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Anaïs Coffinet, David Specklin, Laure Vendier, Michel Etienne, Antoine Simonneau. Frustrated Lewis Pair Chemistry Enables N₂ 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-02324912v1>

Submitted on 22 Oct 2019

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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]

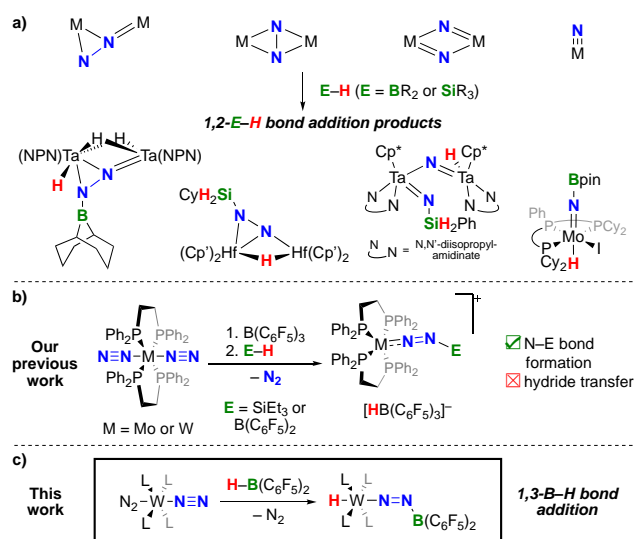
Dedicated to Professor Max Malacria on the occasion of his 70th birthday.

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-^{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).



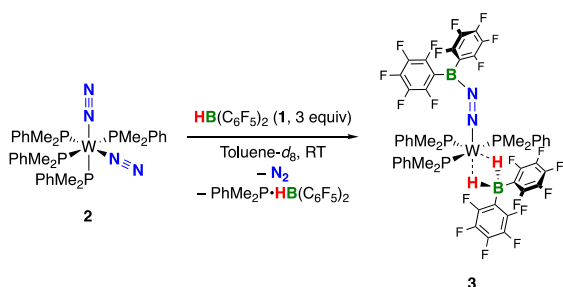
Scheme 1. a) 1,2-E–H bond addition across M–N bonds in strongly activated N₂ complexes (NPN = (PhNSiMe₂CH₂)₂PPh, Cp* = 1,2,4-trimethylcyclopentadienyl, Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl).^[5b,6e,9,8b] b) FLP-inspired functionalization of N₂.^[5c] c) 1,3-B–H bond addition reported in this study.

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

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

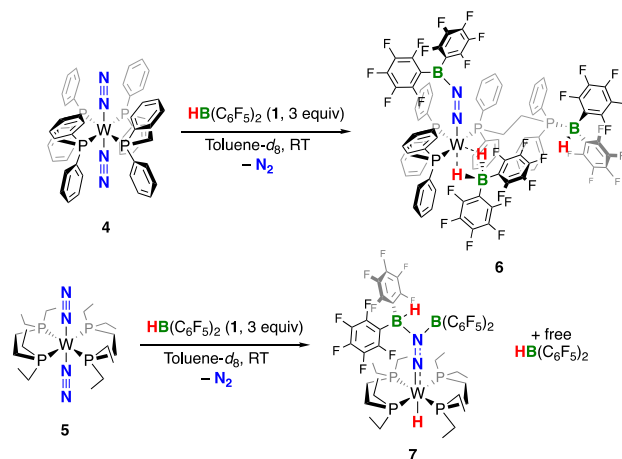
[HB(C₆F₅)₂•PMe₂Ph], two different resonances for **3** at δ 30.5 and -1.6 . An X-ray diffraction study performed on crystals of **3** confirmed that one N₂ ligand was borylated (Figure 1).^[20] The N–N bond length is 1.280(4) Å, in the range of NN double bonds.^[21] Interestingly, the [H₂B(C₆F₅)₂][−] 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, ²J_{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**.

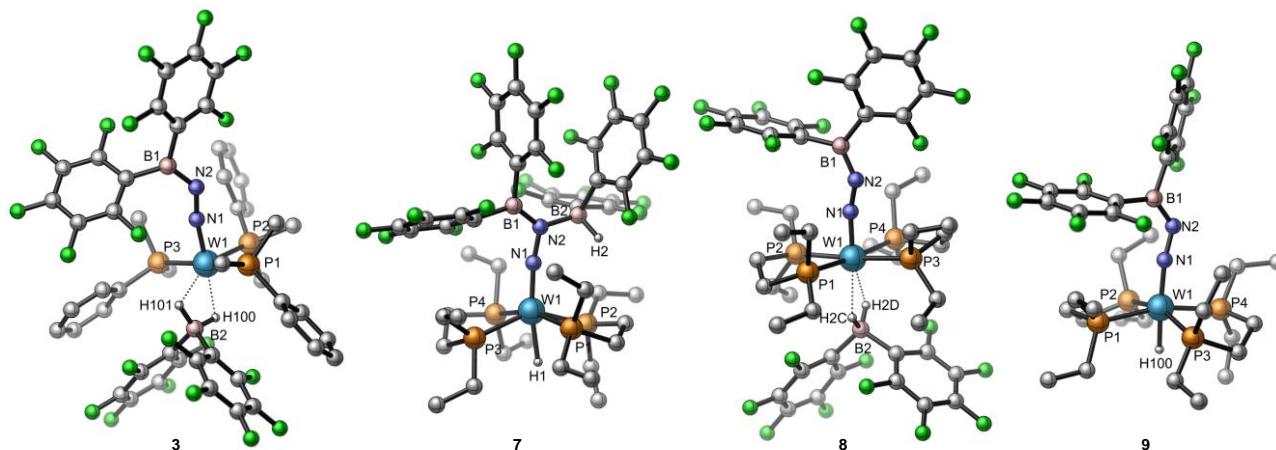
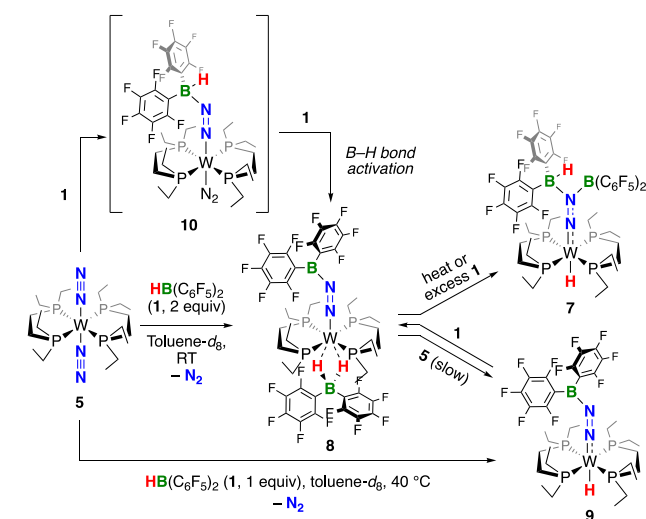


Figure 1. Molecular structures of compounds **3** and **7–9** in the solid state. All hydrogens have been omitted except those bound to B or W. Selected distances (Å) for **3**: W1–N1, 1.781(3); N1–N2, 1.280(4); N2–B1, 1.373(5); B2–H100, 1.15(4); B2–H101, 1.06(6); W1–H100, 2.05(5); W1–H101, 2.05(4). 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.

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

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