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Frustrated Lewis Pair Chemistry Enables N₂ 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^{*[a]}

Dedicated to Professor Max Malacria on the occasion of his 70th 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(C₆F₅)₂ **1** was essential to observe this reactivity and it plays a triple role in this transformation: i) electrophilic N₂-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 N₂ occurred without hydride transfer.

The mild conditions under which the inert N₂ molecule can be activated with metal complexes have sparked continual research efforts devoted to the fixation of nitrogen into N-containing compounds.^[1] A distinct property of soluble transition-metal N₂ complexes is that, beyond formation of N–H bonds of relevance for ammonia synthesis,^[2–4] N–B,^[5] N–Si^[5c,6] and N–C bonds^[7] can be formed by the reaction of metal-bound dinitrogen with various functionalizing agents, paving the way for the direct conversion of N₂ 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-^[5b,6c–g] or 6-^[8] e[−]-reduced^[8] N₂ ligand (Scheme 1a). Diphenyldiazomethane (Ph₂CN₂), the formal addition product of N₂ with diphenylcarbene, undergoes 1,1-hydroboration of the terminal N using Piers' borane HB(C₆F₅)₂ (**1**).^[9] Applications of these transformations towards the synthesis of nitrogen compounds have remained restricted to N₂-derived nitrides.^[8]

We reported recently the silylation and borylation of a non-reduced N₂ ligand using a hydro-silane or -borane.^[5c] Our method took advantage of the formation of a frustrated Lewis pair (FLP)^[10] between an end-on dinitrogen complex and B(C₆F₅)₃ that could heterolytically cleave Si–H^[11] and B–H bonds.^[12] This allowed functionalization of the terminal N, while the hydride issued by the silane or borane was trapped in the inert anion [HB(C₆F₅)₃][−] (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(C₆F₅)₃][−], appeared detrimental. Indeed, the reuptake of N₂ by group 6 phosphine complexes upon photolysis of the corresponding hydrides^[13] represents an attractive route to close a synthetic cycle.^[14] This prompted us to examine the reactivity of HB(C₆F₅)₂ (**1**),^[15] speculating it could act both as a Lewis acidic borylation agent and as a more potent,^[16] less sterically hindered boron-to-metal hydride shuttle in the form of the [H₂B(C₆F₅)₂][−] 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 N₂ 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 N₂ complexes (NPN = (PhNSiMe₂CH₂)₂PPh, Cp* = 1,2,4-trimethylcyclopentadienyl, Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl).^[5b,6c,8b] b) FLP-inspired functionalization of N₂.^[5c] c) 1,3-B–H bond addition reported in this study.

We reacted *cis*-[W(N₂)₂(PMe₂Ph)₄] (**2**)^[17] with 1 equivalent of **1** at room temperature in toluene-*d*₈. Analysis of the reaction mixture by ³¹P NMR showed diagnostic signals of the [HB(C₆F₅)₂•PMe₂Ph] adduct, characterized by a poorly resolved quartet at δ −4.9 (*J*_{PB} = 122 Hz, no ¹⁸³W satellites).^[18,19] To reach full and selective conversion of **2**, we had to add up to three equivalents of **1**. The ¹H NMR spectrum of the reaction mixture showed two broad signals (δ 3.63, −0.75) that sharpened upon ¹¹B decoupling, suggesting the presence of B–H moieties. The deshielded signal characterizes [HB(C₆F₅)₂•PMe₂Ph] 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 ³¹P{¹H} NMR spectrum of **3** showed a A₂X system and a ¹¹B NMR experiment revealed, in addition to the signal for

[a] A. Coffinet, Dr. D. Specklin, Dr. L. Vendier, Prof. Dr. M. Etienne, Dr. A. Simonneau
LCC-CNRS, Université de Toulouse, CNRS, UPS
205 route de Narbonne, BP44099, F-31077 Toulouse cedex 4, France.
E-mail: antoine.simonneau@lcc-toulouse.fr
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[HB(C₆F₅)₂•PMe₂Ph], 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 N₂ ligand was borylated (Figure 1).^[20] The N–N bond length is 1.280(4) Å, in the range of NN double bonds.^[21] Interestingly, the [H₂B(C₆F₅)₂][−] 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 N₂ and one PMe₂Ph 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 N₂-complex **2** with **1**.

Next, we checked the reactivity of *trans*-[W(N₂)₂(dppe)₂]**(4)**^[22] [dppe = 1,2-bis(diphenylphosphino)ethane] and its depe [1,2-bis(diethylphosphino)ethane] analogue **5**^[23], with the assumption that chelation could prevent phosphine dissociation. This would force a modified geometry for the [H₂B(C₆F₅)₂][−]-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.^[24] One phosphorus dissociated from tungsten and was trapped by **1**. A [H₂B(C₆F₅)₂][−] anion was formed concomitantly with the borylation of one N₂ 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 ³¹P NMR spectrum (δ 39.9 vs. δ 36.2 for **5**). A hydride signal showing coupling to four equivalent phosphorus was found in the ¹H NMR spectrum (δ -4.47 , quintet, ²*J*_{HP} = 38 Hz). Borane **1** was still present, but the anion [H₂B(C₆F₅)₂][−] was not detected. Crystallization of **7** (84% yield) confirmed borylation of the N₂ 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^[25]]. The electron-richness of the depe ligand combined with the chelate effect prevents phosphine dissociation, leading to effective hydride transfer.

Scheme 3. Reactions of N₂-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**. ³¹P 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 ¹H and ¹¹B NMR spectra assignable to the [H₂B(C₆F₅)₂][−] anion (¹H{¹¹B}: δ -1.6 , singlet; ¹¹B: δ -40.8 , triplet, *J*_{BH} = 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 [H₂B(C₆F₅)₂][−] formed after borylation of the N₂ 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 N₂-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 (³¹P NMR δ 35.6) was obtained after 10 min at room temperature. On the basis of ¹H{¹¹B}, ¹⁹F 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 ¹H NMR spectrum, a characteristic hydride quintet at δ –2.62 (²J_{HP} = 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^[26] and 4.^[27] 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 N₂ complexes, we have shown herein the possibility to achieve 1,3-B–H bond addition across a W–N≡N unit in which the N₂ ligand is only weakly activated. This was made possible by taking inspiration from the FLP chemistry of hydroboranes^[12] and from a rational experimental approach based on our previous findings.^[9] 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.

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- [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. Sempronio, 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. Makhayev, 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 ΔG_{H^-} of the $[\text{H}_2\text{B}(\text{C}_6\text{F}_5)_2]^-$ anion is 61 kcal/mol vs. 65 kcal/mol for $[\text{HB}(\text{C}_6\text{F}_5)_3]^-$: 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 $[\text{HB}(\text{C}_6\text{F}_5)_3 \cdot \text{PMe}_2\text{Ph}]$.
- [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 $[\text{W}(\text{N}_2\text{H}_2)\text{Cl}(\text{dppe})_2][\text{BPh}_4]$: 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.