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Recent advances in transition metal-free catalytic hydroelementation (E = B, Si, Ge, and Sn) of alkynes

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Catalytic hydroelementation of alkynes mainly with hydroboranes and hydrosilanes gives a straightforward and atom-economical access to a wide range of vinylmetalloids, which are used as synthetically useful and/or reactive species in both synthetic and materials chemistry. Thus far, although numerous transition metal catalysts with well-defined ligand systems have been developed for alkyne hydroelementation, the employed catalysts are mainly based on expensive and potentially toxic metals such as Rh, Pt, and Ir, and their conventional inner-sphere hydride transfer pathways are susceptible to reaction systems, often making it difficult to control the selectivity. In this regard, transition metal-free catalysts for hydroelementation (E = B, Si, *etc.*) have intensively been reported as an alternative to the conventional metal catalytic regimes over the last decade. In this review, we describe the recent advances in transition metal-free catalytic procedures for alkyne hydroelementation using hydrides based on Si, B, Sn, and Ge with strong emphasis on the variation in the catalytic working mode depending on the intrinsic nature of the reaction systems.

1. Introduction

Alkynes, a class of unsaturated hydrocarbons, are important platform chemicals for the synthesis of various functions.[1–6] Among the organic transformations of alkynes, catalytic hydroelementation leading to a broad range of functionalized vinyl molecules is of particular interest since the resultant vinyl moieties have versatile reactivities as nucleophiles to diverse electrophilic counterparts in organic synthesis.[7–16] Accordingly, B, Si, and Sn-based metalloid hydrides are widely employed and studied as a reducing agent in combination with transition metal catalysts for alkyne hydroelementation.[17–25] This reaction involves both regio- and stereochemical considerations, where the regiochemistry defines the position of incorporating metalloids between two carbons of unsymmetrical alkynes (α *vs.*

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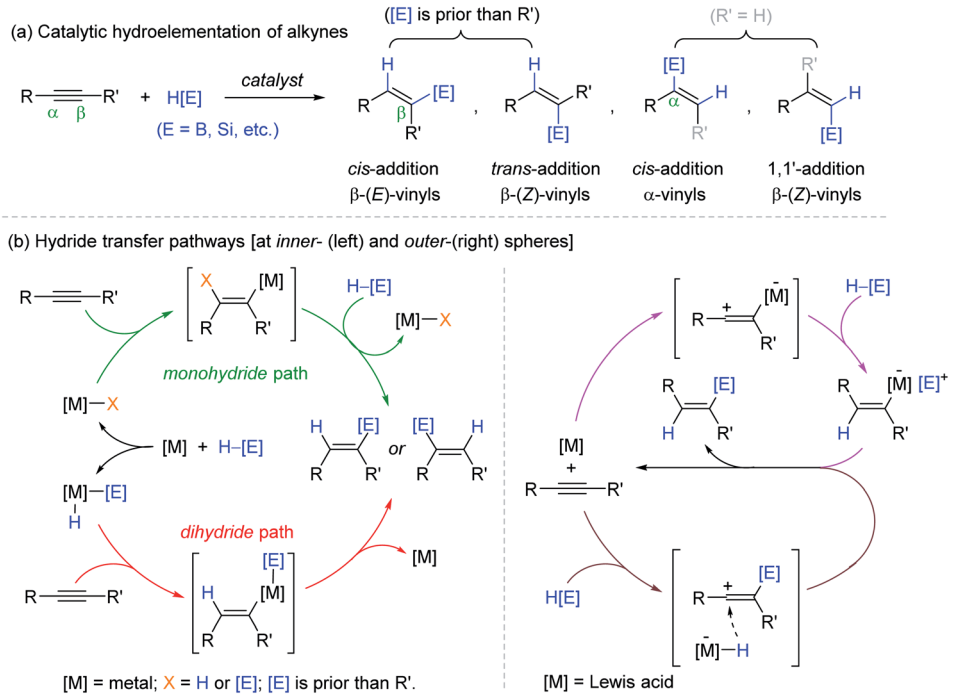
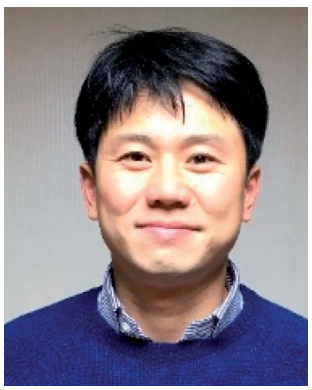
Ruibin Wang was born in China in 1986. He received his Master's Degree (2011) in Medicine Chemistry from Sun Yat-sen University (Prof. Gui Lu). From February 2012 to July 2016, he worked at the Chinese Academy of Sciences as a Research Fellow. Then, he moved to Guangdong Shunde Industrial Design Institute to work as a Research Fellow (2016–2020). In early 2020, he started his PhD degree under the guidance of Prof. Sehoon Park at Guangdong Technion Israel Institute of Technology (GTIIT). His research is focused on the synthetic and mechanistic organometallic chemistry particularly involved in catalysis.



Scheme 1 (a) Regio- and stereoselectivity and (b) general mechanisms of the catalytic hydroelementation of alkynes.

β), and the stereochemistry indicates the olefinic geometry of the resultant vinyl products (*trans vs. cis* or *E vs. Z*) (Scheme 1a). The possible selectivity outcomes are highly sensitive to the reaction components including metal, ligand, and/or metalloid hydride, which often render multiple catalytic pathways operative to bring about undesirable side products.[26–35] There are mainly two types of inner-sphere pathways known for the transition metal-mediated alkyne hydroelementation, where the metal center initially undergoes oxidative addition to afford an active metal species possessing M–H and/or M–[E] bonds ([E] = metalloids), into which alkynes are inserted in a *cis*-manner to eventually deliver (*E*)-vinylmetalloids (Scheme 1b, left).[18,25,26,28] On the other hand, the outer-sphere pathway involving hydride transfer from an outer-sphere of catalytic species is another important mechanism in the context of alkyne reduction, and the majority of these catalytic systems are based on Lewis acids. In the proposed mechanism, alkyne substrates react with either Lewis acid catalysts or highly electrophilic metalloid ions generated *in situ* to form zwitterion or vinyl carbocation intermediates, respectively. These intermediates are finally reduced *via* the outer-sphere hydride transfer to release the β-(*Z*)-vinyl products (Scheme 1b, right).[36]

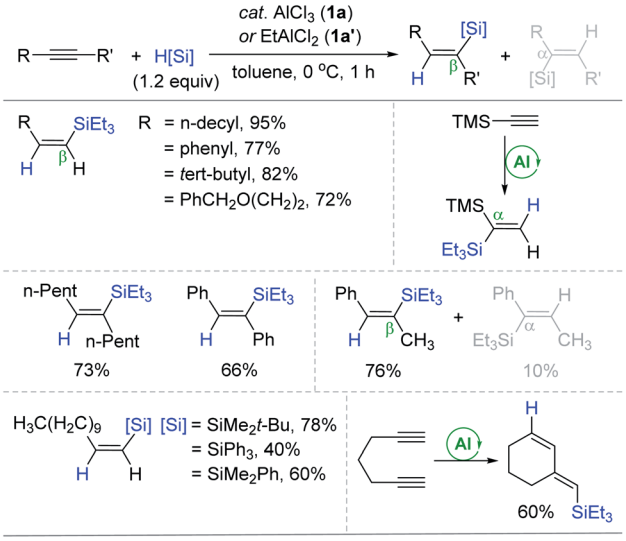
Although numerous well-defined organometallic complexes are known to promote the selective alkyne reduction, this conventional procedure still has a range of cons in terms of practicality, namely the use of expensive metals (*e.g.* Ru, Rh, Pd, and Pt), instability of the metal complexes under ambient conditions, and difficult separation of the transition metals from crude reaction mixtures, which can be linked to toxicity in the pharmaceutical industry.[37–40] In this regard, a significant number of transition metal-free, organo(metallic) catalyst systems for alkyne hydroelementation have recently been disclosed as a competent alternative by many research groups. However, to date, there have been no reviews documenting the transition metal-free catalytic procedures, whereas several reviews on the transition metal-catalyzed alkyne hydroelementation have been published.[22,23,25,26,28,36] For example in 2000, Yamamoto reviewed the Lewis acid-promoted hydrometalation of unactivated alkynes, where various outer-sphere hydride transfer pathways were described.[36] In 2005, Trost published a seminal review on transition metal-catalyzed alkyne hydrometallation with metalloid hydrides based on boron, silicon, and tin.[28] In 2019, Alami and Provot reported a review



Sehoon Park was born in Seoul (Korea). He received his Ph.D. (2008) from the Tokyo Institute of Technology (Prof. Kohtaro Osakada). He then moved to the University of North Carolina at Chapel Hill to work as a Postdoctoral Fellow with Prof. Maurice Brookhart (2009–2012). From April 2013 to February 2019, he worked at the Institute for Basic Science (Korea) as a Senior Research Fellow with a mentorship by Prof. Sukbok Chang. In early 2019, he started his independent research as an Assistant Professor at Guangdong Technion Israel Institute of Technology (GTIIT). His research interests are synthetic and mechanistic organometallic chemistry.

on the hydrostannation of alkynes, focusing on the reaction mechanism and selectivity.[23]

In this review article, we aim to outline the recent examples of diverse transition metal-free catalysts ranging from Lewis acids (based on B, Mg, Al, Si, and P) and bases (based on Li, Mg, P, and K) to Brönsted acids (carboxylic acids) and a Brönsted base (NaOH) for the hydroelementation of alkynes with Si, B, Sn, and Ge-based hydrides (Scheme 2). The term "transition metal" in this review is defined as an element in the d-block of groups 3 to 12 in the periodic table.[41,42] The representative catalytic working modes will be described by the type of catalysts in combination with hydride metalloids. In addition, the regio- and stereo-outcomes of the resultant vinylmetalloids will be discussed with emphasis on the hydride transfer pathway (inner- or outer-sphere mechanisms). The scope of the present review excludes Arase-Hoshi-type alkyne hydroboration involving R_nBH_{3-n} ($n = 0, 1, 2$) catalytic species,[43–46] and transfer hydroelementation of alkynes using cyclohexa-1,4-diene-based metalloid hydride surrogates.[47,48] This review covers the literature up to July, 2020.



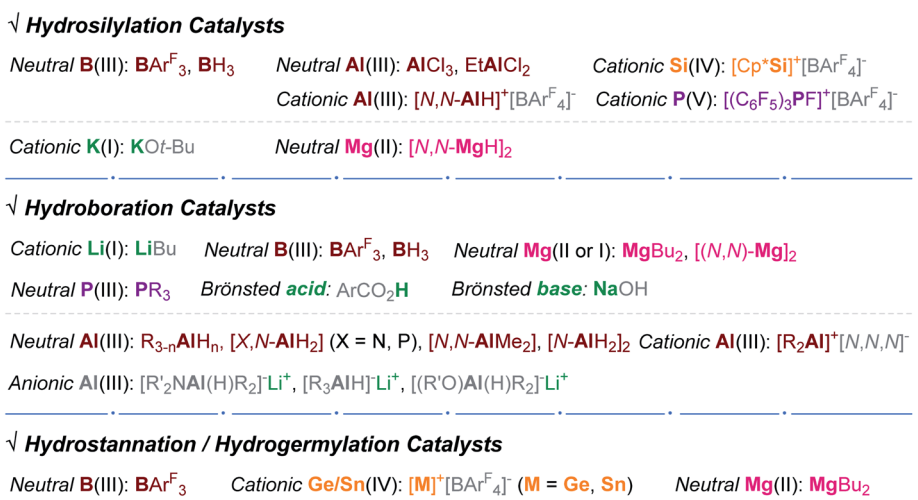
Scheme 3 Al(III)-catalyzed *trans*-hydrosilylation of alkynes. TMS = trimethylsilyl.

2. Hydrosilylation

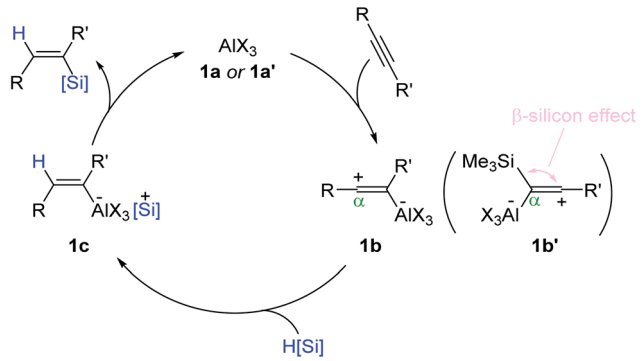
The transition metal-catalyzed hydrosilylation of alkynes is one of the most utilized methods to synthesize a broad range of vinyl compounds since hydrosilanes are cheap, variable, and/or commercially accessible reducing agents.[17–19] The majority of organometallic catalysts for alkyne hydrosilylation are based on precious metals, and their conventional inner-sphere pathways leading to *cis*-hydrosilylation are susceptible to the reaction system, usually giving a mixture of regioisomers. Accordingly, environmentally benign and selective transition metal-free catalysts can be a promising alternative to the conventional metal catalysts.

In 1996, Yamamoto reported the electron-deficient Al(III)-catalyzed *trans*-hydrosilylation of alkynes (Scheme 3).[49,50] This work represents the first transition metal-free catalytic hydrosilylation of alkynes. A broad range of terminal and internal alkynes reacted with Et_3SiH at 0 °C in the presence of $AlCl_3$ (**1a**) or $EtAlCl_2$ (**1a′**) (20 mol%) to give the corresponding β-(*Z*)-vinylsilanes in good to high yields. Notably, the hydrosilylation of trimethylsilylacetylene yielded the α-vinylsilane exclusively. The reactions of unsymmetrical acetylenes led to a mixture of β- and α-vinylsilanes, and their ratios increased up to 7.6 : 1 depending on the differential steric effects of the alkyne substituents. It is interesting that Et_2AlCl was an inactive catalyst possibly due to its low Lewis acidity, while **1a**, which was insoluble in toluene, catalyzed the hydrosilylation in a heterogeneous manner. The scope of silanes was broad to include bulky silanes such as Ph_3SiH. The present catalytic procedure was applicable to the hydrosilylative cyclization of 1,6-heptadiyne, affording the six-membered cyclization product.

Based on the precedence of Lewis acid-catalyzed alkyne reduction,[51–54] a reaction pathway for the Al-catalyzed alkyne



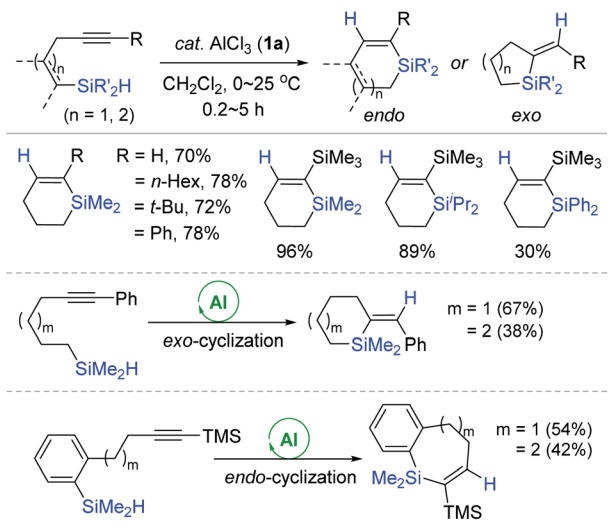
Scheme 2 Transition metal-free catalysts for alkyne hydroelementation (this review).



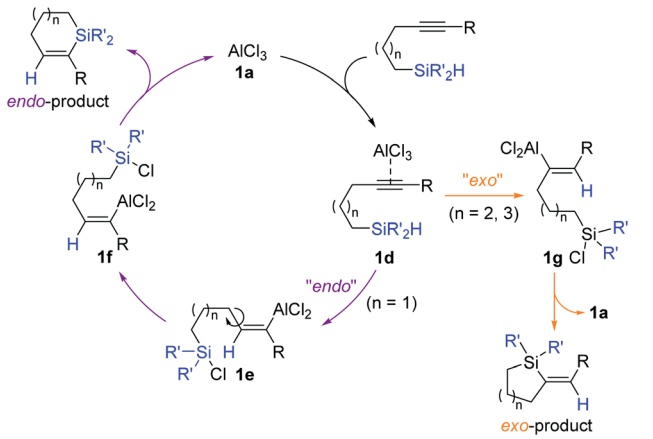
Scheme 4 Proposed pathway for the Al-catalyzed *trans*-hydrosilylation of alkynes.

hydrosilylation was proposed (Scheme 4). Initially, the Al catalyst (**1a** or **1a**′) is assumed to react with an alkyne to form zwitterionic intermediate **1b**, where the sp-hybridized vinyl carbocation is positioned β to the aluminum atom. The carbocation is likely reduced by a hydrosilane from the opposite side of the C(sp^2)–Al moiety to generate aluminum ate-complex **1c**. Then, **1c** is suggested to be converted in a stereo-retentive manner to the (*Z*)-vinylsilane and the Al catalyst. This outer-sphere mechanism involving the vinyl carbocation intermediacy was corroborated by the α-selectivity observed in the hydrosilylation of trimethylsilylacetylene, involving an intermediate such as **1b**′ under the β-silicon effect.

Considering the preliminary result of the hydrosilylative cyclization of a diyne (*vide supra*),[49,50] the Yamamoto group developed the **1a**-catalyzed intramolecular hydrosilylation of alkynes bearing a hydrosilyl moiety to produce various silacycles (Scheme 5).[55] A range of alkynes linked to an SiR′$_2$H (R′ = Me, ^{i}Pr, Ph) moiety by three methylene groups smoothly underwent cyclizative hydrosilylation in an *endo-trans* fashion in the presence of **1a** (20 mol%) to produce the corresponding six-



Scheme 5 $AlCl_3$-catalyzed intramolecular *trans*-hydrosilylation of alkynes possessing a hydrosilyl moiety.



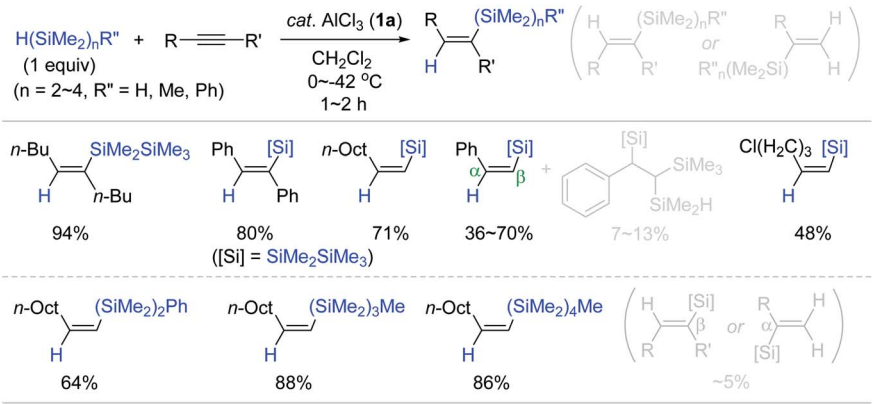
Scheme 6 Proposed pathway for the Al-catalyzed regiodivergent cyclizative hydrosilylation of alkynes.

membered silacycles in 30–96% yield. Notably, the substituents ^{i}Pr and Ph on the silicon retarded the cyclizative hydrosilylation to require a prolonged reaction time of up to 5 h. The phenyl-substituted alkynes possessing four to five methylene tethers were cyclized in an *exo*-mode to give the six- and seven-membered *exo*-silacycles, whereas the cyclization of substituted alkynes bearing a benzene ring spacer proceeded in an *endo*-mode to give the *endo-trans* products with seven to eight-membered ring sizes.

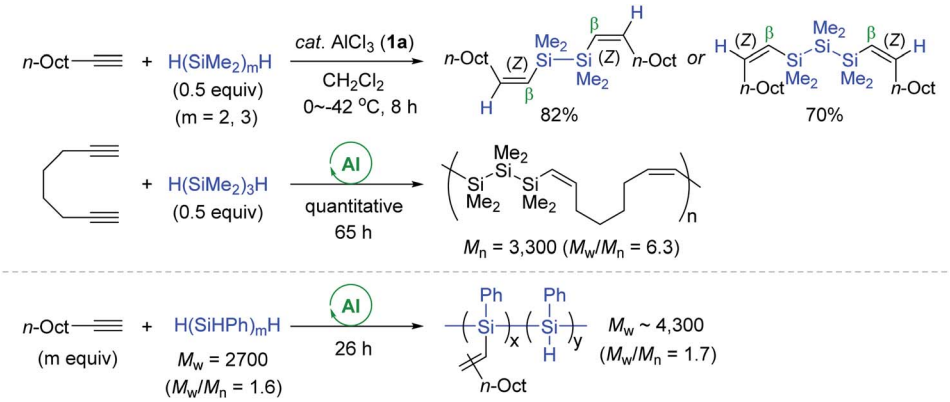
A reaction pathway for the Al-catalyzed regiodivergent cyclizative hydrosilylation of alkynes was proposed (Scheme 6). $AlCl_3$ **1a** is assumed to initially interact with an alkynyl group to form a π-complex **1d**. The species **1d**, where the acetylenic bond is highly activated, is presumed to undergo intramolecular hydride transfer selectively to one of the acetylenic carbons depending on the identity of tethers, generating intermediate **1e** or **1g** bearing a C(sp^2)–Al bond. Intermediates **1e** and **1g** are suggested to be cyclized to furnish the *endo*- and *exo*-silacycles, respectively with the regeneration of **1a**.

Based on Yamamoto's Al catalysis using hydromonosilanes as a reducing agent, Tanaka conceived the $AlCl_3$ (**1a**)-catalyzed hydrosilylation of alkynes with hydrooligosilanes H(SiMe$_2$)$_n$R; [n = 2–4, R = H, Me, Ph] as a reducing agent (Scheme 7).[56] The hydrosilylation of internal and terminal alkynes with pentamethyldisilane (HSiMe$_2$SiMe$_3$, 1 equiv.) occurred at 0 to −42 °C to furnish the β-(*Z*)-vinylsilanes as the major product with small amounts of β-(*E*)- or α-vinylsilanes (~5%). Interestingly, the reaction of phenylacetylene with HSiMe$_2$SiMe$_3$ not only gave the desired *trans*-addition products, but also 1,1,2-trisilyl-substituted ethylbenzene as a minor product (7–13%) depending on reaction temperature and concentration.

Next, α,ω-dihydrooligosilanes [H(SiMe$_2$)$_n$H (n = 2, 3)] were subjected to alkyne hydrosilylation and hydrosilylative polymerization of 1,7-octadiyne (Scheme 8). The reactions with 0.5 equivalents of α,ω-dihydrooligosilanes provided the corresponding β,β-(*Z*,*Z*)-bis-vinylsilanes in good yields. The reaction of 1,7-octadiyne with 1,3-dihydrohexamethyltrisilane in the presence of **1a** (10 mol%) gave a mixture of oligomeric and



Scheme 7 $AlCl_3$-catalyzed *trans*-hydrosilylation of alkynes with monohydrooligosilanes.



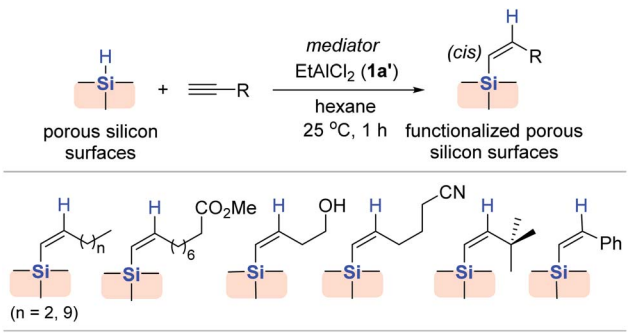
Scheme 8 $AlCl_3$-catalyzed *trans*-hydrosilylation of alkynes with polyhydrosilanes.

polymeric materials [$M_n = 3300$ ($M_w/M_n = 6.3$)]. This Al catalysis was useful in modifying the backbone of poly(hydrosilylene)s. For example, poly(phenylsilylene) ($M_w = 2700$, $M_w/M_n = 1.63$) reacted with 1-decyne *via* multiple hydrosilylations to yield a polymer having decenyl pendants ($M_w = 4260$, $M_w/M_n = 1.74$).

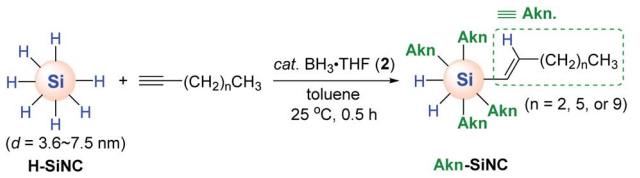
Porous silicon, which has a high surface area morphology of hydride-terminated silicon, exhibits photoluminescence upon UV light irradiation, and has wide applications such as electroluminescent displays,[57] photodetectors,[58] and chemical/biosensing.[59–61] However, silicon materials often suffer from corrosion and instability in highly oxidative and basic media, which are needed for practical applications.[62,63]

Considering this, Buriak *et al.* modified the surface of porous silicon *via* Al (**1a′**) catalysis in an attempt to strengthen its chemical stability (Scheme 9).[64,65] The hydrosilylation of 1-dodecyne occurred on the porous silicon surface at 25 °C upon the addition of $EtAlCl_2$ (**1a′**) to allow the clean incorporation of dodecenyl groups on the silicon surface. Under similar conditions, a range of alkynes bearing various functionalities were hydrosilylated on the surface, resulting in the corresponding alkenyl group-terminated surfaces. It is noteworthy that excess $EtAlCl_2$ (**1a′**) was required for the hydrosilylation of alkynes bearing Lewis basic functional groups, such as cyano and ester groups. The incorporated alkenyl moieties on the surface were characterized *via* FT-IR and NMR spectroscopy, while elemental analysis and secondary ionization mass spectrometry (SIMS) depth profiling indicated a consistent level of alkenyl group incorporated throughout the porous silicon.

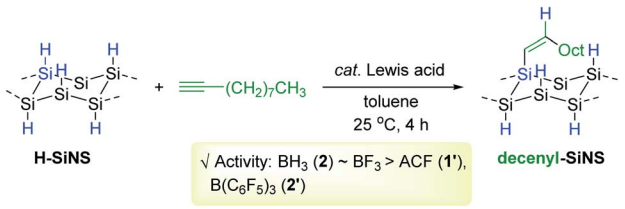
Although the work by Buriak *et al.* showcased silicon surface modification *via* Al-mediated alkyne hydrosilylation, this process required a stoichiometric amount of $EtAlCl_2$ **1a′**. Accordingly, Veinot and coworkers conceived to apply $BH_3 \cdot THF$ (**2**) as a catalyst for the hydrosilylative modification of the



Scheme 9 $EtAlCl_2$-mediated hydrosilylation of various alkynes on porous silicon surfaces.



Scheme 10 BH_3-catalyzed hydrosilylation of alkynes on silicon nanocrystals.



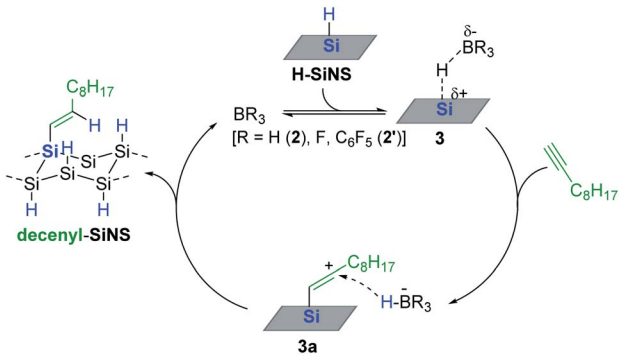
Scheme 12 Transition metal-free Lewis acid-catalyzed hydrosilylation of 1-decyne on silicon nanosheets.

surface of hydride-terminated silica nanocrystals (**H-SiNC**).[66] This work represents the first borane-catalyzed surface modification of nanoscale silicon. The hydrosilylation of terminal alkynes on **H-SiNC** occurred at 25 °C in the presence of **2** (2.5 mol%) to yield the alkenyl-functionalized **SiNC** (**Akn-SiNC**) (Scheme 10). The degree of **SiNC** surface coverage was found to decrease with an increase in the chain length of the alkyne substrates, and terminal alkynes were more reactive than internal alkynes in terms of surface functionalization probably due to steric hindrance. It is noteworthy that the catalytic activity was dependent on the size of **SiNC**, where the hydrosilylation of larger **H-SiNC** ($d = 7.5$ nm) required 12 h, whereas the same reaction on smaller **SiNC** ($d = 3.6$ nm) was faster and was completed within 0.5 h.

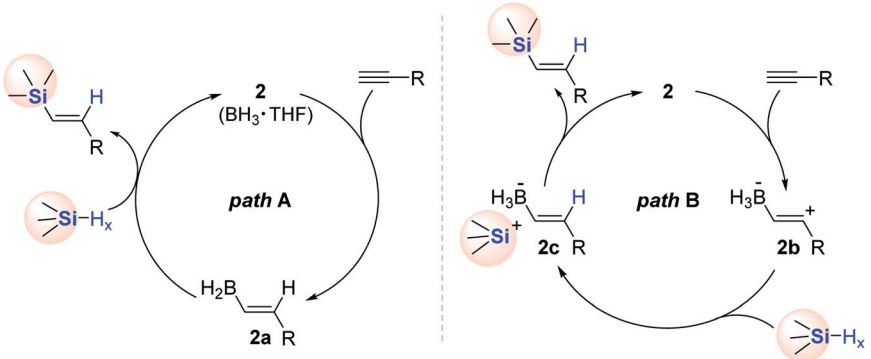
Two reaction pathways were proposed for the **2**-catalyzed alkyne hydrosilylation on the surface of **H-SiNC** (Scheme 11). One possible mechanism (path A) involves the *syn*-addition of **2**, followed by a metathesis process with the Si–H moiety on **SiNC** (Scheme 11, left). The alternative pathway (path B) is assumed to form zwitterionic vinyl carbocation **2b** in the initial step upon the reaction of alkyne with **2**. Subsequently, **2b** is suggested to be reduced with **H-SiNC** to generate a vinyl borohydride having a silylium ion site (**2c**). Finally, **2c** is likely converted to **Akn-SiNCs** with the liberation of **2** (Scheme 11, right).

As a continuing effort for the catalytic surface modification of silicon, Rieger and Venoit examined various transition metal-free Lewis acids as alkyne hydrosilylation catalysts to modify the surface of hydride-terminated silicon nanosheets (**H-SiNS**) (Scheme 12).[67] The hydrosilylation of 1-decyne on the surface of **H-SiNS** proceeded at 25 °C with the Lewis acid catalysts (0.7 mol%) to provide the decenyl-functionalized silicon nanosheets. Less bulky catalysts such as BH_3 (**2**) and BF_3 were more active towards hydrosilylation than the bulky ones [tris(pentafluorophenyl)alane (ACF, **1′**) and $B(C_6F_5)_3$ **2′**]. Considering the poor reactivity of **2′** in the case of porous silicon[64,65] and silicon nanocrystals,[66] the observed catalytic reactivity of $B(C_6F_5)_3$ **2′** with **H-SiNS** suggests two insights: (i) the hydride donor ability of **H-SiNS** is higher than the precedent silicon materials, and (ii) the reaction proceeds *via* an outer-sphere mechanism involving a silylium ion. It is interesting to see that the Lewis acidity of the catalysts (*e.g.* BF_3 *vs.* $BH_3 \cdot SMe_2$) did not influence the degree of functionalization, implying that the steric effect of the catalyst is a major factor in determining its reactivity with **H-SiNS**.

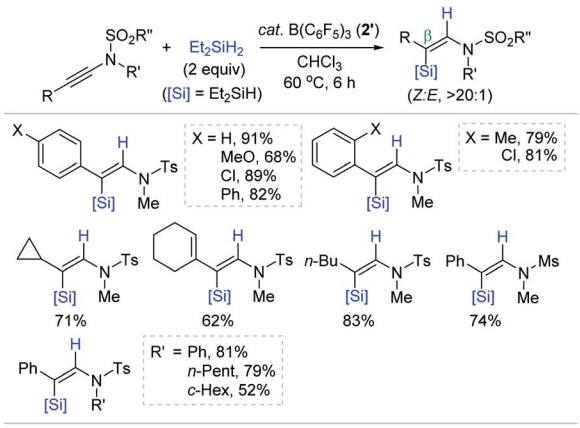
Based on experimental observations, a borane-catalyzed outer-sphere hydrosilylation mechanism was proposed



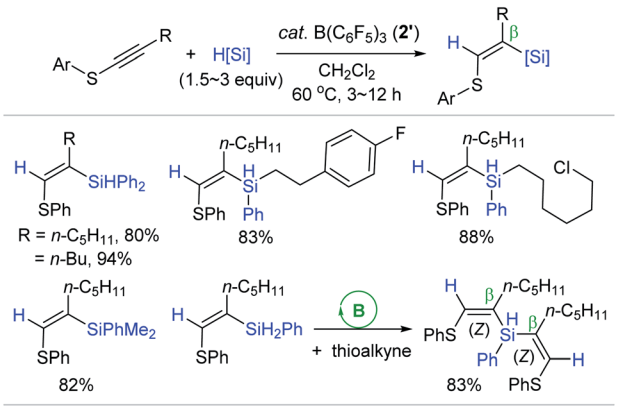
Scheme 13 Proposed pathway for the Lewis acidic borane-catalyzed alkyne hydrosilylation on H-SiNS.



Scheme 11 Two possible pathways for the BH_3-catalyzed alkyne hydrosilylation on H-SiNC.



Scheme 14 $B(C_6F_5)_3$-catalyzed *trans*-hydrosilylation of internal ynamides. Ms = methanesulfonyl.



Scheme 16 $B(C_6F_5)_3$-catalyzed *trans*-hydrosilylation of internal thioalkynes.

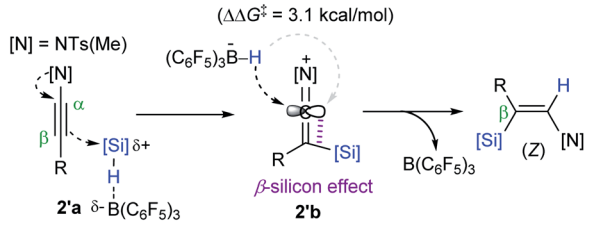
(Scheme 13). Borane is assumed to initially form an adduct with a hydrosilane on the surface (**3**), which generates a silylium ion site, at which 1-decyne reacts to generate a vinyl carbocation (**3a**) bearing a borohydride anion (HBR_3^-). Then **3a** likely undergoes hydride transfer from the borohydride to yield **decenyl-SiNS** with the regeneration of active site **3**.

Motivated by the precedent Lewis acidic Al-catalyzed alkyne hydrosilylation, Chang *et al.* developed for the first time the $B(C_6F_5)_3$ (**2′**)-catalyzed hydrosilylation of internal ynamides, furnishing a broad range of β-silyl (*Z*)-enamides (Scheme 14).[68] The hydrosilylation of ynamides having various substituents in the β-position occurred at 60 °C in the presence of **2′** (3 mol%) with Et_2SiH_2 (2 equiv.). Variation of the *N*-substituents in ynamides from *N*-methyl to -phenyl or -cycloalkyl, and from *N*-tosyl to -mesyl groups did not hamper the reactivity and selectivity (52–81%; *Z*/*E*, >20 : 1). This catalysis was also operative with other hydrosilanes except bulky tertiary silanes such as $^iPr_3SiH$ (not shown).

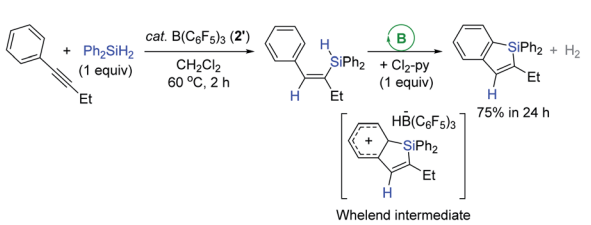
Based on computational studies, a catalytic working mode was proposed (Scheme 15). The initial step is presumed to transfer a silylium ion from the $B(C_6F_5)_3$-silane adduct **2′a** to the β-carbon of an ynamide to form a ketene iminium bearing a $HB(C_6F_5)_3^-$ (**2′b**). Subsequently, **2′b** undergoes hydride attack by the borohydride from the opposite side of the silyl group, leading to a (*Z*)-β-silyl enamide. Density functional theory (DFT) calculations suggested that the *anti*-addition path of a hydrosilane is preferred by 3.1 kcal mol^{-1} over the *syn*-addition path, which is consistent with the observed high (*Z*)-stereoselectivity. The origin of the differential activation energy ($\Delta\Delta G^{\ddagger}$ = 3.1 kcal mol^{-1}) was attributed to the β-silicon effect, resulting in geometrical bias between the same and opposite sides from the silyl group in **2′b**.

Following the Chang's report, Shen reported a similar outer-sphere *trans*-hydrosilylation of internal thioalkynes catalyzed by $B(C_6F_5)_3$ **2′** (Scheme 16).[69] The hydrosilylation of phenyl(1-heptynyl)sulfane cleanly proceeded at 60 °C with **2′** (1.5 mol%) to give the β-(*Z*)-silylated vinyl phenyl sulfide in 85% yield in 12 h. Under the borane catalytic regime, a broad range of 1°, 2°, and 3° hydrosilanes were viable for the (*Z*)-selective hydrosilylation reactions. It is noteworthy that the reaction with bulky silanes required a greater catalyst loading (up to 10 mol%) and/or increased silane quantities (up to 3 equiv.) to achieve reasonable yields of the silylated vinyl sulfides. The borane catalyst was proven to be applicable for double hydrosilylation with $PhSiH_3$ furnishing the β-silylated bis-vinyl sulfide as a single (*Z*,*Z*)-isomer in good yield.

In 2014, Ingleson *et al.* utilized $B(C_6F_5)_3$ (**2′**) as a catalyst for the synthesis of silaindenes from aryl-alkynes *via* a cascade hydrosilylation (Scheme 17).[70] For example, the reaction of 1-phenyl-1-butyne with Ph_2SiH_2 in the presence of **2′** (5 mol%) at 60 °C gave the vinyl silane, which was fully converted to the corresponding silaindene *via* an intramolecular sila-Friedel–Crafts reaction upon the addition of 2,6-dichloropyridine (Cl_2-py, 1 equiv.). The added Cl_2-py was presumed to serve as a Lewis base for the deprotonation of the presupposed Wheland intermediate.



Scheme 15 Proposed working mode for the $B(C_6F_5)_3$-catalyzed hydrosilylation of internal ynamides.

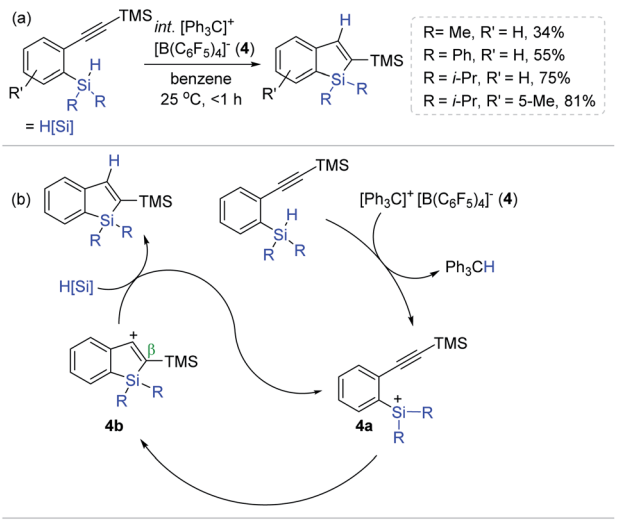


Scheme 17 $B(C_6F_5)_3$-catalyzed one-pot, two-step synthesis of a silaindene from an internal alkyne. Cl_2-py = 2,6-dichloropyridine.

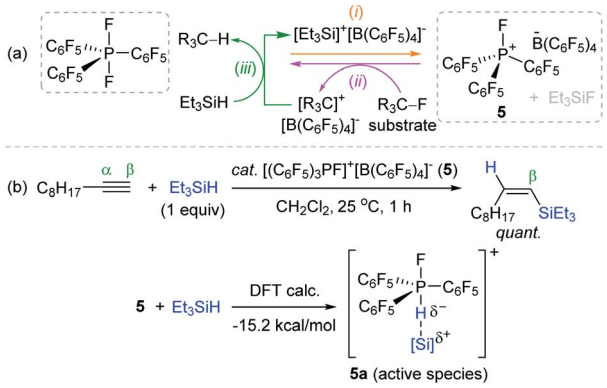
Inspired by Ingleson's Lewis acid-mediated intramolecular sila-cyclization, Kawashima *et al.* developed an intramolecular alkyne hydrosilylation route, leading to silaindenes from 2-alkynylphenylsilane derivatives using trityl tetrakis(pentafluorophenyl)borate ($[Ph_3C]^+[B(C_6F_5)_4]^-$ **4**) as an initiator (Scheme 18a).[71] A substoichiometric amount of **4** (1 mol%) initiated the sila-cyclization of a series of [2-(trimethylsilylethynyl)phenyl]silanes at 25 °C to provide the trimethylsilyl-substituted silaindenes in 34–81% yield within 1 h. It is noteworthy that this catalysis was susceptible to the substituents at the silicon center of the substrates, where the methyl- or phenyl moiety induced low to moderate yields (34–55%), whereas a bulky diisopropyl silyl group gave a higher yield of the silaindene of up to 75%. Interestingly, replacing the alkynyl TMS group with a butyl gave no hydrosilylation, suggesting that the alkynyl TMS moiety is essential for the catalytic turnover and serves as a neighboring group participating in the stabilization of a presumed vinyl carbocation by the β-silicon effect.[72–74]

A prototypical silylium ion-involved, outer-sphere mechanism of the trityl borate-initiated sila-cyclization was proposed (Scheme 18b). Specifically, **4** initially abstracts a hydride from the Si–H group of the substrates to generate active species **4a**, which intramolecularly reacts with an adjacent alkynyl unit to form ethenyl carbocation **4b**. This cationic intermediate is suggested to be stabilized by the (pre)installed silyl groups (β-silicon effect). The catalytic cycle is assumed to be closed upon hydride reduction by another hydrosilyl alkyne substrate, accompanied by the liberation of the silaindene product and the active catalyst **4a**.

In 2013, Stephan *et al.* synthesized an electrophilic organofluorophosphonium salt $[(C_6F_5)_3PF]^+[B(C_6F_5)_4]^-$ **5** through the reaction of a difluorophosphorane $(C_6F_5)_3PF_2$ with the salt reported by Lambert *et al.*, $[Et_3Si]^+[B(C_6F_5)_4]^-$.[75] The highly electrophilic P(v) center in **5** was capable of abstracting a fluoride anion from fluoroalkanes to generate $(C_6F_5)_3PF_2$ and



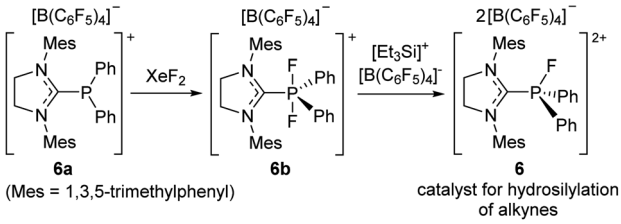
Scheme 18 (a) Trityl borate salt-initiated intramolecular sila-cyclization of alkynes and (b) their catalytic pathway.



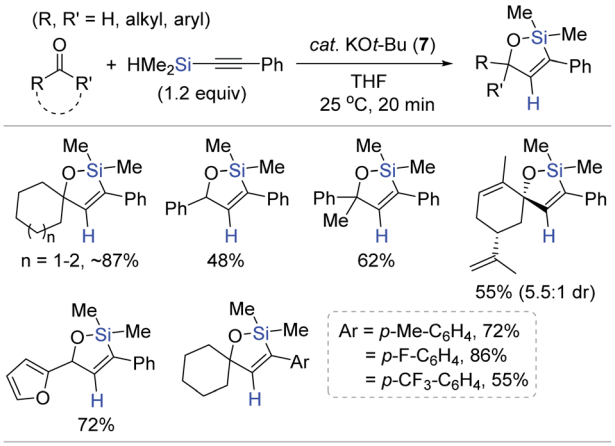
Scheme 19 (a) Generation of an electrophilic phosphonium salt and (b) its catalytic application for alkyne hydrosilylation.

a carbocation. This carbocation was reduced by a hydrosilane to release an alkane with the regeneration of Lambert's salt for catalytic turnover (Scheme 19a). Based on the observed high electrophilicity of **5**, Stephan *et al.* further applied **5**/silane as a catalytic system for the hydrosilylation of alkynes.[76] The hydrosilylation of 1-decyne with Et_3SiH occurred at 25 °C by **5** (1.5 mol%) to quantitatively afford the β-*cis*-vinylsilane within 1 h, suggesting the *anti*-1,2-addition of hydrosilanes to an alkyne. DFT calculations suggested that the LUMO of **5** contains the σ* orbital oriented opposite to the P–F bond to promote the formation of η^1-silane adduct **5a** ($\Delta H = -15.2$ kcal mol^{-1}), which was regarded as an active catalytic species and indeed observed by ^{1}H NMR (Scheme 19b).

Although the electrophilic phosphonium salt **5** displayed unique Lewis acidic catalytic reactivity, the fluoroarene substituents in **5** limit structural variations. Considering this, Stephan *et al.* reported a new synthetic strategy, leading to a highly electrophilic phosphonium salt that does not bear electron-deficient aryl groups. Specifically, NHC-ligated cationic phosphine(III) **6a** is oxidized by XeF_2 to a P(v) cationic difluorophosphorane **6b**, which subsequently undergoes fluoride abstraction by Lambert's salt to eventually afford a fluorophosphonium dication supported by an NHC ligand $[(NHC)PFPh_2]^{2+}[B(C_6F_5)_4]^{2-}$ (**6**) (Scheme 20).[77] To demonstrate the Lewis acidity of **6** in catalytic reactions, Stephan *et al.* performed the hydrosilylation of 1,2-diphenylacetylene in the presence of a catalytic amount of **6**, giving the (*Z*)-vinylsilane in excellent yield at 45 °C within 24 h.



Scheme 20 Synthetic route to a dicationic imidazolium–phosphonium salt **6** as a hydrosilylation catalyst.



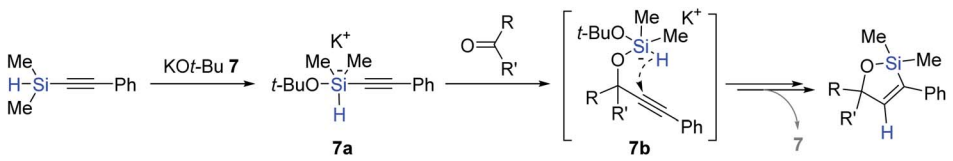
Scheme 21 KO*t*-Bu-promoted tandem alkynylation of carbonyls and intramolecular *trans*-hydrosilylation.

Pentacoordinate hydrosilicates *in situ*-generated from hydrosilanes and Lewis base activators are well-known catalytic species for the reduction of carbonyl functions,[78,79] and alkynylsilanes have been utilized for the alkynylation of carbonyls and imines *via* the corresponding hypervalent silicate intermediates.[80–84] Based on this background, Lee developed a KO*t*-Bu (7)-catalyzed tandem alkynylation and hydrosilylative cyclization of carbonyls with alkynylhydrosilanes (Scheme 21).[85] A range of aldehydes and ketones reacted with alkynylsilanes at 25 °C by catalyst 7 (10 mol%), providing diverse oxasilacyclopentenes in 48–87% yield within 20 min. This catalysis was highly sensitive to electronic and steric variations in substrates, where less bulky and electron-neutral or -deficient aryl-substituted alkynylsilanes were only viable for the tandem transformation.

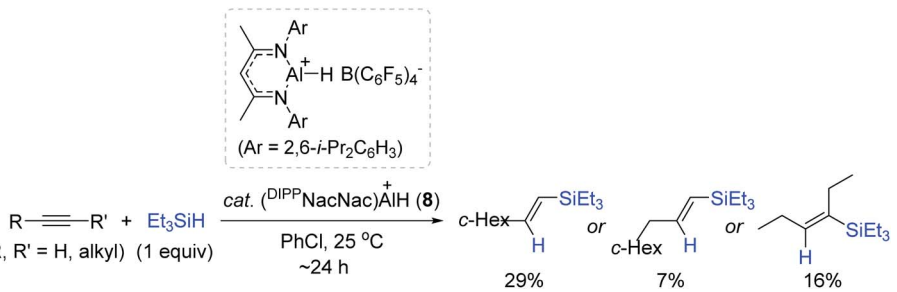
The key steps for the 7-catalyzed tandem alkynylation and hydrosilylation sequence were proposed (Scheme 22). Initially, *tert*-butoxide attacks the silicon center of an alkynylsilane to form a pentavalent silicate intermediate **7a**, which transfers the alkynyl group to the carbonyl to generate an activated hydridosilyl ether **7b**. This species is assumed to undergo intramolecular *trans*-hydrosilylation over the triple bond to liberate an oxasilacyclopentene. A cross-over experiment using two similar alkynylsilanes suggested a naked alkynyl anionic species is involved in the alkynylation step for ketones.[86–89]

Recently, a series of Al complexes with various β-diketiminate [^{Ar}NacNac=CH{C(Me)NAr}$_2$] ligands have emerged as competent catalysts for hydroelementation of unsaturated functions.[90–92] Additionally, neutral ^{Ar}NacNacAl complexes [*e.g.* ^{DIPP}NacNacAl(OTf)H, ^{DEP}NacNacAlH$_2$; DIPP = 2,6-*i*-Pr$_2$C$_6$H$_3$, DEP = 2,6-Et$_2$C$_6$H$_3$] were reported to catalyze the hydroboration of alkynes and carbonyls,[90,91] but the cationic ^{Ar}NacNacAl complexes remained unexplored. In this regard, Nikonov *et al.* prepared the cationic ^{DIPP}NacNacAlH complex (**8**) through the reaction of ^{DIPP}NacNacAlH$_2$ with [Ph$_3$C]$^+$[B(C$_6$F$_5$)$_4$]$^-$ (**4**), and examined its catalytic activity towards the alkyne hydrosilylation.[93] The reactions of a few alkyne substrates with Et$_3$SiH proceeded *via* the action of **8** (5 mol%) with high conversions to afford the vinylsilanes, albeit in low yields (7–29%) (Scheme 23). The observed low yields were ascribed to the facile redistribution of hydrosilanes by **8**. Although the exact catalytic working mode of **8** was unclear, the experimental observations implied that the cationic Al center in **8** serves as a Lewis acid for the activation of Et$_3$SiH.

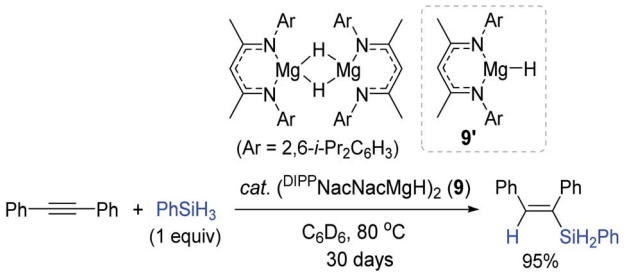
Similar to the Nikonov's work, Hill *et al.* reported a neutral NacNac-Mg hydride dimer (^{DIPP}NacNacMgH)$_2$ (**9**) as a catalyst for alkyne hydrosilylation.[94] The reaction of diphenylacetylene with PhSiH$_3$ slowly proceeded to give the β-(*E*)-vinylsilane in 95% yield in 30 days (Scheme 24). Unlike Al (**8**) catalysis under the Lewis acid-activation mode,[93] its isoelectronic monomeric magnesium hydride **9′** was found to work *via* the classical inner-sphere pathway, involving alkyne insertion, followed by a metathesis reaction with a hydrosilane.



Scheme 22 Proposed key steps for the KO*t*-Bu-catalyzed tandem alkynylation and hydrosilylation.



Scheme 23 Cationic Al(III)-catalyzed hydrosilylation of alkynes.



Scheme 24 Mg(II)-catalyzed *cis*-hydrosilylation of diphenylacetylene.

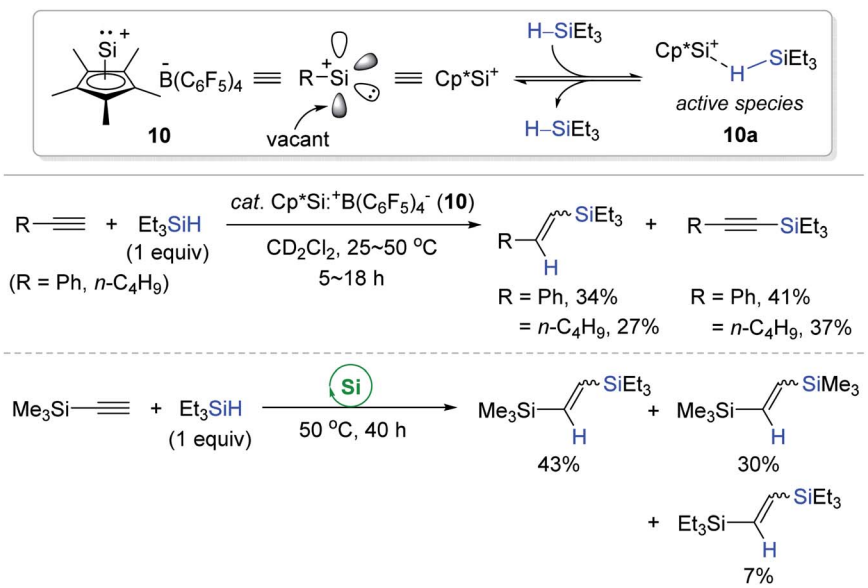
Recently, Fritz-Langhals *et al.* reported the catalytic use of a silyliumylidene cation **10** [Cp*Si:$^{+}$B$(C_6F_5)_4^{-}$; Cp* = pentamethylcyclopentadienyl] having a vacant coordination site.[95] The hydrosilylations of some terminal alkynes proceeded in the presence of **10** (0.04–0.1 mol%) at 25–50 °C to bring about a complex mixture of the corresponding vinylsilanes (*cis*/*trans*) and alkynylsilanes in poor yields, while in the case of ethynyltrimethylsilane, it underwent both hydrosilylation and redistribution reactions to give various vinylsilanes as a mixture (Scheme 25). As similar as the borane-silane adduct **2′a**,[68–70] the η^1-silane adduct (**10a**) was proposed to act as an active catalyst for the outer-sphere hydrosilylation of alkynes. In fact, the η^1-Si–H coordination to the cationic Si center at **10a** was evidenced by the coalescence of the Si–H signal in the time-dependent ^{1}H NMR spectra.

3. Hydroboration

Vinylboranes and vinylboronate esters have been widely utilized as coupling reagents and/or intermediates in the context of synthetic organic chemistry to construct new bonds of C–*C*, C–*N*, and C–*O* on the vinyl skeleton.[12,14,16] Hydroboration of alkynes is the most straightforward method to access the vinylborane reagents, while their regio- and stereoselectivity (α/β and *E*/*Z* issues) are variable and closely related to the possible catalytic working modes.[20–22,28] Conventional transition metal catalytic systems tend to yield (*E*)-vinyl products *via* the *syn*-addition of a B–H moiety (*cis*-hydroboration) at an inner-sphere of the active catalytic species, whereas metal-catalyzed *trans*-hydroboration affording (*Z*)-vinyl products is relatively less documented.

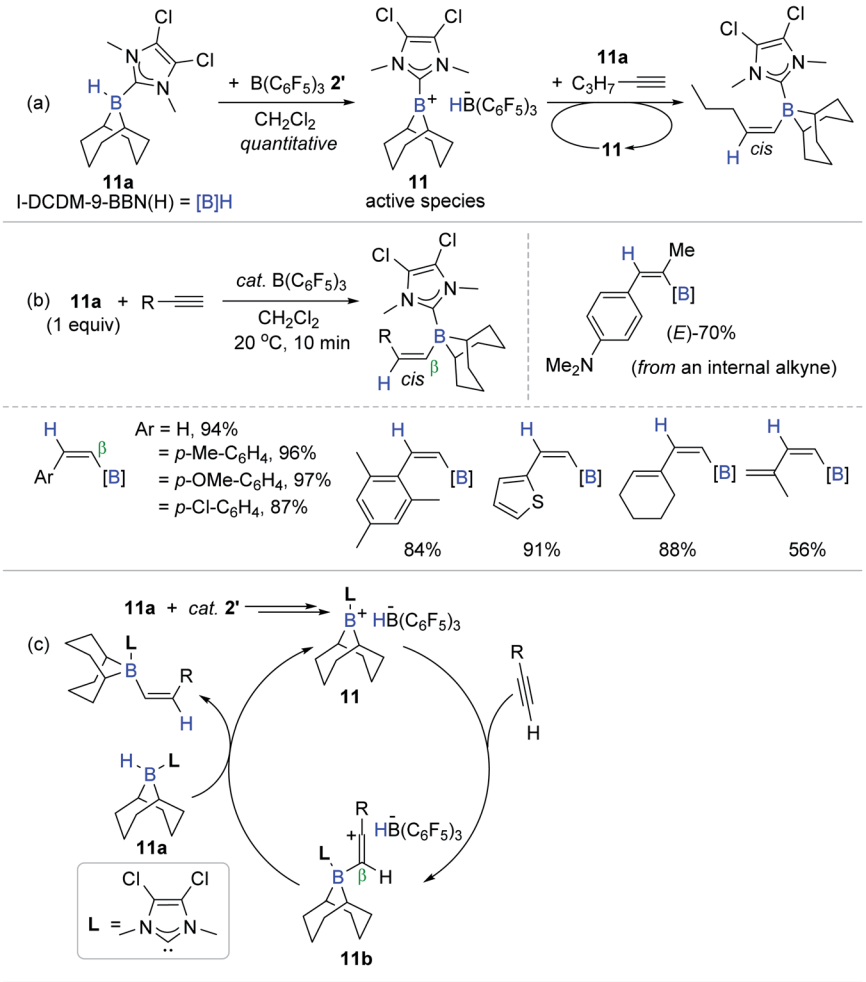
With this background, Ingleson *et al.* reported the $B(C_6F_5)_3$ **2′**-catalyzed *trans*-hydroboration of terminal alkynes (Scheme 26).[96] Their work represents the first transition metal-free *trans*-hydroboration of alkynes. The hydroboration process was proposed to involve an electrophilic borenium cation possessing a borohydride $HB(C_6F_5)_3^{-}$ (**11**) as the active species, which was generated *in situ* upon the 1 : 1 reaction of I-DCDM-9-BBN(H) (**11a**) [(I-DCDM = 1,3-dimethyl-4,5-dichloroimidazolylidene; 9-BBN(H) = 9-borabicyclo3.3.1]nonane) and **2′**. Consistent with **11** as the presumed active species, the stoichiometric reaction of **11**, **11a**, and 1-pentyne gave the corresponding β-*trans*-hydroboration product with the constant observation of **11** (Scheme 26a). Having this stoichiometric insight, the hydroboration of a range of terminal alkynes with **11a** as a reducing agent was conducted in the presence of **2′** (5 mol%) to reveal that the reaction was completed within 10 min at 20 °C to afford the *cis*-vinylboranes in 56–97% yield (Scheme 26b). Although most of the internal alkynes remained inert, the nucleophilic internal alkyne 4-(1-propynyl)-*N*,*N*-dimethylaniline reacted with **11a** under the $B(C_6F_5)_3$ catalytic regime to yield the corresponding vinylborane in 70% in 3 h.

A deuterium labelling study and stoichiometric and catalytic reactions supported a stepwise ionic hydroboration mechanism, involving the β-addition of a borenium cation,[97,98] leading to a vinyl carbocation intermediate **11b**, followed by hydride



Scheme 25 Cp*Si:$^{+}$-catalyzed hydrosilylation of alkynes. Cp* = pentamethylcyclopentadienyl.

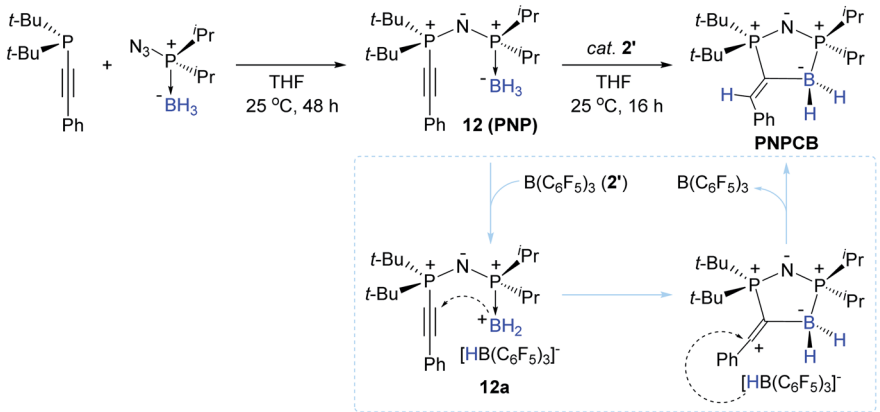
trans-hydroboration product (Scheme 26c).



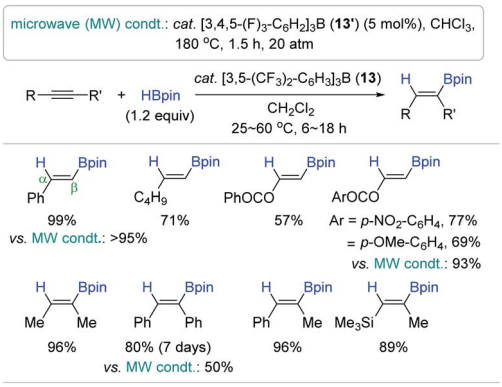
Scheme 26 (a) Stoichiometric and (b) catalytic *trans*-hydroboration of alkynes mediated by $B(C_6F_5)_3$, and (c) its plausible catalytic pathway.

transfer mainly from **11a** to the less hindered face of **11b** to release the *trans*-hydroboration product (Scheme 26c).

With interest in the synthesis of boron-containing heterocycles,[99–103] Stephan *et al.* previously reported a synthetic route to obtain unique B–N heterocycles *via* "click reactions" of boron-azides with (phospha)alkynes.[104] In a related effort, in 2016, Stephan *et al.* reported the stoichiometric reactions of alkynylphosphines with azido-phosphine-borane adducts,



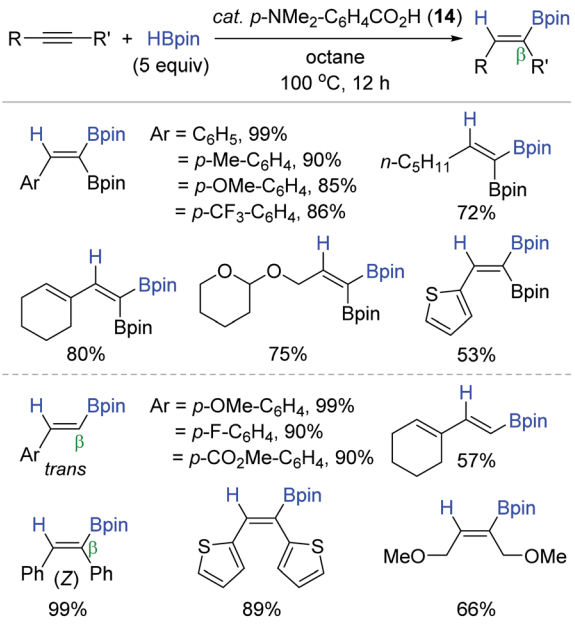
Scheme 27 $B(C_6F_5)_3$-catalyzed intramolecular *trans*-hydroboration of alkynylphosphines leading to B–P heterocycles.



Scheme 28 Lewis acidic borane-catalyzed *cis*-hydroboration of alkynes under conventional and microwave conditions.

forming a series of **PNP** species [representatively, *t*-Bu_2-P(C≡CPh)NP(BH_3)^iPr_2 (**12**)].[105] Interestingly, species **12** underwent an intramolecular *trans*-hydroboration at the phosphaalkynyl unit by the catalytic action of **2′** (10 mol%) to liberate the corresponding **PNPCB** heterocycle in 64% yield (Scheme 27). The reaction pathway leading to **PNPCB** from **12** was proposed to involve a borenium cation bearing $HB(C_6F_5)_3^-$ (**12a**) as the key intermediate. This outer-sphere mechanism was corroborated by the *trans*-added B–H moiety on **PNPCB**, as also shown in the report by Ingleson *et al.*[96]

Having sought a highly Lewis acidic, but functional group tolerant boron-based reduction catalyst, the Oestreich group previously synthesized tris[3,5-bis(trifluoromethyl)phenyl] borane as a catalyst for the hydroboration of alkenes and imines, and demonstrated its superior catalytic activity over the typical borane catalyst $B(C_6F_5)_3$ **2′**.[106,107] Motivated by Oestreich's work, the Melen group applied tris(2,4,6-trifluorophenyl)borane

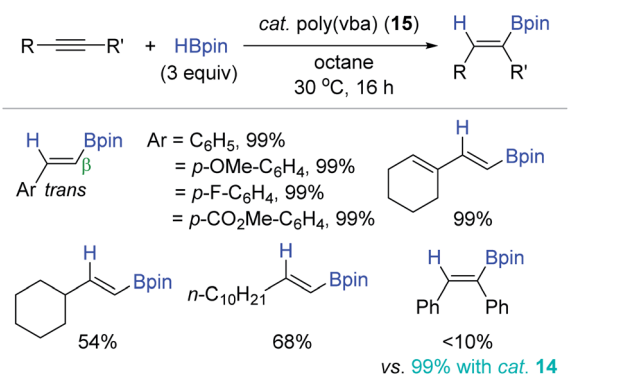


Scheme 29 Benzoic acid-catalyzed *cis*-hydroboration of alkynes.

13 as a mild Lewis acid catalyst for the hydroboration of alkynes.[108] It is noteworthy that the 1 : 1 reaction of **2′** and an alkyne led to 1,1-carboboration, whereas this carboboration did not occur with **13**. The hydroboration of a range of alkynes smoothly proceeded at 60 °C in the presence of **13** (2 mol%) to provide a range of β-vinyl boranes with good functional group tolerance (Scheme 28). It is intriguing to see that the alkenyl geometry of the resultant vinylboronate esters was determined to be a *trans* or (*Z*)-geometry, which was opposite to the stereo-outcome (*cis* or *E*) shown in Ingleson's reaction system.[96] Next, in an attempt to improve the catalytic efficiency, Melen *et al.* carried out the same hydroboration reaction under microwave irradiation conditions with a tris(3,4,5-trifluorophenyl)borane catalyst (**13′**).[109] The hydroboration was completed within 1.5 h under the microwave conditions (180 °C, 20 atm) to afford the *trans* or (*Z*)-products in good to high yields.

With an interest in the selective synthesis of 1,1-diborylalkenes[110–114] *via* the direct hydroboration of alkynylboronates, Jin and coworkers found that carboxylic acids were capable of catalyzing the targeted hydroboration reaction (Scheme 29).[115] This work represents the first direct hydroboration of alkynylboronates, and the first alkyne hydroboration catalyzed by carboxylic acids. A range of carboxylic acids with a pK_a of 4.2–5.0 worked well as the catalyst. The hydroboration of 2-phenyl-1-ethynylboronic acid pinacol ester with HBpin (5 equiv.) in the presence of 4-(dimethylamino)benzoic acid (**14**) (5 mol%) gave the 1,1-diborylalkene in quantitative yield in 12 h. Under these conditions, various alkynylboronates, and common terminal and internal alkynes were smoothly reduced with exclusive regio (β)- and stereoselectivity (*trans* or *Z*), and functional group compatibility with polar groups. Although the working mode of **14** remained unclear, a tentative pinacolboronate ester generated from **14** and HBpin was suggested as a key catalytic species for this hydroboration.[116–118]

Highly motivated by Jin's molecular benzoic acid catalyst, Jones *et al.* applied poly(vinyl benzoic acid) [poly(vba)] **15** as a heterogeneous catalyst for the hydroboration of alkynes (Scheme 30).[119] Phenylacetylene was cleanly hydroborated in the presence of **15** (5 mol%) to give the corresponding *trans*-2-styryl-Bpin in quantitative yield in 16 h. A variety of terminal alkynes were viable, in which aryl-substituted terminal alkynes were

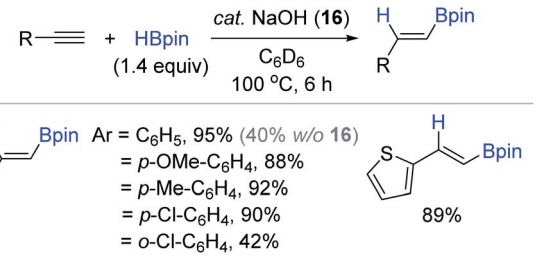


Scheme 30 Poly(vinyl benzoic acid)-catalyzed *cis*-hydroboration of alkynes.

more reactive than the alkyl-substituted alkynes toward hydroboration. However, unlike the catalyst system of **14**, the reactivity of internal alkynes with **15** was poor under the conditions presumably due to their steric effect, limiting access to the catalytic site on the polymer. Catalyst **15** was sparsely soluble in octane solvent, and thus was readily recycled up to the 3rd catalytic batch, maintaining its catalytic activity.

Based on the experimental mechanistic observations (1°-order in [**15**] and [HBpin], and fractional-order in [alkyne]; kinetic isotope effect KIE (k_H/k_D) ~ 0.5), a hypothetical reaction pathway was depicted, as shown in Scheme 31. The initial step is assumed to involve the interaction between a proton of a carboxylic acid and an alkyne to induce polarization over the alkyne unit. An HBpin bound at another acid site has close contact with the polarized alkyne moiety, where the turnover-limiting *syn*-addition of H–Bpin *via* a four-membered transition state occurs to release the β-*trans*-vinylborane with the regeneration of the catalytic site of **15**.

In addition to these Brönsted acid catalysts, Liu and Zhao reported the NaOH (**16**)-initiated hydroboration of terminal alkynes with HBpin.[120] This work is the first example of Brönsted base-catalyzed alkyne hydroboration. The preliminary NBO (natural bond orbital) calculations suggested that the HBpin-NaOH adduct would enhance its hydride character (hydricity) relative to free HBpin,[121,122] which was envisioned to facilitate the hydroboration process. Encouraged by this preliminary theoretical insight, a range of simple terminal alkynes were subjected to catalytic conditions [cat. NaOH (8 mol%), HBpin (1.4 equiv.), C_6D_6, 100 °C, 6 h] to reveal that the *trans*-vinyl products were obtained in moderate to excellent yields *via* the *syn*-addition of H–Bpin (Scheme 32). Notably, the product yield significantly decreased when the phenyl ring possessed an *ortho*-substituent. The stoichiometric reaction of HBpin with NaOH implied that various borohydride species including BH_3–NaOH could be responsible for the observed catalytic activity, as supported by the reports of Clark[123] and

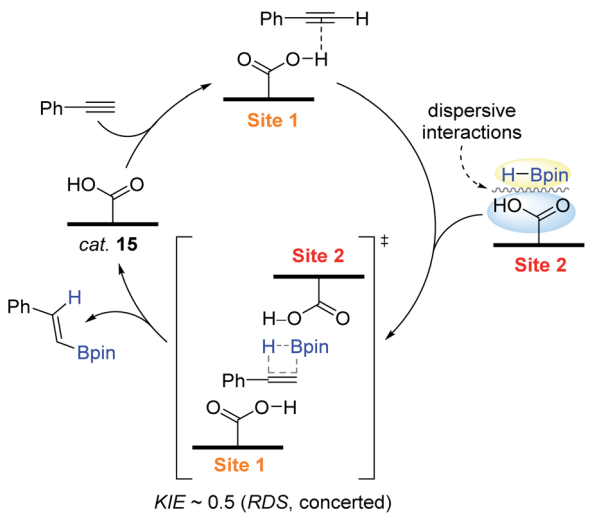


Scheme 32 NaOH-catalyzed *cis*-hydroboration of terminal arylalkynes.

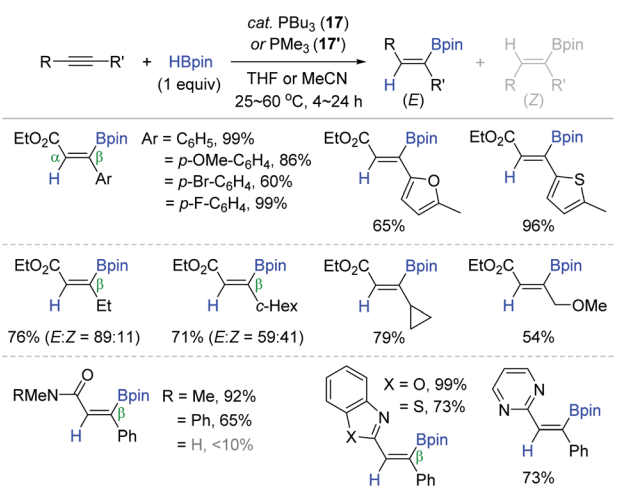
Fu,[124] where BH_3-base adducts generated from the reaction with NaO*t*-Bu or *N*,*N*-dimethylacetamide were observed.

Recently, Ohmiya and Sawamura documented the phosphine-catalyzed *trans*-addition of boron-containing interelement compounds across the C–C triple bond in alkynyloates, in which the electrophilic boron moiety was installed onto the electropositive carbon β to the carbonyl group to form a C(sp^2)–B bond.[125] As a continuing work, the Sawamura group succeeded in the phosphine-catalyzed *trans*-hydroboration of alkynoic acid derivatives, providing the β-(*E*)-alkenylboronates (Scheme 33).[126] Among various tertiary phosphines, the less bulky and electron-donor PBu_3 (**17**) or PMe_3 (**17′**) (2.5–20 mol%) showed the best catalytic performance with anti-selectivity. The reaction of a broad range of β-substituted alkynoates, alkynylamides, or alkynylazoles with HBpin afforded the β-borylated (*E*)-vinyl products in 54–99% yield at 25–60 °C, and various reducible groups were tolerant. It is noteworthy that the β-alkyl substituents on the alkyne substrates led to lower anti-selectivity, while primary and secondary alkynylamides were barely reactive.

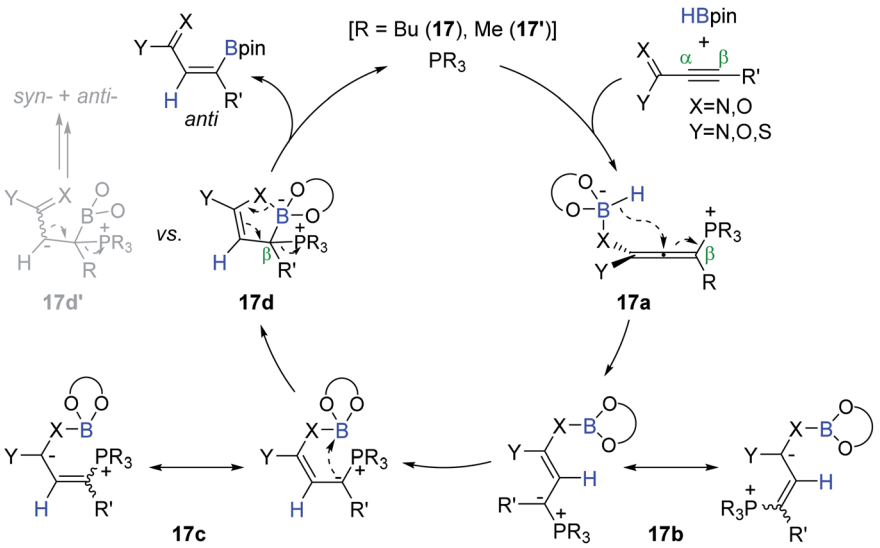
Based on their earlier work,[125,127,128] the catalytic pathway for the phosphine-catalyzed *trans*-hydroboration was proposed (Scheme 34). Initially, the alkyne is assumed to undergo conjugate addition of the phosphine (**17** or **17′**) to the electropositive β-carbon to form zwitterionic allene intermediate **17a**.



Scheme 31 Proposed pathway for the poly(vba)-catalyzed hydroboration of terminal alkynes.



Scheme 33 Trialkylphosphine-catalyzed *trans*-hydroboration of alkynoic acid derivatives.



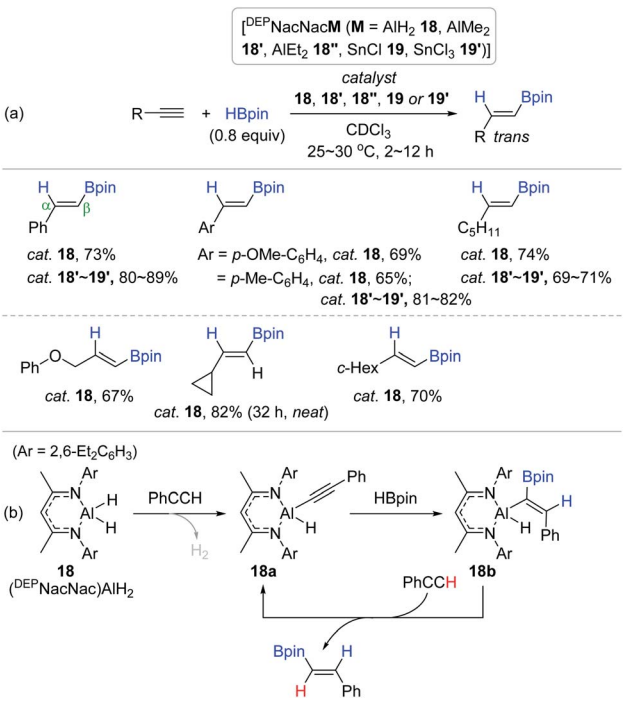
Scheme 34 Proposed pathway for the phosphine-catalyzed hydroboration of alkynoic acid derivatives.

The intramolecular hydride transfer to the allenyl central carbon in **17a** generates ylide intermediates **17b** and **17c**. The ylide carbon in **17c** is presumed to attack the proximal boron atom to form the corresponding cyclic borate **17d**. Finally, the phosphine catalyst is assumed to be regenerated with the release of the anti-hydroboration product upon concerted B–X (X = O, N) bond cleavage associated with the electron rearrangement on **17d**. When the Lewis acidity of a boron center in **17d** is lowered by β-alkyl-substituents, **17d** can be isomerized to **17d′** to eventually bring about a mixture of *anti*/*syn*-products.

Shortly after Sawamura's work, Santos *et al.* also reported the **17**-catalyzed *trans*-hydroboration of alkynoate esters and alkynylamides.[129] They reported similar reaction features to that observed previously. For example, the alkyl-substituted alkynoates at the β-position were converted to the β-borylacrylates with decreased (*E*)-selectivity, and the secondary alkynylamides were unreactive within the phosphine catalytic system.

Together with the transition metal-free organocatalysts for the hydroboration of alkynes, environmentally benign and commercially useful main-group catalysts based on Al,[90,130–139] Li,[138–142] and Mg[143,144] have been recently developed as alternatives to transition metal catalysts.[145] In 2016, Roesky *et al.* reported the *cis*-hydroboration of alkynes catalyzed by a neutral ^{DEP}NacNacAlH$_2$ (**18**).[90] This work represents the first hydroboration reaction catalyzed by a Group 13-based complex. A broad range of terminal alkynes reacted with HBpin in $CDCl_3$ in the presence of **18** (3 mol%) to afford the β-*trans*-vinylboronate esters in good yields in 12 h. Notably, the hydroboration of ethynylcyclopropane was sluggish (82% in 32 h in neat), and the reaction of internal alkynes did not proceed at all. Similar to Roesky's work, Ma and Yang prepared ^{DEP}NacNac-ligated Al and Sn complexes ($AlMe_2$ **18′**, $AlEt_2$ **18″**, SnCl **19**, and $SnCl_3$ **19′**) and demonstrated their good catalytic efficiency towards the *cis*-hydroboration of terminal alkynes (Scheme 35a).[130]

Based on DFT calculations, Roesky *et al.* proposed a catalytic pathway for the Al dihydride **18**-mediated hydroboration of phenylacetylene (Scheme 35b). The key step is suggested to involve the turnover-liming, dehydrogenative σ-bond metathesis between the Al–H in **18** and PhCC(sp)–H bonds, leading to aluminum acetylide **18a**. The alkynyl unit in **18a** is assumed to undergo *syn*-addition of HBpin to generate the alkenyl aluminium hydride **18b**, which likely reacts with the second molecule of phenylacetylene to release the (*E*)-vinylborane with the regeneration of the **18a** active species. Although the catalytic working modes of **18′**, **18″**, **19**, and **19″** remain unknown, the

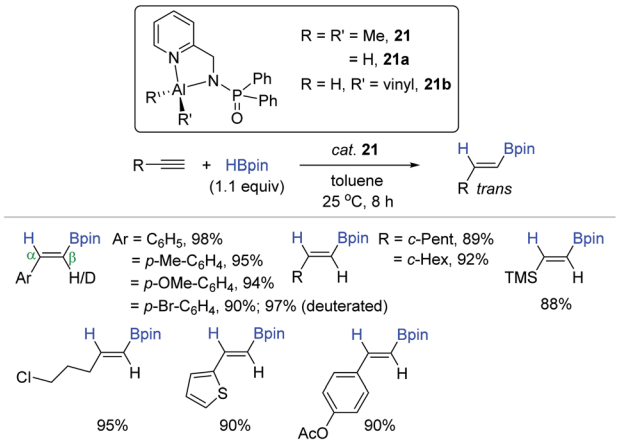


Scheme 35 (a) ^{DEP}NacNac-ligated Al or Sn complex-catalyzed *cis*-hydroboration of terminal alkynes and (b) proposed catalytic working mode of ^{DEP}NacNac-ligated AlH_2.

almost same yields by these catalysts indicate their similar reactivities towards alkyne hydroboration.[130]

Inspired by Roesky's NacNac-ligated Al(III) dihydride **18**, Nembenna *et al.* recently synthesized a bidentate bis-guanidinate-ligated Al(III) dihydride complex **20** as a multifunctional catalyst for the reduction of unsaturated functions including alkynes.[131] The reactions of various terminal alkynes with HBpin (1 equiv.) at 60 °C produced the β-*trans*-vinylboronate esters in 40–82% yield over 12 h in neat conditions (Scheme 36a). Notably, catalyst **20** enabled the hydroboration of internal alkynes, giving the (*Z*)-vinyl products in 30–40% yield, which could not be realized with the catalytic system of **18**.[90] The working mode of **20** in the hydroboration of terminal alkynes is assumed to involve aluminum acetylide species **20a**, which is the same as that proposed by Roesky.[90] However, the mechanism of the internal alkyne hydroboration is presumed to be associated with insertion of the alkyne into the Al–H bond of **20** as the key step to form aluminium vinyl intermediate **20b**, as previously proposed by Cowley and Thomas.[132] Subsequently, **20b** reacts with HBpin *via* transmetallation to liberate the (*Z*)-vinylboronate ester and active catalyst **20** (Scheme 36b). In fact, **20a** and **20b** were observed in the stoichiometric reactions of **20** with phenylacetylene and 1-phenyl-1-propyne, respectively.

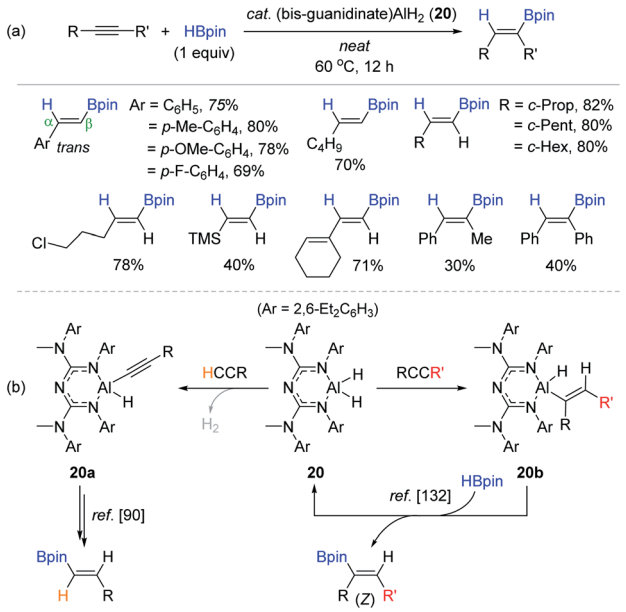
As another example of the *N*,*N*-bidentate ligand-based Al complex, Panda *et al.* synthesized an aluminum dimethyl complex supported by a functionalized amidophosphine ligand [κ^2-{$Ph_2P(=Se)NCH_2(C_5H_4N)$}$AlMe_2$, **21**][146] and applied it as a precatalyst for hydroboration of terminal alkynes (Scheme 37).[133] A range of terminal alkynes possessing electronically variable and/or reducible functional moieties were chemoselectively reduced with HBpin to the corresponding anti-Markovnikov alkenyl boronate esters with exclusive *trans*-selectivity under mild conditions [cat. **21** (3 mol%), toluene, 25 °C, 8 h]. The *trans* selectivity as the outcome of the *syn*-addition of HBpin into the alkyne was further confirmed in the hydroboration of 4-bromo-phenylacetylene-d_1. As proposed by Thomas and Cowley,[132] and Nembenna,[131] the **21**-catalyzed alkyne hydroboration proceeds *via* a "hydroalumination-metathesis" mechanism, where an aluminum dihydride (**21a**) and an aluminium vinyl hydride (**21b**) are regarded as the key species.



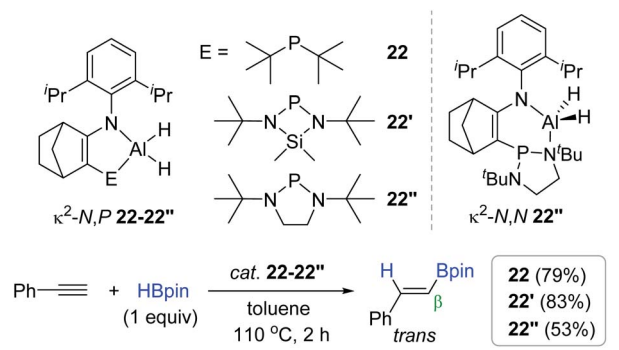
Scheme 37 *N*,*N*-Bidentate Al(III) complex-catalyzed *cis*-hydroboration of terminal alkynes.

Together with a range of bidentate Al hydroboration catalysts,[90,130,131,133] Cowley recently communicated a series of new aluminium dihydride complexes with bidentate *N*,*P*-ligands (**22**, **22′**, and **22″**) as the alkyne hydroboration catalyst.[134] These dihydride species (10 mol%) were found to catalyze the hydroboration of phenylacetylene at 110 °C to give the *trans*-vinylboronate ester with excellent β-selectivity in good yields. It is noteworthy that catalyst **22″** exhibited a slightly lower catalytic activity (53%) than that (79–83%) of **22**–**22′**. This lower activity was ascribed to the reversible phosphine slip on **22″** involving an isomer of κ^2-*N*,*N* geometry (κ^2-*N*,*N* **22″**) during the catalysis (Scheme 38).

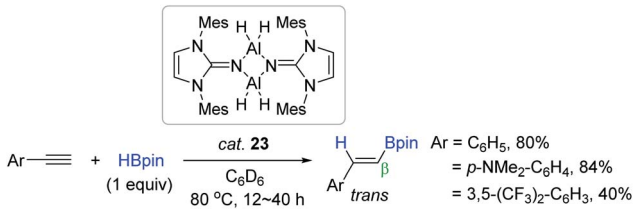
Inoue synthesized a monodentate *N*-heterocyclic imine-stabilized dimeric aluminium dihydride [$^{Mes}LNAlH_2]_2$ **23**



Scheme 36 (a) Bis-guanidinate-ligated Al dihydride-catalyzed *cis*-hydroboration of alkynes and (b) its dual catalytic working modes depending on the type of alkyne substrate (terminal *vs.* internal).



Scheme 38 *N*,*P*-Bidentate Al(III) complex-catalyzed *cis*-hydroboration of phenylacetylene.



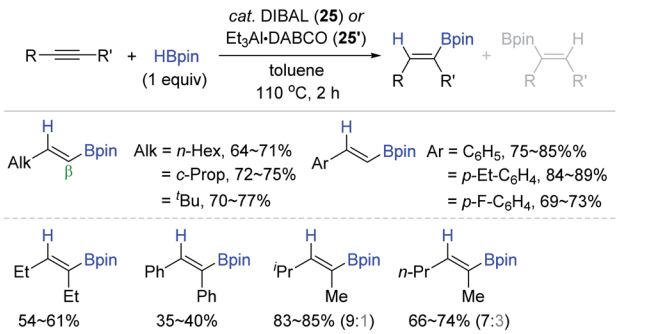
Scheme 39 *N*-heterocyclic imine-ligated Al dihydride-catalyzed *cis*-hydroboration of terminal alkynes.

(^{Mes}LN = 1,3-dimesityl-imidazolin-2-imino, Mes = 2,4,6-trimethylphenyl) and utilized it as a catalyst for the hydroboration of alkynes. The reaction of electron-neutral or -rich terminal arylalkynes proceeded with good efficiency in the presence of **23** (4 mol%) at 80 °C to afford the β-*trans*-vinylboronate esters, while an electron-deficient arylalkyne was slowly converted to the desired vinyl product (40% in 40 h) (Scheme 39).[135] In the proposed catalytic cycle, **23** is assumed to be transformed to an alkynyl aluminium species, which is similar to Roesky's catalytic working mode.[90]

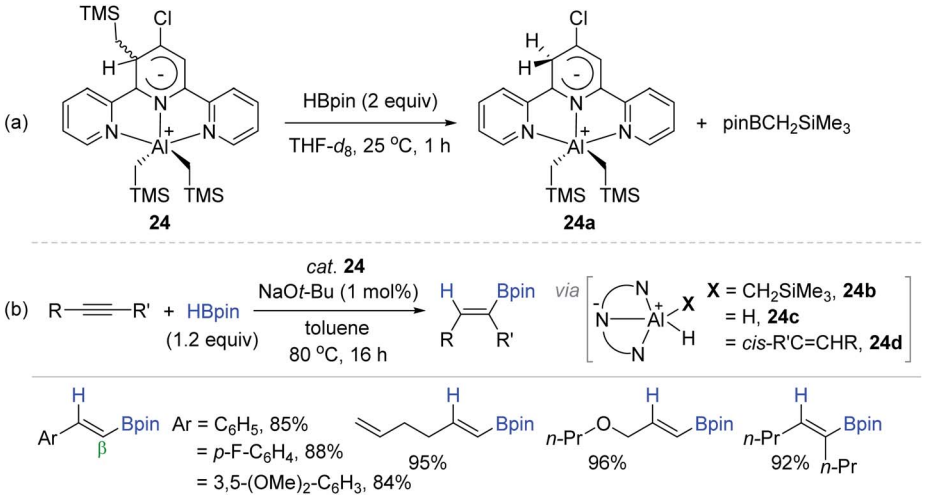
Dub and coworkers were interested in terpyridine (tpy)-based redox active Al complexes[147] and finally serendipitously synthesized a tridentate tpy-ligated aluminium dialkyl complex (**24**)[136] that uniquely featured a zwitterionic Meisenheimer-type nature.[148] The stoichiometric reaction of **24** with 2 equivalents of HBpin at 25 °C generated complex **24a** with the byproduct ($pinBCH_2SiMe_3$) formation (Scheme 40a). Based on this result and computational studies, species **24a** was assumed to be converted to the aluminium (di)hydride species (**24b–c**) *via* consecutive metathesis processes of **24a** with excess HBpin, which was active species for hydroboration of alkynes. Indeed, **24** was shown to serve as a precatalyst for the *cis*-hydroboration of alkynes at 80 °C, providing a range of β-*trans*- or (*Z*)-vinylboronate esters in 84–96% yield with remarkable functional group tolerance. It needs to be emphasized that precatalyst **24** displayed a TON of 910, the highest among the Al-catalyzed alkyne hydroboration reactions. The hydroboration of alkyne was suggested to proceed *via* hydroalumination-metathesis processes involving alkenyl aluminium intermediate **24d** (Scheme 40b).

Considering the practicality of the Al catalytic procedure, Thomas and Cowley developed a more convenient aluminium catalytic system for alkyne hydroboration by employing the commercially available diisobutylaluminium hydride [DIBAL, (^{i}Bu$_2$AlH)$_2$] **25** and bench-stable Et$_3$Al·DABCO **25′** (DABCO = 1,4-diazabicyclo[2.2.2]octane) as (pre)catalysts.[132] It is noteworthy that these (pre)catalysts required no external ligand(s) in accomplishing the anti-Markovnikov (β), *cis*-selective hydroboration. Although the hydroboration occurred at 110 °C higher than Roesky's condition (30 °C), the substrate scope was broad, including various terminal and (non)symmetrical internal alkynes with moderate to high catalytic efficiency (Scheme 41).

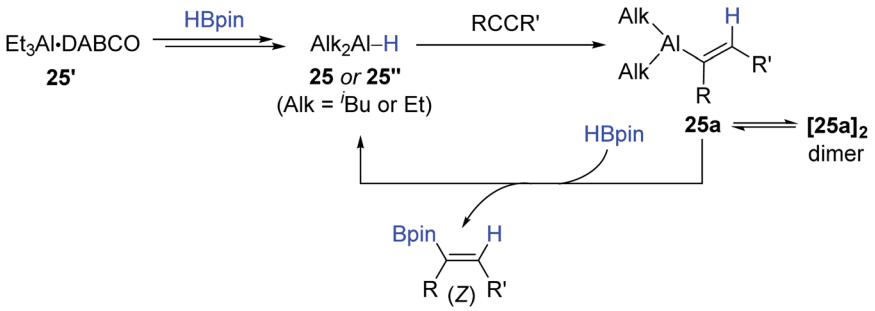
A plausible mechanism for the **25**- or **25′**-catalyzed alkyne hydroboration was proposed (Scheme 42). Initially, the aluminium hydride, which can be **25** or a hydridoalane **25″**, is assumed to undergo the anti-Markovnikov-selective insertion of an alkyne to form alkenyl aluminum species **25a**, which reacts



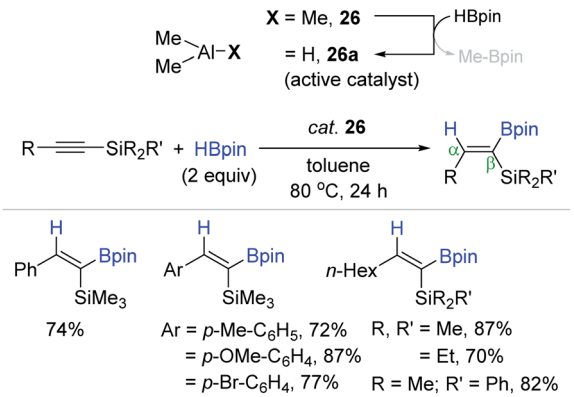
Scheme 41 External ligand-free Al(III)-catalyzed *cis*-hydroboration of alkynes. DIBAL = diisobutylaluminium hydride.



Scheme 40 (a) Stoichiometric reaction of the zwitterionic Meisenheimer Al(III) complex with HBpin, and (b) its catalytic scope towards the *cis*-hydroboration of alkynes. tpy = terpyridine.



Scheme 42 Proposed pathway for the external ligand-free Al(III)-catalyzed *cis*-hydroboration of alkynes.

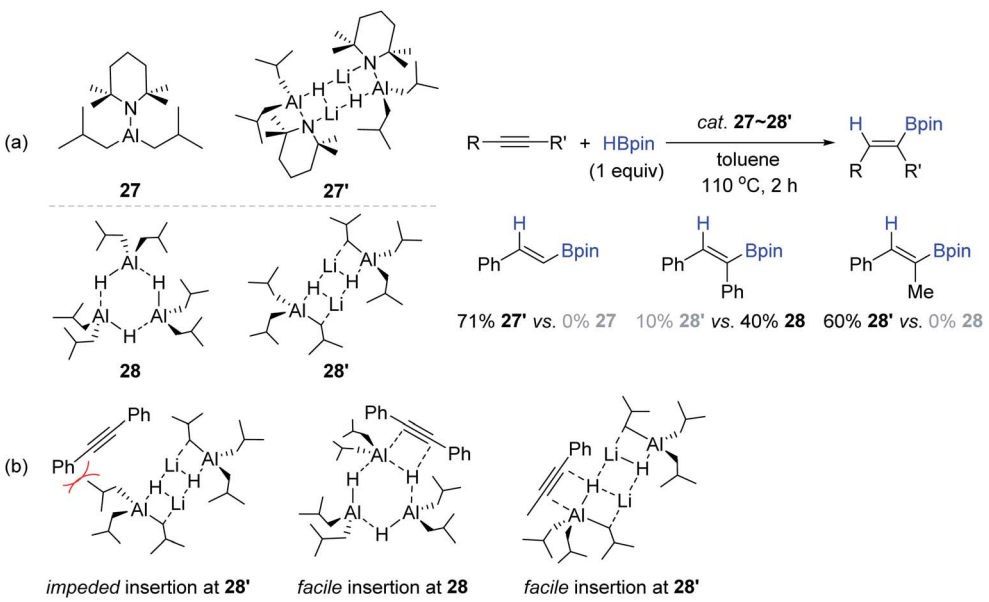


Scheme 43 $AlMe_3$-catalyzed *cis*-hydroboration of alkynylsilanes.

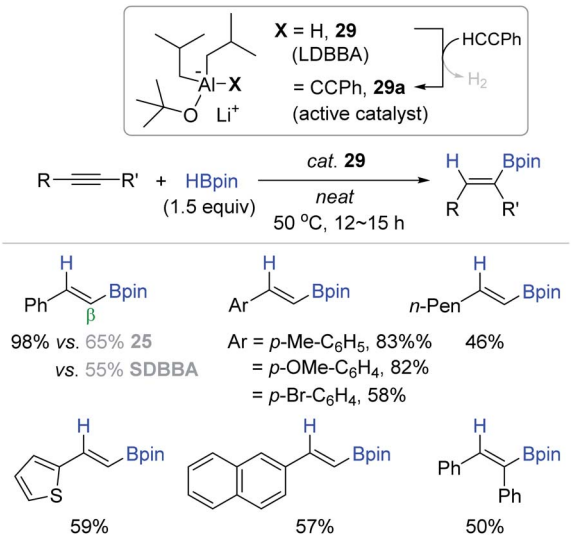
with HBpin *via* a turnover-limiting σ-bond metathesis to deliver the *trans*- or (*Z*)-hydroboration products and regenerate the active catalyst **25** or **25″**. In fact, the stoichiometric reaction of an isolated dimer $[\mathbf{25a}]_2$ with HBpin gave the borylated alkene, and **25a** turned out to work as a catalyst for the alkyne hydroboration, corroborating the alkyne hydroalumination–σ-bond metathesis mechanism. DABCO as a base on **25′** was suggested to play a role in inhibiting the decomposition of the aluminium catalyst, as evidenced by the outcome from the stoichiometric reaction of Et_3Al, HBpin, and DABCO.

Following the work by Thomas and Cowley,[132] Shi *et al.* recently reported the *cis*-hydroboration of alkynylsilanes catalyzed by the commercially available and external ligand-free $AlMe_3$ (**26**). The reaction occurred at 80 °C in the presence of **26** (20 mol%) to produce a range of β-(*Z*)-alkenes bearing both $C(sp^2)$–Si and $C(sp^2)$–B moieties in moderate to high yields in 24 h (Scheme 43).[137] $HAlMe_2$ (**26a**) as an active catalyst for the alkyne hydroboration was suggested to be generated *in situ via* an σ-bond metathesis reaction between **26** and HBpin.

With interest in the possible influence of the lithium element within bimetallic Al–Li catalysts,[149–151] Mulvey compared the catalyst reactivity for the alkyne hydroboration between neutral monometallic Al complexes (**27** and **27′**) and their corresponding anionic bimetallic lithium aluminates (**28**



Scheme 44 (a) Neutral or anionic Al(III)-catalyzed *cis*-hydroboration of alkynes, and (b) comparative insertion modes of alkynes into the Al–H bonds.

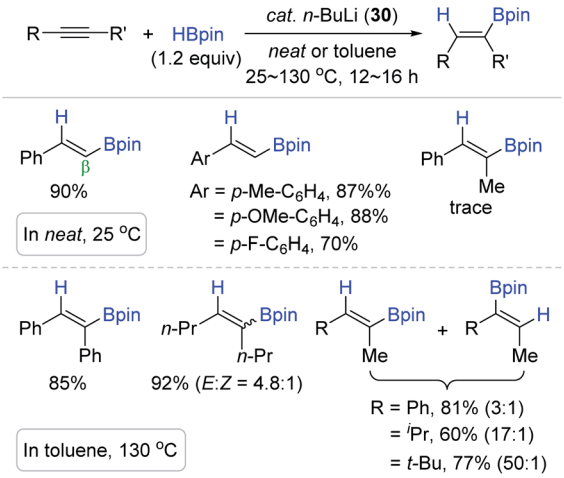


Scheme 45 Anionic Al(III)-catalyzed *cis*-hydroboration of alkynes. LDBBA = lithium diisobutyl-*tert*-butoxyaluminum hydride; SDBBA = sodium diisobutyl-*tert*-butoxyaluminum hydride.

and **28′**) (Scheme 44a).[138] Under identical catalytic conditions [cat. Al (10 mol%), toluene-d_8, 110 °C, 2 h], three types of simple alkynes were examined for hydroboration, revealing that the lithium aluminates **27′** and **28′** exhibited superior reactivity to phenylacetylene and 1-phenyl-propyne, respectively, when compared in parallel to their counterparts of monometallic aluminium catalysts (**27** and **28**). However, catalyst **28** was found to be more active than **28′** in the hydroboration of diphenylacetylene. The lower reactivity of **28′** was attributed to the steric repulsion between the isobutyl moiety on **28′** and phenyl group on the substrate (Scheme 44b).

Based on the report by Mulvey, the An group successfully applied lithium diisobutyl-*tert*-butoxyaluminum hydride (LDBBA, **29**) as a bimetallic lithium aluminate catalyst for the hydroboration of alkynes.[139] The reactions of a range of alkynes occurred in neat conditions at 50 °C with catalyst **29** (5 mol%) to furnish the corresponding β-*trans*-alkenyl boronates in 46–98% yield (Scheme 45). Electron-deficient or internal alkynes were less reactive relative to electron-rich or terminal alkynes, giving moderate yields of the desired vinyl products. It is noteworthy that **29** displayed higher hydroboration activity compared to a series of neutral or anionic Al-based (pre)catalysts including DIBAL **25** and SDBBA (sodium diisobutyl-*tert*-butoxyaluminum hydride). As proposed by the Roesky group,[90] the catalytic pathway was suggested to involve the dehydrogenative C–H alumination of a terminal alkyne to generate an acetylide aluminium species (**29a**) in the initiation step.

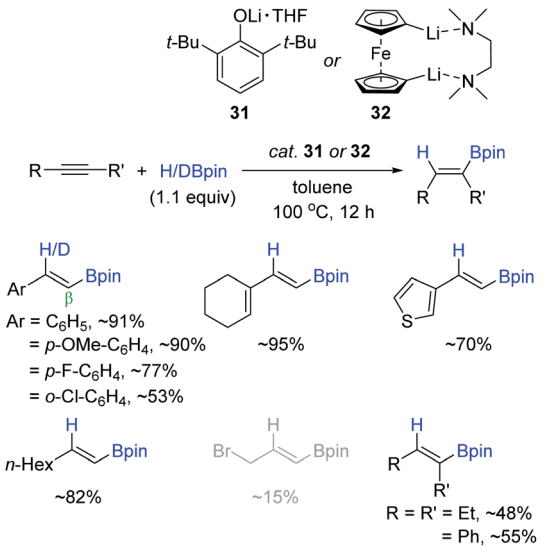
Recently, the groups of Xue[140] and Xu[141] independently demonstrated that highly basic and commercially available *n*-BuLi (**30**) catalyzes the *cis*-hydroboration of terminal and internal alkynes to produce the β-*trans*-alkenyl boronic esters (Scheme 46). Under the *n*-BuLi (**30**) catalytic system, terminal alkynes were hydroborated with HBpin in neat conditions at 25 °C, while the hydroboration of (un)symmetrical internal



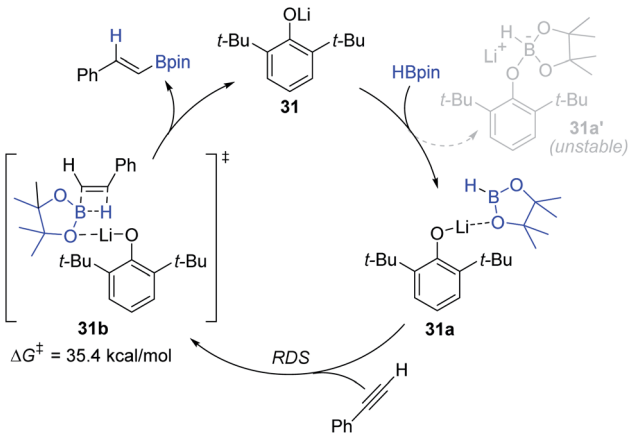
Scheme 46 *n*-BuLi-catalyzed *cis*-hydroboration of alkynes.

alkynes occurred at 130 °C to give a mixture of regio- or stereoisomers of the vinyl products. It is interesting to see that the regioselectivity was improved from 3 : 1 to 50 : 1 with an increase in the steric difference between the two substituents on the unsymmetrical internal alkynes.

Although *n*-BuLi (**30**) worked as a hydroboration catalyst, its instability and inferior functional group compatibility were problematic. In this regard, Sen *et al.* applied sterically protected lithium complexes [2,6-ditertbutyl phenolatelithium (**31**) and 1,1′-dilithioferrocene (**32**)] as the alkyne hydroboration catalyst (Scheme 47).[142] The reactions proceeded at 100 °C with 2 mol% of catalyst **31** or **32** to provide the β-*trans*-alkenyl boronate esters in good to high yields in 12 h. However, internal alkynes were relatively less reactive (up to ~50% yield), and halogen substituents on the alkyne substrates partially underwent lithium–halide exchange, resulting in a decrease in catalytic efficiency.



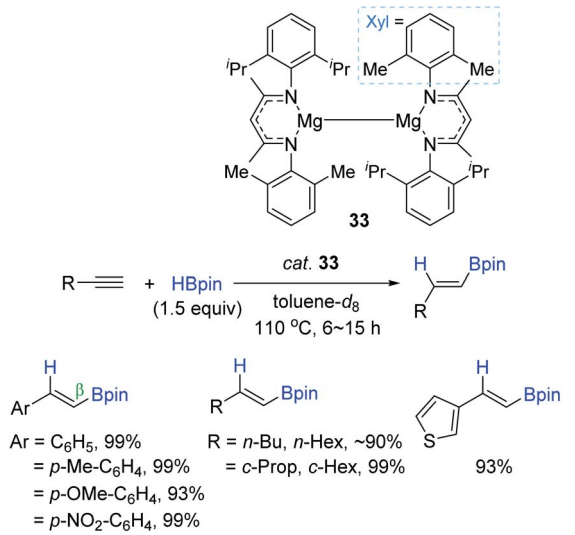
Scheme 47 Sterically demanding Li complex-catalyzed *cis*-hydroboration of alkynes.



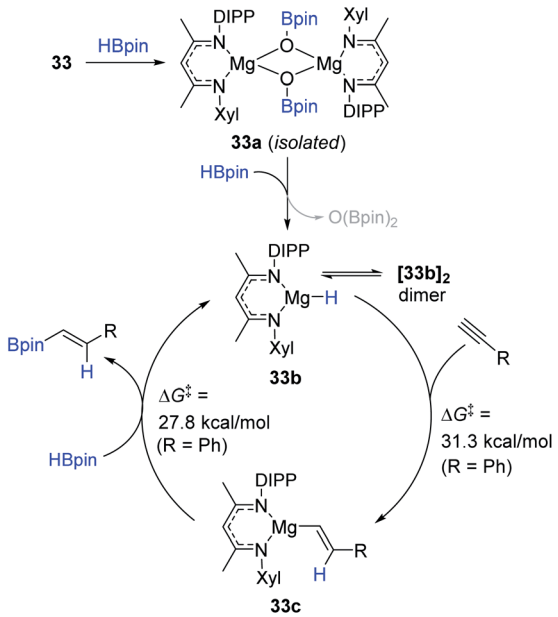
Scheme 48 Proposed pathway for the Li-catalyzed hydroboration of alkynes.

Based on DFT calculations, the **31**-mediated reaction mechanism was proposed (Scheme 48). Initially, a lithium cation in **31** weakly coordinates to the oxygen atom of HBpin to form adduct **31a**, which is calculated to be more stable than lithium borate salt **31a′**. The polarized H–B bond in **31a** is presumed to insert into the alkyne in an anti-Markovnikov manner *via* transition state **31b** ($\Delta G^{\ddagger}$ = 35.4 kcal mol^{-1}) to deliver the alkenyl boronate ester with the regeneration of **31**. This step is regarded as the rate-determining step (RDS).

In parallel with aluminium-based catalysts, a few Mg complexes were shown to catalyze the *cis*-hydroboration of alkynes.[143,144] In 2018, Ma *et al.* synthesized a dimeric Mg(I) complex with unsymmetrical ^{Ar}NacNac ligands as a hydroboration catalyst (**33**).[143] Notably, the dimeric Mg(I) complex **33** was prepared through the reduction of ^{Ar}NacNacMg(II) halide with excess sodium metal. Also, **33** (5 mol%) with HBpin (1.5 equiv.) was found to enable hydroboration of terminal alkynes,



Scheme 49 Unsymmetrical NacNac-ligated dimeric Mg(I)-catalyzed *cis*-hydroboration of terminal alkynes.



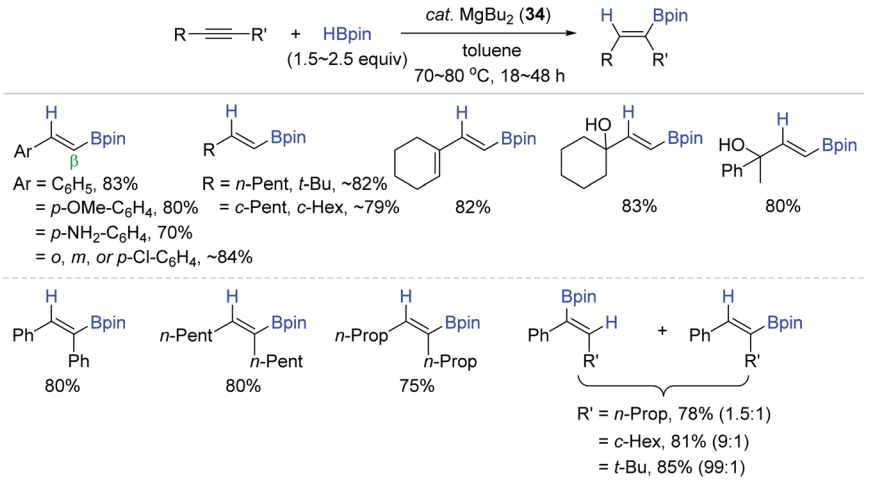
Scheme 50 Proposed pathway for the Mg(I)-catalyzed hydroboration of terminal alkynes.

producing the β-*trans*-alkenyl boronates in excellent yields at 110 °C. However, the dimeric Mg(I) with the symmetrical ligand (^{DIPP}NacNac) displayed a slightly lower catalytic performance in the hydroboration of phenylacetylene [88% (not-shown) *vs.* 99% **33**] (Scheme 49). This work represents the first Mg(I)-catalyzed hydroboration of alkynes.

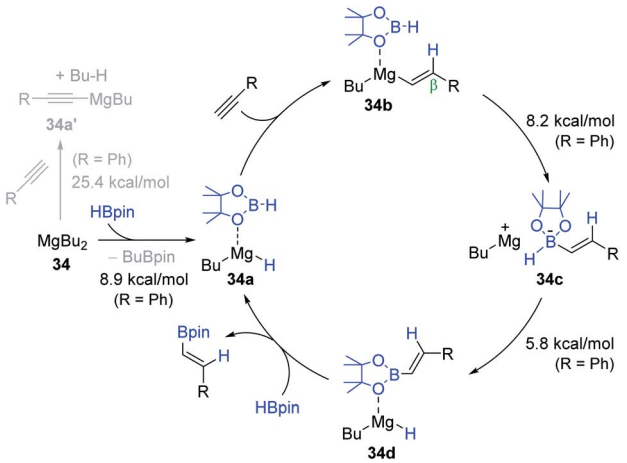
Based on experimental observations in combination with computational studies, a catalytic pathway for the **33**-promoted hydroboration of terminal alkynes was proposed (Scheme 50). Specifically, **33** is assumed to react with HBpin to lead to a dimeric Mg boryloxide complex (**33a**).[152] Indeed, **33a** was isolated as crystals during the catalysis. Species **33a** is subsequently transformed to monomeric Mg hydride **33b** with HBpin. Subsequently, **33b** as the active catalyst likely undergoes turnover-liming *syn*-addition of the alkyne (R = Ph, $\Delta G^{\ddagger}$ = 31.3 kcal mol^{-1}) to form **33c**, which is further metathesized with HBpin to release the *trans*-vinyl product (R = Ph, $\Delta G^{\ddagger}$ = 27.8 kcal mol^{-1}) with the regeneration of **33b**.

Motivated by Ma's work, where the Mg(II) hydride was regarded as the active catalytic species, Rueping *et al.* reported a simpler and external ligand-free Mg catalyst [$MgBu_2$ (**34**)] for alkyne hydroboration.[144] Precatalyst **34** (7–10 mol%) with HBpin catalyzed the hydroboration of a broad range of alkynes at 80 °C with wide functional compatibility to alkoxy, amino, halide, alkenyl, and hydroxy groups, giving the β-*trans*-vinylboronate esters in good to high yields (Scheme 51). As observed in the lithium catalysis,[141] the regioselectivity in the case of unsymmetrical internal alkynes was improved from 1.5 : 1 up to >99 : 1 by increasing the differential steric effect of the substituents (R and R′).

Based on stoichiometric reactions and DFT calculations, a catalytic cycle for **34**-promoted alkyne hydroboration was proposed (Scheme 52). Initially, $MgBu_2$ in the presence of



Scheme 51 $MgBu_2$-catalyzed *cis*-hydroboration of alkynes.



Scheme 52 Proposed pathway for the $MgBu_2$-mediated hydroboration of terminal alkynes.

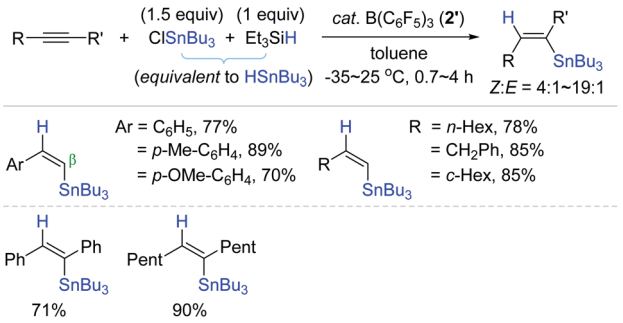
HBpin likely prefers to be BuMgH (**34a**) over an alkynyl MgBu (**34a′**), as predicted by the computational study (R = Ph, $\Delta\Delta G^{\ddagger}$ = 16.5 kcal mol^{-1}). Indeed, the stoichiometric reaction of **34** and excess HBpin was found to generate **34a**. Specifically, **34a** is assumed to undergo β-selective, *syn*-addition of an alkyne to afford Mg-vinyl intermediate **34b**. The next step is suggested to involve the inner-sphere nucleophilic migration of the vinyl moiety to the coordinated HBpin to form zwitterionic intermediate **34c**, which is subsequently isomerized to BuMg–H species **34d** *via* hydride migration from the boron to magnesium centers. These inner-sphere migration processes were calculated to require activation energy of less than 10 kcal mol^{-1}, and thus are highly facile (R = Ph). The vinyl product is suggested to be liberated from **34d** with the regeneration of **34a**.

Recently, Thomas *et al.* re-investigated the alkyne hydroboration promoted by a series of nucleophiles with strong focus on the elucidation of the dominant active catalytic species.[153] Surprisingly, the results suggested that several nucleophilic (pre)catalysts promote the decomposition of HBpin to generate BH_3 and its borohydride species *in situ*, which are potentially active species for the alkyne hydroboration. Among the tested (pre)catalysts, particularly NaOt-Bu, $MgBu_2$ (**34**), and *n*-BuLi (**30**) indeed turned out to serve as a promoter only for the HBpin decomposition, not for the main hydroboration process.

4. Hydrostannation and hydrogermylation

Alkenylstannes are valuable synthetic intermediates, allowing mild cross-coupling reactions and leading to $C(sp^2)$–$C(sp^2)$ bonds with high functional group tolerance,[7,15] and thus are applied in the synthesis of densely functionalized (un)natural compounds.[154–158] In this regard, the transition metal-catalyzed hydrostannation of alkynes providing alkenylstannes has been extensively studied to date,[23–25] while the transition metal-free catalysts have been relatively less highlighted, and thus are detailed in this section (*vide infra*). In 1998, Yamamoto *et al.* reported the $B(C_6F_5)_3$ **2′**-catalyzed hydrostannation of a range of terminal and internal alkynes with Bu_3SnH, *in situ* generated from Bu_3SnCl and Et_3SiH in one pot. This study represents the first transition metal-free hydrostannation of alkynes. The reactions proceeded at −35–25 °C to give the β-*cis*-vinylstannes in 70–90% yield *via* the *trans*-addition of an Sn–H bond (Scheme 53).[159]

The Maleczka group previously reported the *in situ* reduction of organotin halides to organotin hydrides involving an organotin oxide intermediate in the presence of aqueous Na_2CO_3 and PMHS (polymethylhydrosiloxane).[160–162] Based on this and Yamamoto's protocol,[159] Maleczka *et al.* developed a one-pot allylation-hydrostannation sequence for the reduction of alkynals, in which tin halide as the initial product was reduced to an organotin hydride, and this tin hydride was subsequently consumed for the hydrostannation of the alkyne unit on the allylated intermediate in the catalytic system of **2′**/PMHS (Scheme 54).[163] Under the optimal conditions [(i) $BF_3{\cdot}OEt_2$ and allylstannes (1 equiv.), toluene, −35 °C, ~1.5 h and (ii) $B(C_6F_5)_3$



Scheme 53 $B(C_6F_5)_3$-catalyzed *trans*-hydrostannation of alkynes.

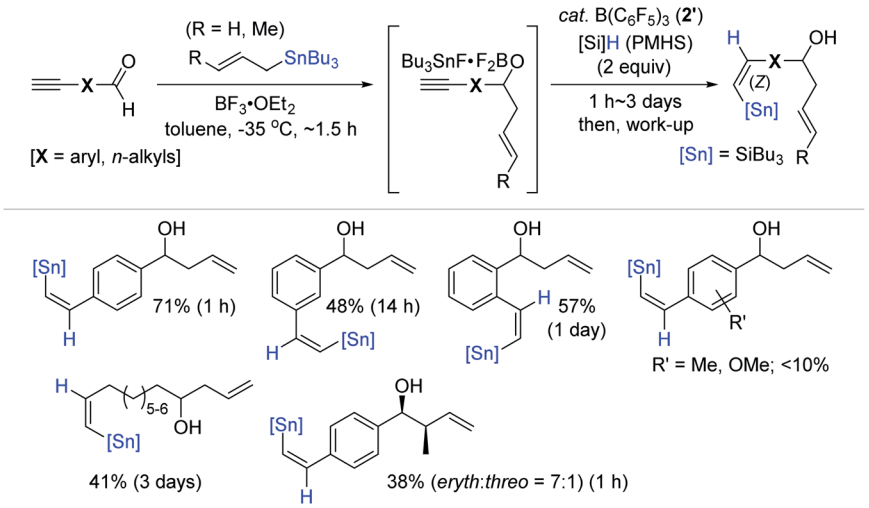
(20 mol%), PMHS (2 equiv.), ~3 days], the sequential reduction of a series of alkynals was performed, demonstrating that this tandem reaction is highly susceptible to both steric and electronic factors. For example, an electron-donating or any substituent close to the aldehyde moiety on the aromatic alkynal substrates halted or slowed down the desired one-pot process, while aliphatic alkynals were less reactive compared to aromatic alkynals, requiring 3 days to achieve ~40% yield.

Based on the NMR-monitoring of the reaction progress, a catalytic pathway for the tandem reductive transformation of alkynals was proposed (Scheme 55). Initially, the aldehyde likely forms an adduct with $BF_3{\cdot}OEt_2$, which rapidly undergoes allylation by tributyl(allyl)tin (^{119}Sn δ −18) to form a boryl ether complexed with a stannyl cation species (**35a**, ^{119}Sn δ 156).[164–166]

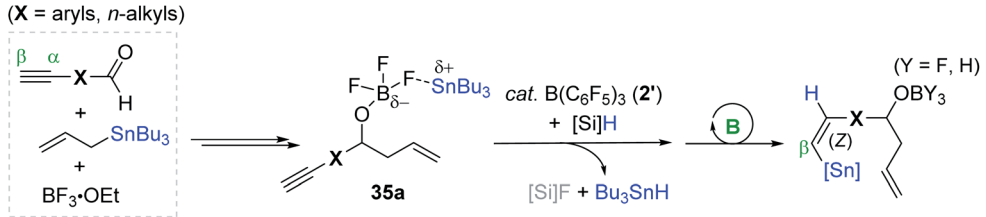
Subsequently, **35a** is suggested to react with the $B(C_6F_5)_3$-PMHS adduct to generate tributyltin hydride (Bu_3SnH; ^{119}Sn δ −88),[167] which is then *trans*-added to the alkyne moiety on **35a** by the action of **2′** to eventually yield the allylation-hydrostannation (*Z*)-product (^{119}Sn δ −56).

Based on Yamamoto's hydrostannation procedure,[159] Organ *et al.* conceived to hydrostannylate complex internal alkynes using catalyst **2′**, and found that $B(C_6F_5)_3$ **2′** enabled the regio- and stereoselective hydrostannation of densely functionalized, internal propargylic alcohol derivatives (Scheme 56).[168] This work represents the first metal-free catalytic hydrostannation of propargylic alcohols. The reaction of 1-*tert*-butyldimethylsilyloxy-2-butene with Bu_3SnH (2 equiv.) smoothly proceeded at 50 °C in toluene in the presence of $B(C_6F_5)_3$ **2′** (20 mol%) to quantitatively give the β-(*Z*)-vinylstannane. However, the reactions of hindered alkynes occurred only in THF solvent in high yields rather than in toluene. The observed solvent-specificity of the $B(C_6F_5)_3$ catalysis was explained by the fact that THF, as a coordinating solvent, assists in stabilizing the stannyl cation (*in situ* generated) by forming a solvated adduct $[Bu_3Sn{\cdot}THF]^+$ $HB(C_6F_5)_3^-$ (**35b**),[169,170] whereas less bulky alkynes in toluene can directly coordinate to the stannyl cation to form adduct **35c**. Indeed, **35b** was found to be quantitatively generated from the reaction of **2′** with excess Bu_3SnH in C_6D_6/THF (1 : 1).

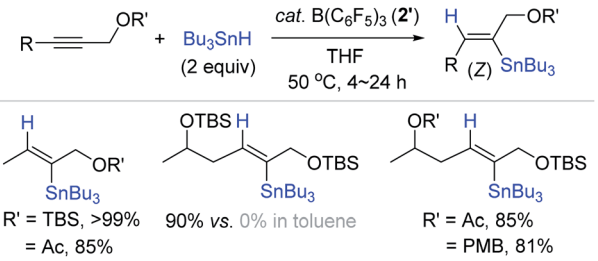
An outer-sphere ionic pathway was proposed for the $B(C_6F_5)_3$-catalyzed alkyne hydrostannation (Scheme 57). Species **35b** or **35c** is presumed to insert into the β-position of the



Scheme 54 $B(C_6F_5)_3$-mediated one-pot allylation-hydrostannation of alkynals.



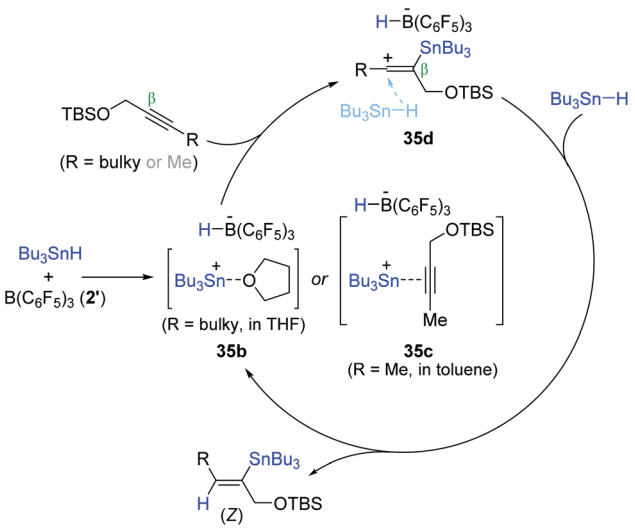
Scheme 55 Proposed reaction pathway for the $B(C_6F_5)_3$-mediated allylation-hydrostannation of alkynals.



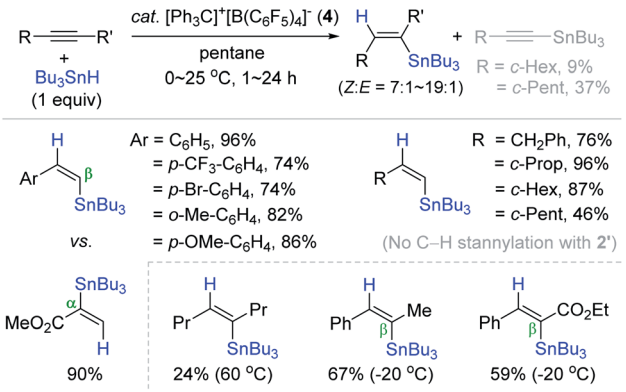
Scheme 56 $B(C_6F_5)_3$-catalyzed *trans*-hydrostannation of internal propargylic alcohol derivatives. TBS = *tert*-butyldimethylsilyl, Ac = acyl, PMB = *p*-methoxybenzyl.

alkyne molecule to form a vinylcation bearing a $HB(C_6F_5)_3^-$ anion (**35d**), which is reduced by "Bu_3SnH" not $HB(C_6F_5)_3^-$ to deliver the hydrostannation product with the regeneration of the stannyl cation. It is noteworthy that the stoichiometric reaction of **35b** with 1-*tert*-butyldimethylsilyloxy-2-butene in the presence of Bu_3SnH (2 equiv.) gave the (*Z*)-vinylstanne in quantitative yield, but no hydrostannation product was observed in the absence of Bu_3SnH, corroborating the role of $HB(C_6F_5)_3^-$ and Bu_3SnH as a spectator counterion and a hydride donor, respectively.[171–173]

Based on Yamamoto and Organ's outer-sphere hydrostannation reactions,[159,168] Oestreich *et al.* reported the catalytic system of $[Ph_3C]^+[B(C_6F_5)_4]^-$ (**4**)/Bu_3SnH, generating a catalytically competent stannyl cation species *in situ* for the *trans*-hydrostannation of alkynes.[174] The hydrostannation of phenylacetylene derivatives proceeded under mild conditions [cat. **4** (1 mol%), pentane, 0–25 °C, 1–24 h] to furnish the desired β-vinylstannes in 74–96% yield with *cis*-selectivity ranging from 87% to 95% (Scheme 58). It is interesting that propiolic acid methyl ester cleanly reacted with α-regioselectivity. This catalytic system was well-tolerant of halogen, alkoxy, and ester groups, whereas an amino substituent



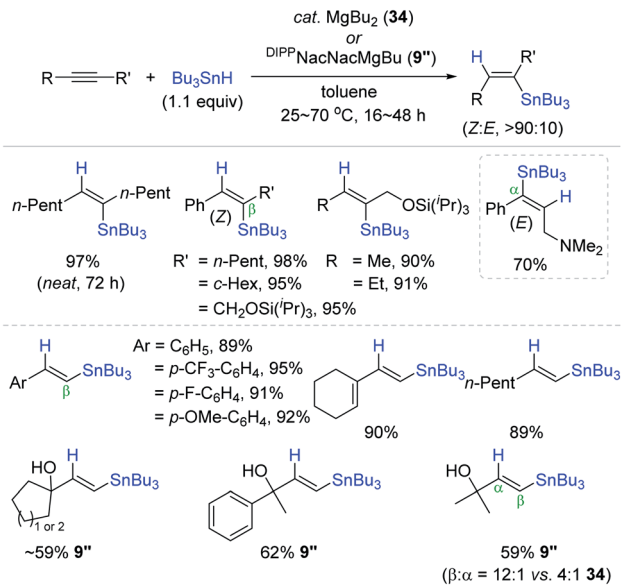
Scheme 57 Proposed pathway for the $B(C_6F_5)_3$-catalyzed hydrostannation of propargylic alcohol derivatives.



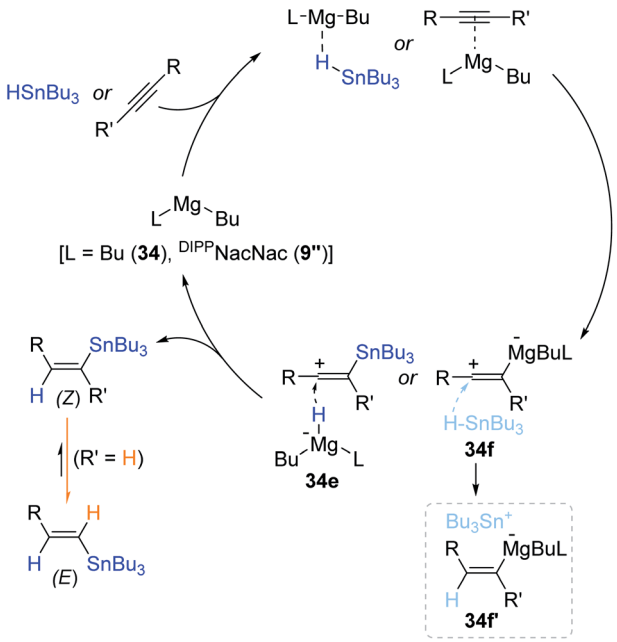
Scheme 58 Trityl borate salt-catalyzed *trans*-hydrostannation of alkynes.

deactivated the catalyst. Only few alkyl-substituted terminal alkynes were cleanly converted to the corresponding β-*cis*-vinylstannes. Some of the hindered alkynes underwent the undesirable dehydrogenative C–H stannylation (*ca.* 10–40%). Interestingly, the C–H stannylation products were not observed under the catalytic system of $B(C_6F_5)_3$, **2′** (*vide supra*).[159] Internal alkynes were also reduced with excellent (*Z*)-selectivity, and the regioselectivity in the case of unsymmetrical internal alkynes possessing a phenyl group was well controlled to be β-preferred.

Recently, Reuping *et al.* successfully expanded the scope of $MgBu_2$ (**34**) catalysis from hydroboration[144] to the hydrostannation of alkynes (Scheme 59).[175] A range of (un)symmetrical internal alkynes were cleanly reduced with Bu_3SnH at 50 °C in the presence of **34** (10 mol%) to the β-vinylstannes in 70–98% yield with high (*Z*)-selectivity as the outcome of the anti-addition of H–$SnBu_3$. Intriguingly, an internal alkyne bearing an NMe_2 substituent was reduced in the opposite manner of



Scheme 59 Alkyl Mg(II)-catalyzed hydrostannation of alkynes.

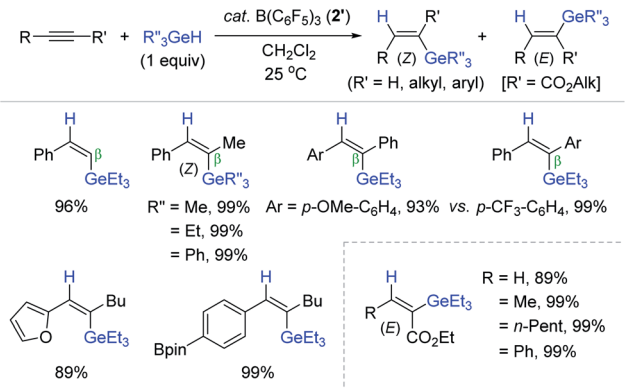


Scheme 60 Proposed outer-sphere mechanism of the alkyl Mg(II)-catalyzed hydrostannation of alkynes.

regio- and stereoselectivity to afford the corresponding α-(*E*)-vinylstanne. Unlike the case of internal alkynes, the hydrostannation of a broad range of terminal alkynes produced the β-*trans*-products in high yields under similar conditions [cat. **34** (7 mol%), toluene, 70 °C, 16 h]. This indicated that the initially formed *cis*-hydrostannation product is isomerized to the *trans*-vinylstannes during the Mg catalysis. Indeed, **34** was found to catalyze the isomerization of *cis*-vinylstannes to *trans*-vinylstannes presumably *via* reversible vinylstanne/organomagnesium exchange, as reported by Still and Seyferth.[176,177] In addition to catalyst **34**, ^{DIPP}NacNacMgBu, **9″**, as a catalyst was shown to improve the β-selectivity up to 12 : 1 for the hydrostannation of particularly terminal propargylic alcohols, in which the bulky *N*-aryl ligand on **9″** was assumed to protect the active Mg center from coordination of the hydroxyl moiety on the substrate.[178,179]

Based on a series of control experiments, a reaction pathway for the Mg(II)-catalyzed hydrostannation of alkynes was proposed (Scheme 60). The present catalysis is suggested to operate *via* the outer-sphere hydride transfer pathway[180–182] rather than an inner-sphere mechanism involving a Mg(II) hydride species.[144] Indeed, a Mg hydride (BuMgH) was barely formed in the 1 : 5 reaction of **34** and Bu_3SnH, not supporting the inner-sphere path. Species **34** is assumed to activate either Bu_3SnH or the alkyne to form a vinyl carbocation as the key intermediate(s) (**34e** or **34f**/**34f′**), which is supposed to undergo hydride reduction by the Bu_2MgH anion or Bu_3SnH to finally deliver the (*Z*)-vinylstanne. The resultant (*Z*)-product is likely isomerized to the more thermodynamically stable (*E*)-isomer in the hydrostannation of terminal alkynes.

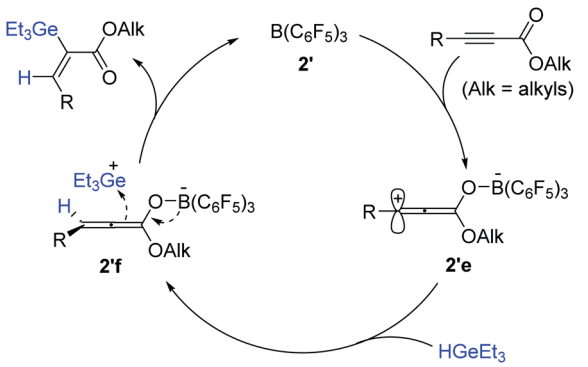
In 2005, Gevorgyan *et al.* communicated the $B(C_6F_5)_3$ **2′**-catalyzed *trans*-hydrogermylation of alkynes with



Scheme 61 $B(C_6F_5)_3$-catalyzed stereodivergent hydrogermylation of alkynes.

trialkylgermanes.[183] This work represents the first transition metal-free hydrogermylation of alkynes. The hydrogermylation worked over a broad range of unsymmetrical internal alkynes to provide the β-(*Z*)-vinylgermanes in excellent yields at 25 °C (Scheme 61). It is interesting that electronically-bias internal alkynes dictated the insertion of a germyl moiety exclusively into the position β to a more e⁻-rich aryl group. This catalysis exhibited functional group tolerance to various reducible groups, which was not observed in the $B(C_6F_5)_3$-catalyzed hydrosilylation[181] and hydrostannation[168,175] reactions. It is striking that substituted propiolates were reduced in an exclusively *cis*-fashion to give the corresponding (*E*)-vinylgermanes, in all high yields under the same conditions. The observed (*E*)-selectivity in the reaction of propiolates implied a mechanistic path different from the prototypical $B(C_6F_5)_3$-mediated outer-sphere *trans*-hydroelementation.[68,96]

A reaction pathway for the *cis*-hydrogermylation of propiolates was proposed (Scheme 62). Initially, $B(C_6F_5)_3$ is assumed to bind the carbonyl moiety of the propiolate to form zwitterionic complex **2′e**, where the carbocation is reduced by a hydrogermane[184] to generate allenolate **2′f** possessing a germylium ion. Subsequently, **2′f** is suggested to combine the germylium species from the less congested face *cis* to H[50] to deliver the *cis*-hydrogermylation product (Scheme 62).



Scheme 62 Proposed pathway for the $B(C_6F_5)_3$-catalyzed *cis*-hydrogermylation of propiolates.

5. Summary and outlook

This review described a broad range of transition metal-free molecular catalysts for the hydroelementation of terminal and internal alkynes with metalloid hydrides based on Si, B, Sn, and Ge, straightforwardly providing an array of functionalized vinyl compounds. Starting from Yamamoto's work using $AlCl_3$ as the first transition metal-free Lewis acid catalyst for the alkyne hydrosilylation in 1996, a handful of research groups including Buriak, Veinot, Ingleson, Stephan, Nikonov, and Hill successfully applied their catalysts for alkyne hydrosilylation in solution or on the surface. In parallel with hydrosilylation, a range of Lewis acid and neutral complexes based on Al and Mg have been utilized as hydroboration catalysts mainly by the groups of Ingleson, Stephan, Melen, Roesky, Cowley, Ma, and Reuping, while several types of simple (Lewis) bases have been demonstrated to mediate the hydroboration of alkynes with high regio- and stereoselectivity over the last decade. The hydrostannation catalyzed by Lewis acids was recently reported by the groups of Maleczka, Organ, Oestreich, and Reuping, whereas only one report on the hydrogermylation was published by Gevorgyan *et al.*

Overall, the viable metal-free catalysts for alkyne hydroelementation are highly diverse to include Lewis acids based on B, Al, Si, and P, and Lewis bases based on Li, Mg, P, and K, as well as Brönsted acids (carboxylic acids) and a Brönsted base (NaOH). Most of the Lewis acid catalysts are proposed to operate *via* an outer-sphere ionic mechanism, where the catalysts activate either the alkyne substrates or metalloid hydrides to form a vinyl carbocation as the key intermediate, which is reduced *via* the *trans*-oriented hydride transfer from the outer-sphere of the catalytic species to eventually deliver the hydroelementation products with high *cis*-selectivity. In contrast with the Lewis acid catalysis, a range of neutral hydride complexes based on Al and Mg, which are often *in situ* generated, catalyze particularly the hydroboration of alkynes *via* the inner-sphere mechanism involving alkyne insertion into an M–H bond (M = Al, Mg) or the *syn*-addition of HBpin into an alkyne unit of the alkynyl metal species to produce the *trans*-borylated vinyl compounds. Unlike alkyne hydrosilylation and hydroboration, the hydrostannation and hydrogermylation of alkynes known thus far are proposed to proceed *via* the outer-sphere mechanism by Lewis acid catalysts. It is interesting to compare that a neutral Mg(II) complex is supposed to serve as a Lewis acid catalyst for the outer-sphere alkyne hydrostannation through the activation of tin hydrides or alkyne molecules, whereas the same Mg complex is assumed to be readily converted to the magnesium hydride to catalyze the inner-sphere hydrosilylation and hydroboration reactions.

Despite the intensive surge in the study of environmentally and economically benign transition metal-free catalysts for the hydroelementation of alkynes, there are still some critical issues to be addressed as follows to compete with the traditional transition metal catalysis: (i) relatively lower turnover numbers, (ii) inferior regioselectivity in the case of unsymmetrical internal alkynes, (iii) limited mechanistic insights with a lack of characterized key catalytic intermediates, and (iv) facile disproportionation of metalloid hydrides such as HBpin. Thus, considering the limitations of the current metal-free catalytic systems, well-defined and robust complexes of alkaline or main group elements that are supported by finely tunable and strongly coordinating phosphine or NHC ligands can be next-generation catalysts for alkyne hydroelementation. Within the development of catalytic systems, robust chelation structures are supposed to suppress the decomposition of catalysts and/or metalloid hydrides to lead to improved catalytic efficiency, while tunable electronic and steric effects in the ligand are envisaged to enable regio- or stereodivergent hydroelementation with a broad substrate scope, including the challenging unsymmetrical internal alkynes. We hope that this review will draw significant interest from the community of organometallic catalysis and inspire synthetic chemists to develop elegant transition metal-free catalytic systems for the divergent hydroelementation of readily accessible olefins as a common chemical feedstock.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Notes and references

1 P. J. Stang and F. Diederich, *Modern acetylene chemistry*, John Wiley & Sons, 2008.
2 R. A. Raphae, *Acetylene compounds in organic synthesis*, Academic Press, New York, 1955.
3 V. V. Voronin, M. S. Ledovskaya, A. S. Bogachenkov, K. S. Rodygin and V. P. Ananikov, *Molecules*, 2018, **23**, 2442.
4 A. M. Haydl, B. Breit, T. Liang and M. J. Krische, *Angew. Chem., Int. Ed.*, 2017, **56**, 11312–11325.
5 J. P. Brand and J. Waser, *Chem. Soc. Rev.*, 2012, **41**, 4165–4179.
6 B. A. Trofimov, *Curr. Org. Chem.*, 2002, **6**, 1121–1162.
7 M. Pereyre, J.-P. Quintard and A. Rahm, *Tin in organic synthesis*, Butterworth-Heinemann, 2013.
8 E. W. Colvin, *Silicon reagents in organic synthesis*, Academic Press, 1988.
9 W. P. Weber, *Silicon reagents for organic synthesis*, Springer, Berlin, 1983.
10 K. Indukuri, L. Cornelissen and O. Riant, *Synthesis*, 2016, **48**, 4400–4422.
11 B. Hu and S. G. DiMagno, *Org. Biomol. Chem.*, 2015, **13**, 3844–3855.
12 A. J. Lennox and G. C. Lloyd-Jones, *Chem. Soc. Rev.*, 2014, **43**, 412–443.
13 E. Langkopf and D. Schinzer, *Chem. Rev.*, 1995, **95**, 1375–1408.

14 N. Miyaura and A. Suzuki, *Chem. Rev.*, 1995, **95**, 2457–2483.
15 J. K. Stille, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 508–524.
16 H. C. Brown, *Pure Appl. Chem.*, 1976, **47**, 49–60.
17 B. Marciniec, *Hydrosilylation: a comprehensive review on recent advances*, Springer Berlin, 2009.
18 D. S. W. Lim and E. A. Anderson, *Synthesis*, 2012, **44**, 983–1010.
19 B. Marciniec, *Silicon Chem.*, 2002, **1**, 155–174.
20 J. Carreras, A. Caballero and P. J. Pérez, *Chem.–Asian J.*, 2019, **14**, 329–343.
21 R. Barbeyron, E. Benedetti, J. Cossy, J.-J. Vasseur, S. Arseniyadis and M. Smietana, *Tetrahedron*, 2014, **70**, 8431–8452.
22 I. Beletskaya and A. Pelter, *Tetrahedron*, 1997, **53**, 4957–5026.
23 M. Alami, A. Hamze and O. Provot, *ACS Catal.*, 2019, **9**, 3437–3466.
24 H. Yoshida, *Synthesis*, 2016, **48**, 2540–2552.
25 N. D. Smith, J. Mancuso and M. Lautens, *Chem. Rev.*, 2000, **100**, 3257–3282.
26 I. P. Beletskaya, C. Nájera and M. Yus, *Chem. Rev.*, 2018, **118**, 5080–5200.
27 T. G. Frihed and A. Fürstner, *Bull. Chem. Soc. Jpn.*, 2016, **89**, 135–160.
28 B. M. Trost and Z. T. Ball, *Synthesis*, 2005, **2005**, 853–887.
29 W. J. Jang, W. L. Lee, J. H. Moon, J. Y. Lee and J. Yun, *Org. Lett.*, 2016, **18**, 1390–1393.
30 B. Sundararaju and A. Fürstner, *Angew. Chem., Int. Ed.*, 2013, **52**, 14050–14054.
31 H. Katayama, K. Taniguchi, M. Kobayashi, T. Sagawa, T. Minami and F. Ozawa, *J. Organomet. Chem.*, 2002, **645**, 192–200.
32 S. E. Denmark and W. Pan, *Org. Lett.*, 2001, **3**, 61–64.
33 Y. Maruyama, K. Yamamura, I. Nakayama, K. Yoshiuchi and F. Ozawa, *J. Am. Chem. Soc.*, 1998, **120**, 1421–1429.
34 R. S. Tanke and R. H. Crabtree, *J. Am. Chem. Soc.*, 1990, **112**, 7984–7989.
35 I. Ojima, N. Clos, R. J. Donovan and P. Ingallina, *Organometallics*, 1990, **9**, 3127–3133.
36 N. Asao and Y. Yamamoto, *Bull. Chem. Soc. Jpn.*, 2000, **73**, 1071–1087.
37 C.-J. Li, *Chem*, 2016, **1**, 423–437.
38 J. L. Tucker, *Org. Process Res. Dev.*, 2010, **14**, 328–331.
39 C.-J. Li and B. M. Trost, *Proc. Natl. Acad. Sci.*, 2008, **105**, 13197–13202.
40 P. T. Anastas and M. M. Kirchhoff, *Acc. Chem. Res.*, 2002, **35**, 686–694.
41 R. H. Petrucci, W. S. Harwood, G. F. Herring and J. D. Madura, *General chemistry : principles and modern applications*, Pearson Prentice Hall, Upper Saddle River; New Jersey, 2007.
42 C. Housecroft; and A. G. Sharpe, *Inorganic Chemistry*, 2nd edn, 2005.
43 E. Nieto-Sepulveda, A. D. Bage, L. A. Evans, T. A. Hunt, A. G. Leach, S. P. Thomas and G. C. Lloyd-Jones, *J. Am. Chem. Soc.*, 2019, **141**, 18600–18611.
44 K. Shirakawa, A. Arase and M. Hoshi, *Synthesis*, 2004, **2004**, 1814–1820.
45 M. Hoshi, K. Shirakawa and A. Arase, *Chem. Commun.*, 1998, 1225–1226.
46 A. Arase, M. Hoshi, A. Mijin and K. Nishi, *Synth. Commun.*, 1995, **25**, 1957–1962.
47 S. Keess and M. Oestreich, *Chem. Sci.*, 2017, **8**, 4688–4695.
48 M. Oestreich, *Angew. Chem., Int. Ed.*, 2016, **55**, 494–499.
49 T. Sudo, N. Asao, V. Gevorgyan and Y. Yamamoto, *J. Org. Chem.*, 1999, **64**, 2494–2499.
50 N. Asao, T. Sudo and Y. Yamamoto, *J. Org. Chem.*, 1996, **61**, 7654–7655.
51 E. Yoshikawa, V. Gevorgyan, N. Asao and Y. Yamamoto, *J. Am. Chem. Soc.*, 1997, **119**, 6781–6786.
52 V. Gevorgyan, J.-X. Liu and Y. Yamamoto, *J. Org. Chem.*, 1997, **62**, 2963–2967.
53 N. Asao, E. Yoshikawa and Y. Yamamoto, *J. Org. Chem.*, 1996, **61**, 4874–4875.
54 N. Asao, Y. Matsukawa and Y. Yamamoto, *Chem. Commun.*, 1996, 1513–1514.
55 T. Sudo, N. Asao and Y. Yamamoto, *J. Org. Chem.*, 2000, **65**, 8919–8923.
56 N. Kato, Y. Tamura, T. Kashiwabara, T. Sanji and M. Tanaka, *Organometallics*, 2010, **29**, 5274–5282.
57 V. V. Doan and M. J. Sailor, *Science*, 1992, **256**, 1791–1792.
58 M. Sailor, J. Heinrich and J. Lauerhaas, in *Stud. Surf. Sci. Catal.*, Elsevier Science, New York, 1996, vol. 103.
59 A. Janshoff, K.-P. S. Dancil, C. Steinem, D. P. Greiner, V. S. Y. Lin, C. Gurtner, K. Motesharei, M. J. Sailor and M. R. Ghadiri, *J. Am. Chem. Soc.*, 1998, **120**, 12108–12116.
60 V. S.-Y. Lin, K. Motesharei, K.-P. S. Dancil, M. J. Sailor and M. R. Ghadiri, *Science*, 1997, **278**, 840–843.
61 J. Harper and M. J. Sailor, *Anal. Chem.*, 1996, **68**, 3713–3717.
62 L. T. Canham, *Adv. Mater.*, 1995, **7**, 1033–1037.
63 K. H. Li, C. Tsai, S. Shih, T. Hsu, D. Kwong and J. Campbell, *J. Appl. Phys.*, 1992, **72**, 3816–3817.
64 J. M. Buriak, M. P. Stewart, T. W. Geders, M. J. Allen, H. C. Choi, J. Smith, D. Raftery and L. T. Canham, *J. Am. Chem. Soc.*, 1999, **121**, 11491–11502.
65 J. M. Buriak and M. J. Allen, *J. Am. Chem. Soc.*, 1998, **120**, 1339–1340.
66 T. K. Purkait, M. Iqbal, M. H. Wahl, K. Gottschling, C. M. Gonzalez, M. A. Islam and J. G. Veinot, *J. Am. Chem. Soc.*, 2014, **136**, 17914–17917.
67 T. Helbich, A. Lyuleeva, P. Marx, L. M. Scherf, T. K. Purkait, T. F. Fässler, P. Lugli, J. G. Veinot and B. Rieger, *Adv. Funct. Mater.*, 2017, **27**, 1606764.
68 Y. Kim, R. B. Dateer and S. Chang, *Org. Lett.*, 2017, **19**, 190–193.
69 Y. Zhang, Y. Chen, Z. Zhang, S. Liu and X. Shen, *Org. Lett.*, 2020, **22**, 970–975.
70 L. D. Curless and M. J. Ingleson, *Organometallics*, 2014, **33**, 7241–7246.
71 H. Arii, K. Nakabayashi, K. Mochida and T. Kawashima, *Molecules*, 2016, **21**, 999.
72 K. Müther, J. Mohr and M. Oestreich, *Organometallics*, 2013, **32**, 6643–6646.

73 K. Müther and M. Oestreich, *Chem. Commun.*, 2011, **47**, 334–336.
74 J. B. Lambert, Y. Zhao and H. Wu, *J. Org. Chem.*, 1999, **64**, 2729–2736.
75 C. B. Caputo, L. J. Hounjet, R. Dobrovetsky and D. W. Stephan, *Science*, 2013, **341**, 1374–1377.
76 M. Perez, L. J. Hounjet, C. B. Caputo, R. Dobrovetsky and D. W. Stephan, *J. Am. Chem. Soc.*, 2013, **135**, 18308–18310.
77 M. H. Holthausen, M. Mehta and D. W. Stephan, *Angew. Chem., Int. Ed.*, 2014, **53**, 6538–6541.
78 R. R. Holmes, *Chem. Rev.*, 1996, **96**, 927–950.
79 C. Chuit, R. J. P. Corriu, C. Reye and J. C. Young, *Chem. Rev.*, 1993, **93**, 1371–1448.
80 R. B. Lettan and K. A. Scheidt, *Org. Lett.*, 2005, **7**, 3227–3230.
81 G. A. Kraus and J. Bae, *Tetrahedron Lett.*, 2003, **44**, 5505–5506.
82 J. E. Baldwin, G. J. Pritchard and R. E. Rathmell, *J. Chem. Soc., Perkin Trans. 1*, 2001, 2906–2908.
83 J. Busch-Petersen, Y. Bo and E. J. Corey, *Tetrahedron Lett.*, 1999, **40**, 2065–2068.
84 I. Kuwajima, E. Nakamura and K. Hashimoto, *Tetrahedron*, 1983, **39**, 975–982.
85 S. V. Maifeld and D. Lee, *Org. Lett.*, 2005, **7**, 4995–4998.
86 B. M. Trost and Z. T. Ball, *J. Am. Chem. Soc.*, 2004, **126**, 13942–13944.
87 L. A. Aronica, F. Morini, A. M. Caporusso and P. Salvadori, *Tetrahedron Lett.*, 2002, **43**, 5813–5815.
88 M. E. Jung and G. Piizzi, *J. Org. Chem.*, 2002, **67**, 3911–3914.
89 I. Fleming, T. W. Newton, V. Sabin and F. Zammattio, *Tetrahedron*, 1992, **48**, 7793–7802.
90 Z. Yang, M. Zhong, X. Ma, K. Nijesh, S. De, P. Parameswaran and H. W. Roesky, *J. Am. Chem. Soc.*, 2016, **138**, 2548–2551.
91 Z. Yang, M. Zhong, X. Ma, S. De, C. Anusha, P. Parameswaran and H. W. Roesky, *Angew. Chem., Int. Ed.*, 2015, **54**, 10225–10229.
92 L. Bourget-Merle, M. F. Lappert and J. R. Severn, *Chem. Rev.*, 2002, **102**, 3031–3066.
93 K. Jakobsson, T. Chu and G. I. Nikonov, *ACS Catal.*, 2016, **6**, 7350–7356.
94 L. Garcia, C. Dinoi, M. F. Mahon, L. Maron and M. S. Hill, *Chem. Sci.*, 2019, **10**, 8108–8118.
95 E. Fritz-Langhals, *Org. Process Res. Dev.*, 2019, **23**, 2369–2377.
96 J. S. McGough, S. M. Butler, I. A. Cade and M. J. Ingleson, *Chem. Sci.*, 2016, **7**, 3384–3389.
97 M. A. Dureen, C. C. Brown and D. W. Stephan, *Organometallics*, 2010, **29**, 6594–6607.
98 M. A. Dureen and D. W. Stephan, *J. Am. Chem. Soc.*, 2009, **131**, 8396–8397.
99 D. N. Lastovickova and C. W. Bielawski, *Organometallics*, 2016, **35**, 706–712.
100 L. Xie, J. Zhang and C. Cui, *Chem. - Eur. J.*, 2014, **20**, 9500–9503.
101 H. Asakawa, K.-H. Lee, Z. Lin and M. Yamashita, *Nat. Commun.*, 2014, **5**, 1–9.
102 T. K. Wood, W. E. Piers, B. A. Keay and M. Parvez, *Chem. - Eur. J.*, 2010, **16**, 12199–12206.
103 E. R. Abbey, L. N. Zakharov and S.-Y. Liu, *J. Am. Chem. Soc.*, 2008, **130**, 7250–7252.
104 R. L. Melen, A. J. Lough and D. W. Stephan, *Dalton Trans.*, 2013, **42**, 8674–8683.
105 L. Fan and D. W. Stephan, *Dalton Trans.*, 2016, **45**, 9229–9234.
106 Q. Yin, Y. Soltani, R. L. Melen and M. Oestreich, *Organometallics*, 2017, **36**, 2381–2384.
107 Q. Yin, S. Kemper, H. F. Klare and M. Oestreich, *Chem. - Eur. J.*, 2016, **22**, 13840–13844.
108 J. R. Lawson, L. C. Wilkins and R. L. Melen, *Chem. - Eur. J.*, 2017, **23**, 10997–11000.
109 J. L. Carden, L. J. Gierlichs, D. F. Wass, D. L. Browne and R. L. Melen, *Chem. Commun.*, 2019, **55**, 318–321.
110 M. Shimizu, I. Nagao, S.-i. Kiyomoto and T. Hiyama, *Aust. J. Chem.*, 2012, **65**, 1277–1284.
111 J. Takaya and N. Iwasawa, *ACS Catal.*, 2012, **2**, 1993–2006.
112 J. Takaya, N. Kirai and N. Iwasawa, *J. Am. Chem. Soc.*, 2011, **133**, 12980–12983.
113 M. Shimizu, C. Nakamaki, K. Shimono, M. Schelper, T. Kurahashi and T. Hiyama, *J. Am. Chem. Soc.*, 2005, **127**, 12506–12507.
114 T. Hata, H. Kitagawa, H. Masai, T. Kurahashi, M. Shimizu and T. Hiyama, *Angew. Chem., Int. Ed.*, 2001, **40**, 790–792.
115 H. E. Ho, N. Asao, Y. Yamamoto and T. Jin, *Org. Lett.*, 2014, **16**, 4670–4673.
116 Z. Zhang, P. Jain and J. C. Antilla, *Angew. Chem., Int. Ed.*, 2011, **50**, 10961–10964.
117 D. B. Collum, S.-C. Chen and B. Ganem, *J. Org. Chem.*, 1978, **43**, 4393–4394.
118 H. C. Brown and B. S. Rao, *J. Am. Chem. Soc.*, 1960, **82**, 681–686.
119 C. B. Hoyt, M. L. Sarazen and C. W. Jones, *J. Catal.*, 2019, **369**, 493–500.
120 Y. Wu, C. Shan, J. Ying, J. Su, J. Zhu, L. L. Liu and Y. Zhao, *Green Chem.*, 2017, **19**, 4169–4175.
121 J. H. Docherty, J. Peng, A. P. Dominey and S. P. Thomas, *Nat. Chem.*, 2017, **9**, 595–600.
122 J. M. Farrell, R. T. Posaratnanathan and D. W. Stephan, *Chem. Sci.*, 2015, **6**, 2010–2015.
123 I. P. Query, P. A. Squier, E. M. Larson, N. A. Isley and T. B. Clark, *J. Org. Chem.*, 2011, **76**, 6452–6456.
124 C. E. Garrett and G. C. Fu, *J. Org. Chem.*, 1996, **61**, 3224–3225.
125 K. Nagao, H. Ohmiya and M. Sawamura, *J. Am. Chem. Soc.*, 2014, **136**, 10605–10608.
126 K. Nagao, A. Yamazaki, H. Ohmiya and M. Sawamura, *Org. Lett.*, 2018, **20**, 1861–1865.
127 K. Nagao, H. Ohmiya and M. Sawamura, *Org. Lett.*, 2015, **17**, 1304–1307.
128 A. Yamazaki, K. Nagao, T. Iwai, H. Ohmiya and M. Sawamura, *Angew. Chem., Int. Ed.*, 2018, **57**, 3196–3199.
129 R. Fritzemeier, A. Gates, X. Guo, Z. Lin and W. L. Santos, *J. Org. Chem.*, 2018, **83**, 10436–10444.
130 Y. Ding, X. Liu, X. Ma, Y. Liu, M. Zhong, W. Li, Z. Yang and Y. Yang, *J. Organomet. Chem.*, 2018, **868**, 55–60.

131 N. Sarkar, S. Bera and S. Nembenna, *J. Org. Chem.*, 2020, **85**, 4999–5009.
132 A. Bismuto, S. P. Thomas and M. J. Cowley, *Angew. Chem., Int. Ed.*, 2016, **55**, 15356–15359.
133 A. Harinath, I. Banerjee, J. Bhattacharjee and T. K. Panda, *New J. Chem.*, 2019, **43**, 10531–10536.
134 R. L. Falconer, G. S. Nichol and M. J. Cowley, *Inorg. Chem.*, 2019, **58**, 11439–11448.
135 D. Franz, L. Sirtl, A. Pöthig and S. Inoue, *Z. Anorg. Allg. Chem.*, 2016, **642**, 1245–1250.
136 G. Zhang, J. Wu, H. Zeng, M. C. Neary, M. Devany, S. Zheng and P. A. Dub, *ACS Catal.*, 2018, **9**, 874–884.
137 F. Li, X. Bai, Y. Cai, H. Li, S.-Q. Zhang, F.-H. Liu, X. Hong, Y. Xu and S.-L. Shi, *Org. Process Res. Dev.*, 2019, **23**, 1703–1708.
138 V. A. Pollard, M. A. Fuentes, A. R. Kennedy, R. McLellan and R. E. Mulvey, *Angew. Chem., Int. Ed.*, 2018, **57**, 10651–10655.
139 A. K. Jaladi, H. Kim, J. H. Lee, W. K. Shin, H. Hwang and D. K. An, *New J. Chem.*, 2019, **43**, 16524–16529.
140 D. Yan, X. Wu, J. Xiao, Z. Zhu, X. Xu, X. Bao, Y. Yao, Q. Shen and M. Xue, *Org. Chem. Front.*, 2019, **6**, 648–653.
141 Z.-C. Wang, M. Wang, J. Gao, S.-L. Shi and Y. Xu, *Org. Chem. Front.*, 2019, **6**, 2949–2953.
142 M. K. Bisai, S. Yadav, T. Das, K. Vanka and S. S. Sen, *Chem. Commun.*, 2019, **55**, 11711–11714.
143 J. Li, M. Luo, X. Sheng, H. Hua, W. Yao, S. A. Pullarkat, L. Xu and M. Ma, *Org. Chem. Front.*, 2018, **5**, 3538–3547.
144 M. Magre, B. Maity, A. Falconnet, L. Cavallo and M. Rueping, *Angew. Chem., Int. Ed.*, 2019, **58**, 7025–7029.
145 K. Revunova and G. Nikonov, *Dalton Trans.*, 2015, **44**, 840–866.
146 A. Harinath, J. Bhattacharjee and T. K. Panda, *Adv. Synth. Catal.*, 2019, **361**, 850–857.
147 L. A. Berben, *Chem. - Eur. J.*, 2015, **21**, 2734–2742.
148 G. A. Artamkina, M. P. Egorov and I. P. Beletskaya, *Chem. Rev.*, 1982, **82**, 427–459.
149 V. A. Pollard, S. A. Orr, R. McLellan, A. R. Kennedy, E. Hevia and R. E. Mulvey, *Chem. Commun.*, 2018, **54**, 1233–1236.
150 L. E. Lemmerz, R. McLellan, N. R. Judge, A. R. Kennedy, S. A. Orr, M. Uzelac, E. Hevia, S. D. Robertson, J. Okuda and R. E. Mulvey, *Chem. - Eur. J.*, 2018, **24**, 9940–9948.
151 Y. Zhang, J. Wei, W.-X. Zhang and Z. Xi, *Inorg. Chem.*, 2015, **54**, 10695–10700.
152 Y. Yang, M. D. Anker, J. Fang, M. F. Mahon, L. Maron, C. Weetman and M. S. Hill, *Chem. Sci.*, 2017, **8**, 3529–3537.
153 A. D. Bage, T. A. Hunt and S. P. Thomas, *Org. Lett.*, 2020, **22**, 4107–4112.
154 G. W. O'Neil, A. M. Craig, J. R. Williams, J. C. Young and P. C. Spiegel, *Synlett*, 2017, **28**, 1101.
155 D. Mailhol, J. Willwacher, N. Kausch-Busies, E. E. Rubitski, Z. Sobol, M. Schuler, M.-H. Lam, S. Musto, F. Loganzo and A. Maderna, *J. Am. Chem. Soc.*, 2014, **136**, 15719–15729.
156 M. Dieckmann, M. Kretschmer, P. Li, S. Rudolph, D. Herkommer and D. Menche, *Angew. Chem., Int. Ed.*, 2012, **51**, 5667–5670.
157 J. Gagnepain, E. Moulin and A. Fürstner, *Chem. - Eur. J.*, 2011, **17**, 6964–6972.
158 A. Fürstner, J.-A. Funel, M. Tremblay, L. C. Bouchez, C. Nevado, M. Waser, J. Ackerstaff and C. C. Stimson, *Chem. Commun.*, 2008, 2873–2875.
159 V. Gevorgyan, J.-X. Liu and Y. Yamamoto, *Chem. Commun.*, 1998, 37–38.
160 W. P. Gallagher, I. Terstiege and R. E. Maleczka Jr, *J. Am. Chem. Soc.*, 2001, **123**, 3194–3204.
161 R. E. Maleczka Jr and W. P. Gallagher, *Org. Lett.*, 2001, **3**, 4173–4176.
162 R. E. Maleczka Jr and I. Terstiege, *J. Org. Chem.*, 1998, **63**, 9622–9623.
163 B. Ghosh, M. D. R. I. Amado-Sierra, D. Holmes and R. E. Maleczka Jr, *Org. Lett.*, 2014, **16**, 2318–2321.
164 W. Plass and J. G. Verkade, *Inorg. Chem.*, 1993, **32**, 5153–5159.
165 D. Dakternieks and H. Zhu, *Organometallics*, 1992, **11**, 3820–3825.
166 S. S. Al-Juaid, S. M. Dhaher, C. Eaborn, P. B. Hitchcock and J. D. Smith, *J. Organomet. Chem.*, 1987, **325**, 117–127.
167 A. G. Davies, *Organotin Chemistry*, Wiley-VCH, Weinheim, 2nd edn, 2004.
168 M. S. Oderinde and M. G. Organ, *Angew. Chem., Int. Ed.*, 2012, **51**, 9834–9837.
169 J. Lambert, Y. Zhao and S. Zhang, *J. Phys. Org. Chem.*, 2001, **14**, 370.
170 J. B. Lambert and B. Kuhlamann, *J. Chem. Soc., Chem. Commun.*, 1992, 931–932.
171 G. E. Keck and D. Krishnamurthy, *J. Org. Chem.*, 1996, **61**, 7638–7639.
172 N. Asao, J.-X. Liu, T. Sudoh and Y. Yamamoto, *J. Org. Chem.*, 1996, **61**, 4568–4571.
173 N. Asao, J.-X. Liu, T. Sudoh and Y. Yamamoto, *J. Chem. Soc., Chem. Commun.*, 1995, 2405–2406.
174 F. Forster, V. M. Rendón López and M. Oestreich, *Organometallics*, 2018, **37**, 2656–2659.
175 M. Magre, M. Szewczyk and M. Rueping, *Org. Lett.*, 2020, **22**, 1594–1598.
176 W. C. Still, *J. Am. Chem. Soc.*, 1978, **100**, 1481–1487.
177 D. Seyferth and M. A. Weiner, *J. Am. Chem. Soc.*, 1962, **84**, 361–364.
178 M. B. Rice, S. L. Whitehead, C. M. Horvath, J. A. Muchnij and R. E. Maleczka Jr, *Synthesis*, 2001, **2001**, 1495–1504.
179 H. Zhang, F. Guibé and G. Balavoine, *J. Org. Chem.*, 1990, **55**, 1857–1867.
180 M. Rubin, T. Schwier and V. Gevorgyan, *J. Org. Chem.*, 2002, **67**, 1936–1940.
181 D. J. Parks, J. M. Blackwell and W. E. Piers, *J. Org. Chem.*, 2000, **65**, 3090–3098.
182 D. J. Parks and W. E. Piers, *J. Am. Chem. Soc.*, 1996, **118**, 9440–9441.
183 T. Schwier and V. Gevorgyan, *Org. Lett.*, 2005, **7**, 5191–5194.
184 H. Mayr and N. Basso, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1046–1048.