ph, Ar = Ph, E = S/Se
1.100b : R = Ph, Ar = 2-MeC_6H_5, E = Se
1.100c : R = Ph, Ar = 2,4,6-$Me_3C_6H_2$, E = Se
1.100d : R = 4-MeC_6H_5, Ar = Ph, E = Se
1.100e : R = 4-ClC_6H_5, Ar = Ph, E = Se

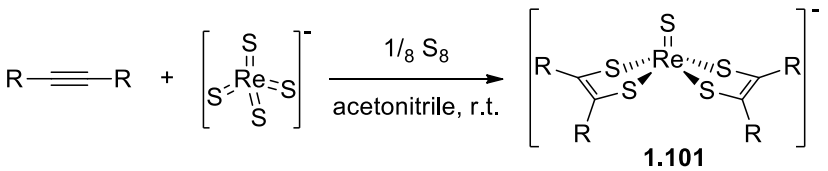
Scheme 1.59 Copper catalysed *E*-dithiolation and diselenation of terminal alkynes

Nickel

The only examples of nickel-catalysed diaryldisulphide addition to alkynes were developed by Beletskaya and co-workers. The use of 3 mol% [$Ni(acac)_2$] and 30 mol% $PMePh_2$ at 100 °C under solvent-free conditions resulted in the stereoselective dithiolation of both internal and terminal alkynes to form *Z*-dithiolated alkene products. The reaction temperature was important: too low meant incomplete reactivity and too high led to a mixture of stereoisomers.[169]

Rhenium

The stoichiometric reaction between the tetrathiometallate anion $[ReS_4]^-$ and diphenylacetylene, 2-butyne and bis(trimethylsilyl)acetylene in the presence of elemental sulphur yielded the dithiolation adducts **1.101** (Scheme 1.60).[170]

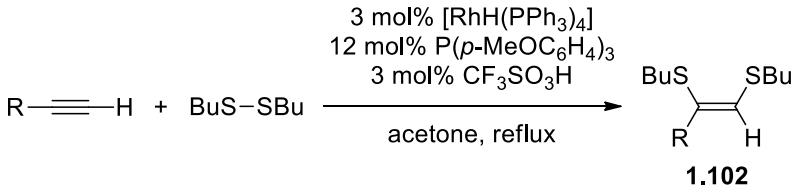


1.101a : R = Ph **1.101c** : R = CO_2Me
1.101b : R = Me

Scheme 1.60 Rhenium mediated stoichiometric dithiolation of internal alkynes

Rhodium

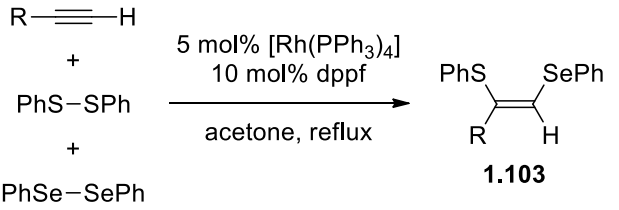
Yamaguchi and co-workers showed that it was possible to dithiolate terminal alkynes using the dialkyl disulphide, Bu_2S_2, employing catalytic quantities of a Rh-phosphine complex, tris(*p*-methoxyphenyl)phosphine and trifluoromethane sulfonic acid affording the corresponding *Z*-bis(alkylthio)alkenes (**1.102**) (Scheme 1.61). A range of functionality at the terminal alkyne substituent was accessible including hydroxyl, *tert*-butyldimethylsiloxy and nitrile. However, internal alkynes were not accessible with this protocol.[171]



1.102a : R = ^{n}Hex
1.102b : R = cyclohexyl
1.102c : R = $(CH_2)_2OH$
1.102d : R = $(CH_2)_2OSiMe_2{}^{t}Bu$
1.102e : R = $(CH_2)_3CN$
1.102f : R = CH_2Ph
1.102g : R = Ph
1.102h : R = $SiMe_3$

Scheme 1.61 Rhodium(I) catalysed dithiolation of terminal alkynes

Yamaguchi and co-workers extended their studies to the addition of disulphides and diselenides to alkynes in cross-over experiments. A 1:1 mixture of diaryl disulphides and diaryl diselenides were reacted with terminal alkynes using the same Rh-complex and 1,1'-bis(diphenylphosphino)ferrocene (dppf). This resulted in the formation of *Z*-1-arylseleno-2-(arylthio)-1-alkenes (**1.103**) as the major product (Scheme 1.62). The amounts of minor products *Z*-2-arylseleno-1-(arylthio)-1-alkene, *Z*-1,2-bis(arylthio)alkene and *Z*-1,2-bis(arylseleno)alkene were insubstantial. However, the minor product ratio became significant upon removal of trifluorosulfonic acid or when increasing the steric hindrance surrounding the alkynes.[172]



1.103

1.103a : R = ^{n}Hex
1.103b : R = $(CH_2)_2Ph$
1.103c : R = ^{t}Bu
1.103d : R = $(CH_2)_2OH$
1.103e : R = $(CH_2)_2OAc$
1.103f : R = $(CH_2)_2OSiMe_2{}^{t}Bu$

Scheme 1.62 Cross-over addition of diphenyldisulphide/diselenide to terminal alkynes

1.2.8 Sulphur-Silicon (S-Si)

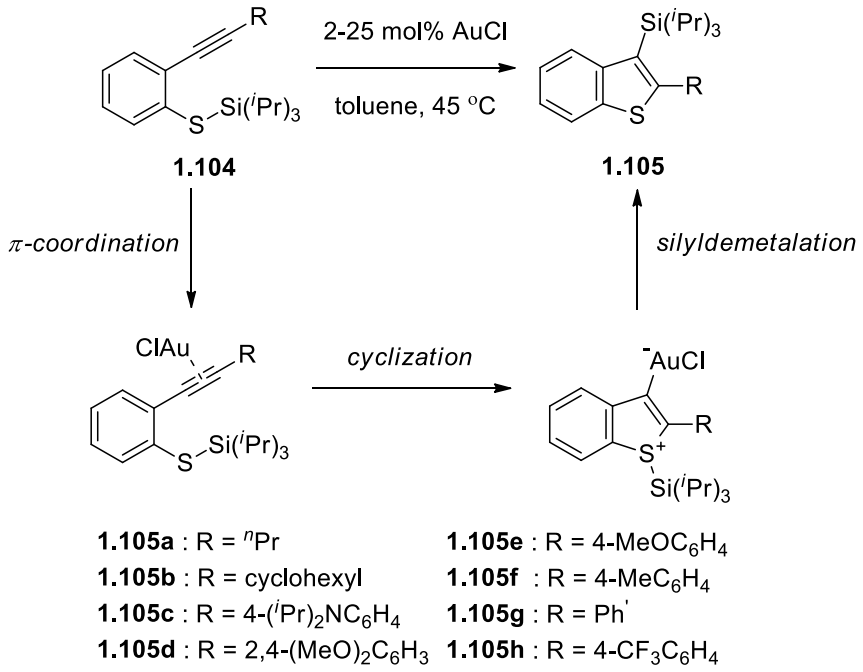
Gold

Nakamura and co-workers reported the AuCl-catalysed cyclization of (*o*-alkynylphenylthio)silanes (**1.104**) to form the corresponding 3-silylbenzo[*b*]thiophenes (**1.105**). The reaction was proposed to proceed initially by coordination of the gold species to the alkynyl moiety. The sulphur atom then acts as an intramolecular nucleophile, attacking the electron deficient alkyne which results in a silylsulfonium intermediate. Subsequently, [1,3]-migration of the silyl group and elimination of AuCl yielded **1.105** (Scheme 1.63). The yield was highly dependent on the nature of the alkyne substituents with electron rich aromatic rings producing higher yields than electron poor or bulky groups (which inhibited the reaction).[173]

1.2.9 Sulphur-Boron (S-B)

Palladium

Suzuki and Miyuara reported the palladium(0) catalysed thioboration of terminal alkynes employing 9-(alkylthio)-9-borabicyclo[3.3.1]nonane to produce 9-[*Z*-2-(alkylthio)-1-alkenyl]-9-borabicyclo[3.3.1]nonane derivatives. These reactions were highly regio-



Scheme 1.63 Gold(I) catalysed cyclization of (*o*-alkynylphenylthio)silanes

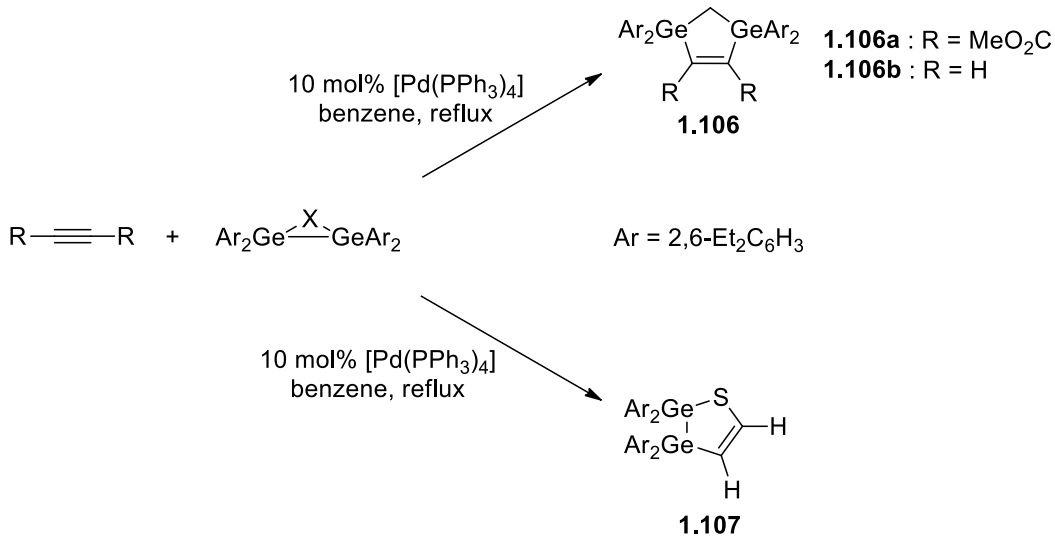
and stereoselective with the boryl group adding to the terminal carbon in all cases. The reactions were sufficiently mild that a variety of functionalities were tolerated.[174]

1.2.10 Germanium-Germanium (Ge-Ge)

Palladium

In contrast to Si-Si and Sn-Sn bonds, the insertion of alkynes into Ge-Ge bonds has been investigated to a much lesser extent. The resulting compounds are expected to have a reactivity profile somewhere in-between their Si-Si and Sn-Sn analogues. The majority of alkyne digermylations in the literature are palladium catalysed. The first example was reported by Ando and co-workers. In their work, a strained cyclic digermirane was reacted with acetylene and dimethyl acetylenedicarboxylate in the presence of 10 mol% [$Pd(PPh_3)_4$] resulting in the formation of the digermacyclopentene **1.106**. When X was a

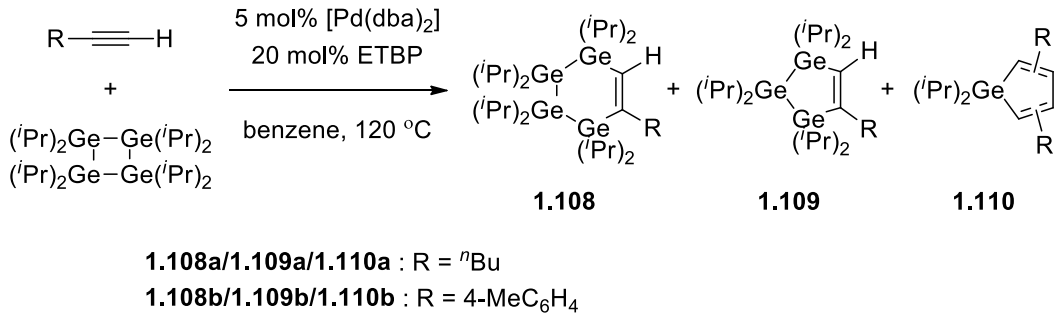
sulphur atom, it was possible to selectively cleave the Ge-S bond to afford **1.107** (Scheme 1.64).[175]



Scheme 1.64 Linker-atom dependent addition strained digermane to alkynes

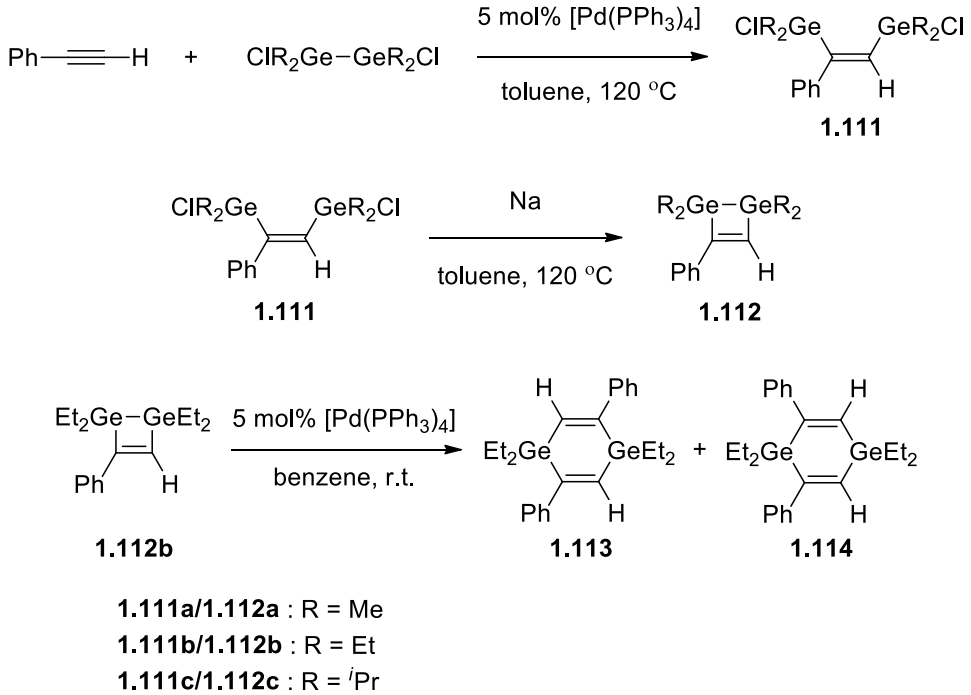
Mochida and co-workers reacted 1,1,2,2,3,3,4,4-octaisopropyltetragermetane ($\{^{i}Pr_2Ge\}_4$) with various terminal alkynes in the presence of palladium complexes to synthesise 1,2,3,4-tetrahydro-1,2,3,4-tetragermins (**1.108**), Δ^4-1,2,3-trigemolene (**1.109**) and 1H-germoles (2,4-, 3,4- and 2,3-disubstituted) (**1.110**) (Scheme 1.65). The yields of **1.109** and **1.110** increased with time and this was attributed to the thermoylsis of **1.108** in the presence of excess alkyne. The formation of **1.109** from **1.108** suggested extrusion of diisopropylgermylene (iPr$_2$Ge:), which was readily trapped by two equivalents of alkyne to give **1.110**.[176]

In 1991, Tanaka reported the first use of linear non-strained digermanes in digermylation of alkynes. 1,2-Dichloro-1,1,2,2-tetramethyldigermane was reacted with phenylacetylene in the presence of a palladium(0) catalyst to form **1.111** (Scheme 1.66). The extension of



Scheme 1.65 Addition of a tetragermetane to internal alkynes

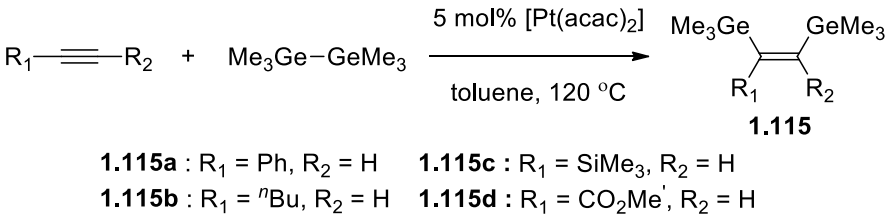
the protocol to hexamethyldigermane resulted in very low conversions.[177] Following studies detailed the conversion of **1.111** to 1,2-digermacyclobut-2-enes (**1.112**) by reductive cyclization in the presence of sodium metal. The treatment of **1.112** with alkynes in the presence of palladium catalysts resulted in the digermylation and the formation of the corresponding 1,4-digermacyclohex-2,5-dienes **1.113** and **1.114** (Scheme 1.66).[178]



Scheme 1.66 Digermylation, reductive cyclization and digermylation employing dichlorodigermanes and terminal alkynes

Platinum

The digermylation of terminal alkynes with hexamethyldigermane has only been accessible employing a platinum catalyst at 120 °C, affording the corresponding *Z*-1,2-bis(trimethylgermyl)ethenes (**1.115**) (Scheme 1.67). Lowering the temperature resulted in deterioration of the yields.[179] Internal alkynes were unreactive.



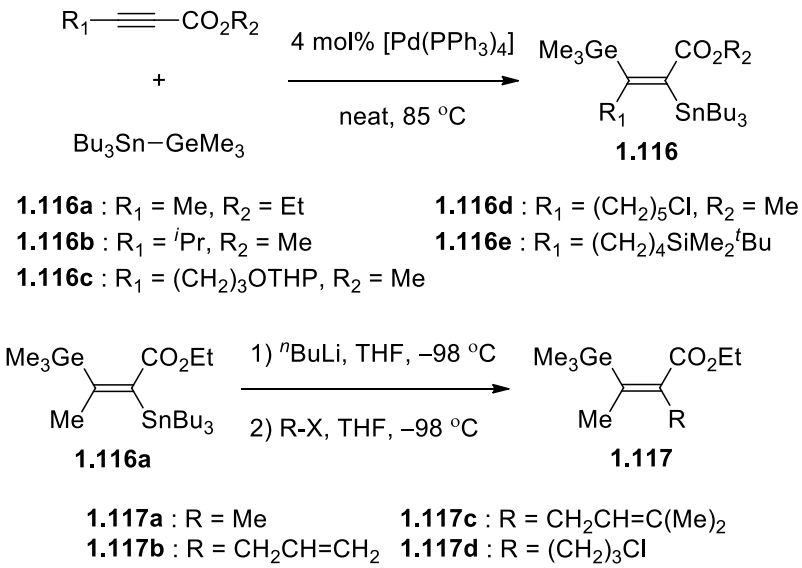
Scheme 1.67 Platinum-catalysed digermylation of alkynes with hexamethyldigermane

1.2.11 Germanium-Tin (Ge-Sn)

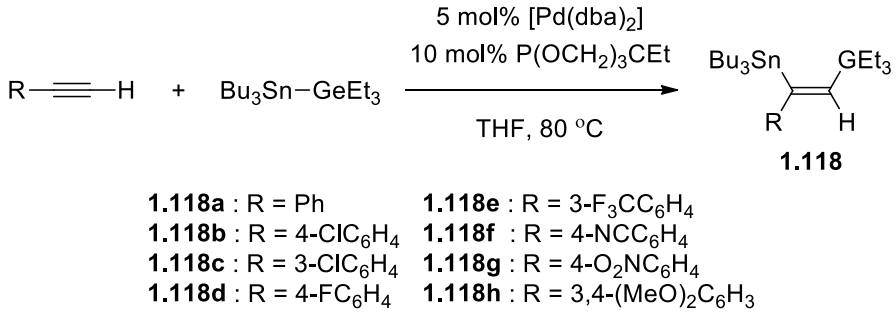
Palladium

Piers and co-workers reported the germylstannation of *α,β*-acetyleneic esters with $Bu_3SnGeMe_3$ to afford *E*-2-(tri-*n*butylstannyl)-3-(trimethylgermyl)alk-2-enoates (**1.116**) as the major product. The reactivity of the resulting germyl and stannyl groups were separately assessed. **1.116** was treated with *n*BuLi and an alkyl halide to form **1.117** *via* the transmetallation of Bu_3Sn. The germyl moiety was also transformed into a C-I bond upon addition of iodine (Scheme 1.68).[180]

Nakano reported the synthesis of *Z*-1-aryl-2-germyl-1-stannylethenes (**1.118**) by the addition of tributyl(triethylgermyl)stannane to aryl terminal alkynes in the presence of catalytic amounts of $[Pd(dba)_2]$ and 4-ethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane (Scheme 1.69). This protocol was extended to ethynylthiophene and 2-methyl-3-butyn-2-ol. The germyl group regioselectively added to the terminal carbon.[181]



Scheme 1.68 *E*-Germylstannation of *α,β*-acetyleneic esters



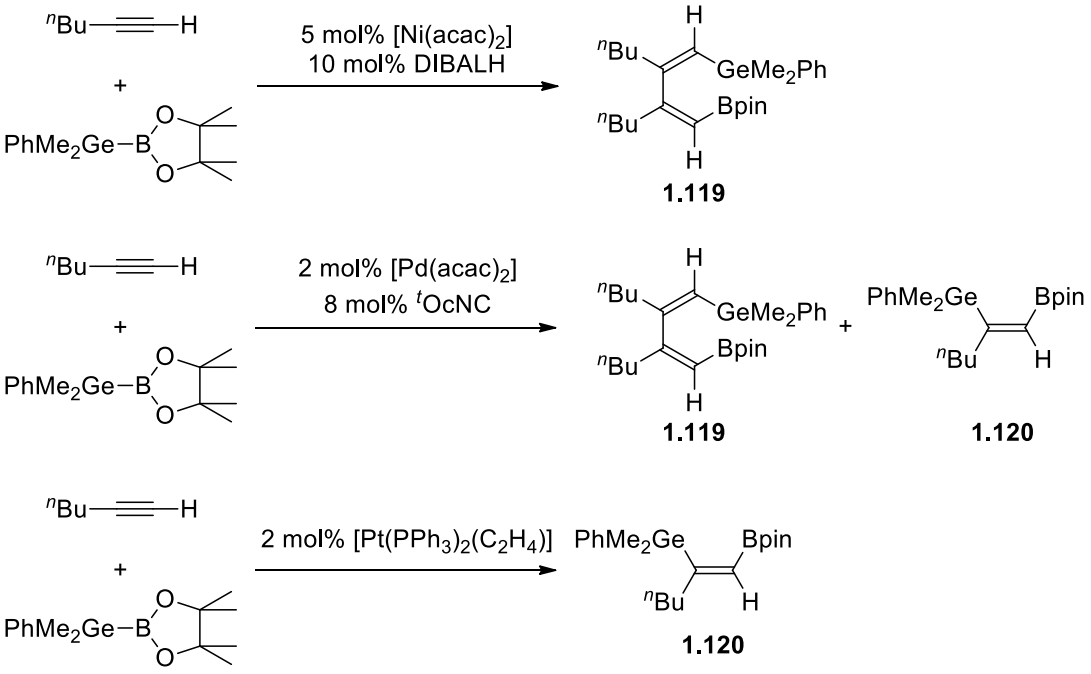
Scheme 1.69 *Z*-Germylstannation of aryl terminal alkynes

1.2.12 Germanium-Boron (Ge-B)

Nickel, Palladium and Platinum

In their investigation into the silaborative dimerization of alkynes catalysed by nickel complexes, Ito and co-workers reported the analogous germylborane reaction. The products obtained in the germylboration of 1-hexyne were highly dependent on the metal catalyst used. In the presence of [Ni(acac)$_2$]/DIBALH the germylborated dimerized product **1.119** was obtained. By altering the catalyst to [Pd(OAc)$_2$]/isocyanide a 1:1

mixture of **1.119** and the germylboration adduct **1.120** was isolated, whereas catalytic-quantities of $Pt(PPh_3)_2(C_2H_4)$ resulted in exclusively **1.120** (Scheme 1.70).[122]



Scheme 1.70 Catalyst-dependent germylboration of 1-hexyne

1.3 Carbenes

Carbenes are electronically neutral divalent carbon atoms with 6 valence electrons. This term is derived from the parent hydride, methylene (H_2C:), whose synthesis was first attempted by Dumas and Regnault in the dehydration of methanol.[182] Early carbenes were generally very reactive species with half-lives less than 1s,[183–185] and their existence was often alluded to by the use of low temperature matrix isolation spectroscopy,[186–188] or trapping reagents.[189–193] Isolable or persistent carbenes are now prominent in the literature.[194,195] The following sections will focus on the properties, synthesis and the transition metal complexes of this set of carbenes with particular emphasis on the largest subgroup, N-heterocyclic carbenes (NHCs).

1.3.1 Stable Carbenes – Electronic and Steric Properties

The divalent carbon atom of carbenes (R_2C:) possesses four bonding and two non-bonding electrons.[196] The geometry surrounding the central carbon is heavily dependent upon the degree of hybridization and ranges from linear to bent. This shape is linked to the ground-state multiplicities of the carbene and the reactivity modes it exhibits. A linear geometry suggests sp-hybridization and two degenerate p-orbitals (p_x and p_y). As this geometry bends to angles <180° sp^2-hybridization dominates and the degeneracy of the p_x and p_y orbitals is lost. In this instance, the p_y (p_π) remains unchanged and the p_x (σ) orbital is stabilized due to an increase in its s-character. Linear carbenes are extreme cases and variations in the bent geometry are often observed.[195] Four electronic configurations involving the non-bonding electrons can be envisaged for a bent carbene. These electrons can be paired with opposite spins in either the σ or p_π orbitals giving rise to a singlet state. The two non-bonding electrons can also singly occupy the σ and p_π orbitals with parallel spins otherwise known as a triplet state.[197] The final electronic configuration is deemed an excited singlet state with the non-bonding electrons again singly occupying the σ and p_π, but with opposite spins (Figure 1.4).

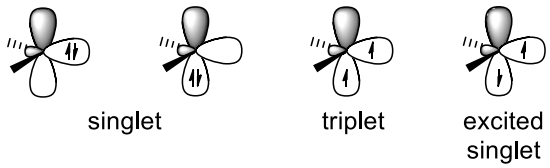


Figure 1.4 carbene electronic configurations – singlet and triplet states

The ground-state multiplicity of the carbene controls its reactivity.[198] Singlet carbenes possess a filled and empty set of frontier orbitals. They are therefore described as ambiphilic demonstrating both electrophilic and nucleophilic tendencies. Triplet carbenes

have two singly occupied molecular orbitals (SOMOs) and are regarded to react in a biradical fashion. Hoffmann calculated that a carbene singlet ground state is favoured when the σ-p_π separation is at least 2 eV and a triplet ground state is favoured when this separation is <1.5 eV.[199] Tuning of the σ-p_π energy gap is possible by altering the electronic and steric properties of the substituents attached to the carbene carbon. Harrison and co-workers reported that manipulations to the inductive properties of the carbene substituents modified the favoured ground state multiplicity.[200] It was demonstrated that fluorine substituents with a greater σ-electron withdrawing character inductively stabilized the σ-orbital on the carbene carbon atom by the introduction of more s-character (leaving p_π unchanged).[201] A singlet ground state was therefore favoured, with the singlet to triplet state energy gap approximately 45 kcal mol^{-1}. On changing the substituents to two lithium atoms, σ-donating substituents, a lowering of the σ-p_π energy gap was observed and a triplet state was favoured by 23 kcal mol^{-1}.[200] Mesomeric effects tend to be more significant in influencing the ground state multiplicity. When the carbenic carbon has for example, two π-donating substituents (*e.g.* -NR_2 and -OR) it exhibits a singlet state. The substituents' lone pairs symmetrically overlap with the vacant p_π-orbital increasing its energy and therefore the σ-p_π separation (Figure 1.5).

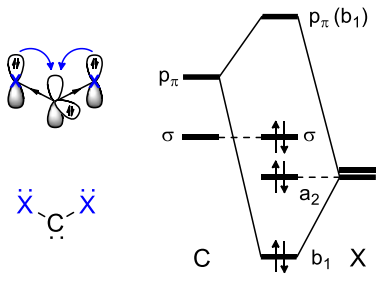
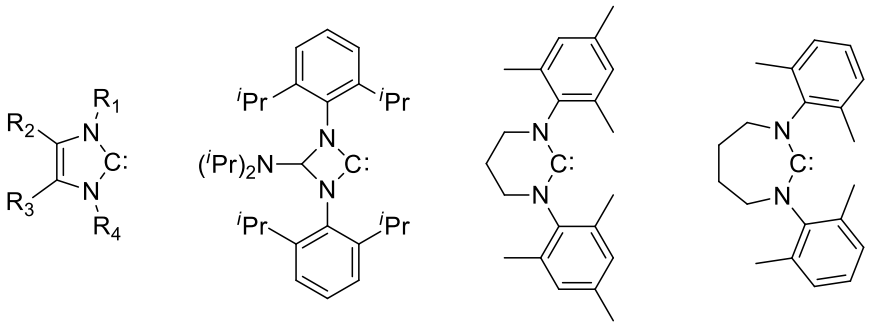


Figure 1.5 Orbital diagram of carbenic carbon with adjacent π-donating substituents

If electronics are negligible, then steric effects dictate the ground state multiplicity of the carbene. Increasing the steric bulk around the carbenic carbon forces the geometry towards 180^{o} (linear) and a triplet state multiplicity.[202,203] Although the triplet state is slightly destabilized by the expansion of this angle, the singlet state is destabilized to a much greater extent.

1.3.2 N-Heterocyclic Carbenes: Background and Synthesis

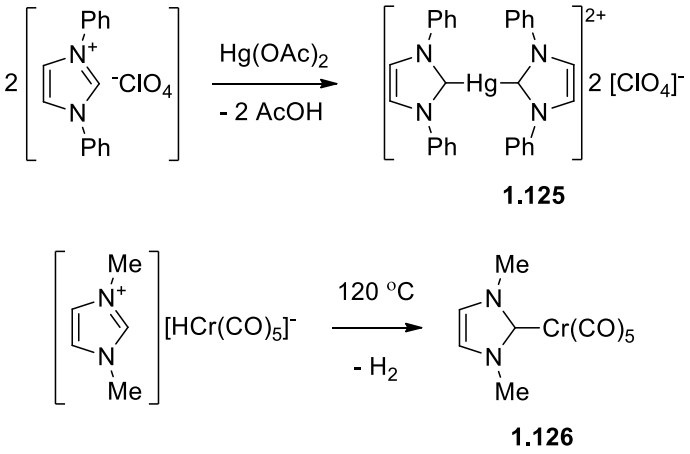
N-Heterocyclic carbenes (NHCs) are defined as heterocyclic species containing a carbenic carbon with at least one adjacent nitrogen atom. The 5-membered imidazole based carbenes are the most widely studied form, although 4,[204] 6 and 7-membered analogues are known (Figure 1.6).[205]



1.121 **1.122** **1.123** **1.124**

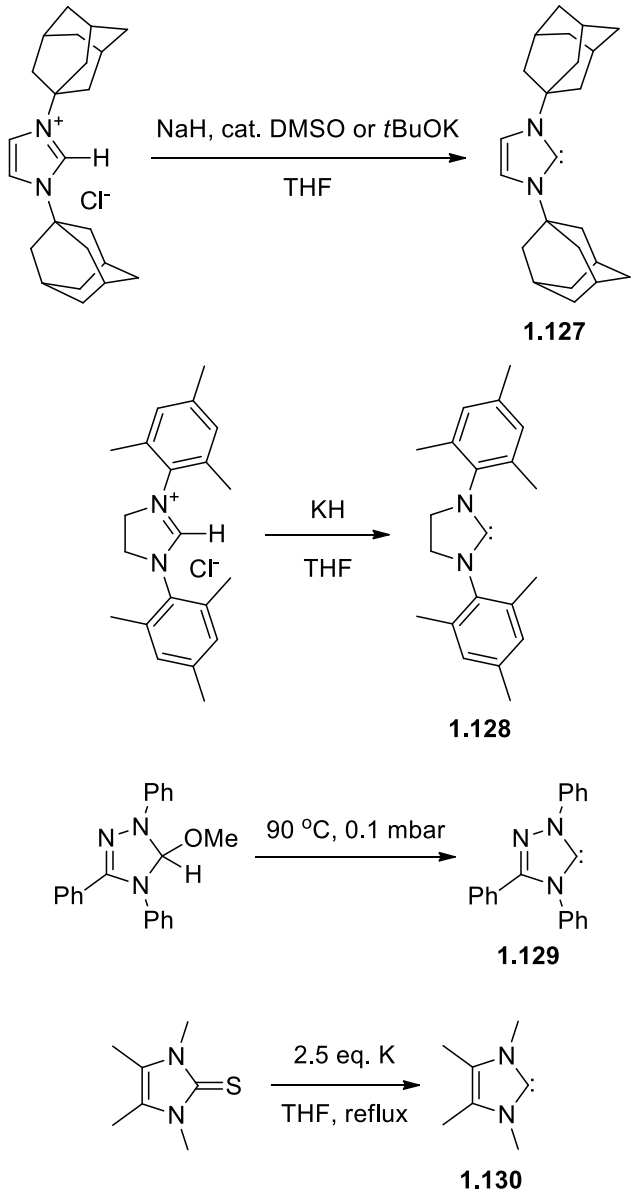
Figure 1.6 General structure of 4, 5, 6 and 7-membered N-heterocyclic carbenes

Early attempts at synthesizing NHCs were reported by Wanzlick,[206,207] and Öfele (Scheme 1.74).[208] However, these accounts were limited to coordination complexes of transition-metals or carbene dimers in order to stabilize the carbenic carbon.



Scheme 1.74 Wanzlick and Öfele synthesis of NHC-transition metal complexes

The first isolation of a stable free-NHC was reported by Arduengo in the form of 1,3-di-1-adamantyl-imidazol-2-ylidene (**1.127**).[209] The kinetic and thermodynamic stability of **1.127** was attributed to the steric bulk provided by the adamantyl moieties as well as the π-donating and σ-withdrawing abilities of the two nitrogen- atoms. This discovery ignited rapid growth of this research area and now a variety of stable NHCs with diverse steric and electronic properties are assessable.[210] Synthesis of isolable NHCs include: base deprotonation of imidazolium,[211] and dihydroimidazolium salts,[212] vacuum thermolysis to liberate methanol from 5-methoxytriazole,[213] and reductive desulfurization of imidazole-2-thiones (Scheme 1.75).[214]

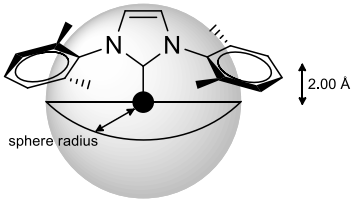


Scheme 1.75 Synthesis of NHCs

1.3.3 N-Heterocyclic Carbene: Bonding to Transition-Metal Centres

NHCs are capable of forming a σ-bond with transition-metal centres (TM) *via* an NHC based nucleophilic lone pair. By adjusting the NHCs steric and electronic properties it is possible to tune the reactivity profile of the resulting NHC-TM complexes. Electron donating substituents (*e.g.* alkyl) on the N-atoms and/or at the C4 and C5 positions increases the strength of the σ-donation to and thus electron density at the TM

centre.[215,216] Alternatively, electron-withdrawing groups (*e.g.* aryl or halogens, respectively) decrease this σ-donation. Altering the steric bulk of substituents at the N-atoms allows for modification of the reactive pocket size and therefore the facile nature of reactivity pathways (*e.g.* oxidative addition and reductive elimination), as well as the stability of the TM centre.[217] The steric bulk of NHCs is measured and quantified by the percent buried volume model, which is defined as the percent of the total volume of a sphere occupied by a ligand at a fixed M-L bond length. This method allows for a quantitative comparison between the coordination complexes of NHC ligands with varying steric properties and can be extended to tertiary phosphine analogues.[217]



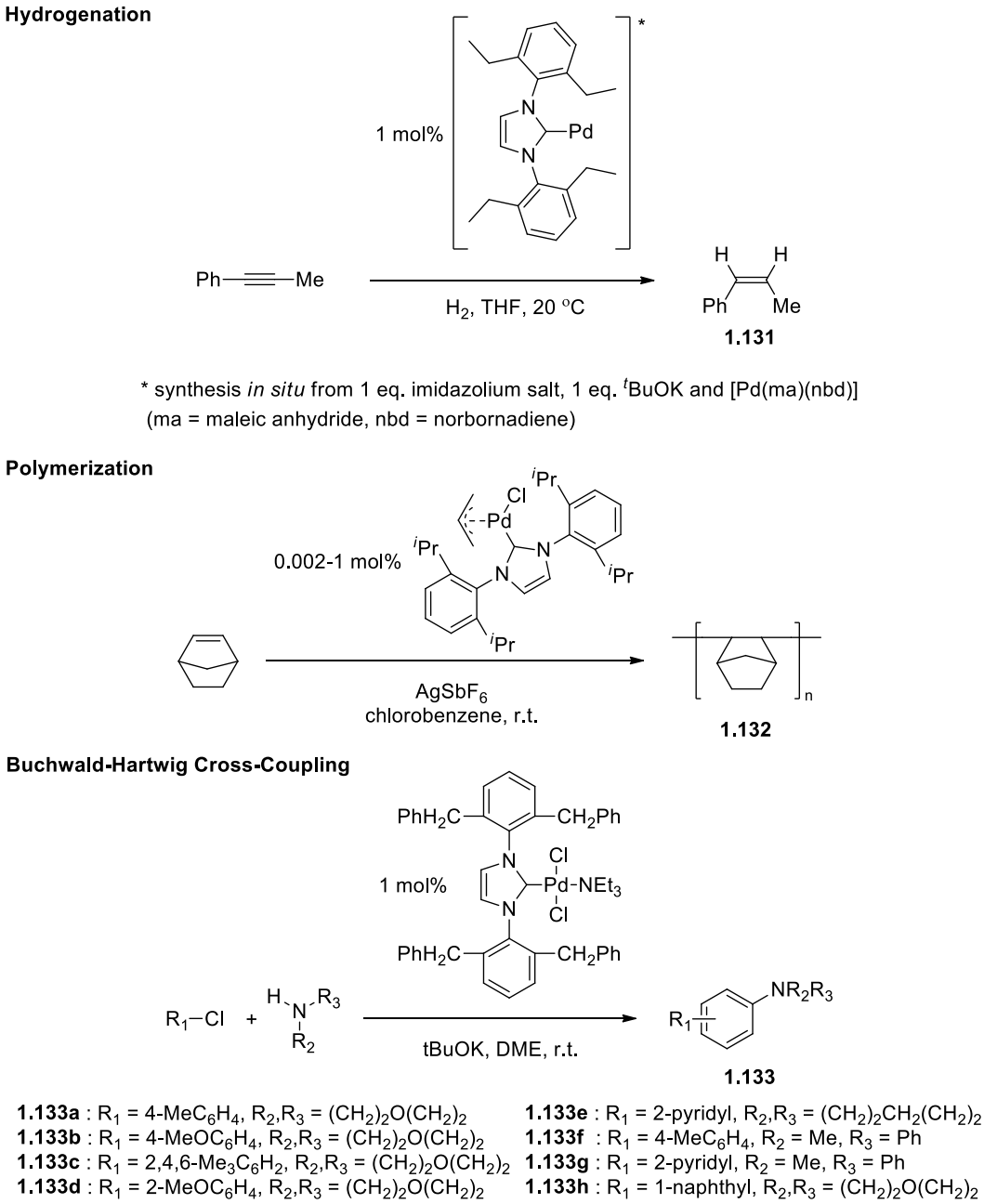
Scheme 1.76 Percent buried volume

Initially, NHCs were considered to bind to metals purely in a σ-donating fashion. It has since been shown that NHCs also accept electron density from the metal centre into the π*-orbitals and this is calculated to account for 15-30% of the overall bonding energy.[218,219]

1.3.4 N-Heterocyclic Carbene-Palladium Complexes in Organic Transformations

NHC-TM complexes are abundant within the literature and are exploited in an array of stoichiometric and catalytic transformations. In particular, palladium examples are the largest sub-group. The reactivity of NHC-palladium complexes is vast and includes chemo- and stereoselective hydrogenation of alkynes,[220] diboration of styrenes,[221]

polymerization and telomerisation reactions,[222,223] cross-coupling (Suzuki-Miyaura,[224] Mizoroki-Heck,[225] Buchwald-Hartwig,[226] Sonagashira,[227] to name a few), oxidation reactions,[228] and C-H activation (Scheme 1.77).[229]



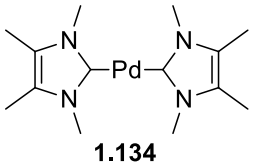
Scheme 1.77 Representative examples of NHC-Pd complexes used in organic synthesis

1.3.5 N-Heterocyclic Carbenes versus Phosphines

NHCs have replaced phosphines as ancillary ligands in many organometallic/organic reactions. NHCs have been shown to be stronger σ-donors than the most common phosphines – this enhances the electron density at the TM centre and for example, enables more favourable rates of oxidative addition.[230] The strong bonds between NHCs and metals means NHC-TM complexes are less prone to ligand dissociation, therefore increasing the thermal and hydrolytic durability of the TM complex and reducing the need for excess ligand.[231] NHC salts are easy to prepare on large scales and are stable without decomposition in air, whereas phosphines degrade at higher temperature and often oxidise under aerobic conditions. The structural versatility of NHCs versus phosphines results in a greater ability to fine tune and modify the resulting NHC-TM complexes. This culminates in more facile introduction of chirality, stability and immobilisation, as well as precise altering of reactivity to suit the chemical needs.[232]

1.4 Aim of This Thesis

The above review demonstrates that a range of element-element additions to alkynes are feasible employing transition-metal mediators with complexes of the type PdL_2 (L = phosphines or isocyanides), the most widely utilized. N-Heterocyclic carbene-palladium species are much more effective in a variety of organic transformations than their phosphine analogues. Yet, they have not been successfully exploited in the hetero element-element addition to alkynes and other unsaturated bonds. 1,3,4,5-Tetramethylimidazol-2-ylidene (ITMe) is an interesting NHC that demonstrates a low percent buried volume and high σ-donating character. Consequently, the bis-NHC-Pd^0 complex $[Pd^0(ITMe)_2]$ (**1.134**, Figure 7) is expected to exhibit a unique reactivity profile.



1.134

Figure 7 Structure of [Pd(ITMe)$_2$]

However, limitations in synthetic routes to **1.134**, such as harsh reaction conditions or coordination of ligands that deactivate the metal centre,[233,234] have resulted in an unexplored assessment of its reactivity. The following chapters will aim to demonstrate a facile synthetic route to **1.134** that overcomes these constraints and subsequently **1.134**'s ability to mediate, stoichiometrically and catalytically, the element-element' additions to alkynes and other unsaturated bonds in an unprecedented manner.

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Chapter 2

Synthesis of [(N-Heterocyclic Carbene)$_2$Pd(SiR$_3$)$_2$] Complexes: Catalytic *cis*-Bis(silyl)ations of Alkynes with Unactivated Disilanes

2.1 Introduction

The transition metal catalysed activation of disilanes for the synthesis of high-value organosilicon compounds has received a significant amount of attention from industry and academia. Applications encompass the formation of silanes,[1] bis(silyl)ation of unsaturated compounds,[2–4] aryl/acyl silane synthesis,[5,6] and protection of alcohols.[7] Since the oxidative cleavage of the Si-Si bond by a low-valent platinum-group transition-metal centre is proposed as a vital step for some of these processes,[8,9] the isolation of the resulting bis(silyl) transition-metal complexes is of great interest for elucidating reaction mechanisms. Unfortunately, the synthesis of such complexes has been largely limited to the oxidative addition of strained or activated disilanes.[10–12]

The cleavage of non-activated hexamethyldisilane ($Me_3SiSiMe_3$) is particularly challenging.[13,14] Examples of the resulting bis(trimethylsilyl) platinum-group metal complexes are rare: only two have been described in the literature, and bear either phosphine or isocyanide ligands. Braun and co-workers reported that [Pt(PEt_3)$_3$] reacted with a large excess of $Me_3SiSiMe_3$ to yield *cis*-[Pt(PEt_3)$_2$($SiMe_3$)$_2$] at ambient temperature, but it only went to 50% completion after three weeks.[15] Earlier, Ito and co-workers synthesized *cis*-[Pt(CNAd)$_2$($SiMe_3$)$_2$] (CNAd = 1-adamantyl isocyanide) from [Pt_3(CNAd)$_6$] using 30 equivalents of $Me_3SiSiMe_3$ at 80 °C.[16] Prior to this work there were no examples in the literature of palladium complexes capable of this reaction.

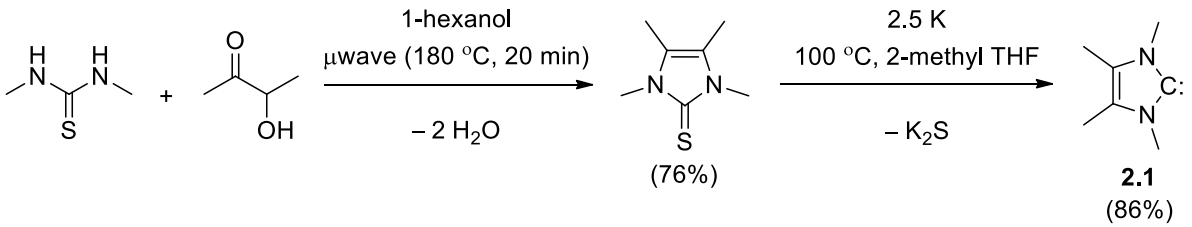
As described in Chapter 1, it is well documented that N-heterocyclic carbenes (NHCs) have equivalent or better σ-donor character than the most common phosphines and that

NHC/M complexes (M = metal) are less prone to decomposition by cleavage of the (NHC)-M bond.[17–21] These properties increase the propensity of the corresponding NHC-palladium complexes towards oxidative cleavage of hetero element-element' bonds. Herein the synthesis of a $(NHC)_2Pd(SiMe_3)_2$ complex and its inclusion in a catalytic cycle leading to the *cis*-bis(silyl)ation of alkynes is reported.

2.2 Synthesis of *cis*-[Pd(ITMe)$_2$(SiMe$_3$)$_2$]

2.2.1 Synthesis of ITMe

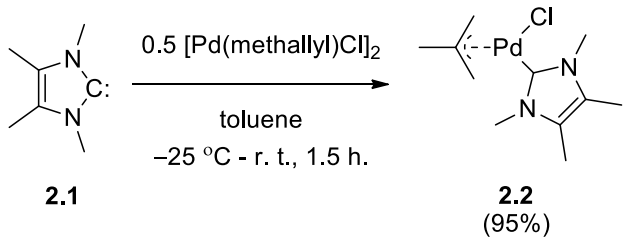
While very recent literature on NHC-Pd complexes features the use of large NHCs as a common denominator,[22–24] attention was instead turned to one of the smallest NHCs available, that is, 1,3,4,5-tetramethylimidazol-2-ylidene (ITMe; **2.1**). ITMe exhibits a very small percent buried volume and a high σ-donor character.[25] The conventional synthetic route to **2.1** was established by Kuhn and co-workers.[26] It involves the formation of the corresponding thione by a ring-forming double condensation of *N*,*N*'-dimethyl-thiourea and acetoin, and subsequent reductive desulfurization of the thione using potassium metal, with an overall yield of about 76%. A thorough modification of the synthetic protocol, including a microwave-mediated cyclization step, allowed **2.1** to be obtained in 86% overall yield even on a gram scale (Scheme 2.1).[27]



Scheme 2.1 Modified synthesis of ITMe (**2.1**)

2.2.2 Synthesis of [(ITMe)Pd(methallyl)Cl]

The second step involved the synthesis of [(ITMe)Pd(methallyl)Cl] (**2.2**). The synthesis of this complex has not been reported, although unsuccessful attempts were detailed by Cavell and co-workers.[28] The conventional synthetic route to [(NHC)Pd(R-allyl)Cl] species involves the reaction of the corresponding [Pd(R-allyl)Cl}$_2$] dimer with a free NHC.[29,30] It was found that reacting [{Pd(methallyl)Cl}$_2$] with a slight excess of **2.1** in toluene, initially led to the formation of **2.2** in 95% yield (Scheme 2.2). The reaction was solvent and temperature dependent with more polar solvents, such as THF, and higher reaction temperatures resulting in the precipitation of elemental palladium.

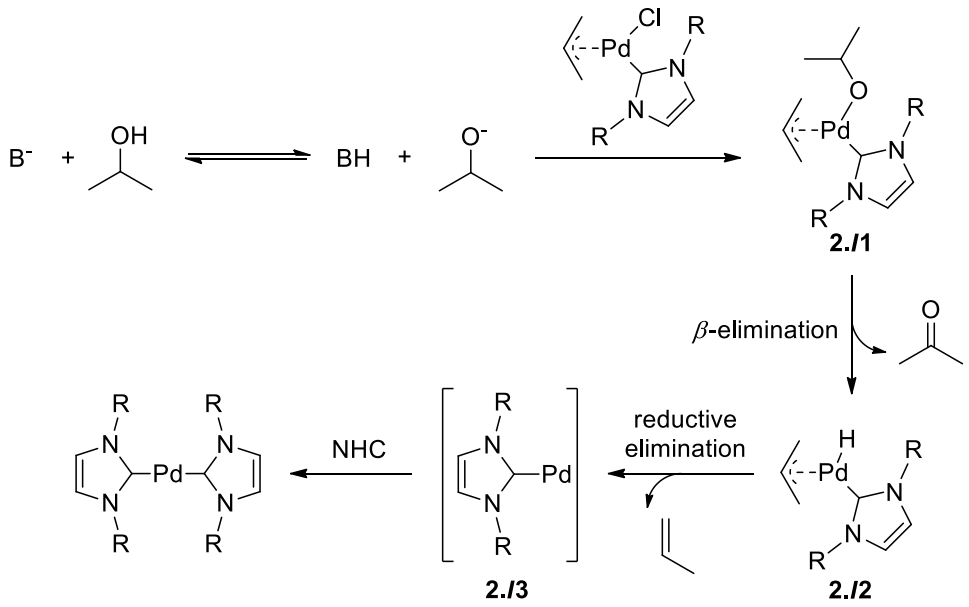


Scheme 2.2 Synthesis of [(ITMe)Pd(methallyl)Cl] (**2.2**)

2.2.3 Synthesis of [Pd^0(ITMe)$_2$] and *in situ* Synthesis of *cis*-[Pd(ITMe)$_2$(SiMe$_3$)$_2$]

[Pd^0(ITMe)$_2$] (**2.3**) has been proposed as the active catalytic species in a number of reactions.[31] The only reported synthesis of **2.3** was achieved through metal vapor synthesis (MVS).[32] Recently, Fantasia and Nolan used [(NHC)Pd(allyl)Cl] complexes as precursors to easily synthesize a series of [Pd^0(NHC)$_2$] complexes,[33] suggesting that the solvent employed in these reactions (isopropanol) was also a reagent and essential to the mechanism of these transformations. The authors proposed that the isopropoxide anion, generated from deprotonation of isopropanol by ^{t}BuOK, replaces the chloride in [(NHC)Pd(allyl)Cl] to form **2.*I*1**. The coordinated isopropoxide subsequently undergoes

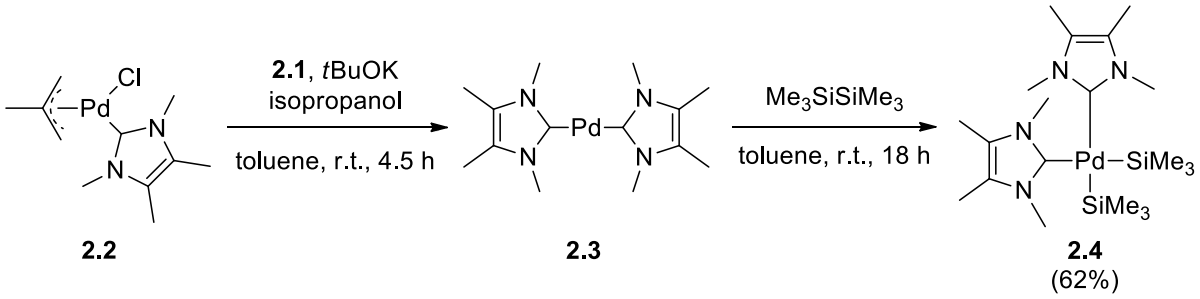
a β-elimination to form acetone and **2.*I*2**. **2.*I*2** then undergoes facile reductive elimination to **2.*I*3**. Coordination of an NHC ligand results in [$Pd^0(NHC)_2$] (Scheme 2.3).[34]



Scheme 2.3 Proposed mechanism for formation of [$Pd^0(NHC)_2$] from [(NHC)Pd(allyl)Cl][33]

Unfortunately, the application of this methodology to the synthesis of **2.3** resulted in the precipitation of large quantities of Pd black. Modifying this procedure by using isopropanol in stoichiometric quantities resulted in the first solution-based synthesis of **2.3**, which was formed as a yellow crystalline precipitate. Its isolation, however, proved difficult because of its limited solubility in toluene, THF and pyridine, and its instability in alcohols or halogenated solvents. Consequently, the reaction mixture was directly reacted with $Me_3SiSiMe_3$ at room temperature for 18 hours. *cis*-[$Pd(ITMe)_2(SiMe_3)_2$] (**2.4**) was collected as an off-white solid in 62% yield (Scheme 2.4). Single crystals of **2.4** were isolated from a saturated solution of toluene at −30 °C, and X-ray analysis revealed that **2.4** displays a marginally distorted square-planar geometry with the two NHCs in a *cis*-configuration and orthogonal to the Si-Pd-Si plane (Figure 2.1). The Pd-Si bond

lengths are comparable to those found in similar complexes such as *cis*-[(dcpe)Pd($SiMe_2H$)$_2$] (dcpe = 1,2-bis(dicyclohexylphosphino)ethane).[8]



Scheme 2.4 Formation of [Pd^0(ITMe)$_2$] and *in situ* oxidative cleavage of $Me_3SiSiMe_3$ yielding **2.4**

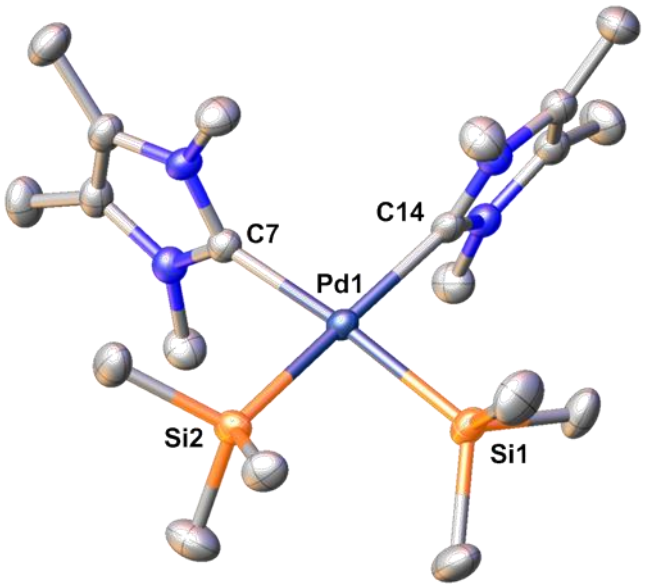
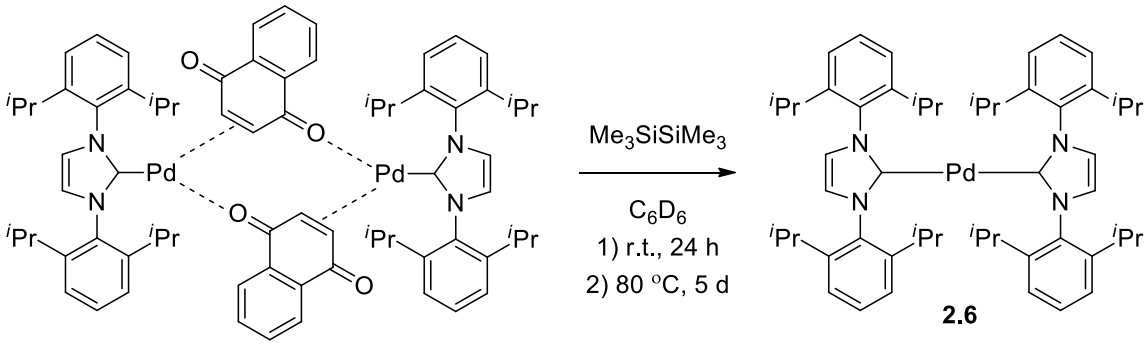


Figure 2.1 Molecular structure of **2.4** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd-Si1 2.3557(6), Pd-Si2 2.3468(6), Pd-C7 2.102(2), Pd-C14 2.119(2); Si1-Pd-Si2 88.65(2), Si1-Pd-C14 88.44(6), Si2-Pd-C7 88.74(6), C7-Pd-C14 94.74(8).

Attempts at oxidative cleavage of $Me_3SiSiMe_3$ utilizing other NHC-Pd complexes were unsuccessful. [(ITMe)$_2$$Pd^0$(ma)] (**2.5**; ma = maleic anhydride), synthesized from the

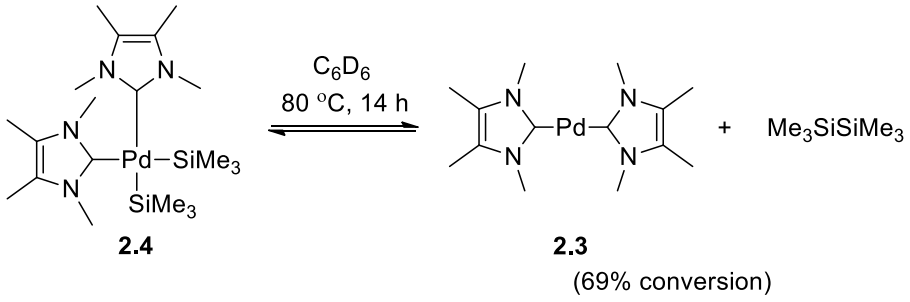
reaction of two equivalents of **2.1** and [Pd^0(cod)(ma)] (cod = 1,5-cyclooctadiene) and previously limited to oxidative cleavage of activated aryl halides,[31,35] in the presence of $Me_3SiSiMe_3$ afforded elemental palladium. The reaction of [(Pd^0{IPr}{nq})$_2$] (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene; nq = 1,4-naphthoquinone) and a slight excess of $Me_3SiSiMe_3$ at elevated temperatures did not result in oxidative addition of the disilane, but instead the thermal decomposition product, [Pd(IPr)$_2$] (**2.6**; Scheme 2.5). Pörschke and co-workers noted a similar decomposition route in the synthesis of monophosphine-Pd(1,6-diene) complexes.[36]



Scheme 2.5 Thermal decomposition of [(Pd^0{IPr}{NQ})$_2$] to **2.6**

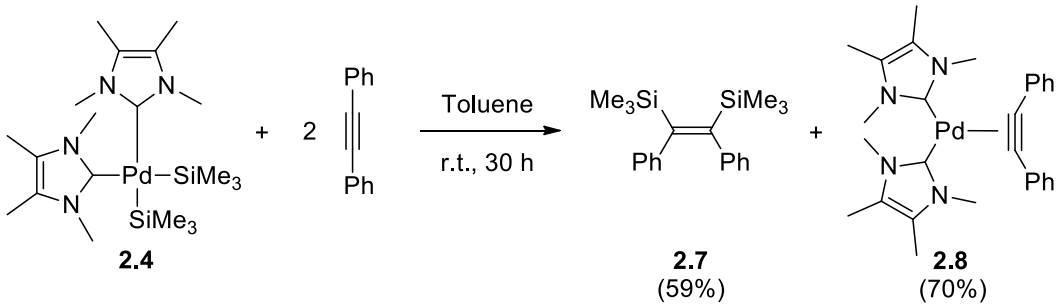
2.3 Stoichiometric Reactivity of *cis*-[Pd(ITMe)$_2$(SiMe$_3$)$_2$]

The reactivity of **2.4** was then investigated. A solution of **2.4** in C_6D_6 was heated to 85 °C and resulted in an intense yellow solution in less than 1.5 hours. ^{1}H NMR analysis showed the formation of $Me_3SiSiMe_3$ and **2.3**. The formation of these reductive elimination products was limited to 69% conversion, even upon increasing the temperature and heating time, probably because of the recombination of the two products to form **2.4** (Scheme 2.6).



Scheme 2.6 Reversible reductive elimination of **2.4** to **2.3** and $Me_3SiSiMe_3$

The bis(silyl)ation of disubstituted alkynes with $Me_3SiSiMe_3$ has not been previously reported. The stoichiometric reaction of **2.4** with diphenylacetylene at room temperature yielded the corresponding *cis*-bis(silyl)ated product **2.7** within 30 hours in a quantitative yield.[37] This reaction also resulted in the quantitative formation of the novel complex $[(ITMe)_2Pd(PhC{\equiv}CPh)]$ (**2.8**), which could be easily isolated after hexane extraction (Scheme 2.7).



Scheme 2.7 Stoichiometric bis(silyl)ation of diphenylacetylene mediated by **2.4**

X-ray crystallography established the *cis*-configuration in **2.7** (Figure 2.2). Compound **2.8** was fully characterized by NMR spectroscopy and elemental analysis. Single crystals of **2.8** were obtained from a saturated toluene solution upon cooling to –30 °C and the result of X-ray analysis is depicted in Figure 2.3, featuring a Y-shaped structure. There is a clear and expected elongation of the C≡C bond and a shortening of the C≡C- bond when

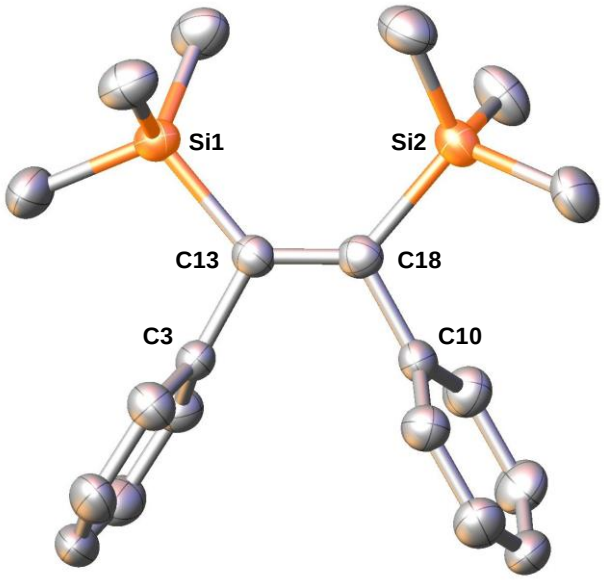


Figure 2.2 Molecular structure of **2.7** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [º]: C13-C18 1.353(3); C3-C13-Si1 111.20(13), C18-C13-Si1 130.13(15) C18-C13-C3 118.60(18), C10-C18-Si2 110.77(14), C13-C18-Si2 130.10(16), C13-C18-C10 119.12(18).

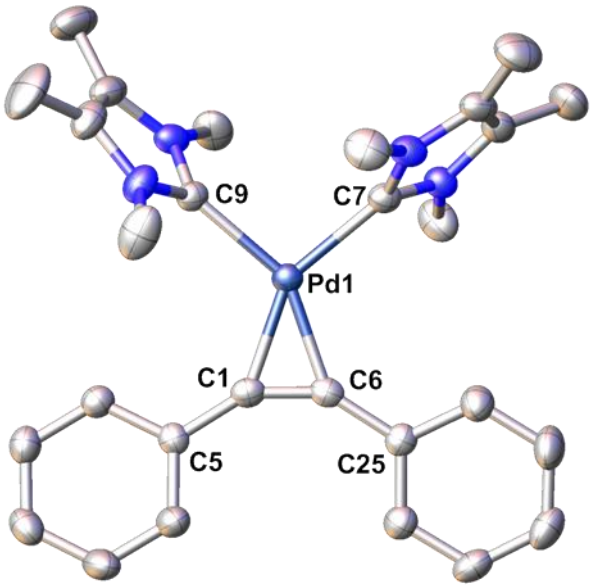
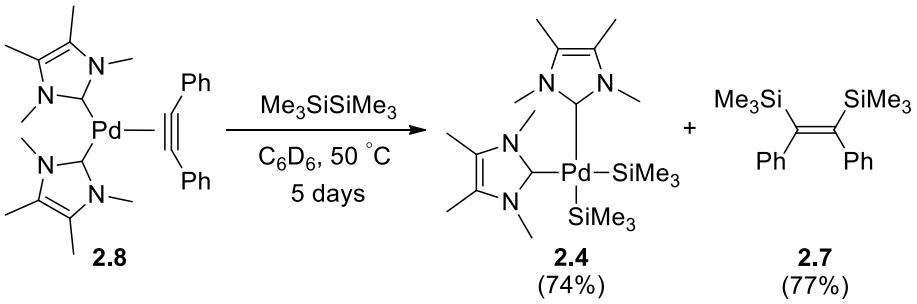


Figure 2.3 Molecular structure of **2.8** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd-C1 2.033(3), Pd-C6 2.029(3), C1-C6 1.290(4); C6-C1-C5 147.5(3), C1-C6-C25 146.03(3).

compared to free diphenylacetylene.[38] Although analogous phosphine-group 10 metal complexes are known,[39–41] this represents the first example of an NHC-Pd^0 complex bearing an η^2-bound alkyne. This species can react with an excess of $Me_3SiSiMe_3$ at 50 °C for over 5 days, resulting in the formation of **2.4** and **2.7** (Scheme 2.8).



Scheme 2.8 Stoichiometric bis(silyl)ation of **2.8** yielding **2.4** and **2.7**

2.4 Catalytic Bis(silyl)ation of Alkynes

With all this information in hand, catalytic bis(silyl)ations of alkynes with $Me_3SiSiMe_3$ were carried out. Diphenylacetylene and $Me_3SiSiMe_3$ were selected as model substrates for the initial optimization of the reaction parameters. A 100% stereoselective conversion into **2.7** (yield = 94%) was observed using 1 mol% of **2.4** (100 °C for 24 h in C_6D_6) (Table 2.1).[37]

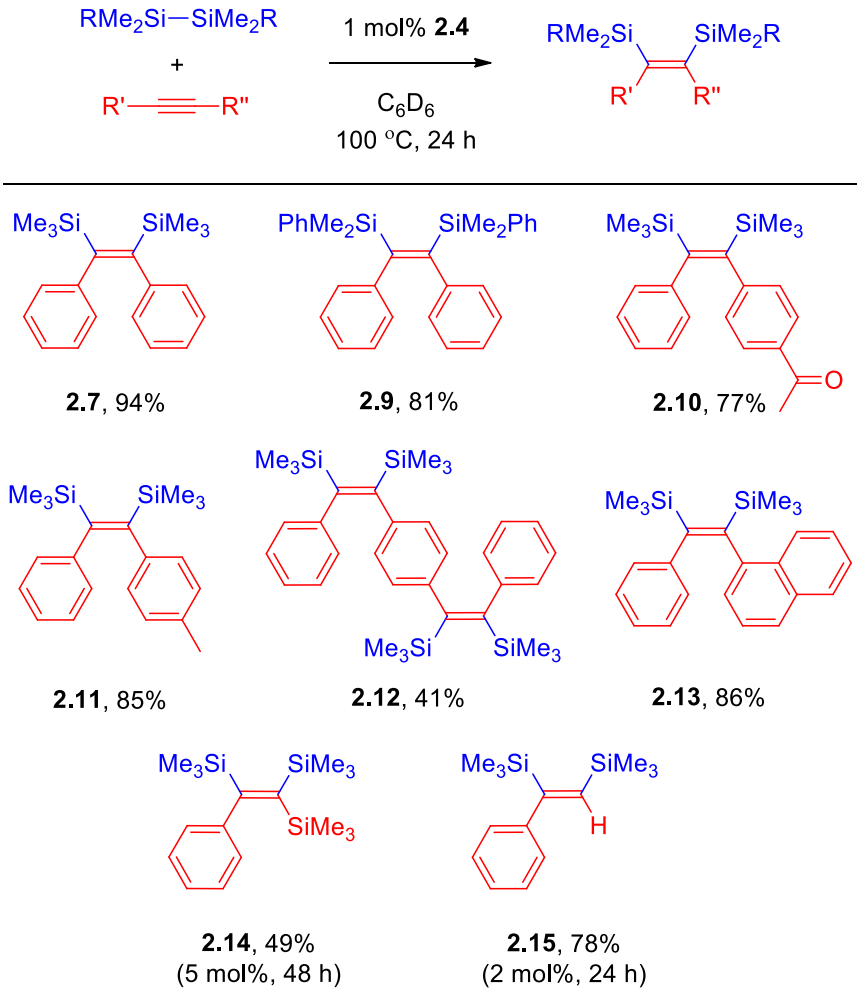


Table 2.1 Catalytic bis(silyl)ation of internal and terminal alkynes employing **2.4** as a catalyst

This reaction is the first reported catalytic synthesis of **2.7**. To test the versatility of **2.4** towards a range of challenging electronic and steric factors surrounding the C≡C bond, a series of internal alkynes and non-activated disilanes were also used as substrates. For instance, the reaction of diphenylacetylene and excess of $PhMe_2SiSiMe_2Ph$ yielded compound **2.9**. The only synthesis reported for this compound involved the stoichiometric reaction of *cis*-$[(PPh_2Me)_2Pt(SiMe_2Ph)_2]$ with diphenylacetylene.[42] The novel compounds **2.10**, **2.11**, **2.12** and **2.13** were all synthesized as *Z*-isomers from the corresponding unsymmetrical internal acetylenes and excess $Me_3SiSiMe_3$, as established by NOESY NMR experiments or X-ray crystallography (Table 2.1).

Compound **2.12** was synthesized with greater than 90% conversion into the desired product. However, its isolation from the crude reaction mixture proved troublesome, and after numerous attempts a maximum of 41% of the desired compound was obtained. During spectroscopic analysis of **2.12**, broad double resonances for the aromatic protons were noted in a 4:1 ratio, as deduced by the integration of these signals. A plausible rationale behind this observation is free-rotation around the two alkenes which results in two conformational isomers, **2.12a** and **2.12b** (Figure 2.4).[43]

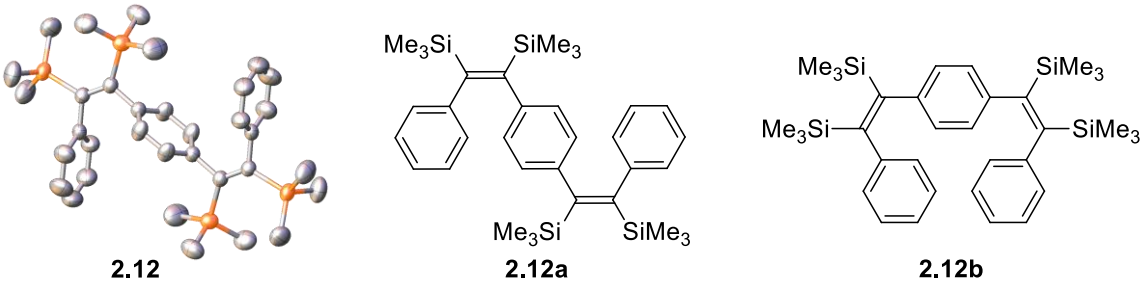


Figure 2.4 X-ray crystal structure and possible rotational isomers of **2.12**

A variable-temperature ^1H NMR study was subsequently undertaken to determine the co-existence of multiple conformers on the NMR time scale (Figure 2.5). At low

temperatures, ≤15 °C, all resonances sharpened with the multiplicity of the minor signals identical to the corresponding major signals. These data were consistent with the slowing down of the rotation rate around the alkenes. Upon elevating the temperature to ≥50 °C the minor isomer receded. This implied the rotation was sufficiently fast that energetically a single conformer was favoured, likely to be the least sterically hindered structure **2.12a**.[44,45]

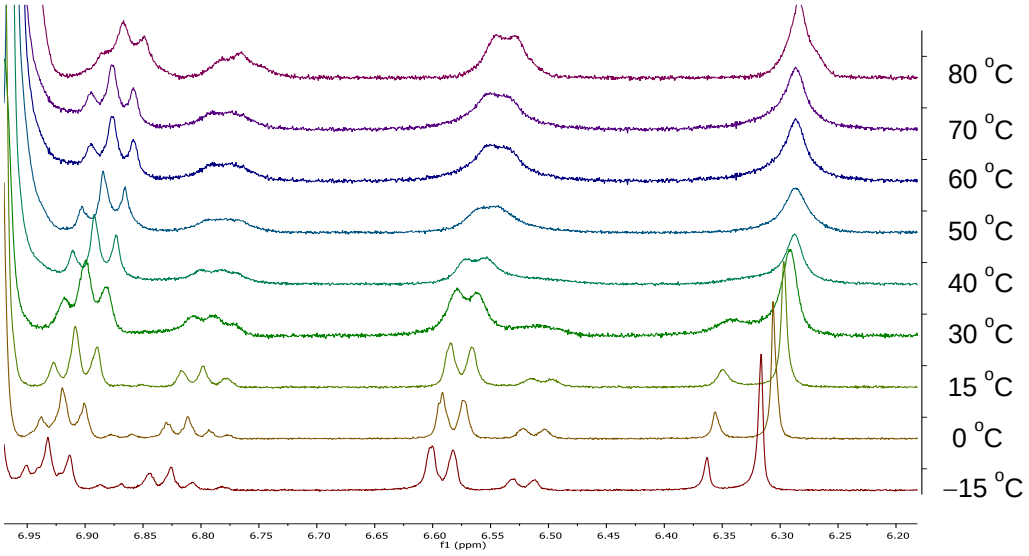
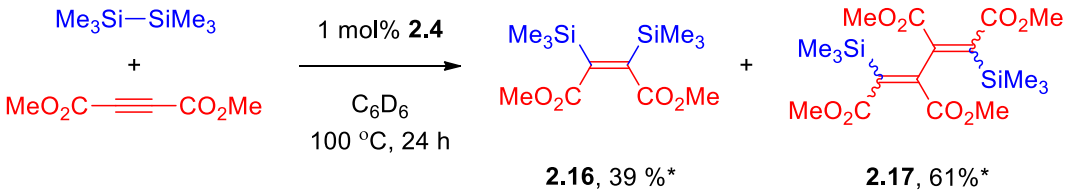


Figure 2.5 Variable-temperature ^{1}H NMR spectra for **2.12** ranging from –15-80 °C

The reaction of $Me_3SiSiMe_3$ with 1-phenyl-2-trimethylsilylacetylene resulted in the formation of **2.14** (49% yield), but it required a considerable increase in catalyst loading and reaction time. The only previous reported synthesis of **2.14** required either stoichiometric addition of Grignard reagents with acetylenes,[46] or the addition of methyl lithium to silyldisilacyclobutene.[47] The protocol was applied to a terminal alkyne, phenylacetylene, affording compound **2.15**, which was synthesized in a yield comparable to that of the best catalytic protocol in the literature.[48] Unfortunately, the reaction of $Me_3SiSiMe_3$ with 2-heptyne and 3-(phenylethynyl)thiophene under these reaction conditions gave very low conversion into the desired products (<5%). On the other hand,

the reaction of $Me_3SiSiMe_3$ with dimethyl acetylenedicarboxylate resulted in the isolation of two products, the bis(silyl)ation alkene adduct **2.16** and the novel 1,4-disilyl diene **2.17** (Scheme 2.9). To date, attempts to crystallize **2.17** remain unsuccessful and therefore the exact stereochemistry is unknown. Examples of palladium catalysed dimerization of dimethyl acetylenedicarboxylate are known in the literature, however, these are limited to the use of strained cyclic disilanes.[49,50]

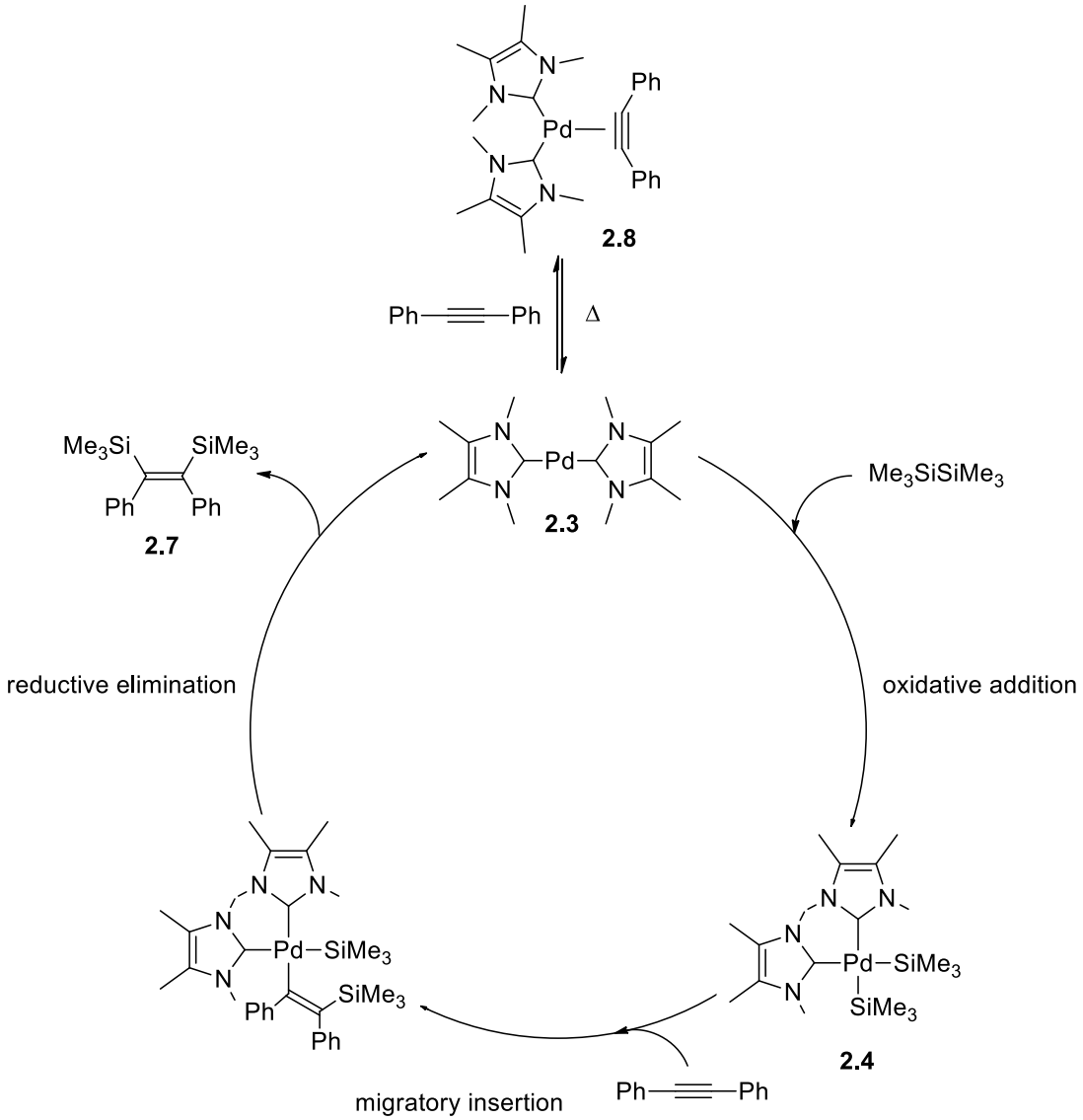


*conversions with respect to dimethyl acetylenedicarboxylate

Scheme 2.9 Bis(silyl)ation of dimethyl acetylenedicarboxylate

2.4.1 Proposed Catalytic Cycle for Bis(silyl)ation

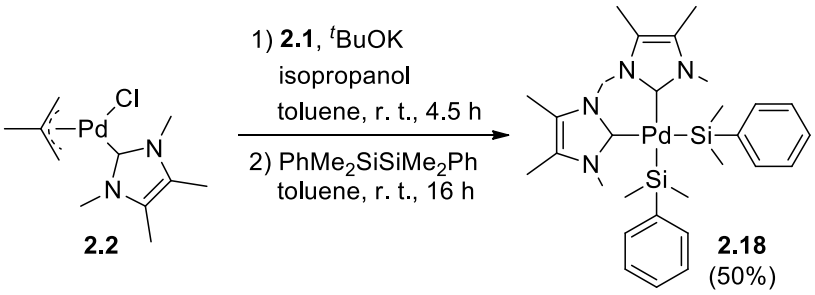
The results from the catalytic reactions and the isolation of **2.4** and **2.7** prompted the proposal of a catalytic cycle, in which **2.3** is the catalytic active species. This 14-electron species can oxidatively add $Me_3SiSiMe_3$, thus yielding **2.4**, followed by a migratory insertion of the alkyne into a Pd-silyl bond to give the corresponding vinyl-palladium-silyl complex.[51–53] This complex would be stabilized by a weak interaction between the silicon from the vinylsilyl moiety and the palladium centre,[54] thus allowing a stereoselective reductive elimination to yield **2.7**. The coordination of diphenylacetylene to **2.3** affords **2.8**, which could be considered the resting state of **2.3** (Scheme 2.10). This mechanism differs from what was known in the literature as it is proposed that the NHCs stay coordinated throughout the catalytic cycle.



Scheme 2.10 Proposed catalytic cycle with **2.3** as the active catalyst

2.5 Synthesis of [(NHC)$_2$Pd(SiR$_3$)$_2$] Analogues

It was possible to extend the methodology in the synthesis of **2.4** to other non-activated disilanes. Replacing $Me_3SiSiMe_3$ with 1,1,2,2-tetramethyl-1,2-diphenyldisilane and 1,2-bis(2-methoxyphenyl)-1,1,2,2-tetramethyldisilane afforded **2.18** and **2.19**, respectively. **2.18** was synthesized under the same conditions as **2.4** and was isolated with moderate yields (50%) (Scheme 2.11).



Scheme 2.11 Formation of **2.18**

Single crystals of **2.18** were acquired from a saturated toluene/benzene (10:1) solution at room temperature. The X-ray crystal structure of **2.18**, like **2.4**, exhibited a distorted square planar geometry with comparable bond angles surrounding the Pd centre. The carbenic carbon-Pd bond lengths were identical to **2.4** and the Pd-Si bond lengths were marginally shorter (≤0.01 Å) (Figure 2.6).

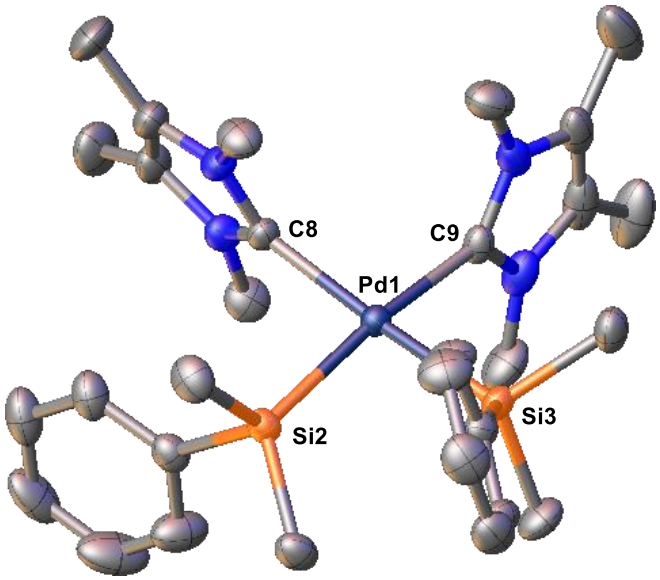
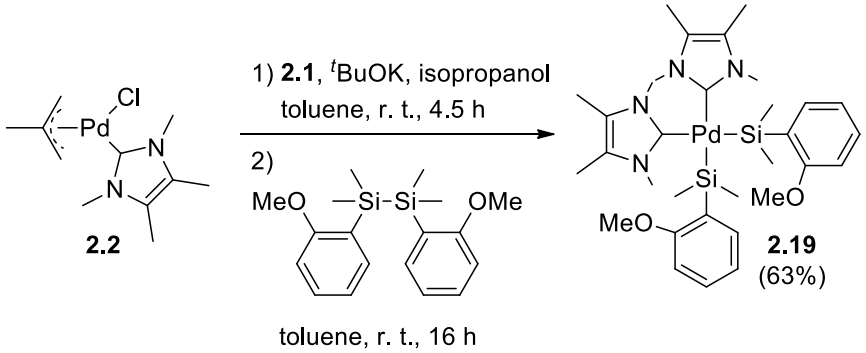


Figure 2.6 Molecular structure of **2.18** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd-Si2 2.3445(8), Pd-Si3 2.3346(8), Pd-C8 2.105(3), Pd-C9 2.123(3); Si2-Pd-Si3 89.81(3), C8-Pd-Si2 89.34(8), C9-Pd-Si3 89.68(8), C8-Pd-C9 92.60(11).

The synthesis of **2.19** required an elevated temperature of 60 °C on adding the disilane to **2.3**. An identical work-up procedure was employed to give **2.19** in a 63% yield (Scheme 2.12). The isolation of single crystals that were suitable for X-ray analysis was unsuccessful. The *cis*-configuration was assumed based on the known structures of **2.4** and **2.18**.



Scheme 2.12 Formation of **2.19**

The $^{13}C\{^1H\}$ NMR resonance for the carbeneic carbon in **2.4**, **2.18** and **2.19** was 196.7, 193.4 and 194.4 ppm, respectively. The insignificant differences between the X-ray crystallographic data and $^{13}C\{^1H\}$ NMR shifts did not give any indication as to the potential diversity in reactivity between these three complexes. The disilane, 1,2-bis(dimethylamino)tetramethyldisilane, was not oxidatively cleaved by **2.3**, an observation that was attributed to the high nucleophilic character of the amino groups.

2.6 Conclusions

In conclusion, the first NHC-bearing complex resulting from the oxidative addition of $Me_3SiSiMe_3$ to a palladium centre was synthesized under mild reaction conditions. This complex was used as a pre-catalyst for the bis(silyl)ation of electronically and sterically challenging internal acetylenes using non-activated disilanes. A series of novel 1,2-disilylstilbenes were synthesized in high yield and with 100% Z-stereoselectivity. Much

of this work is published in *Angewandte Chemie International Edition*.[55] It was also possible to oxidatively cleave the Si-Si bond in other non-activated disilanes utilizing **2.3**. Future work will include a comparative reactivity study into the ability of these complexes to mediate the bis(silyl)ation of alkynes.

2.7 Experimental Details for Chapter 2

General experimental details are given in appendix A1.

2.7.1 Improved Synthesis of 1,3,4,5-tetramethylimidazol-2-thione

A microwave vial was charged with *N*,*N*'dimethylthiourea (4.34 g, 41.67 mmol), acetoin (3.74 g, 42.43 mmol), 1 spatula of $MgSO_4$ and 1-hexanol (60.0 mL). The resulting mixture was heated in the microwave at 185 ^oC for 20 mins (Dynamic mode – 300 W). After removing all volatiles, the resulting off-white solid was washed with cold diethyl ether (3 x 20.0 mL). Yield: 5.70 g, 76%. ^1H NMR (399.5 MHz, C_6D_6): δ_H = 3.13 [s, 6H, N(1,3)-C**H**$_3$], 1.25 [s, 6H, C(4,5)-C**H**$_3$]. ^1H NMR (499.9 MHz, $CDCl_3$): δ_H = 3.55 [s, 6H, N(1,3)-C**H**$_3$], 2.09 [s, 6H, C(4,5)-C**H**$_3$]. $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$): δ_C = 161.8 [**C**(2)], 121.1 [C(4,5)], 32.3 [N(1,3)-**C**H_3], 9.6 [C(4,5)-**C**H_3].

2.7.2 Improved Synthesis of 1,3,4,5-tetramethylimidazol-2-ylidene (ITMe, 2.1)

In an ampoule, 1,3,4,5-tetramethylimidazol-2-thione (1.50 g, 9.58 mmol) and potassium (0.95 g, 24.30 mmol) were suspended in 2-methyl THF (45.0 mL). The resulting reaction mixture was heated to 100 ^oC for 20 h. After cooling the mixture was filtered by an air-sensitive frit, the volatiles were removed in vacuo and the resulting off-white solid was dried under vacuum. Yield: 1.02 g, 86%. ^1H NMR (399.5 MHz, C_6D_6): δ_H = 3.37 [s, 6H, N(1,3)-C**H**$_3$], 1.60 [s, 6H, C(4,5)-C**H**$_3$].

2.7.3 Synthesis of [(ITMe)Pd(methallyl)Cl] (2.2)

[(Pd{methallyl}Cl)$_2$] (0.44 g, 1.12 mmol) in toluene (20.0 mL) was cooled to –25 ^{o}C. A toluene (15.0 mL) solution of **2.1** (0.28 g, 2.225 mmol) was added dropwise over a 20 min period. After stirring at –25 ^{o}C under an Ar atmosphere for 1 h, the reaction mixture was then allowed to warm to room temperature and stirred for a further 1.5 h. The solution was then filtered by cannula, volatiles were removed in vacuo and the pale brown-grey solid was washed with hexanes (3 x 10.0 mL). Yield: 0.68 g, 95%. ^{1}H NMR (399.5 MHz, C_6D_6): δ_H = 4.18 [s, 1H, **H**$_2$CCMeCH$_2$], 3.27 [s, 6H, N(1,3)-C**H$_3$**], 3.25 [s, 1H, **H**$_2$CCMeCH$_2$], 2.86 [s, 1H, H2CCMeC**H**$_2$], 2.16 [s, 1H, H$_2$CCMeC**H**$_2$], 1.73 [s, 3H, H$_2$CC**Me**CH$_2$], 1.33 [s, 6H, C(4,5)-C**H$_3$**]. ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6): δ_C = 178.7 [**C**(2)], 124.6 [**C**(4,5)], 124.6 [H$_2$C**C**MeCH$_2$], 70.3 [H$_2$**C**CMeCH$_2$], 47.1 [H$_2$CCMe**C**H$_2$], 35.1 [N(1,3)-**C**H$_3$], 23.7 [H$_2$CC**Me**CH$_2$], 8.5 [C(4,5)-**C**H$_3$]. Elem. Anal.: Calcd for $C_{11}H_{19}N_2ClPd$: C, 41.10%; H, 5.96%; N, 8.72%. Found: C, 40.98%; H, 5.92%; N, 8.75%.

2.7.4 Synthesis of *cis*-[Pd(ITMe)$_2$(SiMe$_3$)$_2$] (2.4)

In the glove box **2.2** (0.50 g, 1.55 mmol), ^{t}BuOK (0.17 g, 1.55 mmol) and **2.1** (0.20 g, 1.57 mmol) were suspended in toluene (20.0 mL). An isopropanol (0.09 g, 1.55 mmol) toluene (5.0 mL) solution was added and the reaction mixture was stirred at room temperature for 4.5 h. $Me_3SiSiMe_3$ (1.14 g, 7.81 mmol) was then added and the solution stirred for a further 18 h. The mixture was then filtered by cannula, volatiles were removed in vacuo and the resulting off-white solid was washed with hexane (3 x 5.0 mL). Yield: 0.48 g, 62%. ^{1}H NMR (399.5 MHz, C_6D_6): δ_H = 3.35 [s, 12H, N(1,3)-C**H$_3$**], 1.41 [s, 12H, C(4,5)-C**H$_3$**], 0.59 [s, 18 H, Si**Me$_3$**]. ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6): δ_C = 196.7 [**C**(2)], 123.6 [**C**(4,5)], 35.2 [N(1,3)-**C**H$_3$], 9.5 [C(4,5)-**C**H$_3$], 8.8 [Si**Me$_3$**]. ^{29}Si{^{1}H}

NMR (79.4 MHz, C_6D_6): δ_{Si} = 0.46. Elem. Anal.: Calcd for $C_{20}H_{42}N_4Si_2Pd$: C, 47.93%; H, 8.45%; N, 11.18%. Found: C, 47.96%; H, 8.51%; N, 11.04%.

Crystal data for **2.4**: $C_{20}H_{42}N_4PdSi_2$, M_r = 501.15 g mol^{-1}, triclinic, space group P-1 (no. 2), a = 9.7136(4) Å, b = 10.2767(6) Å, c = 20.1800(7) Å, α = 91.163(5)°, β = 100.298(4)°, γ = 108.564(4)°, V = 1463.19(13) Å^3, Z = 2, T = 173 K, λCu(Kα) = 1.5184, R_1 [$I > 2\sigma(I)$] = 0.0271, wR_2 (all data) = 0.0659, $GooF$ = 0.996.

2.7.5 Synthesis of [Pd^0(cod)(ma)]

$[Pd_2(dba)_3]$ (0.40 g, 0.44 mmol), ma (0.17 g, 1.75 mmol) and 1,5-cyclooctadiene (0.54 mL, 4.37 mmol) were suspended in dry acetone (10.0 mL). This reaction mixture was then left to stir under a N_2 atmosphere at room temperature for 50 mins. The reaction mixture was then filtered *via* cannula and the solution was concentrated. Dry diethyl ether (10.0 mL) was then added and the mixture was cooled in an ice bath. The resulting yellow crystals were collected by filtration and dried in vacuo. Yield: 0.04 g, 15%. ^{1}H NMR (499.9 MHz, $\{CD_3\}_2CO$): δ_H = 5.83 [m, 4H, cod-C**H**], 4.40 [s, 2H, ma-C**H**], 2.44 [m, 8H, cod-C**H$_2$**].

2.7.6 Synthesis of [(ITMe)$_2$Pd^0(ma)] (2.5)

To a stirred solution of [Pd^0(cod)(ma)] (0.04 g, 0.11 mmol) in THF (5.0 mL) at –84 °C, a solution of **2.1** (0.03 g, 0.22 mmol) in THF (5.0 mL) was added dropwise over a 10-minute period. The reaction mixture was stirred at ≤ –50 °C for 2 h under a N_2 atmosphere. The reaction mixture was warmed to room temperature and concentrated. A pink solid precipitated upon the addition of dry diethyl ether (10.0 mL), it was collected by filtration and washed with dry diethyl ether (2 x 10.0 mL). Yield: 0.03 g, 66%. ^{1}H NMR (499.9 MHz, C_6D_6): δ_H = 3.91 [s, 2H, MAH-C**H**], 3.26 [s, 12H, N(1,3)-C**H$_3$**], 1.34 [s, 12H,

C(4,5)-C**H**$_3$]. ^{1}H NMR (399.5 MHz, {CD_3}$_2$CO): δ_H = 3.62 [s, 12H, N(1,3)-C**H**$_3$], 3.37 [s, 2H, MAH-C**H**], 2.09 [s, 12H, C(4,5)-C**H**$_3$].

2.7.7 Attempted Reaction of 2.5 with $Me_3SiSiMe_3$

In a J Young tap NMR tube, **2.5** (0.003 g, 7.07 µmol) and $Me_3SiSiMe_3$ (0.011 g, 71.73 µmol) were dissolved in C_6D_6 (0.7 mL). The reaction mixture was stirred at room temperature under an N_2 atmosphere for 3 days and heated at 80 ^{o}C for 21 h. Visually, large quantities of elemental palladium started to form, and the absence of resonances in NMR spectrum suggested complete decomposition.

2.7.8 Synthesis of [Pd^0(IPr)$_2$] (2.6)

In a J Young tap NMR tube, [(Pd^0{IPr}{nq})$_2$] (0.002 g, 1.15 µmol) and $Me_3SiSiMe_3$ (0.004 g, 28.70 µmol) were dissolved in C_6D_6 (1.0 mL). The resulting reaction mixture was stirred at room temperature for 24 h and heated at 80 ^{o}C for 5 days. After cooling, the solution was filtered through flame dried Celite, the filtrate volatiles were removed in vacuo and an orange solid was isolated. Yield: 0.001, 51%. ^{1}H NMR (399.5 MHz, C_6D_6): δ_H = 7.29 [t, $^3J_{HH}$ = 7.8 Hz, 4H, *p*-Ph**H**], 7.09 [d, $^3J_{HH}$ = 7.6 Hz, 8H, *m*-Ph**H**], 6.22 [s, 4H, NHC-C**H**], 2.89 [sept, $^3J_{HH}$ = 7.0 Hz, 8H, C**H**(CH_3)$_2$], 1.21 [d, $^3J_{HH}$ = 7.0 Hz, 24H, CH(C**H**$_3$)$_2$], 1.12 (d, $^3J_{HH}$ = 7.0 Hz, 24H, CH(C**H**$_3$)$_2$]. ^{13}C{^{1}H} NMR (125.7 MHz, C_6D_6): δ_C = 199.3 [N**C**N], 1.46.1 [Ph**C**], 139.2 [Ph**C**], 128.6 [*p*-Ph**C**H], 123.4 [*m*-Ph**C**H], 121.2 [NHC-**C**H], 28.7 [**C**H(CH_3)$_2$], 25.2 [CH(**C**H$_3$)$_2$], 24.1 [CH(**C**H$_3$)$_2$].

2.7.9 Heating of 2.4

In a J Young tap NMR tube a solution of **2.4** (0.01 g, 19.36 µmol) in C_6D_6 (0.7 mL) was heated in a heating block to 85 ^{o}C over 24 h. This resulted in partial reductive elimination

to **2.3** and $Me_3SiSiMe_3$. The maximum conversion to **2.3** and $Me_3SiSiMe_3$ was observed as 69% (suggested by integration of the $SiMe_3$ resonances in the ^1H NMR spectrum). Heating to higher temperatures (95 ^oC) did not supersede this conversion. A small quantity of $Me_3SiOSiMe_3$ was observed over times (9% of all $SiMe_3$ present).

2.3: ^1H NMR (399.5 MHz, C_6D_6): δ_H = 3.93 [s, 12H, N(1,3)-C**H$_3$**], 1.55 [s, 12H, C(4,5)-C**H$_3$**].

2.4: ^1H NMR (399.5 MHz, C_6D_6): δ_H = 3.35 [s, 12H, N(1,3)-C**H$_3$**], 1.42 [s, 12H, C(4,5)-C**H$_3$**], 0.58 [s, 18H, Si**Me$_3$**].

$Me_3SiSiMe_3$: ^1H NMR (399.5 MHz, C_6D_6): δ_H = 0.08 [s, 18H, Si**Me$_3$**].

$Me_3SiOSiMe_3$: ^1H NMR (399.5 MHz, C_6D_6): δ_H = 0.12 [s, 18H, Si**Me$_3$**].

2.7.10 Synthesis of (*Z*)-1,2-diphenyl-1,2-bis(trimethylsilyl)ethene (2.7) and [Pd(ITMe)$_2$(PhC≡CPh)] (2.8)

Isolation of 2.8

In an ampoule, a solution of **2.4** (0.05 g, 96.4 µmol) and diphenylacetylene (0.03 g, 193.0 µmol) in C_6D_6 (5.0 mL) was stirred at ambient temperature for 30 h. The volatiles were then removed in vacuo. The resulting yellow solid was washed with hexane (3 x 10.0 mL). Yield: 0.04 g, 70%. ^1H NMR (399.5 MHz, C_6D_6): δ_H = 7.99 [dd, $^3J_{HH}$ = 9.1, $^4J_{HH}$ = 1.3 Hz, 4H, *m*-C_6H_5], 7.27 [m, 4H, *o*-C_6H_5], 7.05 (tt, $^3J_{HH}$ = 7.3, $^4J_{HH}$ = 1.2 Hz, 2H, *p*-C_6H_5], 3.49 [s, 12H, N(1,3)-C**H$_3$**], 1.54 [s, 12H, C(4,5)-C**H$_3$**]. $^{13}C\{^1H\}$ NMR (100.5 MHz, C_6D_6): δ_C = 198.7 [**C**(2)], 138.6 [**C**≡C], 130.1 [*o*-C_6H_5], 128.2 [*m*-C_6H_5], 126.3 [*i*-C_6H_5], 124.2 [*p*-C_6H_5], 123.1 [**C**(4,5)], 35.2 [N(1,3)-**C**H_3], 8.0 [C(4,5)-**C**H_3]. Elem. Anal.: Calcd for $C_{28}H_{34}N_4Pd$: C, 63.03%; H, 6.43%; N, 10.51%. Found: C, 62.87%; H, 6.56%; N, 10.46%.

Crystal data for **2.8**: $C_{28}H_{43}N_4Pd$, M_r = 532.99 g mol^{-1}, triclinic, space group P-1 (no. 2), a = 10.3873(6) Å, b = 11.4638(5) Å, c = 11.6798(5) Å, α = 68.640(4)°, β = 87.052(4)°, γ = 88.047(4)°, V = 1293.37(11) Å^3, Z = 2, T = 173 K, λCu(Kα) = 1.5184, R_1 [$I > 2\sigma(I)$] = 0.0281, wR_2 (all data) = 0.0702, *GooF* = 1.019.

Isolation of 2.7

The hexane washes from the previous reaction were concentrated down and washed with water (3 x 1.0 mL). The organic layer was collected and dried with anhydrous $MgSO_4$. After filtering and washing the $MgSO_4$ with hexane (3 x 5.0 mL). The filtrate's volatiles were removed in vacuo to reveal a white crystalline solid. Melting point: 87.4 – 88.7 °C. Yield: 0.02 g, 59%. ^{1}H NMR (399.5 MHz, C_6D_6): δ_H = 6.93 [m, 4H, *o*-C_6H_4], 6.76 [m, 2H, *p*-C_6H_4], 6.69 [m, 4H, *m*-C_6H_4], 0.21 [s, 18H, Si**Me$_3$**]. ^{1}H NMR (499.9 MHz, $CDCl_3$): δ_H = 6.97 [m, 4H, C_6H_5], 6.85 [m, 2H, *p*-C_6H_5], 6.63 [m, 4H, C_6H_5], 0.13 [s, 18H, Si**Me$_3$**]. ^{1}H NMR (399.5 MHz, CCl_4): δ_H = 6.73 [m, 10H, C_6H_5], 0.15 [s, 18H, Si**Me$_3$**]. ^{13}C{^{1}H} NMR (125.7 MHz, C_6D_6): δ_C = 158.9 [C=C]. 146.8 [*i*-C_6H_5], 128.4 [*m*-C_6H_5], 127.6 [*o*-C_6H_5], 124.8 [*p*-C_6H_5], 1.8 [Si**Me$_3$**]. ^{29}Si{^{1}H} NMR (79.4 MHz, C_6D_6): δ_{Si} = –7.75. Elem. Anal.: Calcd for $C_{20}H_{28}Si_2$: C, 74.00%, H, 8.69%. Found: C, 73.86%; H, 8.63%. HRMS (APCI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{28}SiH$ 325.1802; Found 325.1809.

Crystal data for **2.7**: $C_{20}H_{28}Si_2$, M_r = 324.60 g mol^{-1}, monoclinic, space group I2/a, a = 14.9857(7) Å, b = 11.5692(5) Å, c = 22.8580(12) Å, α = 90°, β = 91.020(5)°, γ = 90°, V = 3962.2(3) Å^3, Z = 8, T = 173 K, λCu(Kα) = 1.5184, R_1 [$I > 2\sigma(I)$] = 0.0517, wR_2 (all data) = 0.1326, *GooF* = 1.061.

2.7.11 Synthesis of 2.4 and 2.7 from 2.8

Isolation of 2.4

In an ampoule, **2.7** (0.02 g, 41.28 µmol) and $Me_3SiSiMe_3$ (0.03 g, 206.31 µmol) in toluene (5.0 mL) under a N_2 atmosphere was heated at 50 ^oC for 5days. On cooling the volatiles were removed in vacuo and the off-white solid was washed with hexane (3 x 3.0 mL). Yield: 0.015 g, 74%. ^1H NMR (399.5 MHz, C_6D_6): δ_H = 3.34 [s, 12H, N(1,3)-C**H**$_3$], 1.41 [s, 12H, C(4,5)-C**H**$_3$], 0.59 [s, 18H, Si**Me**$_3$].

Isolation of 2.7

The hexane washes from the previous reaction were concentrated and washed with water (3 x 15.0 mL). The organic layer was collected and its volatiles were removed in vacuo to reveal **2.7**, a white crystalline solid. Yield: 0.01 g, 77%. ^1H NMR (399.5 MHz, C_6D_6): δ_H = 6.93 [m, 4H, *o*-C_6H_5], 6.77 [m, 2H, *p*-C_6H_5], 6.70 [m, 4H, *m*-C_6H_5], 0.21 [s, 18H, Si**Me**$_3$].

Catalysis using 2.4 (1 mol%)

2.7.12 Synthesis of 2.7

In separate ampoules two reacton mixture containing $Me_3SiSiMe_3$ (153.0 µL, 0.75 mmol), diphenylacetylene (0.05 g, 0.25 mmol) and **2.4** (0.001 g, 2.49 µmol) in C_6D_6 (0.25 mL) was heated to 100 ^oC for 24 h under a N_2 atmosphere. After cooling the samples were combined. The volatiles were removed in vacuo to reveal an off-white solid. This was re-dissolved in hexane (30.0 mL), filtered through a plug of silica and washed with H_2O (3 x 20.0 mL). The hexane solution was collected and its volatiles were removed in vacuo. The resulting off-white solid was washed with water (1 x 20.0 mL) and dried under vacuum. A white powdered solid resulted. Yield: 0.37 g, 94%. ^1H NMR (399.5 MHz,

C_6D_6): δ_H = 6.92 [m, 4H, C_6H_5], 6.76 [m, 2H, *p*-C_6H_5], 6.70 [m, 4H, C_6H_5], 0.21 [s, 18H, Si**Me**$_3$].

2.7.13 Synthesis of (*Z*)-1,2-bis(dimethyl(phenyl)silyl)-1,2-diphenylethene (2.9)

In an ampoule, a mixture of $PhMe_2SiSiMe_2Ph$ (0.10 g, 0.37 mmol), diphenylacetylene (0.05 g, 0.25 mmol) and **2.4** (0.001 g, 2.49 µmol) in C_6D_6 (0.25 mL) was heated to 100 ^oC for 24 h under a N_2 atomsphere. After cooling the volatiles were removed in vacuo. The resulting solid was re-dissolved in hexane (30.0 mL) and subsequently washed with H_2O (3 x 20.0 mL). The organic fraction was collected and concentrated. The crude material was purified on silica gel (hexane) to afford pure white powdered solid. Yield: 0.18 g, 81%. ^{1}H NMR (399.5 MHz, $CDCl_3$): δ_H = 7.47 [m, 4H], 7.32 [m, 6H], 6.92 [m, 4H], 6.83 [m, 2H], 6.67 [m, 2H], 0.09 [s, 12H, Si**Me$_2$**Ph]. ^{1}H NMR (399.5 MHz, C_6D_6): δ_H = 7.57 [m, 4H], 7.23 [m, 6H], 6.87 [m, 4H], 6.78-6.70 [m, 6H], 0.21 [s, 12H, Si**Me$_2$**Ph]. $^{13}C\{^1H\}$ NMR (125.7 MHz, C_6D_6): δ_C = 158.9 [**C**=C], 146.4 [*i*-Ph], 139.9 [$SiMe_2$**Ph**], 134.9 [$SiMe_2$**Ph**], 129.7 [$SiMe_2$**Ph**], 128.7 [$SiMe_2$**Ph**], 128.4 [Ph], 127.5 [Ph], 125.0 [*p*-Ph], 1.0 [Si**Me$_2$**Ph].

2.7.14 Synthesis of (*Z*)-1-(4-(2-phenyl-1,2-bis(trimethylsilyl)vinyl)phenyl)ethenone (2.10)

In an ampoule, a mixture of 1-(4-(phennylethynl)phenyl)ethenone (0.04 g, 0.19 mmol), $Me_3SiSiMe_3$ (59.0 µL, 0.29 mmol) and **2.4** (0.001 g, 1.94 µmol) in C_6D_6 (0.2 mL) was heated to 100 ^oC for 24 h under a N_2 atmosphere. After cooling the volatiles were removed in vacuo. The purple solid was re-dissolved in chloroform (20.0 mL) and washed with H_2O (3 x 20.0 mL). The chloroform fraction was collected and filtered through a plug of silica. The resulting filtrates solvent was removed in vacuo to reveal a pale yellow

crystalline solid. This was washed with H_2O (15.0 mL) and dried under vacuum. Melting point: 65.1 – 68.3 ºC. Yield: 0.05 g, 74%. ^{1}H NMR (399.5 MHz, C_6D_6): δ_H = 7.60 [m, 2H, *m*-$C_6H_4C(O)CH_3$], 6.931 [m, 2H, *m*-C_6H_5], 6.74 [m, 1H, *p*-C_6H_5], 6.67 [m, 2H, *o*-$C_6H_4C(O)CH_3$], 6.64 [m, 2H *o*-C_6H_5], 1.92 [s, 3H, C6H4C(O)C**H$_3$**], 0.19 [s, 9H, Si**Me$_3$**], 0.17 [s, 9H, Si**Me$_3$**]. ^{1}H NMR (399.5 MHz, $CDCl_3$): δ_H = 7.60 [d, $^3J_{HH}$ = 8.0 Hz, 2H, *m*-$C_6H_4C(O)CH_3$], 6.97 [m, 2H, *m*-C_6H_5], 6.85 [m, 1H, *p*-C_6H_5], 6.74 [d, $^3J_{HH}$ = 8.0Hz, *o*-$C_6H_4C(O)CH_3$], 6.62 [m, 2H, *o*-C_6H_5], 2.46 [s, 3H, $C_6H_4C(O)C$**H$_3$**], 0.14 [s, 9H, Si**Me$_3$**], 0.14 [s, 3H, Si**Me$_3$**]. ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6): δ_C = 195.8 [C_6H_4**C**$(O)CH_3$], 159.5 [Ph**C**=C], 158.1 [PhC=**C**], 152.0 [*i*-$C_6H_4C(O)CH_3$], 146.4 [*i*-C_6H_5], 134.3 [*p*-$C_6H_4C(O)CH_3$], 128.4 [*o*-$C_6H_4C(O)CH_3$], 128.1 [*m*-$C_6H_4C(O)CH_3$], 127.8 [*o*-C_6H_5], 127.7 [*m*-C_6H_5], 25.8 [$C_6H_4C(O)$**C**H_3], 1.7 [Si**Me$_3$**], 1.7 [Si**Me$_3$**]. ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$): δ_C = 198.0 [C_6H_4**C**$(O)CH_3$], 159.4 [Ph(Me_3Si)**C**=C], 157.7 [Ph(Me_3Si)C=**C**], 152.6 [*i*-$C_6H_4C(O)CH_3$], 146.2 [*i*-C_6H_5], 133.6 [*p*-$C_6H_4C(O)CH_3$], 128.1 [*o*-$C_6H_4C(O)CH_3$], 127.6 [*o*-C_6H_5], 127.6 [*m*-$C_6H_4C(O)CH_3$], 127.4 [*m*-C_6H_5], 124.7 [*p*-C_6H_5], 26.5 [$C_6H_4C(O)$**C**H_3], 1.7 [Si**Me$_3$**], 1.6 [Si**Me$_3$**]. ^{29}Si{^{1}H} NMR, 79.4 MHz, C_6D_6): δ_{Si} = –7.38 [$SiMe_3$], –7.77 [$SiMe_3$], Elem. Anal.: Calcd for $C_{22}H_{30}OSi_2$: C, 72.07%; H, 8.25%. Found: C, 72.02%; H, 8.37%. HRMS (APCI) m/z $[M+H]^+$ Calcd for $C_{22}H_{20}Si_2OH$ 367.1908; Found 367.1907

2.7.15 Synthesis of (*Z*)-(1-phenyl-2-(*p*-tolyl)ethene-1,2-diyl)bis(trimethylsilane) (2.11)

In an ampoule, a mixture of $Me_3SiSiMe_3$ (54.0 µl, 0.26 mmol), 1-methyl-4-(phenylethynyl)benzene (0.03 g, 0.18 mmol) and **2.4** (0.001 g, 1.80 µmol) in C_6D_6 (0.25 mL) was heated to 100 ºC for 24 h under a N_2 atmosphere. After cooling the volatiles were removed in vacuo. The resulting solid was re-dissolved in $CHCl_3$ (20.0 mL), filtered

through a plug of silica and washed with H_2O (30.0 mL). The organic fraction was collected, the volatiles removed and the resulting off-white powdered solid was washed with H_2O (20.0 mL). Melting point: 62.2 - 64.6 °C. Yield: 0.05 g, 90%. ^{1}H NMR (399.5 MHz, C_6D_6): δ_H = 6.94 [m, 2H, *m*-C_6H_5], 6.74 [m, 5H, C_6H_5], 6.64 [m, 2H, *o*- $C_6H_4CH_3$], 1.92 [s, 3H, $C_6H_4C\mathbf{H_3}$], 0.24 [s, 9H, Si**Me$_3$**], 0.22 [s, 9H, Si**Me$_3$**]. ^{1}H NMR (399.5 MHz, $CDCl_3$): δ_H = 6.98 [m, 2H, *m*- C_6H_5], 6.86 [m, 2H, *p*-C_6H_5], 6.77 [d, $^3J_{HH}$ = 7.6 Hz, 2H, *m*-$C_6H_4CH_3$], 6.63 [m, 2H, *o*-C_6H_5], 6.51 [d, $^3J_{HH}$ = 7.6 Hz, 2H, *o*-$C_6H_4CH_3$], 2.13 [s, 3H, $C_6H_4C\mathbf{H_3}$], 0.12 [s, 9H, Si**Me$_3$**], 0.12 [s, 9H, Si**Me$_3$**]. ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6): δ_C = 158.9 [**C**=**C**], 147.0 [*i*-C_6H_5], 143.8 [*i*- $C_6H_4CH_3$], 133.9 [*p*-$C_6H_4CH_3$], 128.4 [*m*-$C_6H_4CH_3$], 128.1 [*o*-C_6H_5], 128.0 [*o*-$C_6H_4CH_3$], 124.8 [*p*-C_6H_5], 21.0 [$C_6H_4\mathbf{C}H_3$], 1.9 [Si**Me$_3$**], 1.9 [Si**Me$_3$**]. ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$): δ_C = 158.5 [-C=**C**($SiMe_3$)($C_6H_4CH_3$)], 158.4 [(C_6H_5)($SiMe_3$)**C**=C-], 146.8 [*i*-C_6H_5], 143.5 [*i*-$C_6H_4CH_3$], 133.5 [*p*-$C_6H_4CH_3$], 127.9 [*o*-C_6H_5], 127.9 [*m*-$C_6H_4CH_3$], 127.7 [*o*-$C_6H_4CH_3$],127.1 [*m*-C_6H_5], 124.2 [*p*-C_6H_5], 21.4 [$C_6H_4\mathbf{C}H_3$], 1.8 [Si**Me$_3$**], 1.8 [Si**Me$_3$**]. ^{29}Si{^{1}H} (79.4 MHz, C_6D_6): δ_{Si} = −7.84, −7.84. Elem. Anal.: Calcd for $C_{20}H_{30}Si_2$: C, 74.48 %; H, 8.93 %. Found: C, 74.35 %; H, 9.03 %. HRMS (APCI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{30}Si_2H$ 339.1959; Found 339.1965.

2.7.16 Synthesis of 1,4-bis((*Z*)-2-phenyl-1,2-bis(trimethylsilyl)vinyl)benzene (2.12)

1,4-bis(phenylethynyl)bezene (0.05 g, 0.17 mmol), $Me_3SiSiMe_3$ (95.0 µl, 0.46 mmol) and **2.4** (0.002 g, 3.39 µmol) was dissolved in C_6D_6 (0.6 mL). The resulting reaction mixture was heated to 100 °C for 24 h under a N_2 atmosphere. On cooling the volatiles were removed in vacuo. The oily solid was washed with H_2O (20.0 mL) and extracted using $CHCl_3$ (30.0 mL). The organics were collected and filtered through a plug of silica. 1,4-bis((*Z*)-2-phenyl-1,2-bis(trimethylsilyl)vinyl)benzene was obtained by preparative TLC

(100 % hexane). Melting point: 203.4 - 204.5 ºC. Yield: 0.039 g, 41.0 %. ^{1}H NMR (499.9 MHz, $CDCl_3$): δ_H = 6.89 [t, $^{3}J_{HH}$ = 7.7 Hz, 4H, *o*-Ph], 6.77 [t, $^{3}J_{HH}$ = 7.2 Hz, 2H, *p*-Ph], 6.53 [dd, $^{3}J_{HH}$ = 7.4, 0.9 Hz, 4H, *m*-Ph], 6.21 [s, 4H, brid-Ph], 0.08 [s, 18H, Si**Me**$_3$], −0.06 [s, 18H, Si**Me**$_3$]. ^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$): δ_C = 159.1 [C=**C**], 158.0 [**C**=C], 146.7 [*i*-Ph], 142.5 [*i*-brid-Ph], 127.9 [*o*-Ph], 127.1 [*m*-Ph], 126.6 [brid-Ph], 124.1 [*p*-Ph], 1.7 [Si**Me**$_3$], 1.7 [Si**Me**$_3$]. ^{29}Si{^{1}H} NMR (79.4 MHz, $CDCl_3$): δ_{Si} = −7.95. Elem. Anal.: Calcd for $C_{34}H_{50}Si_4$: C, 71.50 %; H, 8.82 %. Found: C, 71.34 %; H, 8.70 %. HRMS (ESI) m/z: [M + Na]+ Calcd for $C_{34}H_{50}Si_4$ 593.2882; Found 593.2890.

Crystal data for **2.12**: 0.67($C_{34}H_{50}Si_4$), M_r = 380.75 g mol^{-1}, monoclinic, space group C2/c, a = 15.2223(6) Å, b = 11.1780(4) Å, c = 21.3358(8) Å, α = 90º, β = 95.192(3)º, γ = 90º, V = 3615.5(2) Å^3, Z = 6, T = 298 K, λMo(Kα) = 0.71073, R_1 [$I > 2\sigma(I)$] = 0.0517, wR_2 (all data) = 0.1733, *GooF* = 0.989.

2.7.17 Synthesis of (*Z*)-(1-(naphthalen-1-yl)-2-phenylethene-1,2-diyl)bis(trimethylsilane) (2.13)

In an ampoule, a mixture of 1-(phenylethynyl)naphthalene (0.08 g, 0.35 mmol), $Me_3SiSiMe_3$ (106.0 μmL, 0.52 mmol) and **2.4** (0.002 g, 3.39 μmol) in C_6D_6 (0.35 mL) was heated to 100 ºC for 24 h under a N_2 atmosphere. After cooling all volatiles were removed in vacuo revealing a brown oil. This was re-dissolved in $CDCl_3$ (20.0 mL), filtered through a plug of silica and washed with H_2O (3 x 20.0 mL). The organic layer was collected, the volatiles removed and the resulting off-white powdered solid was washed with H_2O (20.0 mL). Melting point: 75.2-78.3 ºC. Yield: 0.11 g, 86 %. ^{1}H NMR (499.9 MHz, $CDCl_3$): δ_H = 7.82 [d, $^{3}J_{HH}$ = 8.0 Hz, 1H, 10-NA], 7.62 [d, $^{3}J_{HH}$ = 7.9 Hz, 1H, 7-NA], 7.39 [m, 2H, 4,9-NA], 7.34 [dd, $^{3}J_{HH}$ = 9.1, 7.0 Hz, 1H, 8-NA], 7.15 [dd, $^{3}J_{HH}$ = 8.5, 6.8 Hz, 1H, 3-NA], 6.90 [br, 1H, *m*-C_6H_5], 6.78 [dd, $^{3}J_{HH}$ = 6.9, 1.4 Hz, 1H, 2-NA],

6.69 [br, 1H, *o*-C_6H_5], 6.69 [dd, $^3J_{HH}$ = 8.7, 6.9 MHz, 1H, *p*-C_6H_5], 6.64 [br, 1H, *m*-C_6H_5], 6.52 [br, 1H, *o*-C_6H_5]. $^{13}C\{^1H\}$ (125.7 MHz, $CDCl_3$): δ_C = 160.1 [(Ph)(Me_3Si)**C**=C-], 156.8 [-C=**C**($SiMe_3$)(NA)], 146.4 [*i*-C_6H_5], 144.5 [*i*-NA], 133.3 [5-NA], 131.3 [6-NA], 128.1 [7-NA], 128.1, 126.8 [10-NA], 126.8, 125.2 [4-NA], 125.2, 125.2, 125.2 [8-NA], 124.8 [2-NA], 124.8 [9-NA], 124.8, 124.4 [3-NA], 124.4. $^{29}Si\{^1H\}$ NMR (79.4 MHz, $CDCl_3$): δ_{Si} = −7.00, −7.51. Elem. Anal.: Calcd for $C_{24}H_{30}Si_2$: C, 76.94 %; H, 8.07 %. Found: C, 76.87 %; H, 7.96 %. HRMS (APCI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{30}Si_2H$ 375.1959; Found 375.1957.

Crystal data for **2.13**: 0.8($C_{24}H_{30}Si_2$), M_r = 299.74 g mol^{-1}, monoclinic, space group $P2_1/C$, *a* = 11.5212(3) Å, *b* = 15.2445(5) Å, *c* = 12.6733(3) Å, α = 90°, β = 90.765(2)°, γ = 90°, *V* = 2225.68(11) $Å^3$, *Z* = 5, *T* = 173 K, λMo(Kα) = 0.71073, R_1 [$I > 2\sigma(I)$] = 0.0429, wR_2 (all data) = 0.1455, *GooF* = 0.963.

2.7.18 Synthesis of 1-phenyl-1,2,2-tris(trimethylsilyl)ethylene (2.14)

In an ampoule, 1-phenyl-2-trimethylsilylacetylene (60.0 µl, 0.30 mmol), $Me_3SiSiMe_3$ (94.0 µl, 0.46 mmol) and **2.4** (0.008 g, 15.16 µmol) were dissolved in C_6D_6 (0.5 mL). The resulting reaction mixture was heated to 100 ºC for 48 h under a N_2 atmosphere. On cooling the volatiles were removed in vacuo. The white oily solid was re-dissolved in DCM and filtered through a plug of silica. The DCM was removed in vacuo and the white solid washed with H_2O (20.0 mL). Yield: 0.048 g, 49.1 %. ^1H NMR (499.9 MHz, $CDCl_3$): δ_H = 7.19 [t, *J* = 7.1 Hz, 2H, Ph], 7.13 [tt, *J* = 7.2, 1.0 Hz, 1H, *p*-Ph], 6.82 [dd, *J* = 7.4, 1.0 Hz, 2H, Ph], 0.32 [s, 9H, Si**Me$_3$**], 0.06 [s, 9H, Si**Me$_3$**], −0.27 [s, 9H, Si**Me$_3$**].

2.7.19 Synthesis of (*Z*)-1,2-bis(trimethylsilyl)-1-phenylethene (2.15)

In an ampoule, phenylacetylene (40.0 µl, 0.36 mmol), $Me_3SiSiMe_3$ (112.0 µl, 0.54 mmol) and **2.4** (0.004 g, 7.18 µmol) were dissolved in C_6D_6 (0.35 mL). The resulting reaction mixture was heated to 100 ºC under a N_2 atmosphere for 24 h. On cooling the reaction mixture hexane (20.0 mL) was added. This solution was washed with H_2O (3 x 20.0 mL). The organic fractions were collected and filtered through a plug of silica. The low boiling point volatiles were then removed in vacuo. Crude product was purified on silica gel (hexane) to afford a colourless oil. Yield: 0.070 g, 77.8 %. ^{1}H NMR (399.5 MHz, $CDCl_3$): δ_H = 7.25 [m, 2H, Ph], 7.16 [t, $^3J_{HH}$ = 7.6 Hz, 1H, *p*-Ph], 7.03 [dd, *J* = 7.6, 1.2 Hz, 2H, Ph], 6.43 [s, 1H, =C**H**], 0.21 [s, 9H, Si**Me**$_3$], 0.15 [s, 9H, Si**Me**$_3$]. ^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$): δ_C = 164.4, 151.1, 149.0, 127.9, 126.4, 125.7, 1.3, 1.1. ^{29}Si{^{1}H} NMR (79.4 MHz, $CDCl_3$): δ_{Si} = −7.19, −10.67.

2.7.20 Synthesis of dimethyl 2,3-bis(trimethylsilyl)maleate (2.16) and tetramethyl 1,4-bis(trimethylsilyl)buta-1,3-diene-1,2,3,4-tetracarboxylate (2.17)

In an ampoule, dimethyl acetylenedicarboxylate (44.0 µL, 0.36 mmol), $Me_3SiSiMe_3$ (108.0 µL, 0.5 mmol) and **2.4** (0.002 g, 3.59 µmol) were dissolved in C_6D_6 (0.35 mL). The resulting reaction mixture was heated to 100 ºC for 24 h under an N_2 atmosphere. Crude NMR analysis indicated a 39:61 ratio of **2.16**:**2.17**. Upon cooling the volatiles were removed in vacuo and the crude material was separated and purified on silica gel (hexane/ethyl acetate 4:1).

Dimethyl 2,3-bis(trimethylsilyl)maleate **(2.16)**:

Yield: 0.038 g, 95%. ^{1}H NMR (499.9 MHz, $CDCl_3$): δ_H = 3.70 [s, 6H, CO_2**Me**], 0.27 [s, 18H, Si**Me**$_3$]. ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$): δ_C = 172.4 [**C**=O], 153.7 [**C**=C], 51.8 [O**Me**], 0.2 [Si**Me**$_3$].

Tetramethyl 1,4-bis(trimethylsilyl)buta-1,3-diene-1,2,3,4,-tetracarboxylate (2.17): Melting point: 72.6 – 73.2 ºC. Yield: 0.043 g, 88%. ^{1}H NMR (499.9 MHz, $CDCl_3$): δ_H = 3.82 [s, 6H, CO_2**Me**], 3.72 [s, 6H, CO_2**Me**], 0.18 [s, 18H, Si**Me**$_3$]. $^{13}C\{^{1}H\}$ NMR (125.7 MHz, $CDCl_3$): δ_C = 171.3 [**C**=O], 164.7 [**C**=O], 153.7 [**C**=C], 136.7 [C=**C**], 52.7 [O**Me**], 52.0 [O**Me**], –0.8 [Si**Me**$_3$]. $^{29}Si\{^{1}H\}$ NMR (79.4 MHz, $CDCl_3$): δ_{Si} = -1.13. Elem. Anal.: Calcd for $C_{18}H_{30}O_8Si_2$: C, 50.21%; H, 7.02%. Found: C, 50.10%; H, 7.12%. HRMS (APCI) m/z: $[M + NH_4]^+$ Calcd for $C_{18}H_{30}O_8Si_2NH_4$ 448.1817; Found 448.1820.

Catalysis with [Pd(ITMe)$_2$(PhC≡CPh)] (2.8) (1 mol%)

2.7.21 Synthesis of 2.7

In an ampoule, a mixture of diphenylacetylene (0.03 g, 0.17 mmol), $Me_3SiSiMe_3$ (55.0 µl, 0.27 mmol) and **2.8** (0.001 g, 1.69 µmol) in C_6D_6 (0.2 mL) was heated to 100 ºC for 24 h under a N_2 atmosphere. After cooling the volatiles were removed in vacuo. The resulting off-white solid was re-dissolved in $CHCl_3$ (20.0 mL) and was filtered through a plug of silica. The filtrates volatiles were removed in vacuo to reveal white solid. This was washed with H_2O (20.0 mL). Yield: 0.05 g, 90 %. ^{1}H NMR (499.9 MHz, $CDCl_3$): δ_H = 6.97 [m, 4H, Ph], 6.85 [m, 2H, *p*-Ph], 6.62 [dd, $^{3}J_{HH}$ = 8.2, 1.4 Hz, 4H, Ph], 0.13 [s, 18H, Si**Me**$_3$].

2.7.22 Synthesis of *cis*-[Pd(ITMe)$_2$(SiMe$_2$Ph)$_2$] (2.18)

2.1 (0.21 g, 0.17 mmol), **2.2** (0.051 g, 0.16 mmol) and ^{t}BuOK (0.018 g, 0.16 mmol) were suspended in toluene (7.0 mL). Isopropanol (12.0 µL, 0.16 mmol) was added and the resulting reaction mixture was stirred at room temperature for 4.5 h under an N_2 atmosphere. At this point, $PhMe_2SiSiMe_2Ph$ (0.128 g, 0.47 mmol) was added and the reaction mixture was stirred for a further 16 h at room temperature. The solution was then

filtered through flame dried Celite, the filtrate's volatiles were removed in vacuo and the crude material was washed with hexane (3 x 5.0 mL) to give an off-white solid. Yield: 0.049 g, 50.0%. ^{1}H NMR (399.5 MHz, C_6D_6): δ_H = 7.71 [m, 4H, Ph], 7.23 [m, 4H, Ph], 7.13 [m, 2H, *p*-Ph], 3.14 [s, 12H, N(1,3)-C**H$_3$**], 1.34 [s, 12H, C(4,5)-C**H$_3$**], 0.77 [s, 12H, Si**Me$_2$**Ph]. ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6): δ_C = 193.4 [N**C**N], 156.3 [*i*-Ph], 134.2 [Ph], 126.6 [Ph], 125.2 [*p*-Ph], 123.8 [**C**(4,5)-CH_3], 34.9 [N(1,3)-**C**H_3], 9.6 [C(4,5)-**C**H_3], 6.9 [Si**Me$_2$**Ph]. ^{29}Si{^{1}H} NMR (79.4 MHz, C_6D_6): δ_{Si} = 0.50. Elem. Anal.: Calcd for $C_{30}H_{46}N_4Si_2Pd$: C, 57.62%; H, 7.41%; N, 8.96%. Found: C, 57.51%; H, 7.52%; N, 8.85%. Crystal data for **2.18**: $C_{33}H_{49}N_4PdSi_2$, M_r = 664.37 g mol^{-1}, triclinic, space group P-1, a = 11.8802(6) Å, b = 12.1897(5) Å, c = 13.9679(5) Å, α = 86.341(3)^o, β = 73.708(4)^o, γ = 63.295(5)^o, V = 1729.87(15) Å^3, Z = 2, T = 173 K, λCu(Kα) = 1.54184, R_1 [$I > 2\sigma(I)$] = 0.0396, wR_2 (all data) = 0.1171, $GooF$ = 0.902.

2.7.23 Synthesis of *cis*-[Pd(ITMe)$_2$(SiMe$_2${2-MeOPh})$_2$] (2.19)

Isopropanol (13.0 µL, 0.17 mmol) was added to stirred mixture of **2.1** (0.023 g, 0.19 mmol), **2.2** (0.055 g, 0.17 mmol) and ^{t}BuOK (0.020 g, 0.17 mmol) in toluene (12.0 mL). The resulting reaction mixture was stirred at room temperature for 4 h. At this stage, 1,2-bis(2-methoxyphenyl)-1,1,2,2-tetramethyldisilane (0.141 g, 0.43 mmol) was added and the mixture was stirred for a further 18 h at 60 ^{o}C. On cooling the reaction mixture was filtered by cannula, the filtrate's volatiles were removed in vacuo and the off-white solid was washed with hexane (3 x 5.0 mL). Yield: 0.075 g, 63%. ^{1}H NMR (399.5 MHz, C_6D_6): δ_H = 7.66 [d, $^{3}J_{HH}$ = 7.0 Hz, 2H, 6-Ph], 7.20 [m, 2H, 4-Ph], 6.94 [m, 2H, 5-Ph], 6.62 [d, $^{3}J_{HH}$ = 8.0 Hz, 2H, 3-Ph], 3.58 [s, 6H, O**Me**], 3.29 [s, 12H, N(1,3)-C**H$_3$**], 1.40 [s, 12H, C(4,5)-C**H$_3$**], 0.73 [s, 12H, Si**Me$_2$**Ar]. ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6): δ_C = 194.4 [N**C**N], 164.0 [2-Ph], 143.5 [1-Ph], 135.6 [6-Ph], 126.9 [4-Ph], 123.5 [**C**(4,5)-CH_3],

119.9 [5-Ph], 109.0 [3-Ph], 54.6 [O**Me**], 34.9 [N(1,3)-**C**H_3], 8.7 [C(4,5)-**C**H_3], 6.6 [Si**Me**$_2$Ar]. ^{29}Si{^{1}H} NMR (79.4 MHz, C_6D_6): δ_{Si} = –1.41. Elem. Anal. Calcd for $C_{32}H_{50}O_2Si_2Pd$: C, 56.08%; H, 7.35%; N, 8.17%. Found: C, 55.98%; H, 7.38%; N, 8.13%.

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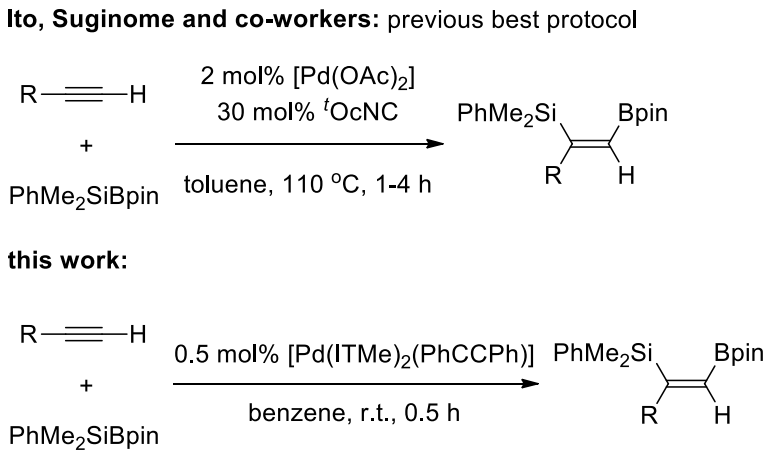
Chapter 3

(N-Heterocyclic Carbene)$_2$Pd(0)-Catalysed Silaboration of Internal and Terminal Alkynes: Scope and Mechanistic Studies

3.1 Introduction

The regio- and stereoselective synthesis of multi-substituted alkenes is a challenging reaction, recurrent in the formation of organic structures. In particular, tri- and tetra-substituted alkenes are present in many pharmaceuticals,[1–5] dipeptide mimetics,[6] polymers,[7] and columnar liquid crystals.[8] There are now many reported methods for the synthesis of such alkenes including olefin metathesis,[9–11] and carbonyl olefination,[12] among others.[13,14] Notably, the transition metal catalysed π-insertion of an alkyne into a bond between two elements of the p-block (*e.g.*, Si-Si, Si-Sn, Sn-Sn, B-B, and Si-B) has received a significant amount of attention (Chapter 1).[15] One of the most interesting examples is arguably the 1,2-addition of a silicon-boron bond (silaboration).[16–18] The resulting 1-silyl-2-boryl alkenes have the potential to independently undergo, for example, a cross-coupling reaction at the boryl (Suzuki-Miyaura) fragment,[19] and Fleming-Tamao oxidative addition or cross-coupling (Hiyama) at the silyl fragment.[20–22] Arguably, the most effective alkyne silaboration protocol is the palladium diacetate/isocyanide combination reported by Ito and co-workers (Scheme 3.1).[23–25] The reactions proceed with high stereoselectivity towards the *syn*-1,2-addition products and in the case of terminal alkynes high regioselectivity, with the boryl fragment attached to the terminal position. Recently, Suginome and co-workers reported that the reverse regioselectivity was possible by changing the palladium source and using a sterically encumbered phosphine ligand, albeit using the more reactive (chlorodimethylsilyl)boronic acid pinacol ester.[26–28] "Abnormal" regioselectivity was



Scheme 3.1 Silaboration of terminal alkynes

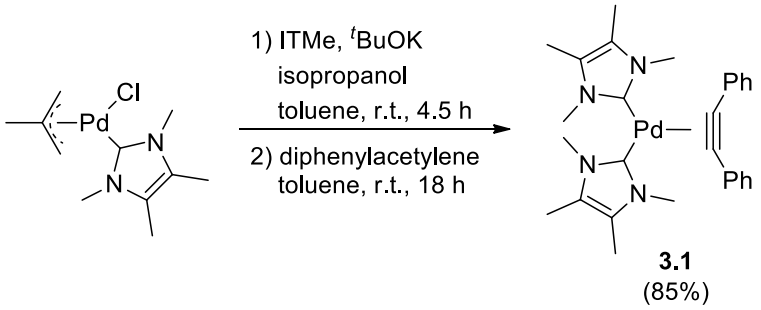
also reported by Stratakis and co-workers using a supported gold nanoparticle catalyst.[29] However, alkyne silaboration protocols have been largely limited to high reaction temperatures, long reaction times, and moderately high catalyst loadings. The most challenging aspect of silaboration chemistry remains the silaboration of unsymmetrical internal alkynes and the resulting formation of regioisomeric mixtures; there are limited examples that remedy this.[30,31]

The use of NHCs,[32–34] as ligand sets in the first isolation of a bis(trimethylsilyl)palladium complex, *cis*-[Pd(ITMe)$_2$(SiMe$_3$)$_2$] (ITMe = 1,3,4,5-tetramethylimidazol-2-ylidene) and the first example of a bis(NHC)-palladium alkyne complex, [Pd(ITMe)$_2$(PhC≡CPh)] was reported in Chapter 2.[35] Both complexes acted as highly active pre-catalysts for the *cis*-bis(silyl)ation of sterically and electronically demanding internal and terminal alkynes. The high activity exhibited by [Pd(ITMe)$_2$(PhC≡CPh)] prompted an investigation into its effectiveness at catalysing the silaboration of alkynes. Herein, the use of [Pd(ITMe)$_2$(PhC≡CPh)] in the silaboration of sterically and electronically demanding terminal and symmetrical internal alkynes is reported. Unprecedented low catalytic loadings, short reaction times, and mild reaction temperatures for terminal alkynes are

presented. Initial experimental investigations into the mechanism of the reaction and the isolation of important intermediates are also described.

3.2 Improved Synthesis of [Pd(ITMe)$_2$(PhC≡CPh)] (3.1)

[Pd(ITMe)$_2$(PhC≡CPh)] (**3.1**) was previously synthesized in what was effectively a three-step process.[35] An improved synthesis of **3.1** has since been devised: [(ITMe)Pd(methallyl)Cl] was reacted with one equivalent of each of potassium *tert*-butoxide, isopropanol, and ITMe at room temperature forming [Pd(ITMe)$_2$], which was then exposed *in situ* to a slight excess of diphenylacetylene at room temperature for 18 h in toluene. After workup, **3.1** was isolated in an 85% yield (Scheme 3.2). **3.1** is deemed as a more soluble analogue of [Pd(ITMe)$_2$].



Scheme 3.2 Improved synthesis of **3.1**

3.3 Catalytic Silaboration of Alkynes

With large quantities of **3.1** in hand, its capacity to catalyse the silaboration of alkynes was investigated. Diphenylacetylene and (dimethyphenyl)silyl boronic acid pinacol ester ($PhMe_2SiBpin$) were chosen as model substrates for the optimization of the initial reaction parameters. The reaction was carried out in C_6D_6 in order to monitor its progression. (*E*)-(1,2-diphenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)dimethyl(phenyl)-silane (**3.2**) was obtained in 96% yield (100%

stereoselectivity) using 0.5 mol% of **3.1** at room temperature and in less than 30 min. A comparable isolated yield was obtained in benzene. The only report for a catalytic synthesis of this compound required 2 mol% of $[Pd(OAc)_2]$/30 mol% *tert*-octyl isocyanide at 110 ºC over 2 h.[24] Single crystals of **3.2** were obtained by slow evaporation of a saturated acetone solution and the X-ray analysis is depicted in Figure 3.1.

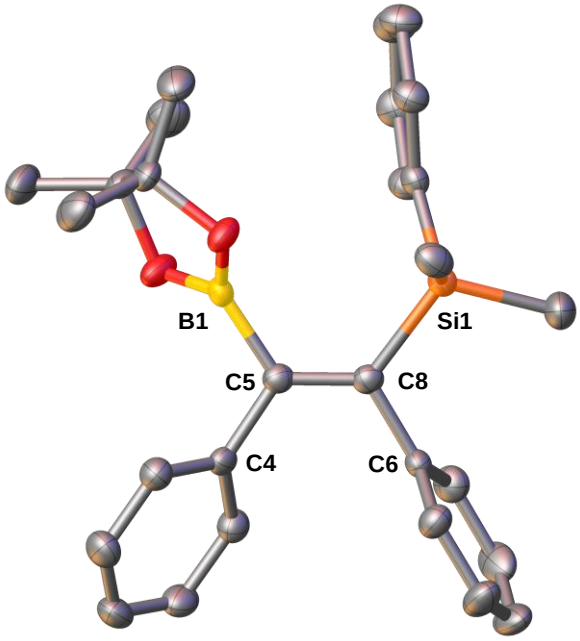
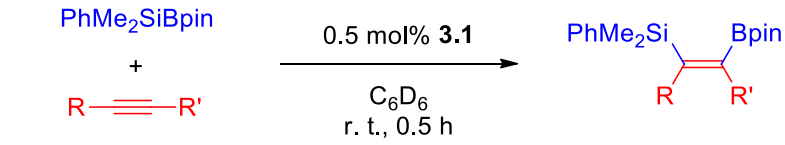
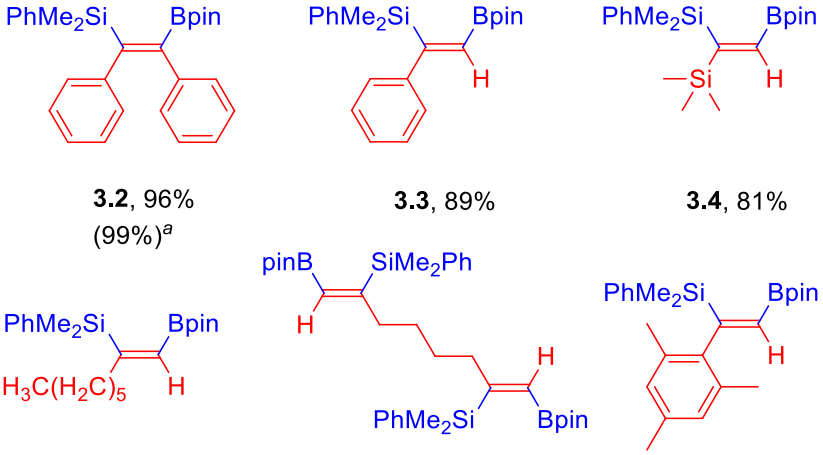


Figure 3.1 Molecular structure of **3.2** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [º]: Si1-C8 1.9015(17), B1-C5 1.577(2), C5-C8 1.355(2); C4-C5-B1 112.83(14), C8-C5-C4 123.02(15), C8-C5-B1 124.15(15), C5-C8-Si1 124.84(13), C5-C8-C6 121.34(15), C6-C8-Si1 113.28(11).

To scope the versatility of this protocol, a series of sterically and electronically challenging alkynes were reacted with $PhMe_2SiBpin$ (Table 3.1). The silaboration of terminal aryl, alkyl, silyl, and even diterminal alkynes proceeded at room temperature





3.2, 96% (99%)[a]

3.3, 89%

3.4, 81%

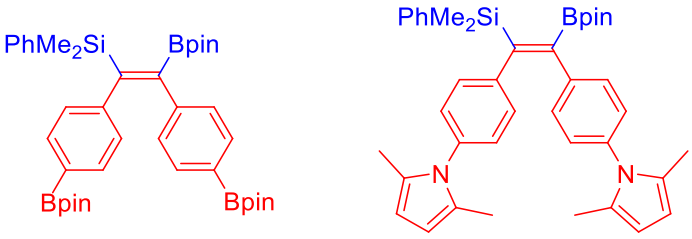
3.5, 88%

3.6, 93%

3.7, 80%

3.8, 86%
(0.5 mol%, 100 °C, 24 h)

3.9, 69%
(0.5 mol%, 100 °C, 6 h)



3.10, 71%
(2.5 mol%, 100 °C, 3 h)

3.11, 64%
(4 mol%, 100 °C, 36 h)

3.12a, 74%
(0.5 mol%, 100 °C, 1 h)[b]

3.13a, 87%
(0.5 mol%, 100 °C, 1h)[c]

[a]Yield in C_6H_6 under same reaction conditions; [b]Major isomer isolated from a mixture that included 20% of the other regiosomer; [c]Major isomer iolated from a mixture that included 7% of the other regioisomer.

Table 3.1 Silaboration of terminal and internal alkynes

using 0.5 mol% of **3.1** in less than 30 min with 100% regio- and stereoselectivity. As for compound **3.2**, the only previous synthesis of compounds **3.3**, **3.4**, **3.5** and **3.6** required 2 mol% of [$Pd(OAc)_2$]/30 mol% *tert*-octyl isocyanide at 110 ^oC, in reaction times varying from 1 to 4 h, whereas compound **3.7** has not been previously reported (Table 3.1).

There are only a few examples of catalytic silaborations of symmetrical and unsymmetrical alkynes in the literature: namely, Ito and co-workers' silaboration of diphenylacetylene, 1-phenyl-1-propyne and dec-5-yne,[24] Sawamura and co-workers' organocatalytic silaboration of polar coordinating internal alkynes,[30] and Sato and co-workers' ynamide silaboration.[31] Mixtures of regioisomers are usually observed in the silaboration of unsymmetrical internal alkynes. However, a more thorough investigation into the silaboration of symmetrical alkynes that are electronically challenging was not reported prior to this investigation. Albeit requiring temperature of 100 ^oC, the novel compounds **3.8**, **3.9**, **3.10** and **3.11** were all synthesized with 100% *cis*-stereoselectivity as established by NOESY NMR (Table 3.1). Both alkyl-alkyl and aryl-aryl internal alkynes bearing functionalities such as carboxylic ester, boronate ester, pyrrole, and ether reacted well under these conditions. Silaboration of internal alkynes with extreme steric hindrance such as 1,2-di(naphthalen-1-yl)ethyne and 1,2-bis(trimethylsilyl)ethyne, was not accessible utilizing this protocol.

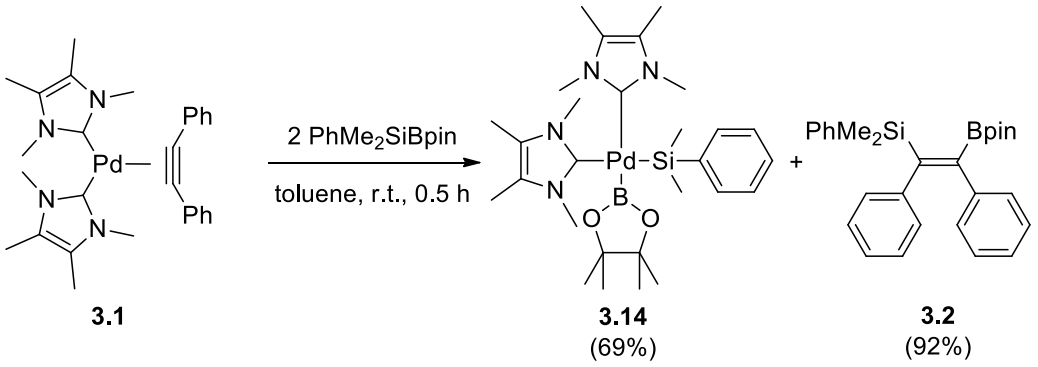
Unsymmetrical alkynes were also subjected to these reaction conditions. The silaboration of unsymmetrical alkyne 1-phenyl-2-trimethylsilylacetylene resulted in the isolation of the novel compound **3.12a** as a major product from an 80:20 mixture of regioisomers. On the other hand, the silaboration of 1-phenyl-1-propyne afforded compound **3.13a**, isolated as the major regioisomer of a mixture containing 7% of the other isomer. This is a similar result to that obtained by Ito,[24] albeit in a shorter reaction time and using a lower catalyst loading (Table 3.1). The silaboration of 1-(*tert*-butyl)-4-(phenylethynyl)benzene and 1-

(phenylethynl)naphthalene afforded near statistical mixture of their corresponding regioisomers. It is therefore considered that unsymmetrical bis-aryl internal alkynes are a limitation to this protocol.

3.4 Mechanistic Study

3.4.1 Synthesis of *cis*-[Pd(ITMe)$_2$(SiMe$_2$Ph)(Bpin)] (3.14)

Next, the attention was turned to the mechanism of these reactions. The proposed catalytic cycle for "normal" silaboration using Pt group catalyst involves an initial oxidative addition resulting in a *cis*-(silyl)(boryl)M(II) complex. The alkyne then undergoes migratory insertion into the M-B bond to form the corresponding (silyl)-M(II)-(borylvinyl) species, followed by a reductive elimination to form the 1-silyl-2-borylalkene.[36–38] The isolation of the oxidative addition products for Pt group complexes is extremely rare due to their low stability: the only previous examples were a series of (phosphine)-Pt complexes reported by Ozawa and co-workers,[37] and one Pd complex reported by Onozawa and Tanaka.[39] The stoichiometric reactivity of **3.1** was investigated in the hope of isolating this important intermediate in the catalytic cycle. On reacting two equivalent of PhMe$_2$SiBpin with **3.1** in toluene, *cis*-[Pd(ITMe)$_2$(SiMe$_2$Ph)(Bpin)] (**3.14**) and **3.2** formed at room temperature in under 30 min (Scheme 3.3).



Scheme 3.3 Synthesis of compound **3.14**

Single crystals of **3.14** were isolated from a double recrystallization in acetonitrile at −30 ^{o}C. X-ray analysis indicated a distorted square planar geometry with the NHCs orthogonal to the Si-Pd-B plane (Figure 3.2). To gain further insights on the reactivity of **3.14**, its stoichiometric reaction with diphenylacetylene was carried out, leading to the quantitative formation of **3.1** and **3.2** at room temperature in only 10 min. Unfortunately attempts of isolating the borylvinyl-Pd-silyl intermediate generated after the migratory insertion were unsuccessful.

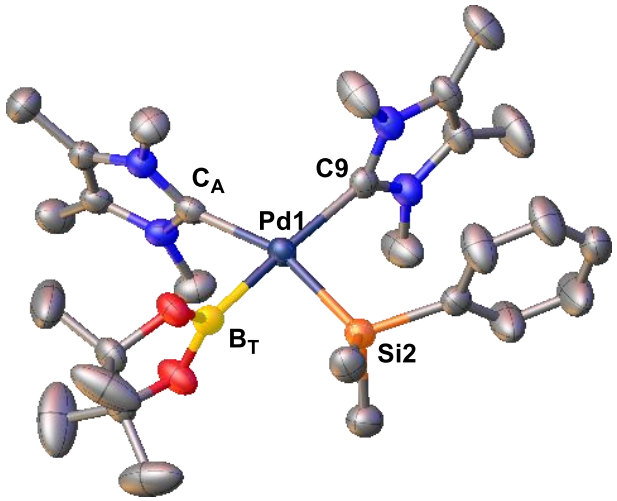
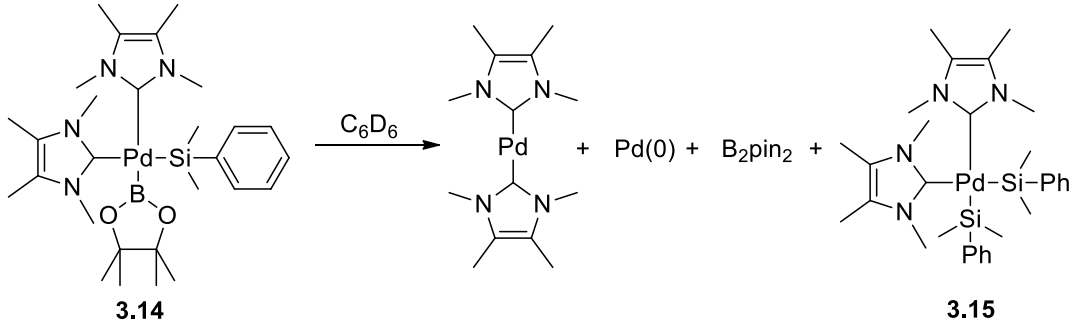


Figure 3.2 Molecular structure of **3.14** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [^{o}]: Pd1-C_A 2.091(3), Pd1-C9 2.120(3), Pd1-B_T 2.038(4), Pd1-Si2 2.3352(9); C_A-Pd1-C9 103.26(12), C9-Pd1-Si2 94.71(9), B_T-Pd1-Si2 81.49(11), C_A-Pd1-B_T 80.89(13).

3.4.2 Decomposition of 3.14

Complex **3.14** seems indefinitely stable to decomposition as a solid under inert conditions. It however rapidly decomposes in solution in non-polar aromatic solvents such as toluene and benzene and at a slower rate in acetonitrile. By monitoring the mixture in C_6D_6 by ^{1}H NMR, the decomposition products were assigned as [Pd(ITMe)$_2$], B_2pin_2, palladium black and *cis*-[Pd(ITMe)$_2$(SiMe$_2$Ph)$_2$] (**3.15**) (Scheme 3.4). The identity of **3.15**

was already known through its independent synthesis, reacting [Pd(ITMe)$_2$] with 1,1,2,2-tetramethyl-1,2-diphenyldisilane (PhMe$_2$SiSiMe$_2$Ph), reported in Chapter 2.[35,40] This decomposition of **3.14** in solution leading to Pd black could very well explain catalyst death with times as the concentration of the alkyne in solution decreases.



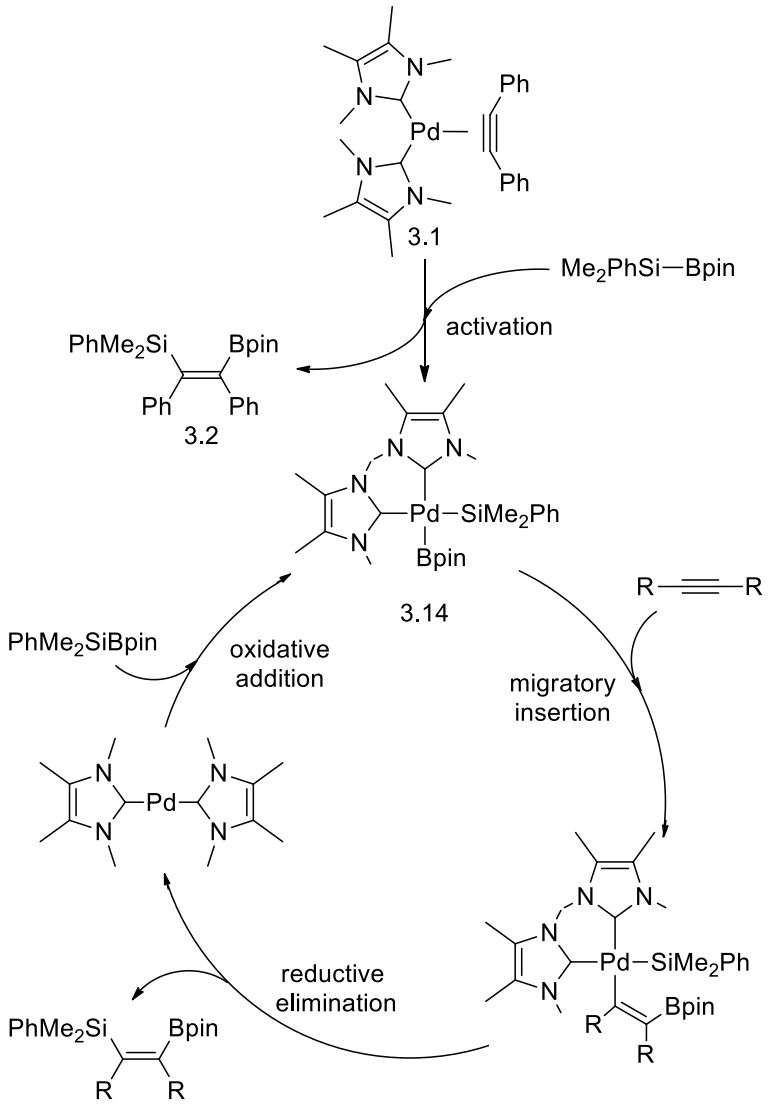
3.14 **3.15**

Scheme 3.4 Decomposition of **3.14** in solution

3.4.3 Proposed Catalytic Cycle for Silaboration

With all this information in hand, a mechanism similar to that in Chapter 2 and depicted in Scheme 6 is proposed, starting with the activation of complex **3.1** leading to the formation of complex **3.14**, as shown in the mechanistic studies. An approach of the alkyne above the plane of the molecule is suggested because, due to their nature, it is unlikely that neither the NHCs, silyl nor boryl groups would detach prior the coordination of the alkyne. A subsequent migratory insertion of the alkyne in to the M-boryl results in the formation of a borylvinyl-palladium-silyl intermediate. This preferred boryl migration over silyl migration has been thoroughly investigated in the literature and is believed to be both a kinetically and thermodynamically favourable process.[41,42] A weak coordination of the boryl moiety to the Pd centre would stabilize the borylvinyl palladium intermediate and allow for a stereoselective reductive elimination,[43] generating the

desired silaborated product and 14 e^- complex [Pd(ITMe)$_2$], the catalytically active species in the cycle (Scheme 3.5).

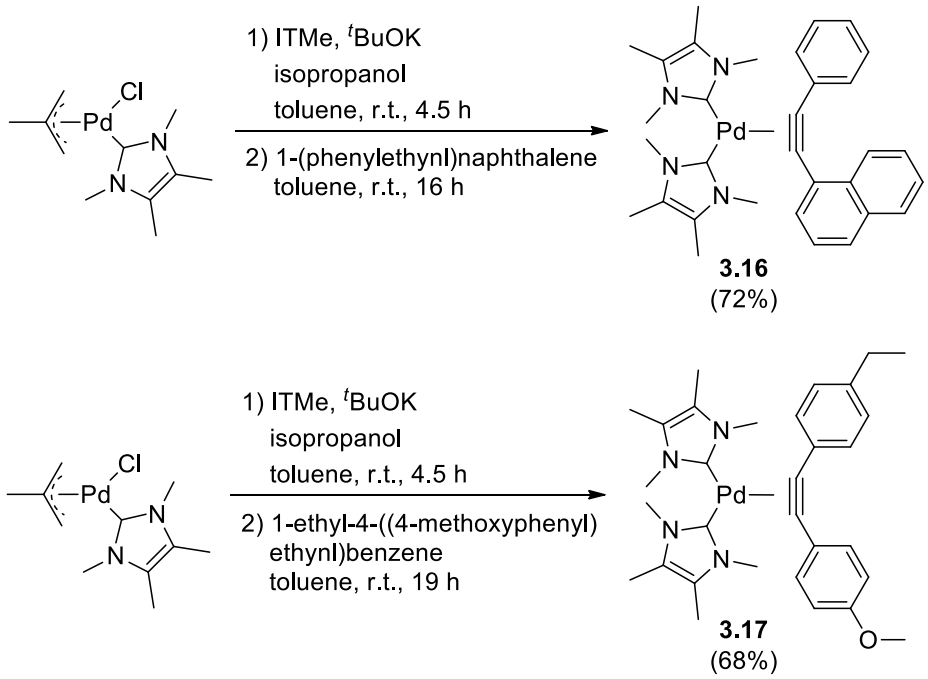


Scheme 3.5 Proposed catalytic cycle

3.5 Synthesis of [Pd(ITMe)$_2$(RC≡CR')] Analogues

The synthesis of **3.1** was extended to other internal aryl alkynes including 1-(phenylethynl)naphthalene and 1-ethyl-4-((4-methoxyphenyl)ethynl)benzene to yield **3.16** and **3.17**, respectively. Full NMR spectroscopic data and elemental analysis were collected for **3.16** and **3.17** (Scheme 3.6). Attempts at the isolation of crystals suitable for

X-ray analysis were unsuccessful. However, the $^{13}C\{^{1}H\}$ NMR resonances for the carbenic carbons of **3.1** (198.7 ppm), **3.16** (198.1 and 197.7 ppm) and **3.17** (199.4 and 199.4 ppm) suggested that the electron density at the palladium centre was not significantly altered by these subtle changes in electronic properties of the alkyne substituents. Electron rich and/or bulky internal alkynes such as 1-phenyl-2-silylacetylene, 1-phenyl-1-propyne, 2-heptyne and 4-octyne did not result in adduct formation and only [Pd(ITMe)$_2$] was observed. These observations were consistent with the absence of, or sluggish bis(silyl)ation (see Chapter 2) and silaboration with these alkynes.



Scheme 3.6 Synthesis of **3.16** and **3.17**

3.6 Conclusions

In conclusion, it was shown that complex **3.1** is a very reactive pre-catalyst in the silaboration of sterically and electronically demanding internal and terminal alkynes proceeding at much lower catalyst loadings, milder temperatures (in the case of terminal

alkynes), and in much faster reaction times than in previous protocols reported in the literature. Investigations into the mechanism for this reaction resulted in the synthesis of *cis*-[Pd(ITMe)$_2$(SiMe$_2$Ph)(Bpin)]. This represents a very rare example of a (silyl)(boryl)palladium complex isolated from the oxidative addition of a Si-B reagent to a Pd(0) centre. This study was reported in the journal *ACS Catalysis*.[44] Other [Pd(ITMe)$_2$(RC≡CR')] analogues have been synthesized and an initial structural comparison suggests there is little difference in their electronic properties. A future direction of this work would be to compare their stoichiometric/catalytic activities in E-E' additions to alkynes in order to understand how tuning of the electronic and steric properties may facilitate or hinder reactivity.

3.7 Experimental Details for Chapter 3

General experimental details are given in appendix A1.

3.7.1 Improved Synthesis of [Pd(ITMe)$_2$(PhC≡CPh)] (3.1)

In a vial, isopropanol (6.8 μl, 0.09 mmol) was added to a mixture of [(ITMe)Pd (methalllyl)Cl] (0.028 g, 0.09 mmol), ^{t}BuOK (0.011 g, 0.11 mmol) and ITMe (0.013 g, 0.10 mmol) in toluene (5.0 mL). The resulting reaction mixture was stirred at room temperature under a N_2 for 4.5 h. At this point, diphenylacetylene (0.020 g, 0.11 mmol) was added and the reaction mixture was stirred for a further 18 h. At this stage the reaction mixture was filtered through a plug of flame dried Celite. A yellow solid settle on top of the Celite and on washing with THF (3 x 4.0 mL) resulted in a yellow filtrate. On removal of the volatiles a yellow powdered solid persisted. Yield: 0.040 g, 84.7 %. ^{1}H NMR (399.5 MHz, C_6D_6): δ_H = 7.99 [dd, $^3J_{HH}$ = 8.1, $^4J_{HH}$ = 1.3 Hz, 4H, *m*-Ph], 7.27 [m, 4H, *o*-Ph], 7.05 [tt, $^3J_{HH}$ = 7.3, $^4J_{HH}$ = 1.3 Hz, 2H, *p*-Ph], 3.49 [s, 12H, N(1,3)-C**H**$_3$], 1.54 [s, 12H, C(4,5)-C**H**$_3$]. ^{13}C{^{1}H} NMR (100.46 MHz, C_6D_6): δ_C = 198.7 [N**C**N], 138.6 [C≡**C**], 130.1

[*o*-Ph], 128.2 [*m*-Ph], 126.3 [*i*-Ph], 124.2 [*p*-Ph], 123.1 [**C**(4,5)-CH_3], 35.2 [N(1,3)-**C**H_3], 9.0 [C(4,5)-**C**H_3].

Catalysis using 3.1

3.7.2 Synthesis of (*E*)-(1,2-diphenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)dimethyl(phenyl)silane (3.2)

In an ampoule equipped with a stirrer bar, (dimethylphenylsilyl)boronic acid pinacol ester (44.0 μl, 0.16 mmol) was added to stirred mixture of diphenyl acetylene (0.028 g, 0.16 mmol) and **3.1** (0.42 mg, 0.79 μmol) in C_6D_6 (0.35 mL). The resulting reaction mixture was stirred at ambient temperature for 19 h. At this stage the volatiles were removed in vacuo, the resulting off-white solid was re-dissolved in CH_2Cl_2 (DCM) (15.0 mL) and filtered through a plug of silica. The filtrates were collected and the volatiles removed in vacuo to reveal a white solid. Yield: 0.038 g, 96.6 %. ^{1}H NMR (399.5 MHz, $CDCl_3$): δ_H = 7.65 [m, 2H, SiMe$_2$**Ph**], 7.34 [m, 3H, SiMe$_2$**Ph**], 6.97 [m, 8H, Ph], 6.71 [m, 2H, *p*-Ph], 1.05 [s, 12H, Bpin], 0.34 [s, 6H, Si**Me$_2$**Ph]. ^{1}H NMR (399.5 MHz, C_6D_6): δ_H = 7.84 [m, 2H], 7.29 [m, 2H], 7.23 [m, 3H], 6.98 [m, 2H], 6.90 [m, 4H], 6.81 [m, 2H], 0.87 [s, 12H, Bpin], 0.51 [s, 6H, Si**Me$_2$**Ph]. ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$): δ_C = 155.1, 144.6, 142.9, 139.8, 134.5, 129.1, 128.8, 128.6, 127.8, 127.3, 127.3, 125.5, 124.8, 84.0, 25.0, −0.1. ^{11}B{^{1}H} NMR (128.2 MHz, $CDCl_3$): δ_B = 30.0. ^{29}Si{^{1}H} NMR (79.4 MHz, $CDCl_3$): δ_{Si} = −9.32. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{28}H_{33}O_2BSiNa$ 463.2235; Found 463.2239.

Crystal data for **3.2**: $C_{28}H_{33}BO_2Si$, M_r = 440.44 g mol^{-1}, triclinic, space group P-1, a = 9.8337(10) Å, b = 11.7927(10) Å, c = 12.4336(11) Å, α = 112.475(8)°, β = 96.966(8)°, γ =104.180(8)°, V = 1254.0(2) Å^3, Z = 2, T = 173 K, λMo(Kα) = 0.71073, R_1 [$I > 2\sigma(I)$] = 0.0463, wR_2 (all data) = 0.1037, *GooF* = 1.023.

3.7.3 Synthesis of (*Z*)-dimethyl(phenyl)(1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)silane (3.3)

A stock solution of **3.1** (0.85 mg, 1.59 µmol) in C_6D_6 (961.6 µL) was added to a mixture of phenylacetylene (35.0 µL, 0.32 mmol) and (dimethylphenylsilyl)boronic acid pinacol ester (87.0 µL, 0.32 mmol). The resulting reaction mixture was stirred at room temperature for 0.5 h. The crude reaction mixture was purified by column chromatography (eluent: hexane/ethyl acetate, 19:1) yielding a colorless oil. Yield: 0.103 g, 89 %. ^{1}H NMR (399.5 MHz, $CDCl_3$): δ_H = 7.58 [m, 2H, $SiMe_2Ph$], 7.29 [m, 3H, $SiMe_2Ph$], 7.22 [m, 2H, Ph], 7.15 [m, 1H, *p*-Ph], 7.06 [m, 2H, Ph], 6.33 [s, 1H, C=C**H**], 1.09 [s, 12H, Bpin], 0.38 [s, 6H, Si**Me$_2$**Ph]. ^{13}C{^{1}H} NMR (100.46 MHz, $CDCl_3$): δ_C = 165.9, 149.2, 140.2, 134.2, 128.6, 127.9, 127.6, 126.6, 126.1, 83.6, 24.9, 0.0. ^{11}B{^{1}H} NMR (128.2 MHz, $CDCl_3$): δ_B = 29.4. ^{29} Si{^{1}H} NMR (79.4 MHz, CDCl3): δ_{Si} = –9.91 (spectroscopic data in agreement with the literature).

3.7.4 Synthesis of (*Z*)-(1-(dimethyl(phenyl)silyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)trimethylsilane (3.4)

A stock solution of **3.1** (0.71 mg, 1.33 µmol) in C_6D_6 (660.0 µL) was added to a mixture of trimethylsilyl acetylene (35.0 µL, 0.25 mmol) and (dimethylphenylsilyl)boronic acid pinacol ester (70.0 µL, 0.26 mmol). The resulting reaction mixture was stirred at ambient temperature for 0.5 h. At this point the crude material was purified by column chromatography (eluent: hexane/ethyl acetate, 19:1) resulting in the isolation of a colorless oil. Yield: 0.072 g, 81 %. ^{1}H NMR (399.5 MHz, $CDCl_3$): δ_H = 7.50 [m, 2H $SiMe_2$**Ph**], 7.28 [m, 3H, $SiMe_2$**Ph**], 7.13 [s, 1H, C=C**H**], 1.05 [s, 12H, Bpin], 0.45 [s, 6H, Si**Me$_2$**Ph], 0.08 [s, 9H, Si**Me$_3$**]. ^{13}C{^{1}H} NMR (100.46 MHz, $CDCl_3$): δ_C = 169.3, 151.0 [v br], 141.4, 134.4, 128.5, 127.6, 83.6, 24.9, 0.7, 0.0. ^{11}B{^{1}H} NMR (128.2 MHz,

$CDCl_3$): δ_B = 29.1. $^{29}Si\{^1H\}$ NMR (79.4 MHz, $CDCl_3$): δ_{Si} = 0.25, –11.28 (spectroscopic data in agreement with the literature).

3.7.5 Synthesis of (*Z*)-dimethyl(phenyl)(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oct-1-en-2-yl)silane (3.5)

A stock solution of **3.1** (0.51 mg, 0.96 µmol) was added to a mixture of 1-octyne (15.0 µL, 0.19 mmol) and (dimethylphenylsilyl)boronic acid pinacol ester (60.0 µL, 0.22 mmol). The resulting reaction mixture was stirred at ambient temperature for 0.5 h. At this point the crude material was purified by column chromatography (eluent: hexane), resulting in the isolation of a colourless oil. Yield: 0.062 g, 88 %. ^1H NMR (399.5 MHz, $CDCl_3$): δ_H = 7.53 [m, 2H, $SiMe_2$**Ph**], 7.29 [m, 3H, $SiMe_2$**Ph**], 6.18 [pseudo-t, $^4J_{HH}$ = 1.4 Hz, 1H, C=C**H**], 2.21 [m, 2H, CH_2], 1.24 [m, 8H, (C**H**$_2$)$_4$], 1.07 [s, 12H, Bpin], 0.85 [t, $^3J_{HH}$ = 6.9 Hz, 3H, C**H**$_3$], 0.44 [s, 6H, Si**Me**$_2$Ph]. $^{13}C\{^1H\}$ NMR (100.46 MHz, $CDCl_3$): δ_C = 166.8, 140.7, 134.2, 128.5, 127.5, 83.2, 42.8, 31.8, 29.8, 29.3, 24.8, 22.7, 14.2, –0.7. $^{11}B\{^1H\}$ NMR (128.2 MHz, $CDCl_3$): δ_B = 29.3. $^{29}Si\{^1H\}$ NMR (79.4 MHz, $CDCl_3$): δ_{Si} = –9.79 (spectroscopic data in agreement with the literature).

3.7.6 Synthesis of ((1*Z*,7*Z*)-1,8-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octa-1,7-diene-2,7-diyl)bis(dimethyl(phenyl)silane) (3.6)

A stock solution of **3.1** (0.60 mg, 1.13 µmol) in C_6D_6 (1204.0 µL) was added to a mixture of 1,7-octadiyne (15.0 µL, 0.11 mmol) and (dimethyphenylsilyl)boronic acid pinacol ester (61.6 µL, 0.22 mmol). The resulting reaction mixture was stirred at ambient temperature for 0.5 h. At this point the crude material was purified by column chromatography (eluent: 100 % hexane followed by 100 % ethyl acetate), resulting in a white solid. Yield: 0.066 g, 93 %. ^1H NMR (399.5 MHz, $CDCl_3$): δ_H = 7.51 [m, 4H,

SiMe$_2$**Ph**], 7.28 [m, 6H, SiMe$_2$**Ph**], 6.14 [s, C=C**H**], 2.14 [m, 4H, CH$_2$], 1.28 [m, 4H, CH$_2$], 1.06 [s, Bpin], 0.42 [s, Si**Me$_2$**Ph]. ^{13}C{^{1}H} NMR (100.46 MHz, CDCl$_3$): δ_C = 166.5, 140.6, 134.2, 128.5, 127.5, 83.2, 42.6, 29.7, 24.8, –0.7, C=**C**BpinH not observed due to quadrapolar broadening. ^{11}B(^{1}H) NMR (128.2 MHz, CDCl$_3$): δ_B = 29.0. ^{29}Si{^{1}H} NMR (79.4 MHz, CDCl$_3$): δ_{Si} = –9.79.

3.7.7 Synthesis of (*Z*)-(1-mesityl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)dimethyl(phenyl)silane (3.7)

A stock solution of **3.1** (0.60 mg, 1.12 µmol) in C$_6$D$_6$ (596.0 µL) was added to a mixture of 2,4,6-trimethylphenylacetylene (35.0 µL, 0.22 mmo1) and (dimethylphenyl)boronic acid pinacol ester (62.5 µL, 0.23 mmol). The resulting reaction mixture was stirred at ambient temperature for 0.5 h. At this point the crude material was concentrated *in vacuo* then purified by column chromatography (100 % hexane followed by 100 % ethyl acetate), resulting in the isolation of a white solid. Yield: 0.073 g, 80 %. ^{1}H NMR (399.5 MHz, CDCl$_3$): δ_H = 7.65 [m, 2H, SiMe$_2$**Ph**], 7.30 [m, 3H, SiMe$_2$**Ph**], 6.80 [s, 2H, MesC**H**], 6.25 [s, 1H, C=C**H**], 2.26 [s, 3H, 4-MesC**H$_3$**], 2.16 [s, 6H, 2,6-MesC**H$_3$**], 2.16 [s, 12H, Bpin], 0.35 [s, 6H, Si**Me$_2$**Ph]. ^{13}C{^{1}H} NMR (100.46 MHz, CDCl$_3$): δ_C = 167.6 [(1)**C**=C], 145.4 [*i*-Mes], 140.1 [SiMe$_2$*i*-Ph], 137.0 [s, (2)C=**C**, vbr], 134.6 [*p*-Mes], 134.4 [SiMe$_2$Ph], 133.0 [*o*-Mes], 128.4 [SiMe$_2$*p*-Ph], 128.1 [*m*-Mes], 127.4 [SiMe$_2$Ph], 83.5 [Bpin], 24.9 [Bpin], 21.4 [2,6-Mes**C**H$_3$], 20.1 [4-Mes**C**H$_3$], 0.2 [Si**Me$_2$**Ph]. ^{11}B{^{1}H} NMR (128.2 MHz, CDCl$_3$): δ_B = 29.7. ^{29}Si{^{1}H} NMR (79.4 MHz, CDCl$_3$): δ_{Si} = –12.20. HRMS (ESI) *m/z*: [M + Na]$^+$: Calcd for C$_{25}$H$_{35}$O$_2$BSiNa 429.2392; Found 429.2376. Elem. Anal.: Calcd for C$_{25}$H$_{35}$O$_2$BSi: C, 73.88%; H, 8.68%. Found: C, 73.72%; H, 8.59%.

3.7.8 Synthesis of dimethyl 2-(dimethyl(phenyl)silyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)maleate (3.8)

Dimethyl acetylenedicarboxylate (37.0 µl, 0.30 mmol) and $PhMe_2SiBpin$ (82.0 µl, 0.30 mmol) were dissolved in C_6D_6 (420 µl). To this stirred mixture, a stock solution of **3.1** (0.16 mg, 0.30 µmol) in C_6D_6 (181 µl) was added. The resulting reaction mixture was heated to 100 °C for 24 h. At this stage, the volatiles were removed under reduced pressure. The crude product was purified by column chromatography (eluent: hexane/EtOAc, 4:1) resulting in a colourless oil. Yield: 0.111 g, 86%. ^{1}H NMR (399.5 MHz, $CDCl_3$): δ_H = 7.55 [m, 2H, $SiMe_2$**Ph**], 7.33 [m, 3H, $SiMe_2$**Ph**], 3.71 [s, 3H, CO_2**Me**], 3.63 [s, 3H, CO_2**Me**], 1.05 [s, 12H, Bpin], 0.49 [s, 6H, Si**Me**$_2$Ph]. ^{13}C{^{1}H} NMR (100.46 MHz, $CDCl_3$): δ_C = 172.2 [**C**(O)Me], 167.6 [**C**(O)Me], 160.2 [**C**=C], 136.4 [$SiMe_2$*i*-Ph], 134.4 [$SiMe_2$**Ph**], 129.6 [$SiMe_2$***p*-Ph**], 127.9 [$SiMe_2$**Ph**], 84.6 [Bpin], 52.2 [CO_2**Me**], 51.6 [CO_2**Me**], 24.8 [Bpin], −1.5 [Si**Me**$_2$Ph]. ^{11}B{^{1}H} NMR (128.2 MHz, $CDCl_3$): δ_B = 29.8. ^{29}Si{^{1}H} NMR (79.4 MHz, $CDCl_3$): δ_{Si} = −7.74. HRMS (ESI) *m/z*: [M + Na]+ Calcd for $C_{20}H_{29}O_6BSiNa$ 427.1719; Found 427.1713. Elem. Anal.: Calcd for $C_{20}H_{29}O_6BSi$: C, 59.41%; H, 7.23%. Found: C, 59.50%; H, 7.14%.

3.7.9 Synthesis of (*E*)-(1,2-bis(4-methoxyphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)dimethyl(phenyl)silane (3.9)

Bis(4-methoxyphenyl) acetylene (0.114 g, 0.47 mmol) and **3.1** (0.002 g, 0.47 µmol) were dissolved in C_6D_6 (1.0 mL). To this mixture $PhMe_2SiBpin$ (130.0 µL, 0.47 mmol) was added and the resulting reaction mixture was heated to 100 °C for 6 h. On cooling, the volatiles were removed *in vacuo*. The resulting oily solid was purified by column chromatography (eluent: hexane/ethylacetate, 20:1) yielding a white solid. Yield: 0.164 g, 69%. ^{1}H NMR (399.5 MHz, C_6D_6): δ_H = 7.88 [m, 2H, $SiMe_2$(***o*-Ph**)], 7.31 [m, 2H,

$SiMe_2$(***m*-Ph**)], 7.24 [m, 1H, $SiMe_2$(***p*-Ph**)], 7.24 [m, 2H, *o*-anisole(**2**)], 6.86 [m, 2H, *o*-anisole(**1**)], 6.63 [m, 2H, *m*-anisole(**2**)], 6.57 [m, 2H, *m*-anisole(**1**)], 3.15 [s, 3H, O**Me**(**1**)], 3.12 [s, 3H, O**Me**(**2**)], 0.92 [s, 12H, Bpin], 0.56 [s, 6H, Si**Me₂**Ph]. $^{13}C\{^1H\}$ NMR (100.46 MHz, C_6D_6): δ_C = 158.1 [*p*-anisole(**2**)], 157.6 [*p*-anisole(**1**)], 154.3 [C=C(**1**)], 140.7 [$SiMe_2$(***i*-Ph**)], 137.3 [*i*-anisole(**1**)], 135.8 [*i*-anisole(**2**)], 134.8 [$SiMe_2$(***o*-Ph**)], 133.5 [C=C(**2**)], 130.8 [*o*-anisole(**2**)], 129.9 [*o*-anisole(**1**)], 129.0 [$SiMe_2$(*p*-Ph)], 128.0 [$SiMe_2$(***m*-Ph**)], 113.6 [*m*-anisole(**1**)], 113.4 [*m*-anisole(**2**)], 83.8 [Bpin(quaternary C)], 54.4 [O**Me**(**1**)], 54.4 [O**Me**(**2**)], 25.1 [Bpin], 0.5 [Si**Me₂**Ph]. $^{11}B\{^1H\}$ NMR (128.2 MHz, C_6D_6): δ_B = 30.5. $^{29}Si\{^1H\}$ (79.4 MHz, C_6D_6): δ_{Si} = −9.37. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{30}H_{37}O_4BSiNa$ 523.2446; Found 523.2441. Elem. Anal.: Calcd for $C_{30}H_{37}O_4BSi$: C, 71.99%; H, 7.45%. Found: C, 71.88%; H, 7.52%.

3.7.10 Synthesis of (*E*)-dimethyl(phenyl)(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)vinyl)silane (3.10)

A stock solution of **3.1** (0.24 mg, 0.45 µmol) in C_6D_6 (242.0 µL) was added to a mixture of 4,4'-(acetylene-1,2-diyl)bis(phenylboronic acid pinacol ester) (0.039 g, 0.09 mmol) and (dimethylphenylsilyl)boronic acid pinacol ester (25.0 µL, 0.09 mmol). The resulting reaction mixture was heated to 100 °C for 3 h. Upon cooling the crude reaction mixture was purified by column chromatography (Eluent: hexane/ethyl acetate, 6:1) yielding a white solid. Yield: 0.044 g, 71 %. ^1H NMR (399.5 MHz, $CDCl_3$): δ_H = 7.63 [m, 2H, $SiMe_2$**Ph**], 7.45 [d, $^3J_{HH}$ = 7.9 Hz, 2H, (2)*m*-Ph], 7.43 [d, $^3J_{HH}$ = 7.9 Hz, 2H, (1)*m*-Ph], 7.33 [m, 3H, $SiMe_2$**Ph**], 6.96 [d, $^3J_{HH}$ = 7.9 Hz, 2H, (2)*o*-Ph], 6.73 [d, $^3J_{HH}$ = 7.9 Hz, 2H, (1)*o*-Ph], 1.30 [s, 12H, (2)Ph**Bpin**], 1.29 [s, 12H, (1)Ph**Bpin**], 1.01 [s, 12H, Bpin], 0.30 [s, 6H, Si**Me₂**Ph]. $^{13}C\{^1H\}$ NMR (100.46 MHz, $CDCl_3$): δ_C = 155.2 [(1)**C**=C], 147.7

[(1)***i*-Ph**Bpin], 145.9 [(2)***i*-Ph**Bpin], 139.6 [SiMe$_2$***i*-Ph**], 134.4 [SiMe$_2$Ph], 134.0 [(1)***m*-Ph**Bpin], 133.9 [(2)***m*-Ph**Bpin], 128.8 [SiMe$_2$*p*-Ph], 128.3 [(2)***o*-Ph**Bpin], 127,8 [(1)***o*-Ph**Bpin], 127.8 [SiMe$_2$**Ph**], 84.0 [Bpin], 83.6 [(1)Ph**Bpin**], 83.6 [(2)Ph**Bpin**], 25.1 [Ph**Bpin**], 25.1 [Ph**Bpin**], 25.0 [Bpin], –0.1 [Si**Me$_2$**Ph], 3 x B-C peaks are not observed due to quadrapolar broadening. $^{11}B\{^1H\}$ NMR (128.2 MHz, $CDCl_3$): δ_B = 31.5 (v. br.). $^{29}Si\{^1H\}$ NMR (79.4 MHz, $CDCl_3$): δ_{Si} = –9.30. HRMS (ESI) m/z: $[M + Na]^+$: Calcd for $C_{40}H_{55}O_6B_3SiNa$ 715.3939; Found 715.3973. Elem. Anal.: Calcd for $C_{40}H_{55}O_6B_3Si$: C, 69.39%; H, 8.01%. Found: C, 69.28%; H, 7.99%.

3.7.11 Synthesis of (*E*)-1,1'-((1-(dimethyl(phenyl)silyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethene-1,2-diyl)bis(1,4-phenylene))bis(2,5-dimethyl-1H-pyrrole) (3.11)

A stock solution of **3.1** (0.002 g, 7.02 µmol) in C_6D_6 (230.0 µL) was added to a mixture of 1,2-bis(4-(2,5-dimethyl-1H-pyrrol-1-yl)phenyl)ethyne (0.032 g, 0.08 mmol) and (dimethylphenylsilyl)boronic acid pinacol ester (24.5 µL, 0.09 mmol). The resulting reaction mixture was heated to 100 ^oC for 36 h. Upon cooling the crude reaction mixture was purified by column chromatography (Eluent: hexane/ethyl acetate, 4:1) yielding a colourless oily solid. Yield: 0.035 g, 64.0 %. ^1H NMR (399.5 MHz, $CDCl_3$): δ_H = 7.62 [m, 2H, SiMe$_2$**Ph**], 7.33 [m, 3H, SiMe$_2$**Ph**], 7.08 [d, $^3J_{HH}$ = 8.3 Hz, 2H, (2)*o*-Ph], 6.89 [d, $^3J_{HH}$ = 8.3 Hz, 2H, (2)*m*-Ph], 6.84 [m, 2H, (1)*m*-Ph], 6.80 [m, 2H, (1)*o*-Ph], 5.83 [s, 2H, (1)3,4-Pyr**H**], 5.83 [s, 2H, (2)3,4-Pyr**H**], 1.88 [s, 6H, (2)2,5-Py**Me$_2$**], 1.86 [s, 6H, (1)2,5-Pyr**Me**$_2$], 1.12 [s, 12H, Bpin], 0.45 [s, 6H, Si**Me$_2$**Ph]. $^{13}C\{^1H\}$ NMR (100.46 MHz, $CDCl_3$): δ_C = 155.6 [(1)**C**=C], 144.0 [(1)Ph-C], 142.2 [(2)Ph-C], 139.0 [SiMe$_2$***i*-Ph**], 136.3 [(2)Ph-C], 135.7 [(1)Ph-C], 134.2 [SiMe$_2$**Ph**], 129.5 [(2)*o*-Ph**C**H], 128.9 [(1)*o*-Ph**C**H], 128.8 [SiMe$_2$***p*-Ph**], 128.6 [(2)2,5-Pyrr**C**], 128.6 [(1)2,5-Pyrr**C**], 127.6

[SiMe$_2$**Ph**], 127.1 [(2)*m*-Ph**C**H], 127.0 [(1)*m*-Ph**C**H], 105.2 [(2)3,4-Pyrr**C**], 105.2 [(1)3,4-Pyrr**C**], 84.1 [Bpin], 24.8 [Bpin], 12.7 [(2)2,5-Pyrr**C**H$_3$], 12.6 [(1)2,5-Pyrr**C**H$_3$], –0.4 [Si**Me$_2$**Ph]. ^{11}B{^{1}H} NMR (128.2 MHz, CDCl$_3$): δ_B = 29.4. ^{29}Si{^{1}H} NMR (79.4 MHz, CDCl$_3$): δ_{Si} = –9.00. HRMS (ESI) *m/z*: [M + H]$^+$: Calcd for $C_{40}H_{47}O_2N_2BSiH$ 627.3573; Found 627.3569. Elem. Anal.: Calcd for $C_{40}H_{47}O_2N_2BSi$: C, 76.66%; H, 7.56%; N, 4.47%. Found: C, 76.55%; H, 7.38%; N, 4.54%.

3.7.12 Synthesis of (*E*)-(2-(dimethyl(phenyl)silyl)-2-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)trimethylsilane (3.12a)

A stock solution of **3.1** (0.001 g, 2.06 µmol) in C_6D_6 (1083.0 µL) was added to a mixture of 1-phenyl-2-trimethylsilylacetylene (80.0 µL, 0.41 mmol) and (dimethylphenylsilyl)boronic acid pinacol ester (111.0 µL, 0.41 mmol). The resulting reaction mixture was heated to 100 ^{o}C for 1 h. Upon cooling, ^{1}H NMR analysis of the crude material suggested an 80:20 ratio of regioisomers. The crude mixture was purified by column chromatography (Eluent: hexane) resulting in the isolation of **3.12a** as a colourless oil (the major isomer and a coeluted mixture of **3.12**/minor regioisomer was also obtained). Yield: 0.131 g, 74 %. ^{1}H NMR (499.5 MHz, CDCl$_3$): δ_H = 7.53 [m, 2H, SiMe$_2$**Ph**], 7.30 [m, 3H, SiMe$_2$**Ph**], 7.17 [m, 2H, *m*-Ph], 7.11 [pseudo-tt, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, *p*-Ph], 6.84 [m, 2H, *o*-Ph], 1.15 [s, 12H, Bpin], 0.25 [s, 6H, Si**Me$_2$**Ph], –0.18 [s, 9H, Si**Me$_3$**]. ^{13}C{^{1}H} NMR (100.46 MHz, CDCl$_3$): δ_C = 170.6 [(PhMe$_2$Si)**C**=C], 153.7 [C=**C**(Bpin)], 148.1 [*i*-Ph], 139.2 [SiMe$_2$***i*-Ph**], 134.6 [SiMe$_2$***o*-Ph**], 128.8 [SiMe$_2$***p*-Ph**], 127.7 [SiMe$_2$***m*-Ph**], 127.6 [*m*-Ph], 127.4 [*o*-Ph], 125.6 [*p*-Ph], 83.7 [Bpin], 26.1 [Bpin], 1.4 [Si**Me$_3$**], –0.1 [Si**Me$_2$**Ph]. ^{11}B{^{1}H} NMR (128.2 MHz, CDCl$_3$): δ_B = 30.6. ^{29}Si{^{1}H} NMR (79.4 MHz, CDCl$_3$): δ_{Si} = –7.52 (SiMe$_3$), –10.81 (s, SiMe$_2$Ph). HRMS

(ESI) *m/z*: $[M + Na]^+$: Calcd for $C_{25}H_{37}O_2BSi_2Na$ 459.2317; Found 459.2313. Elem. Anal.: Calcd for $C_{25}H_{37}O_2BSi_2$: C, 68.78%; H, 8.54%. Found: C, 68.64%; H, 8.63%.

3.7.13 Synthesis of (*E*)-dimethyl(phenyl)(1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1/2-yl)silane (3.13a/3.13b)

A stock solution of **3.1** (0.43 mg, 0.80 µmol) was added to a mixture of 1-phenyl-1-propyne (20.0 µL, 0.16 mmol) and (dimethylphenylsilyl)boronic acid pinacol ester (44.0 µL, 0.16 mmol). The resulting reaction mixture was heated to 100 ˚C for 1 h. Upon cooling, ^{1}H NMR analysis of the crude material suggested a 93:7 mixture of regioisomers. The crude mixture was purified by column chromatography (Eluent: 100 % hexane followed by 100 % ethylacetate) resulting in isolation of **3.13a** as a white solid (the major isomer; the minor regioisomer of **3.13b** was also obtained). **Major (3.13a)**: Yield: 0.053 g, 87 %. ^{1}H NMR (399.5 MHz, $CDCl_3$): δ_H = 7.56 [m, 2H, $SiMe_2$**Ph**], 7.28 [m, 5H, $SiMe_2$**Ph** and Ph], 7.12 [m, 1H, *p*-Ph], 6.88 [m, 2H, Ph], 1.65 [s, 3H, ≡C**Me**], 1.04 [s, 12H, Bpin], 0.21 [s, 6H, Si**Me$_2$**Ph]. ^{13}C{^{1}H} NMR (100.46 MHz, $CDCl_3$): δ_C = 156.1, 145.9, 140.9, 134.2, 128.4, 128.2, 127.6, 127.2, 125.1. 83.6, 24.9, 20.6, –0.1. ^{11}B{^{1}H} NMR (128.2 MHz, $CDCl_3$): δ_B = 30.2. ^{29}Si{^{1}H} NMR (79.4 MHz, $CDCl_3$): δ_{Si} = –11.13. **Minor (3.13b)**: ^{1}H NMR (399.5 MHz, $CDCl_3$): δ_H = 7.60 [m, 2H, $SiMe_2$**Ph**], 7.32 [m, 5H, $SiMe_2$**Ph** and Ph], 7.19 [m, 1H, *p*-Ph], 7.09 [m, 2H, Ph], 1.68 [s, 3H, =C**Me**], 1.04 [s, 12H, Bpin], 0.49 [s, 6H, Si**Me$_2$**Ph]. ^{13}C{^{1}H} NMR (100.46 MHz, $CDCl_3$): δ_C = 152.8 [**C**=C], 148.8 [C=**C**], 143.7 [*i*-Ph], 140.2 [$SiMe_2$*i*-Ph], 134.2 [$SiMe_2$**Ph**], 128.7 [$SiMe_2$**Ph**], 128.5 [Ph], 128.0 [Ph], 127.8 [$SiMe_2$**Ph**], 125.8 [*p*-Ph], 83.6 [Bpin], 25.0 [Bpin], 21.5 [=C**Me**], –0.7 [Si**Me$_2$**Ph]. ^{11}B{^{1}H} NMR (128.2 MHz, $CDCl_3$): δ_B = 29.9. ^{29}Si{^{1}H} NMR (79.4 MHz, $CDCl_3$): δ_{Si} = –8.24. HRMS (ESI) *m/z*: $[M + Na]^+$: Calcd for $C_{23}H_{31}O_2BSiNa$ 401.2079; Found 401.2080.

3.7.14 Synthesis of *cis*-[Pd(ITMe)$_2$(SiMe$_2$Ph)(Bpin)] (3.14) and 3.2

Isolation of 3.14

3.1 (0.022 g, 0.04 mmol) was partially dissolved in toluene (5.0 mL). PhMe$_2$SiBpin (25.0 µL, 0.09 mmol) was added to this stirred suspension. The reaction mixture was subsequently stirred for 0.5 h. The volatiles were removed in vacuo. The resulting off--white solid dissolved in a minimum volume of CH_3CN and crystallized by leaving in a –30 ^oC freezer for 2 days. The mother liquor was decanted and the remaining crystals were dried *in vacuo*. Yield: 0.018 g, 69 %. ^{1}H NMR (399.5 MHz, CD_3CN): δ_H = 7.22 [dd, $^3J_{HH}$ = 7.8, 1.6 Hz, 2H, SiMe$_2$**Ph**], 7.00 [m, 2H, SiMe$_2$**Ph**], 6.96 [m, 1H, SiMe$_2$***p*-Ph**], 3.62 [s, 6H, N(1,3)-C**H$_3$**], 3.34 [s, 6H, N(1,3)-C**H$_3$**], 1.99 [s, 6H, C(4,5)-C**H$_3$**], 1.90 [s, 6H, C(4,5)-C**H$_3$**], 0.91 [s, 12H, Bpin], 0.12 [s, 6H, Si**Me$_2$**Ph]. ^{1}H NMR (399.5 MHz, C_6D_6): δ_H = 7.82 [m, 2H, SiMe$_2$**Ph**], 7.22 [m, 2H, SiMe$_2$**Ph**], 7.13 [m, 1H, SiMe$_2$***p*-Ph**], 3.55 [s, 6H, N(1,3)-C**H$_3$**], 3.23 [s, 6H, N(1,3)-C**H$_3$**], 1.49 [s, 6H, C(4,5)-CH_3], 1.46 [s, 6H, C(4,5)-CH_3], 1.14 [s, 12H, Bpin], 0.91 [s, 6H, Si**Me$_2$**Ph]. ^{13}C{^{1}H} NMR (100.46 MHz, CD_3CN): δ_C = 196.5 [N**C**N], 192.4 [N**C**N], 157.2 [*i*-Ph], 134.15 [Ph], 126.9 [Ph], 125.3 [*p*-Ph], 125.0 [**C**(4,5)-CH_3], 124.6 [**C**(4,5)-CH_3], 80.35 [Bpin], 35.7 [N(1,3)-**C**H_3], 35.3 [N(1,3)-**C**H_3], 25.8 [Bpin], 9.0 [C(4,5)-**C**H_3], 9.0 [C(4,5)-**C**H_3], 6.8 [Si**Me$_2$**Ph]. ^{11}B{^{1}H} NMR (128.2 MHz, CD_3CN): δ_B = 46.2. ^{29}Si{^{1}H} NMR (79.4 MHz, CD_3CN): δ_{Si} = –5.35. Elem. Anal.: Calcd for $C_{28}H_{47}N_4O_2BSiPd$: C, 54.50%; H, 7.68%; N, 9.08%. Found: C, 54.40%; H, 7.65%, N, 9.02%.

Crystal data for **3.14**: $C_{28}H_{47}BN_4O_2SiPd$, M_r = 616.99 g mol^{-1}, monoclinic, space group $P2_1/n$, a = 12.9381(3) Å, b = 17.8318(3) Å, c = 14.8311(4) Å, α = 90^o, β = 113.454(3)^o, γ = 90^o, V = 3138.99(13) Å^3, Z = 4, T = 173 K, λCu(Kα) = 1.54184, R_1 [$I > 2\sigma(I)$] = 0.0350, wR_2 (all data) = 0.0880, *GooF* = 1.044.

Isolation of 3.2

The mother liquor decanted above was filtered through a plug of silica in air. The volatiles from the filtrate collected were removed under reduced pressure to reveal a white powdered solid. Yield: 0.017 g, 92%. ^{1}H NMR (399.5 MHz, $CDCl_3$): δ_H = 7.65 [m, 2H, $SiMe_2$**Ph**], 7.34 [m, 3H, $SiMe_2$**Ph**], 6.97 [m, 8H, Ph], 6.71 [m, 2H, *p*-Ph], 1.05 [s, 12H, Bpin], 0.34 [s, 6H, Si**Me$_2$**Ph]. ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$): δ_C = 155.1, 144.6, 142.9, 139.8, 134.5, 129.1, 128.8, 128.6, 127.8, 127.3, 127.3, 125.5, 124.8, 84.0, 25.0, −0.1. ^{11}B{^{1}H} NMR (128.2 MHz, $CDCl_3$): δ_B = 30.0. ^{29}Si{^{1}H} NMR (79.4 MHz, $CDCl_3$): δ_{Si} = −9.32. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{28}H_{33}O_2BSiNa$ 463.2235; Found 463.2239.

3.7.15 Stoichiometric Synthesis of 3.1 and 3.2 from 3.14

In a J Young tap NMR tube, **3.14** (0.006 g, 9.72 µmol) and diphenylacetylene (0.005 g, 28.05 µmol) were dissolved in C_6D_6 (1.0 mL). The resulting reaction mixture was agitated for 10 min at room temperature. ^{1}H NMR analysis indicated full conversion of **3.14** to **3.1** and **3.2**.

3.7.16 Synthesis of [Pd(ITMe)$_2$(PhC≡CNA)] (3.16)

An isopropanol (9.5 µL, 0.12 mL) toluene (2.0 mL) solution was added to a mixture of [(ITMe)Pd(methallyl)Cl] (0.040 g, 0.12 mmol), ITMe (0.017 g, 0.14 mmol) and ^{t}BuOK (0.014 g, 0.13 mmol) were suspended in toluene (10.0 mL). The resulting reaction mixture was stirred at room temperature for 4.5 h. At this stage, the volatiles were removed in vacuo, the crude material was re-dissolved in toluene (15.0 mL) and 1-(phenylethynl)naphthalene (0.032 g, 0.14 mmol) was added. The reaction mixture was stirred at room temperature for a further 16 h and then the solution was filtered *via*

cannula. The filtrate's volatiles were removed in vacuo and the orange solid was washed with hexane (3 x 5.0 mL). Yield: 0.052 g, 72%. ^{1}H NMR (399.5 MHz, C_6D_6): δ_H = 8.98 [d, $^{3}J_{HH}$ = 8.2 Hz, 1H, 10-NA], 7.95 [m, 1H, 2-NA], 7.79 [dd, *J* = 8.1, 1.2 Hz, 2H, *o*-Ph], 7.76 [m, 1H, 9-NA], 7.57 [d, $^{3}J_{HH}$ = 8.2 Hz, 1H, 7-NA], 7.39 [m, 1H, 3-NA], 7.29 [m, 1H, 8-NA], 7.25 [m, 1H, 4-NA], 7.19 [m, 2H, *m*-Ph], 7.02 [m, 1H, *p*-Ph], 3.54 [s, 6H, N(1,3)-C**H**$_3$], 3.40 [s, 6H, N(1,3)-C**H**$_3$], 1.56 [s, 6H, C(4,5)-C**H**$_3$], 1.44 [s, 6H, C(4,5)-C**H**$_3$]. ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6): δ_C = 198.1 [N**C**N], 197.7 [N**C**N], 140.0 [1-NA], 137.5 [*i*-Ph], 134.8 [5-NA], 131.4 [6-NA], 130.9 [*o*-Ph], 129.0 [10-NA], 128.1 [*m*-Ph], 128.1 [9-NA], 127.5 [**C**=C], 126.4 [3-NA], 125.5 [8-NA], 125.2 [C=**C**], 124.7 [2-NA], 124.5 [*p*-Ph], 124.4 [4-NA], 123.7 [7-NA], 123.2 [**C**(4,5)-CH_3], 123.0 [**C**(4,5)-CH_3], 35.3 [N(1,3)-**C**H_3], 35.1 [N(1,3)-**C**H_3], 9.0 [C(4,5)-**C**H_3], 8.9 [C(4,5)-**C**H_3]. Elem. Anal.: Calcd for $C_{32}H_{36}N_4Pd$: C, 65.92%; H, 6.22%; N, 9.61%. Found: C, 65.76%; H, 6.31%, N, 9.57%.

3.7.17 Synthesis of [Pd(ITMe)$_2$({4-Et}PhC≡CPh{4-OMe})] (3.17)

An isopropanol (8.5 µL, 0.11 mmol) toluene (2.0 mL) solution was added to a mixture of [(ITMe)Pd(methallyl)Cl] (0.036 g, 0.11 mmol), ^{t}BuOK (0.014 g, 0.12 mmol) and ITMe (0.016 g, 0.13 mmol) suspended in toluene (10.0 mL). The resulting reaction mixture was stirred at room temperature for 4.5 h. At this the volatiles were removed *in vacuo*, the crude material was re-dissolved in toluene (15.0 mL) and 1-ethyl-4-((4-methoxyphenyl)ethynl)benzene (0.032 g, 0.13 mmol) was added. The reaction mixture was stirred for a further 19 h at room temperature and then the solution was filtered *via* cannula. The filtrate's volatiles were removed in vacuo and the yellow solid was washed with hexane (3 x 5.0 mL). Yield: 0.045 g, 68%. ^{1}H NMR (399.5 MHz, C_6D_6): δ_H = 7.96 [m, 4H, *o*-PhEt and *o*-PhOMe], 7.16 [m, 2H, *m*-PhEt], 6.89 [m, 2H, *m*-PhOMe], 3.52 [s,

12H, N(1,3)-C**H**$_3$], 3.36 [s, 3H, O**Me**], 2.54 [q, $^3J_{HH}$ = 7.7 Hz, 2H, C**H**$_2$CH$_3$], 1.57 [s, 12H, C(4,5)-C**H**$_3$], 1.15 [t, $^3J_{HH}$ = 7.7 Hz, 3H, CH$_2$C**H**$_3$]. ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6): δ_C = 199.4 [N**C**N], 199.4 [N**C**N], 157.4 [*p*-PhOMe], 139.4 [*p*-PhEt], 136.3 [*i*-PhEt], 131.6 [*o*-PhOMe], 131.0 [*i*-PhOMe], 130.3 [*o*-PhEt], 127.8 [*m*-PhEt], 124.3 [C≡**C**], 123.3 [**C**≡C], 123.0 [**C**(4,5)-CH$_3$], 113.9 [*m*-PhOMe], 54.8 [O**Me**], 35.2 [N(1,3)-**C**H$_3$], 29.2 [**C**H$_2$CH$_3$], 16.1 [CH$_2$**C**H$_3$], 9.0 [C(4,5)-**C**H$_3$]. Elem. Anal.: Calcd for $C_{31}H_{40}N_4OPd$: C, 62.99%; H, 6.82%; N, 9.48%. Found: C, 62.90%; H, 6.89%, N, 9.39%.

3.8 References

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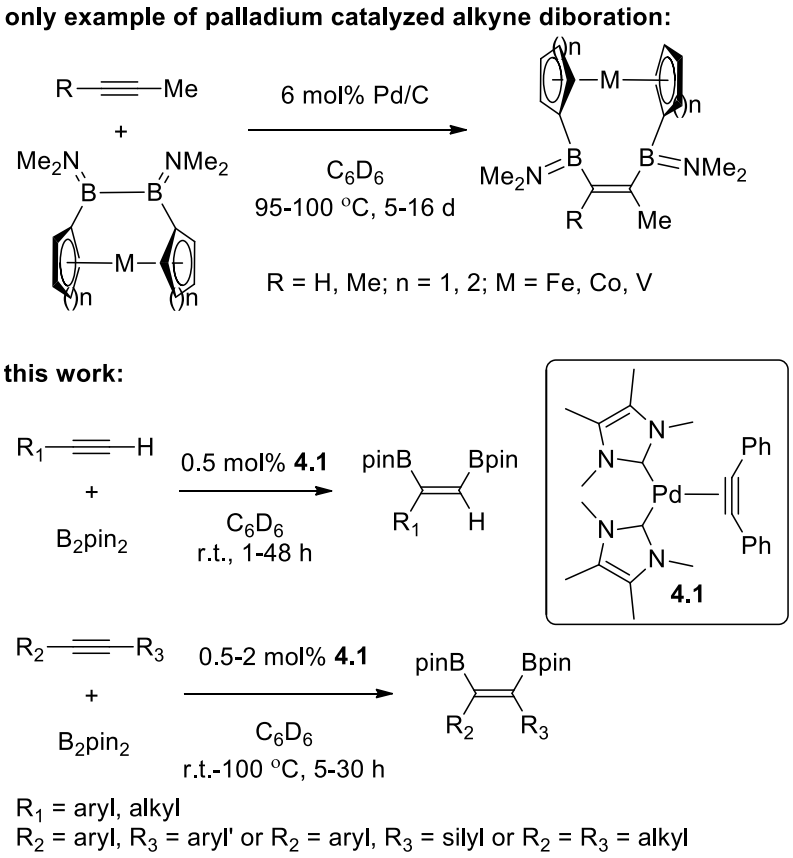
Chapter 4

(N-Heterocyclic-Carbene)$_2$Pd(0) Catalyzed Diboration of Internal and Terminal Alkynes

4.1 Introduction

The transition metal catalyzed π-insertion of alkynes into homo and hetero element-element (E-E') bonds provides the most atom economical route for the stereoselective synthesis of tri- and tetra-substituted alkenes.[1] Among the various E-E' reagents used in such transformations, B-B bonds (diborons) in particular have attracted substantial interest.[2–6] The resulting 1,2-diboryl alkenes, due to their participation in Suzuki-Miyaura cross-coupling,[7–9] are recognized as important building blocks in, for example, the synthesis of pharmaceuticals,[10–12] chirotopical devices,[13] and optically/electronically active polymeric materials.[14] A number of transition metals have been utilized in both homogeneous and heterogeneous catalytic addition of B-B bonds (diboration) to alkynes including cobalt,[15] copper,[16] iridium,[17] rhodium,[17] iron,[18] platinum,[19] and palladium.[20,21] To date, platinum is by far the most effective and widely studied;[22–26] this is attributed to the facile cleavage of the B-B bond and the lability of the corresponding bis(boryl)platinum complexes.[27,28] As a result, even easily handled and often air stable tetraalkoxy- and tetraaryloxydiboron reagents can be utilized, regardless of their relatively high B-B bond strength.[29] However, despite the extensive studies, a number of general limitations remain: the use of elevated temperatures, high catalyst loadings and long reaction times. Only two examples of palladium catalysed alkyne diborations have been described in the literature, both by Braunschweig and co-workers involving the heterogeneous catalysed diboration of alkynes using [2]borametalloarenophanes.[20,21] The reactions required 6 mol% of Pd/C and proceeded

over a period of 5-16 days at temperatures of 95-100 °C (Scheme 4.1). The dearth of reported palladium examples is attributed to the energetics of the B-B oxidative addition. The process is endothermic with a very low reverse activation barrier,[30] and therefore kinetically and thermodynamically unfavourable.



Scheme 4.1 Palladium catalysed diboration of alkynes

The synthesis of the N-heterocyclic carbene bearing[31–33] complex [Pd(ITMe)$_2$(PhC≡CPh)] (ITMe = 1,3,4,5-tetramethylimidazol-2-ylidene) (**4.1**) and its high catalytic reactivity in bis(silyl)ation,[34] and silaboration of internal and terminal alkynes,[35] were reported in Chapter 2 and 3. This prompted an investigation into the potential of **4.1** for the diboration of alkynes. Herein, the use of **4.1** in the unprecedented palladium catalysed diboration of sterically demanding internal and terminal alkynes,

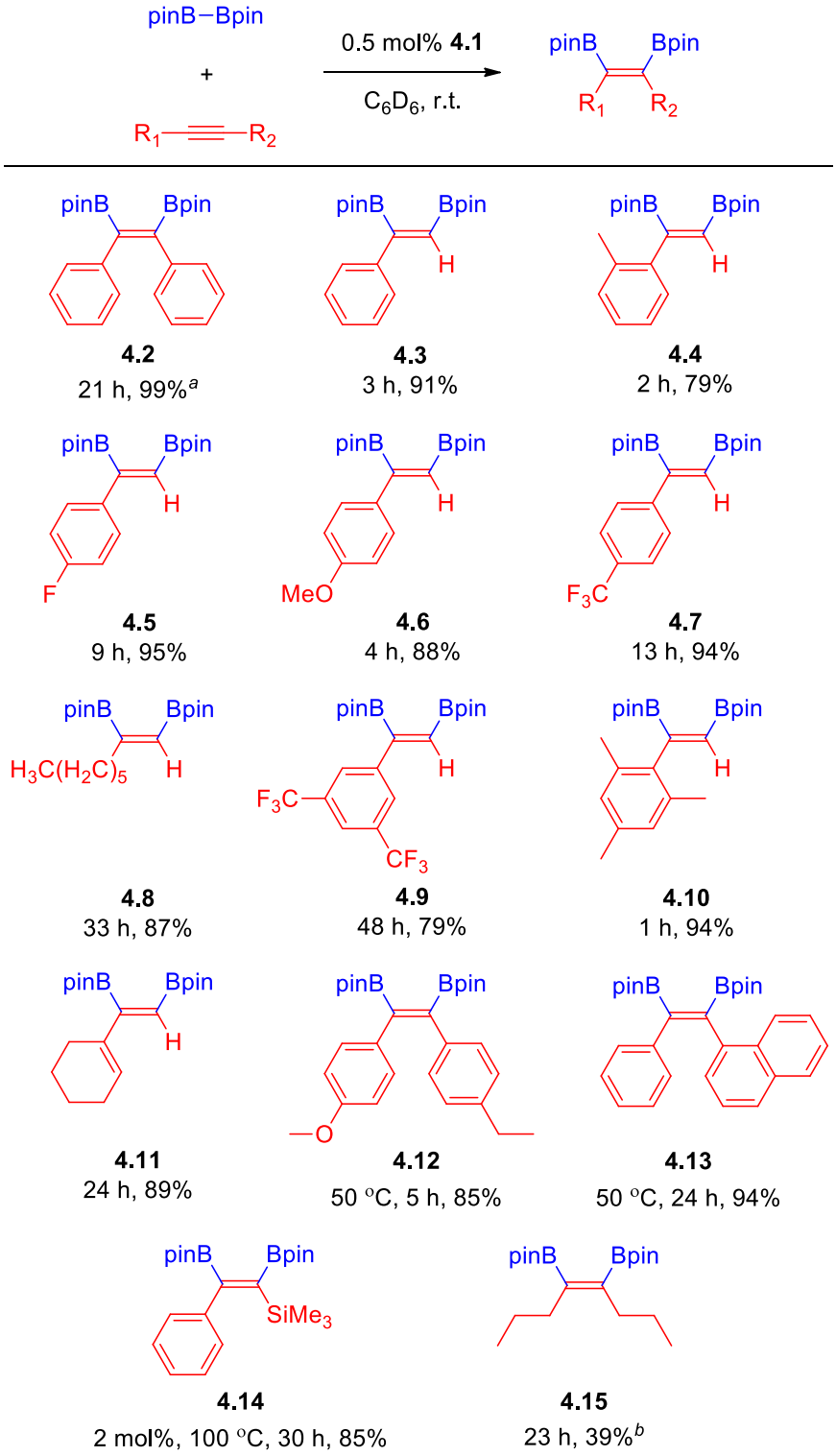
employing low catalytic loadings and mild reaction temperatures is detailed. In addition, a summary of a thorough density functional theory (DFT) study that establishes a likely mechanistic pathway explaining this reactivity, conducted by collaborators at the Universidade de São Paulo, Brazil, is reported.

4.2 Catalytic diboration of alkynes

The reaction parameters were optimized using diphenylacetylene and commercially available bis(pinacalato)diboron (B_2pin_2) as the model substrates, with C_6D_6 as the solvent in order to monitor the progression by ^1H NMR spectroscopy. 100% stereoeselective conversion to (*Z*)-1,2-diphenyl-1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethane (**4.2**) was observed using 0.5 mol% of **4.1** at room temperature in 21 h. Unfortunately, initial workup procedures proved troublesome, with the use of either silica and alumina columns resulting in very low isolated yields presumably due to reactivity with, or strong binding to the stationary phase. Kugelrohr distillation is an alternative methodology reported in the literature,[36] but is generally applicable to small quantities of material and therefore unviable as a scalable procedure. The more noticeable impurity was unreacted B_2pin_2. To remove it, the crude dry material was stirred in deionized H_2O at room temperature over 24 h.[37] Subsequent filtration and drying resulted in the clean isolation of **4.2** in a 99% yield. While there are several protocols in the literature for the synthesis of **4.2**, the previous highest yield was reported by Jin and co-workers who obtained a comparable yield using 2 mol% of nanoporous gold at 100 ^oC over 12 h.[38] To test the potential of this protocol for scaling-up, the synthesis of **4.2** was also carried out in non-deuterated benzene and toluene on a larger practical scale, resulting in comparable isolated yields (Table 4.1). The potential of **4.1** to catalyse this reaction using other diboron reagents was also investigated, but unfortunately neither

bis(catecholato)diboron (B_2cat_2) nor bis(neopentylglycolato)diboron (B_2neop_2) afforded any of the diboration products.

With this information in hand, a series of sterically and electronically demanding alkynes were reacted with B_2pin_2 (Table 4.1). The diboration of alkyl and aryl terminal alkynes proceeded using 0.5 mol% of **4.1** at room temperature over 1-48 h with 100% stereoselectivity. A wide range of functionalities on the aryl moiety was tolerated including fluoro, trifluoromethyl, methoxy and alkyl groups in the *ortho*, *meta* and *para* positions. Compounds **4.3**, **4.4**, **4.5** and **4.6** were synthesized using lower catalyst loadings, milder temperatures and in higher or comparable yields to the highest yielding protocols in the literature (using 2 mol% nanoporous gold at 100 ^oC),[38] and **4.5** and **4.6** were synthesized with comparatively higher stereoselectivities (Table 4.1). Low reaction temperatures have been reported for the synthesis of these compound using both homo- and heterogeneous platinum complexes, although at the expense of lower yields and in many cases higher catalyst loadings.[22–26,39,40] Compound **4.7** was synthesized in a higher yield than the highest yielding protocol in the literature (using 0.2 mol% Pt/TiO_2 at 70 ^oC, 16 h).[25] The previous highest yielding synthesis for compound **4.8** was reported by Miyaura and co-workers (94% yield) using 3 mol% $[Pt(CO)_2(PPh_3)_2]$ at 80 ^oC in DMF over 24 h.[22] The novel compounds **4.9**, **4.10** and **4.11** were synthesized with 100% *syn*-stereoselectivity as established by NOESY NMR spectroscopy (Table 4.1). In the case of **4.11** chemoselectivity is achieved since the olefin remains unreacted. Unsymmetrical internal alkynes also reacted well under these conditions, albeit at higher -but still mild- temperatures (50 ^oC). The novel compounds **4.12** and **4.13** were synthesized with 100% *syn*-stereoselectivities. The diboration of 1-phenyl-2-trimethylsilane, resulting in the formation of **4.14**, required an increased catalyst loading of 2 mol% and a higher



B_2pin_2: 1-1.5 equiv. (see experimental for details). [a]Scale-up synthesis of **4.2**: 0.8 mmol of substrate, benzene, r.t., 24 h (92%); 0.95 mmol of substrate, toluene, r.t, 24 h (95%). [b]Conversion of starting alkyne to **4.15**.

Table 4.1 Diboration of terminal and internal alkynes

temperature (100 °C). The previous best procedure for the synthesis of **4.14** was detailed by Nishihara, obtaining a comparable yield using 5 mol% of [$Pt(PPh_3)_4$] at 80 °C.[26] Finally, the diboration of 4-octyne resulted in a maximum conversion to **4.15** of 39%. Even lower conversions and the formation of palladium black were observed when the reaction was carried out at higher temperatures. It is presumed that the electron-rich nature of the alkyne results in a low binding affinity to the very electron-rich, active catalyst and therefore discourages diboration.

4.3 Mechanism

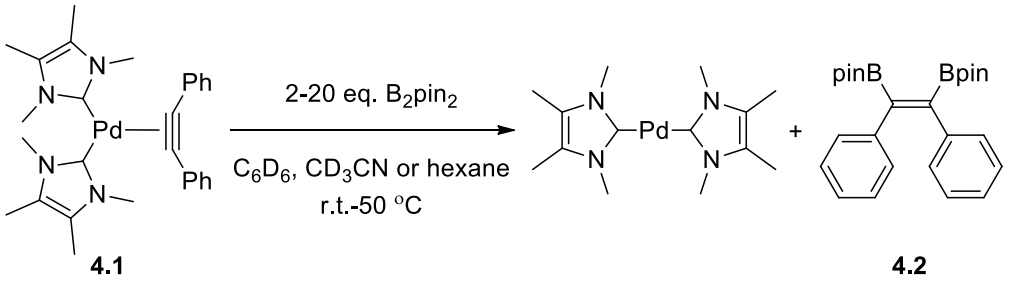
4.3.1 General Mechanism

The accepted experimental and theoretical mechanism for platinum group transition metal catalysed diboration of alkynes involves: (i) oxidative addition of the B-B bond to a $M(0)L_2$ centre forming $L_2M(II)(B)_2$, (ii) dissociation of an L ligand (a phosphine) and coordination of an alkyne in its place, (iii) insertion of the alkyne into the M-B bond, (iv) isomerization of the resulting complex, followed by re-coordination of the L ligand, and (v) stereoselective reductive elimination.[30,41] This mechanism is general and applies to other E-E' bond additions to alkynes.[42–47] In Chapter 2 and 3 it was proposed that the use of NHCs as a ligand set results in a different mechanism, in which both NHCs remain coordinated throughout. This alternative pathway was used as an explanation for the observed increase in reactivity of **4.1** compared to their phosphine an isocyanide analogues in alkyne bis(silyl)ations[34] and silaborations.[35]

4.3.2 Attempted Synthesis of [$(NHC)_2Pd(Bpin)_2$] Complexes

Within Chapter 2 and 3 the corresponding (element)(element')Pd(II) intermediates were isolated with ease. However, the oxidative addition of B-B bonds at a palladium centre

has not been reported in the literature. Computational studies predicted that this oxidative addition step possessed an activation barrier of 8.6 kcal mol^{-1}. However, the B-B oxidative addition to Pd(0) was characterized as an endothermic process with a reverse barrier of only 0.1 kcal mol^{-1}.[30] The cause of this low reverse barrier was attributed to the promotion energy from $d^{10}Pd(0)L_2$ with linear geometry (singlet – ground state) to $d^9s^1Pd(0)L_2$ with bent geometry (triplet – excited state). The energy difference between these two electronic configurations is larger for $Pd(0)L_2$ than for $Pt(0)L_2$ with phosphines. Despite this damning report, attempts at isolation of such oxidative addition complexes were undertaken by reacting the diboron reagent B_2pin_2 with **4.1**. The reactions were performed in C_6D_6, CD_3CN and hexane at room temperature and 50 °C (Scheme 4.2). However, in all instances the only palladium species observed was $[Pd(ITMe)_2]$, as determined by the NHC based CH_3 resonances in the ^1H NMR spectrum at 3.93 and 1.55 ppm. ^1H NMR analysis of crude material also indicated a 100% conversion of diphenylacetylene to the organic product **4.2**. These observations suggest that at least on an isolable level oxidative addition of a B-B at a NHC-Pd(0) centre is not, as predicted, a favourable process. Extension to other diboron reagents, B_2cat_2 and B_2neop_2, was unsuccessful.

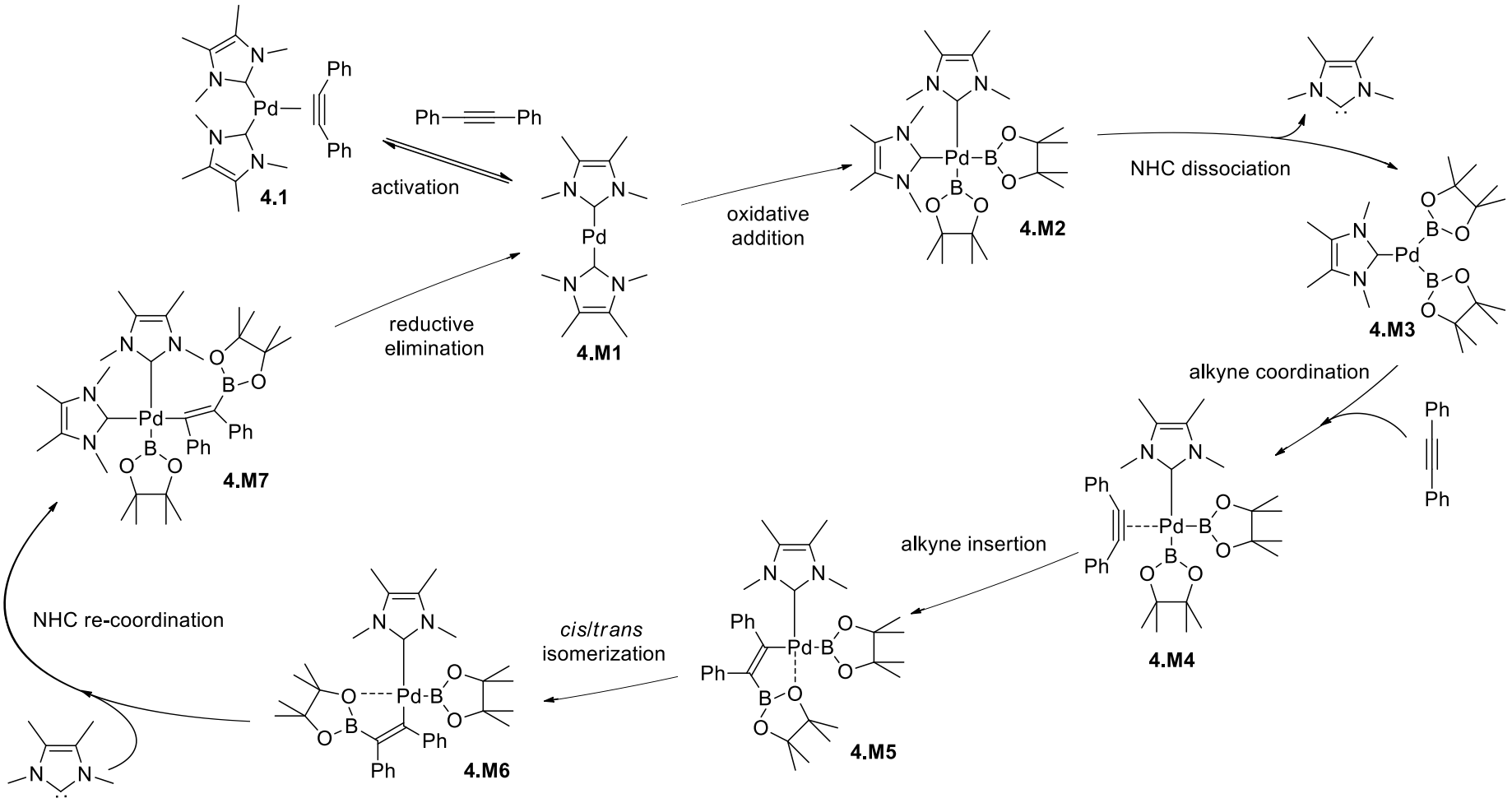


4.1 **4.2**

Scheme 4.2 Stoichiometric addition of B_2pin_2 to **4.1**

4.3.3 Computationally Calculated Mechanism

To gain insight into the mechanism and role of **4.1** in the diboration of alkynes, a density functional theory study was carried out on the optimized model substrates employing a M06-L/BSI level of theory by our collaborators, Professor Ataualpa A. C. Braga and his group. Their investigations suggested that the Pd(0)-catalyzed alkyne diboration supported by NHC ligands proceeded through the same mechanism as the phosphine analogues. This mechanism, depicted in Scheme 4.3, can therefore be summarized as (i) activation of the catalyst by alkyne dissociation from **4.1**, (ii) oxidative addition of the B-B to Pd(0), (iii) ligand dissociation from bis(boryl)palladium(II) complex **4.M3**, (iv) insertion of the alkyne into a Pd-B bond *via* migratory insertion, (v) *cis-trans* isomerization involving the C-Bpin and the allyl ligands, and (vi) reduction of Pd(II) to Pd(0) with the elimination of the *syn*-1,2-diborylated product.[48]



Scheme 4.3 Proposed mechanism for [Pd(NHC)$_2$] catalysed diboration of alkynes

Sasaki and co-workers, studied the activity of $Pd(0)L_2$ and $Pt(0)L_2$ catalyst (L = phosphine) in the C-H activation of methane by oxidative additions.[49] They observed that chelating phosphines destabilize the $M(0)L_2$ complexes bringing the reactants closer and promoting the oxidative addition transition state, [(diboron)$Pd(0)L_2$]. (NHC)-Pd(0) catalysts were also investigated in the activation of methane by oxidative addition,[50] and considered better candidates as catalyst than the analogous phosphines-based Pd(0) complexes. Based on these results, it is proposed that the considerably increased reactivity of NHC-bearing complex **4.1** in the alkyne diboration is a consequence of oxidative addition step. More specifically, on the destabilization of [(diboron)$Pd(0)L_2$] adduct by the NHC ligands resulting in a lower activation free energy for the oxidative addition (3.9 kcal mol^{-1})

4.4 Conclusions

Catalytic investigations have shown that complex **4.1** acts as highly active catalyst in the diboration of sterically and electronically demanding alkynes. For terminal alkynes, low catalyst loadings and temperatures were used for the 100% stereoselective synthesis of *syn*-1,2-diborylalkenes. Internal alkynes can react using this protocol, albeit requiring elevated temperatures. This represents the first example of homogeneous palladium catalysed diboration of alkynes. DFT calculations were performed by collaborators to understand the activity of the NHC-bearing catalyst **4.1**. The results suggest that **4.1** follows the same mechanistic path as the corresponding analogous phosphine system. The dissociation of one NHC is a crucial part of the mechanism, unaccounted for in the proposed pathways for the other E-E' bond additions to alkynes (Chapter 2 and 3). Despite their strong coordination to metal centres, it has been previously shown that the

reversible dissociation of an NHC from an oxidative addition products is a mechanistic possibility.[51,52] The DFT study also showed that the destabilization of the (diboron)Pd(0)L_2 adduct by the NHCs was key to the successful oxidative addition of the B-B bond. This study was reported in the journal *Catalysis Science and Technology*.[48]

4.5 Experimental Details for Chapter 4

General experimental details are given in appendix A1.

4.5.1 Scaled Synthesis of [Pd(ITMe)$_2$(PhC≡CPh)] (4.1)

In a vial, isopropanol (109.0 μL, 1.42 mmol) was added to a mixture of [(ITMe)Pd (methallyl)Cl] (0.457 g, 1.42 mmol), ^{t}BuOK (0.161 g, 1.44 mmol) and ITMe (0.183 g, 1.48 mmol) in toluene (80 mL). The resulting reaction mixture was stirred at room temperature under a N_2 for 4 h. At this point, diphenylacetylene (0.280 g, 1.57 mmol) was added and the reaction mixture was stirred for a further 18 h. At this stage, the volatiles were removed in vacuo. Crude **4.1** was dissolved in CH_3CN (100 mL) and filtered. The filtrate volatiles were removed under reduced pressure and yellow powdered solid was washed with a 1:1 toluene/hexane solution (3 x 20 mL) followed by pentane (3 x 20 mL). Yield: 0.407 g, 54 %. ^{1}H NMR (399.5 MHz, C_6D_6): δ_H = 7.99 [dd, $^3J_{HH}$ = 8.1, $^4J_{HH}$ = 1.3 Hz, 4H, *m*-Ph], 7.27 [m, 4H, *o*-Ph], 7.05 [tt, $^3J_{HH}$ = 7.3, $^4J_{HH}$ = 1.3 Hz, 2H, *p*-Ph], 3.49 [s, 12H, N(1,3)-C**H**$_3$], 1.54 [s, 12H, C(4,5)-CH_3]. ^{13}C{^{1}H} NMR (100.46 MHz, C_6D_6): δ_C = 198.7 [N**C**N], 138.6 [C≡**C**], 130.1 [*o*-Ph], 128.2 [*m*-Ph], 126.3 [*i*-Ph], 124.2 [*p*-Ph], 123.1 [**C**(4,5)-CH_3], 35.2 [N(1,3)-**C**H_3], 9.0 [C(4,5)-**C**H_3].

4.5.2 Stock Solution of 4.1

Stock solutions were made in batches; in a glovebox 5 mg of **4.1** was dissolved in 5 mL of C_6D_6.

4.5.3 Synthesis of (*Z*)-1,2-diphenyl-1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethane (4.2)

A stock solution of **4.1** (0.47 mg, 0.78 μmol) in C_6D_6 (471 μL) was added to a mixture of diphenylacetylene (0.032 g, 0.18 mmol) and bis(pinacolato)diboron (0.046 g, 0.18 mmol). The resulting reaction mixture was stirred at room temperature for 21 h under a N_2 atmosphere. At this point all volatiles were removed in vacuo. Deionized H_2O (35 mL) was added and the mixture was stirred at room temperature for 24 h. Filtration and drying under reduced pressure resulted in the collection of a white solid. Yield: 0.076 g, 99%. ^{1}H NMR (399.5 MHz, $CDCl_3$): δ_H = 7.05 [m, 6H, Ph], 6.95 [m, 4H, Ph], 1.32 [s, 24H, Bpin]. $^{13}C\{^1H\}$ NMR (100.46 MHz, $CDCl_3$): δ_C = 141.4, 129.5, 127.5, 125.9, 84.2, 25.0. $^{11}B\{^1H\}$ NMR (128.2 MHz, $CDCl_3$): δ_B = 30.3 (spectroscopic data in agreement with the literature).

4.5.4 Synthesis of (*E*)-2,2'-(1-phenylethene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (4.3)

To a stock solution of **4.1** (0.61 mg, 1.14 μmol) in C_6D_6 (607 μmol) was added to a mixture of phenylacetylene (25.0 μL, 0.23 mmol) and bis(pinacolato)diboron (0.058 g, 0.23 mmol). The resulting reaction mixture was stirred at room temperature for 3 h under a N_2 atmosphere. The volatiles were removed in vacuo, deionized H_2O (35 mL) was added to the crude material and the mixture was stirred for 24 h. Decanting the H_2O and drying under vacuum resulted in the isolation of a yellow oil. Yield: 0.074 g, 91 %. ^{1}H NMR (399.5 MHz, $CDCl_3$): δ_H = 7.43 [m, 2H, Ph], 7.28 [m, 3H, Ph], 6.28 [s, 1H, =C**H**], 1.37 [s, 12H, Bpin], 1.30 [s, 12H, Bpin]. $^{13}C\{^1H\}$ NMR (100.46 MHz, $CDCl_3$): δ_C = 143.2, 128.4, 127.7, 126.7, 84.3, 83.7, 25.2, 25.0. $^{11}B\{^1H\}$ (128.2 MHz, $CDCl_3$): δ_B = 30.1 (spectroscopic data in agreement with the literature).

4.5.5 Synthesis of (*E*)-2,2'-(1-(*o*-tolyl)ethene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (4.4)

A stock solution of **4.1** (0.42 mg, 0.79 μmol) in C_6D_6 (423 μL) was added to a mixture of 1-ethynyl-2-methylbenzene (20.0 μL, 0.16 mmol) and bis(pinacalato)diboron (0.051 g, 0.20 mmol). The resulting reaction mixture was stirred for 2 h at room temperature under a N_2 atmosphere. At this point all volatiles were removed in vacuo, deionized H_2O (50 mL) was then added and the mixture was stirred for 24 h. The H_2O was decanted, the resulting pale brown solid was washed with more deionized H_2O (3 x 25 mL) and dried thoroughly under a high vacuum. Yield: 0.046 g, 79 %. ^{1}H NMR (399.5 MHz, $CDCl_3$): δ_H = 7.12 [m, 4H, 3,4,5,6-Ph], 6.02 [s, 1H, =C**H**], 2.31 [s, 3H, PhC**H$_3$**], 1.33 [s, 12H, Bpin], 1.29 [s, 12H, Bpin]. ^{13}C{^{1}H} NMR (100.46 MHz, $CDCl_3$): δ_C = 144.8, 134.7, 130.0, 128.1, 126.8, 125.7, 84.1, 83.7, 25.1, 25.0, 20.6, 2 C=C were not observed due to quadrapolar broadening caused by adjacent B atoms. ^{11}B{^{1}H} NMR (128.2 MHz, $CDCl_3$): δ_B = 30.0 (spectroscopic data in agreement with the literature).

4.5.6 Synthesis of (*E*)-2,2'-(1-(4-fluorophenyl)ethene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (4.5)

A stock solution of **1** (0.50 mg, 0.94 μmol) in C_6D_6 (500 μL) was added to a mixture of 1-ethynyl-4-fluorobenzene (0.023 g, 0.19 mmol) and bis(pinacalato)diboron (0.048 g, 0.19 mmol). The resulting reaction mixture was stirred at room temperature for 9 h under a N_2 atmosphere. At this point the volatiles were removed in vacuo, deionized H_2O (35 mL) was added and the resulting mixture was stirred at room temperature for 24 h. The H_2O was then decanted and the resulting yellow oil was dried under vacuum. Yield: 0.067 g, 95 %. ^{1}H NMR (399.5 MHz, $CDCl_3$): δ_H = 7.41 [m, 2H, Ph], 6.98 [m, 2H, Ph], 6.24 [s, 1H, =C**H**], 1.37 [s, 12H, Bpin], 1.30 [s, 12H, Bpin]. ^{13}C{^{1}H} NMR (100.46 MHz, $CDCl_3$):

δ_C = 162.7 [d, $^1J_{CF}$ = 246.6 Hz, *p*-Ph], 139.2 [d, $^4J_{CF}$ = 3.3 Hz, *i*-Ph], 128.3 [d, $^3J_{CF}$ = 8.0 Hz, *o*-Ph], 115.3 [d, $^2J_{CF}$ = 21.4 Hz, *m*-Ph], 84.3 [Bpin], 83.7 [Bpin], 25.2 [Bpin], 25.0 [Bpin], 2 C=C were not observed due to quadrapolar broadening caused by adjacent B atoms. $^{11}B\{^1H\}$ NMR (128.2 MHz, $CDCl_3$): δ_B = 30.1. ^{19}F NMR (375.9 MHz, $CDCl_3$): δ_F = –115.10 (m) (spectroscopic data in agreement with the literature).

4.5.7 Synthesis of (*E*)-2,2'-(1-(4-methoxyphenyl)ethene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (4.6)

A stock solution of **4.1** (0.50 mg, 0.93 µmol) in C_6D_6 (496 µL) was added to a mixture of 1-ethynyl-4-methoxybenzene (0.025 g, 0.18 mmol) and bis(pinacalato)diboron (0.055 g, 0.22 mmol). The resulting reaction mixture was stirred at room temperature for 4 h under a N_2 atmosphere. At this point all volatiles were removed in vacuo, deionized H_2O (35 mL) was then added and the mixture was stirred for 24 h. The H_2O was decanted, the resulting dark yellow oil was washed with more deionized H_2O (2 x 25 mL) and dried thoroughly under a high vacuum. Yield: 0.063 g, 88 %. ^1H NMR (399.5 MHz, $CDCl_3$): δ_H = 7.40 [m, 2H, Ph], 6.84 [m, 2H, Ph], 6.22 [s, 1H, =C**H**], 3.79 [s, 3H, O**Me**], 1.38 [s, 12H, Bpin], 1.30 [s, 12H, Bpin]. $^{13}C\{^1H\}$ NMR (100.46 MHz, $CDCl_3$): δ_C = 159.6, 135.6, 133.7 [**C**=C], 127.9, 114.1 [C=**C**], 113.9, 84.2, 83.6, 55.3, 25.3, 25.0. $^{11}B\{^1H\}$ NMR (128.2 MHz, $CDCl_3$): δ_B = 30.4 (spectroscopic data in agreement with the literature).

4.5.8 Synthesis of (*E*)-2,2'-(1-(4-(trifluoromethyl)phenyl)ethene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (4.7)

A stock solution of **4.1** (0.41 mg, 0.77 µmol) in C_6D_6 (408 µL) was added to a mixture of 1-ethynyl-4-(trifluoromethyl)benzene (25.0 µL, 0.15 mmol) and bis(pinacalato)diboron (0.055 g, 0.22 mmol). The resulting reaction mixture was stirred at room temperature for

13 h under a N_2 atmosphere. At this point the volatiles were removed in vacuo, deionized H_2O (35 mL) was then added and the mixture was stirred for 24 h. The H_2O was then decanted and the resulting product was washed with more deionized H_2O (2 x 25 mL). The off-white solid was then dried under a high vacuum. Yield: 0.061 g, 94 %. ^{1}H NMR (399.5 MHz, $CDCl_3$): δ_H = 7.55 [m, 4H, *o*- and *m*-Ph], 6.35 [s, 1H, C=C**H**], 1.37 [s, 12H, Bpin], 1.32 [s, 12H, Bpin]. $^{13}C\{^{1}H\}$ NMR (100.46 MHz, $CDCl_3$): δ_C = 146.9 [*i*-Ph], 129.5 [q, $^{2}J_{CF}$ = 32.4 Hz, *p*-Ph], 127.0 [*o*-Ph], 125.4 [q, $^{3}J_{CF}$ = 3.8 Hz, *m*-Ph], 124.4 [q, $^{1}J_{CF}$ = 272.8 Hz, **C**F_3], 84.5 [Bpin], 84.0 [Bpin], 25.1 [Bpin], 25.0 [Bpin], 2 C=C were not observed due to quadrapolar broadening caused by adjacent B atoms. $^{11}B\{^{1}H\}$ NMR (128.2 MHz, $CDCl_3$): δ_B = 30.3. ^{19}F NMR (375.9 MHz, $CDCl_3$): δ_F = –62.53 (spectroscopic data in agreement with the literature).

4.5.9 Synthesis of (*E*)-2,2'-(oct-1-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (4.8)

A stock solution of **4.1** (0.51 mg, 0.96 µL) in C_6D_6 (514 µL) was added to a mixture of 1-octyne (15.0 µL, 0.19 mmol) and bis(pinacolato)diboron (0.055 g, 0.21 mmol). The resulting reaction mixture was stirred at room temperature for 33 h under a N_2 atmosphere. At this point, the volatiles were removed in vacuo. The resulting crude product was stirred in deionized H_2O (30 mL) over 24 h, the H_2O was then decanted and colourless oil was dried under vacuum. Yield: 0.070 g, 87 %. ^{1}H NMR (399.5 MHz, $CDCl_3$): δ_H = 5.82 [s, 1H, C=C**H**], 2.18 [t, $^{3}J_{HH}$ = 7.6 Hz, 2H], 1.38 [m, 2H], 1.29 [s, 12H, Bpin], 1.27 [m, 6H], 1.24 [s, 12H, Bpin], 0.84 [t, $^{3}J_{HH}$ = 6.9 Hz, 3H, CH_3]. $^{13}C\{^{1}H\}$ NMR (100.46 MHz, $CDCl_3$): δ_C = 83.5, 83.2, 39.8, 31.7, 29.1, 28.6, 24.9, 24.8, 22.5, 14.0. $^{11}B\{^{1}H\}$ NMR (128.2 MHz, $CDCl_3$): δ_B = 30.5 (spectroscopic data in agreement with the literature).

4.5.10 Synthesis of (*E*)-2,2'-(1-(3,5-bis(trifluoromethyl)phenyl)ethene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (4.9)

A stock solution of **4.1** (0.38 mg, 0.71 µL) in C_6D_6 (377 µL) was added to a mixture of 1-ethynyl-3,5-bis(trifluoromethyl)benzene (25.0 µL, 0.14 mmol) and bis(pinacalato)diboron (0.049 g, 0.19 mmol). The resulting reaction mixture was stirred at room temperature for 48 h under a N_2 atmosphere. At this point all the volatiles were removed in vacuo. Deionized H_2O (50 mL) was added to the reaction mixture and this was allowed to stir for 24 h. The H_2O was decanted and the product was washed with further quantities of deionized H_2O (3 x 20 mL). The yellow oil was dried under a high vacuum. Yield: 0.055 g, 79%. ^{1}H NMR (399.5 MHz, CDCl3): δ_H = 7.88 [s, 2H, *o*-Ph], 7.74 [s, 1H, *p*-Ph], 6.41 [s, 1H, =C**H**], 1.37 [s, 12H, Bpin], 1.33 [s, 12H, Bpin]. ^{13}C{^{1}H} NMR (100.46 MHz, $CDCl_3$): δ_C = 145.3 [*i*-Ph], 131.7 [q, $^2J_{CF}$ = 32.1 Hz, *m*-Ph], 127.0 [*o*-Ph], 123.6 [q, $^1J_{CF}$ = 272.6 Hz, -**C**F_3], 121.1 [*p*-Ph], 84.8 [Bpin], 84.22 [Bpin], 25.1 [Bpin], 25.1 [Bpin], 2 C=C were not observed due to quadrapolar broadening caused by adjacent B atoms. ^{11}B{^{1}H} NMR (128.2 MHz, $CDCl_3$): δ_B = 30.2. ^{19}F NMR (375.9 MHz, $CDCl_3$): δ_F = –63.1. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{22}H_{28}F_6O_4B_2Na$ 515.1970; Found 515.1970. Elem. Anal.: Calcd for $C_{22}H_{28}F_6O_4B_2$: C, 53.70%; H, 5.74%. Found: C, 53.55%; H, 5.67%.

4.5.11 Synthesis of (*E*)-2,2'-(1-mesitylethene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (4.10)

A stock solution of **4.1** (0.51 mg, 0.96 µmol) in C_6D_6 (511 µL) was added to a mixture of 2-ethynl-1,3,5-trimethylbenzene (30.0 µL, 0.19 mmol) and bis(pinacolato)diboron (0.054 g, 0.21 mmol). The reaction mixture was stirred at room temperature for 1 h under a N_2 atmosphere. At this point the volatiles were removed in vacuo, the resulting colourless

oil was washed with deionized water (3 x 30 mL) at which point a white solid precipitated. This white solid was collected by filtration and dried. Yield: 0.072 g, 94 %. ^{1}H NMR (399.5 MHz, $CDCl_3$): δ_H = 6.81 [s, 2H, Ph], 5.85 [s, 1H, =C**H**], 2.25 [s, 3H, *p*-PhCH_3], 2.18 [s, 6H, *o*-PhCH_3], 1.33 [s, 12H, Bpin], 1.24 [s, 12H, Bpin]. ^{13}C{^{1}H} NMR (100.46 MHz, $CDCl_3$): δ_C = 141.6 [*i*-Ph], 135.1 [*p*-Ph], 134.5 [*o*-Ph], 128.0 [*m*-Ph], 83.7 [Bpin], 83.4 [Bpin], 25.1 [Bpin], 24.9 [Bpin], 21.1 [*p*-Ph**C**H_3], 20.8 [s, *o*-Ph**C**H_3], 2 C=C were not observed due to quadrapolar broadening caused by adjacent B atoms. ^{11}B{^{1}H} NMR (128.2 MHz, $CDCl_3$): δ_B = 29.7. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{23}H_{36}O_4B_2Na$ 421.2692; Found 421.2695. Elem. Anal.: Calcd for $C_{23}H_{36}O_4B_2$: C, 69.38%; H, 9.11%. Found: C, 69.29%; H, 9.16%.

4.5.12 Synthesis of (*E*)-2,2'-(1-(cyclohex-1-en-1-yl)ethene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (4.11)

A stock solution of **4.1** (0.34 mg, 0.64 µmol) in C_6D_6 (340 µL) was added to a mixture of 1-ethynylcyclohex-1-ene (15.0 µL, 0.13 mmol) and bis(pinacalato)diboron (0.039 g, 0.15 mmol). The resulting reaction mixture was stirred at room temperature for 24 h under a N_2 atmosphere. At this point all volatiles were removed in vacuo, deionized H_2O (35 mL) was added and the resulting mixture was stirred at room temperature for 24 h. At this point the beige solid was collected by filtration and dried under a high vacuum. Yield: 0.041 g, 89 %. ^{1}H NMR (399.5 MHz, C_6D_6): δ_H = 6.30 [m, 1H, =C**H**CH_2], 6.26 [s, 1H, =C**H**], 2.16 [m, 2H, (2)C**H₂**], 2.05 [m, 2H, (5)C**H₂**], 1.45 [m, 2H, C**H₂**], 1.36 [m, 2H, C**H₂**], 1.31 [s, 12H, Bpin], 1.11 [s, 12H, Bpin]. ^{13}C{^{1}H} NMR (100.46 MHz, C_6D_6): δ_C = 140.8 [(1)cyclohexen-1-yl], 131.2 [(6)cyclohexen-1-yl], 83.6 [Bpin], 83.1 [Bpin], 26.7 [(5)cyclohexen-1-yl], 25.6 [Bpin], 25.5 [(2)cyclohexen-1-yl], 25.0 [Bpin], 23.1 [cyclohexen-1-yl], 22.6 [cyclohexen-1-yl], 2 C=C were not observed due to quadrapolar

broadening caused by adjacent B atoms. $^{11}B\{^{1}H\}$ NMR (128.2 MHz, C_6D_6): δ_B = 30.9. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{20}H_{34}O_4B_2Na$ 383.2535; Found 383.2526. Elem. Anal.: Calcd for $C_{20}H_{34}O_4B_2$: C, 66.71%; H, 9.52%. Found: C, 66.79%; H, 9.43%.

4.5.13 Synthesis of (*Z*)-2,2'-(1-(4-ethylphenyl)-2-(4-methoxyphenyl)ethene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (4.12)

A stock solution of **4.1** (0.35 mg, 0.66 μmol) in C_6D_6 (354 μL) was added to a mixture of 1-ethyl-4-((4-methoxyphenyl)ethynyl)benzene (0.031 g, 0.13 mmol) and bis(pinacolato)diboron (0.043 g, 0.17 mmol). The resulting reaction mixture was heated to 50 ˚C for 5 h under a N_2 atmosphere. Upon cooling the reaction mixture, the volatiles were removed in vacuo. Deionized H_2O (35 mL) was added to the resulting off-white solid and this was stirred at room temperature for 24 h. The white solid was collected by filtration and dried under a high vacuum. Yield: 0.055 g, 85 %. ^{1}H NMR (399.5 MHz, $CDCl_3$): δ_H = 6.88 [m, 6H, *o,m*-Ph(4-Et) and *o*-Ph(4-OMe)], 6.61 [m, 2H, *m*-Ph(4-OMe)], 3.71 [s, 3H, O**Me**], 2.53 [q, $^{3}J_{HH}$ = 7.7 Hz, 2H, **CH$_2$**CH_3], 1.32 [s, 12H, BPin], 1.32 [s, 12H, Bpin], 1.16 [t, $^{3}J_{HH}$ = 7.7 Hz, 3H, CH_2**CH$_3$**]. ^{1}H NMR (499.5 MHz, C_6D_6): δ_H = 7.30 [d, $^{3}J_{HH}$ = 8.2 Hz, 2H, *o*-Ph(4-Et)], 7.26 [d, $^{3}J_{HH}$ = 8.7 Hz, 2H, *o*-Ph(4-OMe)], 6.90 [d, $^{3}J_{HH}$ = 8.2 Hz, 2H, *m*-Ph(4-Et)], 6.60 [d, $^{3}J_{HH}$ = 8.7 Hz, *m*-Ph(4-OMe)], 3.14 [s, 3H, O**Me**], 2.32 [q, $^{3}J_{HH}$ = 7.6 Hz, 2 H, **CH$_2$**CH_3], 1.19 [s, 12H, Bpin], 1.18 [s, 12H, Bpin], 0.95 [t, $^{3}J_{HH}$ = 7.6 Hz, 3H, CH_2**CH$_3$**]. $^{13}C\{^{1}H\}$ NMR (100.46 MHz, $CDCl_3$): δ_C = 157.8 [*p*-Ph(4-OMe)], 141.5 [*p*-Ph(4-Et)], 138.8 [*i*-Ph(4-Et)], 134.0 [*i*-Ph(4-OMe)], 130.7 [*o*-Ph(4-OMe)], 129.5 [*o*-Ph(4-Et)], 127.1 [*m*-Ph(4-Et)], 113.1 [*m*-Ph(4-OMe)], 84.1 [Bpin], 84.1 [Bpin], 55.1 [O**Me**], 28.6 [**C**H_2CH_3], 25.1 [Bpin], 25.1 [Bpin], 15.3 [CH_2**C**H_3], 2 C=C were not observed due to quadrapolar broadening caused by adjacent B atoms. $^{13}C\{^{1}H\}$ NMR (100.46 MHz, C_6D_6): δ_C = 158.4 [*p*-Ph(4-OMe)], 141.6 [*p*-Ph(4-Et)],

140.0 [*i*-Ph(4-Et)], 134.7 [*i*-Ph(4-OMe)], 131.1 [*o*-Ph(4-OMe)], 130.0 [*o*-Ph(4-Et)], 127.6 [*m*-Ph(4-Et)], 113.7 [*m*-Ph(4-OMe)], 83.8 [Bpin], 83.8 [Bpin], 54.5 [O**Me**], 28.8 [**C**H_2CH_3], 25.1 [Bpin], 25.1 [Bpin], 15.3 [CH_2**C**H_3], 2 C=C were not observed due to quadrapolar broadening caused by adjacent B atoms. $^{11}B\{^1H\}$ NMR (128.2 MHz, $CDCl_3$): δ_B = 30.8. $^{11}B\{^1H\}$ NMR (128.2 MHz, C_6D_6): δ_B = 30.8. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{29}H_{40}O_5B_2H$ 491.3135; Found 491.3132. Elem. Anal.: Calcd for $C_{29}H_{40}O_5B_2$: C, 71.05%; H, 8.22%. Found: C, 70.94%; H, 8.26%.

4.5.14 Synthesis of (*Z*)-2,2'-(1-(naphthalen-1-yl)-2-phenylethene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (4.13)

A stock solution of **4.1** (0.39 mg, 0.72 μmol) in C_6D_6 (385 μL) was added to a mixture of 1-(phenylethynyl)naphthalene (0.033 g, 0.14 mmol) and bis(pinacalato)diboron (0.049 g, 0.19 mmol). The resulting reaction mixture was heated to 50 ˚C for 24 h under a N_2 atmosphere. At this point all volatiles were removed in vacuo, deionized H_2O (30 mL) was added and the reaction mixture was stirred for 24 h. The H_2O was removed and the off-white solid was dried under high vacuum. Yield: 0.070 g, 94 %. ^1H NMR (399.5 MHz, CDCl3): δ_H = 7.97 [m, 1H, naphth], 7.70 [m, 1H, naphth], 7.54 [m, 1H, naphth], 7.35 [m, 1H, naphth], 7.35 [m, 1H, naphth], 7.17 [m, 1H, naphth], 6.95 [m, 1H, naphth], 6.86 [m, 5H, Ph], 1.37 [s, 6H, Bpin], 1.35 [s, 6H, Bpin], 1.21 [s, 6H, Bpin], 1.20 [s, 6H, Bpin]. $^{13}C\{^1H\}$ NMR (100.46 MHz, $CDCl_3$): δ_C = 141.6, 140.1, 133.3, 132.2, 128.3, 128.1, 127.4, 126.9, 126.6, 126.3, 126.0, 125.4, 125.4, 125.1, 84.3, 84.2, 25.3, 24.9, 24.9, 24.8. $^{11}B\{^1H\}$ NMR (128.2 MHz, $CDCl_3$): δ_B = 30.7. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{30}H_{36}O_4B_2H$ 483.2872; Found 483.2871. Elem. Anal.: Calcd for $C_{30}H_{36}O_4B_2$: C, 74.72%; H, 7.52%. Found: C, 74.63%; H, 7.46%.

4.5.15 Synthesis of (*Z*)-trimethyl(2-phenyl-1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)silane (4.14)

A stock solution of **4.1** (0.002 g, 3.06 µmol) in C_6D_6 (406 µL) was added to a mixture of trimethyl(phenylethynyl)silane (30.0 µL, 0.15 mmol) and bis(pinacolato)diboron (0.042 g, 0.17 mmol). The resulting reaction mixture was heated to 100 ˚C for 30 h under a N_2 atmosphere. Upon cooling the reaction mixture, the volatiles were removed in vacuo. At this point all volatiles were removed in vacuo, deionized H_2O (30 mL) was added and the reaction mixture was stirred for 24 h. The H_2O was removed and the off-white powdered solid was dried under high vacuum. Yield: 0.056 g, 85 %. ^{1}H NMR (399.5 MHz, $CDCl_3$): δ_H = 7.21 [m, 3H, *m*,*p*-Ph], 7.11 [m, 2H, *o*-Ph], 1.37 [s, 12H, Bpin], 1.22 [s, 12H, Bpin], –0.18 [s, 9H, $SiMe_3$]. ^{13}C{^{1}H} NMR (100.46 MHz, $CDCl_3$): δ_C = 146.0 [*i*-Ph], 128.0 [*o*-Ph], 127.6 [*m*-Ph], 126.3 [*p*-Ph], 84.1 [Bpin], 83.8 [Bpin], 25.7 [Bpin], 24.9 [Bpin], 1.0 (Si**Me$_3$**], 2 C=C were not observed due to quadrapolar broadening caused by adjacent B atoms.. ^{11}B{^{1}H} NMR (128.2 MHz, $CDCl_3$): δ_B = 30.8, 29.1. ^{29}Si{^{1}H} (79.4 MHz, $CDCl_3$): δ_{Si} = –7.43 (spectroscopic data in agreement with the literature.

4.5.16 Synthesis of (*Z*)-2,2'-(oct-4-ene-4,5-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (4.15)

A stock solution of **4.1** (0.45 mg, 0.85 µL) in C_6D_6 (454 µL) was added to a mixture of 4-octyne (25.0 µL, 0.17 mmol) and bis(pinacalato)diboron (0.045 g, 0.18 mmol). The resulting reaction mixture was stirred at room temperature for 23 h under a N_2 atmosphere. At this point no further conversion was observed (39 % conversion). At this point all volatiles were removed in vacuo. The resulting off-white oily solid was stirred in deionized H_2O (35 mL) for 24 h. The H_2O was then decanted and the product was washed with further quantities of deionized H_2O (3 x 25 mL). The resulting colourless oil

was dried under a high vacuum. Yield: 0.012 g, 20 % (39 % conversion). ^{1}H NMR (499.5 MHz, $CDCl_3$): δ_H = 2.17 [m, 4H], 1.37 [m, 4H], 1.28 [s, 24H, Bpin], 0.91 [t, $^{3}J_{HH}$ = 7.4 Hz, 6H, C**H**$_3$]. ^{13}C{^{1}H} (100.46 MHz, $CDCl_3$): δ_C = 83.4, 33.2, 25.1, 23.2, 14.7, 2 C=C were not observed due to quadrapolar broadening caused by adjacent B atoms. ^{11}B{^{1}H} NMR (128.2 MHz, $CDCl_3$): δ_B = 30.6 (spectroscopic data in agreement with the literature).

4.5.17 Stoichiometric Reactivity of 4.1 with B_2pin_2

In a vial, **4.1** (1 equiv.) and B_2pin_2 (2-20 equiv.) were dissolved in solvent (C_6D_6, CD_3CN or hexane) and stirred at either room temperature or 50 ^{o}C. The reaction progress was monitored by ^{1}H NMR spectroscopy.

[Pd(ITMe)$_2$]: ^{1}H NMR (399.5 MHz, C_6D_6): δ_H = 3.93 [s, 12H, N(1,3)-C**H**$_3$], 1.55 [s, 12H, C(4,5)-C**H**$_3$].

4.2: ^{1}H NMR [399.5 MHz, $CDCl_3$]: δ_H = 7.05 [m, 6H, Ph], 6.95 [m, 4H, Ph], 1.32 [s, 24H, Bpin].

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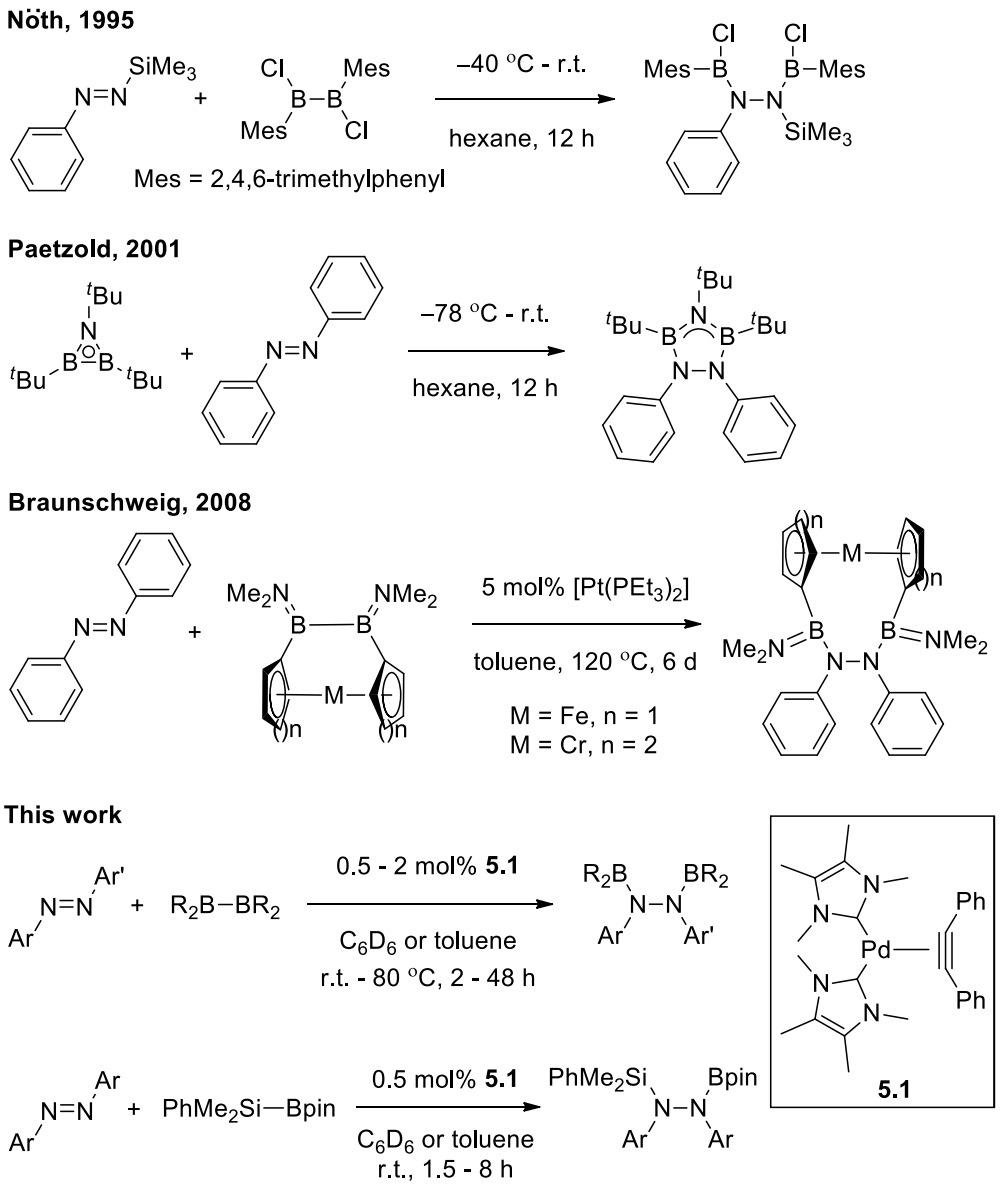
Chapter 5

Synthesis of Functionalized Hydrazines: Facile Homogeneous (N-Heterocyclic Carbene)-Pd(0) Catalyzed Diboration and Silaboration of Azobenezenes

5.1 Introduction

The transition metal catalysed diboration (B-B) and silaboration (Si-B) of carbon-based unsaturated bonds such as alkynes,[1–7] alkenes,[8–12] and 1,3-dienes,[13–15] represents some of the most valuable and widely studied organic transformations in the literature. Nevertheless, the translation of this chemistry to other element-based unsaturated bonds remains a considerable challenge. In particular, the diboration and silaboration of N=N (azo) bonds harnesses the potential for the synthesis of highly functionalized hydrazines as precursors to, for instance, polymeric materials,[16,17] DNA modifiers,[18,19] and glycosidase inhibitors.[20] Despite this potential, such element-element additions to azo moieties are extremely rare. There are only three reported isolated examples of azo diborations to yield the corresponding 1,2-bis(boryl)hydrazines. These require the use of either an extremely reactive B-B bond in the form of azadiboriridenes,[21] or dichlorodiboranes,[22] or a highly strained B-B bond as in [2]borametallarenophanes (Scheme 5.1).[23] Recently however, a combined computational and experimental article from Li and co-workers showed that the diboration of N=N bonds using a commercially available and air stable tetraalkoxydiboron reagent such as bis(pinacolato)diboron is feasible.[24] There were no prior examples in the literature of N=N silaborations.

The synthesis of [Pd(ITMe)$_2$(PhC≡CPh)] (**5.1**) was reported in Chapter 2, 3 and 4,[25] and has showed high catalytic reactivity in the regio- and stereoselective diboration,[26] and silaboration of alkynes.[27] The ability of **5.1** to catalyse the element-element bond



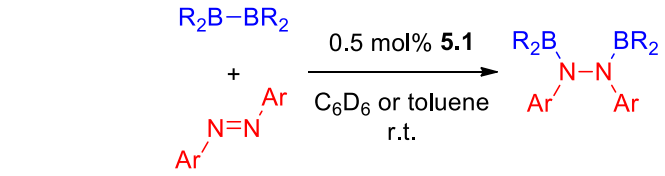
Scheme 5.1 Element-element additions to N=N bonds

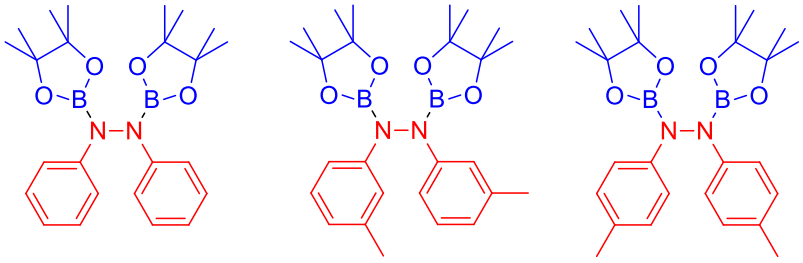
additions to other unsaturated bonds was investigated. Herein, **5.1** is employed as a very active pre-catalyst in the diboration and silaboration of azobenzenes (N=N bonds). The products represent the first isolated examples of 1,2-bis(boryl)hydrazines and 1-silyl-2-borylhydrazines starting from commercially available diboranes and silaboranes, respectively.

5.2 Catalysis

5.2.1 Catalytic Diboration of Azobenzenes

The viability of the diboration of azobenzenes were assessed by combining, under an inert atmosphere and at room temperature, azobenzene (PhN=NPh), bis(pinacolato)diboron (B_2pin_2) and catalytic quantities of **5.1**, in C_6D_6 in order to monitor the reaction progression by ^{1}H NMR spectroscopy. The optimization of the reaction parameters resulted in 100% conversion to 1,2-diphenyl-1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (**5.2**) after 2 h, using as little as 0.5 mol% of **5.1** (Table 5.1). The reaction also proceeded in toluene under the same conditions on a larger scale. After several recrystallizations from hexanes, **5.2** was isolated as an air and moisture sensitive white powder in a 63% yield. Single crystals of **5.2** were isolated from a saturated hexane solution at –30 ^{o}C and the resulting X-ray analysis is depicted in Figure 5.1. The crystalline structure of **5.2** was solved in the $P2_12_12_1$ space group with one of the Bpin functionalities displaying a degree of dynamic disorder. A notable feature of this molecular structure is the length of the N-N bond [1.419(4) Å] which is, as expected, comparable to the N-N bond in diphenylhydrazine [1.394(7) Å],[28] and much longer than the N=N bond of azobenzene [1.25 Å]. Each N atoms exhibits a distorted trigonal planar geometry [115.2(2)-128.4(6)^o; N1, N2: $\Sigma = 360^o$]. The B-N bond lengths [1.410(14) Å and 1.433(4) Å] are in agreement with those of other aminoboranes of the form $R_2BNR'_2$,[23,29,30] and imply partial double bond character.[31] The distorted trigonal planar geometry surrounding each B atom is indicative of sp^2 hybridization [133.0(9)-127.6(9)^o; B1, B12: $\Sigma = 360^o$].

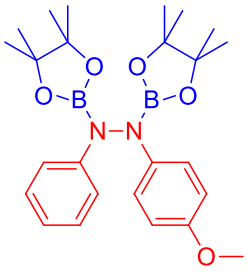




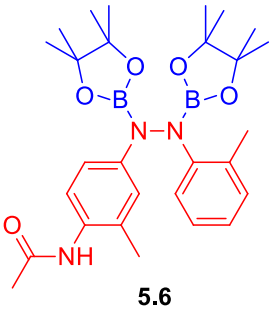
5.2
2 h, 63%[a]

5.3
2.5 h, 72%

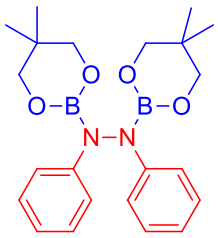
5.4
3 h, 75%



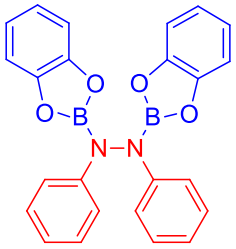
5.5
4 h, 79%



5.6
80 °C, 22 h, 72%[a]



5.7
2 mol%, 80 °C
48 h, 77%



5.8
2 mol%, 80 °C
24 h, 66%[a]

B_2R_4: 1-1.5 equiv. (see experimental for details). [a]Yields from scaled-up reaction in toluene

Table 5.1 Diboration of Azobenzenes

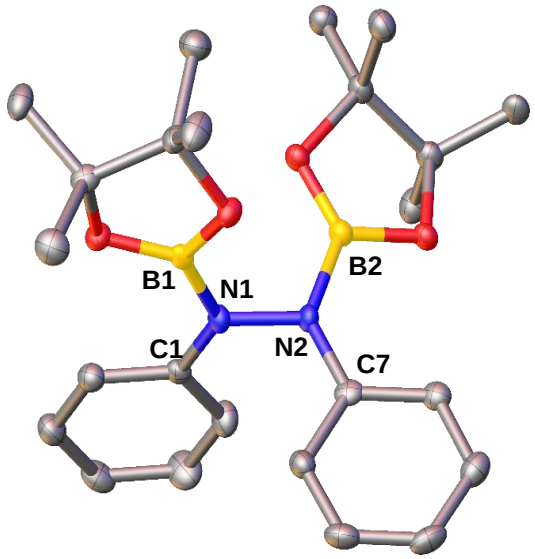


Figure 5.1 Molecular structure of **5.2** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: N1-N2 1.419(4), N1-B1 1.433(4), N2-B2 1.410(14); C1-N1-B1 128.1(3), N2-N1-C1 116.2(2), N2-N1-B1 115.2(2), C7-N2-N1 116.1(2), B2-N2-N1 115.5(6), B2-N2-C7 128.4(6), O1-B1-N1 124.6(3), O1-B1-O2 114.3(3), O2-B1-N1 121.3(3) O13-B2-N2 119.4(12), O13-B2-O13 113.0(9), O14-B2-N2 127.6(9).

The versatility of this catalytic diboration using B_2pin_2 was assessed and this protocol was extended to a series of azobenzenes with a range of functionalities including alkyl, methoxy and amido moieties in the *ortho*, *meta* and *para* positions. As with **5.2**, the synthesis of the novel compounds **5.3**, **5.4** and **5.5** only required 0.5 mol% of **5.1**, proceeded at room temperature and were completed in 2.5-4 h (Table 5.1).

Single crystals of **5.4** suitable for X-ray analysis were grown in a saturated hexane solution at −30 °C. The molecular structure of **5.4** was solved in the same space group, $P2_12_12_1$, and exhibited comparable N-N [1.416(3) Å] and B-N [1.431(4) and 1.440(4) Å] bond lengths as **5.2** (Figure 5.2). The synthesis of **5.6**, required an increase of temperature (80 °C) and reaction time (22 h) to reach completion. This was attributed to the limited

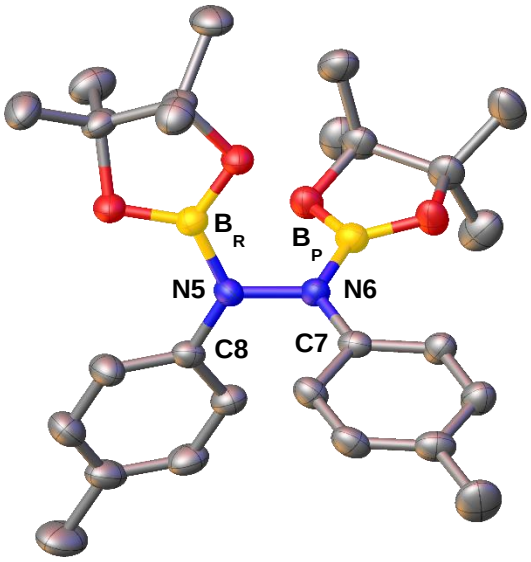
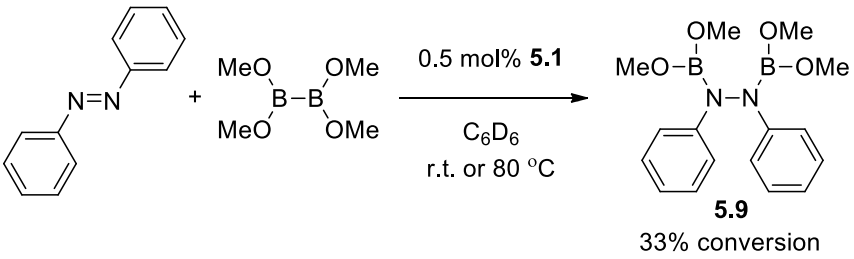


Figure 5.2 Molecular structure of **5.4** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: N5-N6 1.416(3), N5-B_R 1.440(4), N6-C7 1.426(4); N6-N5-C8 116.3(2), N6-N5-B_R 116.0 (2), C8-N5-B_R 127.7(2), N5-N6-C7 116.7(2), N5-N6-B_P 115.8(2), C7-N6-B_P 126.0(2).

solubility of the azobenzene in C_6D_6 and toluene. It was also possible to exchange the diboron reagent for other commercially available B-B analogues such as bis(neopentylglycolato)diboron and bis(catecholato)diboron. This resulted in the formation of **5.7** and **5.8** respectively, albeit employing higher catalyst loadings, higher temperatures, and longer reaction times than those for their B_2pin_2 counterpart. The reaction of tetramethoxy-diborane(4) with PhN=NPh at room temperature resulted in a 33% conversion to **5.9**. This conversion was not improved on extending reaction time or elevating the temperature. Isolation of **5.9** also proved troublesome with starting PhN=NPh and tetramethoxy diboron ($B_2\{OMe\}_4$) persisting, even after multiple re-crystallization attempts (Scheme 5.2).



Scheme 5.2 Synthesis of **5.9**

The diboron, tetrakis(dimethylamino)diboron ($B_2\{NMe_2\}_4$), was unreactive towards diboration of PhN=NPh under optimized conditions.

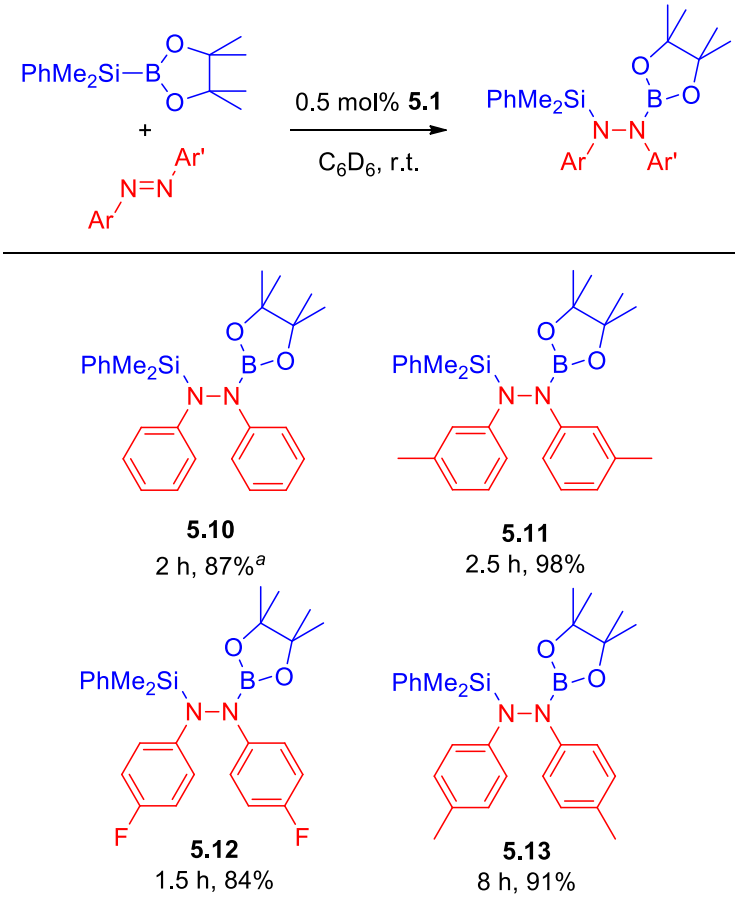
An experimental NMR study by Bryce and co-workers showed that the $J(^{11}B,^{11}B)$ coupling, obtained from ^{11}B DQF *J*-resolved NMR spectroscopic experiments on different diborons, was directly correlated to the B-B bond dissociation energy.[32] These data are also consistent with crystallographic data for the corresponding B-B bond lengths.[33] Studies showed that a decrease in $J(^{11}B,^{11}B)$ coupling was consistent with a B-B bond that possesses a decreased bond energy and increased bond length. Hence, diboron reagents with larger B-B bond lengths are predicted to exhibit higher reactivity. This rationale agrees perfectly with the necessity for harsher reaction conditions in the diboration of azobenzene when employing the diboron, B_2cat_2 over B_2pin_2. B_2cat_2 displays a shorter B-B bond length than B_2pin_2 [1.678(3) Å *vs.* 1.711(6) Å], and a higher $J(^{11}B,^{11}B)$ coupling [135 Hz *vs.* 120 Hz].[32,33]

$B_2(OMe)_4$ [B-B, 1.720(6) Å] and $B_2(NMe_2)_4$ [B-B, 1.762(1) Å], based on the above assumptions, are expected to have an equal and more facile reactivity in comparison to B_2pin_2. However, these reactivity patterns were not observed. A plausible explanation for this phenomenon may be attributed to the dihedral angles between the BO_2 and BN_2 units.[33] B_2pin_2, B_2cat_2 and B_2neop_2 demonstrate dihedral angles of 0°, meaning the BO_2

units are essentially coplanar. This would allow for a favourable interaction between the B-B bond LUMO and the Pd(0) catalyst HOMO, and thus a more facile oxidative addition of the B-B bond. The dihedral angles for $B_2(OMe)_4$ and $B_2(NMe_2)_4$ are 49.5° and 90.0°.[33] The increase in staggered conformation of the B atoms is consistent with the decreased reactivity of the diboron in this reaction. As the dihedral angle distorts from 0°, it is expected that steric clashing, between the B-B bond and Pd(0) species, and misalignment of frontier orbitals will increase. This results in a more difficult oxidative addition and a decrease in the propensity for diboration.

5.2.2 Catalytic Silaboration of Azobenzenes

Attention was next turned to the catalytic silaboration of azobenzenes. The silaborane of choice was the readily available (dimethylphenyl)silyl boronic acid pinacol ester ($PhMe_2SiBpin$). The reaction parameters were optimized using $PhMe_2SiBpin$ and azobenzene as the model substrates. (dimethyl(phenyl)silyl)-1,2-diphenyl-2-yl)hydrazine (**5.10**) was synthesized with a 100% conversion in 2 h in C_6D_6 and toluene. Interestingly, compound **5.10** is air and moisture stable which simplified purification. On stirring the crude reaction mixture in deionized H_2O overnight, **5.10** was recovered as a white powder in 87% yield (Table 5.2).



$PhMe_2SiBpin$: 1.13-1.36 equiv. [a]Isolated yield form scale up reactions in toluene.

Table 5.2 Silaboration of azobenzenes

Single crystals of **5.10** were isolated from the slow evaporation of a saturated acetone solution at room temperature. The molecular structure of **5.10** obtained from X-ray analysis is shown in Figure 5.3. There are some noteworthy features in this molecular structure, the first one was that it was solved in the $P2_1$ space group. The N-N bond length [1.417(4) Å] is comparable to **5.2** [1.419(4) Å] and/or shorter than that for other silyl substituted hydrazines (*e.g.* $Ph_2Si\{NHNH\}SiPh_2$ and $PhSi\{NHNHMe\}_2$) reported in the literature [1.421(5)-1.4820(2) Å].[34–36] The bonding around each N atom, as with **5.2**, showed a distorted trigonal planar geometry [115.3(2)-127.9(2)°; N1, N2: $\Sigma = 360°$]. The

B-N bond length [1.438(5) Å] is in agreement with other aminoboranes including **5.2** and the geometry surrounding the B-atom is distorted trigonal planar [114.6(4)-123.8(3)^{o}; B_p: $\Sigma = 360^{o}$]. The Si-N bond length is longer [1.773(2) Å] than that for other silyl amines of the form $R_3SiNR'_2$.[34–39]

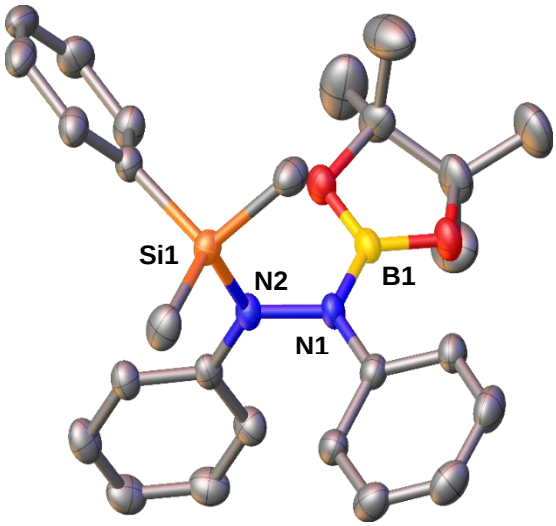


Figure 5.3 Molecular structure of **5.10** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [^{o}]: N1-N2 1.417(4), N1-B1 1.438(5), Si1-N2 1.773(3); N2-N1-C7 115.8(3), N2-N1-B1 116.3(3), C7-N1-B1 127.8(3), N1-N2-Si1 115.3(2), C6-N2-Si1 127.9(2), C6-N2-N1 116.3(3), O2-B1-N1 123.8(3), O3-B1-O2 114.6(3), O3-B1-N1 121.6(3).

The potential of **5.1** in the silaboration of other azobenzenes was extended to *ortho*, *meta* and *para* substituted symmetrical azobenzenes with alkyl and fluoro groups. The novel compounds **5.11**, **5.12** and **5.13** were synthesized using 0.5 mol% of **5.1** at room temperature reaching completion in 1.5 to 8 h (Table 5.2). Compounds **5.11**, **5.12** and **5.13** were also stable to air and moisture. Single crystals of **5.12** were grown from slow evaporation of a saturated acetone solution at room temperature. The molecular structure

of **5.12** is depicted in Figure 5.4 and is, within experimental error, identical to **5.10** in terms of space group, bond lengths and angles.

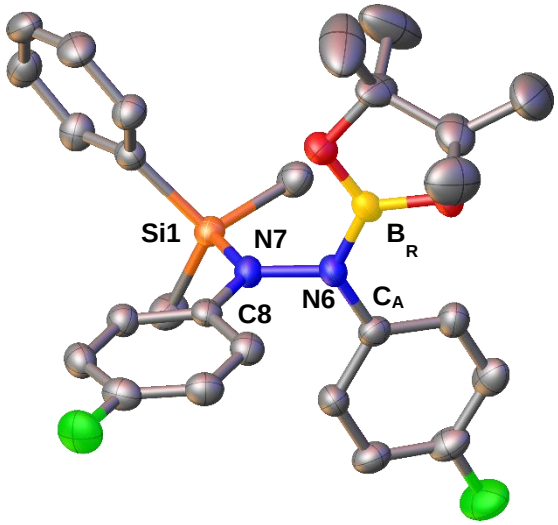


Figure 5.4 Molecular structure of **5.12** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: N6-N7 1.412(5), Si1-N7 1.773(4), N6-B_R 1.433(6); N7-N6-C_A 115.4(4), N7-N6-B_R 116.5(4) C_A-N6-B_R 128.0(4), N6-N7-Si1 115.6(3), C8-N7-Si1 128.1(3), C8-N7-N6 115.8(4).

As expected, the application of this silaboration protocol to unsymmetrical azobenzenes resulted in a statistical mixture of regioisomers (see Experimental Details).

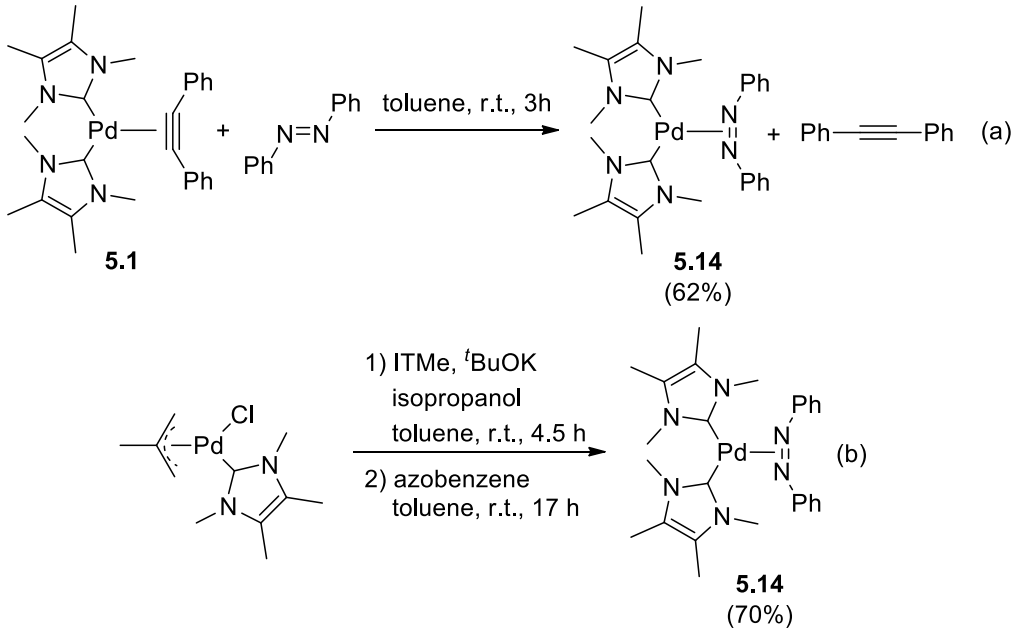
5.3 Mechanism of Diboration/Silaboration of Azobenzenes

5.3.1 Isolation of [Pd(ITMe)$_2$(PhN=NPh)]

The attempts at catalytic bis(silyl)ation of PhN=NPh using hexamethyldisilane and **5.1** at room and elevated temperatures were unsuccessful. However, ^{1}H NMR data suggested the formation of a new NHC-Pd species with NHC based CH_3 resonances at 3.29 and

1.36 ppm. The new NHC-Pd species was tentatively identified as [Pd(ITMe)$_2$(PhN=NPh)] (**5.14**). The identity of the latter was confirmed through its independent synthesis, reacting **5.1** with PhN=NPh (Scheme 5.3, a). The formation of **5.14** through this route represented a ligand displacement reaction and suggested that PhN=NPh has a higher binding affinity to the Pd(0) than diphenylacetylene. Attempts to react **5.14** with diphenylacetylene resulted in a complete recovery of **5.14**.

The synthesis of **5.14** was scaled-up following a similar route to the synthesis of **5.1**. [(ITMe)Pd(methallyl)] was reacted with one equivalent of each of potassium *tert*-butoxide, isopropanol and ITMe at room temperature to form [Pd(ITMe)$_2$], which was then exposed *in situ* to an excess of PhN=NPh at room temperature for 17 h to form **5.14** (Scheme 5.3, b).



Scheme 5.3 Methods for the synthesis of **5.14**

Single crystals of **5.14** were obtained *via* a double recrystallization in a saturated toluene/hexane (2:1) solution and X-ray analysis is depicted in Figure 5.5. **5.14** demonstrates a Y-shaped structure and an elongation of the N-N bond [1.412(6) Å] when

compared to free PhN=NPh [1.25 Å]. The lengthening of the N-N bond is consistent with single bond character between the two N atoms. This feature is commonly observed amongst other transition metal-azobenzene coordination complexes in a zero oxidation state, including in platinum [1.430(13) Å],[40] nickel [1.385(5) Å],[41] and iron [1.398(2) Å] analogues.[42] The NHC Pd-C bond lengths in **5.14** are longer [2.057(5) and 2.075(5) Å] than in **5.1** [2.029(3) and 2.033(3) Å] and $^{13}C\{^{1}H\}$ NMR resonance for the carbenic carbon in **5.14** is significantly shifted upfield (189.0 ppm) in comparison to **5.1** (198.7 ppm). These data suggest that the coordination of PhN=NPh versus diphenylacetylene results in a much greater electron density at the palladium centre. The formation and isolation of **5.14** represented the first NHC-Pd based coordination complex of azobenzenes.

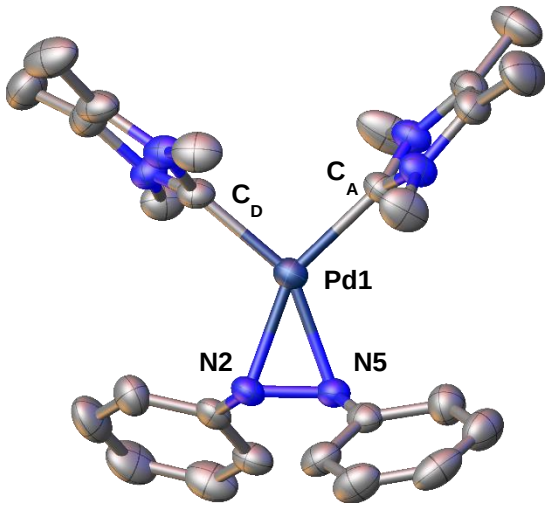
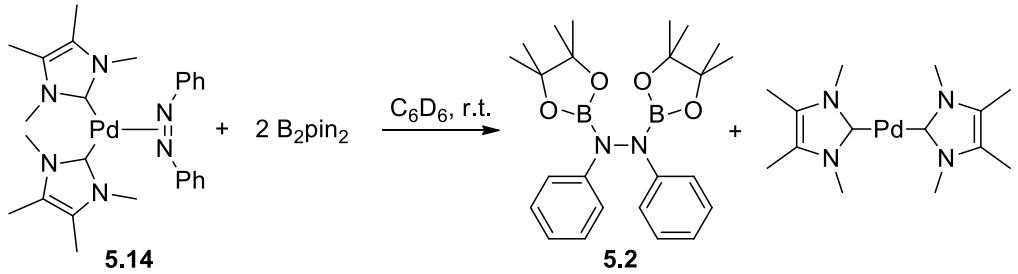


Figure 5.5 Molecular structure of **5.14** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: N2-N5 1.412(5). Pd1-N2 2.066(4), Pd1-N5 2.093(4), Pd1-C_A 2.075(5), Pd1-C_D 2.057(5); N2-Pd1-N5 39.69(17), C_A-Pd1-N5 113.94(18), C_D-Pd1-N2 110.4(2).

5.3.2 Stoichiometric Reactivity between 5.14 and B_2pin_2

The reaction between **5.14** and >2 equivalents of B_2pin_2 in C_6D_6 at room temperature was monitored by ^1H NMR spectroscopy. As expected, **5.2** formed with ease and 100% conversion of the azobenzene was observed. [Pd(ITMe)$_2$] was also found to be the major NHC-Pd species (Scheme 5.4). Minor unassigned NHC based resonances were also noted in the ^1H NMR spectrum. It was not possible to separate and isolate these minor compounds.

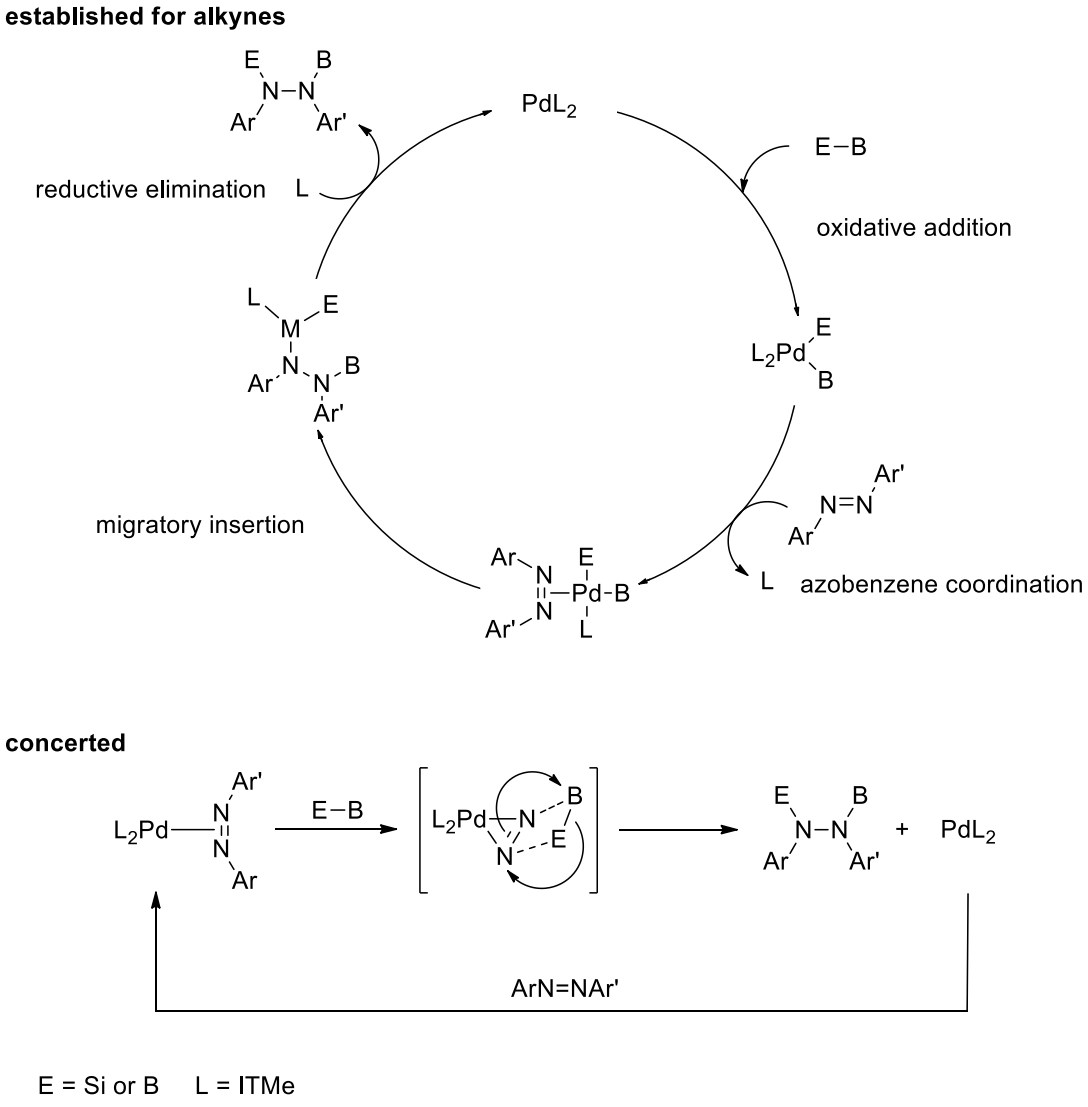


5.14 **5.2**

Scheme 5.4 Stoichiometric reaction between **5.14** and B_2pin_2

5.3.3 Possible Mechanistic Routes

A similar mechanistic pathway, as observed in Chapter 4, may be envisaged for the diboration and silaboration of azobenzenes.[26] This can be summarized as (i) dissociation of the azobenzene from **5.14**, (ii) oxidative addition of an E-B bond (E = Si or B) to Pd(0) centre, (iii) an NHC dissociation from the (E)(B)palladium(II) complex followed by azobenzene coordination, (iv) insertion of azobenzene into a Pd-B bond *via* migratory insertion, and (v) reduction of Pd(II) to Pd(0) with the elimination of 1-element-2-boryl hydrazine (Scheme 5.5). However, due the availability of N lone pairs and the Lewis acidic nature of the B atoms, it is impossible to rule out other mechanistic pathways such as a concerted route (Scheme 5.5).[43–45]

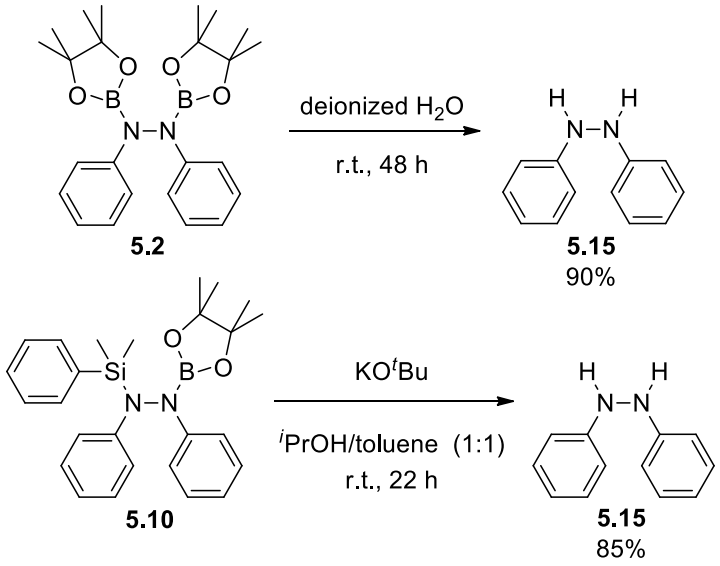


Scheme 5.5 Proposed mechanistic pathways for diboration and silaboration of azobenzenes

5.4 1,2-Bis(boryl)hydrazine and 1-Silyl-2-borylhydrazine Hydrolysis

Upon stirring **5.2** in degassed deionized H_2O overnight the Bpin groups were hydrolytically cleaved to afford the corresponding 1,2-diphenylhydrazines (**5.15**, Scheme 5.6). This result, albeit accessed through palladium catalysis, supported the proposed mechanism by Li and co-workers whereby **5.2** was computationally calculated as an

intermediate in the organocatalytic formation of hydrazines from their corresponding azobenzenes. Interestingly, the same conditions proved to be ineffective for the hydrolysis of **5.10**. Instead the cleavage of both the Si-N and B-N bonds was achieved using KO^{t}Bu in an isopropanol/toluene mixture (Scheme 5.6). The cross-coupling potential of the N-B bond in **5.10** was assessed, however, initial investigations, using standard conditions, proved unsuccessful (see Experimental Details).[46]



Scheme 5.6 Synthesis of **5.15** from **5.2** and **5.10**

5.5 Conclusions

Complex **5.1** acts as a highly active pre-catalyst in the diboration and silaboration of azobenzenes using commercially available diboranes and silaboranes, respectively. Novel 1,2-bis(boryl)hydrazines and 1-silyl-2-borylhydrazines were synthesized using low catalyst loadings, mild temperatures, and short reaction times. Initial reactivity studies show that the 1,2-bis(boryl)hydrazines are highly susceptible to hydrolytic cleavage, whereas 1-silyl-2-borylhydrazines are stable under ambient conditions and require much harsher conditions to form the corresponding hydrazines. **5.14** was synthesized

presumably as a resting state or intermediate in the catalytic cycle of these reactions. This study was reported in *Advanced Synthesis and Catalysis* as a communication.[47] The reactivity potential of the novel 1,2-bis(boryl)hydrazines and 1-silyl-2-boryl hydrazines will be the focus of future investigations.

5.6 Experimental Details for Chapter 5

General experimental details are given in appendix A1.

5.6.1 Synthesis of 1,2-di-*p*-tolyldiazene

p-Toluidine (0.331 g, 3.09 mmol), copper(I) bromide (0.013 g, 0.09 mmol) and pyridine (22.5 µL, 0.28 mmol) were dissolved in toluene (5 mL). The resulting reaction mixture was heated to 60 °C under an atmosphere of air for 3 days. At this point the reaction mixture was cooled to room temperature and filtered through a plug of silica. The resulting filtrate was concentrated and the crude mixture was purified by flash chromatography (eluent: 100% hexane). Yield: 0.110 g, 34%. ^{1}H NMR (399.5 MHz, C_6D_6): δ_H = 7.81 [d, $^{3}J_{HH}$ = 8.0 Hz, 4H], 7.30 [d, $^{3}J_{HH}$ = 8.0 Hz, 4H], 2.43 [s, 6H]. ^{13}C{^{1}H} NMR (100.46 MHz, $CDCl_3$): δ_C = 151.0, 141.3, 129.9, 122.9, 21.6.

5.6.2 Synthesis of 1,2-bis(4-fluorophenyl)diazene

4-Fluoroaniline (94.6 µL, 1.00 mmol), copper(I) bromide (0.004 g, 0.03 mmol) and pyridine (8.9 µL, 0.11 mmol) were dissolved in toluene (4 mL). The resulting reaction mixture was heated to 60 °C for 48 h. Upon cooling, the reaction mixture was filtered through a plug of silica, the filtrate volatiles were removed in vacuo and the crude solid was purified by flash chromatography (eluent: 100% hexane). Yield: 0.100 g, 92%. ^{1}H NMR (399.5 MHz, $CDCl_3$): δ_H = 7.92 [m, 4H], 7.20 [m, 4H]. ^{1}H NMR (399.5 MHz, C_6D_6): δ_H = 7.76 [m, 4H], 6.78 [m, 4H]. ^{13}C{^{1}H} NMR (100.46 MHz, $CDCl_3$): δ_C = 164.6

[d, $^{1}J_{CF}$ = 251.2 Hz], 148.2 [d, $^{4}J_{CF}$ = 2.6 Hz], 125.0 [d, $^{3}J_{CF}$ = 9.0 Hz], 116.2 [d, $^{2}J_{CF}$ = 23.1 Hz]. ^{19}F NMR (375.9 MHz, $CDCl_3$): δ_F = −109.38 [m].

5.6.3 Synthesis of [Pd(ITMe)$_2$(PhC≡CPh)] (5.1)

5.1 was synthesised following previous literature preparation.[27]

5.6.4 Stock Solution of 5.1

Stock solution were made in batches; in a glovebox 5 mg of **5.1** was dissolved in 2 mL of C_6D_6 (9.38 µmol, 4.69 x 10^{-3} M).

5.6.5 Synthesis of 1,2-diphenyl-1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (5.2)

In C_6D_6

PhN=NPh (0.025 g, 0.14 mmol), B_2pin_2 (0.041 g, 0.16 mmol) and **5.1** (0.001 g, 2.62 µmol) were dissolved in C_6D_6 (0.7 mL). The resulting reaction mixture was stirred at room temperature for 2 h. At this point the reaction mixture was filtered by cannula and all volatiles were then removed in vacuo. The resulting off-white solid was recrystallized in hexane at −30 ˚C. On decanting the volatiles, the colourless crystals were dried under a high vacuum to give a white powder.

In toluene

In an ampoule, PhN=NPh (0.101 g, 0.55 mmol), bis(pinacalato)diboron (0.109 g, 0.43 mmol) and **5.1** (0.001 g, 2.06 µmol) were dissolved in toluene (2 mL). The resulting reaction mixture was stirred at room temperature under an N_2 atmosphere for 2 h. At this stage the reaction mixture was filtered *via* cannula and the filtrates volatiles were removed in vacuo. The resulting crude solid was recrystallized in hexane (3 x 5 mL), which resulted

in isolation of an off-white powder. Yield: 0.119 g, 63%. ^{1}H NMR (399.5 MHz, C_6D_6): δ_H = 7.76 [m, 4H, Ph], 7.16 [m, 4H, Ph], 6.81 [m, 2H, *p*-Ph], 1.12 [s, 12H, Bpin], 1.08 [s, 12H, Bpin]. ^{13}C{^{1}H} NMR (100.46 MHz, C_6D_6): δ_C = 146.5 [*i*-Ph], 129.2 [Ph], 121.6 [*p*-Ph], 117.0 [Ph], 83.5 [**C**, Bpin], 24.8 [**C**H$_3$, Bpin], 24.4 [**C**H$_3$, Bpin]. ^{11}B{^{1}H} NMR (128.2 MHz, C_6D_6): δ_B = 25.8. Elem. Anal. Calcd for $C_{24}H_{34}O_4N_2B_2$: C, 66.09%; H, 7.86%; N, 6.42%. Found: C, 66.41%; H, 7.56%; N, 6.62%.

Crystal data for **5.2**: $C_{24}H_{34}N_2B_2O_4$, M_r = 436.15 g mol^{-1}, orthorhombic, space group $P2_12_12_1$, a = 11.248(3) Å, b = 12.019(6) Å, c = 17.861(4) Å, α = 90°, β = 90°, γ = 90°, V = 2414.6(15) Å^3, Z = 4, T = 103 K, λMo(Kα) = 0.71073, R_1 [$I > 2\sigma(I)$] = 0.0483, wR_2 (all data) = 0.0982, *GooF* = 1.017.

5.6.6 Synthesis of 1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-di-*m*-tolylhydrazine (5.3)

3,3'-dimethylazobenzene (0.025 g, 0.12 mmol), B_2pin_2 (0.041 g, 0.16 mmol) and **5.1** (0.32 mg. 0.59 μmol) were dissolved in C_6D_6 (0.7 mL). The reaction mixture was stirred at room temperature under a nitrogen atmosphere for 2.5 h. At this point the volatiles were removed in vacuo. The resulting off-white solid was recrystallized in toluene/hexane (1:3, 5.0 mL) and then hexane (2 x 2.0 mL) at −30 °C. Yield: 0.040 g, 72%. ^{1}H NMR (399.5 MHz, C_6D_6): δ_H = 7.63 [m, 2H, 6-Ph], 7.63 [s, 2H, 2-Ph], 7.13 [m, 2H, 5-Ph], 6.68 [d, $^{3}J_{HH}$ = 7.4 Hz, 2H, 4-Ph], 2.11 [s, 6H, Me], 1.14 [s, 12H, Bpin], 1.11 [s, 12H, Bpin]. ^{13}C{^{1}H} NMR (100.46 MHz, C_6D_6): δ_C = 146.7 [1-Ph], 138.6 [3-Ph], 129.1 [5-Ph], 122.5 [4-Ph], 117.7 [2-Ph], 114.5 [6-Ph], 83.5 [**C**, Bpin], 24.9 [**C**H$_3$, Bpin], 24.4 [**C**H$_3$, Bpin], 21.9 [**Me**]. ^{11}B{^{1}H} NMR (128.2 MHz, C_6D_6): δ_B = 25.5. Elem. Anal. Calcd for $C_{26}H_{38}O_4N_2B_2$: C, 67.27%; H, 8.25%; N, 6.03%. Found: C, 67.33%; H, 8.27%; N, 6.10%.

5.6.7 Synthesis of 1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-di-*p*-tolylhydrazine (5.4)

1,2-di-*p*-Tolyldiazene (0.025 g, 0.11 mmol), B_2pin_2 (0.033 g, 0.13 mmol) and **5.1** (0.30 mg, 0.56 μmol) were dissolved in C_6D_6 (0.7 mL). The resulting reaction mixture was stirred at room temperature under a N_2 atmosphere for 3 h. At this point, the volatiles were removed in vacuo and the crude reaction mixture was recrystallized in hexane (3 x 2 mL) at –30 ^oC resulting in the isolation of a white powder. Yield: 0.040 g, 75%. ^1H NMR (399.5 MHz, C_6D_6, 400 MHz): δ_H = 7.69 [m, 4H, *o*-PhMe], 7.00 [m, 4H, *m*-PhMe], 2.07 [s, 6H, Ph**Me**], 1.15 [s, 12H, Bpin], 1.11 [s, 12H, Bpin]. $^{13}C\{^1H\}$ NMR (100.46 MHz, C_6D_6): δ_C = 144.2 [*i*-PhMe], 130.4 [*p*-PhMe], 129.7 [*m*-PhMe], 117.3 [*o*-PhMe], 83.4 [**C**, Bpin], 24.9 [**C**H_3, Bpin], 24.5 [**C**H_3, Bpin], 20.6 [Ph**Me**]. $^{11}B\{^1H\}$ NMR (128.2 MHz, C_6D_6): δ_B = 25.5. Elem. Anal. Calcd for $C_{26}H_{38}O_4N_2B_2$: C, 67.27%; H, 8.25%; N, 6.03%. Found: C, 67.19%; H, 8.27%; N, 6.12%.

Crystal data for **5.4**: $C_{26}H_{38}N_2B_2O_4$, M_r = 464.20 g mol^{-1}, orthorhombic, space group $P2_12_12_1$, a = 11.3842(5) Å, b = 12.2242(5) Å, c = 19.0048(8) Å, α = 90°, β = 90°, γ = 90°, V = 2644.75(19) $Å^3$, Z = 4, T = 173 K, λCu(Kα) = 1.54184, R_1 [$I > 2\sigma(I)$] = 0.0503, wR_2 (all data) = 0.1288, *GooF* = 0.970.

5.6.8 Synthesis of 1-(4-methoxyphenyl)-2-phenyl-1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (5.5)

1-(4-Methoxyphenyl)-2-phenyldiazene (0.099 g, 0.46 mmol), B_2pin_2 (0.144 g, 0.61 mmol) and **5.1** (0.001 g, 0.24 μmol) were dissolved in C_6D_6 (0.7 mL). The resulting reaction mixture was stirred at room temperature under a N_2 atmosphere for 4 h. At this stage the sample was filtered *via* a cannula, the filtrate volatiles were removed in vacuo and the resulting off-white solid was recrystallized in hexane (3 x 4 mL). Yield: 0.170 g,

79%. ^{1}H NMR (399.5 MHz, C_6D_6): δ_H = 7.77 [m, 2H, *m*-Ph], 7.62 [m, 2H, **Ph**OMe], 7.18 [m, 2H, *o*-Ph], 6.83 [m, 1H, *p*-Ph], 6.75 [m, 2H, **Ph**OMe], 3.28 [s, 3H, O**Me**], 1.15 [s, 6H, Bpin], 1.14 [s, 6H, Bpin], 1.11 [s, 6H, Bpin], 1.10 [s, 6H, Bpin]. ^{13}C{^{1}H} NMR (100.46 MHz, C_6D_6): δ_C = 155.2 [*p*-PhOMe], 146.7 [*i*-Ph], 139.7 [*i*-PhOMe], 129.1 [*o*-Ph], 121.5 [*p*-Ph], 118.6 [**Ph**OMe], 117.2 [*m*-Ph], 114.6 [**Ph**OMe], 83.5 [**C**, Bpin], 55.0 [O**Me**], 24.9 [**C**H_3, Bpin], 24.5 [**C**H_3, Bpin]. ^{11}B{^{1}H} NMR (128.2 MHz, C_6D_6): δ_B = 25.3. Elem. Anal. Calcd for $C_{25}H_{36}O_5N_2B_2$: C, 64.41%; H, 7.78%; N, 6.01%. Found: C, 64.28%; H, 7.65%; N, 6.09%.

5.6.9 Synthesis of *N*-(4-(1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(*o*-tolyl)hydrazinyl)-2-methylphenyl)acetamide (5.6)

4-Acetamido-2',3-dimethylazobenzene (0.120 g, 0.45 mmol), B_2pin_2 (0.144 g, 0.57 mmol) and **5.1** (0.001 g, 2.25 µmol) were dissolved in toluene (1.5 mL). The resulting reaction mixture was heated to 80 °C under a N_2 atmosphere for 22 h. At this point, the reaction mixture was cooled to room temperature, dissolved in dioxane (15 mL) and filtered *via* cannula. The filtrate volatiles were removed in vacuo. The off-white solid was recrystallized in toluene/hexane (5:1, 2 x 5 mL) at −30 °C and then washed with hexane (5 mL). Yield: 0.169 g, 72%. ^{1}H NMR (399.5 MHz, C_6D_6): δ_H = 7.92 [d, $^{3}J_{HH}$ = 8.7 Hz, 1H, (1)5-PhH], 7.74 [m, 1H, (2)4-PhH], 7.63 [d, $^{3}J_{HH}$ = 8.7 Hz, (1)6-PhH], 7.47 [s, 1H, (1)2-PhH], 7.06 [m, 2H, (2)3-PhH/(2)5-PhH], 6.88 [m, 1H, (2)6-PhH], 5.84 [s, 1H, C(O)N**H**], 2.63 [s, 3H, (2)2-Ph**Me**], 1.83 [s, 3H, (1)3-Ph**Me**], 1.51 [s, 3H, **Me**C(O)NH-], 1.15 [s, 12H, Bpin], 1.13 [s, 12H, Bpin]. ^{13}C{^{1}H} NMR (100.46 MHz, C_6D_6): δ_C = 166.7 [**C**(O)NH], 144.9 [(2)1-Ph], 143.8 [(1)1-Ph], 132.9 [(2)2-Ph], 131.5, 131.4 [(2)3-Ph], 129.8, 126.6 [(2)5-Ph], 125.0 [(2)6-Ph], 124.7 [(2)4-Ph], 124.2 [(1)5-Ph], 122.0 [(1)2-Ph], 118.6 [(1)6-Ph], 83.5 [**C**, Bpin], 25.1 [**C**H_3, Bpin], 25.1 [**C**H_3, Bpin], 24.6 [**C**H_3,

Bpin], 24.4 [Bpin], 23.6 [**Me**C(O)NH], 19.8 [(2)2-Ph**Me**], 18.1 [(1)3-Ph**Me**]. $^{11}B\{^{1}H\}$ (128.2 MHz, C_6D_6): δ_B = 25.2. Elem. Anal. Calcd for $C_{28}H_{41}O_5N_3B_2$: C, 64.52%; H, 7.93%; N, 8.06%. Found: C, 64.66%; H, 8.07%; N, 8.21%.

5.6.10 Synthesis of 1,2-bis(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)-1,2-diphenylhydrazine (5.7)

PhN=NPh (0.025 g, 0.14 mmol), 5,5,5',5'-tetramethyl-2,2'-bi(1,3,2-dioxaborinane) (0.035 g, 0.15 mmol) and **5.1** (0.001 g, 2.63 µmol) were dissolved in C_6D_6 (0.7 mL). The resulting reaction mixture was heated to 80 °C under an N_2 atmosphere for 48 h. At this stage, the reaction mixture was cooled to room temperature, the volatiles were removed in vacuo. The resulting brown oily solid was recrystallized in toluene/hexane (2:3, 2 mL) and then hexane (2 x 2 mL) at −30 °C. A colourless crystalline solid was obtained as a result. Yield: 0.043 g, 77%. ^{1}H NMR (399.5 MHz, C_6D_6): δ_H = 7.83 [d, $^{3}J_{HH}$ = 8.1 Hz, 4 H, Ph], 7.23 [m, 4H, Ph], 6.86 [pseudo t, $^{3}J_{HH}$ = 7.3 Hz, 2H, *p*-Ph], 3.37 [m, 8H, C**H**$_2$], 0.63 [s, 12H, C**H**$_3$]. $^{13}C\{^{1}H\}$ NMR (100.46 MHz, C_6D_6): δ_C = 147.1 [*i*-Ph], 128.5 [Ph], 120.8 [*p*-Ph], 118.0 [Ph], 72.2 [**C**H_2], 31.4 [**C**$(CH_3)_2$], 21.1 [**C**H_3]. $^{11}B\{^{1}H\}$ NMR (128.2 MHz, C_6D_6): δ_B = 21.3. Elem. Anal. Calcd for $C_{22}H_{30}O_4N_2B_2$: C, 64.75%; H, 7.41%; N, 6.86%. Found: C, 64.66%; H, 7.44%; N, 6.90%.

5.6.11 Synthesis of 1,2-bis(benzo[d][1,3,2]dioxaborol-2-yl)-1,2-diphenylhydrazine (5.8)

In C_6D_6

PhN=NPh (0.025 g, 0.14 mmol), 2,2'-bibenzo[d][1,3,2]dioxaborole (0.035 g, 0.15 mmol) and **5.1** (0.001 g, 2.63 µmol) were dissolved in C_6D_6 (0.7 mL). The resulting reaction mixture was heated at 80 °C under a N_2 atmosphere for 24 h. At this stage the volatiles

were removed in vacuo, the crude brown oily solid was then recrystallized in toluene/hexane (1:3, 2 mL) and then toluene (1 x 5 mL) at –30 °C. This resulted in the isolation of an off-white solid.

In toluene

PhN=NPh (0.060 g, 0.32 mmol), 2,2'-bibenzo[d][1,3,2]dioxaborole (0.078 g, 0.33 mmol) and **5.1** (0.003 g, 6.38 μmol) were dissolved in toluene (1.5 mL). The resulting reaction mixture was heated to 80 °C and stirred at this temperature under a N_2 atmosphere for 24 h. The volatiles were removed in vacuo and the crude oily solid was recrystallized in toluene (3 x 3 mL) at –30 °C. The resulting off-white powder was washed with hexane (3 x 3 mL). Yield: 0.089 g, 66%. ^{1}H NMR (399.5 MHz, C_6D_6): δ_H = 7.70 [d, $^{3}J_{HH}$ = 8.3 Hz, 4H, N(*o*-Ph)], 7.13 [m, 4H, N(*m*-Ph)], 6.87 [dd, *J* = 8.3 Hz, 6.6 Hz, 2H, N(*p*-Ph)], 6.81 [m, 4H, cat-3-Ph], 6.64 [m, 4H, cat-2-Ph]. ^{13}C{^{1}H} NMR (100.46 MHz, C_6D_6): δ_C = 148.8 [cat-1-Ph], 144.3 [N(*i*-Ph)], 129.7 [N(*m*-Ph)], 123.6 [N(*p*-Ph)], 122.7 [cat-2-Ph], 117.7 [N(*o*-Ph)], 112.5 [cat-3-Ph]. ^{11}B{^{1}H} (128.2 MHz, C_6D_6): δ_B = 26.7. Elem. Anal. Calcd for $C_{24}H_{18}O_4N_2B_2$: C, 68.63%; H, 4.32%; N, 6.67%. Found: C, 68.63%; H, 4.38%; N, 6.59%.

5.6.12 Synthesis of 1,2-bis(dimethoxyboryl)-1,2-diphenylhydrazine (5.9)

PhN=NPh (0.025 g, 0.14 mmol), $B_2(OMe)_4$ (0.040 g, 0.27 mmol) and **5.1** (0.001 g, 2.63 μmol) were dissolved in C_6D_6 (0.7 mL). The resulting reaction mixture was stirred at room temperature for 40 h and, separately, at 80 °C for 24 h. ^{1}H NMR analysis indicated a maximum 33% conversion to **5.9**. Multiple recrystallization attempts in toluene/hexane solution (1:5 to 5:1) proved unsuccessful with starting material persisting.

5.9: ^{1}H NMR (399.5 MHz, C_6D_6): δ_H = 7.31 [m, 4H, Ph], 7.12 [m, 4H, Ph], 6.80 [m, 2H, *p*-Ph], 3.46 [s, 12H, O**Me**]. ^{11}B{^{1}H} NMR (128.2 MHz, C_6D_6): δ_B = 22.1.

5.6.13 Synthesis of 1-(dimethyl(phenyl)silyl)-1,2-diphenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (5.10)

In C_6D_6

PhN=NPh (0.025 g, 0.14 mmol), $PhMe_2SiBpin$ (46.0 µL, 0.17 mmol) and **5.1** (0.36 mg, 0.68 µmol) were dissolved in C_6D_6 (0.7 mL). The resulting reaction mixture was stirred at room temperature for 2 h. At this point the volatiles were removed in vacuo and the resulting oily solid was washed with cold hexane (4 x 1 mL). Upon drying the title compound was obtained as a white powder without further purification.

In toluene

PhN=NPh (0.070 g, 0.38 mmol), $PhMe_2SiBpin$ (0.120 g, 0.46 mmol) and **5.1** (0.001 g, 1.31 µmol) were dissolved in toluene (1.5 mL). The reaction mixture was stirred at room temperature under a N_2 atmosphere for 2 h. At this stage the volatiles were removed in vacuo, the resulting oily solid was stirred in deionized H_2O overnight and a white powder was obtained upon filtering. Yield: 0.148 g, 87%. ^{1}H NMR (399.5 MHz, C_6D_6): δ_H = 7.85 [m, 2H, $SiMe_2$**Ph**], 7.68 [m, 2H, *o*-Ph(1)], 7.23 [m, 3H, $SiMe_2$**Ph**], 7.16 [m, 2H, *m*-Ph(1)], 7.03 [m, 4H, *o*- and *m*-Ph(2)], 6.85 [m, 1H, *p*-Ph(1)], 6.68 [m, 1H, *p*-Ph(2)], 1.05 [s, 6H, Bpin], 1.01 [s, 6H, Bpin], 0.61 [s, 3H, Si**Me$_2$**Ph], 0.58 [s, 3H, Si**Me$_2$**Ph]. ^{13}C{^{1}H} NMR (100.46 MHz, C_6D_6): δ_C = 149.8 [*i*-Ph(2)], 147.5 [*i*-Ph(1)], 138.3 [$SiMe_2$*i*-**Ph**], 134.8 [$SiMe_2$**Ph**], 129.7 [$SiMe_2$*p*-**Ph**], 129.3 [Ph(2)], 129.1 [*m*-Ph(1)], 128.1 [$SiMe_2$**Ph**], 121.9 [*p*-Ph(1)], 119.1 [*p*-Ph(2)], 118.0 [*o*-Ph(1)], 114.1 [Ph(2)], 83.6 [**C**, Bpin], 24.8 [**C**H_3, Bpin], 24.4 [**C**H_3, Bpin], –0.7 [Si**Me$_2$**Ph], –0.8 [Si**Me$_2$**Ph]. ^{11}B{^{1}H} NMR (128.2 MHz, C_6D_6): δ_B = 25.8. ^{29}Si{^{1}H} NMR (79.4 MHz, C_6D_6): δ_{Si} = 4.59. Elem. Anal. Calcd for $C_{26}H_{33}O_2N_2SiB$: C, 70.26%; H, 7.48%; N, 6.30%. Found: C, 70.18%; H, 7.50%; N, 6.30%.

Crystal data for **5.10**: $C_{26}H_{33}N_2O_4BSi$, M_r = 444.44 g mol^{-1}, monoclinic, space group $P2_1$, a = 8.51365(19) Å, b = 12.4441(3) Å, c = 11.7153(3) Å, α = 90°, β = 91.067(2)°, γ = 90°, V = 1240.96(5) Å^3, Z = 2, T = 103 K, λCu(Kα) = 1.54184, R_1 [$I > 2\sigma(I)$] = 0.0574, wR_2 (all data) = 0.1604, *GooF* = 1.043.

5.6.14 Synthesis of 1-(dimethyl(phenyl)silyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-di-*m*-tolylhydrazine (5.11)

1,2-di-*m*-Tolyldiazene (0.024 g, 0.11 mmol), dimethyl(phenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (0.040 g, 0.15 mmol) and **5.1** (0.30 mg, 0.56 µmol) were dissolved in C_6D_6 (0.7 mL). The resulting reaction mixture was stirred at room temperature under a N_2 atmosphere. After 2.5 h, the volatiles were removed in vacuo, deionized H_2O (100 mL) was added and the crude reaction mixture was stirred at room temperature for 15 h. The product was obtained cleanly as a white powder on filtering the precipitate. Yield: 0.052 g, 98%. ^{1}H NMR (399.5 MHz, C_6D_6): δ_H = 7.88 [m, 2H, SiMe$_2$*o*-**Ph**], 7.62 [dd, J = 8.3, 2.2 Hz, 1H, (2)Ph{6}], 7.55 [s, 1H, (2)Ph{2}], 7.24 [m, 3H, SiMe$_2$*m*/*p*-**Ph**], 7.15 [m, 1H, (2)Ph{5}], 6.96 [m, 3H, (1)Ph{2/5/6}], 6.71 [m, 1H, (2)Ph{4}], 6.53 [m, 1H, (1)Ph{4}], 2.13 [s, 3H, (2)**Me**], 2.01 [s, 3H, (1)**Me**], 1.08 [s, 6H, Bpin], 1.04 [s, 6H, Bpin], 0.67 [s, 3H, Si**Me$_2$**Ph], 0.62 [s, 3H, Si**Me$_2$**Ph]. ^{13}C{^{1}H} NMR (100.46 MHz, C_6D_6): δ_C = 149.9 [(1)Ph{1}], 147.6 [(2)Ph{1}], 138.7 [(1)Ph{3}], 138.6 [(2)Ph{3}], 138.5 [SiMe$_2$*i*-**Ph**], 134.9 [SiMe$_2$*o*-**Ph**], 129.7 [SiMe$_2$*p*-**Ph**], 129.3, 129.1 [(2)Ph{5}], 128.1 [SiMe$_2$*m*-**Ph**], 122.7 [(2)Ph{4}], 120.1 [(1)Ph{4}], 118.4 [(2)Ph{2}], 115.3 [(2)Ph{6}], 114.6, 111.5, 83.5 [**C**, Bpin], 24.8 [**C**H$_3$, Bpin], 24.4 [**C**H$_3$, Bpin], 21.8 [(1)**Me**], 21.8 [(2)**Me**], –0.6 [Si**Me$_2$**Ph], –0.9 [Si**Me$_2$**Ph]. ^{11}B{^{1}H} NMR (128.2 MHz, C_6D_6): δ_B = 25.8. ^{29}Si{^{1}H} NMR (79.4 MHz, C_6D_6): δ = 4.40. Elem. Anal. Calcd for

$C_{28}H_{37}N_2O_2SiB$: C, 71.17%; H, 7.89%; N, 5.93%. Found: C, 71.06%; H, 7.74%; N, 5.75%.

5.6.15 Synthesis of 1-(dimethyl(phenyl)silyl)-1,2-bis(4-fluorophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (5.12)

1,2-bis(4-Fluorophenyl)diazene (0.027 g, 0.12 mmol), $PhMe_2SiBpin$ (0.038 g, 0.14 mmol) and **5.1** (0.33 mg, 0.62 μmol) were dissolved in C_6D_6 (0.7 mL). The resulting reaction mixture was stirred at room temperature for 1.5 h under a N_2 atmosphere. At this stage the volatiles were removed in vacuo, deionized H_2O (100 mL) was added and the reaction mixture was stirred for a further 24 h at room temperature. The H_2O was then decanted and the off-white solid was dried under a high vacuum. Yield: 0.050 g, 84%. ^{1}H NMR (399.5 MHz, C_6D_6): δ_H = 7.68 [m, 2H, $SiMe_2$*o*-**Ph**], 7.37 [m, 2H, (2)*o*-PhF], 7.17 [m, 3H, $SiMe_2$*m*,*p*-**Ph**], 6.74 [m, 2H, (1)*o*-PhF], 6.74 [m, 2H, (2)*m*-PhF], 6.60 [m, 2H, (1)*m*-PhF], 0.97 [s, 6H, Bpin], 0.92 [s, 6H, Bpin], 0.48 [s, 3H, Si**Me$_2$**Ph], 0.43 [s, 3H, Si**Me$_2$**Ph]. ^{13}C{^{1}H} NMR (100.46 MHz, C_6D_6): δ_C = 159.8 [d, $^1J_{CF}$ = 239.7 Hz, (2)*p*-PhF], 158.3 [d, $^1J_{CF}$ = 236.7 Hz, (1)*p*-PhF], 145.6 [(1)*i*-PhF], 143.3 [(2)*i*-PhF], 137.8 [$SiMe_2$*i*-**Ph**], 134.6 [$SiMe_2$*o*-**Ph**], 130.0 [$SiMe_2$*p*-**Ph**], 128.2 [$SiMe_2$*m*-**Ph**], 119.1 [d, $^3J_{CF}$ = 7.6 Hz, (2)*o*-PhF], 115.8 [d, $^2J_{CF}$ = 21.9 Hz, (2)*m*-PhF], 115.6 [d, $^2J_{CF}$ = 21.9 Hz, (1)*m*-PhF], 114.7 [d, $^3J_{CF}$ = 7.6 Hz, (1)*o*-PhF], 83.7 [**C**, Bpin], 24.8 [**C**H_3, Bpin], 24.3 [**C**H_3, Bpin], –0.8 [Si**Me$_2$**Ph], –1.1 [Si**Me$_2$**Ph]. ^{11}B{^{1}H} NMR (128.2 MHz, C_6D_6): δ_B = 25.4. ^{19}F{^{1}H} NMR (375.9 MHz, C_6D_6): δ_F = –122.60 (m), –126.70 (m). ^{29}Si{^{1}H} NMR (79.4 MHz, C_6D_6): δ_{Si} = 4.85. Elem. Anal. Calcd for $C_{26}H_{31}O_2N_2F_2SiB$: C, 65.00%; H, 6.50%; N, 5.83%. Found: C, 64.81%; H, 6.39%; N, 6.00%.

Crystal data for **5.12**: $C_{26}H_{31}N_2O_2F_2BSi$, M_r = 480.43 g mol^{-1}, monoclinic, space group $P2_1$, a = 8.58378(17) Å, b = 12.6067(2) Å, c = 11.7191(2) Å, α = 90°, β = 90.5690(18)°,

$\gamma = 90^{o}$, $V = 1268.10(4)$ Å^3, $Z = 2$, $T = 173$ K, λCu(Kα) = 1.54184, R_1 [$I > 2\sigma(I)$] = 0.0635, wR_2 (all data) = 0.1806, *GooF* = 1.061.

5.6.16 Synthesis of 1-(dimethyl(phenyl)silyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-di-*p*-tolylhydrazine (5.13)

1,2-di-*p*-Tolyldiazene (0.031 g, 0.15 mmol), dimethyl(phenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (45.0 µL, 0.17 mmol) and **5.1** (0.40 mg, 0.74 µmmol) were dissolved in C_6D_6 (0.7 mL). The resulting reaction was stirred at room temperature under a N_2 atmosphere for 8 h. At this stage, the volatiles were removed in vacuo, deionized H_2O (80 mL) was added and the precipitated mixture was stirred at room temperature for 16 h. The H_2O was decanted resulting in isolation of a white powder. Yield: 0.069 g, 91%. ^{1}H NMR (399.5 MHz, C_6D_6): δ_H = 7.90 [m, 2H, SiMe$_2$*o*-**Ph**], 7.64 [m, 2H, (2)*o*-PhMe], 7.26 [m, 3H, SiMe$_2$*m*,*p*-**Ph**], 7.00 [m, 4H, (1)*o*-PhMe and (2)*m*-PhMe], 6.82 [m, 2H, (1)*m*-PhMe], 2.10 [s, 3H, (2)Ph**Me**], 2.04 [s, 3H, (1)Ph**Me**], 1.07 [s, 6H, Bpin], 1.03 [s, 6H, Bpin], 0.65 [s, 3H, Si**Me$_2$**Ph], 0.62 [s, 3H, Si**Me$_2$**Ph]. ^{13}C{^{1}H} NMR (100.46 MHz, C_6D_6): δ_C = 147.5 [(1)*i*-PhMe], 145.2 [(2)*i*-PhMe], 138.7 [SiMe$_2$*i*-**Ph**], 134.8 [SiMe$_2$*o*-**Ph**], 130.8 [(2)*p*-PhMe], 129.9 [(1)*m*-PhMe], 129.7 [(2)*m*-PhMe], 129.7 [SiMe$_2$*p*-**Ph**], 127.9 [SiMe$_2$*m*-**Ph**], 127.7 [(1)*p*-PhMe], 118.1 [(2)*o*-PhMe], 114.1 [(1)*o*-PhMe], 83.4 [**C**, Bpin], 24.8 [**C**H$_3$, Bpin], 24.4 [**C**H$_3$, Bpin], 20.6 [(1)Ph**Me**], 20.4 [(2)Ph**Me**], –0.6 [Si**Me$_2$**Ph], –0.8 [Si**Me$_2$**Ph]. ^{11}B{^{1}H} NMR (128.2 MHz, C_6D_6): δ_B = 25.8. ^{29}Si{^{1}H} NMR (79.4 MHz, C_6D_6): δ_{Si} = 4.10. Elem. Anal. Calcd for $C_{28}H_{37}O_2N_2SiB$: C, 71.17%; H, 7.89%; N, 5.93%. Found: C, 70.99%; H, 8.02%; N, 5.90%.

5.6.17 Reaction of 1-(4-methoxphenyl)-2-phenyldiazene and $PhMe_2SiBpin$

1-(4-Methoxyphenyl)-2-phenyldiazene (0.025 g, 0.12 mmol), dimethyl(phenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (35.0 µL, 0.13 mmol) and **5.1** (0.31 mg, 0.59 µmol) were dissolved in C_6D_6 (0.7 mL). The resulting reaction mixture was stirred at room temperature for 24 h under a N_2 atmosphere. Crude NMR analysis at this stage showed a mixture of inseparable regioisomers (see ^{1}H NMR spectrum in supporting information).

5.6.18 Synthesis of $[Pd(ITMe)_2(PhN{=}NPh)]$ (5.14) from 5.1

5.1 (0.032 g, 0.06 mmol) and PhN=NPh (0.019 g, 0.10 mmol) were dissolved in toluene (5.0 mL). The resulting reaction mixture was stirred at room temperature for 3 h. At this stage, the volatiles were removed in vacuo and the crude material was washed recrystallized in a toluene/hexane solution (3:1, 2 x 2.0 mL). The resulting yellow powder was washed with pentane (3 x 2.0 mL). Yield: 0.020 g, 62%. ^{1}H NMR (399.5 MHz, C_6D_6): δ_H = 7.80 [m, 4H, Ph], 7.26 [m, 4H, Ph], 6.87 [*pseudo*-t, *J* = 7.2 Hz, 2H, *p*-Ph], 3.31 [s, 12H, N(1,3)-C**H**$_3$], 1.38 [s, 12H, C(4,5)-C**H**$_3$]. ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6): δ_C = 189.0 [N**C**N], 163.0 [*i*-Ph], 128.9 [Ph], 124.1 [**C**(4,5)-CH_3], 120.5 [Ph], 117.0 [*p*-Ph], 35.2 [N(1,3)-**C**H_3], 8.7 [C(4,5)-**C**H_3]. Elem. Anal. Calcd for $C_{26}H_{34}N_6Pd$: C, 58.15%; H, 6.38%; N, 15.65%. Found: C, 58.10%; H, 6.47%; N, 15.60%.

Crystal data for **5.14**: $C_{26}H_{34}N_6Pd$, M_r = 721.26 g mol^{-1}, orthorhombic, space group $P2_12_12_1$, *a* = 12.7436(9) Å, *b* = 15.31140(12) Å, *c* = 18.9685(13) Å, α = 90°, β = 90°, γ = 90°, *V* = 3702.0(5) Å^3, *Z* = 4, *T* = 173 K, λCu(Kα) = 1.54184, R_1 [$I > 2\sigma(I)$] = 0.0370, wR_2 (all data) = 0.0964, *GooF* = 1.032.

5.6.19 Scaled-up Synthesis of 5.14

Isopropanol (12.2 µL, 0.16 mmol) was added to a stirred mixture of [(ITMe)Pd(methallyl)Cl] (0.051 g, 0.16 mmol), ITMe (0.024 g, 0.19 mmol) and potassium *tert*-butoxide (0.019 g, 0.17 mmol) suspended in toluene (5.0 mL). The reaction mixture was stirred at room temperature under an N_2 atmosphere for 4.5 h, at which point PhN=NPh (0.036 g, 0.20 mmol) was added and the solution was stirred for a further 17 h at room temperature. The resulting reaction mixture was filtered, the filtrates volatiles were removed in vacuo and the crude material was recrystallized in a toluene/hexane solution (2:1, 2 x 15.0 mL) at –35 ^{o}C. A yellow solid was obtained after filtration and subsequent washes with hexane (3 x 5.0 mL). Yield: 0.060 g, 70%. (See above for NMR assignment).

5.6.20 Hydrolysis of 5.2 to Form 1,2-diphenylhydrazine (5.15)

To **5.2** (0.014 g, 31.49 µmol) degassed deionized H_2O (10 mL) was added. The resulting reaction mixture was stirred for 48 h at room temperature under an argon atmosphere. At this stage the H_2O was filtered off and the resulting white powder was dried in vacuo. Yield: 0.005 g, 90%. ^{1}H NMR (399.5 MHz, C_6D_6): δ_H = 7.08 [m, 4H], 6.76 [m, 2H], 6.62 [m, 4H], 4.71 [s, 2H]. $^{13}C\{^{1}H\}$ NMR (100.46 MHz, C_6D_6): δ_C = 149.4, 129.5, 120.0, 112.7.

5.6.21 Base Driven Alcoholysis of 5.10 to Form 5.15

5.10 (0.025 g, 0.06 mmol) and KO^{t}Bu (0.013 g, 0.12 mmol) was dissolved in ^{i}PrOH/toluene (1:1, 2 mL). The resulting reaction mixture was stirred at room temperature for 22 h under an N_2 atmosphere. The volatiles were removed in vacuo and the product

extracted with hexane (2 x 1 mL). Colourless crystals were obtained on recrystallizing the hexane extracts at –30 °C. Yield: 0.009 g, 85% (see above for NMR assignment).

5.6.22 Attempted Cross-Coupling of 5.10

In an ampoule, 5.10 (0.025 g, 0.06 mmol), potassium carbonate (0.092 g, 0.66 mmol) and [$Pd(PPh_3)_4$] (0.005 g, 4.15 µmol) were stirred under a high vaccum. A solution of iodobenzene (10.0 µL, 0.09 mmol) in THF/H_2O (9:1, 2.0 mL) was added to this stirred mixture of solids. The resulting reaction mixture was then heated to reflux under an argon atmosphere for 24 h. Upon cooling, the volatiles were removed in vacuo and the crude mixture was analysis by ^{1}H NMR spectroscopy. NMR analysis was inconclusive and suggested that both the boryl and silyl moieties were no longer present.

5.7 References

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Chapter 6

Preliminary Investigative Studies and Future Directions

6.1 Prologue

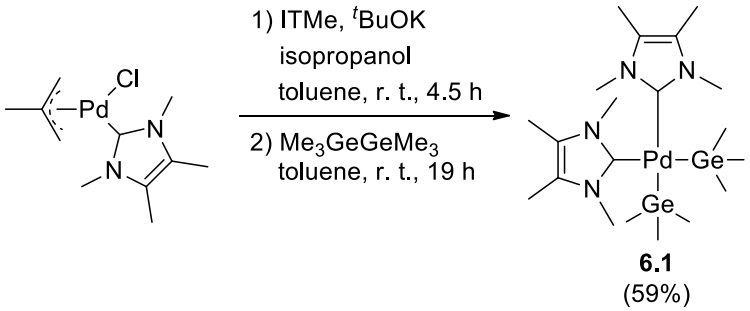
Previous chapters have demonstrated the high degree of success in the use of a $NHC_2Pd(0)$ complex and its derivatives in a range of catalytic transformations. This final chapter outlines some preliminary studies that further explore the reactivity scope of these complexes, and serves as future directions.

6.2 Germanium-Germanium Bond (Ge-Ge) Reactivity

The studies into transition metal mediated element-element bond activations and subsequent alkyne insertions reported in Chapters 2, 3 and 4,[1–3] were extended to an initial examination of Ge-Ge bonds. Ge is directly below silicon (Si) and above tin (Sn) in the periodic table, hence organogermanium compounds are expected to demonstrate properties somewhere in-between their Si and Sn analogues.[4] However, organogermanium chemistry remains relatively unexplored. Palladium mediated digermylation of alkynes has been studied to a much lesser extent than bis(silyl)ation and distannation,[5–7] and this chemistry has been largely limited to the use of strained or activated digermanes (*e.g.* containing at least one electron withdrawing group).[8,9]

Preliminary investigations into the oxidative cleavage of the non-activated hexamethyldigermane ($Me_3GeGeMe_3$) with $[Pd(ITMe)_2]$ resulted in the isolation of *cis*-$[Pd(ITMe)_2(GeMe_3)_2]$ (**6.1**, ITMe = 1,3,4,5-tetramethylimidazol-2-ylidene). **6.1** was synthesized by reacting $[Pd(ITMe)_2]$, formed by combining [(ITMe)Pd(methallyl)Cl] and stoichiometric quantities of ITMe, potassium *tert*-butoxide and isopropanol,[1] with

$Me_3GeGeMe_3$ at room temperature. After work-up, **6.1** was isolated in a 59% yield (Scheme 6.1).



Scheme 6.1 Synthesis of **6.1**

Single crystals of **6.1** suitable for X-ray analysis were isolated from a saturated toluene solution at –30 °C, however it was not possible to refine the data for lengthy discussions on bond lengths and angles (R_1 = 8.8% and wR_2 = 27.7%). Figure 6.1 depicts the molecular structure, displaying connectivity only, proving the *cis*-configuration.

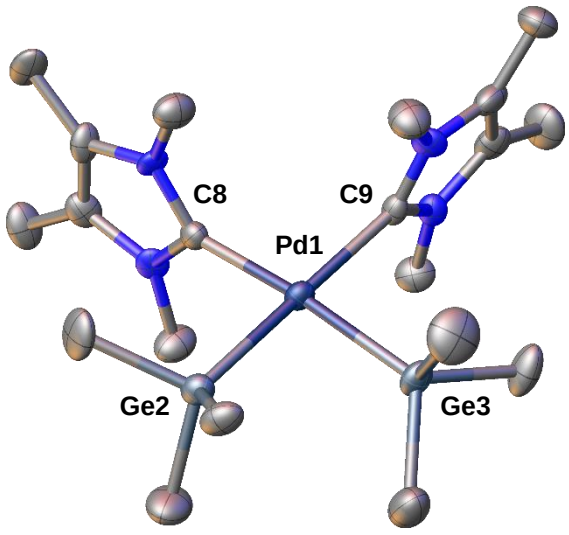
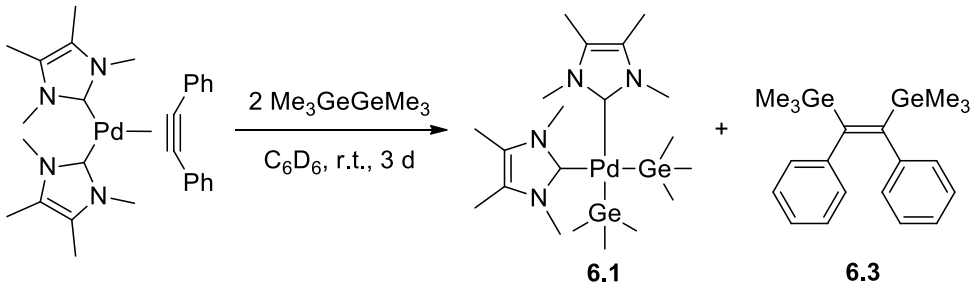


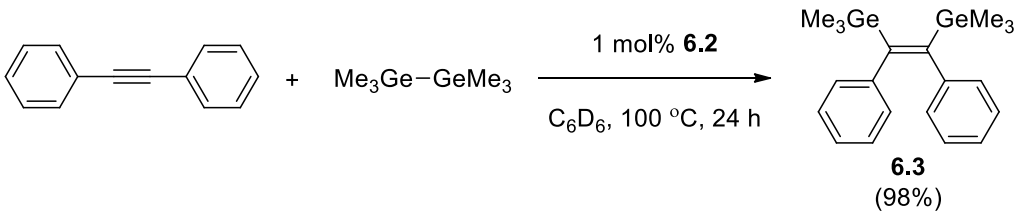
Figure 6.1 Molecular structure of **6.1** with thermal ellipsoids at the 50% probability level. Structural data suitable for connectivity analysis only.

6.1 was also formed by exposing [Pd(ITMe)$_2$(PhC≡CPh)] (**6.2**) to 2 equivalents of $Me_3GeGeMe_3$.[2] Additionally, by following the reaction using ^{1}H NMR spectroscopy, it was observed that all the diphenylacetylene was converted to the air and moisture stable, novel compound (*Z*)-1,2-diphenyl-1,2-bis(trimethylgermyl)ethene (**6.3**, Scheme 6.2).



Scheme 6.2 Synthesis of **6.1** and stoichiometric digermylation to form **6.3**

Previous attempts at performing digermylations of alkynes employing $Me_3GeGeMe_3$ in the literature were limited to the use of terminal alkynes, high loadings of platinum catalysts and elevated temperatures of 120 ^{o}C.[10] **6.2** capacity to catalyse the digermylation of diphenylacetylene using $Me_3GeGeMe_3$ was assessed. The digermylated stilbene **6.3** was obtained in a 98% yield (100% stereoselectivity) employing 1 mol% of **6.2** at 100 ^{o}C in 24 h (Scheme 6.3).



Scheme 6.3 Catalytic digermylation of diphenylacetylene to form **6.2**

Single crystals of **6.3** were isolated from slow evaporation of a saturated acetone solution at room temperature and the molecular structure is depicted in Figure 6.2.

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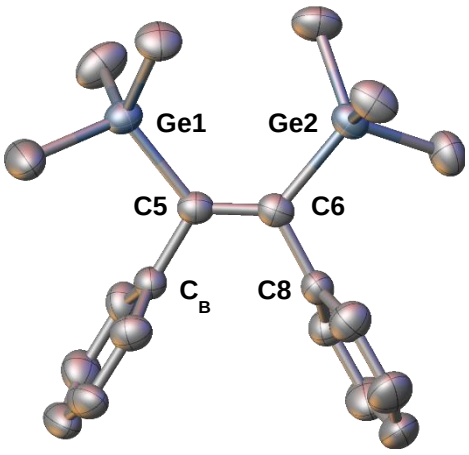


Figure 6.2 Molecular structure of **6.3** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C5-C6 1.358(7), Ge1-C5 1.973(5), C5-C_B 1.489(6), Ge2-C6 1.977(4), C6-C8 1.498(6); C6-C5-Ge1 128.1(4), C6-C5-C_B 120.0(4), C_B-C5-Ge1 111.9(3), C5-C6-Ge2 129.6(3), C5-C6-C8 119.2(4), C8-C6-Ge2 111.2(3).

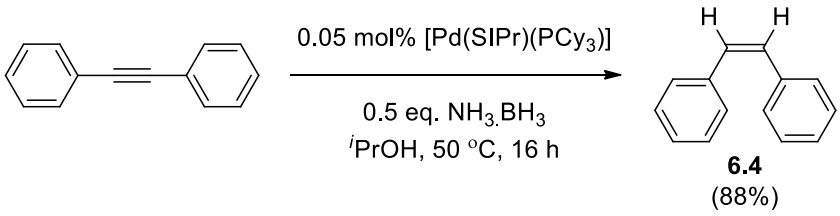
Further examination is necessary in order to assess the scope and limitations of this catalytic protocol.

6.3 Semi-Hydrogenation of Diphenylacetylene

Semi-hydrogenation of alkynes to *Z*-alkenes is traditionally mediated by the improved Lindlar's catalyst (Pd black on $BaCO_3$ that is poisoned with PbOAc and quinoline).[11,12] However, this procedure is often limited by the necessity for elaborate equipment set up, partial *Z* to *E* alkene isomerization, double-bond shifts and the requirement of pressurized molecular hydrogen. Transition metal catalysed transfer hydrogenation provides a promising alternative.[13] During these reactions, a molecule of hydrogen is effectively

moved from one compound (a hydrogen source) to another. This circumvents the use of hydrogen gas, providing a more practical and safer protocol. Sources of stored hydrogen include formic acid and ammonia-borane.[14,15] Although other transition metal mediators are known,[16–18] the semi-hydrogenation of alkynes to *Z*-alkenes *via* transfer hydrogenation frequently employs palladium catalysts,[13] sometimes with N-heterocyclic carbenes as a ligand set.[19–22]

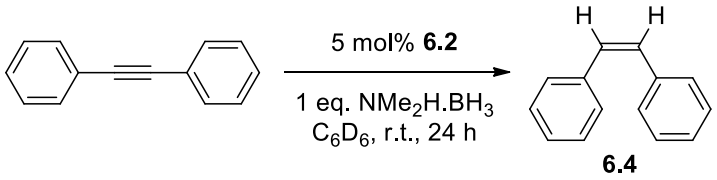
A recent report from Cazin and co-workers detailed the semi-hydrogenation of diphenylacetylene to form **6.4** with a high *Z*-stereoselectivity using ammonia-borane and a mixed N-heterocyclic carbene-phosphine Pd(0) catalyst, [Pd(SIPr)(PCy_3)] (SIPr = 1,3-bis(2,6-diisopropylphenyl)imidazolidine; Cy = cylcohexyl). The reaction was carried out with catalyst loadings of 0.05 mol% at 50 °C over 16 h (Scheme 6.4).



Scheme 6.4 Cazin's N-heterocyclic carbene or NHC-Pd(0) catalysed semi-hydrogenation of diphenylacetylene using ammonia borane as the hydrogen source

Cazin observed that bis(NHC)Pd(0) complexes, *e.g.* [Pd($IPr)_2$] (IPr = 1,3-bis-(2,6-diisopropylphenyl)imidazole-2-ylidene), were ineffective under these standard conditions and resulted in low yields of the semi-hydrogenation products. Despite this, the unprecedented catalytic conditions accessible in element-element additions to alkynes utilizing **6.2**,[1–3] prompted a preliminary investigation into its ability to mediate transfer hydrogenation of alkynes using the amine-borane, $Me_2NH{\cdot}BH_3$.

Diphenylacetylene was reacted with $Me_2NH{\cdot}BH_3$ in the presence of 5 mol% of **6.2** at room temperature under an N_2 atmosphere. The reaction reached completion after 24 h and crude ^1H NMR analysis suggested the formation of primarily **6.4** (Scheme 6.5).



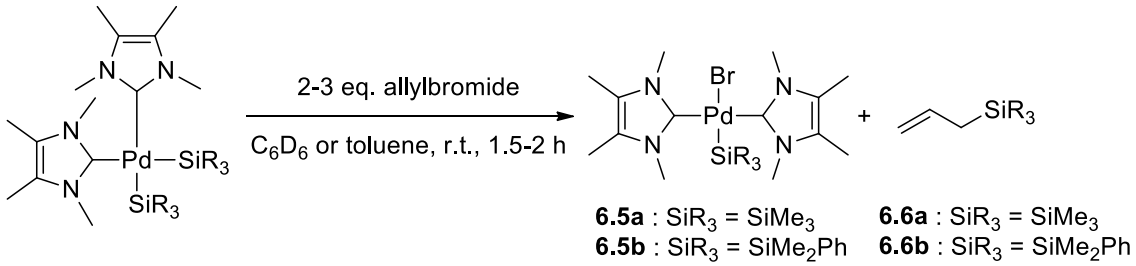
Scheme 6.5 Semi-hydrogenation of diphenylacetylene using $Me_2NH{\cdot}BH_3$ and catalytic quantities of **6.2**

Although a thorough optimization of this protocol and work-up procedure were not established, this early result suggests that **6.2** could very well be an efficient semi-hydrogenation catalyst. However, catalyst loading must be significantly reduced.

6.4 Synthesis of Mono(silyl)palladium(II) Bromide Complexes

Mono(silyl)palladium(II) halide species are proposed as key intermediates in the synthesis of allylsilanes.[23,24] Although abundant in palladium pincer chemistry,[25–29] examples of their isolation in this catalytic cycle are rare. Ozawa and co-workers detailed the reaction between *trans*-$[Pd(L)_2(SiF_2Ph)]$ (L = PMe_3, PMe_2Ph and $PMePh_2$) and allyl bromide to afford *trans*-$[Pd(L)_2(SiF_2Ph)(Br)]$ and the corresponding allylsilane.[23] Later, Watson and co-workers synthesized $[(^tBuPAr_2)Pd(SiMe_3)(I)]$ (Ar = 3,5-Me_2-4-OMe-C_6H_2) from stoichiometric quantities of $[(cod)Pd(CH_2SiMe_3)_2]$ (cod = 1,5-cyclooctadiene), $^tBuPAr_2$ and Me_3SiI.[24]

Preliminary studies revealed the first synthesis of non-pincer mono(silyl)palladium bromide complexes bearing a NHC ligand set. The bis(silyl)palladium complexes, *cis*-[Pd(ITMe)$_2$(SiR$_3$)$_2$] (SiR$_3$ = SiMe$_3$ and SiMe$_2$Ph), synthesized in Chapter 2,[1,2] were reacted with excess allylbromide at room temperature under an N_2 atmosphere to yield *trans*-[Pd(ITMe)$_2$(SiMe$_3$)(Br)] (**6.5a**) and *trans*-[Pd(ITMe)$_2$(SiMe$_2$Ph)Br] (**6.5b**) in a 92% and 93% yield respectively (Scheme 6.6).



Scheme 6.6 Stoichiometric synthesis of mono(silyl)palladium bromide complexes

In following the reaction progress by ^{1}H NMR spectroscopy, characteristic resonances of the corresponding allylsilanes (**6.6a**, allyltrimethylsilane and **6.6b**, allyldimethylphenylsilane) were also observed. However, these compounds were not isolated.

Single crystals of **6.5a**, suitable for X-ray analysis, were grown by slow evaporation of a saturated deuterated benzene solution at room temperature. However, it was not possible to refine the data for lengthy discussions on bond lengths and angles (R_1 = 9.7% and wR_2 = 34.2%). The unit cell consisted of three molecules of **6.5a** and two molecules of benzene, each exhibiting varying degrees of structural disorder. Figure 6.3 depicts the molecular structure of a single molecule of **6.5a**, proving its *trans*-configuration.

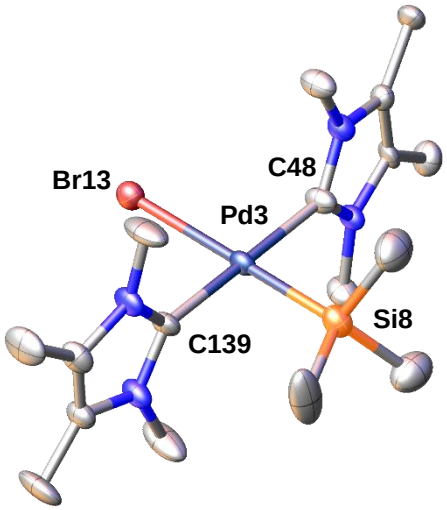


Figure 6.3 Molecular structure of **6.5a** with thermal ellipsoids at the 50% probability level. Structural data suitable for connectivity analysis only.

Single crystals of **6.5b** were isolated by slow evaporation of a saturated deuterated benzene solution at room temperature. X-ray analysis revealed that **6.5b** displays a marginally distorted square-planar geometry with the two NHCs in a *trans*-configuration and orthogonal to the Br-Pd-Si plane (Figure 6.4).

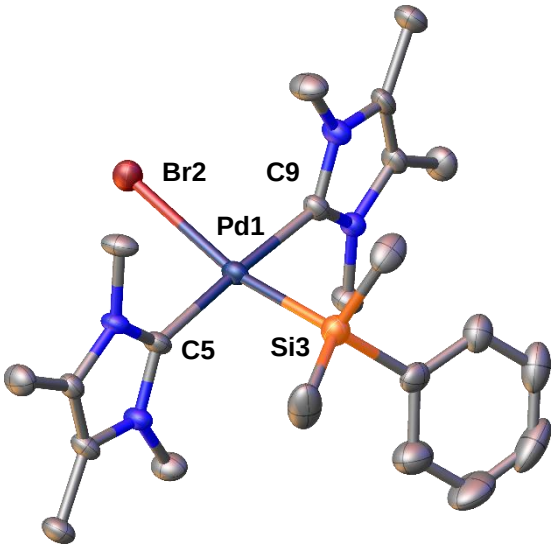
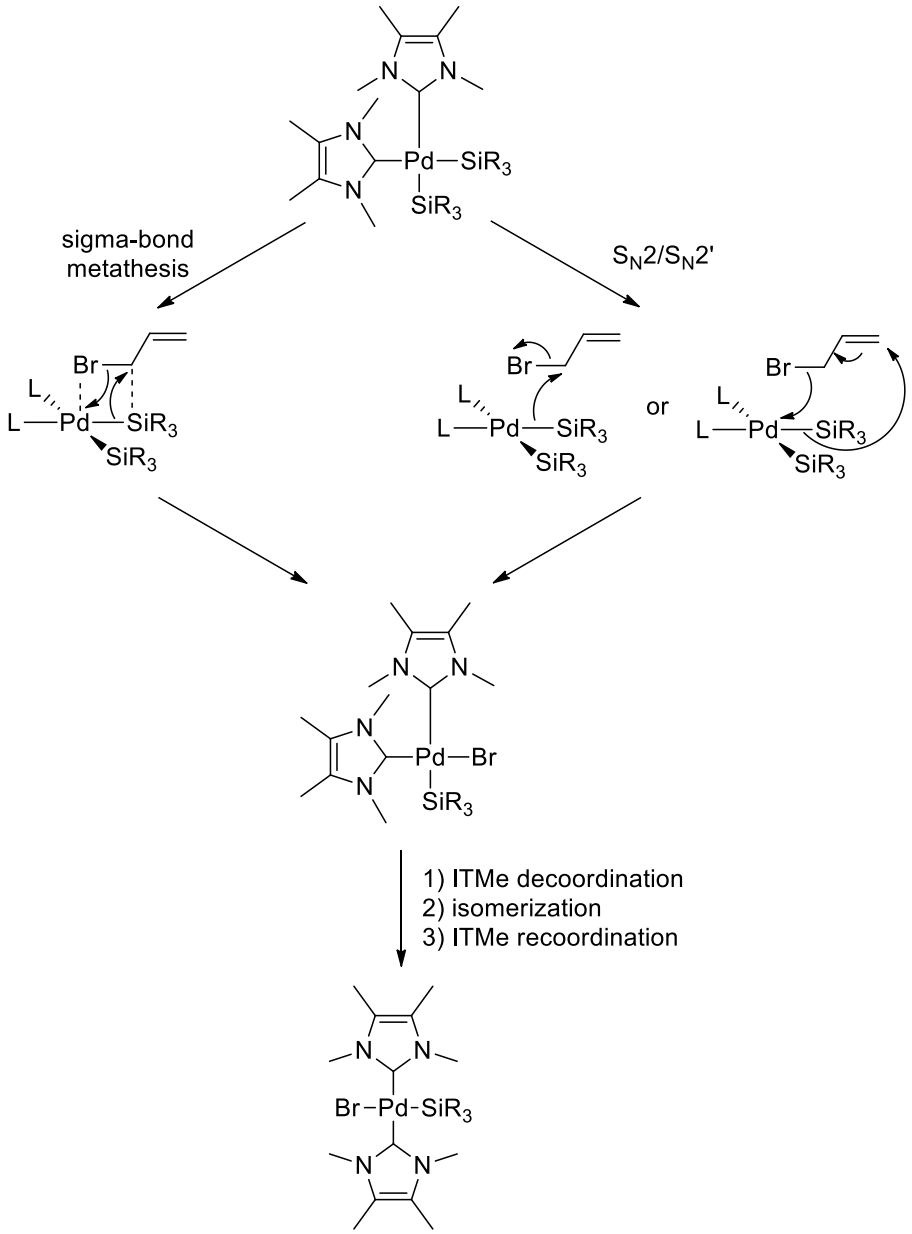


Figure 6.4 Molecular structure of **6.5b** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]:

Pd1-Br2 2.6334(7), Pd-Si3 2.2945(17), Pd1-C5 2.027(4), Pd1-C9 2.025(5); C5-Pd1-Br2 94.96(15), C5-Pd1-Si3 89.16(16), C9-Pd1-Br2 87.63(16), C9-Pd1-Si3 88.60(17).

The carbenic carbon-Pd bond lengths in **6.5b** [2.027(4) and 2.025(5) Å] are significantly shorter than in *cis*-[Pd(ITMe)$_2$(SiMe$_2$Ph)$_2$] [2.105(3) and 2.123(3) Å] suggesting SiMe$_2$Ph exhibits a stronger *trans*-influence than ITMe.[30] The decreased length of the Pd-Si bond in **6.5b** [2.2945(17) Å] versus *cis*-[Pd(ITMe)$_2$(SiMe$_2$Ph)$_2$] [2.3445(8) and 2.3346(8) Å] infers a stronger Pd-Si bond in **6.5b** and demonstrates the weak *trans*-influence of Br. Based on these data, the intensity of the *trans*-influence in these two structures follows the sequence: Br < ITMe < SiMe$_2$Ph. The *trans*-configuration observed in **6.5b** is thought to be favoured, thermodynamically and kinetically, as a result of the high *trans*-influence of SiMe$_2$Ph and relatively large steric size of Br.

A possible mechanism for the formation of **6.5** includes either a σ-bond metathesis between a Pd-Si, in *cis*-[Pd(ITMe)$_2$(SiR$_3$)$_2$], and Br-C bond, in allylbromide, or an S_N2/S_N2' by the nucleophilic Pd-Si bond at the electrophilic sites in the allylhalide. An NHC would then dissociate from the palladium centre, a *cis* to *trans* isomerization of the Br and Si moieties would follow and finally the dissociated NHC would re-coordinate (Scheme 6.7).[31,32]



Scheme 6.7 Possible mechanistic routes for **6.5**

Although not evaluated, it is predicted that the facile formation and apparent stability of **6.5** would prohibit catalytic silylation of allylhalides. This is attributed to a *cis*-configuration being a requirement for reductive elimination, the re-formation of the active catalyst and therefore completion of the catalytic cycle.

6.5 Conclusions

This chapter demonstrates preliminary studies that further explore the reactivity scope of (ITMe)-Pd based complexes. [Pd(ITMe)$_2$] and [Pd(ITMe)$_2$(PhC≡CPh)] oxidatively cleaved the Ge-Ge bond in hexamethyldigermane to afford *cis*-[Pd(ITMe)$_2$(GeMe$_3$)$_2$]. This represents the first bis(trimethylgermanium)Pd complex bearing NHC ligands. Furthermore, [Pd(ITMe)$_2$(PhC≡CPh)] acts as a highly active pre-catalyst in the digermylation of diphenylacetylene to form the novel compound (*Z*)-1,2-diphenyl-1,2-bis(trimethylgermyl)ethene. As a future study, this catalytic protocol should be extended to a range of alkynes, with contrasting electronic and steric properties, in order to assess the scope and limitations.

[Pd(ITMe)$_2$(PhC≡CPh)] was also assessed as semi-hydrogenation catalyst. Although not fully optimized, an initial experiment showed that it was possible to catalyse the semi-hydrogenation of diphenylacetylene to (*Z*)-stilbene, utilizing an amine-borane as a transfer hydrogenation source. Future work should involve optimization of this procedure including an extensive study into the source of hydrogen and alkyne scope. Additionally, a computational study should also be undertaken for a greater understanding of this system.

Finally, the first non-pincer NHC mono(silyl)palladium halide complexes were synthesized, *trans*-[Pd(ITMe)$_2$(SiR$_3$)(Br)] (SiR$_3$ = SiMe$_2$Ph and SiMe$_3$), in the reaction of allylbromide with the corresponding *cis*-[Pd(ITMe)$_2$(SiR$_3$)$_2$] under mild conditions. A possible mechanistic route for the formation of *trans*-[Pd(ITMe)$_2$(SiR$_3$)(Br)] includes either a σ-bond metathesis or an S_N2/S_N2' reaction between allybromide and *cis*-[Pd(ITMe)$_2$(SiR$_3$)$_2$]. This is then followed by a *cis*-*trans* isomerization that involves an NHC dissociation. The reactivity of *trans*-[Pd(ITMe)$_2$(SiR$_3$)(Br)] is unexplored, however future work may include attempts at halide abstraction to form

[$Pd(ITMe)_2(SiR_3)$][Anion],[33–35] and utilization of these cationic palladium(II) complexes as catalysts in polymerization reactions.[36–38]

6.6 Experimental Details for Chapter 6

General experimental details are given in appendix A1.

6.6.1 Synthesis of *cis*-[$Pd(ITMe)_2(GeMe_3)_2$] (6.1) from [(ITMe)Pd(methallyl)Cl]

Isopropanol (10.0 µL, 0.14 mmol) was added to a suspension of [(ITMe)Pd(methallyl)Cl] (0.046 g, 0.14 mmol), ITMe (0.019 g, 0.16 mmol) and potassium *tert*-butoxide (0.017 g, 0.15 mmol) in toluene (10.0 mL). The resulting reaction mixture was stirred at room temperature under an N_2 atmosphere for 4.5 h. At this stage, $Me_3GeGeMe_3$ (58.0 µL, 0.29 mmol) was added and the reaction mixture was stirred for a further 19 h at room temperature. The solution was then filtered *via* cannula, the filtrate's volatiles were removed in vacuo and the resulting off-white solid was washed with hexane (3 x 5.0 mL). Yield: 0.050 g, 59%. ^{1}H NMR (399.5 MHz, C_6D_6): δ_H = 3.33 [s, 12H, N(1,3)-C**H**$_3$], 1.42 [s, 12H, C(4,5)-C**H**$_3$], 0.64 [s, 18H, Ge**Me**$_3$]. ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6): δ_C = 193.6 [N**C**N], 123.5 [**C**(4,5)-CH_3], 35.0 [N(1,3)-**C**H_3], 8.6 [C(4,5)-**C**H_3], 7.6 [Ge**Me**$_3$]. Elem. Anal. Calcd for $C_{20}H_{42}N_4Ge_2Pd$: C, 40.70%; H, 7.17%; N, 9.49%. Found: C, 41.13%; H, 7.44%; N, 9.46% (repeated analysis did not lead to improved results – decomposition may be a result of exposure to air or moisture during analysis).

6.6.2 Synthesis of 6.1 from 6.2

In a Young's tap NMR tube, **6.2** (0.004 g, 8.23 µmol) and $Me_3GeGeMe_3$ (0.005 g, 22.93 µmol) were dissolved in C_6D_6 (0.7 mL). The progress of the reaction was monitored by ^{1}H NMR spectroscopy showing full conversion to **6.1** and (*Z*)-1,2-diphenyl-1,2-bis(trimethylgermyl)ethene (**6.2**) after stirring at room temperature under an N_2

atmosphere for 3 days. See sections **6.5.1** and **6.5.3** for spectroscopic analysis of **6.1** and **6.2**, respectively.

6.6.3 Catalytic Formation of 6.3

Diphenylacetylene (0.025 g, 0.14 mmol), $Me_3GeGeMe_3$ (45.0 µL, 0.22 mmol) and **6.2** (0.75 mg, 1.41 µmol) were dissolved in C_6D_6 (0.7 mL). The resulting reaction mixture was heated under an N_2 atmosphere to 100 ^oC for 24 h. Upon cooling the volatiles were removed in vacuo, the crude material was re-dissolved in CH_2Cl_2 (10.0 mL) and subsequently filtered through flame dried Celite. The filtrate volatiles were removed in vacuo to reveal an off-white solid. Yield 0.057 g, 98%. ^1H NMR (399.5 MHz, $CDCl_3$): δ_H = 6.99 [m, 4H, Ph], 6.87 [m, 2H, *p*-Ph], 6.66 [m, 4H, Ph], 0.24 [s, 18H, $GeMe_3$]. $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$): δ_C = 157.2 [**C**=C], 146.1 [*i*-Ph], 127.7 [Ph], 127.3 [Ph], 124.4 [*p*-Ph], 1.5 [Ge**Me**$_3$]. Elem. Anal. Calcd for $C_{20}H_{28}Ge_2$: C, 6.82%; H, 58.06%. Found: C, 6.89%; H, 58.07%.

Crystal data for **6.3**: $C_{20}H_{28}Ge_2$, M_r = 413.60 g mol^{-1}, triclinic, space group P-1, a = 11.5360(8) Å, b = 12.4807(7) Å, c = 15.1324(8) Å, α = 75.511(5)^o, β = 89.743(5)^o, γ = 73.967(5)^o, V = 2022.5(2) Å^3, Z = 4, T = 173 K, λCu(Kα) = 1.54184, R_1 [$I > 2\sigma(I)$] = 0.0610, wR_2 (all data) = 0.1841, *GooF* = 1.175.

6.6.4 Synthesis of (*Z*)-1,2-diphenylethene (6.4)

Diphenylacetylene (0.050 g, 0.28 mmol), $Me_2NH{\cdot}BH_3$ (0.017 g, 0.29 mmol) and **6.2** (0.008 g, 14.07 µmol) were dissolved in C_6D_6 (0.7 mL). The resulting reaction mixture was stirred at room temperature under an N_2 atmosphere for 24 h. At this stage, crude ^1H NMR analysis suggested 100% conversion of starting diphenylacetylene and formation of **6.4** as the major product.

6.4: ^{1}H NMR (399.5 MHz, C_6D_6): δ_H = 7.23 [m, 4H, Ph], 7.01 [m, 6H, Ph], 6.47 [s, 2H, C**H**=].

[Chemical shifts agree with those reported in the literatures].[39]

6.6.5 Synthesis of *trans*-[Pd(ITMe)$_2$(SiMe$_3$)(Br)] (6.5a) and allyltrimethylsilane (6.6a)

Allylbromide (0.032 g, 0.26 mmol) was added to a solution of *cis*-[Pd(ITMe)$_2$(SiMe$_3$)$_2$] (0.043 g, 0.09 mmol) in C_6D_6 or toluene (3.0 mL) and the resulting reaction mixture was stirred at room temperature for 1.5 h. At this stage, the volatiles were removed in vacuo and the off-white powder was washed with hexane (3 x 4.0 mL).

6.5a, Yield: 0.040 g, 92%. ^{1}H NMR (399.5 MHz, C_6D_6): δ_H = 3.68 [s, 12H, N(1,3)-C**H$_3$**], 1.42 [s, 12H, C(4,5)-C**H$_3$**], 0.12 [s, 9H, SiMe$_3$]. ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6): δ_C = 184.9 [N**C**N], 124.0 [**C**(4,5)-CH$_3$], 35.1 [N(1,3)-**C**H$_3$], 8.5 [C(4,5)-**C**H$_3$], 6.9 [Si**Me$_3$**]. ^{29}Si{^{1}H} NMR (79.4 MHz, C_6D_6): δ_{Si} = 7.68. Elem. Anal. Calcd. for $C_{17}H_{33}N_4SiBrPd$: C, 40.20%; H, 6.55%; N, 11.03%. Found: C, 40.15%; H, 6.54%; N, 10.95%.

6.6a (from crude reaction solution), ^{1}H NMR (399.5 MHz, C_6D_6): δ_H = 5.77 [m, 1H, C**H**=], 4.92 [m, 1H, C**H**=], 4.89 [m, 1H, C**H**=], 1.44 [m, 2H, C**H$_2$**], –0.03 [s, 9H, Si**Me$_3$**]. [Agrees with an independently taken NMR sample of allyltrimethylsilane].

6.6.6 Synthesis of *trans*-[Pd(ITMe)$_2$(SiMe$_2$Ph)(Br)] (6.5b)

Allybromide (6.0 µL, 0.07 mmol) and *cis*-[Pd(ITMe)$_2$(SiMe$_2$Ph)] (0.021 g, 0.03 mmol) were dissolved in C_6D_6 or toluene (1.0 mL). The resulting reaction mixture was stirred at room temperature for 2 h under an N_2 atmosphere. At this stage, all volatiles were removed in vacuo and the resulting white solid was washed with hexane (3 x 2.0 mL). Yield: 0.018 g, 93%. ^{1}H NMR (399.5 MHz, C_6D_6): δ_H = 7.20 [m, 2H, SiMe$_2$**Ph**], 7.07 [m,

3H, SiMe$_2$**Ph**], 3.51 [s, 12H, N(1,3)-C**H$_3$**], 1.42 [s, 12H, C(4,5)-C**H$_3$**], 0.31 [s, 6H, Si**Me$_2$**Ph]. ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6): δ_C = 183.4 [N**C**N], 149.6 [SiMe$_2$***i*-Ph**], 133.1 [SiMe$_2$**Ph**], 127.0 [SiMe$_2$**Ph**], 126.5 [SiMe$_2$***p*-Ph**], 124.2 [**C**(4,5)-CH_3], 34.9 [N(1,3)-**C**H$_3$], 8.5 [C(4,5)-**C**H$_3$], 4.2 [Si**Me$_2$**Ph]. ^{29}Si{^{1}H} NMR (79.4 MHz, C_6D_6): δ_{Si} = 2.44. (It was not possible to obtain elemental analysis for **6.5b** – every attempt resulted in numbers that were inconsistent with calculated values. A possible reason for this is decomposition of **6.5b** by exposure to air or moisture on transit to data collection).

Crystal data for **6.5b**: $C_{22}H_{35}N_4SiBrPd$, M_r = 569.94 g mol^{-1}, orthorhombic, space group P2=2$_1$2$_1$, a = 10.5467(4) Å, b = 14.3455(3) Å, c = 16.7301(4) Å, α = 90°, β = 90°, γ = 90°, V = 2531.23(13) Å^3, Z = 4, T = 173 K, λMo(Kα) = 0.71073, R_1 [$I > 2\sigma(I)$] = 0.0345, wR_2 (all data) = 0.0677, *GooF* = 1.011.

[Crude ^{1}H NMR data is consistent with the formation of allyldimethylphenylsilane (**6.6b**) as a product of this reaction. However, this was not isolated in this instance].[40]

6.7 References

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Chapter 7

Thesis Summary

7.1 Summary

7.1.1 Chapter 1

This chapter introduced the transition metal (TM) mediated element-element' (E-E') additions to alkynes and provided a thorough literature review on this topic. The chapter began by providing an initial background of alkenes and outlined their properties, geometry, importance in industrially relevant compounds, and methods of stereoselective synthesis. TM mediated E-E' additions to alkynes was described as the most atom economical route to *Z* or *syn*-alkenes. The subsequent section illustrated the general mechanism of this process (platinum group mediated) and provided a comprehensive literature review covering a range of E-E' bonds including Si-Si, B-B, Si-B, Sn-Sn, Sn-Si, Sn-B, S-S, Se-Se, S-Si, S-B, Ge-Ge, Ge-Sn and Ge-B. This review presents the scope and limitations in this area of chemistry.

The final segment of this introductory chapter detailed the background, properties, binding modes to TMs and benefits in palladium catalysis of N-heterocyclic carbenes (NHCs). A concluding paragraph sets the scene for the subsequent chapters and defines the chemical target, $[Pd(ITMe)_2]$ (**7.1**, ITMe = 1,3,4,5-tetramethylimidazol-2-ylidene).

7.1.2 Chapter 2

Arguably, chapter 2 is the seminal chapter to this thesis and describes the first solution-based synthetic route to **7.1**. Initially an improved synthesis of ITMe was detailed. ITMe was then reacted with $[Pd(methallyl)Cl]_2$ to afford the novel complex [(ITMe)Pd(methallyl)Cl]. An experimental investigation, based on a fundamental

understanding of the possible mechanism, resulted in the formation of **7.1** by exposure of [(ITMe)Pd(methallyl)Cl] to stoichiometric quantities of ITMe, ^{t}BuOK and isopropanol. However, the isolation of **7.1** proved troublesome; this was attributed to its limited solubility in most organic solvents and its reactivity with others (*e.g.* chlorinated and protic solvents). Instead, **7.1** was reacted *in situ* with hexamethyldisilane ($Me_3SiSiMe_3$) resulting in the isolation of *cis*-[$Pd(ITMe)_2(SiMe_3)_2$] (**7.2**) under mild conditions. This represented the first isolated example of a bis(trimethylsilyl)palladium complex obtained from the oxidative addition of $Me_3SiSiMe_3$ at a Pd(0) centre. This oxidative addition procedure in the synthesis of *cis*-bis(silyl)palladium complexes was deemed general and extended to other non-activated disilanes (1,2-diphenyl-1,1,2,2-tetramethyldisilane and 1,2-bis(2-methoxyphenyl)-1,1,2,2-tetramethyldisilane). Attempts at oxidatively cleaving the Si-Si bond in $Me_3SiSiMe_3$ employing other low valent NHC-Pd(0) complexes including [$(ITMe)_2Pd^0$(ma)] and [$(Pd^0\{IPr\}\{nq\})_2$] (ma = maleic anhydride, nq = 1,4-naphthoquinone) were unsuccessful.

Stoichiometric reactivity studies showed that **7.2** can undergo, in solution, a temperature dependent reversible reductive elimination. Furthermore, **7.2** mediated the stoichiometric bis(silyl)ation of diphenylacetylene at room temperature to afford (*Z*)-1,2-diphenyl-1,2-bis(trimethylsilyl)ethene (**7.3**) and [$Pd(ITMe)_2$(PhC≡CPh)] (**7.4**), the first bis(NHC)Pd(0)-alkyne complex reported in the literature. **7.4** was shown to stoichiometrically react with $Me_3SiSiMe_3$ to reform **7.2** and afforded another equivalent of **7.3**. This effectively completed a cycle with promise for catalytic applicability.

7.2 was subsequently utilized as a pre-catalyst in the bis(silyl)ation of electronically and sterically demanding internal and terminal alkynes to yield the corresponding 1,2-disilylalkenes with a 100% *Z*-stereoselectivity. The reaction proceeded employing 1 mol% of **7.2** at 100 ^{o}C in 24 h. This catalytic protocol demonstrated the first bis(silyl)ation

of internal alkynes using $Me_3SiSiMe_3$. A proposed catalytic cycle suggested **7.4** to be a resting state of **7.1**, the active catalytic species. **7.1** oxidatively cleaved $Me_3SiSiMe_3$ to yield **7.2**. An alkyne then binds in the *z*-plane of the Pd metal, followed by its migratory insertion into a Pd-Si bond and the formation of the corresponding silyl-palladium-vinylsilyl intermediate. A subsequent stereoselective reductive elimination generated the active catalyst, **7.1** and a *Z*-1,2-disilylalkene. The enhanced reactivity observed with **7.2** was suggested to be a result of the NHCs remaining coordinated throughout the cycle.

7.1.3 Chapter 3

In chapter 3, the investigations into E-E' additions to alkynes were extended to Si-B bonds. This chapter started with an improved synthesis for **7.4** from the reaction between *in situ* formed **7.1** and diphenylacetylene. Other bis(NHC)Pd(0)-alkyne complexes were also accessible utilizing this protocol including [Pd(ITMe)$_2$(PhC≡CNA)] (NA = naphthyl) and [Pd(ITMe)$_2$({4-Et}PhC≡CPh{4-OMe})]. The silaboration of alkynes was initially pursued using the model substrates diphenylacetylene and (dimethylphenylsilyl)boronic acid pinacol ester ($PhMe_2SiBpin$) with catalytic quantities of **7.4**. After optimization of the reaction parameters, (*E*)-(1,2-diphenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxanborolan-2-yl)vinyl)dimethyl(phenyl)silane was formed in the presence of 0.5 mol% **7.4** at room temperature in 0.5 h. This procedure was then extended to a range of electronically and sterically challenging terminal alkynes to synthesize the corresponding 1-silyl-2-boryl alkenes with a 100% regio- and *Z*-stereoselectivity. These reaction conditions were unprecedented in terms of catalyst loadings, reaction temperatures and times. Despite requiring temperatures of 50-100 ^oC, symmetrical and unsymmetrical internal alkynes were also accessible under these conditions.

Investigation into the catalytic cycle resulted in the isolation of *cis*-[Pd(ITMe)$_2$(SiMe$_2$Ph)(Bpin)] (**7.5**) from the reaction of **7.4** and PhMe$_2$SiBpin at room temperature. **7.5** represented a very rare example of an isolated (silyl)(boryl)palladium complex. Mechanistically, a similar pathway to that in Chapter 2 was proposed for the silaboration of alkynes. Again, the reluctance of NHCs to decoordinate being the suggested reasoning behind the enhanced activity of **7.4** in this reaction.

7.1.4 Chapter 4

The dearth of reported palladium catalysed diborations of alkynes in the literature is attributed to the energetics of the B-B oxidative addition. The process is endothermic with a very low reverse activation barrier and therefore kinetically and thermodynamically unfavourable. Despite this, chapter 4 describes the use of **7.4** as a highly active pre-catalyst in such a reaction.

Initial catalysis was carried out using the model substrates diphenylacetylene and bis(pinacolato)diboron (B$_2$pin$_2$). A thorough optimization of this protocol, employing 0.5 mol% of **7.4** at room temperature, resulted in the formation of (*Z*)-1,2-diphenyl-1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethane in near quantitative yields. A range of alkyl and aryl terminal alkynes bearing a variety of functionalities were accessible under these conditions. The diboration of internal alkynes was also possible, but required elevated temperatures of 50-100 ^{o}C. In all cases, 100% *Z*-stereoselectivity was observed.

Our collaborators carried out a density functional theory (DFT) study to highlight the reasoning as to why **7.4** mediated diboration of alkynes. Calculations showed that the reaction followed a similar mechanistic pathway to that of analogous phosphine platinum catalysts *e.g.* (i) oxidative addition of B$_2$pin$_2$ by **7.1** resulted in the formation of *cis*-

[Pd(ITMe)$_2$(Bpin)$_2$], (ii) an NHC would then dissociate followed by coordination of an alkyne in its place, (iii) the alkyne would then undergo a migratory insertion into a Pd-B bond to form a boryl-palladium-vinylboryl intermediate, (iv) a *cis*-*trans* isomerization of the boryl and vinylboryl moieties would follow, (v) the NHC would recoordinate inducing a stereoselective reductive elimination and the formation of the corresponding *Z*-1,2-diborylalkene. It was suggested that successful oxidative addition and thus diboration was due to the destabilization of the (diboron)Pd(0)L$_2$ adduct by the NHCs. This mechanism differs from the proposed mechanisms for the bis(silyl)tion and silaboration of alkynes reported in Chapter 2 and 3. In these chapters, it was suggested that the NHCs remain coordinated throughout (due to their strong σ-donor character) and the alkyne would coordinate above the plane of the palladium to form an 18-electron, penta-coordinate nearly square based pyramidal complex. However, calculations for the diboron system suggest this intermediate is highly unstable with a large free energy of 41.7 kcal mol^{-1} (*vs. cis*-[(NHC)$_2$Pd(B)$_2$]). On the other hand, the decoordination of an NHC from *cis*-[(NHC)$_2$Pd(B)$_2$], followed by the coordination of an alkyne requires an input energy of 10.1 kcal mol^{-1}. This is an energetically more favoured route and it is therefore envisaged that the calculated mechanism reported in Chapter 4 is pertinent to the bis(silyl)ation and silaboration systems.

7.1.5 Chapter 5

Chapter 5 describes the B-B and Si-B additions to the N=N bond in azobenzenes. Literature precedence for such reactivity was scarce with only B-B examples reported. Even then, the diborons employed exhibited highly strained or reactive B-B bonds. **7.4** was observed to catalyse the diboration and silaboration of azobenzenes using commercially available diboron and silaborane reagents under mild conditions.

The catalytic optimization for the diboration of azobenzenes concentrated on azobenzene and B_2pin_2 as the model substrates. The novel compound, 1,2-diphenyl-1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (**7.6**) was isolated using 0.5 mol% of **7.4** at room temperature. This protocol was extended to a range of azobenzenes, bearing alkyl, alkoxy and amido functionalities, and to alternative diboron reagents *e.g.* bis(catecholato)diboron and bis(neopentyl glycolato)diboron. The resulting novel 1,2-diborylated hydrazines were noted to be extremely sensitive to air and moisture. A controlled reaction of **7.6** with degassed deionized H_2O resulted in the formation of diphenylhydrazine (**7.7**) at room temperature.

The silaboration of azobenzenes was also achieved under these optimized conditions using the silaborane, $PhMe_2SiBpin$. The resulting novel 1-silyl-2-borylhydrazines formed contained alkyl or fluoro moieties in *ortho*, *meta* and *para* positions on the aryl rings. In contrast to the 1,2-diborylhydrazines, 1-silyl-2-borylhydrazines were stable to air and moisture. However, it was possible to remove the Si and B groups to form **7.7** from [dimethyl(phenyl)silyl]-1,2-diphenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine under base driven alcoholysis conditions.

In an unsuccessful attempt to extend these additions to disilanes, the formation of $[Pd(ITMe)_2(PhN{=}NPh)]$ (**7.8**) was observed. **7.8** was independently synthesized from the reaction of **7.1** or **7.4** with azobenzene, and represents the first NHC-Pd azobenzene complex.

The diboration and silaboration of azobenzenes using **7.4** as a catalyst was proposed to proceed either through a similar mechanism to that of alkyne diboration reported in chapter 4 or through a concerted mechanism involving **7.8**.

7.1.6 Chapter 6

Chapter 6 details preliminary further reactivity investigations of the ITMe-Pd complexes reported in the preceding chapters, and serves as a basis for future work in this area of chemistry. The E-E' additions to alkynes was extended to Ge-Ge bonds. Initial stoichiometric reactivity between **7.1** or **7.4** and hexamethyldigermane ($Me_3GeGeMe_3$) resulted in the isolation of *cis*-[$Pd(ITMe)_2(GeMe_3)_2$] (**7.9**). **7.9** represents the first bis(trimethylgermyl)palladium complex reported. In the case of the reaction involving **7.4**, the novel compound (*Z*)-1,2-diphenyl-1,2-bis(trimethylgermyl)ethene (**7.10**) was also obtained. Furthermore, **7.10** was catalytically formed in the digermylation of diphenylacetylene with $Me_3GeGeMe_3$ using 1 mol% of **7.4** at 100 ^oC in 24 h.

Additionally, **7.4** acted as a pre-catalyst in the semi-hydrogenation of diphenylacetylene to *Z*-stilbene employing dimethylamine-borane as a transfer hydrogenation source. Although the catalytic procedure was not optimized this provided substantial evidence that an alkyne semi-hydrogenation study was worthwhile.

In previous chapters the reactions of complexes of the type *cis*-[$Pd(ITMe)_2(SiR_3)_2$] (SiR_3 = $SiMe_3$ {**7.2**} or $SiMe_2Ph$) were limited to alkynes. Mono(silyl) palladium halides are reported in the literature as important intermediates in the formation of allylsilanes, however isolation of these complexes in the catalytic cycle were limited. It was observed that *trans*-[$Pd(ITMe)_2(SiR_3)Br$] (**7.11**) and the corresponding allylsilane formed on reacting *cis*-[$Pd(ITMe)_2(SiR_3)_2$] with allyl halide. A possible mechanism for the formation of **7.11** was proposed: *cis*-[$Pd(ITMe)_2(SiR_3)_2$] either undergoes a σ-bond metathesis or an S_N2/S_N2' reaction with allyl bromide to form *cis*-[$Pd(ITMe)_2(SiR_3)Br$]. One NHC would decoordinate, an isomerization would occur and recoordination of the NHC to form **7.11** would follow. Initial reactivity studies of **7.11** were not established, but it is anticipated that these complexes would undergo a halide abstraction to form the

cationic palladium complexes, [Pd(ITMe)$_2$(SiR$_3$)][anion] (**7.12**). **7.12** could then serve as polymerization catalysts.

7.2 Thesis Outputs

7.2.1 Published Work

- M. B. Ansell, D. E. Roberts, F. G. N. Cloke, O. Navarro, J. Spencer, *Angew. Chem. Int. Ed.* **2015**, *54*, 5578-5582. Highlighted in EPSRC UK National Mass Spectrometry Facility Annual Report 2015/2016, p27.
- M. B. Ansell, J. Spencer, O. Navarro, *ACS Catal*, **2016**, *6*, 2192-2196.
- M. B. Ansell, V. H. Menezes de Silva, G. Heerdt, A. A. C. Braga, J. Spencer, O. Navarro, *Catal. Sci. Technol.* **2016**, *6*, 7461-7467.
- M. B. Ansell, G. E. Kostakis, H. Braunschweig, O. Navarro, J. Spencer, *Adv. Synth. Catal.* **2016**, *358*, 3765-3769.
- M. B. Ansell, O. Navarro, J. Spencer, *Coord. Chem. Rev.* **2017**, *36*, 54-77.

7.2.2 Honours and Awards

- Royal Society of Chemistry Research Mobility Grant (2016 – to visit the Braunschweig Lab).
- Royal Society of Chemistry Dalton Division Travel Grant (2015 – attendance at the 250th American Chemical Society Meeting, Boston MA, USA).
- University of Sussex Doctoral Overseas Conference Grant (2015 – attendance at the 250th American Chemical Society Meeting, Boston MA, USA).
- University of Sussex Alumni Study Award (2013, 2014, 2015).

7.2.3 Presentations

- *'Synthesis of a (N-Heterocyclic Carbene)$_2$Pd(0) Complex: Catalytic Element-Element 1,2-Additions to Alkyne and Azo Moieties'* CheM62 Meeting, AstraZeneca, Macclesfield, UK, November 2016. *Poster*.
- *'The Synthesis of a (N-Heterocyclic Carbene)$_2$Pd(0) Complex: Catalytic Element-Element 1,2-Additions to Alkyne and Azo Moieties with Mechanistic Insights'* 2nd Southern Dalton Meeting, University of Reading, UK, September 2016. *Talk*.
- *'Synthesis of an (NHC)$_2$Pd(SiMe$_3$)$_2$ Complex. Catalytic, cis-Bis-Silylations of Internal Alkynes with Unactivated Disilanes'* 1st Dalton Young Members Event, University of Leeds, UK, September 2015. *Talk*.
- *Synthesis of an [(NHC)$_2$Pd(SiMe$_3$)$_2$] Complex and Catalytic cis-Bis(silyl)ations of Alkynes with Unactivated Disilanes'* 250th American Chemical Society Meeting, Boston MA, USA, August 2015. *Poster*.
- *'Synthesis of an (NHC)$_2$Pd(SiMe$_3$)$_2$ Complex. Catalytic, cis-Bis-Silylations of Internal Alkynes with Unactivated Disilanes'* 26th SCI Postgraduate Symposium on Novel Organic Chemistry, University of Southampton, UK, May 2015. *Talk*.
- *'Synthesis of an[(NHC)$_2$Pd(SiMe$_3$)$_2$] Complex and Catalytic cis-Bis(silyl)ations of Alkynes with Unactivated Disilanes'* Southern Dalton Meeting, University of Sussex, UK, April 2015. *Poster*.

Appendix 1: Experimental Details

A1.1 General Procedures

The manipulation of air sensitive compounds and their spectroscopic measurements were undertaken using standard Schlenk line techniques under pre-dried Ar (using a BASF R3-11(G) catalyst and 4 Å molecular sieves), or in a MBraun glovebox under N_2 (O_2 < 10.0 ppm). All glassware was dried in a 160 ^oC oven prior to use. Celite was pre-dried in a 200 ^oC oven and then dried with a heat gun under a dynamic vacuum prior to use. Filter cannulae equipped with microfibre filters were dried in an oven at 160 ^oC prior to use.

A1.2 Purification of Solvents

All solvents used for air sensitive compounds were dried by vacuum distillation followed by distillation of potassium (*e.g.* hexane and toluene) or stored over activated 4 Å molecular sieves under an Ar atmosphere (*e.g.* 2-methyl tetrahydrofuran). Dried solvents were degassed and stored over Ar in ampoules containing activated molecular sieves. For reactions carried out under ambient conditions solvents were used as purchased.

Deuterated benzene, C_6D_6, was degassed and dried by refluxing over potassium for 3 days, vacuum transferred into ampoules and stored under N_2. Deuterated chloroform, $CDCl_3$, was used as purchased.

A1.3 Instrumentation

A1.3.1 NMR Spectroscopy

NMR spectra were recorded on a Varian VNMRS 400 (^1H 399.5 MHz; $^{13}C\{^1H\}$ 100.5 MHz; $^{11}B\{^1H\}$ 128.2 MHz; ^{19}F 375.9 MHz; $^{29}Si\{^1H\}$ 79.4 MHz) or 500 (^1H 499.9 MHz; $^{13}C\{^1H\}$ 125.7 MHz). Chemical shifts are reported in ppm. The spectra were referenced to the corresponding protic solvent (^1H) or signals of the solvent (^{13}C). $^{11}B\{^1H\}$, ^{19}F and

$^{29}Si\{^{1}H\}$ NMR spectra were referenced externally relative to $BF_3.OEt_2$, $CFCl_3$ (10%) and $SiMe_4$ respectively.

A1.3.2 Mass Spectrometry

High resolution mass spectrometry was carried out by Dr A. Abdul-Sada at the University of Sussex or by the EPSRC UK Nation Mass Spectrometry Facility, University of Swansea.

A1.3.3 Elemental Analysis

Elemental analyses were carried out by Stephen Boyer at the Elemental, Analysis Service, London Metropolitan University.

A1.3.4 X-Ray Crystallography

Single crystal X-ray diffraction data for **2.4**, **2.7**, **2.8**, **2.12**, **2.13**, **2.18**, **3.2**, **3.14**, **5.4**, **5.10**, **5.12**, **5.14**, **6.1**, **6.3**, **6.5a** and **6.5b** were collected at the University of Sussex on an Agilent Technologies Xcalibur Gemini Ultra diffractometer (λCu(Kα) = 1.54184 or λMo(Kα) = 0.71073) equipped with a Eos CCD area detector. The data were collected at 173 K using an Oxford Cryosystems Cobra low temperature device. Data were processed using CrysAlisPro, and the unit cell parameters were refined against all data. Semi empirical absorption corrections were carried out using the MULTI-SCAN program.[1] The structures were solved by using an intrinsic phasing method (SHELXT),[2] and refined F0 by full matrix least squares refinement using SHELXL-2013,[3] within OLEX2.[4] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were added at calculated positions and refined using riding models with isotropic displacement parameters based on the equivalent isotropic displacement parameter (Ueq)

of the parent atoms. The crystal data of **5.2** was collected on a BRUKER X8-APEC II diffractometer with a CCD area detector and multi-layer mirror monochromated Mo(Kα) radiation. The structure was solved using intrinsic phasing method (SHELXT),[2] refined with the SHELXL program,[5] and expanded using Fourier techniques. All non-hydrogen atoms were refined anistropically. Hydrogen atoms were included in structure factor calculations. All hydrogen atoms were assigned to idealised geometric positions.

Structures **2.4**, **2.7**, **2.8**, **2.12**, **2.13**, **2.18**, **3.2**, **3.14**, **5.2**, **5.4**, **5.10**, **5.12**, **5.14**, **6.1**, **6.3**, **6.5a** and **6.5b** were solved by M. B. Ansell, with special thanks to Dr George E. Kostakis for patience, advice and support with crystallography.

Structures **2.4**, **2.7**, **2.8**, **2.12**, **2.13**, **2.18**, **3.2**, **3.14**, **5.2**, **5.4**, **5.10** and **5.12** were submitted to the Cambridge Crystallographic Data Centre (CCDC) and assigned the numbers 1029150, 1045559, 1029151, 1053253, 1053277, 1434732, 1442149, 1432628, 1501645, 1501646 and 1501647 respectively.

A1.4 References

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