Transition metal catalyzed element–element additions to alkynes

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The efficient and stereoselective synthesis of, or precursors to, multi-substituted alkenes has attracted substantial interest due to their existence in various industrially and biologically important compounds. One of the most atom economical routes to such alkenes is the transition metal catalyzed hetero element–element insertion into alkynes. This article provides a thorough up-to-date review on this area of chemistry, including discussions on the mechanism, range of E–E bonds accessible and the stoichiometric/catalytic transition metal mediators employed.

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1. Introduction

Alkenes are defined as either branched or unbranched hydrocarbons that possess at least one carbon–carbon double bond (C=C) and have a general formula of C\textsubscript{n}H\textsubscript{2n+2} [1]. Each carbon atom in a C=C bond is sp\textsuperscript{2}-hybridized, forming \(\sigma\)-bonds to three other atoms (Scheme 1) [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 \(\text{trans}\) or \(\text{cis}\), respectively originating from the German words ‘entgegen’ meaning opposite and ‘zusammen’ meaning together) (Fig. 1).

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 (Fig. 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. A range of stereoselective syntheses are reported in the literature, methods 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 (Fig. 2) [19,20].

Arguably, one of the most atom economical routes (maximum number of atoms of the reactants appearing in the product(s)) [21] in the synthesis of multi-substituted alkenes is alkyn e reduction by its \(\pi\)-insertion into hetero element–element\(^*\) (E–E, where E and E\(^*\) \(\neq\) H) bonds (albeit the newly formed C–C and E–E bonds are then further functionalized) [22]. These \(\pi\)-insertions result in the regio- and stereoselective formation of cis-1-element-2-element\(^*\)-alkenes in a single step (Scheme 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.

Despite the chemical importance of this reaction and the industrial relevance of the 1-element-2-element\(^*\)-alkenes as precursors to highly functionalized multi-substituted alkenes, the last thorough review on this topic was reported by Moberg and Beletskaya in 1999 (with a revised edition in 2006) [22,23]. A substantial volume of papers has since been published, and we believe there is a strong argument for an updated review that includes these more recent developments.

2. Transition metal mediated \(\text{EE}^*\) additions to alkenes

2.1. Mechanism

The main mediators in the E–E\(^*\) additions to alkenes 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 [24,25]. The first step in this catalytic cycle is the oxidative cleavage of a E–E\(^*\) bond by a M(\text{II})\textsubscript{2} (M = platinum...
group metal, \( L = \text{phosphine/isocyanide} \) species to form cis-(E)(E')M \((\text{II})_2 \) (\( \text{MI1} \)). \( \text{MI1} \) is often kinetically stable and is isolated experimentally for many of the E\( A \)E\( 0 \) bonds discussed above (the relevant oxidative additions will be discussed in the appropriate chapters) [26–30]. A ligand exchange then occurs with decoordination of a single \( L \) ligand and coordination of the alkyne in its place to yield \( \text{MI2} \). This is swiftly followed by an insertion of the alkyne into a \( M - E \) or \( M - E' \) bond (\( \text{MI3} \)). The regioselectivity of the E\( A \)E\( 0 \) 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 [33,34]. Experimental studies suggest that the insertion is often the rate-limiting step in these reaction pathways [31]. An isomerization and re-coordination of the \( L \) ligand results in the \( E \) and (E\( 0 \)) 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 2).

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

### 2.2. Silicon–Silicon (\( \text{Si–Si} \))

#### 2.2.1. Palladium

The \( \pi \)-insertion of unsaturated moieties into \( \text{Si–Si} \) bonds is often called bis(silylation). Palladium mediated bis(silylation) of alkenes is one of the most investigated reactions within this area of chemistry [35]. 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 $X_3 \text{Me}_{3-m} \text{Si-SiMe}_3 X_n$ ($X = \text{H, F, Cl or OMe}; m = 1-2, n = 1-2$), added to various alkynes when catalytic quantities of $[\text{Cl}_2\text{Pd(PR}_3)_2]$ or $[\text{Pd(PR}_3)_4]$ ($R = \text{Et or Ph and } R' = \text{Ph}$) were employed (Scheme 3) [36,37]. The extension of this protocol to non-activated disilanes, such as hexamethyldisilane ($\text{Me}_3\text{Si-SiMe}_3$), was unsuccessful. Elsewhere, Sakurai showed that the extent of alkyne bis(silylation) using the strained cyclic disilane, 1,1,2,2-tetramethyl-1,2-disilacyclopentane, was dependent upon the choice of alkyne [38]. Dimethyl acetylenedicarboxylate, phenylacetylene and ethylene all underwent bis(silylation) (Scheme 3). However, no reaction was observed with the internal alkynes diphenylacetylene and bis(trimethylsilyl)acetylene.

Watanabe performed the bis(silylation) of acetylene using chlorinated disilanes, $\text{Me}_n\text{Si}_2\text{Cl}_{6-n}$ ($n = 2-5$) [39]. The formation of the Z-1,2-disilylated alkenes was favored, 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, $\text{(MeO)}_m\text{Me}_{3-m}\text{Si-SiMe}_3 \text{(OMe)}_n$, as well as the acetylenes, 1-hexyne and trimethylsilylacetylene [40]. Bis(silylation) with $\text{Me}_3\text{Si-SiMe}_3$ was extremely sluggish even at temperatures of 140°C [40].

Hiyama and co-workers utilized these chlorinated disilanes in the palladium catalyzed bis(silylation) of bis(trimethylsilyl)butadiyne [41]. Subsequent treatment of the reaction mixture with $\text{MeMgBr}$ resulted in the formation of 1,1,4,4-tetrakis(trimethylsilyl)-1-buten-3-yne (4) (Scheme 4).

**Scheme 3.** Kumada’s activated and Sakurai’s strained disilane bis(silylations) [36–38].

**Scheme 4.** Bis(silylation) of diynes using chlorinated disilanes [41].

**Scheme 5.** Bis(silylation) of 1,4-diethynylbenzene towards crack free sol-gels [43].

**Scheme 6.** Palladium catalyzed ferrocenyldisilane insertion into alkynes [45].

Fig. 3. Ko’s o-carborane disilane 7 and Braunschweig’s [2]silachromoarenophanes 8 [47,48] and Sakurai utilizing activated and strained disilanes, respectively. Kumada and co-workers demonstrated that activated disilanes, of the form $X_3 \text{Me}_{3-m} \text{Si-SiMe}_3 X_n$ ($X = \text{H, F, Cl or OMe}; m = 1-2, n = 1-2$), added to various alkynes when catalytic quantities of $[\text{Cl}_2\text{Pd(PR}_3)_2]$ or $[\text{Pd(PR}_3)_4]$ ($R = \text{Et or Ph and } R' = \text{Ph}$) were employed (Scheme 3) [36,37]. The extension of this protocol to non-activated disilanes, such as hexamethyldisilane ($\text{Me}_3\text{Si-SiMe}_3$), was unsuccessful. Elsewhere, Sakurai showed that the extent of alkyne bis(silylation) using the strained cyclic disilane, 1,1,2,2-tetramethyl-1,2-disilacyclopentane, was dependent upon the choice of alkyne [38]. Dimethyl acetylenedicarboxylate, phenylacetylene and ethylene all underwent bis(silylation) (Scheme 3). However, no reaction was observed with the internal alkynes diphenylacetylene and bis(trimethylsilyl)acetylene.

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Seyferth and co-workers demonstrated that the very reactive and strained Si–Si σ bond in octamethyl-1,2-disilacyclobutane was capable of bis(silylating) a number of alkynes including acetylene, phenylacetylene and dimethyl acetylenedicarboxylate when using catalytic quantities of [Cl₂Pd(PPh₃)₂]. However, extension of this protocol to other internal alkynes was unsuccessful, even at temperatures of 140 °C [44].

Manners showed that the ferrocenyldisilane, [Fe(η⁵-C₅H₄)₂]-(SiMe₃)₂] inserted into acetylene or phenylacetylene to form the organometallic rings 6a and 6b, respectively (Scheme 6) [45]. 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 [46]. Other palladium mediated bis(silylations) of alkynes using strained disilanes have appeared in the literature: Ko’s ‘super-aromatic’ o-carborane disilane 7 [47], and Braunschweig’s [2]silachromoarenophane 8 [48], bis(silylated) terminal and internal alkynes, respectively (Fig. 3). The cyclic nature of these disilanes pre-conditioned the formation of the Z-configured 1,2-disilylated alkene products.

In 1991, a communication from Ito and co-workers revolutionised the field of alkyne bis(silylation) by the introduction of the pre-catalytic combination of [Pd(OAc)₂] and isocyanide ligands [49]. As a result, the bis(silylation) 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(silylation) of terminal alkynes such as 1-phenylpropyne, 1-phenylhexyne, 1-nonyne and phenylacetylene using the non-activated disilane, Me₃SiSiMe₃. Reactions proceeded at 110 °C and resulted in unprecedented high stereoselectivities. Ito and co-workers extended this protocol to a range of bis(silylations) including the intramolecular bis(silylation) of alkynes in the stereoselective synthesis of 1,2,4-triols [50], cyclic tetrakis(organosilyl) ethenes as organic chromophores [51], chiral allenylsilanes [52], and enantioenriched propargyl silanes [53].

Many authors since have utilized the [Pd(OAc)₂]/isocyanide combination within their own work. For example, Strohmahn

The bis(silylation) of a number of internal and terminal alkynes using the activated disilane Me₃SiSiMe₃-Ph was achieved by Ozawa [42]. The catalyst was generated in situ from the mixture of 1 mol% [Pd(η³-allyl)Cl] and 2 mol% PMe₂Ph. 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 Me₃SiSiMe₃ or Ph₂SiSiMe₃-Ph.

Loy and co-workers employed the activated disilane, 1,2-dime thoxy-1,1,2,2-tetramethyldisilane in the bis(silylation) of 1,4-diethynylbenzene to form 5 (Scheme 5). Then ring closed at each alkenyl unit to form the corresponding disilaoxacyclopentenes. 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 [43].
and co-workers used the pre-catalytic combination above in a number of alkyne bis(silylations) using 1,1,2,2-tetramethyl-1,2-bis(phenylthiomethyl)disilane as the disilane source [54]. In particular, the bis(silylation) of ethynyl[2.2]paracyclophanes resulted in the formation of 9 (Scheme 7), which have potential applications in chiral catalysis and optoelectronic materials [55]. The addition of Me₃SiSiMe₃ to internal alkynes is considered one of the most challenging reactions in alkyne bis(silylation) chemistry. Even Ito's [Pd(OAc)₂]/isocyanide combination was catalytically inactive [49]. Navarro, Spencer and co-workers reported the synthesis of the novel compound cis-[Pd(ITMe)₂(SiMe₃)₂] (10, ITMe = 1,3,4,5-tetramethylimidazol-2-ylidene), via the oxidative addition of Me₃SiSiMe₃ to [Pd(0)(ITMe)₂] under mild conditions. 10 was subsequently employed as a pre-catalyst in the bis(silylation) of a range of 1,2-diarylalkynes using Me₃SiSiMe₃ (Scheme 8) [57]. The resulting stilbenes 11 were synthesized with 100% Z-stereoselectivity and were either novel or previously only synthesized in a stoichiometric manner. This unprecedented protocol was also extended to the bis(silylations) of two alkynes separated by a phenyl linker, to 1-silyl-2-aryl alkynes and to terminal alkynes.

2.2.2. Platinum

In contrast, the platinum catalyzed bis(silylation) of alkynes has been investigated to a lesser extent. The most common
bis(silylation) mediator is [(η2-ethylene)Pt(PPh3)2]. Ishikawa detailed the bis(silylation) of a number of alkynes using 3,4-benz o-1,1,2,2-tetra(isopropyl)-1,2-disilacyclobut-3-ene [58]. The reac tivity 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 12 and 13. The bulky mono-substituted alkynes mesitylacetylene and (phe nyldimethylsilyl)acetylene formed 13 as the sole product, whereas diphenylacetylene resulted in only the 1,2-disilylated alkene 14 (Scheme 9).

Investigations into the reactivity of 1,2-bis(dimethylsilyl)carb opane by Ko and co-workers were extended to the platinum cata lyzed bis(silylation) of alkynes. Normal 1,2-bis(silylation) 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 (silylation) and the formation of a five-membered disilyl ring [59]. A later report by Ishikawa described the bis(silylation) of range of terminal and internal alkynes using cis- and trans-1,2-di methyl-1,2-diphenyl-disilacycloptane. The reactions proceeded with high stereospecificity and translation of the cis or trans nature of disilane in all cases [60].

2.2.3. 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 [61–63]. Despite this effort, gold catalysis is very much in its infancy with the only reports of alkyne bis(silylation) in the literature being mediated by gold nanoparticles supported on titanium oxide (Au/TiO2) [64]. Stratakis and co-workers showed that the bis(silylation) of a range of terminal alkynes using hexamethyldisilane and 1,2-diphe nyl-1,2,2-tetramethyldisilane was possible [65]. In all cases, the Z-alkenes were favored 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-tetramethyldisilane (HMe2SiSiMe2H). However, two isomers (15, major, and 16, minor) were isolated (Scheme 10). Mechanistically, this observation was explained by an initial bis(silylation) followed by a dehydrogenative addition to a second alkyne [66].

2.2.4. Iron

Sunada and co-workers reacted 1,2-bis(dimethylsilyl)benzene with [Fe(mesityl)_2] (mesityl = 2,4,6-Me_C6H3) in aromatic solvents under a nitrogen (N2) atmosphere to form 17 (Scheme 11). Subsequent addition of 2-butyne or phenylacetylene resulted in the quantitative formation of the disilacarbocycles 18a and 18b, respectively (Scheme 11) [67]. This process was made catalytic upon addition of 1,2-bis(dimethylsilyl)benzene to phenylacetylene and 20 mol% of Fe [68]. Although this is not a bis(silylation) 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(silylation) of alkynes.

2.2.5. Nickel

Kumada and co-workers accomplished the first examples of alkyne bis(silylation) using a nickel mediator. Bis(silyl)biptyridyl-nickel(II) complex 19 reacted with diphenylacetylene to form 20. Treatment of the latter with MeMgBr, followed by an acidic work up, resulted in the isolation of E,1,2-bis(trimethylsilyl)stilbene (21) (Scheme 12) [69]. Extension to other alkynes yielded mixtures of Z- and E-alkene products.

At the same time, Liu showed that a tetrafluorodisilacyclobutene underwent oxidative addition to [Ni(CO)4]. The corresponding bis[silyl]Ni(II) complex 22 was reacted with tert-butylacetylene to form the two new 1,4-disilacyclohexadienes 23 and 24, where the tBu groups are syn and anti, respectively (Scheme 13) [70].

The first catalytic bis(silylation) 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(PMe3)4] formed the Z-alkene 25 [71]. As well as bis(silylation), an alkyne insertion into one of the phenylene-Si bonds occurred, with 26 isolated as a minor product (Scheme 14). This type of insertion was consistently observed on applying the methodology to other alkynes [72].

2.2.6. Rhodium

Examples of rhodium mediated alkyne bis(silylations) are rare. Tilley and co-workers carried out the stoichiometric reaction of [(Me3P)3RhSi(Me2Si)2] (27) with 2-butyne, resulting in the

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Scheme 15. Stoichiometric bis(silylation) of 2-butyne mediated by Rh(I) species [73].
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Scheme 16. Rh(I)-catalyzed intramolecular trans-bis(silylation) of alkynes [74].
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Scheme 17. The first diboration of alkynes catalyzed by [Pt(PPh3)4] [80].
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The protocol was then extended to a variety of (2-alkynylphenyl)diloxanes affording the corresponding 3-silyl-1-benzosiloles (30) (Scheme 16).

2.3. Boron–Boron (B–B)

2.3.1. Platinum

Due to their low toxicity, high stability under atmospheric conditions, and versatility, the synthesis of organoboron reagents has attracted significant interest. In particular, there is substantial focus towards 1,2-diborylated alkenes as the products of alkyne diboration [75]. The resulting newly formed B–B bonds are able to participate in Suzuki-Miyaura cross-coupling reactions [76], 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 destabilizes the boron based p-orbital, this increases the Lewis acidity of the boron atoms and therefore their susceptibility towards nucleophilic attack) and often react with unsaturated organic substrates without the need for a transition metal mediator or catalyst [77]. However, the preparations of diboron tetrahalides are difficult, and this therefore limits their synthetic utility [78,79]. 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 alkenes. 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. Seminal results by Suzuki and Miyaura [80] indicated that 1-octyne inserted into the B–B bond of bis(pinacolato)diboron (B2pin2) using catalytic quantities of [Pt(PPh3)4] to form 31 (Scheme 17). 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 [81]. Other transition metal complexes proved ineffective within this study, e.g. [Pd(PPh3)4] and [Pd(OAc)2]/isocyanide (the best catalysts in the bis(silylation) of alkynes). Suzuki-Miyaura’s coupling protocols have
Smith and co-workers carried out a stoichiometric diboration by reacting commercially available bis(catecolato)diboron (B\(_2\)cat\(_2\)) with [(\(\eta^2\)-4-octyne)Pt(PPh\(_3\)\(_2\))]\(_2\). This resulted in the oxidative addition bis(boryl)Pt(II) complex 32, and the Z-1,2-diborylated alkene 33 (Scheme 18) [87].

Marder and Norman extended the synthesis of bis(boryl)platinum(II) complexes to the use of other diborons including B\(_2\)pin\(_2\) and B\(_2\)(4-Bucat)\(_2\) (4-Bucat = 1,2-O\(_2\)-BuCaH\(_3\)). [(\(\eta^2\)-ethylene)Pt(PPh\(_3\)\(_2\))]\(_2\) and 34 were then used as catalysts in the diboration of terminal and internal alkynes employing B\(_2\)pin\(_2\) and B\(_2\)cat\(_2\) as B-B bond sources (Scheme 19). These catalysts were more efficient in the stereoselective formation of Z-1,2-diborylated alkynes than [Pt(PPh\(_3\)\(_2\))]\(_2\), 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 alkene and the diboron reagent. The presence of \(\pi\)-donating moieties on the alkene resulted in faster reactions than \(\pi\)-withdrawing substituents and the fastest conversions proceeded in the order of B\(_2\)cat\(_2\) > B\(_2\)pin\(_2\) > B\(_2\)(4-Bucat)\(_2\) [88].

The platinum catalyzed diboration of internal and terminal alkynes using diboron 1,2-B\(_2\)Cl\(_2\)(NMe\(_2\))\(_2\), affords cyclic 1-azonia-2-borata-5-boroles (36) (Scheme 20). The key feature within these structures was that the boron and nitrogen atoms exhibited both a terminal and internal alkynes employing B\(_2\)pin\(_2\) and B\(_2\)cat\(_2\) as B-B bond sources (Scheme 19). These catalysts were more efficient in the stereoselective formation of Z-1,2-diborylated alkynes than [Pt(PPh\(_3\)\(_2\))]\(_2\), 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 alkene and the diboron reagent. The presence of \(\pi\)-donating moieties on the alkene resulted in faster reactions than \(\pi\)-withdrawing substituents and the fastest conversions proceeded in the order of B\(_2\)cat\(_2\) > B\(_2\)pin\(_2\) > B\(_2\)(4-Bucat)\(_2\) [88].

The platinum catalyzed diboration of 1-octyne and di-p-methylenepherylacetylene using B\(_2\)cat\(_2\) [90]. The reactions proceeded using 5 mol% of the commercially available [Cl\(_2\)Pt(cod)] (cod = 1,5-cyclooctadiene) at 55 °C. This protocol was highly dependent on the choice of diboron source, no catalytic activity was observed using B\(_2\)pin\(_2\), as well as the choice of halide and diene on the platinum metal. [Br\(_2\)Pt(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

\[
\begin{align*}
\text{Scheme 22. Stepwise diboration/fluorodeboronation of alkynes} & \text{ [93].} \\
\text{Scheme 23. Synthesis of NHC-platinum-based catalysts in diboration of alkynes} & \text{ [98].} \\
\text{Scheme 24. Stoichiometric and catalytic diboration of alkynes using \([2]\)boramet}-
\]
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 sp²-organobismetallic derivatives, Srebnik and co-workers demonstrated the platinum catalyzed diboration of 1-alkynylphosphonates and 1-alkynylboronates afforded the Z-1,2-diborylated vinylphosphonates and trisboration alkene products 37 and 38, respectively (Scheme 21) [91]. 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 catalyzed diboration of phenylethynyl MIDA (MIDA = N-methylimidic acid) boronate with B₂pin₂ to form 1,1,2-triboryl-2-phenylethene [92].

Fernandez and co-workers reported the preparation of α,α’-difluorinated carbonyl compounds. The reactions proceeded by an initial platinum(0) catalyzed 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 diterfluoroborate (or Selectfluor) resulted in formation of the 1-(chloromethyl)-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane ditefluorinated carbonyls. If trace amounts of water were found within the solvent or reaction mixture the difluoromethyl alcohols resulted in the formation of the α,α’-difluorinated carbonyls. If trace amounts of water were found within the solvent or reaction mixture the difluoromethyl alcohols resulted in the formation of the α,α’-difluorinated carbonyls. If trace amounts of water were found within the solvent or reaction mixture the difluoromethyl alcohols resulted in the formation of the α,α’-difluorinated carbonyls. If trace amounts of water were found within the solvent or reaction mixture the difluoromethyl alcohols resulted in the formation of the α,α’-difluorinated carbonyls. If trace amounts of water were found within the solvent or reaction mixture the difluoromethyl alcohols resulted in the formation of the α,α’-difluorinated carbonyls. If trace amounts of water were found within the solvent or reaction mixture the difluoromethyl alcohols resulted in the formation of the α,α’-difluorinated carbonyls. If trace amounts of water were found within the solvent or reaction mixture the difluoromethyl alcohols resulted in the formation of the α,α’-difluorinated carbonyls. If trace amounts of water were found within the solvent or reaction mixture the difluoromethyl alcohols resulted in the formation of the α,α’-difluorinated carbonyls. If trace amounts of water were found within the solvent or reaction mixture the difluoromethyl alcohols resulted in the formation of the α,α’-difluorinated carbonyls. If trace amounts of water were found within the solvent or reaction mixture the difluoromethyl alcohols resulted in the formation of the α,α’-difluorinated carbonyls. If trace amounts of water were found within the solvent or reaction mixture the difluoromethyl alcohols resulted in the formation of the α,α’-difluorinated carbonyls.
(pin = pinacolato; dan = naphthalene-1,8-diaminato) (Scheme 25) [101]. In the presence of phosphine-platinum catalysts, the diboration of terminal alkynes resulted in the regioselective formation of 43 with Bdan, a boryl protecting group, in the terminal position. The palladium-catalyzed Suzuki-Miyaura cross-coupling occurred chemoselectively on the more reactive internal Bpin. This was in sharp contrast to the B2pin2 based diborations, where the coupling selectively proceeds initially at the more reactive terminal Bpin group.

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/TiO2. A range of electron-donating and withdrawing aromatic or alkyl, branched and cycloalkyl substituents were accessible. Exclusively Z-1,2-diborylated alkene were observed in all cases [102]. In contrast, when the support was magnesia (MgO), higher loadings and the use of solvent and elevated temperatures of 130 °C were required [103].

2.3.2. Palladium

Palladium-catalyzed diborations of alkynes are rare. Examples employing [2]borametalloarenophanes were reported by Braunschweig and co-workers. Palladium on carbon was utilized as a heterogeneous catalytic source, however the diborations required higher temperatures and much longer conversion times than their platinum analogues [99,100]. The rarity of palladium mediated alkyne diborations can be attributed to the energetics of the B–B bond oxidative addition at the Pd(0) center. Theoretical calculations suggest that this is both a kinetically and thermodynamically unfavorable process [104]. Despite this, Spencer, Navarro and co-workers recently accomplished the facile diboration of terminal and internal alkynes using catalytic amounts of \( \text{[Pd(ITMe)2(PhC} \] \( \text{52a–} \) \( \text{52e} \) \( \text{52i} \)) (Scheme 25). These diborations proceeded in high yields and/or under milder reaction conditions than their platinum analogues.

A computational study to determine the mechanistic route suggested that Pd(0) catalyzed alkyne diborations using NHC ligands followed the same catalytic cycle as phosphines (as detailed in the introduction of Section 2) [105]. An integral process in this pathway was, as in the case of phosphines, the reversible dissociation of an NHC ligand. These NHC ligands were also key to a successful oxidative addition of the B–B bond at the Pd(0) center. They destabilize the (diboron)Pd(0)L2 (L = ITMe) adduct resulting in a sufficient lowering of the free energy for oxidative addition.

2.3.3. 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 \( \text{B2cat}_{2} \) (Scheme 27) using a \( \text{[Co(PMe}_{3} \text{)}]_{3} \) catalyst. Compound 46 was isolated as the major product of this reaction, with small quantities of the \( \text{E-isomer} \) detected [106].

2.3.4. Iron

The only example of iron catalyzed diboration of alkynes was detailed by Nakamura in 2015. Initial optimizations focused on the diboration of 4-octyne using \( \text{B2pin}_{2} \). Catalytic quantities of \( \text{FeBr}_{2} \) and \( \text{LiOMe} \) with 1.5 equivalents of MeOBpin were enough to afford 47 in high yields [107]. 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 48 was isolated as the major product (Scheme 28), suggesting that the incorporation of the second boryl unit was introduced by an electrophilic substitution reaction with MeOBnep or MeOBpin.

2.3.5. 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 49 as a catalyst. Degassing this reaction mixture followed by the introduction of a CO atmosphere generated the new catalyst 50, which mediated the dehydrogenative diboration of the newly formed alkynylboronate with HBpin to form 51 (Scheme 29) [108]. This reaction was extended to a range of alkyl and aryl terminal alkynes. The authors proposed the reaction to proceed via a hydroboration intermediate or via \( \text{B2pin}_{2} \).

2.3.6. Copper

Examples of group 11 transition metal catalyzed diboration of alkynes are very rare, with only one example of copper and one of gold described in the literature [109]. The first diboration of alkynes employing a copper catalyst was performed by Yoshida.
The diboration of alkyl and aryl internal alkynes using $\text{B}_2\text{pin}_2$ in the presence of $[\text{Cu(OAc)}_2]$ and PCY$_3$ resulted in high yields of the corresponding Z-1,2-diborylated alkenes [110]. The authors also extended this to the diboration of benzynes to form the resulting 1,2-diborylated benzenes (Scheme 30). Changing the phosphine to P(tBu)$_3$, P(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 53 was exclusively isolated (Scheme 30).

2.3.7. Gold

Nanoporous gold (AuNPore), prepared by dealloying the monolithic Au$_{30}$Ag$_{70}$ alloy in a 70% nitric acid electrolyte, is a highly active catalyst in the diboration of alkynes. Jin and co-workers optimized a system with phenylacetylene and B$_2$pin$_2$ utilizing 2 mol% of AuNPore at 100°C [111]. 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$_2$pin$_2$ onto the AuNPore surface. The B-A-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.

2.4. Silicon–Boron (Si–B)

2.4.1. Palladium

Silylboranes 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 [112], is such that 1-boryl-2-silyl alkenes are synthesized with chemo-, regio- and stereoselective control in a single transformation [113,114]. 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 [115,116]. The most widely used catalysts for the silaboration of...
alkynes are group 10 transition metal complexes, specifically palladium-containing complexes.

Ito’s palladium/tert-alkyl isocyanide catalyst combination, previously detailed in alkyne bis(silylations), was effective in the silaboration of both terminal and internal alkynes to form syn-1-boryl-2-silyl alkenes (54) with high regio- and stereoselectivities (Scheme 31) [117]. The silylborane of choice was (dimethylphenylsilyl)boronic acid pinacol ester (PhMe₂SiBpin);

\[
\begin{align*}
R & \equiv H \\
\text{excess alkyne} & \equiv >99 : <1 \\
\text{excess silylborane} & \equiv 8-11 : 89-92
\end{align*}
\]

Scheme 34. Reagent dependent stereoselective silaboration of terminal alkynes [124].

\[
\begin{align*}
\text{R} & \equiv \text{H} \\
\text{Si B} & \equiv \text{Cl} \\
\text{O} & \equiv \text{O}
\end{align*}
\]

\[
1) \text{1 mol\% } [\eta^3\text{-C}_3\text{H}_5\text{PdCl}L] \\
\text{toluene, r.t., 2 h}
\]

\[
2) \text{PrOH, pyridine, r.t., 1 h}
\]

\[
\begin{align*}
\text{R} & \equiv \text{Bu} \\
\text{Si} & \equiv \text{OCH(Me)}
\end{align*}
\]

Scheme 35. Ligand controlled, stereoselective ‘abnormal’ regioselective silaboration [125].

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. Attempts at silaboration employing other metal complexes resulted in either lower yields and mixtures of regioisomers (e.g. [Pt(PPh₃)₄]) or no activity (e.g. [RhCl(PPh₃)₃]).

The authors later extended this protocol to other silylboranes (i.e. PhMe₂SiB(NEt₂)₂ and PhMe₂SiBcat) and to a larger array of
terminal and internal alkynes, including 1,7-octadiyne to afford the double silaboration product 55 (Scheme 31). The reactivity of the \textit{syn}-1-boryl-2-silyl alkenes was also assessed. Suzuki-Miyaura cross-coupling and conjugate additions to methyl vinyl ketones at the alkenyl boryl group were possible, leading to cross-coupling and conjugate additions to methyl vinyl ketones \textit{syn} the double silaboration product \textit{syn} including in the synthesis of \textit{syn}-alkylboryl carbocyclization of hepta-1,6-diyne to form 59 (Scheme 33) [122].

Pilet and co-workers synthesized stable organosilylboranes possessing mesityl groups on the boryl atom, (diphenylmethylsilyl)dimeitylsilylborane (PhMe2SiBMe2) and (diphenyl-tetra-butylsilyl)dimesitylborane (Ph3BuSiBMe2). These silylboranes 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 alkenes such as phenylacetylene, using the [Pd\textsubscript{2}(dba)\textsubscript{3}] / epto catalytic combination. Steric clashing between the substituents of the alkene and the boryl moiety precluded the silaboration of internal alkynes [123].

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\textsubscript{2}SiBpin) with 1-octyne in the presence of 1 mol\% \{[\eta\textsuperscript{3}-C\textsubscript{3}H\textsubscript{3}]Pd(PPh\textsubscript{3})Cl\}, followed by subsequent addition of isopropyl alcohol (IPA) and pyridine. When excess 1-octyne was used the \textit{Z}-isomer 60 was isolated as the sole product. However, excess ClMe\textsubscript{2}SiBpin results in the formation of the \textit{E}-isomer 61 as the major product (Scheme 34). This observation was applicable to a range of terminal alkynes, although sterically hindered substituents on the alkene restricted \textit{E}-silaboration [124].

It was also possible to tune the regioselectivity in the silaboration of terminal alkynes. The silaboration proceeds with ‘normal’ regioselectivity in the presence of catalytic quantities of \{[\eta\textsuperscript{3}-C\textsubscript{3}H\textsubscript{3}]Pd(PPh\textsubscript{3})Cl\}. However, using the more sterically hindered phosphine P(Bu\textsubscript{3})\textit{b} (biphenyl-2-\textit{y}) an inverse or ‘abnormal’ regioselectivity was observed, with \textit{Z}-2-boryl-1-silyl-1-alkenes 62 isolated as the major product (Scheme 35) [125].

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 63 via intramolecular attack of the resulting silanol oxygen with the tricoordinated boron atom. The potassium borates 63\textsubscript{a} and 63\textsubscript{h}}
were then subjected to external-base free Suzuki-Miyaura cross-coupling with 4-iodoanisole to form 64 and 65, respectively (Scheme 36) [126].

The authors achieved a different mode of reactivity by substituting one of the substituents of the silicon atom of a silylborane for an amino group. The reaction of (Et₂N)Me₂SiBpin with aliphatic or aryl terminal alkynes resulted in the formation of 2,4- and 3,4-disubstituted siloles, 66 and 67 respectively (Scheme 37). Isomer 66 was favored in most cases and this was attributed to steric clashes with 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(Bu)₂(2-biphenyl), resulted in a higher ratio of 66 vs. 67. The synthesis of siloles was also accompanied by the formation of the corresponding aminopinacolborane, and was extended to other silylboranes including (Me₂N)Me₂SiBpin and (pyrrolidino)Me₂SiBpin [127].

Moberg and co-workers subjected a number of 1,3-enynes to palladium catalyzed silaborations using PhMe₂SiBpin. The reactions required relatively high loadings of palladium and phosphine ligand, as well as catalytic quantities of disobutylaluminum hydride (DIBALH). 1,2-Silaboration led to dienes 68 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 69 (Scheme 38) [128]. Later, Moberg altered the silylborane to CiMe₂SiBpin and, in the presence of isopropanol and pyridine, this resulted in formation of the corresponding highly substituted 1,3-dienyl-2-silanols. Subsequent Suzuki-Miyaura and Hiyama-Denmark cross-coupling reactions yielded tri- and tetra-substituted 1,3- or 1,2-dienes in a chemo-, regio- and diastereoselective manner [129].

Most of the reports to date utilize either phosphine or iso-cyanide ligand sets. In their investigations into NHC-palladium catalysis, Spencer, Navarro and co-worker observed that [Pd{(ITMe)₂(PPh₃)₄}]+ ([44]) catalyzed the silaborations of terminal and internal alkynes with PhMe₂SiBpin to afford a number of known and novel 1-silyl-2-boryl alkenes 54 and 70 (Scheme 39) [130]. This protocol represented the first example of alkynyl silaborations employing NHC ligands. All reactions proceeded with 100% syn-stereoselectivity and in the case of terminal alkynes 100% ‘normal’ regioselectivity. High regioselectivities were also noted when using unsymmetrical internal alkynes, with the silyl moiety favoring a position that is geminal to the aryl ring. Unprecedented mild reaction temperatures for terminal alkynes, short reaction times, and low catalyst loadings were reported.

2.4.2. Nickel

Ito reported the double insertion of terminal alkynes into the Si–B bond of PhMe₂SiBpin to afford ZZ-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 reduncant DIBALH to afford a 3:1 mixture of 71 and 72 (Scheme 40). The major product 71 was a result of head-to-head dimerization of the alkyne, whereas head-to-tail dimerization gave 72. Dimerization yields were increased by using a large excess of alkyn 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 [131].

2.4.3. Gold

The only other metal-mediated alkyne silaboration in the literature utilized gold nanoparticles supported on titania (Au/TiO₂).

Stratakis and co-workers used 1 mol% Au/TiO₂ to catalyze the silaboration of terminal alkynes at room temperature to form syn-2-boryl-1-silyl-1-alkenes 73 (Scheme 41). 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-distannation of alkynes. Side products in this reaction were the ‘normal’ regioselective silylborated alkenes, the competing reaction in this silaboration protocol. Extension to internal alkynes resulted in mixtures of regioisomers or no yield at all [132].

2.5. Tin–Tin (Sn–Sn)

2.5.1. Palladium

Organostannanes are often utilized in the chemoselective formation of C–C bonds through Migita-Kosugi-Stille reactions [133]. The development of new methodologies in the construction of C–Sn bonds is therefore of high interest [134]. A particularly attractive example is the insertion of alkynes into Sn–Sn bonds, distannation. The resulting alkynes have two new C–C bonds through Migita-Kosugi-Stille reactions [135]. 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 sulfur oxides [141].

Recently, Foucher and co-workers depicted the insertion of acetylene and phenylacetylene into the backbone of poly[di(n-buty)|stannane. This resulted in the formation of new alken-tin polymers 78 and 79, respectively (Scheme 46) [142].

was also observed in the absence of catalyst under photolysing conditions [135].

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 presursor was also extended to other hexaalkyldistannanes (hexaethyl and hexabutyl ditin) [136], and to 1,2,4,5-tetrasstannacyclohexanes [137]. The latter were further employed in the distannation of trimethylstannylenethane to synthesize the first 1,1,2-tristannylalkene derivatives 75 (Scheme 43) [138].

Piers and co-workers reported the distannation of alkyl-2-alkynoatoles using Me3SnSnMe3 and a [Pd(PPh3)4] catalyst in THF at room temperature (or reflux) to form Z-2,3-bis(trimethylstannyl)-2-alkenoates 76 (Scheme 44). A vast array of functionality was tolerated including alkenyls, ethers, silyl ethers and primary halides [139]. Alkenoates with an α-halogeno-alkyl group were treated with MeLi which resulted in a transmetallation-cyclization reaction to afford 2-trimethylstannylcycloalk-1-enes 77 (Scheme 45) [140]. The distannation protocol was also extended to N,N-dimethyl-2-alkynlamides and the formation of Z,N,N-dime thyl-2,3-bis(trimethylstannyl)-2-alkenamide 76q. Compounds 76 were thermally labile and transferred upon heating or at room temperature to the thermodynamically stable E-isomers [139]. 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-tolysulphonylisocyanate (TSI), dichloromethylmethylether (DCME), trimethylsilyl chlorosulphonates and sulfur oxides [141].

Some of the first investigations into distannation of alkynes were carried out by Mitchell and co-workers. Hexamethyldistannane (Me6SnSnMe6) and terminal alkynes were mixed in the presence of catalytic quantities of [Pd(PPh3)4] to form Z-1,2-distannyl alkynes 74 (Scheme 42). 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
terminal alkenes to form the corresponding 1,4-distanna-[4]
ferrocenophanes 80 (Scheme 47) [143]. Both terminal and internal
alkynes were accessible. However, dimethyl acetylatedicarbox-
ylate gave the distannation product in a side reaction while favoring
cyclotrimerization to form hexamethylbenzene hexacarboxylate.
Extension to analogous palladium catalysts such as [Pd(PPh3)4]
and [Pd(dba)2] were unsuccessful [144].

2.5.3. Copper

In 2013, Yoshida carried out the first catalytic distannation of
alkynes using a copper catalyst, [Cu(OAc)2(PPh3)2] in the presence
of Cs2CO3 was used to optimize the reaction between Me3SnSnMe3,
and CuOR derived from a CuOR as the reaction proceeded through a Cu
resulted in sluggish reactions and low yields. It was proposed that
alkynes bearing isoamyl, isobutyl and cyclopentyl, as well as chloro,
amino and cyano functionalities. Alkynes that were sterically congested
formed alkenes with a new C
A
Sn bond, often in a
regio- and stereoselective manner. Palladium catalyzed silylstannation
was a useful tool for the construction of 1,2-distannylated alkene.

2.6. Tin–Silicon (Sn–Si)

2.6.1. Palladium

Sn–Si bond (silylstannation) addition to alkenes results in the
formation of alkenes with a new C–Sn and C–Si bond, often in a
regio- and stereoselective manner. Palladium catalyzed silylstannation
of alkenes are by far the most reported examples within
the literature and have found application in the synthesis of natu-
ral products [146,147], and pharmaceuticals [148]. The first palladi-
um catalyzed examples of alkylene silylstannations were shown by
Mitchell and co-workers. The authors reacted a range of terminal alkenes
with (trimethylsilyl)trimethylstannane (Me3SiSnMe3) in the presence of [Pd(PPh3)4] under solvent-free conditions to yield

Scheme 50. Palladium(0)-catalyzed silylstannation followed by regioselective
cyclization [150].

Scheme 51. Silylstannation of 1-alkoxyalkynes [151].

Scheme 52. Alkyne silylstannation using ionic liquid immobilised palladium(0)
[152].

Scheme 53. Silylstannation and bismetallative cyclization of 1,3-enynes [154].

2.5.2. Platinum

The only examples of distannation of alkenes employing a plat-
inum catalyst were carried out by Wrackmeyer and co-workers.
The distannane, 1,2-distanna-[2]ferrocenophane reacted sequentially
or in one pot with [Pt(PPh3)2(η2-C5H4)] and a range of

Scheme 54. Palladium catalyst-dependent regioselective silylstannation [155].

Scheme 55. Cu(I) catalyzed ‘abnormal’ silylstannation of terminal alkenes [156].
the corresponding Z-1-silyl-2-stannyl-1-alkenes \( \text{alkenes (82)} \) (Scheme 49). In all cases the silyl moiety added regioselectively at the terminal carbon [149].

Ito extended the use of \([\text{Pd(PPh}_3]_4\) as a catalyst in the reaction of the disilanylstannane 83 with alkynes affording the \((\beta\text{-disilylalkenyl})stannanes 84.\) The reaction proceeded with the \(Z\)-addition of the Si–Sn bond to the C–C triple bond. 84, in the presence of phenylacetylene and further quantities of \([\text{Pd(PPh}_3]_4\), then underwent regioselective cyclization to form the silastannacyclohexadiene 85 as a single isomer (Scheme 50) [150]. Ito later accomplished the silystannination of 1-alkoxyalkynes employing the pre-catalytic combination of \([\text{Pd(OAc)}_2]\)/tert-octylisocyanide. The reactions proceeded at room temperature and yielded the syn-addition products 86, with the silyl group regioselectively introduced at the carbon atom bearing the alkoxy moiety (Scheme 51).

\([\text{Pd(PPh}_3]_4\) was inactive in these transformations at both room and elevated temperatures [151]. The resulting alkyne 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 silystannination of terminal alkynes with \(\text{Bu}_3\text{SnSiMe}_2\text{Ph} \) using catalytic quantities of \([\text{Pd(PPh}_3]_4\) immobilised in the ionic liquid 1-\(\text{butyl}-3\)-methylimidazolium hexafluorophosphate ([bmim][PF\(_6\)]). High stereo- and regioselectivities were observed and simple ether extraction resulted in isolation of the Z-1-silyl-2-stannyl-1-alkenes 87 (Scheme 52) [152]. The palladium(0)-ionic liquid combination was recyclable with no loss of activity even after 10 cycles [153].

The bismetallative cyclization of 1,3-enzymes, using \(\text{Bu}_3\text{SnSiMe}_3\), is dependent on the choice of ligand and palladium source. The use of \([\text{Pd(PPh}_3]_4\) results in ‘normal’ silystannination of the alkyne affording 88. However, upon removing the phosphine and using \([\text{Pd}_2(\text{dba})_3\cdot\text{CHCl}_3\) or \([\text{Pd(OH)}_2\cdot\text{C}],\) cyclized compounds 89 can be isolated as the major products of the reaction (Scheme 53). The bistetallative cyclization can also be observed on employing nucleophilic \(\text{N-heterocyclic carbines with bulky alkyl N-substituents} [154].\)

It is possible to tune the regioselectivity of alkyne silystannination by changing the ligand of a palladium(II) catalyst. Treatment of fluorine containing internal alkynes with \(\text{Bu}_3\text{SnSiMe}_3\) in the presence of 2.5 mol% \([\text{Cl}_2\text{Pd(PPh}_3]_2\) yields the silylstannlated adducts 90. However, by switching the palladium catalyst to \([\text{Cl}_2\text{Pd}('\text{Bu}_3\text{NC})_2]\), the opposite regioselectivities 91 are observed (Scheme 54) [155].

2.6.2. Copper

The only example of a copper-catalyzed alkyne silylstannation was carried out by Yoshida and co-workers. The authors detailed a three-component coupling reaction employing terminal alkynes, a silylborane (\(\text{PhMe}_2\text{SiBpin}\)) and a tin alkoxide (\(\text{Bu}_3\text{SnO} + \text{Bu}_)\)) in the presence of a Cu(I) catalyst (\([\text{CuCl-P}^\text{Bu}_3\text{]}\)). The observed regioselectivities were inverse to those of conventional silylstannation under palladium catalyzed conditions, with the stannyl moiety predominantly adding to the terminal carbon as shown in 92. A range of alkyl branched and unbranched alkynes bearing cyano, bromo, hydroxyl or amino functionalities were accessible (Scheme 55). The authors proposed a similar mechanism to the distannation of alkynes mediated by a copper(I) catalyst. A silylcopper species, \(\text{CuSiMe}_2\text{Ph}\), is initially formed via a sigma-bond metathesis between a copper alkoxide and a silylborane. An alkyn could then insert into the Cu–Si bond to give a \(\beta\)-silylalkenylcopper intermediate, which is subsequently trapped by a tin alkoxide to furnish the silylstannation alkene adduct and regenerated the copper alkoxide [156].

2.7. Tin–Boron (Sn–B)

2.7.1. Palladium

The borylstannation of alkynes results in the formation of alkynes with a new C–Sn and C–B bond. The first palladium-catalyzed example was shown by Tanaka and co-workers in 1996. The borylstannane 1,3-dimethyl-2-(trimethylstannyl)-2-bora-1,3-diazacyclopentine \((\text{Me}_3\text{SnB[NMe(CH_2)_3NMMe]}\) was added to alkynes using catalytic quantities of \([\text{Pd(PPh}_3]_4\) (Scheme 56). The reagents were added together in benzene at 0°C and then warmed to room temperature. Terminal alkynes yielded \(\text{syn}-1\)-boryl-2-stannyl-1-alkenes 93 as the sole product. Internal alkynes were also accessible, although a higher temperature (80°C) was necessary [157]. Weber later extended this protocol to the more sterically hindered borylstannane, 1,3-di-tert-butyl-2,3-(trimethylstannyl)-2-bora-1,3-diazacyclopentine \((\text{Me}_3\text{SnB[NBu(CH_2)_3NKBu]}\) [158]. RajanBabu developed Tanaka’s methodology and extended it to the borylstannation of 1,3-enzymes. This protocol resulted in the isolation of the \(\text{syn}-1\)-boryl-2-stannyl-1-alkenes 94 in chemo-, regio- and stereoselective fashions with no complications arising due to the adjacent alkene. However, the boryl group in 94 was hydrolytically unstable. In situ treatment with pinacol and \(\text{p-toluenesulfonic acid (PTSA)}\) yielded the hydrolytically stable 95 (Scheme 57) [159].
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 [160]. 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 [156].

2.8. Sulfur–Sulfur and Selenium–Selenium (S–S and Se–Se)

2.8.1. Palladium

Organochalcogens are known to exhibit a range of pharmacological activity profiles including as potential anticancer [161], anti-inflammatory [162], and antibacterial agents [163]. The introduction of chalcogens into alkynes to form 1,2-bis(chalcogen) alkynes is challenging. The formation of 1,2-bis(chalcogen) alkynes often requires the use of heavy metals, high temperatures and results in a mixture of stereoisomers. Such methods include the reaction vinyl dichlorides with thiolate anions [164] and radical reactivity between chalcogen species and alkynes [165]. The transition-metal catalyzed addition of dichalcogens to alkynes is a possible alternative to synthesizing 1,2-bis(chalcogen)alkynes 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 (96), respectively (Scheme 58). 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 (97) (Scheme 58). A stepwise attempt at carbonylation of 96 with CO to yield 97 resulted in the isolation of only 96, suggesting that CO insertion was part of dichalcogen additions in the first instance [166].

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) alkene (98). Subsequent treatment with tetra-‘butylammonium fluoride (TBAF) in the presence of excess methyl iodide (MeI)
other electrophiles including halides, epoxides and acyl chlorides [167].

\[ \text{Scheme 63. Rhenium mediated stoichiometric dithiolation of internal alkynes} \]

Beletskaya and co-workers reported an alternative methodological addition of \( \text{S}_\text{Ph} \text{Ph} \text{S}_2 \) and diphenyl diselenide (PhSeSePh) were reacted with a variety of terminal alkynes in the presence of catalytic quantities of \( [\text{Cl}_2\text{Pd}(\text{PPh}_3)_2] \), PhEH (E = S or Se) and triethylamine \( \text{NEt}_3 \) to yield the bidentate phosphine \( \text{Pd}(0) \) catalyst reported by Cai [174].

Additionally, Careau investigated the reactivity of \( \text{98} \) towards other electrophiles including halides, epoxides and acyl chlorides [168]. Furthermore, treatment of \( \text{98} \) with \( \text{HCl} \) in the presence of a Lewis acid \( ([\text{Zn}(\text{OTf})_2]) \) yielded the bicyclic adducts 2,5,7-trithiabiocyclo[2.2.1]heptane [100, Scheme 60] [169].

Beletskaya and co-workers reported an alternative methodology in the addition of \( \text{S-S} \) and \( \text{Se-Se} \) bonds to alkynes. Diphenyl disulfide \( (\text{Ph}_2\text{S}_2) \) and diphenyl diselenide \( (\text{Ph}_2\text{Se}_2) \) were reacted with a variety of terminal alkynes within the literature [170]. It was later shown that excess \( \text{PPh}_3 \) prevented the rapid polymerization to \( [\text{Pd(ER)}_2] \) and therefore the inhibition of the palladium catalyst [171].

Beletskaya also reported the dithiolation of terminal alkynes utilizing a \( \text{Pd}(0) \) catalyst supported by a triphenylphosphine resin under conventional [172], and microwave heating conditions [173]. Simple filtration resulted in the isolation of the \( \text{Z}-1,2\)-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 \( \text{Pd}(0) \) catalyst reported by Cai [174].

Zeni described the addition of diorganyl diselenides and disulfides to terminal alkynes in the presence of an iron(III) chloride \( (\text{FeCl}_3) \) 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 [175]. Iron catalyzed addition to \( 1,4\)-butyn-diols, pentyne-1,5-diol and \( 4\)-amino-1-butynol afforded \( \text{3,4-bis(organochalcogen)-2,5-dihydrofurans} \) [101], \( \text{4,5-bis(organochalcogen)-3,6-dihydro-2H-pyrans} \) (Scheme 62) [102] and \( \text{2,5-dihydro 1H-pyrrole derivatives} \) (Scheme 63), respectively, under mild aerobic conditions (Scheme 61) [176]. 1,3-Diyynes in the presence of dibutyldiselenide or dimethyldisulfide and stoichiometric quantities of \( \text{FeCl}_3 \) yielded symmetrical and unsymmetrical 3,4-bis[butyldiselenyl]chalcogenophanes [184]. In the synthesis of the \( \text{104} \), the cyclization was stereoselective providing exclusively the desired \( \text{E}-\text{selenoencynes} \) as intermediates. The selenenophanes then formed via an intramolecular 5-endoid cyclization [177].

2.8.3. Copper

The addition of the catalytic mixture of \( \text{Cu} \), zinc dust and glycerol resulted in the stereoselective addition of diaryl dichalcogenides to form a variety of \( 
\text{E}-1,2\)-bis-chalcogen alkynes (105) (Scheme 62). Zinc and glycerol were essential to the reaction; \( \text{Zn} \) reduced \( \text{Cu(I)} \) to \( \text{Cu(0)} \) while glycerol acted as a solvent, but also as a possible reducing agent for the reduction of \( \text{Zn(II)} \) to \( \text{Zn(0)} \) [178].

2.8.4. Nickel

The only examples of nickel-catalyzed addition of diaryldisulfides to alkynes were developed by Beletskaya and co-workers.
The use of 3 mol% [Ni(acac)₂] and 30 mol% PMePh₂ at 100 °C under solvent-free conditions resulted in the stereoselective dithiolation of both internal and terminal alkynes to form 2-dithiolated alkene products. The reaction temperature was important: too low meant incomplete reactivity and too high led to a mixture of stereoisomers [179].

2.8.5. Rhenium
The stoichiometric reaction between the tetrathiometallate anion [ReS₄]²⁻ and diphenylacetylene, 2-butyne and bis(trimethylsilyl)acetylene in the presence of elemental sulfur yielded the dithiolation adducts 106 (Scheme 63) [180].

2.8.6. Rhodium
Yamaguchi and co-workers showed that it was possible to dithiolate terminal alkynes using the dialkyl disulphide, Bu₂S₂, employing catalytic quantities of a Rh-dialkylphosphine complex, tris(p-methoxyphenyl)phosphine and trifluoromethane sulfonic acid affording the corresponding Z-bis(alkylthio)alkenes (107) (Scheme 64). A range of functionality at the terminal alkynyl substituent was accessible including hydroxyl, tert-butylidemethylsiloxyl and nitrile. However, internal alkynes were not accessible with this protocol [181].

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 disulfides and diaryl diselenides were reacted with terminal alkynes using the same Rh complex and 1,1'-bis(diphenylphosphino)ferrocene (dpdf). This resulted in the formation of Z-1-arylseleno-2-(arylthio)-1-alkenes (108) as the major product (Scheme 65). The amounts of minor by-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 [182].

2.9. Sulfur–Silicon (S–Si)

2.9.1. Gold
Nakamura and co-workers developed the AuCl-catalyzed cyclization of o-alkynylphenylthio)siolanes (109) to form the corresponding 3-silylbenzo[b]thiophenes (110). The reaction was proposed to proceed initially by coordination of the gold species to the alkynyl moiety. The sulfur 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 110 (Scheme 66). 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) [183].

2.10. Sulfur–Boron (S–B)

2.10.1. Palladium
Suzuki and Miyaura employed 9-(alkylthio)-9-borabicyclo[3.3.1]nonane in the palladium(0) catalyzed thiorotation of terminal alkynes to produce 9-[Z-2-(alkylthio)-1-alkenyl]-9-borabicyclo[3.3.1]nonane derivatives. These reactions were highly regio- 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 [184].

2.11. Germanium–Germanium (Ge–Ge)

2.11.1. 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 alkylene digermylations in the literature are palladium-catalyzed. The first example was reported by Ando and co-workers. In their work, a strained cyclic digerminane was reacted with acetylene and dimethyl acetylenedicarboxylate in the presence of 10 mol% [Pd(PPh₃)₄] resulting in the formation of the digermacyclopentene 111. When X was a sulfur atom, it was possible to selectively cleave the Ge–S bond to afford 112 (Scheme 67) [185].

Mochida and co-workers reacted 1,1,2,2,3,3,4,4-octaisopropyldigermane ((Pr₂Ge)₄) with various terminal alkynes in the presence of palladium complexes to synthesise 1,2,3,4-tetrahydro-1,2,3,4-tetrahydropyrene (113). Δ²-1,2,3-trigemolene (114) and 1H-germolems (2,4-, 3,4- and 2,3-disubstituted) (115). The yields of 114 and 115 increased with time, a fact attributed to the thermolysis of 113 in the presence of excess alkyne. The formation of 114 from 113 suggested extrusion of disiropolygermylene (iPrGe)₂,
which was readily trapped by two equivalents of alkyne to give 115 [186] (Scheme 68).

In 1991, Tanaka used linear non-strained digermales in the 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 116 (Scheme 69). The extension of the protocol to hexamethyldigermane resulted in very low conversions [187]. Following studies accomplished the conversion of 116 to 1,2-digermacyclobut-2-enes (117) by reductive cyclization in the presence of sodium metal. The treatment of 117 with alkynes in the presence of palladium catalysts resulted in the digermylation and the formation of the corresponding 1,4-digermacyclohex-2,5-dienes 118 and 119 (Scheme 69) [188].

### 2.11.2. Platinum

The digermylation of terminal with hexamethyldigermane has only been accessible employing a platinum catalyst at 120 °C, affording the corresponding Z,1,2-bis(trimethylgermyl)ethenes (120) (Scheme 70). Lowering the temperature resulted in deterioration of the yields [189]. Internal alkynes were unreactive.

### 2.12. Germanium–Tin (Ge–Sn)

#### 2.12.1. Palladium

Piers and co-workers reported the germylstannation of α,β-acetyleneic esters with Bu$_3$SnGeMe$_3$ to afford E-2-(tri-butylstannylethyl)-3-(trimethylgermyl)alk-2-enotes (121) as the major product. The reactivity of the resulting germyl and stannyl groups were separately assessed. 121 was treated with BuLi and an allyl halide to form 122 via the transmetalation of Bu$_3$Sn. The germyl moiety was also transformed into a C–I bond upon addition of iodine (Scheme 71) [190].

Nakano synthesized Z-1-aryl-2-germyl-1-stannylethenes (123) by adding tributyl(triethylgermyl)stannane to aryl terminal alkynes in the presence of catalytic amounts of [Pd(dba)$_2$] and 4-ethy l-1-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane (Scheme 72). This protocol was extended to ethynylthiophene and 2-methyl-3-buty n-2-ol. The regioselective addition of the germyl moiety at the terminal carbon was favored in all cases [191].

### 2.13. Germanium–Boron (Ge–B)

#### 2.13.1. Nickel, palladium and platinum

In their investigation into the silaborative dimerization of alkynes catalyzed by nickel complexes, Ito and co-workers developed the analogous germylborane reaction. The product/s 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 124 was obtained. By altering the catalyst to [Pd(OAc)$_2$/isoanisidine, a 1:1 mixture of 124 and the germylboration adduct 125 was isolated, whereas catalytic-quantities of Pt[PPh$_3$_2](C$_2$H$_4$)$_2$ resulted in exclusively 125 (Scheme 73) [131].
3. Conclusions

This review presents the state-of-the-art in homo- and hetero-
geneous transition metal catalyzed hetero element–element
additions to alkenes. These reactions yield highly functionalized
multi-substituted alkenes with high regio- and stereoselectivities.
The early literature was limited to reactive or unstable E–E bonds,
and reactions were primarily mediated by platinum group
transition metal complexes with phosphine or isocyanide ligands.
Developments over the past decade made it possible to employ
other transition metals such as coinage metal complexes, and uti-
lize commercially available E–E bonds that are air and moisture
stable. Furthermore, the application of NHCs as ligands has vastly
improved conditions in an unprecedented manner. However,
E–E bonds are still restricted in their application and the state-of-the-art catalysts remain flawed. Continuing efforts are
likely to focus on earth abundant transition metal complexes
and new E–E bonds that improve current regio- and
stereoselectivities.

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