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Anaïs Coffinet, David Specklin, Laure Vendier, Michel Etienne, Antoine Simonneau. Frustrated Lewis Pair Chemistry Enables N<sub>2</sub> Borylation by Formal 1,3-Addition of a B–H Bond in the Coordination Sphere of Tungsten. *Chemistry - A European Journal*, 2019, 25, pp.14300-14303. 10.1002/chem.201904084 . hal-02324912

**HAL Id: hal-02324912**

**<https://hal.science/hal-02324912>**

Submitted on 22 Oct 2019

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# Frustrated Lewis Pair Chemistry Enables N<sub>2</sub> Borylation by Formal 1,3-Addition of a B–H Bond in the Coordination Sphere of Tungsten

Anaïs Coffinet, David Specklin, Laure Vendier, Michel Etienne, and Antoine Simonneau\*<sup>[a]</sup>

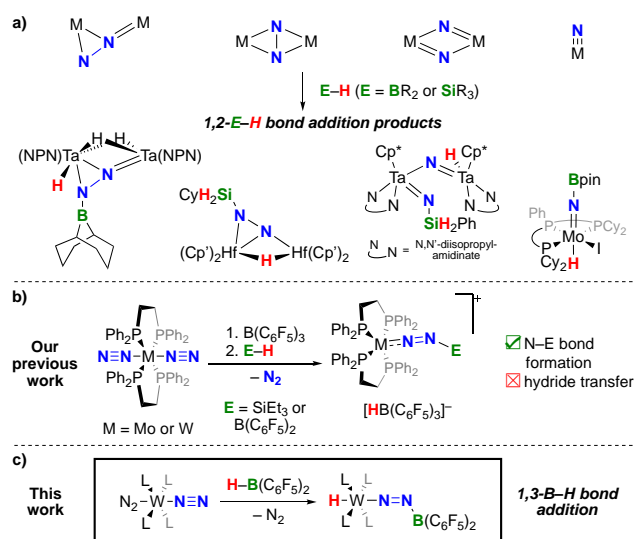
Dedicated to Professor Max Malacria on the occasion of his 70<sup>th</sup> birthday.

**Abstract:** The first example of a formal 1,3-B–H bond addition across the M–N≡N unit of an end-on dinitrogen complex **5** has been achieved. The use of Piers' borane HB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> **1** was essential to observe this reactivity and it plays a triple role in this transformation: i) electrophilic N<sub>2</sub>-borylation agent, ii) Lewis acid in a frustrated Lewis pair-type B–H bond activation and iii) hydride shuttle to the metal center. This chemistry is supported by NMR and solid-state characterization of products and intermediates. The combination of chelate effect and strong σ donation in the diphosphine depe ligand was mandatory to avoid phosphine dissociation that otherwise led to complexes where borylation of N<sub>2</sub> occurred without hydride transfer.

The mild conditions under which the inert N<sub>2</sub> molecule can be activated with metal complexes have sparked continual research efforts devoted to the fixation of nitrogen into N-containing compounds.<sup>[1]</sup> A distinct property of soluble transition-metal N<sub>2</sub> complexes is that, beyond formation of N–H bonds of relevance for ammonia synthesis,<sup>[2–4]</sup> N–B,<sup>[5]</sup> N–Si<sup>[5c,6]</sup> and N–C bonds<sup>[7]</sup> can be formed by the reaction of metal-bound dinitrogen with various functionalizing agents, paving the way for the direct conversion of N<sub>2</sub> into value-added nitrogen compounds. Thanks to the mild hydride donor reactivity and to the thermodynamic driving force offered by the formation of strong N–Si or N–B bonds, hydrosilanes and -boranes are attractive substrates for the synthesis of boryl- or silyl-amines or hydrazines. Indeed, they react across reactive M–N bonds of complexes incorporating a 4-<sup>[5b,6c–g]</sup> or 6-<sup>e-</sup>-reduced<sup>[8]</sup> N<sub>2</sub> ligand (Scheme 1a). Diphenyldiazomethane (Ph<sub>2</sub>CN<sub>2</sub>), the formal addition product of N<sub>2</sub> with diphenylcarbene, undergoes 1,1-hydroboration of the terminal N using Piers' borane HB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> (**1**).<sup>[9]</sup> Applications of these transformations towards the synthesis of nitrogen compounds have remained restricted to N<sub>2</sub>-derived nitrides.<sup>[8]</sup>

We reported recently the silylation and borylation of a non-reduced N<sub>2</sub> ligand using a hydro-silane or -borane.<sup>[5c]</sup> Our method took advantage of the formation of a frustrated Lewis pair (FLP)<sup>[10]</sup> between an end-on dinitrogen complex and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> that could heterolytically cleave Si–H<sup>[11]</sup> and B–H bonds.<sup>[12]</sup> This allowed functionalization of the terminal N, while the hydride issued by the silane or borane was trapped in the inert anion [HB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sup>–</sup> (Scheme 1b). In the prospect of using this approach to realize a synthetic cycle, the absence of hydride transfer to the metal, due to the poor hydride donor ability of

[HB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sup>–</sup>, appeared detrimental. Indeed, the reuptake of N<sub>2</sub> by group 6 phosphine complexes upon photolysis of the corresponding hydrides<sup>[13]</sup> represents an attractive route to close a synthetic cycle.<sup>[14]</sup> This prompted us to examine the reactivity of HB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> (**1**),<sup>[15]</sup> speculating it could act both as a Lewis acidic borylation agent and as a more potent,<sup>[16]</sup> less sterically hindered boron-to-metal hydride shuttle in the form of the [H<sub>2</sub>B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>]<sup>–</sup> anion that would be generated after the B–N bond formation/B–H bond activation event. Herein, we report on our studies of the reactivity of **1** and show that a judicious choice of phosphine ligands in Hidaï-Chatt tungsten N<sub>2</sub> complexes leads to the formal 1,3-B–H bond addition across a W–N≡N moiety (Scheme 1c).



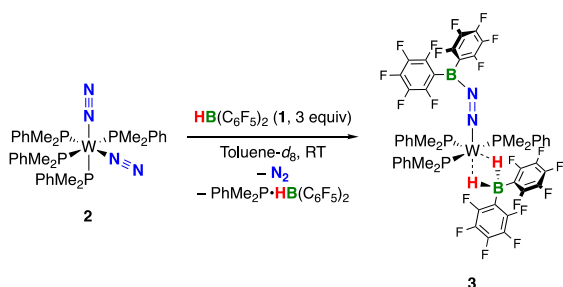
**Scheme 1.** a) 1,2-E–H bond addition across M–N bonds in strongly activated N<sub>2</sub> complexes (NPN = (PhNSiMe<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>PPh, Cp\* = 1,2,4-trimethylcyclopentadienyl, Cp\* = 1,2,3,4,5-pentamethylcyclopentadienyl).<sup>[5b,6e,9,8b]</sup> b) FLP-inspired functionalization of N<sub>2</sub>.<sup>[5c]</sup> c) 1,3-B–H bond addition reported in this study.

We reacted *cis*-[W(N<sub>2</sub>)<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>4</sub>] (**2**)<sup>[17]</sup> with 1 equivalent of **1** at room temperature in toluene-*d*<sub>8</sub>. Analysis of the reaction mixture by <sup>31</sup>P NMR showed diagnostic signals of the [HB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>•PMe<sub>2</sub>Ph] adduct, characterized by a poorly resolved quartet at δ –4.9 (*J*<sub>PB</sub> = 122 Hz, no <sup>183</sup>W satellites).<sup>[18,19]</sup> To reach full and selective conversion of **2**, we had to add up to three equivalents of **1**. The <sup>1</sup>H NMR spectrum of the reaction mixture showed two broad signals (δ 3.63, –0.75) that sharpened upon <sup>11</sup>B decoupling, suggesting the presence of B–H moieties. The deshielded signal characterizes [HB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>•PMe<sub>2</sub>Ph] while the high field one may be assigned to that of protons interacting with the tungsten center in the new complex **3** (Scheme 2). The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **3** showed a A<sub>2</sub>X system and a <sup>11</sup>B NMR experiment revealed, in addition to the signal for

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Supporting information for this article is available free of charge at: <https://doi.org/10.1002/chem.201904084>.

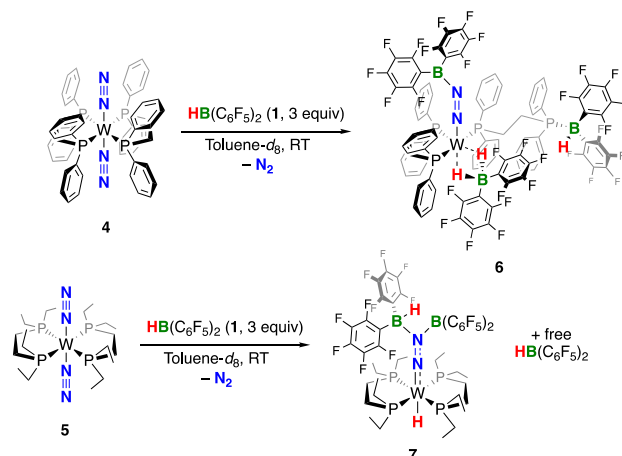
[HB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>]<sup>-</sup>PMe<sub>2</sub>Ph], two different resonances for **3** at δ 30.5 and -1.6. An X-ray diffraction study performed on crystals of **3** confirmed that one N<sub>2</sub> ligand was borylated (Figure 1).<sup>[20]</sup> The N–N bond length is 1.280(4) Å, in the range of NN double bonds.<sup>[21]</sup> Interestingly, the [H<sub>2</sub>B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>]<sup>-</sup> anion coordinates to the metal center, now in the formal oxidation state +II. The two hydrogens occupy the coordination sites left vacant after the loss of one N<sub>2</sub> and one PMe<sub>2</sub>Ph ligands. Prolonged, mild heating of the reaction mixture led to decomposition of **3** without evidence for the formation of metal hydrides.



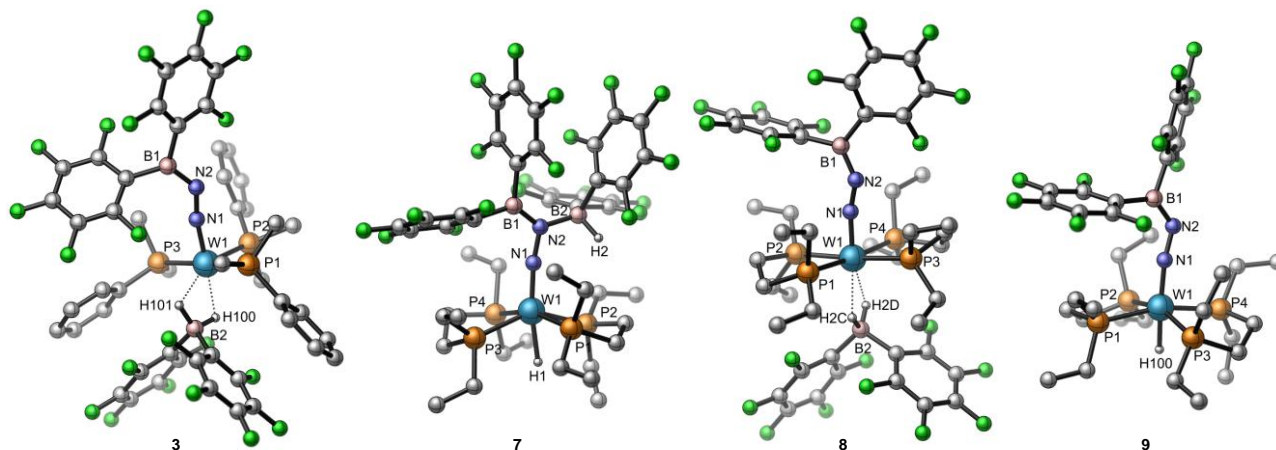
**Scheme 2.** Reaction of N<sub>2</sub>-complex **2** with **1**.

Next, we checked the reactivity of *trans*-[W(N<sub>2</sub>)<sub>2</sub>(dppe)<sub>2</sub>] (**4**)<sup>[22]</sup> [dppe = 1,2-bis(diphenylphosphino)ethane] and its depe [1,2-bis(diethylphosphino)ethane] analogue **5**<sup>[23]</sup>, with the assumption that chelation could prevent phosphine dissociation. This would force a modified geometry for the [H<sub>2</sub>B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>]<sup>-</sup>-W interaction that could promote W–H bond formation. The reaction of **4** with 3 equivalents of **1** yielded a product **6** very similar to **3** as revealed by NMR and confirmed by X-ray diffraction.<sup>[24]</sup> One phosphorus dissociated from tungsten and was trapped by **1**. A [H<sub>2</sub>B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>]<sup>-</sup> anion was formed concomitantly with the borylation of one N<sub>2</sub> ligand (Scheme 3).

Under identical conditions, complex **5** quickly and selectively converted to a new compound **7** without phosphine dissociation, as a singlet was observed in the <sup>31</sup>P NMR spectrum (δ 39.9 vs. δ 36.2 for **5**). A hydride signal showing coupling to four equivalent phosphorus was found in the <sup>1</sup>H NMR spectrum (δ -4.47, quintet, <sup>2</sup>J<sub>HP</sub> = 38 Hz). Borane **1** was still present, but the anion [H<sub>2</sub>B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>]<sup>-</sup> was not detected. Crystallization of **7** (84% yield) confirmed borylation of the N<sub>2</sub> ligand as well as hydride transfer to the metal, realizing the targeted formal 1,3-B–H bond addition (Scheme 3, Figure 1). The thus-formed boryldiazenido ligand trapped another equivalent of **1**, forming a Lewis pair. From the electron-withdrawing effect of the two boron groups ensues a noticeable N–N bond elongation [1.378(4) Å<sup>[25]</sup>]. The electron-richness of the depe ligand combined with the chelate effect prevents phosphine dissociation, leading to effective hydride transfer.



**Scheme 3.** Reactions of N<sub>2</sub>-complexes **4** and **5** with **1**.

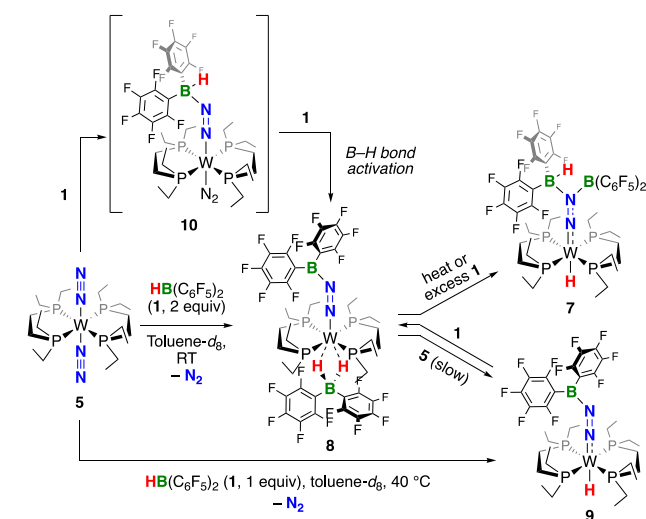


**Figure 1.** Molecular structures of compounds **3** and **7–9** in the solid state. All hydrogens have been omitted except those bound to B or W. Selected distances (Å) for **3**: W1–N1, 1.781(3); N1–N2, 1.280(4); N2–B1, 1.373(5); B2–H100, 1.15(4); B2–H101, 1.06(6); W1–H100, 2.05(5); W1–H101, 2.05(4). For **7**: W1–N1, 1.807(2); N1–N2, 1.378(3); N2–B1, 1.392(5); N2–B2, 1.586(6); W1–H1, 1.91(4). For **8**: W1–N1, 1.789(2); N1–N2, 1.256(3); N2–B1, 1.368(4); B2–H2C, 1.10(3); B2–H2D, 1.17(3); W1–H2C, 2.22(4); W1–H2D, 2.35(3). For **9**: W1–N1, 1.807(2); N1–N2, 1.301(3); N2–B1, 1.369(3); W1–H1, 1.66(2).

Since at least one equivalent of Piers' borane was in excess, we repeated the reaction with only 2 equivalents of **1**. <sup>31</sup>P NMR analysis of the reaction mixture revealed selective transformation to a new compound **8** with equivalent phosphorus nuclei (δ 32.4). Key spectral features for **8** were signals in the <sup>1</sup>H and <sup>11</sup>B NMR spectra assignable to the [H<sub>2</sub>B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>]<sup>-</sup> anion (<sup>1</sup>H(<sup>11</sup>B): δ -1.6, singlet; <sup>11</sup>B: δ -40.8, triplet, J<sub>BH</sub> = 71 Hz); shielding of its proton resonances was a clear indication of

interaction with the W center. Thus, it can be proposed that **8** is an intermediate *en route* to **7** before hydride transfer (Scheme 4). **8** crystallized from the reaction mixture in 79% yield, allowing determination of its structure (Figure 1). As anticipated, the interaction of the W center with [H<sub>2</sub>B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>]<sup>-</sup> formed after borylation of the N<sub>2</sub> ligand is different from that in **3** and **6**. In **8**, the dihydroborate anion occupies a single coordination site *trans* to the boryldiazenido group, while in **3** and **6** the hydrides

occupy one apical and one equatorial sites. The isolation of **8** allowed us to check the influence of **1** on the hydride transfer: indeed, addition of excess **1** to a solution of **8** quickly converted the latter into **7**. Lewis pair formation of **1** with the boryldiazenido ligand in **8** might help trigger W–H bond formation by rendering the metal center more electrophilic. The formation of **8** confirms the triple role of Piers' borane: it acts as a N<sub>2</sub>-borylation agent, a Lewis acid able of B–H bond activation and a hydride shuttle. The two latter roles are performed by the second equivalent of **1**, which is regenerated after the hydride transfer and subsequently trapped by the boryldiazenido ligand. This prompted us to verify whether a slight excess of **1** would be sufficient to perform the 1,3-B–H bond addition, this time affording the tungsten hydride **9**. Upon addition of 1.1 equivalent of **1** to a solution of **5**, a mixture of **5**, **8** and a third major compound (<sup>31</sup>P NMR δ 35.6) was obtained after 10 min at room temperature. On the basis of <sup>1</sup>H{<sup>11</sup>B}, <sup>19</sup>F NMR and IR spectroscopy (Figures S28–32), this compound was formulated as **10**, the adduct of **5** with **1** (Scheme 4). When heated to 40 °C for 4 h, this mixture evolved into a single compound **9** isolated in 78% yield. In the <sup>1</sup>H NMR spectrum, a characteristic hydride quintet at δ –2.62 (<sup>2</sup>J<sub>HP</sub> = 27.6 Hz) was found. An X-ray diffraction study confirmed a structural analogy between **9** and **7**, the difference lying in the absence of interaction of the boryldiazenido ligand with a second equivalent of **1**. **9** could also be selectively prepared by mixing equimolar amounts of **5** and **8** for 10 d at room temperature. **9** reacted with one equivalent of **1** to give a roughly 1:1 mixture of **7** and **8** within 10 min, indicating that W–H bond formation was reversible in the presence of **1**, as observed with hydrides of group 3<sup>[26]</sup> and 4.<sup>[27]</sup> After 1 h, almost all **8** was converted to the tungsten hydride **7** (Figure 1, Scheme 4).



**Scheme 4.** Complexes observed in the reactions of **5** with **1**.

In addition to 1,2-hydroboration of M–N bonds that has been reported for strongly activated N<sub>2</sub> complexes, we have shown herein the possibility to achieve 1,3-B–H bond addition across a W–N≡N unit in which the N<sub>2</sub> ligand is only weakly activated. This was made possible by taking inspiration from the FLP chemistry of hydroboranes<sup>[12]</sup> and from a rational experimental approach based on our previous findings.<sup>[9]</sup> The strong electrophilicity of **1** is essential for the B–H activation step: reactions of **5** with 9-borabicyclo[3.3.1]nonane (9-BBN) or catecholborane were unproductive under the experimental conditions reported herein. We are currently exploring different metal–ligand combinations and other hydroboranes in order to study the generality of this

transformation and apply it to the synthesis of boron–nitrogen compounds.

## Acknowledgements

A. S. would like to thank Dr. Nicolas Mézailles, Dr. E. Alessandra Quadrelli and Dr. Sylviane Sabo-Etienne for insightful discussions. A. C. is grateful to the French Ministry of National and Superior Education and Research (MENESR) for a Ph. D. fellowship. A. S. acknowledges the European Research Council (ERC) for funding (Grant Agreement 757501). All authors are indebted to the French National Center for Scientific Research (CNRS) for financial support.

**Keywords:** bis(pentafluorophenyl)borane • dinitrogen • frustrated Lewis pairs • phosphines • tungsten

- [1] a) *Transition Metal-Dinitrogen Complexes: Preparation and Reactivity*, Y. Nishibayashi, Ed.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2019; b) R. J. Burford, M. D. Fryzuk, *Nat. Rev. Chem.* **2017**, *1*, 26; c) M. D. Walter, *Recent Advances in Transition Metal-Catalyzed Dinitrogen Activation*; P. J. Pérez, Ed.; Advances in Organometallic Chemistry, Vol. 65; Academic Press, 2016; pp 261-377; d) N. Khoenkhoen, B. de Bruin, J. N. H. Reek, W. I. Dzik, *Eur. J. Inorg. Chem.* **2015**, 567-598.
- [2] a) N. Stucke, B. M. Flöser, T. Weyrich, F. Tuczek, *J. Inorg. Chem.* **2018**, 1337; b) *Nitrogen Fixation*; Y. Nishibayashi, Ed.; Topics in Organometallic Chemistry, Vol. 60; Springer International Publishing AG: Cham, Switzerland, 2017; c) Y. Roux, C. Duboc, M. Gennari, *ChemPhysChem* **2017**, *18*, 2606-2617.
- [3] a) Y. Hu, M. W. Ribbe, *Angew. Chem. Int. Ed.* **2016**, *55*, 8216-8226; *Angew. Chem.* **2016**, *128*, 8356-8367; b) B. M. Hoffman, D. Lukoyanov, Z.-Y. Yang, D. R. Dean, L. C. Seefeldt, *Chem. Rev.* **2014**, *114*, 4041.
- [4] (a) G. Ertl, *Angew. Chem. Int. Ed.* **2008**, *47*, 3524-3535; *Angew. Chem.* **2008**, *120*, 3578-3590; b) R. Schlögl, *R. Angew. Chem. Int. Ed.* **2003**, *115*, 2050-2055; *Angew. Chem.* **2003**, *42*, 2004; c) *Catalytic Ammonia Synthesis: Fundamentals and Practice*; J. R. Jennings, Ed.; Springer: New York, NY, 1991.
- [5] Selected examples: a) H. Ishino, Y. Ishii, M. Hidai, *Chem. Lett.* **1998**, *27*, 677-678; b) M. D. Fryzuk, B. A. MacKay, S. A. Johnson, B. O. Patrick, *Angew. Chem. Int. Ed.* **2002**, *41*, 3709-3712; *Angew. Chem.* **2002**, *114*, 3861-3864; c) A. Simonneau, R. Turrel, L. Vendier, M. Etienne, *Angew. Chem. Int. Ed.* **2017**, *56*, 12268-12272; *Angew. Chem.* **2017**, *129*, 12436-12440.
- [6] Selected examples: a) M. Hidai, K. Komori, T. Kodama, D.-M. Jin, T. Takahashi, S. Sugiura, Y. Uchida, Y. Mizobe, *J. Organomet. Chem.* **1984**, *272*, 155-167; b) K. Komori, S. Sugiura, Y. Mizobe, M. Yamada, M. Hidai, *Bull. Chem. Soc. Jpn.* **1989**, *62*, 2953-2959; c) M. D. Fryzuk, J. B. Love, S. J. Rettig, V. G. Young, *Science* **1997**, *275*, 1445-1447; d) M. D. Fryzuk, B. A. MacKay, B. O. Patrick, *J. Am. Chem. Soc.* **2003**, *125*, 3234-3235; e) M. Hirotsu, P. P. Fontaine, A. Epshteyn, L. R. Sita, *J. Am. Chem. Soc.* **2007**, *129*, 9284-9285; f) Y. Lee, N. P. Mankad, J. C. Peters, *Nat. Chem.* **2010**, *2*, 558-565; g) S. P. Semproni, E. Lobkovsky, P. J. Chirik, *J. Am. Chem. Soc.* **2011**, *133*, 10406-10409.
- [7] Selected examples: a) J. Chatt, A. A. Diamantis, G. A. Heath, N. E. Hooper, G. J. Leigh, *J. Chem. Soc. Dalton Trans.* **1977**, 688-697; b) T. Yoshida, T. Adachi, T. Ueda, M. Kaminaka, N. Sasaki, T. Higuchi, T. Aoshima, I. Mega, Y. Mizobe, M. Hidai, *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1040-1042; *Angew. Chem.* **1989**, *101*, 1053-1055; c) L. Morello, J. B. Love, B. O. Patrick, M. D. Fryzuk, *J. Am. Chem. Soc.* **2004**, *126*, 9480-9481; d) T. Kupfer, R. R. Schrock, *J. Am. Chem. Soc.* **2009**, *131*, 12829-12837; f) D. J. Knobloch, E. Lobkovsky, P. J. Chirik, *Nat. Chem.* **2010**, *2*, 30-35; g) J. Ballmann, A. Yeo, B. O. Patrick, M. D. Fryzuk, *Angew. Chem. Int. Ed.* **2011**, *50*, 507-510; *Angew. Chem.* **2011**, *123*, 527-530; h) M. Falcone, L. Chatelain, R. Scopelliti, I. Živković, M. Mazzanti, *Nature* **2017**, *547*, 332-335; k) Y. Nakanishi, Y. Ishida, H. Kawaguchi, *Angew. Chem. Int. Ed.* **2017**, *56*, 9193-9197; *Angew.*

- Chem.* **2017**, *129*, 9321-9325; l) Z.-J. Lv, Z. Huang, W.-X. Zhang, Z. Xi, *J. Am. Chem. Soc.* **2019**, *141*, 8773-8777.
- [8] a) Q. Liao, A. Cavallé, N. Saffon-Merceron, N. Mézailles, *Angew. Chem. Int. Ed.* **2016**, *55*, 11212-11216; *Angew. Chem.* **2016**, *128*, 11378-11382; b) M. F. Espada, S. Bennaamane, Q. Liao, N. Saffon-Merceron, S. Massou, E. Clot, N. Nebra, M. Fustier-Boutignon, N. Mézailles, *Angew. Chem. Int. Ed.* **2018**, *57*, 12865-12868; *Angew. Chem.* **2018**, *130*, 13047-13050.
- [9] a) C. Tang, Q. Liang, A. R. Jupp, T. C. Johnstone, R. C. Neu, D. Song, S. Grimme, D. W. Stephan, *Angew. Chem. Int. Ed.* **2017**, *56*, 16588-16592; *Angew. Chem.* **2017**, *129*, 16815-16819; b) R. L. Melen, *Angew. Chem. Int. Ed.* **2018**, *57*, 880-882; *Angew. Chem.* **2018**, *130*, 890-892.
- [10] a) J. Paradies, *Coord. Chem. Rev.* **2019**, *380*, 170-183; b) Stephan, D. W. *Science* **2016**, *354*, aaf7229; c) D. W. Stephan, G. Erker, *Angew. Chem. Int. Ed.* **2015**, *54*, 6400-6441; *Angew. Chem.* **2015**, *127*, 6498-6541; d) D. W. Stephan, G. Erker, *Angew. Chem. Int. Ed.* **2010**, *49*, 46-76; *Angew. Chem.* **2010**, *122*, 50-81.
- [11] a) M. Oestreich, J. Hermeke, J. Mohr, *Chem. Soc. Rev.* **2015**, *44*, 2202-2220; b) W. E. Piers, A. J. V Marwitz, L. G. Mercier, *Inorg. Chem.* **2011**, *50*, 12252-12262.
- [12] M. A. Dureen, A. Lough, T. M. Gilbert, D. W. Stephan, *Chem. Commun.* **2008**, 4303-4305.
- [13] a) R. Pierantozzi, G. L. Geoffroy, *Inorg. Chem.* **1980**, *19*, 1821-1822; b) A. P. Pivovarov, Y. V Gak, T. N. Doronina, V. D. Makhaev, A. P. Borisov, Y. G. Borod'ko, *Izv. Akad. Nauk SSSR, Seriya Khimicheskaya* **1981**, 1207-1212.
- [14] M. Hidai, *Coord. Chem. Rev.* **1999**, *185-186*, 99-108.
- [15] a) D. J. Parks, R. E. von H. Spence, W. E. Piers, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 809-811; ; *Angew. Chem.* **1995**, *107*, 895-897; b) D. J. Parks, W. E. Piers, G. P. A. Yap, *Organometallics* **1998**, *17*, 5492-5503.
- [16] The hydride donor ability  $\Delta G_{H^-}$  of the  $[H_2B(C_6F_5)_2]^-$  anion is 61 kcal/mol vs. 65 kcal/mol for  $[HB(C_6F_5)_3]^-$ : Z. M. Heiden, A. P. Lathem, *Organometallics* **2015**, *34*, 1818-1827.
- [17] T. A. George, C. D. Seibold, *J. Organomet. Chem.* **1971**, *30*, C13-C14.
- [18] This was confirmed by the separated preparation of  $[HB(C_6F_5)_3 \cdot PMe_2Ph]$ .
- [19] Complex **2** has been reported to lose a phosphine ligand upon treatment with HCl in dimethoxyethane: T. Takahashi, Y. Mizobe, M. Sato, Y. Uchida, M. Hidai, *J. Am. Chem. Soc.* **1979**, *101*, 3405-3407.
- [20] CCDC 1937633-36 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the Cambridge Crystallographic Data Centre.
- [21] 1.189 (*trans*) or 1.251 (*cis*) Å for PhN=NPh: J. Harada, K. Ogawa, S. Tomoda, *Acta Crystallogr. Sect. B* **1997**, *53*, 662-672.
- [22] M. Hidai, K. Tominari, Y. Uchida, A. Misono, *J. Chem. Soc. D Chem. Commun.* **1969**, 1392.
- [23] J. Chatt, G. A. Heath, R. L. Richards, *J. Chem. Soc. Chem. Commun.* **1972**, 1010-1011.
- [24] All attempts to correctly solve the structure of **6** were unsuccessful due to its tendency to give twinned crystals.
- [25] This is comparable to the N-N bond length in the hydrazido complex  $[W(N_2H_2)Cl(dppe)_2][BPh_4]$ : G. A. Heath, R. Mason, K. M. Thomas, *J. Am. Chem. Soc.* **1974**, *96*, 259-260.
- [26] D. J. H. Emslie, W. E. Piers, M. Parvez, R. McDonald, *Organometallics* **2002**, *21*, 4226-4240.
- [27] R. González-Hernández, J. Chai, R. Charles, O. Pérez-Camacho, S. Kniajanski, S. Collins, *Organometallics* **2006**, *25*, 5366-5373.