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Group 6 Transition Metal/Boron Frustrated Lewis Pair Templates Activate N₂ and Allow its Facile Borylation and Silylation

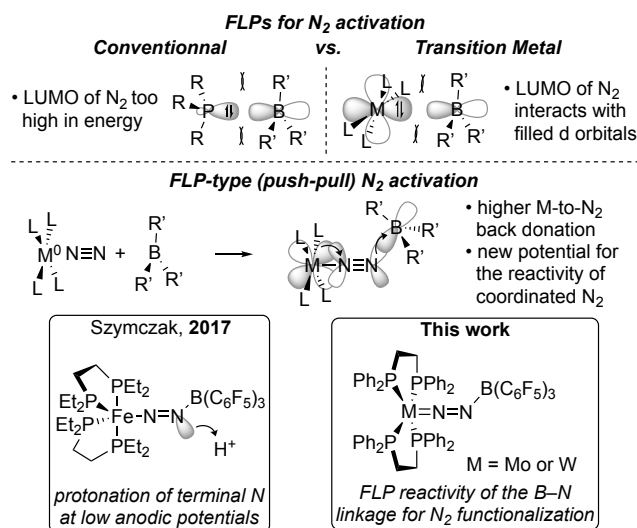
Antoine Simonneau,^{*,[a,b]} Raphaël Turrel,^[a,b] Laure Vendier^[a,b] and Michel Etienne^[a,b]

Abstract: The reaction of *trans*-[M(N₂)₂(dppe)₂] (M = Mo, **1_{Mo}**, M = W, **1_W**) with B(C₆F₅)₃ (**2**) provides the adducts [(dppe)₂M=N=N-B(C₆F₅)₃] (**3**) which can be regarded as M/B transition-metal frustrated Lewis pair (TMFLP) templates activating dinitrogen. Easy borylation and silylation of the activated dinitrogen ligands in complexes **3** with a hydro-borane and -silane occur by splitting of the B–H and Si–H bonds between the N₂ moiety and the perfluoroaryl borane. This reactivity of **3** is reminiscent of conventional frustrated Lewis pairs chemistry and constitutes an unprecedented approach for the functionalization of dinitrogen.

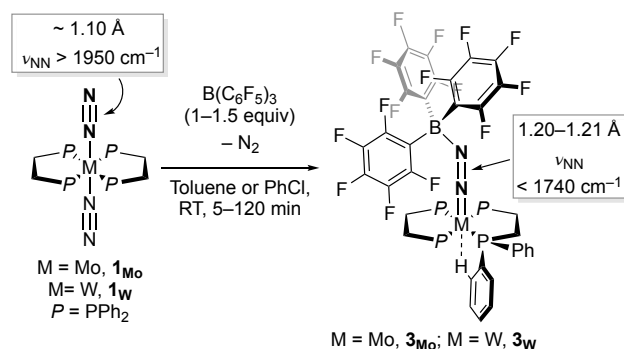
Although the Frustrated Lewis Pair (FLP) chemistry has developed into a powerful tool for the activation of various small molecules over the past decade,^[1] dinitrogen has thus far remained one of its missing targets. While isoelectronic CO has been the object of reactivity studies both with "conventional" FLPs^[2] and with the emerging Transition Metal FLP (TMFLP) systems,^[3,4] the inertness of N₂ and its reluctance to bind other p-block elements^[5] have hampered the development of its FLP chemistry. However, N₂ forms stable complexes with low-valent transition metals which offer platforms to study stoichiometric and catalytic transformation of this molecule. The reactivity of such coordination compounds has been intensively studied for decades and, eventually, some of them have shown catalytic activity for the reduction of N₂ into NH₃ or silylamines under mild

conditions,^[6] thus paving the way for homogeneous alternatives to the energy- and resource-intensive Haber-Bosch process.^[7] Inspired by recent achievements in the TMFLP field, we wanted to check whether a combination of a low-valent transition metal center and a strong, bulky Lewis acid could afford a template for the FLP-type activation of N₂ (Scheme 1, top).^[8] Herein, we wish to share some preliminary achievements pertaining to this concept, which provide new paradigms for the functionalization of coordinated N₂.^[9]

We chose to investigate *trans*-[M(N₂)₂(dppe)₂] (M = Mo, **1_{Mo}**, M = W, **1_W**, dppe = 1,2-bis(diphenylphosphino)ethane) dinitrogen complexes for this study. This choice was driven by the fact that on the one hand a substantial body of work exists on their reactivity,^[10] and, on the other hand, the group 6 M(dppe)₂ platforms have shown interesting reactivity regarding the activation of small organic fragments that are reminiscent of FLP chemistry.^[11] We surmised that **1** could react with the strong electrophile tris(pentafluorophenyl)borane (B(C₆F₅)₃, **2**) and trigger formal reduction of the N₂ ligand, akin to protonation.^[12] During the time this paper was being written, Szymczak and co-workers reported, in a very elegant but contextually different study, that adduct formation of **2** with the [(depe)₂Fe(N₂)] complex (depe = 1,2-bis(diethylphosphino)ethane) enhances activation of the dinitrogen ligand (Scheme 1, bottom).^[13] We treated orange C₆D₆ suspensions of **1** with 1 equivalent of **2** at room temperature and immediately obtained dark green solutions. Spectroscopic analysis indicated the clean formation of new complexes **3**, according to ¹H, ³¹P, ¹⁹F and ¹¹B NMR (≥90% NMR yield) (Scheme 2). The ¹H NMR spectra show inequivalent sets of methylene and aromatic protons, which indicates a loss of symmetry. A set of eight aromatic *ortho* protons is particularly shifted to high field. The ³¹P NMR spectra of **3_{Mo}** and **3_W** display a single peak shifted downfield to 73.1 ppm and 69.2 ppm, respectively (vs. 65.2 for **1_{Mo}** and 46.1 for **1_W**). ¹¹B and ¹⁹F NMR spectra are in accordance with the formation of adducts of borane **2** (shielding of the *para* fluorine atoms and a negative boron chemical shift, see the Supporting Information Fig. S1–4 and S6–9). Repeating these experiments



Scheme 1. Conventional vs. transition metal FLP for N₂ activation (top), and the advantages of such an approach in N₂ chemistry (bottom).



Scheme 2. Activation of N₂ to diazenido by zero-valent group 6 metal/B(C₆F₅)₃ TMFLP templates.

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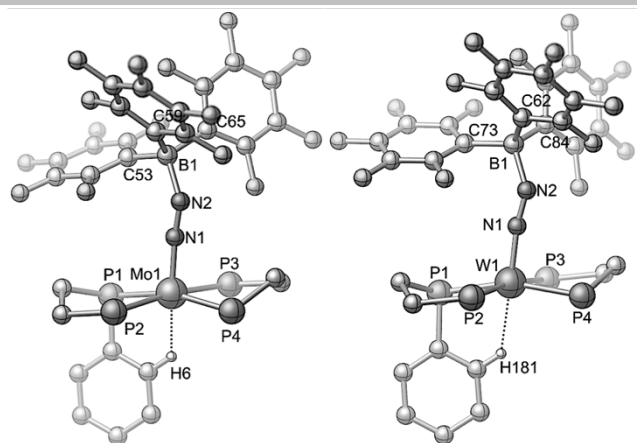
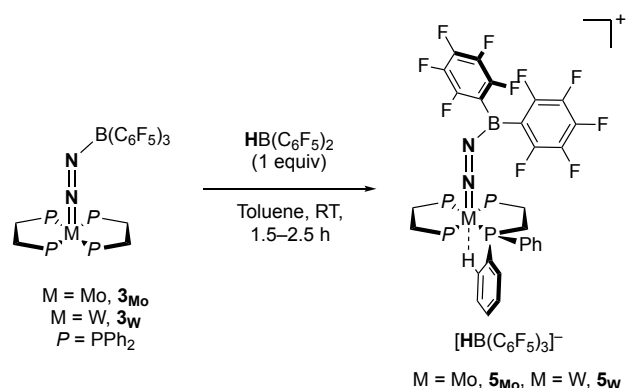


Figure 1. Molecular structures of **3_{Mo}** (left) and **3_W** (right) rendered with CYLView.^[20] Hydrogens (except H6 in **3_{Mo}** and H181 in **3_W**) and all but one aromatic substituents of the dppf ligands omitted for clarity. Relevant bond lengths [Å] and angles [°]: **3_{Mo}**: Mo1–N1 1.841(4), N1–N2 1.196(5), N2–B1 1.567(7), Mo1–H6 2.37, Mo1–N1–N2 174.4(4), N1–N2–B1 141.4(5), N1–Mo1–P1 103.15(13), N1–Mo1–P3 90.08(13), N2–B1–C53 108.6(4), N2–B1–C59 105.0(4), N2–B1–C65 110.3(4), C53–B1–C59 113.5(5), C53–B1–C65 113.7(5), C59–B1–C65 105.4(4). **3_W**: W1–N1 1.841(4), N1–N2 1.212(6), N2–B1 1.570(6), W1–H181 2.49, W1–N1–N2 170.2(3), N1–N2–B1 140.3(4), N1–W1–P1 106.83(13), N1–W1–P3 92.04(13), N2–B1–C62 102.9(4), N2–B1–C73 109.5(4), N2–B1–C84 110.8(4), C62–B1–C73 113.7(4), C62–B1–C84 105.8(4), C73–B1–C84 113.6(4).

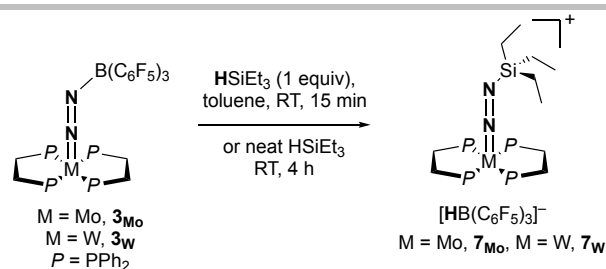
on a larger scale in toluene or chlorobenzene, followed by addition of pentane caused precipitation of dark powders (see the Supporting Information for details) from which single crystals suitable for an X-ray diffraction study could be grown. Indeed, Lewis pairs between **2** and one dinitrogen ligand in complexes **1** were formed. The molecular structures of adducts **3_{Mo}** and **3_W** given in Figure 1 are quite similar.^[14] Short M–N bonds [1.841(4) Å for **3_{Mo}** and **3_W** vs. 2.01(12) for **1_{Mo}**^[15] and long N–N distances [1.196(5) Å for **3_{Mo}** and 1.212(6) for **3_W** vs. 1.096 Å for free N₂ and 1.10(2) for **1_{Mo}**] support a M=N=N depiction,^[16] as a result of enhanced metal-to-N₂ back bonding. The B–N bonds are 1.567(7) Å (**3_{Mo}**) and 1.570(6) Å (**3_W**) and fall within the range of B–N bond lengths typical of classical adducts of **2** with nitrogen bases.^[17] The tetrahedral character^[18] of the boron atom is 87% (**3_{Mo}**) and 85% (**3_W**). **3_{Mo}** and **3_W** can thus be regarded as boratadiazenido complexes. The second dinitrogen ligand of **1** is lost upon reaction with the borane, leaving the other apical site vacant. This likely results from the strong *trans* effect of the diazenido moiety. Remarkably, an agostic interaction exists between the metal atom and an *ortho* hydrogen of one of the phenyl group in the solid state (Mo–H6 2.37 Å and W–H181 2.49 Å), forcing the NMP₄ arrangements to slightly distort from the ideal square pyramidal geometry (the angles between the M–N1 bond and the MP1P2 centroid in **3_{Mo}** and **3_W** are 103° and 105°, respectively).^[19] This might explain why a set of *ortho* protons is shielded in the solution ¹H NMR spectrum of **3**, these protons exchanging rapidly on the NMR time scale. The IR spectra of **3** (Fig. S5 and Fig. S10) show broad, intense bands assigned to the N–N bond stretching of the elongated N₂ moieties at 1744 cm^{−1} for **3_{Mo}** (226 cm^{−1} shift compared to **1_{Mo}**) and 1717 cm^{−1} for **3_W** (236 cm^{−1} shift compared to **1_{Mo}**). According to these data, a superior activation (population of the π*) of the N₂ ligand is noted compared to Szymczak's Fe example (129 cm^{−1} shift).^[13]

3_{Mo} and **3_W** can be viewed as zero-valent group 6 metal/B(C₆F₅)₃ TMFLP templates that activate dinitrogen. Although some p block Lewis acid adducts of metal-ligated dinitrogen are known, very few have been structurally characterized,^[13,21] and their reactivity was generally not explored. The recent report by Szymczak and co-workers has revealed such adducts were worth studying in the context of N₂ protonation. For our part, we were interested to check whether **3_{Mo}** and **3_W** could behave as an FLP, thus providing a new way to functionalize coordinated dinitrogen. In preliminary experiments, we decided to investigate B–H^[22] and Si–H^[23] bond activation. Upon addition of 1 equivalent of HB(C₆F₅)₂ (**4**)^[24] to C₆D₆ solutions of complexes **3**, new species **5** were formed cleanly in less than 3 h (NMR) (Scheme 3). In both cases, a high field shifted signal at ca. −25 ppm in the ¹¹B{¹H} NMR spectra indicated the formation of hydroborate anions. Yet, we were not able to detect a second boron resonance, although the ¹⁹F NMR spectrum showed a correct fluorine atom count (Fig. S11–14 and S16–19). Scale-up of these experiments in toluene followed by addition of pentane afforded the complexes as brown powders with the same spectral signatures. Single crystals suitable for X-ray diffraction studies could be grown,^[14] which allowed us to confirm their structures. However, and despite several attempts, the resulting data for **5_{Mo}** is of low quality, and therefore any geometric parameter should be considered with care. **5_{Mo}** and **5_W** are the products of the FLP-type B–H bond splitting by B(C₆F₅)₃ adducts **3** (Figure 2, left).^[22] They are ionic compounds where the anionic part is a hydrotris(pentafluorophenyl)borate, whose hydride originates from reagent **4**. In the cationic metal counterpart of **5_W**, enhanced back-donation from the metal into the π* orbital of N₂ is evidenced by a shorter M–N [1.841(4) Å for **3_W** vs. 1.755(3) Å for **5_W**] and a remarkably longer N–N bonds [1.212(6) Å for **3_W** vs. 1.274(5) Å for **5_W**]. Close M–H contacts at the vacant apical site [2.36 Å in **5_W**] and a high-field shifted signal integrating for 8 aromatic *ortho* protons in the ¹H NMR spectra again support an agostic interaction. Broad but weak bands at 1550 and 1532 cm^{−1} were assigned to the ν_{NN} of **5_{Mo}** and **5_W**, respectively (Fig. S15 and S20). Such a shift (ca. 190 cm^{−1}) and loss of intensity, as well as a rather short B–N bond in **5_W** [1.378(6) Å] indicate the strong participation of the M⁺≡N⁺–N=B[−] resonance form in the bonding situation.



Scheme 3. FLP-type splitting of a B–H bond by adducts **3**.

The reactions of the dark green complexes **3** with 1 equivalent of triethylsilane (**6**) in toluene-d₈ or with a large excess in neat conditions at room temperature resulted in a



Scheme 4. FLP-type splitting of a Si-H bond by adduct **3**.

color change to dark red. Again, ^{11}B NMR analysis of the isolated solids in C_6D_6 suggested the formation of the $[\text{HB}(\text{C}_6\text{F}_5)_3]^-$ anion (doublet around -24.5 ppm). ^1H NMR showed the disappearance of the SiHEt_3 signal and the appearance of eight shielded aromatic *ortho* protons. The ^{31}P NMR spectra indicated clean conversion to new complexes **7** with phosphorus resonances at 66.0 ($\mathbf{7}_{\text{Mo}}$) and 65.0 ppm ($\mathbf{7}_{\text{W}}$). These observations account for the formation of square pyramidal, ionic complexes again stabilized by an agostic interaction in the vacant apical site. By analogy with the B-H splitting experiments described above, we conclude that $\mathbf{3}_{\text{Mo}}$ and $\mathbf{3}_{\text{W}}$ are also able to perform the FLP-type splitting of Si-H bonds between **2** and their N_2 ligands (Scheme 4). The ^{29}Si HMQC NMR spectra of $\mathbf{7}_{\text{Mo}}$ and $\mathbf{7}_{\text{W}}$ give signals at 2.0 and -1.45 ppm for the Si atoms, respectively (vs. 0.2 ppm for free Et_3SiH), which suggests that the positive charge is not located at the Si atom (Fig. S21–25 and S27–31). It is worth mentioning that the IR spectra of $\mathbf{7}_{\text{Mo}}$ and $\mathbf{7}_{\text{W}}$ both present a broad, weak ν_{BH} band around 2400 cm^{-1} for the hydroborate as well as a broad one at 1664 and 1638 cm^{-1} , respectively, which indicate a stronger activation of the N_2 moiety compared to complexes **3**, but weaker than in **5** (Fig. S26 and S32). While compound $\mathbf{7}_{\text{Mo}}$ precipitated as an oil, crystals of $\mathbf{7}_{\text{W}}$ suitable for an X-ray diffraction study could be grown, allowing us to validate the proposed structures (Figure 2, right).

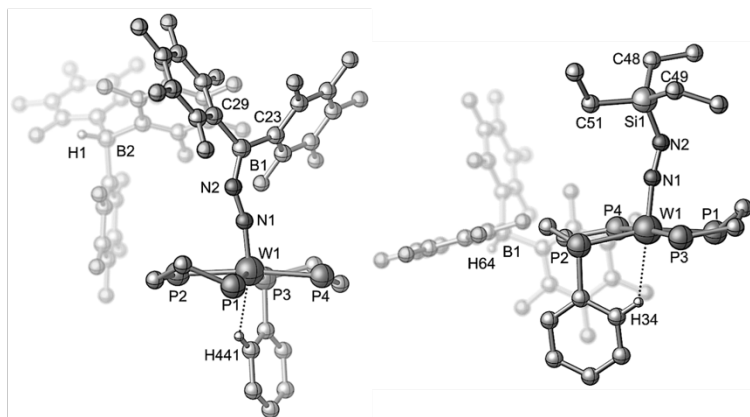


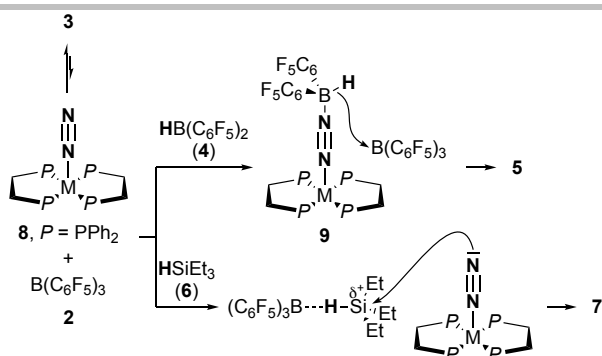
Figure 2. Molecular structures of **5w** (left) and **7w** (right) [ellipsoids at the 50% probability level, hydrogens (except H441 in **5w** and H34 in **7w**) and all but one aromatic substituents of the dppe ligands omitted for clarity]. Relevant bond lengths [Å] and angles [°]: **5w**: W1–N1 1.755(3), N1–N2 1.274(5), N2–B1 1.378(6), W1–H441 2.36, W1–N1–N2 166.8(3), N1–N2–B1 138.5(4), N1–W1–P1 88.42(11), N1–W1–P3 109.45(11), N2–B1–C23 124.3(4), N2–B1–C29 116.3(4), C23–B1–C29 119.4(4). **7w**: W1–N1 1.789(2), N1–N2 1.232(3), N2–Si1 1.735(3), W1–H34 2.57, W1–N1–N2 171.6(2), N1–N2–Si1 139.1(3), N1–W1–P1 88.86(8), N1–W1–P2 106.51(8), N2–Si1–C48 105.49(18), N2–Si1–C49 108.77(16), N2–Si1–C51 110.45(17), C48–Si1–C49 111.3(2), C48–Si1–C51 109.3(2), C49–Si1–C51 111.30(19).

Comparison of the bond lengths of the W–N–N core in $\mathbf{7}_{\text{W}}$ with those of $\mathbf{3}_{\text{W}}$ and $\mathbf{5}_{\text{W}}$ points out a greater back-donation from W to the N_2 moiety [W1–N1 1.789(2) Å, N1–N2 1.232(3) Å] than in $\mathbf{3}_{\text{W}}$, but weaker than in $\mathbf{5}_{\text{W}}$, as a result of lower electronegativity of Si compared to B in the $\text{B}(\text{C}_6\text{F}_5)_2$ group. The N–Si bond length falls within the range of those found in related complexes.^[25]

These reactions support the notion that dinitrogen complexes can serve as the Lewis base component of an FLP, thus providing a basis for the development of new functionalization methods of coordinated dinitrogen. Its borylation and silylation have indeed already been described in the literature; with complexes $\mathbf{1}_{\text{Mo}}$ and $\mathbf{1}_{\text{W}}$,^[25] but also in other end-on dinitrogen complexes,^[25,26] these reactions rely on the use of more electrophilic boron or silicon (pseudo)halides. A notable exception is the related, anionic *trans*- $[\text{NBu}_4][\text{W}(\text{NCS})(\text{N}_2)(\text{dppe})_2]$ complex, which reacted with primary or secondary hydroboranes. In this case, borylation of dinitrogen occurred without transfer of the hydride, which ended up in the ammonium hydroborate byproduct,^[25a] analogously to the $\mathbf{3} \rightarrow \mathbf{5}$ reaction. In dinitrogen-derived hydrazido or nitrido complexes, 1,2 addition of B–H^[27] or Si–H^[28] bonds across the M–N bond can also be an efficient route to borylation or silylation of dinitrogen; however this necessitates 4 or 6 e^- reduction of N_2 by the metal center prior to functionalization. Mild, alternative routes are disclosed herein, as a non-electrophilic main group hydride is made amenable to react with a weakly activated N_2 ligand. As to their mechanisms, direct reactions between the N_2 complexes with an *in situ* generated borinium (R_2B^+) or silylium (R_3Si^+) cation can be ruled out as **2** is not a suitable hydride abstractor to generate these highly reactive species.^[29,30] We suggest instead adducts **3** to be in equilibrium with coordinatively unsaturated complexes **8** and free borane **2** in solution, similarly to conventional B/N FLPs.^[31] In the borylation case, **8** can react with **4** to form a Lewis pair **9**.^[32] Upon formation of **9**, the B–H bond weakens and therefore the hydride is readily abstracted by **2**.^[22] In the silylation case, borane **2** activates the Si–H bond^[23,30] which renders the Si atom electrophilic enough to be attacked by

the terminal nucleophilic nitrogen of **8** (Scheme 5). As preliminary studies to check whether the $\mathbf{3} \rightleftharpoons \mathbf{8} + \mathbf{2}$ equilibrium exists, we performed a variable temperature NMR experiment. At -60°C , a toluene- d_8 solution of $\mathbf{3}_{\text{Mo}}$ revealed the presence of a second phosphorus signal at 62.1 ppm that could correspond to **8** (Fig. S33). In addition, a 2D NOESY ^{19}F NMR experiment (Fig. S34) also showed exchange between an excess of free **2** with its $\mathbf{3}_{\text{Mo}}$ coordinated form.

This work demonstrates that low-valent group 6 metal/Lewis acid TMFLP templates can be valuable tools to activate dinitrogen. In addition, such activation of N_2 permits its borylation and silylation with mild, ubiquitous E–H ($\text{E} = \text{R}_2\text{B}$ or R_3Si) reagents, in a way reminiscent of conventional FLPs. Such an approach has been neglected in the dinitrogen functionalization chemistry so far, and we have shown that molybdenum and tungsten complexes could perform equally well in these transformations. Future work will be directed towards the examination of different dinitrogen complexes and Lewis acids combinations. Special attention will be paid to the nature of the latter, since their ability to deliver back the hydride to the metal after the bond splitting step will be critical for the development of a catalytic N_2 reduction. The synthetic



Scheme 5. Proposed mechanisms for the reactions of **3** with **4** and **6** ($M = \text{Mo}$ or W).

potential of such an FLP-type functionalization of coordinated N_2 is currently under investigation and can be extrapolated from the chemistry of conventional FLPs.

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Keywords: boranes • dinitrogen • frustrated Lewis pairs • group 6 metals • silanes

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