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Antoine Simonneau, Michel Etienne. Enhanced Activation of Coordinated Dinitrogen with p-Block Lewis Acids. *Chemistry - A European Journal*, 2018, 24 (48), pp.12458-12463. hal-01829681

HAL Id: hal-01829681

<https://hal.science/hal-01829681v1>

Submitted on 4 Jul 2018

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Enhanced Activation of Coordinated Dinitrogen with p-Block Lewis Acids

Antoine Simonneau,^{*,[a,b]} and Michel Etienne^[a,b]

LCC, Université de Toulouse, CNRS, UPS; 205, route de Narbonne, BP44099, F-31077 Toulouse Cedex 4, France.

E-mail: antoine.simonneau@lcc-toulouse.fr

Homepage: <https://www.lcc-toulouse.fr/>

In memory of Dr. Julien Louvel

Abstract: This Concept article highlights recent research on Lewis acid adducts of dinitrogen complexes, including our contributions. After a reminder of the early works, it is demonstrated that such kind of species offers a new platform for dinitrogen functionalization as well as valuable models for the understanding of elementary steps of (bio)catalytic cycles. When possible, parallels regarding this mode of activation from the orbital point of view are drawn between the different systems discussed herein.

Keywords: dinitrogen complexes • Lewis acids • p-block • dinitrogen functionalization • Frustrated Lewis Pairs

Introduction

Molecular dinitrogen complexes have been the focus of intensive studies since the mid 1960s when Allen and Senoff disclosed the first coordination compound exhibiting an end-on coordinated N₂ unit (Figure 1, left).^[1] Chemists immediately realized the potential of such entities as a platform to study chemical transformations of the abundant, but very stable and inert N₂ molecule. At the advent of this chemistry, the reactivity of these complexes with Brønsted acids was intensively investigated.^[2] These studies offered simplified models of the reactions occurring at the active site of the nitrogenases (Figure 1, right), i.e. the successive transfers of protons and electrons to the FeMo cofactor necessary for N₂ reduction. At the same time, these investigations paved the way for the development of catalysts for ammonia synthesis that could potentially operate under ordinary pressure and temperature conditions.^[3] The synthesis of organonitrogen compounds also fueled interest in the coordination chemistry community.^[4] Having an estimate of the Brønsted or Lewis basicity of the N₂ ligand appeared to be important for the conception of the above-mentioned reactions. The preparation and characterization of Lewis acid (LA) adducts of dinitrogen complexes was therefore envisaged as a valuable source of information, since it would allow one to judge whether the N₂ ligand is accessible to electrophiles in general, and what response the transition metal center would give upon complexation of the Lewis acid in terms of d→π* electron back donation. Here, key analytical probes are typically the N–N bond stretching frequency ν_{NN} in IR spectroscopy, or metrical parameters from X-ray diffraction studies. Recently, some research groups have revisited combinations of end-on dinitrogen phosphine complexes with p-block Lewis acids. This has allowed for the preparation of models of elusive species relevant to catalytic dinitrogen reduction processes, as well as the discovery of unprecedented reactivity patterns, thus giving a new momentum toward the study of this class of coordination compounds.

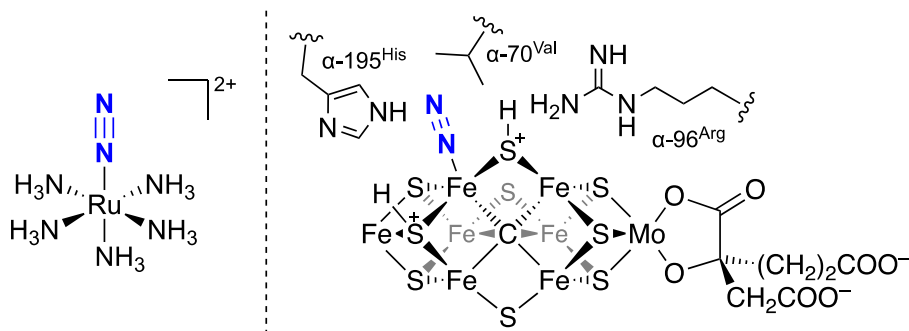
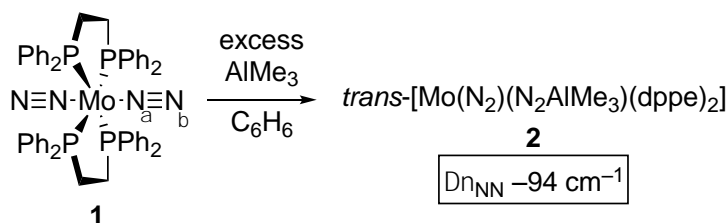


Figure 1. First reported N_2 complex (left) and the active site of the nitrogenase showing N_2 bound to the FeMo cofactor (right).

Early Works

While the nitrogenases had been known for decades when Allen and Senoff made their discovery, knowledge about their mechanism was not as advanced as it is today.^[5] As they were already known to have a bimetallic nature, Chatt and his colleagues at the Nitrogen Fixation Unit of the University of Sussex examined the interaction of some end-on dinitrogen complexes with electrophilic transition metal or main-group compounds in order to get some insights into the mechanism of nitrogen fixing metalloenzymes.^[6] They could prepare and characterize a series of heterobimetallic complexes for which they proposed a structure featuring an N_2 ligand bridging two metals in a $\eta^1:\eta^1$ fashion, as a result of Lewis acid-Lewis base (LB) interaction. In some instances (e.g. with TiF_4 , $TiCl_4$, $FeCl_3$, $CuCl$ or PF_5), these reactions failed to produce a stable N_2 -bridged complex and resulted in oxidation of the starting N_2 complex.^[6b,c] The reactions of isoelectronic group 6–8 dinitrogen phosphine complexes with different aluminum compounds ($AlMe_3$, $AlPh_3$ and $AlCl_3$) were investigated and the isolated adducts, when viable, were characterized by 1H NMR and IR spectroscopy.^[6e,f] Although the complexes investigated [$Mo(0)$, $W(0)$, $Re(I)$ and $Os(II)$] formed stable 1:1 adducts with $AlMe_3$ without noticeable amounts of alkylated products (Scheme 1, adduct formation between the Mo complex **1** and $AlMe_3$), the reaction with $AlPh_3$ was of narrower scope, while treatment with $AlCl_3$ generally resulted in decomposition along with N_2 evolution.^[7] Correlation between d electron delocalization from the metal center into the π^* molecular orbital (MO) of the N_2 ligand and basicity of its β nitrogen was experimentally established. The weakening of the N–N triple bond observed by IR spectroscopy was attributed to a "push-pull" mechanism where electron density withdrawal on one side of the bridging N_2 ligand triggers enhanced $d \rightarrow \pi^*$ back donation from the transition metal center.^[6a,b]

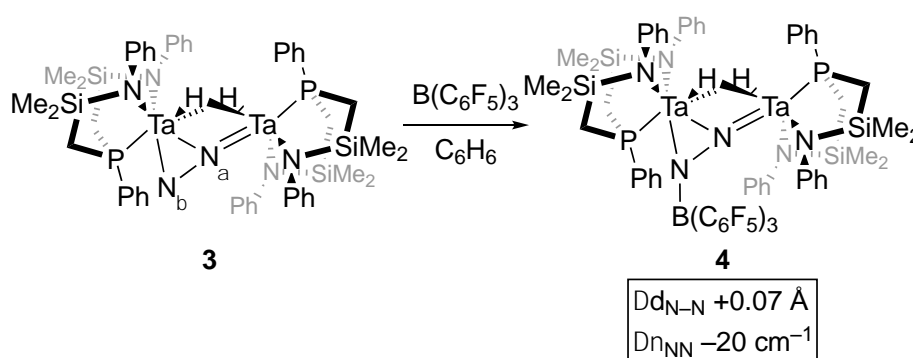


Scheme 1. Adduct of a N_2 complex with an aluminum Lewis acid.

Adducts with a Side-On, End-On N_2 Complex

The late 1990s and early 2000s witnessed major breakthroughs in the chemistry of molecular dinitrogen complexes: N_2 cleavage by low-coordinate, well-defined Mo complexes;^[8] the achievement of catalytic ammonia synthesis,^[9] albeit with limited turn-over numbers and turn-over frequencies; and hydrogenation of coordinated N_2 ,^[10] the latter becoming possible with the discovery of the side-on coordination mode in homobimetallic complexes.^[11] Remarkably, all these processes occurred in

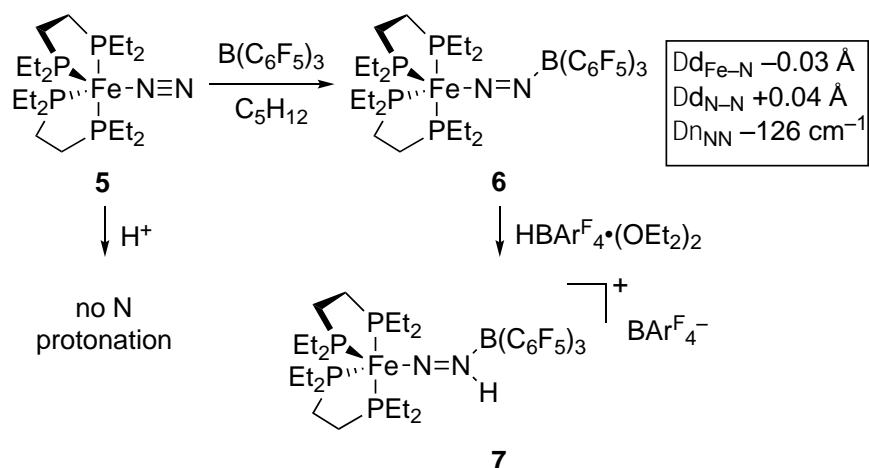
especially mild conditions. In 2005, a joint study on the interaction of the Ta complex $[\{(NPN)Ta\}_2(\mu-H)_2(\mu-\eta^1:\eta^2-N_2)]$ (**3**), with various p-block LA $[AlMe_3, GaMe_3$ (both not shown) and $B(C_6F_5)_3$, Scheme 2]^[12] by Tuczec, Fryzuk and coworkers sporadically brought back into fashion group 13 LA adducts of N_2 complexes. The goal of this investigation was to better apprehend the reactivity of the N_2 ligand in the rare side-on, end-on coordination mode.^[13] LA addition to complex **3** occurred at the β nitrogen to give **4**. A bathochromic shift of the ν_{NN} stretch (-20 cm^{-1}) in the IR spectrum was evidence of further weakening of the N–N bond in **4**. The bonding situation in a model complex, $[\{PH_3(NH_2)_2Ta\}_2(\mu-H)_2(\mu-\eta^1:\eta^2-N_2-BH_3)]$, was investigated by means of DFT calculations. Boron complexation leads to a decrease of the HOMO's energy.^[14] Although the overall symmetry is different than that in the end-on mononuclear complexes, the HOMO also corresponds to a bonding interaction of the metal centers' filled $d\pi$ orbitals with antibonding π^* of the dinitrogen ligand. Increased N_2 polarization can be traced according to Natural Charges (NCs) resulting from a Natural Population Analysis (NPA). The MOs involved in the N–B dative bond are principally a hybrid of the p_σ and a π bond of the N_2 fragment and the empty p orbital at boron.



Scheme 2. Adduct of a side-on, end-on (NPN)Ta complex with $B(C_6F_5)_3$.

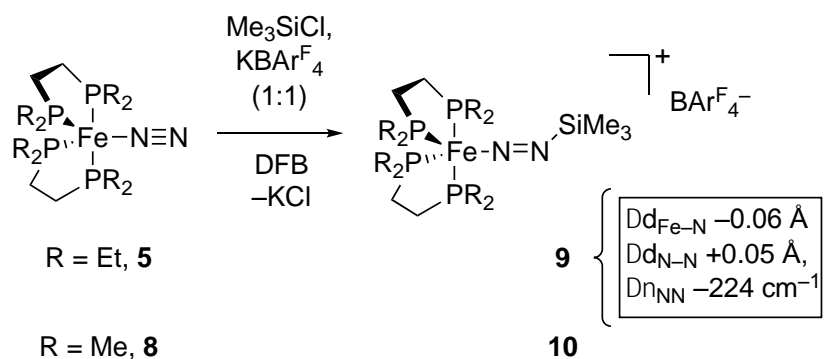
Adducts between Iron- N_2 Complexes and Strong Lewis Acids for the Understanding of Catalytic Processes

Very recently, the team of Szymczak investigated the spectroscopic and electrochemical properties as well as electronic structures of adducts between the end-on iron-dinitrogen complex $[Fe(depe)_2(N_2)]$ (**5**, $depe = 1,2$ -bis(diethylphosphino)ethane) and various LAs. The idea was to test the "push-pull hypothesis" by which acidic residues in the active site of the nitrogenase pull electron density from the reduced iron center onto the N_2 ligand (see Figure 1),^[5] thus rendering it more reactive towards protonation (Scheme 3).^[15] In adducts of the type $[(depe)_2Fe(\eta^1:\eta^1-N_2-BR_3)]$ ($R = 2,6-F_2C_6H_3, 2,4,6-F_3C_6H_2, C_6F_5, OC_6F_5$ or F), a good correlation was found between the Lewis acidity of the boranes^[16] and the activation of the N_2 ligand, as judged by the ν_{NN} stretching frequency in IR spectroscopy. Solid-state (X-ray) and electronic (DFT) structures were reported for the $B(C_6F_5)_3$ adduct **6**. The NNB arrangement is bent [$137.0(3)^\circ$], as a result of $p_B/\pi^*_{N_2}$ mixing for the formation of the B–N dative bond. Activation of the N–N bond (elongation by $+0.04\text{ \AA}$ and ν_{NN} red shift of 126 cm^{-1}) upon LA complexation was explained, in terms of orbital considerations, by (i) a greater stabilization of the HOMO, which consists of a combination of d orbitals with the π^* of N_2 , and (ii) an increase of its π^* character, analogous to **4**. NCs calculations clearly indicate enhanced polarization of the N_2 ligand, with an increase of the negative charge at the terminal N. This is counterintuitive, as one would have expected the acceptor to quench its basicity. An important implication of these observations is that transfer of electron density from the metal favors reactivity of electrophiles at the N_2 ligand instead of the reduced iron center. This assumption was clearly verified by the protonation of **6** with $HBAr^F_4$ ($Ar^F = 3,5-(F_3C)_2C_6H_3$) which smoothly occurred at the terminal N to give **7** in excellent yield (Scheme 3, **6** \rightarrow **7**).



Scheme 3. A Lewis acid adduct of an iron- N_2 complex aimed at verifying the "push-pull hypothesis" regarding the active site of the nitrogenase.

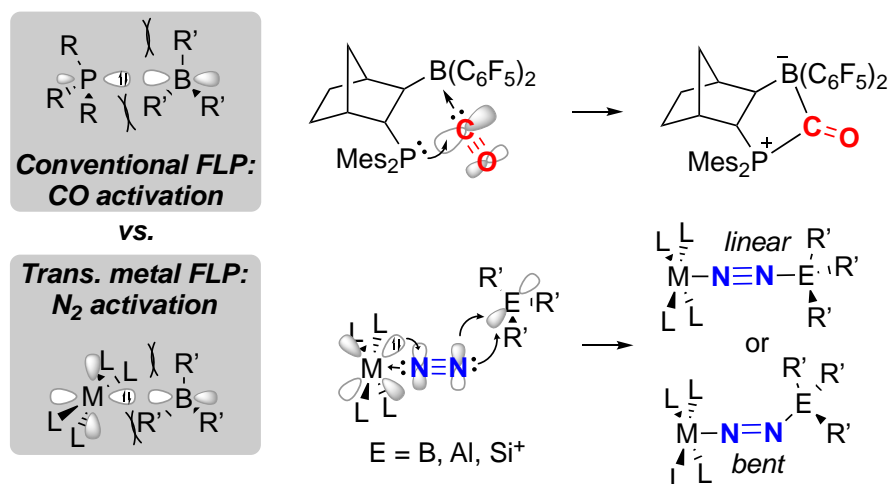
Beyond validating the "push-pull hypothesis", characterization of such mono-protonated species offers a snapshot of what may resemble elusive FeN_2H intermediates in catalytic N_2 reductions.^[3b,17] Ashley and coworkers cleverly made use of the more Lewis acidic Me_3Si^+ silylium ion as a proton mimic to characterize the first cationic silyldiazenido iron complexes (Scheme 4).^[18] Treatment of **5** or $[\text{Fe}(\text{dmpe})_2(\text{N}_2)]$ (**8**, dmpe = 1,2-bis(dimethylphosphino)ethane) with $\text{Me}_3\text{SiCl}/\text{KBARF}_4$ afforded the ionic compounds **9** and **10** bearing a bent NNSi arrangement [$\text{Ar}^{\text{F}} = 3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3$]. IR data were in line with a notable weakening of the N–N bond. As expected with the stronger LA Me_3Si^+ , the ν_{NN} shifted towards lower energies (-224 cm^{-1}) as the consequence of a greater "pull" effect. The X-ray diffraction structures of complexes **9** and **10** show an elongation of the N–N bond of ca. $+0.05 \text{ \AA}$, while the Fe–N bond displays greater double bond character than in **5** or **8**. DFT calculations performed on the silyldiazenido complexes were in line with those run by Szymczak and co-workers (*vide supra*). According to their diamagnetic character, trigonal bipyramid geometry and d orbital-centered HOMOs, the complexes were best described as being Fe(0), d^8 , rather than Fe(II), high spin d^6 . Relevance to the intermediates in catalytic cycles of N_2 reduction to silylamines^[19] can also be invoked here. Indeed, several silyldiazenido complexes have been reported prior to Ashley's work. Such compounds were obtained by substitution of a (pseudo-)halide in R_3SiX compounds,^[20] and occurrence of R_3Si^+ cations is rather unlikely.^[21]



Scheme 4. A cationic Fe-silyldiazenido complex mimics intermediates of catalytic N_2 reduction.

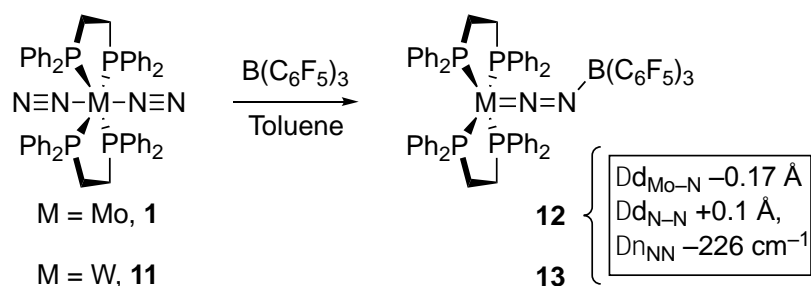
Lewis Acid Adducts of N₂ Complexes and the Frustrated Lewis Pair Chemistry

The "push-pull" paradigm for N₂ activation illustrated by the two previous examples can be extended to the recent chemistry of the frustrated Lewis pairs (FLP).^[22] This now mature field exploits the simultaneous action of a LA and a Lewis base (LB) – prevented from forming a classical LA–LB adduct by steric interactions – for the activation of a vast array of (small) molecules (see scheme 5, top; activation of CO, isoelectronic to N₂, by an intramolecular P/B FLP^[23]).



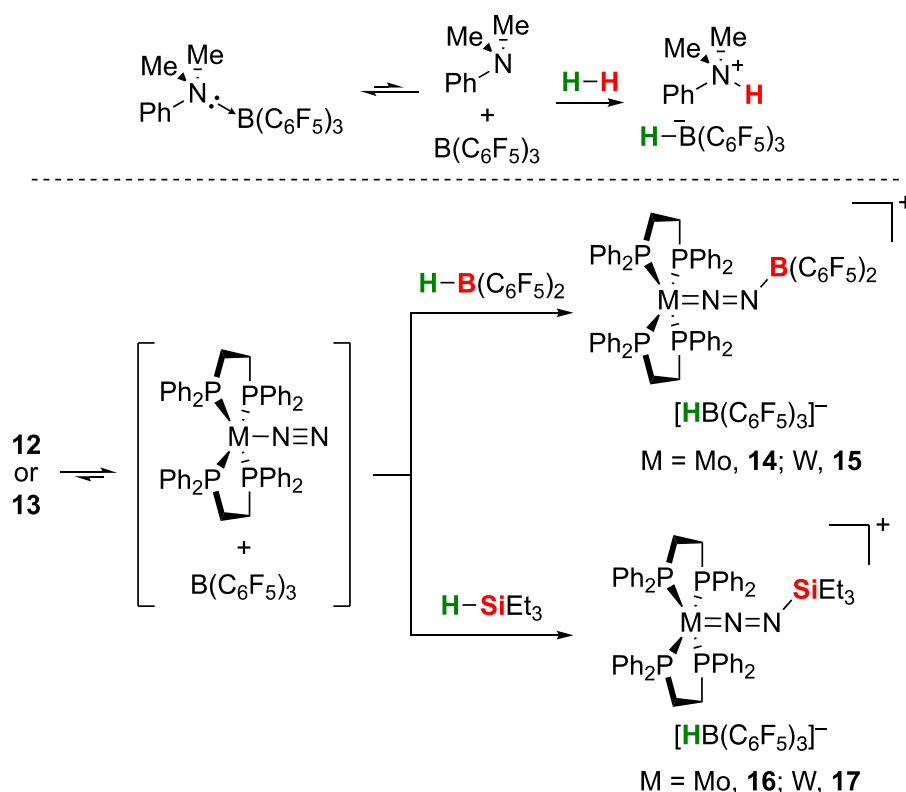
Scheme 5. Comparison of the "conventional" FLP chemistry of isoelectronic CO (top) with the N₂ complexes/LA adducts discussed herein, which can be viewed as transition metal FLP templates (bottom).

Although initially based solely on p-block compounds, mixed systems incorporating a metal complex have started to emerge as alternatives to pure main group combinations.^[24] The iron dinitrogen complexes/LA combinations of Szymczak and Ashley can be viewed as metal/p-block FLP templates that activate N₂, the difference from a conventional FLP being that electron density of the Lewis basic component lies in an orbital of different geometry (see Scheme 5, bottom). The involvement of the metal's filled d orbital in the activation of N₂ is here the key to make N₂ amenable to FLP-type chemistry.^[25] In conventional phosphorus/boron systems, the P-centered HOMO involved in the small molecule activation cannot build a constructive overlap with the high-lying N₂ π*. We recently drew an explicit parallel with this type of N₂ activation with FLPs when we reported the Mo and W complexes **12** and **13**.^[26] Similarly to Szymczak's and Ashley's iron examples, they were prepared from the group 6 dinitrogen complexes **1** and **11**, respectively, by treatment with B(C₆F₅)₃. **12** and **13** share a bent NNB arrangement, with a substantially elongated NN bond. This is reflected by the important bathochromic shift of the ν_{NN} in both complexes (–226 and –236 cm^{–1}, respectively, Scheme 6). Although no calculations were performed on these complexes, it can reasonably be assumed that the same effects explain the activation of the N₂ ligand, i.e., enhanced metal-to-ligand charge transfer triggered by LA's interaction with N₂'s π*.^[27] One N₂ ligand is lost upon complexation, as opposed to Chatt's example of the AlMe₃ adduct with **1**.^[5d] The strong charge transfer caused by the borane may impart a substantial *trans* influence to the N₂ unit, which thus hampers coordination in the second apical site. Compared to the Fe complex **6**, the higher activation of the N₂ ligand, as illustrated by ν_{NN} and N–N bond lengths, correlates with the greater π-donating ability of Mo and W. Similar structural and spectroscopic changes are achieved in the Fe complexes of Ashley and co-workers, as a result of the use of the highly electrophilic silylium cation.



Scheme 6. Adducts of Mo- and W-N₂ complexes with the strong LA B(C₆F₅)₃.

The Mo and W complexes **12** and **13** were shown to react with hydroboranes and hydrosilanes (Scheme 7). It was postulated that the size of the [(dpe)₂M(N₂)] fragment might facilitate dissociation of the borane, which would allow subsequent B–H and Si–H bond splitting and functionalization of the N₂ ligand with boryl and silyl groups in **14–17**. Such reactivity again compares well with that of usual nitrogen/boron (N/B) FLPs (Scheme 7, top).^[28–30] No borylation or silylation of N₂ occurs in the absence of B(C₆F₅)₃. Akin to **9** and **10**, the N–N bonds in the functionalized complexes are rather long (1.23–1.27 Å for the W complexes), with ν_{NN} below 1670 cm⁻¹. These products can be seen as adducts of d⁶ dinitrogen complexes with the elusive [Et₃Si]⁺[HB(C₆F₅)₃]⁻ silylium cation,^[31] or the unknown [(C₆F₅)₂B]⁺[HB(C₆F₅)₃]⁻ borinium ion,^[32] but we proposed to describe these ionic species **14–17** as boryl- or silyl-diazenido complexes with metal centers in the +2 oxidation state.^[33] In the silyldiazenido complexes **16** and **17**, the NMR resonances of the ²⁹Si nucleus are shifted to high field, strongly suggesting that the positive charge is not carried by the Si atom.^[34] The actual electronic situation in the group 6 complexes **14–17** remains debatable and calculations are under way to better appreciate it. This should allow detailed comparison with Szymczak's and Ashley's examples.



Scheme 7. Conventional nitrogen/boron FLP chemistry (top) compares well with the borylation and silylation of N₂ in complexes **12** and **13** (bottom).

These examples of B–H and Si–H bond splitting act as an incentive to extend this N/B FLP-type reactivity. We know from Szymczak's and Ashley's work that d^8 iron dinitrogen complexes form stable adducts with strong Lewis acids. In-depth studies involving complexes of different metals, ligands and LAs are under way. A deeper understanding of such combinations will allow the design of new FLP templates with tailored properties and reactivity. The chemistry of conventional N/B FLPs is very rich, and its extension to M–N \equiv N/B systems gives a glimpse of new possibilities regarding the functionalization of coordinated N₂.

Summary and Outlook

Since the pioneering work led by the group of Chatt during the 1970s, progress has been made in the understanding of the nitrogenases, and catalytic N₂ reductions have been achieved. The field of the Frustrated Lewis pairs has also emerged as a strategy of choice for the activation of small molecules. All these advances of modern chemistry will continue to encourage chemists to give a new look to Lewis acid adducts of (end-on) dinitrogen complexes. This body of recent work clearly demonstrates that combinations of Lewis acids with dinitrogen complexes may develop as a complementary approach for N₂ activation and functionalization. A common feature of the examples discussed above is that LA complexation to coordinated N₂ lowers the energy level of the HOMO of the N₂ complex, a combination of metal-centered d orbitals and N₂ π^* orbitals. As a result, important charge transfer takes place from the metal to N₂, increasing its polarization. In depth understanding of the bonding situation should help predict the reactivity of such adducts, and gain insights into mechanistic pathways. A challenge associated with this chemistry may reside in the occurrence of electron transfer processes,^[6b,c] as (strong) Lewis acids can also behave as one electron oxidants.^[35]

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- [24] a) S. R. Flynn, D. F. Wass, *ACS Catal.* **2013**, *3*, 2574–2581. b) D. F. Wass, A. M. Chapman, *Top. Curr. Chem.* **2013**, *334*, 261–280.
- [25] While this article was being written, Stephan and co-workers reported the isolation of the adduct of diazodiphenylmethane with $\text{B}(\text{C}_6\text{F}_5)_3$, $\text{Ph}_2\text{C}=\text{N}=\text{N}-\text{B}(\text{C}_6\text{F}_5)_3$. A prelude to the FLP chemistry of N_2 with pure main group system is thus composed: 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. This FLP-type activation of N_2 was subsequently highlighted by Melen: b) R. Melen, *Angew. Chem. Int. Ed.* **2017**, *56*, 880–882; *Angew. Chem.* **2017**, *129*, 890–892.
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- [27] Although the Fe complexes **6**, **9** and **10** on the one hand and the Mo and W complexes **12** and **13** on the other hand do not share the same geometries, the orbital involved in the back-bonding are in every case a set of two symmetry-degenerated d_{xy} , d_{xz} or d_{yz} orbitals. This allows, to some extent, comparison of the bonding situations in these different species.
- [28] Formation of a classical $(\text{C}_6\text{F}_5)_3\text{B}\cdot\text{NR}_3$ adduct does not preclude a FLP behavior: a) T. Voss, T. Mahdi, E. Otten, R. Fröhlich, G. Kehr, D. W. Stephan, G. Erker, *Organometallics* **2012**, *31*, 2367–2378; b) T. C. Johnstone, G. N. J. H. Wee, D. W. Stephan, *Angew. Chem. Int. Ed.* **2018**, *57*, 5881–5884. For a review dealing specifically with B/N FLPs, see: c) V. Sumerin, K. Chernichenko, F. Schulz, M. Leskelä, B. Rieger, T. Repo, *Top. Curr. Chem.* **2013**, *332*, 111–155.
- [29] B–H bond activation with FLPs: M. A. Dureen, A. Lough, T. M. Gilbert, D. W. Stephan, *Chem. Commun.* **2008**, 4303–4305.
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- [33] Examples of related complexes: ref. 7d; a) K. Komori, S. Sugiura, Y. Mizobe, M. Yamada, M. Hidai, *Bull. Chem. Soc. Jpn.* **1989**, *62*, 2953–2959; b) M. Hidai, K. Komori, T. Kodama, D.-M. Jin, T. Takahashi, S. Sugiura, Y. Uchida, Y. Mizobe, *J. Organomet. Chem.* **1984**, *272*, 155–167.
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