Personal Account

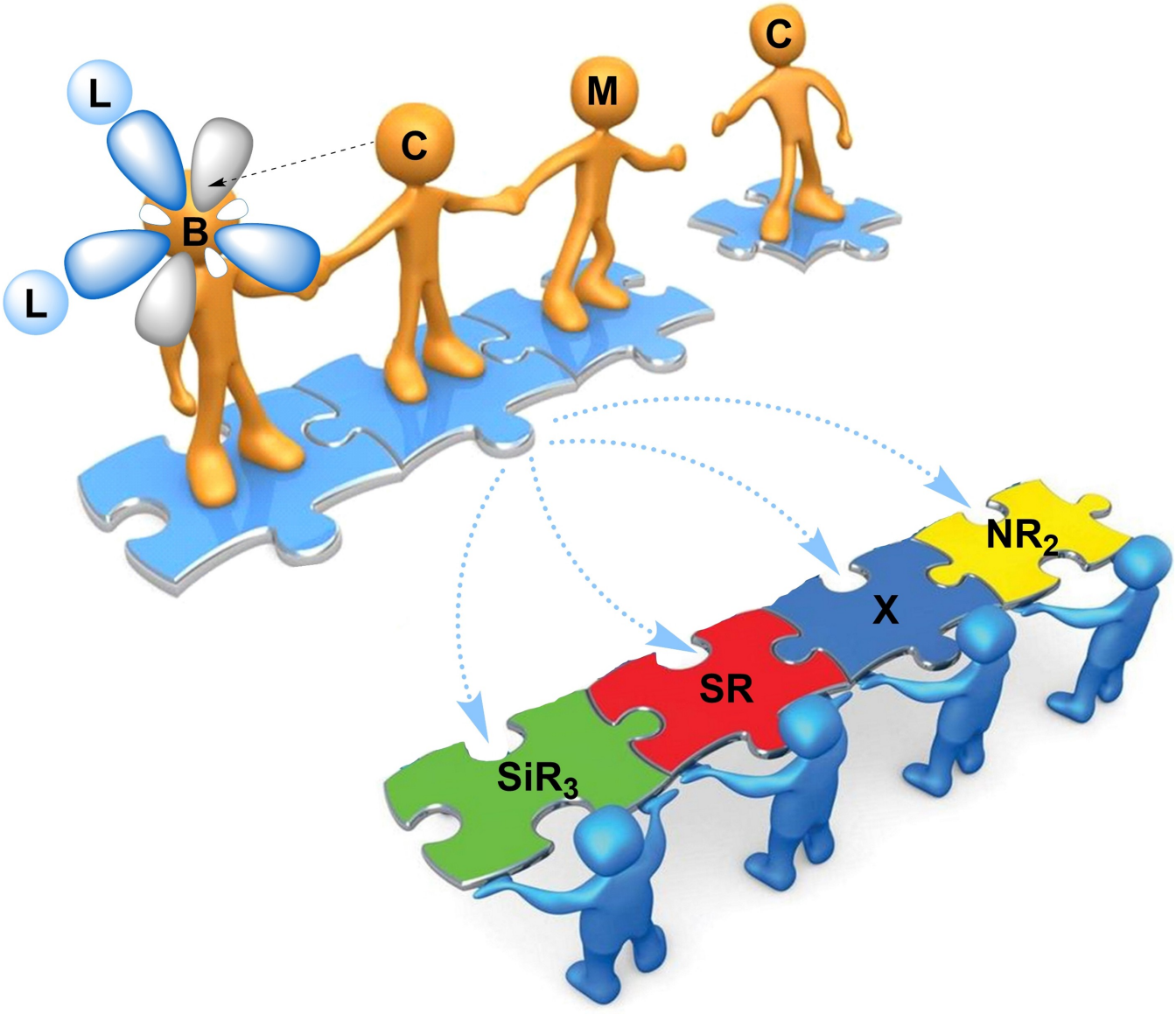
THE CHEMICAL RECORD

doi.org/10.1002/tcr.202300349
tcr.wiley-vch.de

α-Boryl Carbanions: The Influence of Geminal Heteroatoms in C–C Bond Formation

Elena Fernández*[a]

Dedicated to Prof. Norio Miyaura



Abstract: The wide applications of alpha-boryl carbanions in selective coupling with organohalides, imines/carbonyls and conjugated unsaturated substrates has become an interesting tool for organic synthesis. Strategically, the inclusion of heteroatoms, such as Si, S, N, F, Cl, Br and I in the alpha position opens a new venue towards multifunctionalities in molecular design. Here, a conceptual and practical view on powerful carbanions, containing α-silicoboron, α-thioboron, α-haloboron and α-aminoboron is given, as well as a prespective on their efficient application for selective electrophilic trapping.

Keywords: α-boryl carbanion, α-silicoboron carbanion, α-thioboron carbanion, α-aminoboron carbanion, α-haloboron carbanion

1. α-Boryl Carbanions as Functional Synthons

α-Boryl carbanions are strategic ionic species for coupling reactions[1,2] taken advantage of the valence deficiency of the adjacent three coordinate boron center. Species related to the molecular formula $M^+[R"_2B\text{-}CRR']^-$ can be expressed as its resonance form, the borata-alkene systems $M^+[R"_2B{=}CRR']^-$ (Figure 1), acting as a nucleophilic reservoir[3] throughout electrophilic trapping sequences. Depending on the nature of the metal involved, the α-boryl carbanions can be classified in three different type of α-boryl alkylidene metal species: a) nucleophilic borata-alkene salts with alkali and alkali-earth metals, b) nucleophilic η^2-(C–B) borata-alkene complexes with early transition metals, as well as with Cu and Ag, and c) α-boryl alkyl complexes with late transition metals (Figure 1). DFT-derived parameters for capturing the electronic and steric properties of α-boryl alkylidene metal species justify the reactivity trends observed as nucleophiles in coupling reactions.[4] Experimentally, the α-boryl alkylidene lithium or sodium salts can be easily alkylated, as well as promoting ring opening of epoxides and aziridines,[5a–q] and can deliver stereoselective alkenes when react with carbonyl compounds, through the Boron-Wittig reactions.[5r] In those cases, the strong borata-alkene character is characterized by the high Wiberg C–B bond order (about 1.36) and the short C–B distance (about 1.48 Å) with the Li or Na cations interacting electrostatically with the borata-alkene moiety.[6] On the other hand, in the boron-stabilized carbanions involving Cu(I) cations, the $[pinB{=}CH_2]^-$ fragment acts as an anionic η^2-(C,B) ligand and the HOMO orbital shows an overlap between Cu(I) *d* orbitals and the C=B π orbital. Consequently, the reactivity observed by borylalkyde copper (I) complexes accomplishes the coupling with carbonyl groups, towards the formation of 1,2-hydroxyboronates, but also with aldimines or ketimines. Interestingly the allylic alkylation is also efficiently performed as well as aryl and alkyl propargylic substitutions, ring opening of vinyl carbonates or vinyl epoxides, and conjugated additions on α,β-unsaturated carbonyl groups.[7] The addition of stabilizing ligands, such as mono and diphosphines, contribute to enhance the steric and electronic tuning of the borylalkyde copper (I) catalyst towards stereoselective control in the coupling sequence. Complementarily, the α-boryl alkyl Pd complexes generated by treatment of *gem*-diboron alkanes and ArPdX species, allows chemoselective and regiospecific Suzuki-Miyaura coupling at room temperature.[8] The key to success is the generation of the stabilized α-boryl alkyl Pd intermediate, by virtue of the adjacent B atom. That strategy indicates that Suzuki-Miyaura coupling takes place on a multisubstituted sp^3-carbon bearing β-C–H bonds but the σ-borylalkyl-PdAr intermediate is sufficiently stable to prevent undesired reductive elimination pathways. To complement this reflexion on the metal influence to the alpha-boryl carbanions, it is worthy to mention that Zn(II) and Ag(I) have also been used as countercations to provide interesting platform for selective coupling reactions.[9]

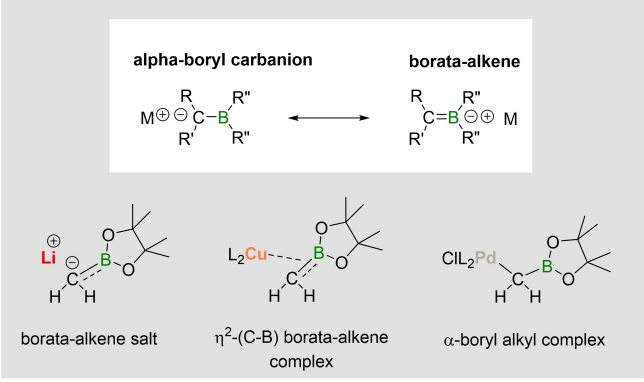


Figure 1. Influence of metal in the alpha-boryl carbanion and resonance borata-alkene structures.

[a] *Prof. E. Fernández*
Dept. Química Física i Inorgànica
University Rovira i Virgili, Tarragona, Spain
E-mail: mariaelena.fernandez@urv.cat

The nature of the boron substituents also influences the relative stability of the corresponding α-boryl carbanions. This is the case of $M^+[CH_2(Bdan)]^-$ (Bdan = 1,8-naphthalenediaminatoboryl) since the stabilization of the carbanion using the α-Bdan moiety is reflected in the HOMO orbital, which shows strong delocalization of the carbanion p-type electron density into the π-channel of the Bdan moiety (Figure 2).[10] For comparison, the α-(pinacolato)boronate carbanion is less stable than the α-(1,8-naphthalenediaminato)boronate carbanion by 12.3 kcal·mol^{-1}.[10] According to NBO analysis, the Bpin fragment supports a less negative charge (−0.14e) than the Bdan fragment (−0.21e), as inferred from the corresponding HOMO orbitals. Thus, preferred selective functionalization of the Bpin moiety is expected versus the Bdan moiety in Pd-catalyzed Suzuki Miyaura coupling of unsymmetrical *gem*-diborylalkane compounds.[11] The α-boryl carbanions, containing the boryl moieties $BMes_2$ and $B(C_6F_5)_2$ have been rationalized to have a higher stability along the carbanion series. Whereas the boron atom in the Bpin and Bdan boryl fragments depict the π-donor ability from the O and N heteroatoms to the empty p orbital of the B atom, the electron deficient boron center in $BMes_2$ and $B(C_6F_5)_2$ is fully available for delocalizing the carbanion negative charge. This also correlates with the stronger borata-alkene character of these species (Wiberg C–B bond order from 1.56 ($BMes_2$) to 1.73 ($B(C_6F_5)_2$).[4,12] The energy of the HOMO corresponds to a C–B π-orbital strongly polarized towards the carbanionic atom in $[CH_2(Bpin)]^-$ correlating with the enhanced nucleophilic reactivity (Figure 2).[4]

The number of boryl fragments also influences the alpha-boryl carbanion stability/reactivity. By comparison of α-mono-, di-, and triboryl carbanions, it has been determined by DFT studies that increasing the number of boryl moieties the stability of the carbanion is enhanced whereas the nucleophilic properties are diminished. Figure 2 shows the HOMO orbitals for $[CH_2(Bpin)]^-$, $[CH(pinB)_2]^-$ and $[C(pinB)_3]^-$ where it can be clearly observed that each boryl moiety contributes to the stabilization of the carbanion through a strong delocalization of the carbanion p-type electron density into the π-channel. Consequently, the α-triboryl carbanion has lower-energy laying HOMO (−2.61 eV) than those for α-diboryl carbanion and α-monoboryl carbanion (−1.85 and −0.58 eV, respectively)

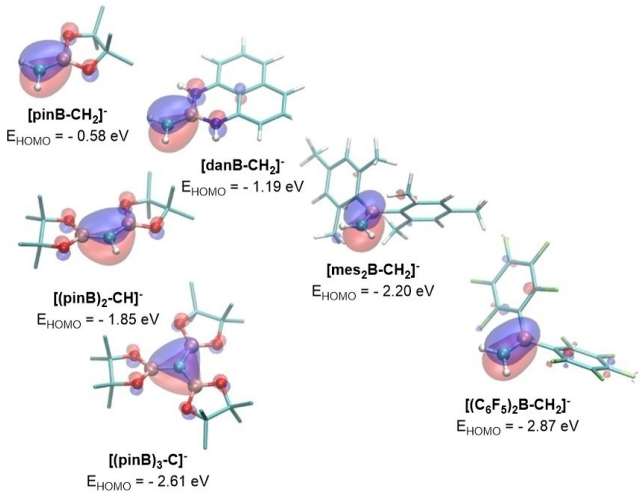
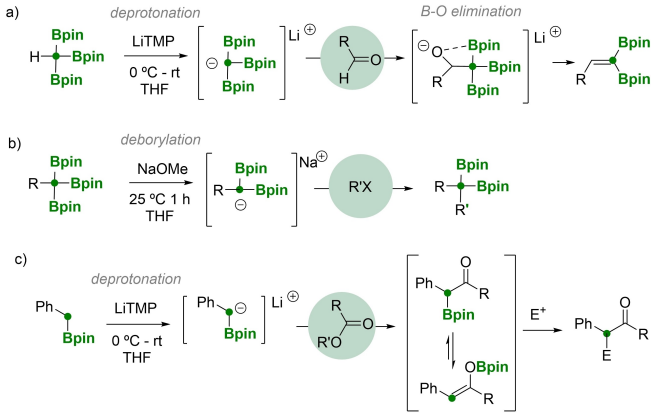


Figure 2. Representation of HOMO orbitals corresponding to the carbanion lone pair for $[CH_2(BR_2)]^-$ with $B(C_6F_5)_2$, $BMes_2$, Bdan and Bpin including the calculated energy of the HOMO orbital (E_{HOMO}) in eV. For comparison the representation of HOMO orbitals for $[CH_2(Bpin)]^-$, $[CH(Bpin)_2]^-$ and $[C(Bpin)_3]^-$.

being the α-triboryl carbanion the least prone to react with electrophiles and the most stable. However, the tris(boryl)methide ions can react with aldehydes to undergo the expected Boron-Wittig reaction to synthetize trisubstituted *gem*-diborylalkenes (Scheme 1a),[13] whereas α-diboryl carbanions not only react with carbonyl compounds, but also participate in alkylation or conjugate addition reactions (Scheme 1b).[14]

The electronic and structural properties of alpha-boryl carbanions can be affected by the influence of the substituents on the carbon atom. For comparison, the replacement of one H in $[CH_2(BR_2)]^-$ by Me or Ph substituents affects significantly, demonstrating that the Ph group stabilises the carbanion lone pair. This is also reflected in the lower energy-laying HOMO (−1.27 eV for $[CHPh(BR_2)]^-$ versus −0.58 eV and −0.56 eV for $[CH_2(BR_2)]^-$ and $[CHMe(BR_2)]^-$, respectively).[4] This descriptor capture the electron withdrawing effect of the Ph group showing a lower reactivity in coupling reactions, although interesting reactivity

Elena Fernández received her degree in chemistry at the University of Barcelona in 1991. She earned her Ph.D. in 1995 on catalytic hydroformylation of sugars with Prof. Sergio Castillón at the University Rovira i Virgili. She moved two years at the University of Oxford (UK) for postdoctoral studies on catalytic asymmetric hydroboration-amination reaction with Prof. John M. Brown. Elena accepted a lecturer position at the University Rovira i Virgili, becoming part of the permanent staff in 2000 and full professor from 2019. Her group's research interests are based on new concepts about activation and reactivity of organoborane compounds.



Scheme 1. a) Boron-Wittig reaction between Li[C(Bpin)$_3$] and aldehydes, b) alkylation reaction between Na[CR(Bpin)$_2$] and alkyl halides, c) coupling reaction between Li[CHPh(Bpin)] and esters.

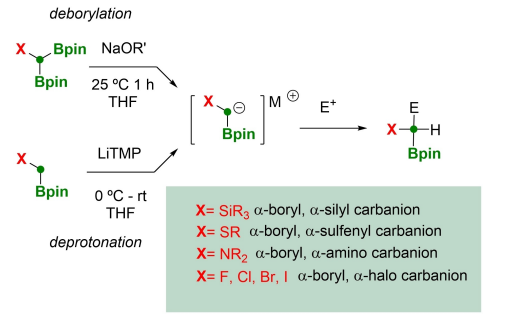
between Li[CHPh(Bpin)] and esters provides direct acces to interesting ketones (Scheme 1c).[15]

gem-Diboryl compounds with an α-hetero substituents are also very versatile since the corresponding α-boryl carbanion, containing an hetero functional group, can enrich the subsequent coupling reaction towards multifunctionalized products. The next sections are devoted to identify the stabilized carbanions with α-silicoboron, α-thioboron, α-aminoboron, α-haloboron moieties and their concomitant electrophilic trapping (Scheme 2).

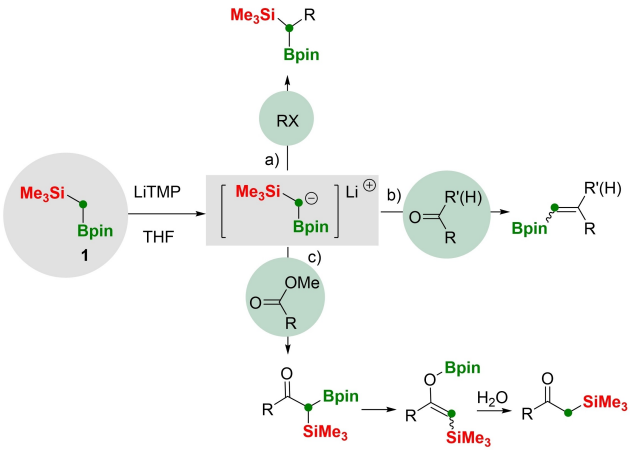
2. α-Silicoboron Carbanions

The introduction of the functional group SiR_3 in the alpha position of α-boryl carbanions has a direct influence on the electronics but also in the structural properties of the carbanion $[CH(Bpin)(SiR_3)]^-$. Several recent studies have been focused on the synthesis of α-borylsilyl compounds since they can be chemoselectively transformed through C–B and/or C–Si functionalizations.[16,17] The *gem*-borylsilylmethane (**1**) was originally synthesized by Matteson and co-workers, in 1980, and the correspsonding carbanion was formed via deprotonation with lithium tetramethylpiperidide (LiTMP) as base, tetramethylethylenediamine (TMEDA) as activator, and tetrahydrofuran (THF) as solvent. The electrophilic trapping could be efficiently performed with primary alkyl halides towards the synthesis of valuable *gem*-borylsilyl alkanes (Scheme 3a).[18] When the carbanion $[CH(Bpin)(SiMe_3)]^-$ reacted with ketones or aldehydes, the corresponding tri- or disubstituted alkenes were generated through an exclusive Si–O elimination pathway (Scheme 3b).[18] Contrarily, the preferential B–O elimination takes place when the carbanion $[CH(Bpin)(SiMe_3)]^-$ reacted with carboxylic esters, presumably throughout boron enolate intermediate (Scheme 3c).[18]

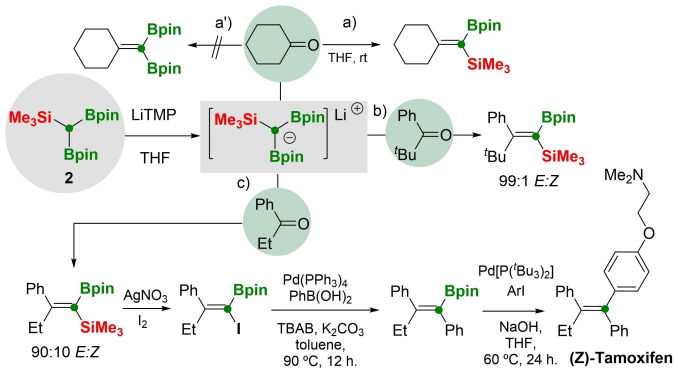
The *gem*-diborylsilylmethane (**2**) can also be deprotonated with hindered bases, such as LiTMP, to form the corresponding carbanion Li[C(Bpin)$_2$(SiR$_3$)] that reacts efficiently with ketones and aldehydes. Our group developed the straightforward synthesis of tetrasubstituted alkenes by addition of the carbanion $[C(Bpin)_2(SiMe_3)]^-$ to symmetric ketones, throughout B–O elimination, which resulted faster than the analogous Si–O Peterson-type reactivity (Scheme 4a).[19] This observation contrasts with the Matteson reactivity between the carbanion $[CH(Bpin)(SiMe_3)]^-$ and ketones or aldehydes, giving access to the alkenes with exclusive Si–O elimination pathway. We also studied the reaction of Li[C(Bpin)$_2$(SiR$_3$)] with non symmetric ketones, containing both aryl and alkyl substituents, and the Boron-Wittig approach delivered the corresponding 1,1-borylsilyl tetrasubstituted alkenes with a high degree of stereocontrol, being the major isomer the one that places the Bpin moiety *cis* to aryl group (Scheme 4b).[19] The reasons for such stereoselectivity might point out an unfavorable steric interaction between the aliphatic substituents on the ketone and the hindered Bpin moiety in the olefination transition



Scheme 2. Schematic representation of the carbanions containing α-boryl and α-hetero substituents and their concomitant coupling reactions



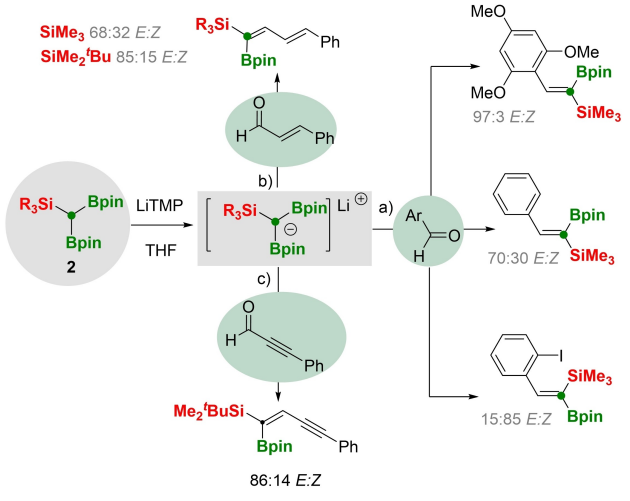
Scheme 3. *In situ* generation of Li[CH(Bpin)(SiMe$_3$)] and subsequent reactivity with alkyl halides, ketones, aldehydes and esters.



Scheme 4. *In situ* generation of Li[C(Bpin)$_2$(SiMe$_3$)] and consequently reactivity with symmetric and non symmetric ketones.

state. We applied our methodology to the synthesis of (*Z*)-Tamoxifen starting from the stereoselective coupling between [C(Bpin)$_2$(SiMe$_3$)]$^-$ and propiophenone, followed by iododesilylation of the 1,1-borylsilyl tetrasubstituted alkene, complementing the synthesis with two consecutive chemoselective Suzuki-Miyaura couplings, leading to Tamoxifen (>93% Z) (Scheme 4c).[19] This modular stereoselective synthesis constitutes one of the most step and cost-economic routes to this antagonistic prodrug.

The reactivity between Li[C(Bpin)$_2$(SiMe$_3$)] and aliphatic/aromatic aldehydes also proved to be efficient towards the synthesis of 1,1-silylborylated trisubstituted alkenes, showing a preference for the *E* stereoisomer, with the Bpin moiety *syn* to the aryl group, but *Z* stereopreference for *ortho* halide substituents on the aryl group (Scheme 5a).[20]

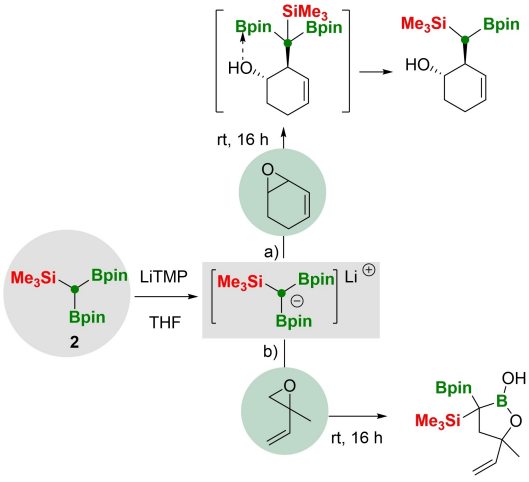


Scheme 5. *In situ* generation of Li[C(Bpin)$_2$(SiMe$_3$)] and reactivity with aromatic aldehydes α,β-unsaturated aldehydes to synthesize 1,1,–silylborylated alkenes, conjugated dienes and enynes.

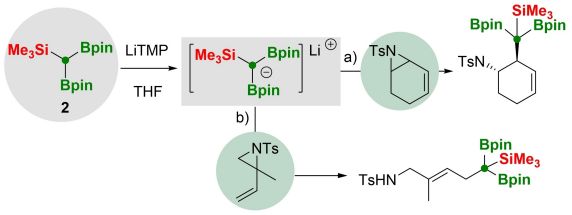
The olefination of α,β-unsaturated aldehydes with the carbanion [C(Bpin)$_2$(SiMe$_3$)]$^-$ resulted in a chemoselective preference for the nucleophilic attack to the aldehyde functionality versus the conjugated β position. Scheme 5b illustrates the reactivity with cinnamaldehyde towards the formation of trisubstituted conjugated dienyl compounds in 68:32 *E:Z* ratio. It is worthy to note that the use of the more sterically hindered carbanion [C(Bpin)$_2$(SiMe$_2$^{t}Bu)]$^-$ contributed to enhance the preference on the *E* stereoisomer (Scheme 5b).[20] The boron-Wittig reaction between Li[C(Bpin)$_2$(SiMe$_2$^{t}Bu)] and 3-phenylpropiolaldehyde allowed the synthesis of the corresponding 1,1,–silylborylated enyne with marked preference on the *E* stereoisomer (Scheme 5c).[20]

The reactivity between Li[C(Bpin)$_2$(SiMe$_3$)] and 3,4-epoxy-1-cyclohexene has proved to be efficient towards the regio- and diastereoselective S$_N$2 ring opening / C–C cross-coupling on the allylic position (Scheme 6a).[5n] It is interesting to note that the final product has suffered a proto-deborylative sequence, probably assisted by the OH functional groups in the products. We also conducted the nucleophilic ring opening / C–C cross-coupling of 2-methyl-2-vinyloxirane with Li[C(Bpin)$_2$(SiMe$_3$)], and we proved not only that the nucleophilic attack occurred exclusively at the homoallylic position, but also that the new product suffered an intramolecular cyclization to give the substituted 3,3-borylsilyl 1,2-oxaborolan-2-ol product (Scheme 6b).[5n]

Complementarily, the reactivity between Li[C(Bpin)$_2$(SiMe$_3$)] and cyclic vinyl aziridines is successfully conducted via exclusive nucleophilic S$_N$2 attack on the allylic position (Scheme 7a) with concomitant ring opening pathway.[5o] In this case the proto-deborylation is not assisted by the NH present in the products. Interestingly, regioselective S$_N$2′ nucleophilic attack occurs on 2-methyl-1-tosyl-2-vinyl-



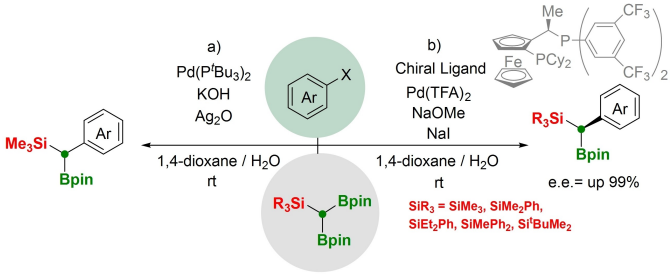
Scheme 6. *In situ* generation of Li[C(Bpin)$_2$(SiMe$_3$)] and nucleophilic ring opening / C–C cross coupling of vinyl epoxides



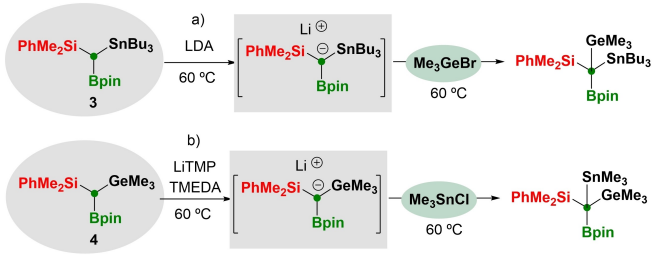
Scheme 7. *In situ* generation of Li[C(Bpin)$_2$(SiMe$_3$)] and nucleophilic ring opening / C–C cross coupling of vinyl aziridines

aziridines forming the homoallylic silyl-diboronates with complete *E* stereoselectivity (Scheme 7b).[5o]

The activation of *gem*-diborylsilylmethane (**2**) can also be conducted with Pd complexes to catalyze the Suzuki-Miyaura cross coupling reactions with aryl halides, giving access to relevant benzylic 1,1-silylboronate esters (Scheme 8a) following the original work by Endo and co-workers.[21] The asymmetric version of this process was accomplished by an elegant work by Cho and co-workers, using a Josiphos type chiral ligand to modify the Pd catalyst. This methodology established the Pd(TFA)$_2$ as catalyst precursor of choice and NaOMe as base, requiring NaI as additive for quantitative conversion, although its role in the mechanism remains unclear (Scheme 8b).[22] The same authors have reported a method for synthesizing various α-silyl-substituted allylic boronate esters through the palladium-catalyzed chemoselective coupling of (diborylmethyl)silanes with alkenyl bromides under mild conditions.[23]



Scheme 8. Palladium catalyzed activation of [CH(Bpin)$_2$(SiMe$_3$)] with concomitant cross-coupling reaction.



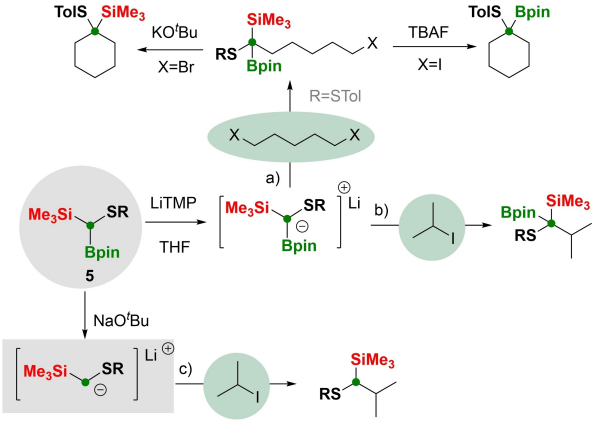
Scheme 9. Synthesis of B-, Ge-, Si-, and Sn-substituted methanes.

Borylsilyl-methanes can also be substituted with heteroatoms as Ge, Sn.[24] Shimizu et al., prepared [CH(SnBu$_3$)(Bpin)(SiMe$_2$Ph)] (**3**) and generated the corresponding carbanion with LDA followed by germylation with Me$_3$GeCl (Scheme 9a). Similarly, starting from the multifunctional species [CH(GeMe$_3$)(Bpin)(SiMe$_2$Ph)] (**4**) after treatment with LiTMP and TMEDA, the corresponding carboanion suffer a stannylation with Bu$_3$SnCl (Scheme 9b).

Our group synthesized the multifunctionalized compound [CH(SR)(Bpin)(SiMe$_3$)] (**5**) that could be eventually deprotonated with LiTMP to give the species Li[C(SR)(Bpin)(SiMe$_3$)] that efficiently performed a S$_N$2 alkylation pathway with primary and secondary alkyl halides (Scheme 10a,b).[25] The polyfunctionalized products could follow a selective intramolecular deborylative cyclization depending on the base involved. In the presence of KO^{t}Bu, deborylation took place and the resulting α-SiMe$_3$ and α-STol carbanion conducted the intramolecular alkylation sequence to deliver a 6-membered ring with *gem*-(SiMe$_3$)(STol) groups. Alternatively, when the base was TBAF, desilylation was preferred and the resulting α-Bpin and α-STol stabilized carbanion promoted the intramolecular alkylation towards the 6-membered ring with *gem*-(Bpin)(STol) groups (Scheme 10a). Similarly, the compound [CH(SR)(Bpin)(SiMe$_3$)] (**5**) could be activated via deborylation with NaO^{t}Bu, and the resulting carbanion performed the expected S$_N$2 alkylation with primary and secondary alkyl halides (Scheme 10c).[25]

3. α-Thioboron Carbanions

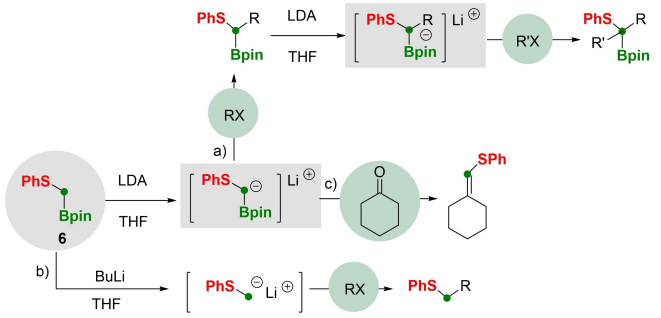
Another interesting route to hetero-substituted alpha-boron carbanions covers the introduction of alkylthio groups (SR). Matteson and co-workers[26] designed in 1978 a convenient approach towards the preparation of pinacol



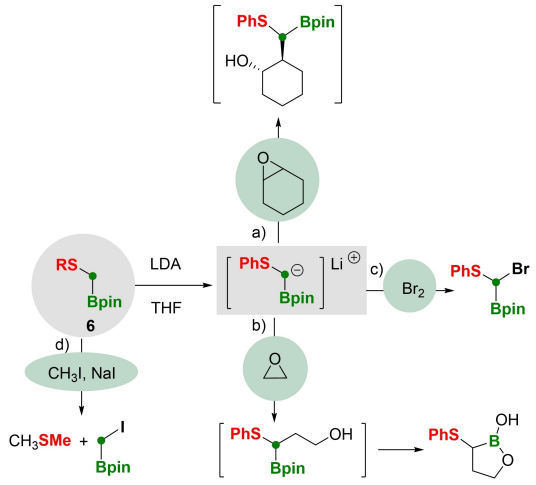
Scheme 10. Coupling reaction between [CH(SR)(Bpin)(SiMe$_3$)] (**5**) and primary or secondary alkyl halides, through selective activation depending on the bases.

(phenylthio)methaneboronate ester (**6**) and its deprotonation by lithium diisopropylamide (LDA) to generate the corresponding stabilized α-phenylthio, α-boryl carbanion (Scheme 11a). Alkylation of the carbanion with primary alkyl halides proceeds efficiently and the product may in turn be deprotonated and alkylated once more (Scheme 11a). The use of BuLi as base provides the C-Bpin cleavage and the subsequent alkylation is produced to give the corresponding thioether compound, instead (Scheme 11b). Besides the previous examples, Matteson also demonstrated that the reaction of α-phenylthio, α-boryl carbanion with cyclohexanone followed a boron-Wittig reaction towards the formation of enethiol ether (Scheme 11c).[26]

The α-phenylthio, α-boryl carbanion reacted with cyclohexene oxide to promote the diastereoselective S_N2 ring opening / C–C cross-coupling giving the *trans* isomer as the exclusive product (Scheme 12a).[26] For comparison, when Li[CH(Bpin)(SPh)] reacted with ethylene oxide, the nucleophilic ring opening / C–C cross-coupling provided the desired



Scheme 11. *In situ* generation of Li[CH(Bpin)(SPh)] and subsequent reactivity with alkyl halides and ketones.



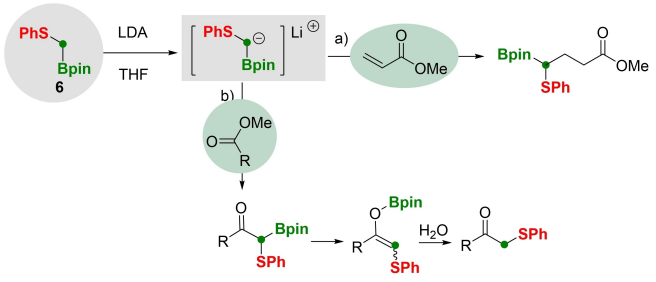
Scheme 12. *In situ* generation of Li[CH(Bpin)(SPh)] and subsequent reactivity with epoxides and Br_2 and MeI/NaI.

lineal product but an intramolecular cyclization between the OH and the Bpin moiety allowed the isolation of the substituted 3-thio-oxaborolan-2-ol product (Scheme 12b).[26] The α-phenylthio, α-boryl carbanion reacted efficiently with Br_2 to produce the interesting α-phenylthio, α-boryl α-bromo methane compound (Scheme 12c).[26] It has been demonstrated that pinacol (methylthio)methaneboronate ester can react with CH_3I to form the corresponding pinacol iodomethaneboronate together with $S(CH_3)_2$ (Scheme 12d).[27]

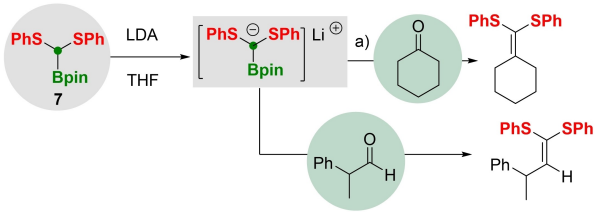
The chemistry of Li[CH(Bpin)(SPh)] with electron deficient alkenes has been illustrated when reacted with the Michael acceptor methylacrylate forming the C–C new bond regioselectively in the beta position (Scheme 13a).[28] However, the acylation of the α-phenylthio, α-boryl carbanion with methyl esters provides an efficient and general methodology to α-phenylthio ketones through a postulated boron enolate intermediate (Scheme 13 b).[26]

The accessibility to bis(phenylthio)boronic esters guarantees the facile deprotonation with LDA, and the new carbanion may react with ketones and aldehydes towards tetra- and trisubstituted 1,1-bis(phenylthio)alkene, which are considered very important ketene thioacetals (Scheme 14).[29] It was found that Li[CH(Bpin)$(SPh)_2$] reacted much better than the trimethylsilyl analogue, Li[$CH(SiMe_3)(SPh)_2$] which fails to homologate ketones having acidic α-hydrogens.

Recent studies have shown that *α*-thiodiboryl alkanes can be efficiently synthetized, however, the generation of the



Scheme 13. *In situ* generation of Li[CH(Bpin)(SPh)] and subsequent reactivity with esters and α,β-unsaturated esters.



Scheme 14. *In situ* generation of Li[CH(Bpin)$(SPh)_2$] and subsequent reactivity with ketones and aldehydes towards ketene thioacetals.

corresponding carbanionic species by treatment with LiTMP or NaO^{t}Bu bases is still underdeveloped.[30,31]

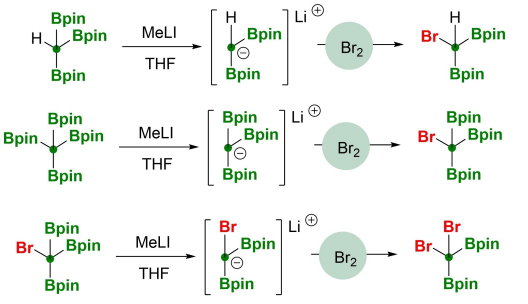
4. α-Haloboron Carbanions

The synthesis of haloboryl methane containing the iodine substituent, [CH_2(Bpin)(I)] (**8**), was designed by Matteson and co-workers since 1979.[32] This reagent and its analogue compounds [CH_2(Bpin)(Br)] (**9**), [CH_2(Bpin)(Cl)] (**10**) and [CH_2(Bpin)(F)] (**11**), have been mainly used as homologating reagents.[33] Halomethyl organoboron metalloids have shown to display several different reactivity profiles including metalation, boronate formation, and α-borylradicals. Cross-coupling reaction involving haloboryl alkane compounds, via oxidative addition, are nowadays strategic pathways to construct C–C bonds.[34]

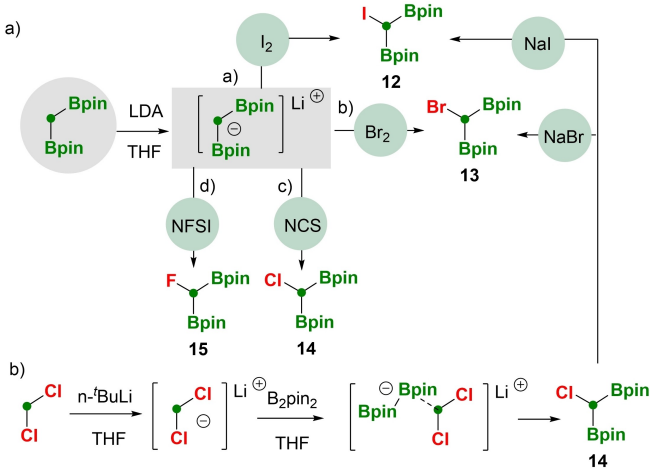
In parallel, halodiboryl methane are considered appealing reagents for the enhanced opportunities to transform both C–B bonds and/or the C-halide bond. Matteson and co-workers established a method for the preparation of bromo-diborylmethane by the activation of trisborylmethane with MeLi followed by treatment with Br_2 (Scheme 15)[35] Although this method is efficient, the preparations of tri- and tetraboryl-methane are still tedious.

Currently, the preparation and isolation of halodiboryl-methanes has been successfully achieved by Cho and co-workers, by reacting (diborymethyl)lithium salt with the corresponding halogenating reagent (Scheme 16a). Compounds [CH(Bpin)$_2$(I)] (**12**), [CH(Bpin)$_2$(Br)] (**13**), [CH-(Bpin)$_2$(Cl)] (**14**) and [CH(Bpin)$_2$(F)] (**15**) have been efficiently prepared and isolated in gram scale.[36,37] Liu and co-workers have also launched an alternative synthetic protocol in large scale, based on the use of B_2pin_2 to react with lithiated dichloromethane to accede chlorodiboryl methane, in which Bpin is the migrating group. Subsequent bromine or iodine substituted halodiboryl-methanes can be prepared by halide exchange with sodium bromide and sodium iodide (Scheme 16b).[38] Also alkyl-substituted *gem*-dichloro compounds serve to be transformed into the corresponding *gem*-halodiboryl alkanes with tetrasubstituted alkanes.

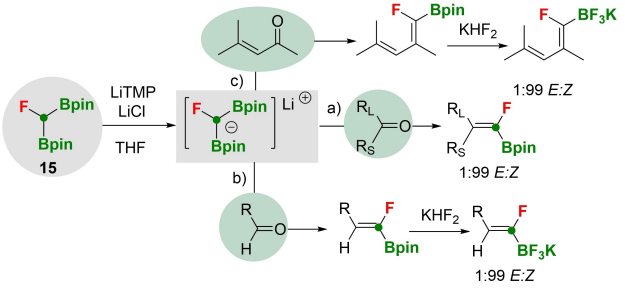
The fluoro-diborylmethyl anion can be generated from **15** by abstraction of the acidic proton in α-CH bond with LiTMP and the corresponding salt can promote an efficient synthesis of tetra- and tri-substituted (*Z*)-fluoroborylalkenes via Boron–Wittig reaction of ketones and aldehydes, respectively (Scheme 17a,b). The additive lithium chloride has been used suggesting a role to preserve monomeric lithium species, thereby facilitating B–O elimination before bond rotation along the intermediates of the Boron-Wittig reaction. The control on the stereoselectivity is justified by the minimization of the steric repulsion through the preferred B–O elimination in which the small fluorine atom is proximal to the large ketone substituent (R_L), delivering (*Z*)-fluoro-borylalkene as the major isomer. The reactivity of Li[C(Bpin)$_2$(F)] with β.β-disubstituted α,β-unsaturated ketones, also resulted chemoselective towards the boron-Wittig reaction (Scheme 17c).[36] This reactivity is very relevant since it is known that the presence of fluorine on a carbanion center dramatically



Scheme 15. Synthetic approach towards bromo-polyborylated methanes.



Scheme 16. Synthesis of halodiboryl-methanes a) from Li[CH(Bpin)$_2$] and b) from Li[CH(Cl)$_2$]

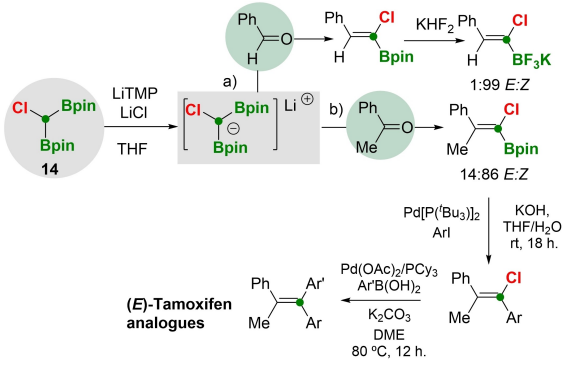


Scheme 17. *In situ* generation of Li[C(Bpin)$_2$(F)] and subsequent reactivity with ketones and aldehydes.

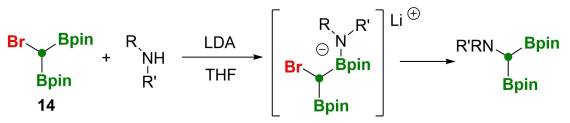
influence the nucleophilic alkylation reactions, due to the negative fluorine effect.[39]

Cho and co-workers also launched the transformation of [CH(Bpin)$_2$(Cl)] (**14**) into chloro-diborylmethane carbanion, by treatment of LiTMP to prove its efficiency towards the reaction with ketones and aldehydes. For instance, benzaldehyde participated in the boron-Wittig protocol affording the corresponding tri-substituted chloro-borylalkene favouring the Z-stereoisomer (Scheme 18a). Several alkyl and aryl ketones were readily converted to the corresponding chloro-borylalkenes in good yields, and subsequent consecutive chemoselective Suzuki-Miyaura couplings, lead to (*E*)-Tamoxifen derivatives (Scheme 18b).[36]

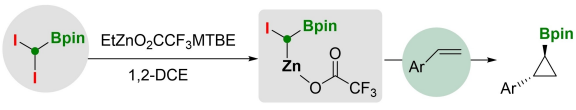
Interestingly, when the Boron-Wittig reaction of acetophenone was conducted with [CH(Bpin)$_2$(Br)] (**13**) / LiTMP the corresponding bromoborylalkene was obtained in high yield but with lower ratio (*E*/*Z* = 33: 67 ratio). However, when [CH(Bpin)$_2$(I)] (**12**) / LiTMP was used instead, no reaction took place under the standard reaction conditions.[37] Alternatively, [CH(Bpin)$_2$(Br)] (**13**) and [CH(Bpin)$_2$(I)] (**12**) were applied to homologative coupling with nitrogen nucleophiles such as carbamates, amides, and aromatic amines (Scheme 19).



Scheme 18. *In situ* generation of Li[C(Bpin)$_2$(Cl)] and subsequent reactivity with ketones and aldehydes.



Scheme 19. Synthesis of nitrogen-substituted diborylmethanes

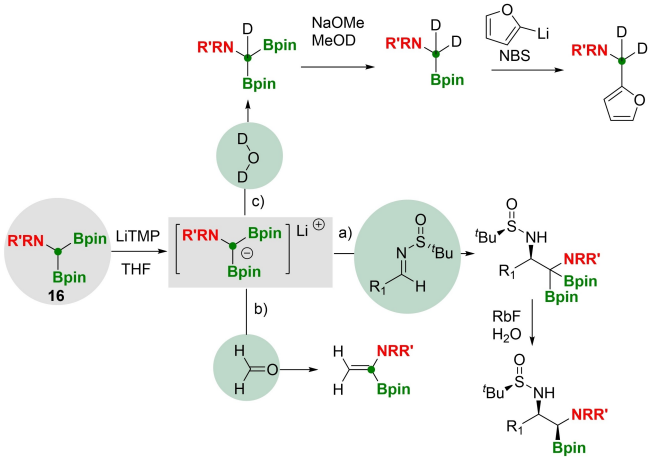


Scheme 20. Activation of diiodo-borylmethane with Zn(II) complexes to achieve borocyclopropanation.

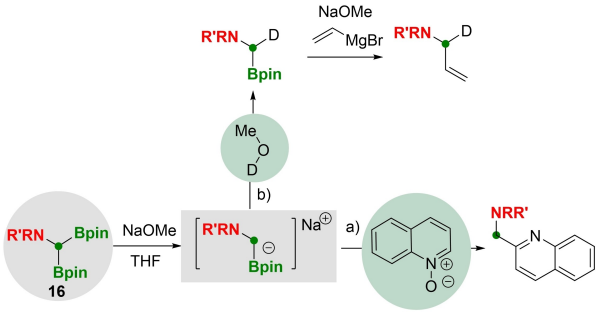
Carbenoid precursor from dichloro-borylmethane is not feasible due to the low C–Cl bond reactivity, however the more reactive diiodo precursor can be activated by zinc complexes to deliver a borocyclopropanation of (*E*)- or (*Z*)-allylic ethers and styrene derivatives via the Simons-Smith reaction (Scheme 20).[40a] Alternatively, the combination of diiodo-borylmethane, $CrCl_2$ with TMEDA can promote the borylcyclopropanation of unactivated alkenes under mild conditions, with the advantages that the reaction proceeds stereoselectively with disubstituted alkenes even without hydroxy or alkoxy groups, and both electron-rich and electron-deficient alkenes can be applicable.[40b]

5. α-Aminoboron Carbanions

Aminomethaneboronic esters are known from early preparations by Matteson and co-workers.[32] Since then α-amino, α-boryl alkanes have become essential synthons in biological application and material science.[41] Early attempts to generate the corresponding α-amino, α-boryl carbanion, by the presence of hindered bases, were unsuccessful. Recently, a series of nitrogen-substituted diborylmethanes have been prepared and the α-CH deprotonation could be achieved with LiTMP.[37] The corresponding carbanion proved to react with chiral *N*-*tert*-butanesulfinyl aldimines in THF at −50 °C or −60 °C affording the desired enantioenriched 1,2-diamino-1,1-diboronate esters in good yields and with high diastereoselectivity (Scheme 21a). Further diastereoselective protodeboronation, in the presence of RbF, and H_2O, produced the enantioenriched 1,2 diamino-1-boronate esters (Scheme 21a). Reactivity of Li[C(Bpin)$_2$(NRR')] with aldehydes, promoted the boron-Wittig reaction (Scheme 21b), whereas in the presence of D_2O the carbanion was deuterated, and further transformed via



Scheme 21. *In situ* generation of Li[C(Bpin)$_2$(NRR')] and subsequent reactivity with aldimines, aldehydes and D_2O.



Scheme 22. *In situ* generation of Na[CH(Bpin)(NRR')] and subsequent reactivity with quinoline-N-oxide or CH_3OD/vinyl magnesium bromide.

OMe- assisted deborylative deuteration and deborylative alkylation with RLi (Scheme 21c).[37]

Alternatively, the nitrogen-substituted diborylmethanes could be activated by NaOMe, throughout deborylation pathway, and the stabilized Na[CH(Bpin)(NRR')] carbanion serves as a convenient platform enabling alkylation with quinoline-N-oxide to yield heteroaryl-containing tertiary amines (Scheme 22a). The latent intermediate Na[CH-(Bpin)(NRR')] can introduce a deuterion atom, trapped from CH_3OD media, with the concomitant $C(sp^2)$-$C(sp^3)$ bond formarion by reaction with vinyl magnesium bromide, (Scheme 22b).

More recently, it has been described the efficient catalytic asymmetric synthesis of α-aminoboronic derivatives, via copper-catalyzed N-alkylation of carbamates by readily available racemic α-chloroboronate esters.[42]

Summarizing the message of this personal account, the role of heteroatom (heteroatom = Si, S, N, I, Br, Cl and F)-substituted boryl and diborylalkanes in organic synthesis is founded in the ability to stabilize the corresponding α-boryl carbanion and react with a great palette of electrophiles to construct a diverse type of functionalized molecules. Carbanions from α-$BSnCH_2$ or α-$BGeCH_2$ species were not considered in this account for the lack of representative examples about their reactivity. A breakthrough was made in this field, especially for the isolation and characterization of α-haloboryl carbanions and α-aminoboryl carbanions with Li as countercation.

It is the seed to experimental and theoretical unpredicted synthetic methodologies with greater confidence for years to come.

Acknowledgements

We thank Ministerio de Economía y Competitividad and Fondo Europeo de Desarrollo Regional FEDER through project PID2022-141693NB–I00.

References

[1] Selected Reviews: a) N. Miralles, R. J. Maza, E. Fernández, *Adv. Synth. Catal.* **2018**, *360*, 1306–1327; b) R. Nallagonda, K. Padala, A. Masarwa, *Org. Biomol. Chem.* **2018**, *16*, 1050–1064; c) Ch. Wu, J. B. Wang, *Tetrahedron Lett.* **2018**, *59*, 2128–2140; d) R. Gava, E. Fernández *Org. Biomol. Chem.* **2019**, *17*, 6317–6325; e) W. Jo, J. H. Lee, S. H. Cho, *Chem. Commun.* **2021**, *57*, 4346–4353; f) Y. Lee, S. Han, S. H. Cho, *Acc. Chem. Res.* **2021**, *54*, 3917–3929; g) C. Zhang, W. Hu, J. P. Morken, *ACS Catal.* **2021**, *11*, 10660–10680; h) M. Corro, O. Salvadó, S. González, P. Dominguez-Molano, E. Fernández, *Eur. J. Inorg. Chem.* **2021**, 2802–2813.

[2] Y. Ping, C. Wu, J. Wang, Chapter 3 in *Advances in Organometallic Chemistry towards Organic Synthesis*, Fernández, E. Ed. *Sci. Synth.* Thieme, **2020**.

[3] a) R. J. Maza, J. J. Carbó, E. Fernández, *Adv. Synth. Catal.* **2021**, *363*, 2274–2289; b) M. Eaton, Y. Zhang, Sh.-Y Liu, *Chem. Soc. Rev.* **2024**, doi-org.sabidi.urv.cat/10.1039/D3CS00730H.

[4] R. J. Maza, J. J. Carbó, E. Fernández, *Chem. Eur. J.* **2021**, *27*, 12352–12361.

[5] Selected coupling reactions with α-boryl alkylidene lithium or sodium salts: a) A. J. Wommack, J. S. Kingsbury, *Tetrahedron Lett.* **2014**, *55*, 3163–3166; b) K. Hong, X. Liu, J. P. Morken, *J. Am. Chem. Soc.* **2014**, *136*, 10581–10584; c) J. R. Coombs, L. Zhang, J. P. Morken, *J. Am. Chem. Soc.* **2014**, *136*, 16140–16143; d) J. R. Coombs, L. Zhang, J. P. Morken, *Org. Lett.* **2015**, *17*, 1708–1711; e) W. Jo, J. Kim, S. Choi, S. H. Cho, *Angew. Chem. Int. Ed.* **2016**, *55*, 9690–9694; f) T. C. Stephens, G. Pattison, *Org. Lett.* **2017**, *19*, 3498–3501; g) S. A. Murray, M. Z. Liang, S. J. Meek, *J. Am. Chem. Soc.* **2017**, *139*, 14061–14064; h) G- Gao, Z. Kuang, Q. Song, *Org. Chem. Front.* **2018**, *5*, 2249–2253; i) W. J. Teo, S. Ge, *Angew. Chem. Int. Ed.* **2018**, *57*, 1654–1658; j) X. Li, D. G. Hall, *Angew. Chem. Int. Ed.* **2018**, *57*, 10304–10308; k) C. E. Iacono, T. C. Stephens, T. S. Rajan, G. Pattison, *J. Am. Chem. Soc.* **2018**, *140*, 2036–2040; l) W. Sun, L. Wang, C. Xia, C. Liu, *Angew. Chem. Int. Ed.* **2018**, *57*, 5501–5505; m) S. A. Murray, E. C. M. Luc, S. J. Meek, *Org. Lett.* **2018**, *20*, 469–472; n) R. Gava, E. Fernández, *Chem. Eur. J.* **2019**, *25*, 8013–8017; o) O. Salvadó, R. Gava, E. Fernández, *Org. Lett.* **2019**, *21*, 9247–9250; p) W. Sun, L. Wang, Y. Hu, X. Wu, C. Xia, C. Liu, *Nat. Commun.* **2020**, *11*, 3113–3124; q) H. Kim, Y. Jung, S. H. Cho, *Org. Lett.* **2022**, *24*, 2705–2710; r) A. B. Cuenca, E. Fernández, *Chem. Soc. Rev.* **2021**, *50*, 72–86.

[6] a) R. Hunold, J. Allwohn, G. Baum, W. Massa, A. Berndt, *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 961–964; b) Ch.-W. Chiu, F. P. Gabbaï, *Angew. Chem. Int. Ed.* **2007**, *46*, 6878–6881; c) J. D. Hoefelmeyer, S. Sole, F. P. Gabbaï, *Dalton Trans.* **2004**, 1254–1258; d) M. M. Olmstead, P. P. Power, K. J. Weese, R. J. Doedens, *J. Am. Chem. Soc.* **1987**, *109*, 2541–2543; e) M. Pilz, J. Allwohn, R. Hunold, W. Massa, A. Berndt, *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1370–1374; f) Y. Sahin, M. Hartmann, G. Geiseler, D. Schweikart, C. Balzereit, G. Frenking, W. Massa, A. Berndt, *Angew. Chem. Int. Ed.* **2001**, *40*, 2662–2665; g) A. Tortajada, L. J. Bole, M. Mu, M.

Stanford, M. N. Peñas-Defrutos, M. García-Melchor, E. Hevia, *Chem. Sci.* **2023**, *14*, 6538–6543.

[7] Selected coupling reactions with α-boryl alkylidene copper complexes: a) P. Knochel, *J. Am. Chem. Soc.* **1990**, *112*, 7431–7433; b) M. Sakai, S. Saito, S. G. Kanai, A. Suzuki, N. Miyaura, *Tetrahedron* **1996**, *52*, 915–924; c) Z.-Q. Zhang, C.-T. Yang, L.-J. Liang, B. Xiao, X. Lu, J.-H. Liu, Y.-Y. Sun, T. B. Marder, Y. Fu, *Org. Lett.* **2014**, *16*, 6342–6345; d) J. M. Joannou, B. S. Moyer, S. J. Meek, *J. Am. Chem. Soc.* **2015**, *137*, 6176–6179; e) S. A. Murray, J. C. Green, S. B. Tailor, S. J. Meek, *Angew. Chem. Int. Ed.* **2016**, *55*, 9065–9069; f) J. Park, Y. Lee, J. Kim, S. H. Cho, *Org. Lett.* **2016**, *18*, 1210–1213; g) J. Kim, S. Park, J. Park, S. H. Cho, *Angew. Chem. Int. Ed.* **2016**, *55*, 1498–1501; h) Z.-Q. Zhang, B. Zhang, X. Liu, J.-H. Liu, B. Xiao, Y. Fu, *Org. Lett.* **2016**, *18*, 952–955; i) Y. Shi, A. H. Hoveyda, *Angew. Chem. Int. Ed.* **2016**, *55*, 3455–3458; j) A. Ebrahim-Alkhalil, Z.-Q. Zhang, T.-J. Gong, W. Su, X.-Y. Lu, B. Xiao, Y. Fu, *Chem. Commun.* **2016**, *52*, 4891–4893; k) N. Miralles, J. E. Gómez, A. W. Kleij, E. Fernández, *Org. Lett.* **2017**, *19*, 6096–6099; l) J. Kim, K. Ko, S. H. Cho, *Angew. Chem. Int. Ed.* **2017**, *56*, 11584–11588; m) J. Park, S. Choi, Y. Lee, S. H. Cho, *Org. Lett.* **2017**, *19*, 4054–4057; n) F. Li, Z.-Q. Zhang, X. Lu, B. Xiao, Y. Fu, *Chem. Commun.* **2017**, *53*, 3551–3554; o) H. Zhao, M. Tong, H. Wang, S. Xu, *Org. Biomol. Chem.* **2017**, *15*, 3418–3422; p) Q. Zhang, B. Wang, J. Q. Liu, Y. Fu, Y.-Ch. Wu, *J. Org. Chem.* **2018**, *83*, 561–570; q) J. Kim, M. Shin, S. H. Cho, *ACS Catal.* **2019**, *9*, 8503–8508; r) J. Kim, Ch. Hwang, Y. Kim, S. H. Cho, *Org. Process Res. Dev.* **2019**, *23*, 1663–1668; s) W. J. Jang, J. Yun, *Angew. Chem. Int. Ed.* **2019**, *58*, 18131–18135; t) S. Nishino, K. Hirano, M. Miura, *Org. Lett.* **2019**, *21*, 4759–4762; u) J. C. Green, J. M. Zanghi, S. J. Meek, *J. Am. Chem. Soc.* **2020**, *142*, 1704–1709; v) E. Wheatley, J. M. Zanghi, S. J. Meek, *Org. Lett.* **2020**, *22*, 9269–9275; w) Ch. Zhang, X. Wu, Ch Wang, Ch. Zhang, J. Qu, Y. Chen, *Org. Lett.* **2020**, *22*, 6376–6381; x) M. Kim, B. Park, M. Shin, S. Kim, J. Kim, M.-H. Baik, S. H. Cho, *J. Am. Chem. Soc.* **2021**, *143*, 1069–1077; y) S. González, D. Del Carratore, R. J. Maza, E. Fernández, *Tetrahedron Chem* **2023**, *8*, 100045.

[8] Selected coupling reactions with α-boryl alkylidene palladium complexes: a) K. Endo, T. Ohkubo, M. Hirokami, T. Shibata, *J. Am. Chem. Soc.* **2010**, *132*, 11033–11035; b) K. Endo, T. Ohkubo, M. Hirokami, T. Shibata, *Org. Lett.* **2011**, *13*, 3368–3371; c) K. Endo, T. Ohkubo, T. Ishioka, T. Shibata, *J. Org. Chem.* **2012**, *77*, 4826–4831; d) K. Endo, T. Ishioka, T. Ohkubo, T. Shibata, *J. Org. Chem.* **2012**, *77*, 7223–7231; e) C. Sun, B. Potter, J. P. Morken, *J. Am. Chem. Soc.* **2014**, *136*, 6534–6537; f) B. Potter, A. A. Szymaniak, E. K. Edelstein, J. P. Morken, *J. Am. Chem. Soc.* **2014**, *136*, 17918–17921; g) S. H. Cho, J. F. Hartwig, *Chem. Sci.* **2014**, *5*, 694–698; h) Z. He, Q. Zhu, X. Hu, L. Wang, C. Xia, C. Liu, *Org. Chem. Front.* **2019**, *6*, 900–907; i) F.-P. Wu, X.-F. Wu, *Angew. Chem. Int. Ed.* **2021**, *60*, 11730–11734.

[9] Selected coupling reactions with α-boryl alkylidene silver or zinc complexes: a) M. V. Joannou, B. S. Moyer, M. J. Goldfogel, S. J. Meek, *Angew. Chem. Int. Ed.* **2015**, *54*, 14141–14145; b) M. Zhan, R.-Z. Li, Z.-D. Mou, Ch.-G. Cao, J. Liu, Y.-W. Chen, D. Niu, *ACS Catal.* **2016**, *6*, 3381–3386; c) Y. Lee, J. Park, S. H. Cho, *Angew. Chem. Int. Ed.* **2018**, *57*, 12930–12934; d) H. Lee, Y. Lee, S. H. Cho, *Org. Lett.* **2019**, *21*, 5912–5916; e) W. Jo, S.-Y. Baek, C. Hwang, J. Heo, M.-H. Baik, S. Cho, *J. Am. Chem. Soc.* **2020**, *142*, 13235–13245; f) P. Guo, M. Zhan, *J. Org. Chem.* **2021**, *86*, 9905–9913; g) P. Guo, H. Jin, J. Han, L. Xu, P. Li, M. Zhan, *Org. Lett.* **2023**, *25*, 1268–1273.

[10] A. B. Cuenca, J. Cid, D. García-López, J. J. Carbó, E. Fernández, *Org. Biomol. Chem.* **2015**,*13*, 9659–9664.

[11] a) J. C. H. Lee, R. Mcdonald and D. G. Hall, *Nat. Chem.* **2011**, *3*, 894–899; b) X. Feng, H. Jeon and J. Yun, *Angew. Chem. Int. Ed.* **2013**, *52*, 3989–3992.

[12] P. Moquist, G.-Q. Chen, Ch. Mück-Lichtenfeld, K. Bussmann, C. G. Daniliuc, G. Kehr, G. Erker, *Chem. Sci.* **2015**, *6*, 816–815.

[13] a) D. S. Matteson, P. B. Tripathy, *J. Organomet. Chem.* **1974**, *69*, 53–55; b) O. Salvadó, P. Dominguez-Molano, E. Fernández, *Org. Lett.* **2022**, *24*, 4949–4953.

[14] a) D. S. Matteson, R. J. Moody, P. K. Jesthi, *J. Am. Chem. Soc.* **1975**, *97*, 5608–5609; b) D. S. Matteson, R. J. Moody, *J. Org. Chem.* **1980**, *45*,1091–1095; c) L. Zhang, Z. Huang, *J. Am. Chem. Soc.* **2015**, *137*, 15600–15603; d) W. N. Palmer, C. Zarate, P. Chirik, *J. Am. Chem. Soc.* **2017**, *139*, 2589–2592; e) S. H. Doan, B. K. Mai, Th. V. Nguyen, *ACS Catal.* **2023**, *13*, 8099–8105.

[15] a) B. Lee, P. J. Chirik, *J. Am. Chem. Soc.* **2020**, *142*, 2429–2437; b) H. Li, L. Wang, Y. Zhang, J. Wang, *Angew. Chem. Int. Ed.* **2012**, *51*, 2943–2946.

[16] W. Sun, Y. Hu, Ch. Xia, Ch. Liu, *New J. Chem.* **2021**, *45*, 14847–1485.

[17] Selected synthetic preparation of *gem*-borylsilylalkanes and subsequent reactivity: a) D. S. Matteson, D. Majumdar, *J. Organomet. Chem.* **1980**, *184*, C41–C43; b) H. Yatagai, Y. Yamamoto, K. Maruyama, *J. Am. Chem. Soc.* **1980**, *102*, 4548–4550; c) D. J. S. Tsai, D. S. Matteson, *Organometallics* **1983**, *2*, 236–241; d) D. Buynak, B. Geng, *Organometallics* **1995**, *14*, 3112–3115; e) M. Shimizu, H. Kitagawa, T. Kurahashi, T. Hiyama, *Angew. Chem. Int. Ed.* **2001**, *40*, 4283–4286; f) M. Murakami, I. Usui, M. Hasegawa, T. Matsuda, *J. Am. Chem. Soc.* **2005**, *127*, 1366–1367; g) O. Toshimichi, S. Michinori, *Bull. Chem. Soc. Jpn.* **2009**, *82*, 29–49; h) V. K. Aggarwal, M. Binanzer, M. C. de Ceglie, M. Gallanti, B. W. Glasspoole, S. J. F. Kendrick, R. P. Sonawane, A. Vázquez-Romero, M. P. Webster, *Org. Lett.* **2011**, *13*, 1490–1493; i) H.-Y. Jung, J. Yun, *Org. Lett.* **2012**, *14*, 2606–2609; j) F. Meng, H. Jang, A. H. Hoveyda, *Chem. Eur. J.* **2013**, *19*, 3204–3214; k) T. Mita, Y. Ikeda, K. Michigami, Y. Sato, *Chem. Commun.* **2013**, *49*, 5601–5603; l) J. H. Li, X. Shangguan, Z. Zhang, S. Huang, Y. Zhang, J. Wang, *Org. Lett.* **2014**, *16*, 448–451; m) A. L. Barsamian, Z. Wu, P. R. Blakemore, *Org. Biomol. Chem.* **2015**, *13*, 3781–3786; n) C. Bomio, M. A. Kabeshov, A. R. Lit, Sh.-H. Lau, J. Ehlert, C. Battilocchio, S. V. Ley, *Chem. Sci.* **2017**, *8*, 6071–6075; T. Bootwicha, J. M. Feilner, E. L. Myers, V. K. Aggarwal, *Nat. Chem.* **2017**, *9*, 896–902; o) H. Zhao, M. Tong, H. Wang, S. Xu, *Org. Biomol. Chem.* **2017**, *15*, 3418–3422; p) L. Wang, T. Zhang, W. Sun, Z. He, C. Xia, Y. Lan,

C. Liu, J . *Am. Chem.* **2017**, *139*, 5257–5264; R. J. Armstrong, V. K. Aggarwal, *Synthesis* **2017**, 3323–3336; q) A. A. Szymaniak, C. Zhang, J. R. Coombs, J. P. Morken, *ACS Catal.* **2018**, *8*, 2897–2901; r) C. Wu, Z. Bao, X. Xu, J. Wang, *Org. Biomol. Chem.* **2019**, *17*, 5714–5724; s) J. Kim, S. H. Cho, *ACS Catal.* **2019**, *9*, 230–235; J. Kim, E. Lee, S. H. Cho, *Angew. Chem. Int. Ed.* **2019**, *8*, 1664–16687; t) Y. Jung, S. Y. Yoo, Y. Jin, J. You, S. Han, J. Yu, Y. Park, S. H. Cho, *Angew. Chem. Int. Ed.* **2023**, *62*, e202218794; u) J. Park, Y. Jung, J. Kim, E. Lee, S. Y. Lee, S. H. Cho, *Adv. Synth. Catal.* **2021**, *363*, 2371–2376.

[18] a) D. S. Matteson, D. Majumdar, *J. Chem. Soc. Chem. Commun.* **1980**, 39–40; b) D. S. Matteson, D. Majumdar, *Organometallics* **1983**, *2*, 230–236; c) M. W. Rathke, R. Kow, *J. Am. Chem. Soc.* **1972**, *94*, 6854–6856.

[19] E. La Cascia, A. B. Cuenca, E. Fernández, *Chem. Eur. J.* **2016**, *22*, 18737–18741.

[20] O. Salvadó, E. Fernández, *Chem. Commun.* **2021**, *57*, 6300.

[21] K. Endo, F. Kurosawa, Y. Ukaji, *Chem. Lett.* **2013**, *42*,1363–1365.

[22] J. Kim and S. H. Cho, *ACS Catal.* **2019**, *9*, 230–235.

[23] J. Kim, E. Lee, S. H. Cho, *Asian J. Org. Chem.* **2019**, *8*, 1664–1667.

[24] M. Shimizu, T. Kurahashi, H. Kitagawa, K. Shimono, T. Hiyama, *J. Organomet. Chem.* **2003**, *686*, 286–293.

[25] M. G. Civit, J. Royes, Ch. M. Vogels, S. A. Westcott, A. B. Cuenca, E. Fernández, *Org. Lett.* **2016**, *18*, 3830–3833.

[26] a) D. S. Matteson, K. Arne, *J. Am. Chem. Soc.* **1978**, *15*, 1325–1326; b) D. S. Matteson, K. Arne, *Organometallics* **1982**, *1*, 280–288.

[27] D. P. Phillion, R. Neubauer, S. S. Andrew, *J. Org. Chem.* **1986**, *51*, 1610–1612.

[28] S. Jagannathan, T. Forsyth, Ch. A. Kettner, *J. Org. Chem.* **2001**, *66*, 6375–6380.

[29] A. Mendoza, D. S. Matteson, *J. Org. Chem.* **1979**, *44*, 1352–1354.

[30] Y. Wang, Y. Li, L. Wang, Sh. Ding, L. Song, X. Zhang, Y.-D. Wu, J. Sun, J . *Am. Chem.* **2023**, *145*, 2305–2314.

[31] V. Sufal, K. Piyush, A. Kashyap, R. Mondal, K. Geetharani, *Org. Lett.* **2023**, *25*, 2901–2906.

[32] a) D. S. Matteson, D. Majumda, *J. Organomet. Chem.* **1979**, *170*, 259–264; b) P. G. M. Wuts, P. A. Thompson, *J. Organomet. Chem.* **1982**, *234*, 137–141.

[33] a) D. S. Matteson, *Chem. Rev.* **1989**, *89*, 1535–1551; b) D. S. Matteson, B. S. Collins, V. K. Aggarwal, E. Ciganek, *Org. React.* **2021**, *105*, 427–860.

[34] Selected works on cross-coupling and reductive coupling with α-halo α-boryl alkanes: a) J. Schmidt, J. Choi, A. T. Liu, M. Slusarczyk, G. C. Fu, *Science* **2016**, *354*, 1265–1269; b) S.-Z. Sun, R. Martin, *Angew. Chem. Int. Ed.* **2018**, *57*, 3622–3625; c) S.-Z. Sun, M. Borjesson, R. M. Martin-Montero, R. Martin, *J. Am. Chem. Soc.* **2018**, *140*, 12765–12769; d) J.-B. Qiao, Z.-Z. Zhao, Y.-Q. Zhang, K. Yin, Z.-X. Tian, X.-Z. Shu, *Org. Lett.* **2020**, *22*, 5085–5089; e) J. Zhou, D. Wang, W. Xu, Z. Hu, T. Xu, *J. Am. Chem. Soc.* **2023**, *145*, 2081–2087; f) K. A. C. Bastick, A. J. B. Watson *ACS Catal.* **2023**, *13*, 7013–7018; g) P. Guo, H. Jin, J. Han, L. Xu, P. Li, M. Zhan, *Org. Lett.* **2023**, *25*, 1268–1273.

[35] D. S. Matteson, R. A. Davis, L. A. Hagelee, *J. Organomet. Chem.* **1974**, *69*, 45–51.

[36] S. Han, Y. Lee, Y. Jung, S. H. Cho, *Angew. Chem. Int. Ed.* **2022**, *61*, No. e20221053.

[37] C. Hwang, Y. Lee, M. Kim, Y. Seo, S. H. Cho, *Angew. Chem. Int. Ed.* **2022**, *61*, No. e202209079.

[38] a) T. Fang, L. Xu, Y. Qin, N. Jiang, Ch. Liu, *Chin. J. Org. Chem.* **2023**, *43*, 777–780; b) T. Fang, L. Wang, M. Wu, X. Qi, Ch. Liu, *Angew. Chem. Int. Ed.* **2024**, *63*, e202315227.

[39] W. Zhang, C. Ni, J. Hu, *Top. Curr. Chem.* **2012**, *308*, 25–44.

[40] a) G. Benoit, A. B. Charette, *J. Am. Chem. Soc.* **2017**, *139*, 1364–1367; b) M. Murai, Ch. Mizuta, R. Taniguchi, K. Takai, *Org. Lett.* **2017**, *19*, 6104–6107.

[41] a) P. Andrés, G. Ballano, M. I. Calaza, C. Cativiela, *Chem. Soc. Rev.* **2016**, *45*, 2291–2307; b) A. Sterman, I. Sosic, S. Gobeca, Z. Casar, *Org. Chem. Front.* **2019**, *6*, 2991–2998.

[42] G. Zuccarello, S. M. Batiste, H. Cho, G. C. Fu *J. Am. Chem. Soc.* **2023**, *145*, 3330–3334.

Manuscript received: November 17, 2023
Revised manuscript received: January 12, 2024
Version of record online: February 2, 2024

