Single Electron Transfer to Diazomethane–Borane Adducts Prompts C−H Bond Activations

Levy L. Cao, Jiliang Zhou, Zheng-Wang Qu,* and Douglas W. Stephan*

In memory of Nicholas C. Payne

Abstract: *While $(Ph_2CN_2)B(C_6F_5)_3$ is unstable, single electron transfer from Cp^*_2Co affords the isolation of stable products $[Cp^*_2Co][Ph_2CNNHB(C_6F_5)_3]$ **1** and $[Cp^*Co(C_5Me_4CH_2B-(C_6F_5)_3)]$ **2**. The analogous combination of Ph_2CN_2 and BPh_3 showed no evidence of adduct formation and yet single electron transfer from Cp^*_2Cr affords the species $[Cp^*_2Cr]-[PhC(C_6H_4)NNBPh_3]$ **3** and $[Cp^*_2Cr][Ph_2CNNHBPh_3]$ **4**. Computations showed both reactions proceed via transient radical anions of the diphenyldiazomethane–borane adducts to effect C−H bond activations.*

The activation of small molecules has been a major driver of organometallic chemistry over the last 60 years. Such efforts have spawned great interest and important developments. In recent years, such inquiries have begun to permeate main group chemistry. One avenue of main group chemistry exploited for the activation of small molecules has been frustrated Lewis pair (FLP) chemistry.[1] While this initially emerged from the finding of the heterolytic activation of H_2 by combinations of Lewis acids and bases,[2] subsequent efforts demonstrated reactivity of FLPs with a wide range of small molecules.[3] Noticeably absence from these investigations have been studies involving dinitrogen.

Organometallic chemists have studied metal–N_2 systems since the seminal report of A. D. Allen[4] who described the first transition metal–dinitrogen complex. Over the past 50 years numerous advances have emerged from the luminaries of organometallic chemistry including Schrock,[5] Cummins,[6] Peters,[7] Fryzuk,[8] Evans,[9] Gambarotta,[10] Nishibiashi,[11] Holland,[12] Chatt,[13] and Liddle[14] among others.[15] Avenues to metal-mediated N_2 chemistry have typically involved stoichiometric reductants.[8d] More recently, in 2017 the Szymczak[16] and Simonneau[17] groups demonstrated the utility of a Lewis acidic borane in promoting reactivity of

metal-bound N_2 fragments, effecting protonation, borylation and silylation of N_2 bound between the metal and boron.

Main group interactions with N_2 have drawn much less attention. A number of computational studies have addressed the interactions of N_2 with Lewis acids, while the species $(N_2)BF_3$ was spectroscopically characterized upon generation by supersonic expansion at 600 torr and 170 K.[18] The compound $Ph_3PNNPPh_3$[19] although not derived from N_2, was controversially described as N_2 stabilized by two phosphine donors.[20] However, in a truly seminal finding, Braunschweig et al.[21] described the first metal-free capture of N_2 using a cAAC-stabilized borylene (cAAC: cyclic (alkyl)(amino) carbene).
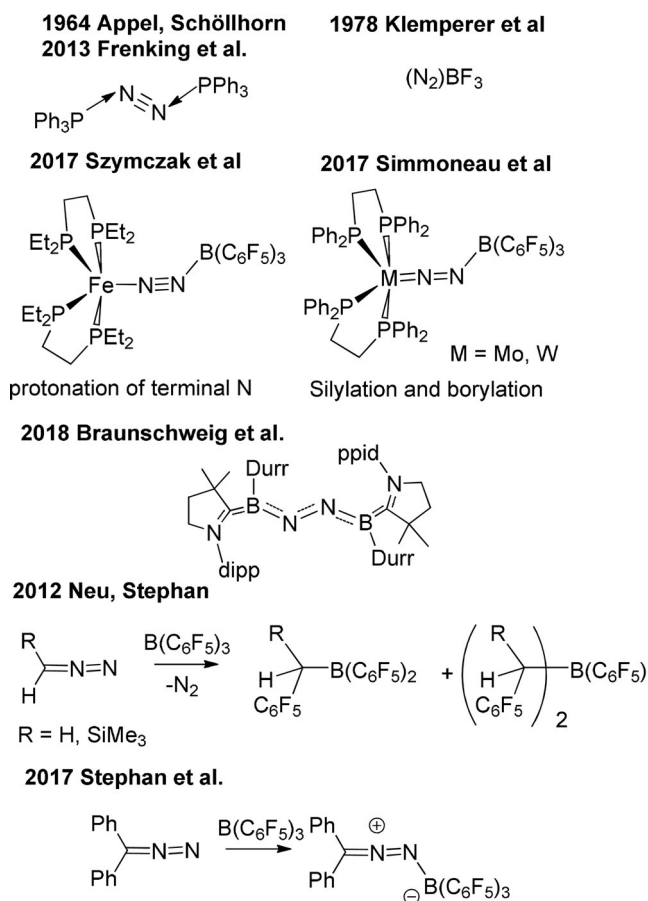
In our own efforts towards main group-N_2 chemistry, we initiated studies of diazomethanes which liberate N_2. Such systems may provide insight for the design of main group-N_2 systems.[22] In 2012, we reported the insertion of diazomethanes into B−C bonds of electrophilic boranes with the liberation of N_2 (Scheme 1).[23] Such insertions were recently exploited in organic synthesis by Melen et al.[24] In recent work,[25] we showed that the sterically-encumbered diazomethane, Ph_2CN_2, does not insert but rather forms a highly reactive, yet isolable borane-adduct, $(Ph_2CN_2)B(C_6F_5)_3$. Moreover, we also showed weak Lewis acid–base adducts were stabilized by stoichiometric reduction.[26] This notion was also exploited by the Erker group in the isolation of Lewis acid stabilized radicals.[27] Herein, we probe the impact of reduction on the reactivity of the unstable $(Ph_2CN_2)B(C_6F_5)_3$, demonstrating that single electron transfer to diazomethane-borane adducts stabilizes weak B···N interactions providing reactive transient radicals which effect C−H bond activation.

A 1:1 combination of diphenyldiazomethane (Ph_2CN_2) with $B(C_6F_5)_3$ in chlorobenzene was stirred at −35 °C. Addition of an equal molar amount of Cp^*_2Co immediately gave a yellow solution. The crude ^{19}F NMR spectrum showed two sets of resonances at −134.0, −163.9, and −167.3 ppm and −130.2, −161.9, −162.7 ppm, attributable to inequivalent C_6F_5 rings. The ^{11}B NMR spectrum showed two resonances at −7.6 and −13.0 ppm attributable to two tetra-coordinated boron species, **1** and **2**, respectively. ^1H NMR data showed resonances at 6.61 and 2.43 ppm attributable to NH and CH_2 fragments. Fractional recrystallization permitted formulation of the two products **1** and **2** by X-ray crystallographic analysis. Compound **1** was found to be the salt $[Cp^*_2Co][Ph_2CNNHB-(C_6F_5)_3]$ (Figure 1a). While the cation was unexceptional, the diazoborate anion was derived from the interaction of the hydrazide bound to borane. The B−N(H) bond length in **1** is 1.539(7) Å, while the N−N and N−C bonds lengths is 1.342(5)
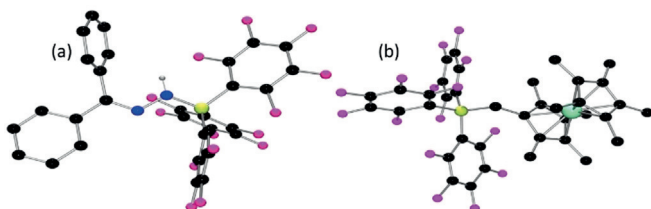
[*] Dr. L. L. Cao, Dr. J. Zhou, Prof. Dr. D. W. Stephan
Department of Chemistry, University of Toronto
80 St. George St., Toronto, Ontario, M5S3H6 (Canada)
E-mail: dstephan@chem.utoronto.ca

Dr. Z.-W. Qu
Mulliken Center for Theoretical Chemistry, Institut für Physikalische und Theoretische Chemie, Rheinische Friedrich-Wilhelms-Universität Bonn
Beringstrasse 4, 53115 Bonn (Germany)
E-mail: qu@thch.uni-bonn.de

1964 Appel, Schöllhorn
2013 Frenking et al.

Ph₃P—N≡N—PPh₃

Scheme graphic: Ph_3P–N=N–PPh_3

1978 Klemperer et al

$(N_2)BF_3$

2017 Szymczak et al

protonation of terminal N

2017 Simmoneau et al

M = Mo, W

Silylation and borylation

2018 Braunschweig et al.

2012 Neu, Stephan

R = H, SiMe₃

2017 Stephan et al.

Scheme 1. Interactions of main group systems with N₂-fragments.


Figure 1. POV-Ray depiction of the anion of a) **1** and b) **2**. The cation and hydrogen atoms (except NH) are omitted for clarity. C: black, N: blue, F: pink, B: yellow-green, Co: green, and H: grey.

and 1.303(7) Å, respectively. The B−N−N angle was determined to be 118.2(3)° while the C−N−N angle is 120.9(4)°. The second isolated product was confirmed to be [Cp*Co(C₅Me₄CH₂B(C₆F₅)₃)] **2** (Figure 1b). In this species, one of the hydrogen atoms in one of the Cp* methyl groups has been replaced by borane, affording the zwitterionic Co^{III}-borate **2**, with a methylene–boron B−C bond length of 1.66(1) Å.

Collectively, the identification of **1** and **2** is consistent with two possible reaction mechanisms involving single electron transfer from a Co^{II} center to either B(C₆F₅)₃[28] or the diazomethane adduct of the borane, (Ph₂CN₂)B(C₆F₅)₃.[25] It is noteworthy that although C−H activation by the radical [B(C₆F₅)₃)]·⁻,[29] is expected to give the anion [HB(C₆F₅)₃]⁻,

independent combination of diazomethane with [HB(C₆F₅)₃]⁻ showed no reaction. This supports the view that compound **1** is formed through hydrogen atom abstraction from Cp*₂Co by the transient diazomethane-borane adduct radical anion [Ph₂CN₂B(C₆F₅)₃]·⁻ (Scheme 2), consistent with the overall reaction ratio of diazomethane:Cp*₂Co:B(C₆F₅)₃ of 1:2:2.
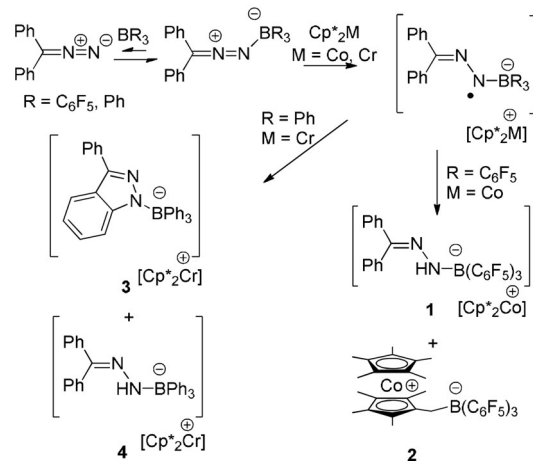
**Scheme 2.** Reactions of Ph₂CN₂ with B(C₆F₅)₃ and Cp*₂Co, and with BPh₃ and Cp*₂Cr.

Ph₂CN₂ was combined with BPh₃ in chlorobenzene at −35 °C. Monitoring the solution by multinuclear NMR spectroscopy revealed no evidence of adduct formation. This is consistent with the poor Lewis basicity of the diazomethane and the weaker Lewis acidity of the BPh₃ in comparison to B(C₆F₅)₃, in line with the computed free energies (see Supporting Information). Addition of Cp*₂Cr to a mixture of BPh₃ and diazomethane at −35 °C generated an orange solution. The ^{11}B NMR spectrum showed resonances at 23.0 and −3.5 ppm consistent with the formation of two products, **3** and **4** which were isolated by fractional crystallization. An X-ray diffraction study revealed species **3** to be [Cp*₂Cr][PhC(C₆H₄)NNBPh₃] (Scheme 2, Figure 2a). While the cation was typical, the anion of **3** was shown to be a borate with a substituent derived from the cyclization of the N₂ fragment onto the *ortho* position of one of the aryl rings on the diazomethane carbon. The resulting five membered ring which is fused to the aryl ring is 1,3-disubstituted with and phenyl ring on carbon and BPh₃ bound to nitrogen. The resulting N−B bond is 1.566(6) Å, while the N−N and new N−
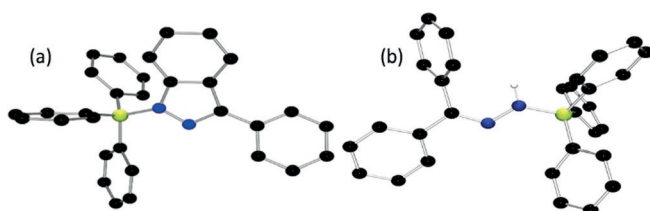
Figure 2. POV-Ray depiction of the anion of a) **3** and b) **4**. The cation and hydrogen atoms (except NH) are omitted for clarity. C: black, N: blue, and B: yellow-green.
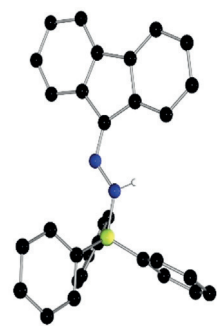
C bond distances are determined to be 1.312(5) and 1.351-(5) Å. The second product **4** was also characterized crystallographically revealing its formulation as [Cp*$_2$Cr][Ph$_2$CNNHBPh$_3$] (Scheme 2, Figure 2 b). The B−N and N−N distances in the anion of **4** were determined to be 1.562(4) Å and 1.322(3) Å, respectively.

In contrast, the reaction of 9-diazofluorene ((C$_{12}$H$_8$)CN$_2$) with B(C$_6$F$_5$)$_3$ did not form an adduct but led to loss of N$_2$ (Scheme 3) and the formation of the carboboration product
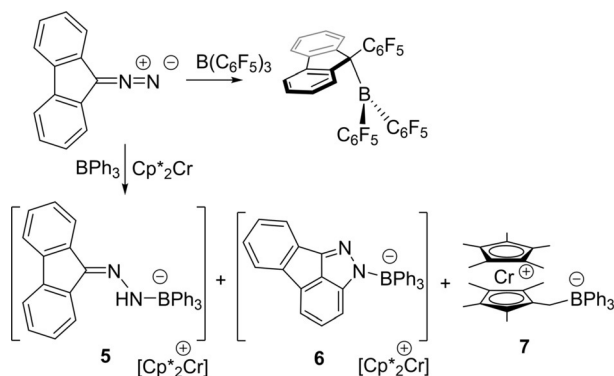
Scheme 3. Reactions of (C$_{12}$H$_8$)CN$_2$ with BPh$_3$ and Cp*$_2$Cr.

(C$_{12}$H$_8$)C(C$_6$F$_5$)(B(C$_6$F$_5$)$_2$) as confirmed spectroscopically and crystallographically (see Supporting Information). This is consistent with observations seen for less sterically encumbered diazomethanes.[23,30] However, monitoring the reaction of (C$_{12}$H$_8$)CN$_2$ with BPh$_3$ and Cp*$_2$Cr by ^{11}B NMR spectroscopy revealed the generation of three products as evidenced by the resonances at 26.2, 2.4, and −1.7 ppm. The peaks at −1.7 and 2.4 ppm were unambiguously assigned to [Cp*$_2$Cr][C$_{12}$H$_8$CNNHBPh$_3$] **5** and [Cp*Cr(C$_5$Me$_4$CH$_2$BPh$_3$)] **7** by NMR and crystallographic methods (Figure 3, see Supporting Information). The remaining resonance at 26.2 ppm, was attributed to the species [Cp*$_2$Cr][C$_{13}$H$_7$N$_2$BPh$_3$] **6** by analogy to **3**. These results suggest that the electron transfer to the weak adducts gives a transient radical [(C$_{12}$H$_8$)CN$_2$BPh$_3$]$^{•-}$, which reacts further through competitive pathways involving either intramolecular cyclization or intermolecular H-atom abstraction.

The mechanism of these reactions were probed by density functional theory (DFT) calculations at the PW6B95-D3/def2-QZVP + COSMO-RS// TPSS-D3/def2-TZVP + COSMO level of theory in chlorobenzene solution.[31] The reaction of Ph$_2$CN$_2$ with BPh$_3$ and Cp*$_2$Cr is initiated by single electron transfer from Cp*$_2$Cr to the unstable Ph$_2$CN$_2$·BPh$_3$ adduct (Figure 4) affording the radical anion [Ph$_2$CNNHBPh$_3$]$^{•-}$ **INT1** (spin on N next to B: 0.53 e) is 4.3 kcal mol^{-1}

Figure 3. POV-Ray depiction of the anion of **5**. The cation and hydrogen atoms (except NH) are omitted for clarity. C: black, N: blue, and B: yellow-green.
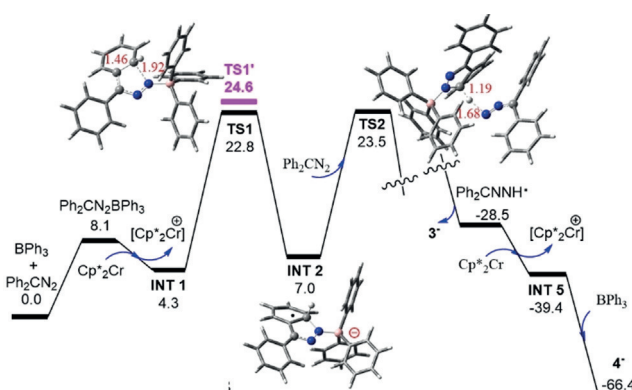
Figure 4. DFT-computed free energy profile (kcal mol^{-1}, at 298 K and 1 mol L^{-1} reference concentration) for the formation of anion of **3** and **4**. Selected bond lengths are given in angstroms while selected C: grey, H: white, N: blue, and B: pink.

endergonic. Alternative pathways involving electron transfers to separated BPh$_3$ and Ph$_2$CN$_2$ species (14.8 and 8.9 kcal mol^{-1}) are significantly less favorable. Similarly, further electron transfer to **INT1** is unlikely (12.2 kcal mol^{-1} endergonic). The N-centered radical **INT1** may then add intramolecularly to the *ortho* position of a phenyl ring (via transition structure **TS1**) to give **INT2** affording delocalization of the spin onto the ring. From here, a highly exergonic H-transfer to another Ph$_2$CN$_2$ molecule (via **TS2**) gives the anion of **3** and the neutral N-radical (Ph$_2$CNNH)$^•$ (spin on N next to H: 0.54 e) with a moderate overall barrier of 23.5 kcal mol^{-1}. The latter radical is readily reduced by Cp*$_2$Cr through electron transfer and trapped by BPh$_3$ giving the anion of **4** (−66.4 kcal mol^{-1}).

For the reaction of Ph$_2$CN$_2$ with the stronger Lewis acid B(C$_6$F$_5$)$_3$ and the more reductive Cp*$_2$Co,[32] electron transfer from Cp*$_2$Co to the reversible adduct (Ph$_2$CNN)B(C$_6$F$_5$)$_3$ is −15.3 kcal mol^{-1} exergonic affording the radical anion [Ph$_2$CN$_2$B(C$_6$F$_5$)$_3$]$^{•-}$. This intermediate is computed to effect H-atom from one methyl group of Cp*$_2$Co over a barrier of 16.6 kcal mol^{-1} to form the stable anion of **1** (see Supporting Information). The alternative intramolecular pathway, analogous to that above encounters a higher overall barrier of 23.3 kcal mol^{-1} (see Supporting Information).

To garner further support for the computed mechanism, efforts to observe the transient radical adducts in the reactions were undertaken, but were unsuccessful. However, monitoring the reaction of (C$_{12}$H$_8$)CN$_2$, Cp*$_2$Fe and Al(C$_6$F$_5$)$_3$ in C$_6$H$_5$Cl at room temperature by EPR spectroscopy revealed a pentet resonance at g(iso) = 2.0039, with (^{14}N) hyperfine couplings of 3.70 G and 3.58 G. This signal was similar to the related N-based radicals[33] and was attributed to the radical species [Ph$_2$CN$_2$Al(C$_6$F$_5$)$_3$]$^{•-}$. This signal slowly degrades at room temperature over 5 h, leaving a broad resonance attributed to an organic radical (see Supporting Information). Subsequent addition of Ph$_3$SnH generated a mixture of products, from which [Cp*$_2$Fe]-[(C$_{12}$H$_8$)CNNHAl(C$_6$F$_5$)$_3$] **8** was identified by NMR spectroscopy while single crystals of [Cp*$_2$Fe][(C$_{12}$H$_8$)CHAl(C$_6$F$_5$)$_3$] **9** were obtained from the reaction mixture (Figure 5). Com-
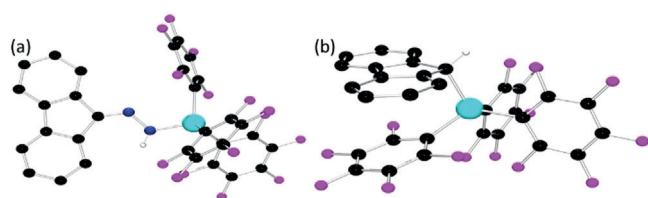
Figure 5. POV-Ray depiction of the anion of a) **8** and b) **9**. The cation and hydrogen atoms (except the NH and the Al-bound CH) are omitted for clarity. C: black, N: blue, Al: Cyan, and F: pink.

pound **8** was independently prepared and crystallographically characterized from the reaction of $(C_{12}H_8)CNNH_2$, $Cp*_2Fe$, and $Al(C_6F_5)_3$. The formulations of **8** and **9** are consistent with the generation of the spectroscopically observed radical anions $[(C_{12}H_8)CN_2Al(C_6F_5)_3]^{\cdot-}$ and $[(C_{12}H_8)CAl(C_6F_5)_3]^{\cdot-}$ (Scheme 4).
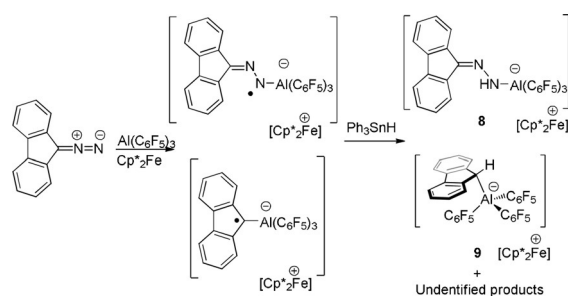
Scheme 4. Reactions of $(C_{12}H_8)CN_2$, $Al(C_6F_5)_3$ and $Cp*_2Fe$ with Ph_3SnH.

In conclusion, we have demonstrated that single electron transfer to unstable diazomethane-borane adducts, accesses reactive radical anions that effect H-atom abstraction from C–H bonds. The resulting anionic species are significantly more stable than the corresponding neutral adducts, suggesting that in situ reductions may be a useful strategy to infer the presence of weakly bound adducts. We suggest that this strategy could be exploited in developing main group-N_2 chemistry. At the same time, the potential utility of main group radical anions in C–H bond homolysis offers an interesting prospect for C–H functionalization.

Acknowledgements

Conflict of interest

The authors declare no conflict of interest.

[1] D. W. Stephan, *Science* **2016**, *354*, aaf7229.
[2] G. C. Welch, R. R. S. Juan, J. D. Masuda, D. W. Stephan, *Science* **2006**, *314*, 1124–1126.
[3] a) J. S. J. McCahill, G. C. Welch, D. W. Stephan, *Angew. Chem. Int. Ed.* **2007**, *46*, 4968–4971; *Angew. Chem.* **2007**, *119*, 5056–5059; b) M. A. Dureen, C. C. Brown, D. W. Stephan, *Organometallics* **2010**, *29*, 6594–6607; c) M. A. Dureen, D. W. Stephan, *J. Am. Chem. Soc.* **2009**, *131*, 8396–8398; d) M. A. Dureen, G. C. Welch, T. M. Gilbert, D. W. Stephan, *Inorg. Chem.* **2009**, *48*, 9910–9917; e) E. Otten, R. C. Neu, D. W. Stephan, *J. Am. Chem. Soc.* **2009**, *131*, 9918–9919; f) R. C. Neu, E. Otten, D. W. Stephan, *Angew. Chem. Int. Ed.* **2009**, *48*, 9709–9712; *Angew. Chem.* **2009**, *121*, 9889–9892; g) J. G. M. Morton, M. A. Dureen, D. W. Stephan, *Chem. Commun.* **2010**, *46*, 8947–8949; h) J. J. Chi, T. C. Johnstone, D. Voicu, P. Mehlmann, F. Dielmann, E. Kumacheva, D. W. Stephan, *Chem. Sci.* **2017**, *8*, 3270–3275; i) J. Chen, L. Falivene, L. Caporaso, L. Cavallo, E. Y. Chen, *J. Am. Chem. Soc.* **2016**, *138*, 5321–5333; j) M. Sajid, L.-M. Elmer, C. Rosorius, C. G. Daniliuc, S. Grimme, G. Kehr, G. Erker, *Angew. Chem. Int. Ed.* **2013**, *52*, 2243–2246; *Angew. Chem.* **2013**, *125*, 2299–2302; k) R. Dobrovetsky, D. W. Stephan, *J. Am. Chem. Soc.* **2013**, *135*, 4974–4977; l) M. Sajid, A. Stute, A. J. P. Cardenas, B. J. Culotta, J. A. M. Hepperle, T. H. Warren, B. Schirmer, S. Grimme, A. Studer, C. G. Daniliuc, R. Frohlich, J. L. Petersen, G. Kehr, G. Erker, *J. Am. Chem. Soc.* **2012**, *134*, 10156–10168; m) D. W. Stephan, G. Erker, *Chem. Sci.* **2014**, *5*, 2625–2641; n) K. Y. Ye, M. Bursch, Z. W. Qu, C. G. Daniliuc, S. Grimme, G. Kehr, G. Erker, *Chem. Commun.* **2017**, *53*, 633–635; o) L. E. Longobardi, V. Wolter, D. W. Stephan, *Angew. Chem. Int. Ed.* **2015**, *54*, 809–812; *Angew. Chem.* **2015**, *127*, 823–826.
[4] A. D. Allen, C. V. Senoff, *J. Chem. Soc. Chem. Commun.* **1965**, 621–622.
[5] a) R. R. Schrock, *Acc. Chem. Res.* **2005**, *38*, 955–962; b) R. R. Schrock, *Philos. Trans. R. Soc. London Ser. A* **2005**, *363*, 959–969; c) R. R. Schrock, *Angew. Chem. Int. Ed.* **2008**, *47*, 5512–5522; *Angew. Chem.* **2008**, *120*, 5594–5605.
[6] C. C. Cummins, *Chem. Commun.* **1998**, 1777–1786.
[7] J. S. Anderson, J. Rittle, J. C. Peters, *Nature* **2013**, *501*, 84.
[8] a) M. D. Fryzuk, S. A. Johnson, *Coord. Chem. Rev.* **2000**, *200–202*, 379–409; b) B. A. MacKay, M. D. Fryzuk, *Chem. Rev.* **2004**, *104*, 385–401; c) E. A. MacLachlan, M. D. Fryzuk, *Organometallics* **2006**, *25*, 1530–1543; d) R. J. Burford, M. D. Fryzuk, *Nat. Rev. Chem.* **2017**, *1*, 0026.
[9] a) D. H. Woen, G. P. Chen, J. W. Ziller, T. J. Boyle, F. Furche, W. J. Evans, *J. Am. Chem. Soc.* **2017**, *139*, 14861–14864; b) W. J. Evans, D. S. Lee, *Can. J. Chem.* **2005**, *83*, 375–384.
[10] a) S. Gambarotta, *J. Organomet. Chem.* **1995**, *500*, 117–126; b) S. Gambarotta, *Inorg. Chem. Highlights* **2002**, 285–295; c) S. Gambarotta, J. Scott, *Angew. Chem. Int. Ed.* **2004**, *43*, 5298–5308; *Angew. Chem.* **2004**, *116*, 5412–5422.
[11] H. Tanaka, Y. Nishibayashi, K. Yoshizawa, *Acc. Chem. Res.* **2016**, *49*, 987–995.
[12] a) P. L. Holland, *Dalton Trans.* **2010**, *39*, 5415–5425; b) K. C. MacLeod, P. L. Holland, *Nat. Chem.* **2013**, *5*, 559–565; c) S. F.

McWilliams, P. L. Holland, *Acc. Chem. Res.* **2015**, *48*, 2059–2065.

[13] J. Chatt, *J. Organomet. Chem.* **1975**, *100*, 17–28.

[14] a) L. R. Doyle, A. J. Wooles, L. C. Jenkins, F. Tuna, E. J. L. McInnes, S. T. Liddle, *Angew. Chem. Int. Ed.* **2018**, *57*, 6314–6318; *Angew. Chem.* **2018**, *130*, 6422–6426; b) B. M. Gardner, S. T. Liddle, *Eur. J. Inorg. Chem.* **2013**, 3753–3770; c) S. T. Liddle, *Angew. Chem. Int. Ed.* **2015**, *54*, 8604–8641; *Angew. Chem.* **2015**, *127*, 8726–8764.

[15] N. Kuganathan, J. C. Green, H.-J. Himmel, *New J. Chem.* **2006**, *30*, 1253–1262.

[16] J. B. Geri, J. P. Shanahan, N. K. Szymczak, *J. Am. Chem. Soc.* **2017**, *139*, 5952–5956.

[17] A. Simonneau, R. Turrel, L. Vendier, M. Etienne, *Angew. Chem. Int. Ed.* **2017**, *56*, 12268–12272; *Angew. Chem.* **2017**, *129*, 12436–12440.

[18] K. C. Janda, L. S. Bernstein, J. M. Steed, S. E. Novick, W. Klemperer, *J. Am. Chem. Soc.* **1978**, *100*, 8074.

[19] R. Appel, R. Schöllhorn, *Angew. Chem. Int. Ed. Engl.* **1964**, *3*, 805; *Angew. Chem.* **1964**, *76*, 992.

[20] N. Holzmann, D. Dange, C. Jones, G. Frenking, *Angew. Chem. Int. Ed.* **2013**, *52*, 3004–3008; *Angew. Chem.* **2013**, *125*, 3078–3082.

[21] a) M.-A. Légaré, G. Bélanger-Chabot, R. D. Dewhurst, E. Welz, I. Krummenacher, B. Engels, H. Braunschweig, *Science* **2018**, *359*, 896–900; b) D. L. Broere, P. L. Holland, *Science* **2018**, *359*, 871; c) M.-A. Légaré, M. Rang, G. Bélanger-Chabot, J. I. Schweizer, I. Krummenacher, R. Bertermann, M. Arrowsmith, M. C. Holthausen, H. Braunschweig, *Science* **2019**, *363*, 1329–1332.

[22] T. Itoh, Y. Nakata, K. Hirai, H. Tomioka, *J. Am. Chem. Soc.* **2006**, *128*, 957–967.

[23] R. C. Neu, C. Jiang, D. W. Stephan, *Dalton Trans.* **2013**, *42*, 726–736.

[24] M. Santi, D. M. C. Ould, J. Wenz, Y. Soltani, R. L. Melen, T. Wirth, *Angew. Chem. Int. Ed.* **2019**, *58*, 7861–7865; *Angew. Chem.* **2019**, *131*, 7943–7947.

[25] C. N. Tang, Q. M. Liang, A. R. Jupp, T. C. Johnstone, R. C. Neu, D. T. Song, S. Grimme, D. W. Stephan, *Angew. Chem. Int. Ed.* **2017**, *56*, 16588–16592; *Angew. Chem.* **2017**, *129*, 16815–16819.

[26] L. Liu, L. L. Cao, Y. Shao, D. W. Stephan, *J. Am. Chem. Soc.* **2017**, *139*, 10062–10071.

[27] X. Tao, C. G. Daniliuc, R. Knitsch, M. R. Hansen, H. Eckert, M. Lübbesmeyer, A. Studer, G. Kehr, G. Erker, *Chem. Sci.* **2018**, *9*, 8011–8018.

[28] R. J. Kwaan, C. J. Harlan, J. R. Norton, *Organometallics* **2001**, *20*, 3818–3820.

[29] C. J. Harlan, T. Hascall, E. Fujita, J. R. Norton, *J. Am. Chem. Soc.* **1999**, *121*, 7274–7275.

[30] R. C. Neu, D. W. Stephan, *Organometallics* **2012**, *31*, 46–49.

[31] a) TURBOMOLE, version 7.3, **2018**; b) A. Klamt, G. Schüürmann, *J. Chem. Soc. Perkin Trans. 2* **1993**, *2*, 799; c) F. Eckert, A. Klamt, *AIChE J.* **2002**, *48*, 369–385; d) F. Eckert, A. Klamt, COSMOtherm, Version C3.0, Release 16.01, **2015**; e) K. Eichkorn, F. Weigend, O. Treutler, R. Ahlrichs, *Theor. Chem. Acc.* **1997**, *97*, 119; f) F. Weigend, M. Häser, H. Patzelt, R. Ahlrichs, *Chem. Phys. Lett.* **1998**, *143*, 294; g) F. Weigend, F. Furche, R. Ahlrichs, *J. Chem. Phys.* **2003**, *119*, 12753; h) F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305; i) F. Weigend, *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057–1065; j) J. Tao, J. P. Perdew, V. N. Staroverov, G. E. Scuseria, *Phys. Rev. Lett.* **2003**, *91*, 146401; k) P. Deglmann, K. May, F. Furche, R. Ahlrichs, *Chem. Phys. Lett.* **2004**, *384*, 103; l) Y. Zhao, D. G. Truhlar, *J. Phys. Chem. A* **2005**, *109*, 5656–5667; m) S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104; n) S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456–1465; o) S. Grimme, *Chem. Eur. J.* **2012**, *18*, 9955.

[32] J. L. Robbins, N. Edelstein, B. Spencer, J. C. Smart, *J. Am. Chem. Soc.* **1982**, *104*, 1882–1893.

[33] a) A. A. Berezin, C. P. Constantinides, S. I. Mirallai, M. Manoli, L. L. Cao, J. M. Rawson, P. A. Koutentis, *Org. Biomol. Chem.* **2013**, *11*, 6780–6795; b) H. J. Cowley, J. J. Hayward, D. R. Pratt, J. M. Rawson, *Dalton Trans.* **2014**, *43*, 1332–1337; c) A. E. Waked, R. O. Memar, D. W. Stephan, *Angew. Chem. Int. Ed.* **2018**, *57*, 11934–11938; *Angew. Chem.* **2018**, *130*, 12110–12114.

[34] CCDC 1917667, 1917668, 1917669, 1917670, 1955444, 1955445, 1955446, 1955447 and 1955448 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.