Synthesis of fused B,N-heterocycles by alkyne cleavage, NHC ring-expansion and C-H activation at a diboryne†

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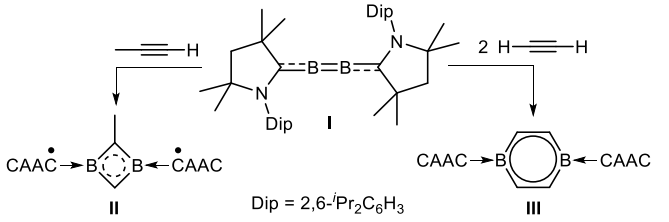
The addition of alkynes to a staturated N-heterocyclic carbene (NHC)-supported diboryne results in spontaneous cycloaddition, with complete B≡B and C≡C triple bond cleavage, NHC ring-expansion and activation of a variety of C-H bonds, leading to the formation of complex mixtures of fused B,N-heterocycles.

Whereas cycloaddition reactions of unactivated alkynes often display high activation barriers requiring the use of catalysts and/or very high temperatures,[1] the cycloaddition of alkynes with other homodinuclear multiple bonds of both groups 13 and 14 (E=E or E≡E) generally proceeds without the need for a catalyst, due to the significantly higher energy of the π-bonding HOMO of the heteroene/yne relative to those of C-C double or triple bonds.[2] Heavier group 14 alkene analogues, for example, undergo [2+2] cycloadditions with terminal acetylenes,[3] while [2+2] and [2+2+2] cycloadditions have been reported for Ge≡Ge and Si≡Si triple bonds, respectively.[4] Among the rare multiply bonded heavier group 13 analogues, both Tokitoh's masked dialumene benzene adduct and Inoue's first Al=Al alkene analogue react with alkynes to form 1,2-dihydro-1,2-dialumetes,[5] while Power's digallene undergoes a [2+2+2] cycloaddition to the corresponding 1,4-digallacyclohexa-2,5-diene.[6] We have reported that the photoactivated cycloaddition of 2-butyne to a phosphine-stabilised diaryldiborene yields a homoaromatic 1,3-dihydro-1,3-diborete, from the rearrangement of an intermediate 1,2-diborete.[7] Furthermore, the cyclic (alkyl)(amino)carbene (cAAC)-stabilised diboracumulene **I**,[8] reacts spontaneously with propyne and acetylene to yield the 2π-aromatic 1,3-diborete biradical **II** and the neutral 1,4-diborabenzene **III**, respectively (Scheme 1).[7] In contrast, neither diborenes nor diborynes stabilised by unsaturated N-heterocyclic carbenes (NHCs) undergo acetylene cycloaddition reactions even under forcing photolytic conditions.



Scheme 1. Previously reported reactions of alkynes with B-B multiple bonds.

We have previously described that the saturated NHC-stabilised diboryne (SIDep)B≡B(SIDep) (**1**, SIDep = 1,3-bis(2,6-diethylphenyl)-4,5-dihydroimidazol-2-ylidene)[9] is significantly more reactive than its unsaturated NHC-stabilised counterpart,[10] presumably due to the higher π-accepting ability of saturated NHCs.[11] Indeed, stirring a benzene solution of **1** under an acetylene atmosphere resulted in a rapid colour change from red to yellow. After workup the zwitterionic $C_5B_2N_2$ fused heterocycle **2-H** was isolated in 91% yield (Scheme 2), its structure being confirmed by X-ray crystallographic analysis (*vide infra*). In solution **2-H** presents ^{11}B NMR resonances at 54.0 (sp^2-*B*) and –10.2 (sp^3-*B*) ppm. The B_2C_3 core displays a diagnostic *H*C=B singlet at δ_{1H} = 4.04 ppm and a highly shielded AB doublet system at δ_{1H} = –0.12 and –0.74 ppm (^2J = 16.3 Hz) for the magnetically inequivalent BCH_2B protons. A 1H singlet at δ_{1H} =1.90 ppm was assigned to the terminal acetylide proton.

The addition of 2 equiv. phenyl-, *p*-trifluoromethylphenyl- and *p*-dimethylaminophenylacetylene to **1** yielded mixtures of three distinct products. Careful analysis of the complex 1D and 2D NMR spectra of these mixtures enabled the identification of the three constitutional isomers **2a-R**, **2b-R** and **3-R** displayed in Scheme 2. The annotated NMR spectra of the **2a/2b/3-Ph^{CF3}** product mixture in Fig. 1 showcase the characteristic resonances enabling the identification of each product. In all cases the major product is **2a-R** (**2a-Ph** 82%; **2a-Ph^{CF3}** 55%; **2a- Ph^{NMe2}** 93%), easily identified by the upfield ^{1}H NMR BCH_2B AB doublet system in the –0.8 to 0.2 ppm region (*H1*$_{2a}$, Fig. 1a) and its ^{11}B NMR *B1*$_{2a}$ resonance around –10 ppm. The minor product is its regioisomer **2b-R** (**2b-Ph** 3%; **2b-Ph^{CF3}** 10%; **2b-Ph^{NMe2}** 1%), identified by its diagnostic ^{1}H NMR *H*C=B singlet around 4.0 ppm (*H2*$_{2b}$, Fig. 1b), a splitting pattern of the ring-expanded NHC methylene protons similar to that of **2a-R** (compare *H4*$_{2a}$ and *H4*$_{2b}$, Fig. 1b), and a minor ^{11}B NMR *B1*$_{2b}$ resonance around –8 ppm (Fig. 1a).

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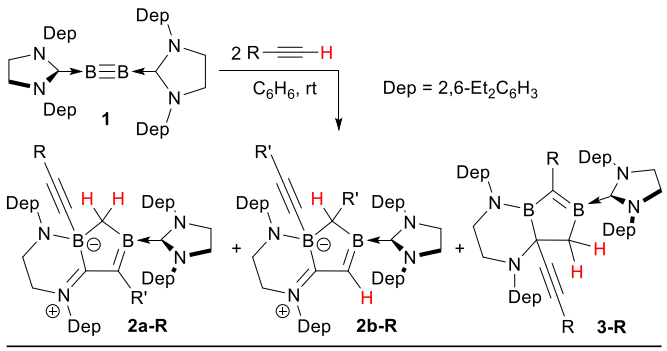
† *Electronic supplementary information (ESI) available: General experimental details, NMR spectra, details of the DFT calculations and crystallographic data. CCDC* 1907157-1907164*. For ESI and crystallographic data in CIF or other electronic format see xxx*



R, R'	2a-R (%)	2b-R (%)	3-R (%)
R = R' = H	100 (**2a/b-H** = **2-H**)		–
Ph	82	3	15
Ph^{CF3} (4-CF_3-C_6H_4)	55	10	35
Ph^{NMe2} (4-NMe_2-C_6H_4)	93	1	6
R = $SiMe_3$, R' = H	78 (**2-TMS**)	22 (**2-H**)	–

Scheme 2. Reaction of diboryne **1** with terminal alkynes and product distributions.

The third product, **3-R** (**3-Ph** 15%; **3-Ph^{CF3}** 35%; **3-Ph^{NMe2}** 6%), was unequivocally identified by the solid-state structure of **3-Fc**, in which the second equivalent of acetylene has added across the C2-C3 bond, generating a stereocentre at C3 (Fig. 2, *vide infra*). **3-R** presents a characteristic BC*H*$_2$B AB doublet system in the 0.5 to 1.2 ppm region (*H1*$_3$, Fig. 1c)‡ as well as a splitting pattern of the ring-expanded NHC methylene protons that is distinct and upfield-shifted from that of **2a/b-R** (*H4*$_3$, Fig. 1b). Very broad and barely distinguishable ^{11}B NMR resonances around 38 and 54 ppm were attributed to *B1*$_3$ and *B2*$_{2a/2b/3}$, respectively (Fig. 1a).§ For the **2a/2b/3-Ph^{CF3}** mixture the additional ^{19}F NMR data confirmed their relative proportions (Fig. 1d). Separation of the three products proved impossible due to near identical solubility and polarity. It is noteworthy that these $C_5B_2N_2$ fused heterocycles are the first of their kind.

For the reaction with trimethylsilylacetylene, a large excess (80 equiv.) were required to reach full conversion of **1** within 18 hours at room temperature to a 78:22 mixture of **2-TMS** and **2-H** (Scheme 2). The loss of the silyl groups was explained by the analysis of the reaction mixture after full consumption of **1**, which revealed that 36 equiv. $Me_3SiC{\equiv}CH$ had been converted to acetylene (δ_{1H} = 1.42 ppm, δ_{13C} = 71.7 ppm)[12] and $Me_3SiC{\equiv}CSiMe_3$ (δ_{1H} = 0.13 ppm, δ_{29Si} = –19.4 ppm).[13] While the latter does not react with **1**, the former is responsible for the incorporation of acetylene into the products, **2-TMS** and **2-H**. It thus appears that **1** catalyses this unusual alkyne C-H/C-$SiMe_3$ σ-bond metathesis, a reaction that has previously only been reported for an oxo-bridged bis(uranium) complex.[14]

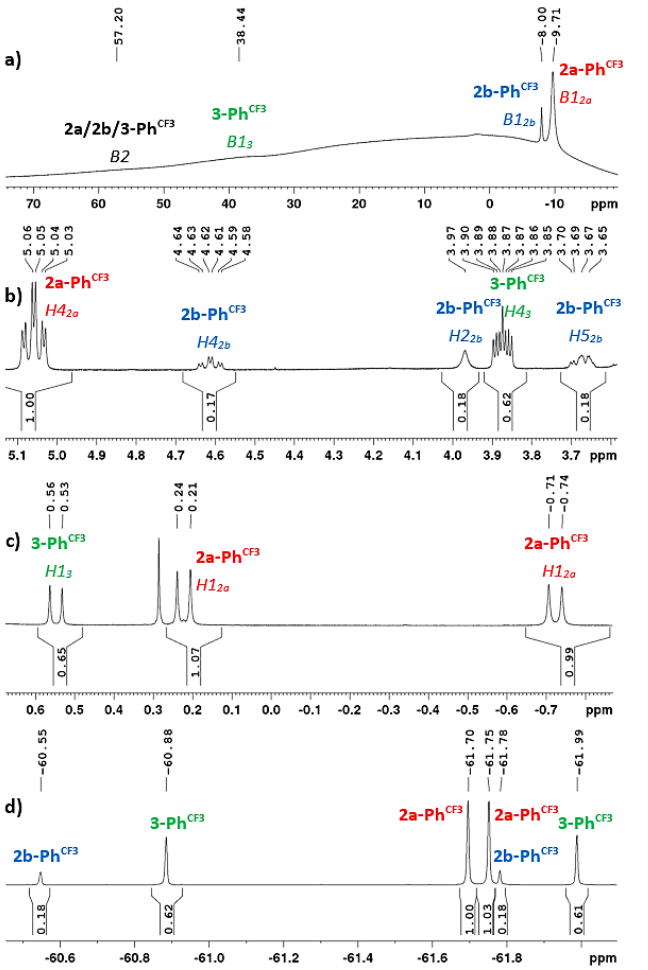


Fig. 1. Annotated NMR spectra of the product mixture **2a/2b/3-Ph^{CF3}** in C_6D_6: **a)** ^{11}B NMR spectrum; **b)** ^{1}H NMR spectrum, 3.6 to 5.2 ppm; **c)** ^{1}H NMR spectrum, –0.8 to 0.6 ppm **d)** ^{19}F NMR spectrum.

Slow evaporation of saturated benzene solutions of the mixtures provided yellow single crystals of the major products, **2-H**, **2a-Ph** (Fig. 2), **2a-Ph^{CF3}**, **2a-Ph^{NMe2}** and **2-TMS** (see Figs S55–S57 in the Supporting Information) suitable for X-ray diffraction analysis. In all these compounds the B_2C_3 core is found in an envelope conformation fused at the B1 and C3 positions to the ring-expanded NHC. The average B1-C2, C2-C3 and C3-N2 bond lengths of 1.47, 1.41 and 1.35 Å, respectively, suggest partial double bonds and delocalisation of π-density over the B2-C2-C3-N2 framework.

The reaction of **1** with ferrocenylacetylene took a different course. Beside minute amounts of **2a-Fc** (< 2%) and ca. 32% **3-Fc**, identified by its ^{1}H NMR BC*H*$_2$B AB doublet system at 0.77 and 0.83 ppm, the major product (66%) presents a ^{1}H NMR BC*H*$_2$B singlet (2H) at –0.07 ppm, as well as three distinctive 1H multiplets at 3.45 (d, ^3J = 8.8 Hz), 3.59 ppm (d, ^3J = 15.2 Hz) and 6.45 ppm (dd, ^3J = 8.8, 15.2 Hz), typical of a vinyl group. Furthermore, the ^{11}B NMR spectrum shows two very broad overlapping resonances in the 24 to 29 ppm region.§ X-ray structural analysis enabled the identification of this compound as **4-Fc** (Fig. 3), which is comprised of a central 3-Fc-1,2-dihydro-1,3-diborete bound via B1 to an *N*-vinylcarbamimide

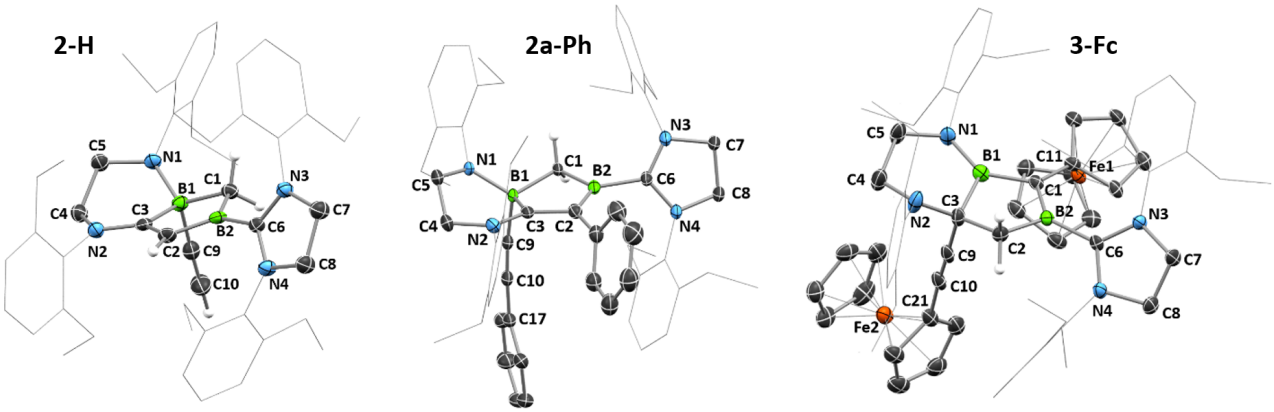


Fig. 2. Crystallographically-derived molecular structures of **2-H**, **2a-Ph** and **3-Fc**. Thermal ellipsoids drawn at the 50% probability level. Dep groups represented in framework style and hydrogen atoms omitted for clarity, except for the diagnostic protons bound to C1 or C2.

ligand, which results from the deprotonation and ring-opening of the SIDep backbone. While backbone deprotonations of unsaturated NHCs[15] and ring-opening at the N-$C_{carbene}$ bond[16] are well-known in NHC chemistry, backbone deprotonation and ring-opening at the N-$C_{backbone}$ bond of a saturated NHC or NHO (N-heterocyclic olefin) have only recently been reported for the first time.[17] The B_2C_2 core of **4-Fc** adopts a butterfly conformation with a B-B axis. The coplanarity of the B1-C2-B2 plane and the Cp ring, as well as the partial B1-C2, C1-B2 and C1-C11 double bonds (1.497(5), 1.490(5) and 1.454(4) Å, respectively) suggest π-delocalization over the entire B1-C2(Cp)-B1 moiety. The planar *N*-vinylcarbamimide ligand framework binds to the B_2C_2 ring via a B2-C3 single bond (1.604(4) Å) and displays C5-C4 (1.321(4) Å) and C3-N1 (1.291(4) Å) double bonds.

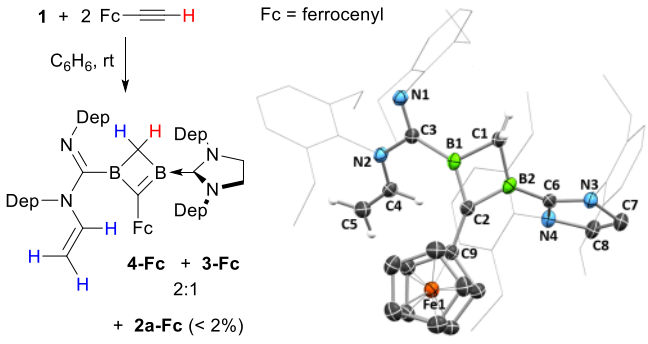


Fig. 3. Reaction of **1** with ferrocenylacetylene and crystallographically-derived molecular structure of **4-Fc**. Thermal ellipsoids drawn at the 50% probability level. Dep groups represented in framework style and hydrogen atoms omitted for clarity, except for the diagnostic protons bound to C1, C4 and C5.

Finally, the reaction of **1** with diphenylacetylene resulted in the formation of **5-Ph₂**, which presents two very broad ^{11}B NMR resonances at 23 and 49 ppm, indicative of two sp^2-boron centres. X-ray crystallographic analysis revealed a complex structure comprised of four fused cycles, including a fused bicyclic $B_2N_2C_5$ core, itself fused at the C3 and N2 positions to an indoline moiety resulting from the C-H activation of a Dep ethyl substituent. Furthermore, due to its three stereocentres (C1, C3, C23) the ^{1}H NMR spectrum of **5-Ph₂** displays six diastereomers. The major one (ca. 77%) shows a BC*H*(Ph)B singlet at 2.08 ppm, as well as a characteristic quartet at 3.96 ppm for *H23*, coupling to a methyl doublet at 1.44 ppm. The solid-state structure shown in Fig. 4 corresponds to the (C1^R,C3^S,C23^S)/(C1^S,C3^R,C23^R) diastereomeric pair.

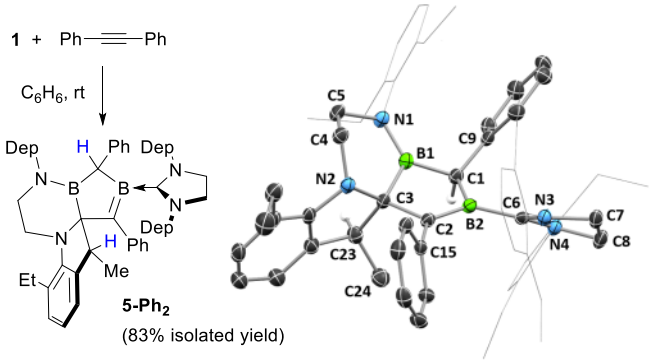
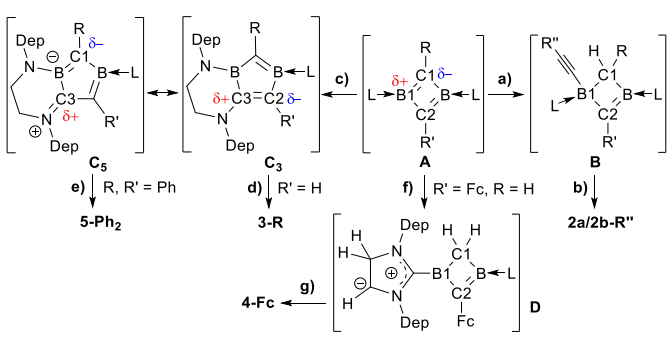


Fig. 4. Reaction of **1** with diphenylacetylene and crystallographically-derived molecular structure of **5-Ph₂**. Thermal ellipsoids drawn at the 50% probability level. Dep groups represented in framework style and hydrogen atoms omitted for clarity, except for the diagnostic protons bound to C1 and C23.

The isolation of the various reaction products of **1** with both terminal and internal alkynes gives us an insight into the possible reaction mechanisms at work. In all cases the first step of the reaction is likely the formation of a transient antiaromatic 1,2-diborete by [2+2] cycloaddition, which instantly rearranges to the thermodynamically more stable 1,3-diborete **A** (Scheme 3). Unlike the CAAC ligands in compound **II**, which are capable of absorbing one electron each and becoming radicals, resulting in a stable 2π-aromatic B_2C_2 core (Scheme 1), the SIDep ligands cannot form stable radicals, making **A** highly reactive. A 1:1 reaction of **1** and phenylacetylene in C_6D_6 showed 50% conversion to the **2a/2b/3-Ph** product mixture, leaving 50% of **1** unreacted, which shows that the formation of **A** is the rate-limiting step in all cases, ring-expansion and C-H activation being significantly faster. For terminal acetylenes, the addition of the C-H bond across the polarized B1=C1 double bond leads to intermediate **B** (Scheme 2, step **a**), which then undergoes NHC ring-

expansion by insertion into the B1-C2 bond, yielding **2a/2b-R** (step b). The regioselectivity of step **a** is likely dictated by sterics, which leads to an overall preference for alkyne addition across B1=C1(H) and ultimately product **2a-R**.



Scheme 3. Proposed intermediates in the formation of **2a/2b/3-R**, **4-Fc** and **5-Ph$_2$**.

There is, however, also an electronic effect: as the electron-withdrawing nature of R increases in the order of Ph^{NMe2} < Ph < Ph^{F}), the B1=C1(R) bond becomes more polarised, thereby facilitating the addition of the second equivalent of alkyne and increasing the proportion of **2b-R** formed. Conversely, intermediate **A** itself may undergo ring-expansion to intermediate **C** (step **c**), the regioselectivity being again dictated by sterics, so that insertion of C3 occurs into the less hindered B1-C2 bond. For terminal alkynes, C-H addition then occurs across the less hindered C3=C2(H) bond (step d), leading to **3-R**. For the diphenyl derivative, the more electronegative C1 atom deprotonates one of the Dep-ethyl groups, leading to **5-Ph$_2$** (step e). Finally, the formation of **4-Fc** must proceed directly from **A**: the strongly electron-donating Fc substituent renders C1 particularly basic, thus promoting the (inter- or intramolecular) deprotonation of the SIDep backbone, yielding a mesoionic intermediate **D** analogous to that recently isolated from the C-F activation of C_6F_6 by SIDip (step **f**).[17a] This can be followed by ring-opening at the N-$C_{backbone}$ bond to yield **4-Fc** (step **g**).[17]

In conclusion, the reactions of terminal and internal alkynes with a saturated NHC-stabilised diboryne result in complex mixtures of fused B,N-heterocycles, which can be deconvoluted using NMR spectroscopic and X-ray crystallographic analyses. The selectivity of the reactions can be rationalised by considering a common, highly reactive 1,3-diborete intermediate, which can undergo further alkyne addition, NHC ring-expansion or NHC backbone deprotonation and rearrangement.

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Notes and references

‡ The second BC*H$_2$*B doublet, identified by a COSY experiment, overlaps with the Dep-C*H$_3$* resonances around δ_{1H} = 1.1 ppm.

§ Experimental ^{11}B NMR resonances were attributed based on theoretical shifts calculated at the B3LYP/6-311G(d) level (Fig. S58 in the Supporting Information).

1 (a) I. A. Maretina and B. I. Ionin, *Regioselective Syntheses of Polysubstituted Benzenes Catalyzed by Transition Metal Complexes.* In *Alkynes in Cycloadditions* (Ed. J. C. Tebby), Wiley-VCH, Weinheim, 2014; (b) F. R. Truscott, G. Maestri, R. Rodriguez and M. Malacria, *Part II: Catalytic Cycloaddition Reactions*. In *Modern Alkyne Chemistry: Catalytic and Atom-Economic Transformations* (Eds. B. M. Trost and C.-J. Li), Wiley-VCH Verlag, 2015.

2 (a) E. Rivard, *Chem. Soc. Rev*., 2016, **45**, 989; (b) R. C. Fischer and P. P. Power, *Chem. Rev*., 2010, **110**, 3877; (c) P. P. Power, *Organometallics*, 2007, **26**, 4362.

3 (a) J. Schneider, J. Henning, J. Edrich, H. Schubert and L. Wesemann, *Inorg. Chem*., 2015, **54**, 6020; (b) V. Y. Lee, T. Fukawa, M. Nakamoto, A. Sekiguchi, B. L. Tumanskii, M. Karni and Y. Apeloig, *J. Am. Chem. Soc*., 2006, **128**, 11643; (c) S. A. Batcheller and S. Masamune, *Tetrahedron Lett*., 1988, **29**, 3383; (d) D. J. De Young and R. West, *Chem. Lett*., 1986, 883.

4 (a) R. Kinjo, M. Ichinohe, A. Sekiguchi, N. Takagi, M. Sumimoto and S. Nagase, *J. Am. Chem. Soc*., 2007, **129**, 7766; (b) C. Cui, M. M. Olmstead and P. P. Power, *J. Am. Chem. Soc*., 2004, **126**, 5062.

5 (a) P. Bag, A. Porzelt, P. J. Altmann and S. Inoue, *J. Am. Chem. Soc*., 2017, **139**, 14384; (b) T. Agou, T. Nagata and T. Tokitoh, *Angew. Chem. Int. Ed*., 2013, **52**, 10818.

6 Z. Zhu, X. Wang, M. M. Olmstead and P. P. Power, *Angew. Chem. Int. Ed*., 2009, **48**, 2027.

7 M. Arrowsmith, J. Böhnke, H. Braunschweig, M. A. Celik, C. Claes, W. C. Ewing, I. Krummenacher, K. Lubitz and C. Schneider, *Angew. Chem. Int. Ed*., 2016, **55**, 11271.

8 J. Böhnke, H. Braunschweig, W. C. Ewing, C. Hörl, T. Kramer, I. Krummenacher, J. Mies, A. Vargas, *Angew. Chem. Int. Ed*., 2014, **53**, 9082.

9 M. Arrowsmith, J. Böhnke, H. Braunschweig, M. A. Celik, T Dellermann and K. Hammond, *Chem. Eur. J*., 2016, **22**, 17169.

10 J. Böhnke, H. Braunschweig, P. Constantinidis, T. Dellermann, W. C. Ewing, I. Fischer, K. Hammond, F. Hupp, J. Mies, H.-C. Schmitt and A. Vargas, *J. Am. Chem. Soc*., 2015, **137**, 1766.

11 S. Fantasia, J. L. Petersen, H. Jacobsen, L. Cavallo and S. P. Nolan, *Organometallics*, 2007, **26**, 5880.

12 T. Zuschneid, H. Fischer, T. Handel, K. Albert, and G. Häfelinger, *Z. Naturforsch*., 2004, **59b**, 1153.

13 F. D. Uhlig and H. C. Marsmann, *Silicon-29 NMR some practical Aspects*. In *Gelest Catalogue, Silicon Compounds: Silanes & Silicones*, 2003, Morrisville, PA. USA: Eigenverlag.

14 J. Wang, Y. Gurevich, M. Botoshansky and M. S. Eisen, *J. Am. Chem. Soc.* 2006, **128**, 9350.

15 (a) M. Uzelac and E. Hevia, *Chem. Commun*., 2018, **54**, 2455; (b) J. B. Waters and J. M. Goicoechea, *Coord. Chem. Rev*., 2015, **293-294**, 80; (c) Y. Wang, Y. Xie, M. Y. Abraham, P. Wei, H. F. Schaefer III, P. v. R. Schleyer and G. H. Robinson, *J. Am. Chem. Soc*., 2010, **132**, 14370.

16 (a) S. Würtemberger-Pietsch, U. Radius and T. B. Marder, *Dalton Trans*., 2016, **45**, 5880; (b) M. R. Momeni, E. Rivard, and A. Brown, *Organometallics*, 2013, **32**, 6201; (c) D. Schmidt, J. H. J. Berthel, S. Pietsch and U. Radius, *Angew. Chem. Int. Ed*., 2012, **51**, 8881; (d) M. Arrowsmith, M. S. Hill, G. Kociok-Köhn, D. J. MacDougall and M. F. Mahon, *Angew. Chem. Int. Ed*., 2012, **51**, 2098.

17 (a) M. Pait, G. Kundu, S. Tothadi, S. Karak, S. Jain, K. Vanka and S. S. Sen, *Angew. Chem. Int. Ed.*, 2019, **58**, 2804; (b) T. X. Gentner, G. Ballmann, J. Pahl, H. Elsen and S. Harder, *Organometallics*, 2018, **37**, 4473.