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Push-Pull Activation of N₂: Coordination of Lewis acids to dinitrogen complexes

Anaïs Coffinet, Antoine Simonneau* and David Specklin

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

Abstract: This article gathers, as of 2020, examples of (hetero)dinuclear dinitrogen complexes that are formed by Lewis acid-base interaction thanks to dative bonding between an electron-deficient s-, p- or d-block species and the electron-rich terminal nitrogen of a neutral end-on dinitrogen complex. Lewis acid (LA) coordination to the dinitrogen ligand results in a higher level of activation (i. e. polarization) according to a push-pull mechanism: electron depletion induced by LA coordination amplifies electron back-donation. The magnitude of such phenomenon will depend on various factors that will be highlighted here, as well as the mean to measure it. In some instances, key reactivities that Lewis acid (LA) coordination has lent to the dinitrogen complex, or how their combination has allowed the discovery of original reactions will be discussed. This review is organized in three main sections according to which block of the Periodic System the Lewis acid component of the complexes discussed belongs to. In a final section, pieces of work issued from main group chemistry and relevant in the context of N₂ push-pull activation will be presented.

Keywords: Dinitrogen; transition metal complexes; Lewis acids; Alkali; Alkali-earth; main group; push-pull; heterobimetallic complexes

1. INTRODUCTION

Since the first preparation of an end-on dinitrogen complex in the mid 1960s by Allen and Senoff,¹ N₂ activation has become an important topic in coordination, inorganic and organometallic chemistries. It remains undebatable that transition metal species are predominant in this field. Today, the metals capable of binding dinitrogen span across the whole d-block. A variety of coordination modes are known, albeit the end-on one is frequently encountered.²⁻¹⁰ Early on, chemists have realized the potential of dinitrogen complexes as platforms to study chemical transformations of the abundant, but very stable and inert N₂ molecule. In relationship with the chemistry occurring in the active site of the nitrogen fixing enzyme nitrogenase,¹¹⁻¹⁶ one remarkable property of end-on coordinated dinitrogen is its propensity to be protonated by Brønsted acids. Indeed, if sufficient electron density is delocalized into the antibonding π^* molecular orbitals of N₂ by back-donation from the metal, significant basicity is imparted to the terminal nitrogen. In some instances, with excess acid and a sufficiently electron-rich metal, some synthetic dinitrogen complexes have afforded ammonia,^{17,18,27-36,19,37-39,20-26} thus mimicking the enigmatic FeMo cofactor necessary for N₂ reduction by the nitrogenases. One great achievement of dinitrogen chemistry is the development of catalytic systems for N₂ reduction by devising sources of protons and electrons that can cohabit long enough within a reactor and that kinetically match NH₃ synthesis over H₂ evolution.⁴⁰⁻⁴⁶ The remarkably mild reaction conditions under which current homogeneous N₂ reduction catalysts perform are often opposed to the functioning of the industrial Haber-Bosch (HB) process, the only artificial nitrogen fixation technology that has met commercial success and that suffers from high energy and fossil fuel consumptions as well as very harsh operating conditions.⁴⁷⁻⁵³

Having an estimate of the Brønsted or Lewis basicity of the end-on N₂ ligand is of primary importance for the conception of the above-mentioned catalyses. At the advent of the chemistry of dinitrogen complexes, 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 $d \rightarrow \pi^*$ electron back donation.^{28,54–58} The term “push-pull effect” was soon given to the mechanism by which coordination of a Lewis acid to the terminal nitrogen of an N₂ ligand enhances its “activation”,^{28,55} a term that has been originally employed for highly polarized olefins featuring electron-withdrawing and -donating groups in a 1,2 relationship.^{59,60} Comparatively, the push-pull polarization of N₂ is the result of electron depletion caused by LA complexation (pull effect), resulting in a more important d electrons delocalization from the metal (push effect). The same effect has been suggested to be a key factor in biological N₂ activation, operating through H-bond donor sites within the active site of the nitrogenase.^{13,61,62} Key analytical probes to measure this effect are typically the N–N bond stretching frequency $\nu(\text{N}_2)$ in IR spectroscopy, metrical parameters from X-ray diffraction studies or in some instances, ¹⁵N NMR.

The purpose of this article is to gather, as of 2020, examples of *(hetero)dinuclear dinitrogen complexes that are formed by Lewis acid-base interaction thanks to dative bonding between an electron-deficient species and the electron rich terminal nitrogen of a neutral end-on or side-on, end-on dinitrogen complex*. In every case, we will pay attention to place the below-described species within a research context and pick the key available parameters that allow the measurement of the push-pull activation. In some cases, we will discuss key reactivities that Lewis acid (LA) coordination has lent to the dinitrogen complex, or how their combination has allowed the discovery of original reactions. We have decided to organize this review in three main sections according to which block of the Periodic System the Lewis acid component of the complexes discussed belongs to. In a final section, pieces of work issued from main group chemistry and relevant in the context of N₂ push-pull activation will be presented.^{63,64}

2. S-BLOCK CATIONS INTERACTION WITH DINITROGEN COMPLEXES

Alkali and alkali-earth cations are used as promoters in a large variety of heterogeneous catalytic processes. Notably, modern catalysts for nitrogen fixation in the Haber-Bosch (H-B) process are incorporating K₂O, CaO and MgO to the iron catalyst bed among other promoters.⁵³ The calcium and magnesium are limited to a structural role by stabilizing the active sites, increasing the surface area and preserving the integrity of the catalyst. On the other hand, potassium is suspected to have an active participation in the catalysis by acting as an “electronic promoter” on the surface of the catalyst.⁴⁹ The effect of such promoters on the catalytic activity has been explored extensively⁶⁵ but the results are often empirical and the mechanisms involving the s-group cations are not well understood. This is due in part to the limitations in the investigation of atomic scale interactions on catalysts surfaces, which make extremely difficult the direct observation of the interplay between active sites, substrates and promoters. Understanding the role of these promoters could allow for the development of better-optimized catalysts with effects on their selectivity, activity and robustness.

By comparison, homogeneous systems are more easily studied, allowing for the observation of dynamic processes through direct observation and the isolation of relevant catalytic products and intermediates. The behavior of s-group cations in solution depends on several parameters. Ion pairing can lead to poor solubility, which can be balanced by the use of non-coordinating anions or O- and N-donor solvents that provide weak bonding interactions.⁶⁶ Crown ether and cryptands are also able to solvate the cations by host-guest interactions but their coordination often introduce a competition with the substrate.⁶⁷ s-Group cations are usually labile, they form interactions lacking significant covalency and are thus mostly electrostatic and non-directional. Despite these limitations, s-group

cations have been found to have an essential role in substrate transformation in molecular catalysis and organic transformations.^{68–70}

Fixation and reduction of dinitrogen in the nitrogenase enzyme involve coordination to a reduced iron center embedded in a multimetallic Fe/Fe, Fe/Mo or Fe/V active site. Under an essentially unknown mechanism, sequential reduction and proton transfer reactions occur with low overpotentials and high protonation selectivity.¹³ This contrasts with typical iron-based synthetic systems that require metal centers with high π -basicity and high reduction potential, which often results in low selectivity toward protonation.^{71,72} A key aspect of biological systems is their use of macroscopic structures to finely control the substrate's environment during enzymatic processes. Secondary-sphere interactions are one of the fundamental tools used by metalloproteins to achieve this control.^{73,74} These interactions often involve hydrogen bonding donors and Lewis acidic sites,^{75,76} simple s-group cations, especially Na^+ and K^+ , are also routinely placed near active sites.^{77,78} Insight gained on the nature of bound N_2 ligand / s-group cations interactions could then benefit both homogeneous and heterogeneous N_2 transformation reactions.

2.1. s-Block cations interaction with formally anionic N_2 complexes

Although out of the scope of this review, the association of s-group cations with the N_2 ligand of a formally anionic complex has been observed with a large variety of transition metal (TM) complexes^{39,79–81} and deserves some words here. Such interactions are almost exclusively the result of s-block metal promoted reduction of a halide TM complex under an N_2 atmosphere in order to obtain a dinitrogen complex. A 2017 review by Holland and colleagues⁸² explored the literature on alkali metal coordination to N_2 complexes, with an emphasis toward insights pertaining to the surface chemistry of the HB process. Typically, coordination of an alkali cation results in a linear $\text{M}-\text{N}\equiv\text{N}-\text{X}$ motif (M: Transition metal, X: alkali cation), the cation being stabilized by coordinating solvent molecules, crown ether solvation or cation- π interactions with the ancillary ligand (Figure 1). By stabilizing electron density on the terminal nitrogen, alkali cation coordination results in activation of the dinitrogen and can promote a nucleophilic reactivity and/or N_2 reduction. At the time of Holland's review, all examples of alkali cations coordination were accompanied with a reduction of the transition metal complex bearing the N_2 ligand and thus the electronic effect of the alkali cations could not be fully resolved. The lack of directly comparable complexes varying the cations also impaired the determination of a clear trend down the alkali group. By comparison, the literature on Alkali-earth cations coordination to dinitrogen is more limited. There is only a handful of studies, which are all restricted to Mg^{2+} . Mirroring most of the alkali cations literature, these examples involve a reduction of the TM complex (directly with Mg^0 or *via* MgEt_2 promoted reductive elimination) prior to Mg^{2+} interaction with N_2 .^{83–87} The coordination of Mg^{2+} generally form a bridging $\text{M}-\text{N}_2-\text{Mg}(\text{L}_n)-\text{N}_2-\text{M}$ motif (M = Mo, Co, Fe; L = THF; n = 2 or 4) with linear or bent N-N-Mg geometries depending respectively on whether the reduction took place at the N_2 ligand to form diazenido (e.g. $[\text{Mo}^0-\text{N}=\text{N}]^{-83-85}$) complexes or at the TM center (e.g. $[\text{Co}^{-1}-\text{N}\equiv\text{N}]^{-88}$). Owing to reduction events occurring concomitantly with Mg^{2+} coordination, the cation effect on N_2 activation cannot be easily discerned from the inherent properties of the anionic TM species and ion pairing interactions.

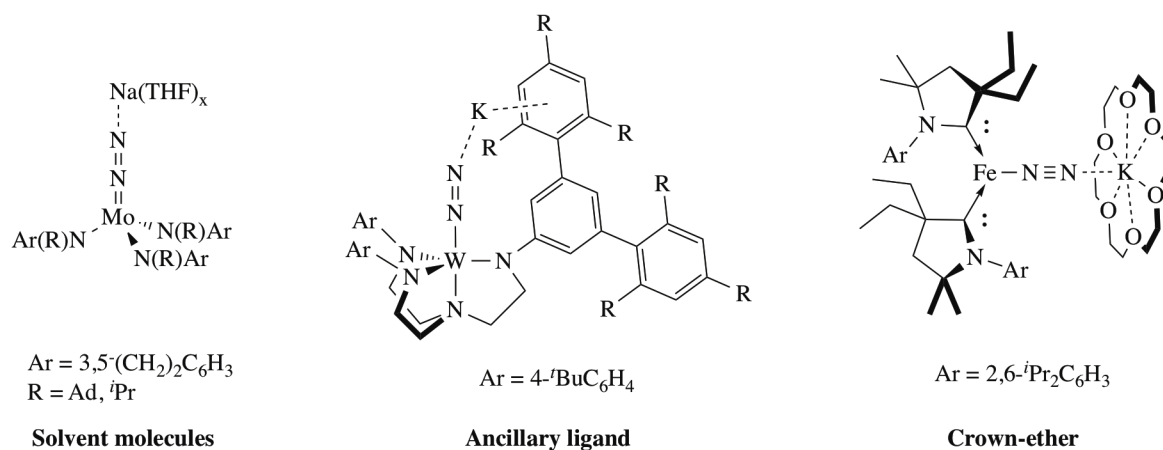
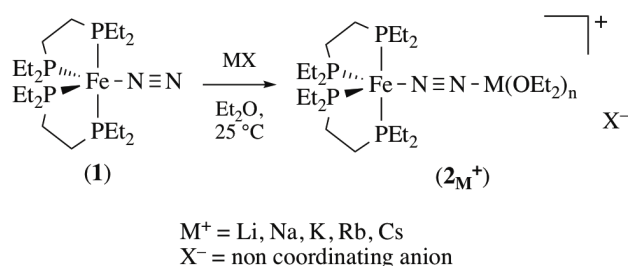


Figure 1. Support of the alkali cations coordination to end-on N₂ ligand.

2.2. Alkali cations interaction with neutral N₂ complexes

In the active site of the nitrogenase enzymes, enhanced N₂ polarization owing to acidic residues (H-bond donors) *via* a “push-pull” mechanism has been proposed to justify the high selectivity and soft conditions required for nitrogen fixation. In this context, the group of Szymczak carried out in 2017 a systematic investigation on the electronic and structural effect of LA coordination to a model iron(0) dinitrogen complex.⁶¹ They reacted [Fe(depe)₂(N₂)] (**1**) (depe: 1,2-bis(diethylphosphino)ethane) with various LAs to afford stable adducts with alkali cations (Scheme 1), Fe^{II} and borane based electrophiles coordinating to the terminal nitrogen of the end-on N₂ ligand. The bulk of their findings concerned the adduct of main group B(C₆F₅)₃ that will be discussed in details in section 4.3.1. Complex (**1**) is especially apt for the evaluation of N₂-alkali cations pairing as its neutral state and ligand design allow the pairs to be devoid of charge pairing and cation-π interactions.



Scheme 1. Formations of adducts (**2_M⁺**) with alkali cations salt of non-coordinating anions [B(C₆F₅)₄]⁻ or [B(3,5-{CF₃}₂C₆H₃)₄]⁻.

The binding of Li⁺, Na⁺, K⁺, Rb⁺ and Cs⁺ to (**1**) were characterized by IR spectroscopy in Et₂O from freshly prepared stoichiometric mixtures of (**1**) and the salts of non-coordinating anions Li[B(C₆F₅)₄] and M[B(3,5-{CF₃}₂C₆H₃)₄] (M = Na, K, Rb, Cs). The ν(N₂) of the corresponding adducts (**2_M⁺**) undergoes bathochromic shifts as a function of the LA strength expressed in Acceptor Number (AN).⁸⁹ The Δν(N₂) are ranging from -51.8 to -68.6 cm⁻¹ compared to (**1**), indicative of a moderate N₂ activation. Contrary to previous examples of N₂-alkali cations pairs, (**1**) and (**2_M⁺**) are in equilibrium with association constants (in Et₂O) varying from 430(80) to 94(5) M⁻¹ down the alkali series. In this simple system, the magnitude of N₂ activation induced by the interaction with alkali cations was following a quasi-linear relationship with the acceptor number of the cations (Figure 2). Dissociation of (**2_M⁺**) was facilitated by the use of a coordinating solvent, which was required to overcome the poor solubilities of the s-group salts.

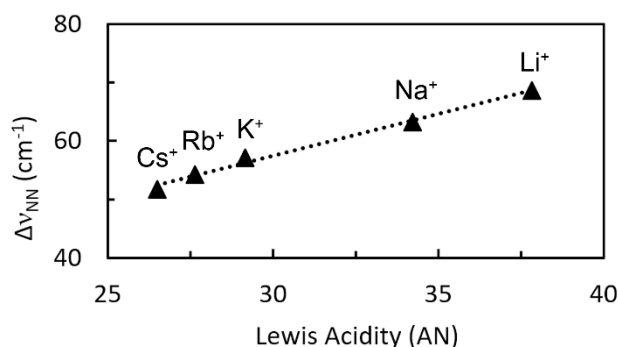


Figure 2. Linear correlation of N_2 stretching frequency and AN for (2_{M}^+) ($\text{M} = \text{Li}^+, \text{Na}^+, \text{K}^+, \text{Rb}^+, \text{Cs}^+$).

In a 2019 study of the alkali series interactions with Molybdenum(0) dinitrogen complexes bearing a family of multidentate lariat ether phosphine ligands, Pap *et al* explored the potential of using tethered crown ethers for alkali cations solvation.⁹⁰ Reaction of the triphosphine ligands ($\{\text{aza-}n\text{-crown}\}\text{CH}_2\text{CH}_2\text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2$ ($n\text{-crown-P}_3\text{-Ph}$, $n = 15, 18$) with $\text{MoCl}_3(\text{THF})_3$ followed by reduction with Na/Hg in presence of PMe_3 afforded the N_2 complexes 3^n . The related complex *mer*-($n\text{-crown-P}_3\text{-}^i\text{Pr}$) $\text{Mo}(\text{N}_2)_2(\text{PPh}_2\text{Me})$ (4^n) was isolated by ligand substitution between $\text{Mo}(\text{N}_2)_2(\text{PPh}_2\text{Me})_4$ and ($n\text{-crown-P}_3\text{-}^i\text{Pr}$). Complexes 3^n and 4^n display tethered crown ethers of different ring sizes in *cis* position to the N_2 ligand, which allowed them to support alkali cations/ N_2 interactions (Figure 3).

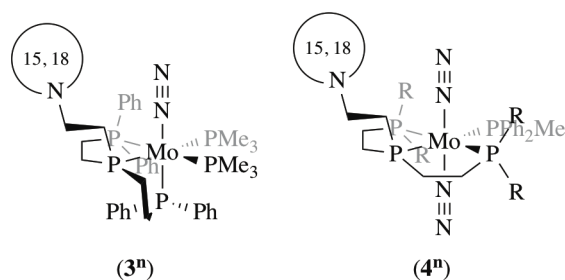
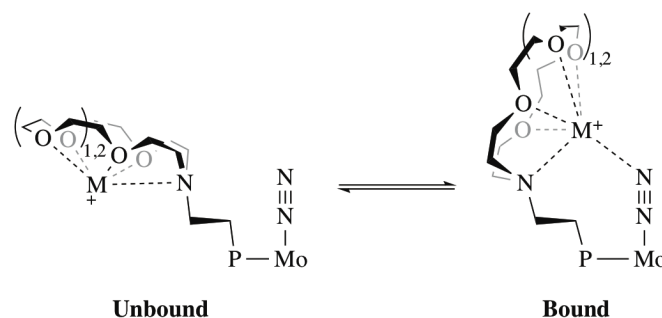


Figure 3. Complexes (3^n) and (4^n) bearing tethered $n\text{-crown}$ ether ($\text{R} = {}^i\text{Pr}$).

Owing to the large cations size disparity within the alkali series, crown ethers of different ring sizes present clear binding selectivities,⁹¹ although the affinity is strong between cations and rings of any size. Salts $\text{M}^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ($\text{M}^+ = [\text{Li}(\text{OEt})_2]^+, \text{Na}^+, \text{K}^+, \text{Rb}^+, \text{Cs}^+$) were reacted with (3^n) and (4^n) in *ortho*-difluorobenzene to observe complex behaviors, the respective predominant species (5^n_{M}) and (6^n_{M}) ($\text{M} =$ alkali cation) resulted from the sequestration of the cations within the crown ether. The N_2 bound and unbound isomers of these species are in equilibrium (Scheme 2), with relative concentrations depending on the alkali cations. The relative amount of (5^n_{M}) bound isomers grew with increasing cations size, up to Rb^+ , then decreased slightly for Cs^+ . This behavior is related to the strength and the structural properties of the crown ether interactions. Small cations such as Li^+ interact strongly with crown ethers, which compete effectively with N_2 interactions. Large cations however tend to “pucker” out of the crown ethers plane, leaving them more exposed for further interactions. On account of steric repulsion from the ${}^i\text{Pr}$ groups, complexes (6^n_{M}) exhibited very little interaction of N_2 with Li^+, Na^+ and K^+ . Activation of N_2 by the cations interaction is rather weak with a maximum $\Delta v(\text{N}_2)$ reached for (5^{15}_{Li}) at -37 cm^{-1} ($\pm 15 \text{ cm}^{-1}$). DFT calculations carried out on (5^n_{M}) and (6^n_{M}) systems suggested that a longer arm between the phosphine ligand and the crown ethers might result in more favorable interactions.



Scheme 2. Equilibrium between bound and unbound isomers of (5^n_M) and (6^n_M).

Despite a very limited number of examples, interactions of N_2 by alkali cations show an evident correlation between the Lewis acidity of the cations and the degree of N_2 activation. By exploring a simple system presenting no significant competing interactions, Szymczak and his team were able to reveal a linear relationship between the acceptor number of alkali cations and the change in $\nu(N_2)$ stretching frequencies of the interacting N_2 ligand. With no other supporting interactions, coordination of alkali cations to N_2 is weak and labile. Competing interactions such as ions pairing, cation- π interactions and cations solvation can readily overshadow or even prevent the formation of N_2 /alkali cations adducts. Taking these considerations into account, careful design of the N_2 complex is needed to profit from alkali cations activation of N_2 .

3. LEWIS ACID-BASE ADDUCTS OF END-ON DINITROGEN COMPLEXES WITH D-BLOCK ELECTROPHILES

Early on, after the first few isolations of complexes bearing an end-on N_2 ligand, the first example of two d-block elements coordinating to a single, bridging N_2 ligand was reported by Taube and coll. with the symmetrical *trans*- $[Ru(NH_3)_5]_2(\mu-N_2)]^{4+}$.⁹² These homobimetallic complexes are typically symmetrical and linear. The resulting lack of N_2 polarization complicate their consideration as mere Lewis pairs, this type of complexes will not be discussed in details, at the exception of two mixed-valence homobimetallic iron complexes presented in section 3.5. Bridged homobimetallic complexes have been reported for a large variety of TMs, encompassing metal centers of group 4 to 10 with end-on, side-on and mixed coordination modes for the N_2 ligand at various activation levels.²⁻¹⁰

Weak N_2 activation where the ligand can be formally considered as $(N_2)^0$ occurs more frequently with 18 electrons, mid to late transition metal complexes. Often, the coordination of the second metal center does not influence significantly the N_2 activation and the parameters determining the formation of bridged N_2 complexes over mononuclear complexes are not well understood. The N_2 ligand is typically easily removed under vacuum and chemical activation is seldom encountered.⁹³ Higher activation of the N_2 ligand (formally $(N_2)^{2-}$ to $(N_2)^{4-}$) occurs more frequently with early TMs with high reducing power to form strong multiple N-Metal bonds. Some of these complexes have been shown to promote the further reduction of N_2 either chemically or electrochemically as well as the reaction of N_2 with small molecules such as H_2 ^{94,95} and CO .⁹⁶⁻¹⁰⁰ High activation of N_2 can also lead to splitting by dinuclear complexes to afford nitride complexes as demonstrated by Cummins with $[(Mo\{N^tBu(C_6H_3Me_2-3,5)\}_3)_2(\mu-N_2)]$.^{101,102}

Comparatively, there has been much less heterobimetallic bridged N_2 complexes reported. The formation of these complexes occurs through several mechanisms that can be separated into two groups: i) reactions involving significant chemical transformations or ii) formation of Lewis pairs. As it does not represent simple Lewis acid-base interactions the former group will not be discussed in this

review; some typical examples are the immediate reduction of the N₂ ligand upon formation of the U^{IV}/Mo^{IV} μ-(N₂)²⁻ complex [(^tBu(3,5-Me₂C₆H₃)N)U(μ-N₂)Mo(N^tBuPh)₃] from the corresponding U^{III}(THF) and Mo^{III} complexes,¹⁰³ the displacement of a chloride ligand by the reaction of [(N(^tBu)(Ar))Mo-N=N]₂[Mg(THF)₂] with two equivalents of the Nb^{IV} complex [(ⁱPr)(Ar)N]₃NbCl to afford [(ⁱPr)(Ar)N]₃Nb(μ-N₂)Mo[N(^tBu)(Ar)]₃¹⁰⁴ or the formal insertion of a W-N₂ moiety into an M-halide bond as disclosed by the team of Hidai^{105,106} with the formation of [WX(PMe₂Ph)₄(μ-N₂)MCp₂Cl] complexes (M = Ti, Zr, Hf; X = Cl, I).

Formal Lewis pairs are formed by the reaction of a terminal dinitrogen TM complex with TM LAs. This interaction typically results in activation of the N₂ ligand *via* a push-pull mechanism. The formation of such Lewis pairs have been explored since the first reported example by Chatt *et al* in 1969 with the formation of Re^I(μ-N₂)Mo^{IV} heterobimetallic complex.²⁸ The number of Lewis pairs that have been characterized is relatively low and limited to N₂ complexes of Mo⁰, Re^I and Fe⁰ as Lewis bases. As for the Lewis acids, TMs ranging from group 4 up to group 11 elements were employed.

3.1. Early works on ClRe(N₂)(PMe₂Ph)₄ adduct with d-block Lewis Acids

The complex *trans*-[ReCl(N₂)(PMe₂Ph)₄] (**7**) is part of a series of rhenium(I) dinitrogen complexes that were among the first well-characterized N₂ complexes¹⁰⁷ and Lewis pair formation between (**7**) and d-block LAs has been extensively exemplified. The idea driving this body of work was to prepare and study polynuclear dinitrogen complexes in order to get some insights into the functioning of the nitrogenase enzymes,¹⁰⁸ of which the bimetallic nature was uncovered at the time. Within the series of adducts they were able to characterize, the N₂ ligand is generally weakly activated with ν(N₂) and d_{NN} in the 1900–2100 cm⁻¹ and 1.1–1.2 Å ranges [1922 cm⁻¹ and 1.06 Å for (**7**)], respectively.¹⁰⁹

The Chatt research group pioneered the exploration on the reactivity of Re^I-N₂ complexes with the report that (**7**) could react in dichloromethane with THF or Et₂O solvates of TiCl₃, CrCl₃, MoCl₃ and MoCl₄.²⁸ They proposed at the time that the new products formed, characterized by color changes and bathochromic shifts of ν(N₂), were adducts of the general formula [Cl(PMe₂Ph)₄Re(μ-N₂)MCl_x(S)_y] (M = Ti^{III} {**8**}, Cr^{III} {**9**}, Mo^{III} {**10**} and Mo^{IV} {**11**}). However, later studies have shown that (**11**) was misidentified and was instead an adduct of a Mo^V complex (*vide infra*). The formation of (**11**) was of special interest to them owing to its possible relevance to the nitrogenase enzyme, which also contains a Mo center. To support the proposed nature of (**11**), tentative analogues such as [Cl(PMe₂Ph)₄Re(μ-N₂)MoCl₄(PEtPh₂)] (**12**) were prepared [ν(N₂) = 1810 cm⁻¹]. The considerable activation of N₂ in (**11**) [Δν(N₂) = -127 cm⁻¹] could be further increased with the use of excess MoCl₄·2Et₂O [Δν(N₂) = -242 cm⁻¹]. Attempts to form adducts with other N₂ complexes characterized at the time were inconclusive, they suggested that a certain level of N₂ activation was necessary to provide sufficient Lewis basicity to the terminal nitrogen atom [ν(N₂) < ~1970 cm⁻¹].

They expanded upon their findings by applying the same synthetic strategy to a large variety of d-block and main group LAs, the latter will be discussed in section 4.⁵⁵ They reacted (**7**) with one to two equivalents of groups 2 to 10 and group 12 transition metal halides. Activation of the N₂ ligand was characterized by their stretching frequencies in infrared spectroscopy whose attribution was validated in some cases with comparison to the ¹⁵N₂ analogous complex (Table 1). Although rhenium(I) is a reasonably stable oxidation state, excess TiCl₄ and TiF₄ promoted the formation of rhenium(II) complexes, characterized by a ~80 cm⁻¹ hypsochromic shift of ν(N₂). A similar reactivity was also observed previously between [ReCl(N₂)(dppe)₂] (dppe: 1,2-bis(diphenylphosphino)ethane) and Ag^I or Cu^{II} salts.⁵⁴

Table 1. Spectroscopic properties (cm⁻¹) of *trans*-[ReCl(N₂)(PMe₂Ph)₄] adducts with d-block LAs.

Lewis acid	$\nu(^{14}\text{N}_2)$	$\nu(^{15}\text{N}_2)$	Ratio
Class (1)			
TiCl ₃ ^a	1805	1750	1:1
[TiCl ₃ (MeCN) ₃] ^a			
[TiCl ₃ (THF) ₃] ^a			
ZrCl ₄	1790	1747	1:1
HfCl ₄	1824	1762	1:2 ^b
[VCl ₃ (MeCN) ₃]	1800	-	1:1
NbCl ₅	1630	-	1:1 ^b
TaCl ₅	1695	1635	1:1 ^b
[MoCl ₄ (Et ₂ O) ₂]	1795	1745	1:1
[MoCl ₄ (THF) ₂]	1795	-	1:1
[MoCl ₄ (PMePh ₂) ₂]	1810	-	1:1
[MoCl ₄ (PEtPh ₂) ₂]	1810	-	1:1
[MoCl ₄ (Et ₂ O) ₂] ^c	1680	1625	1:2
[MoCl ₄ (THF) ₂] ^c	1680	-	1:2
[WCl ₄ (PMe ₂ Ph) ₂]	1730	-	1:1
[ReOCl ₃ (PPh ₃) ₂]	1842	-	^d
Class (2)			
ScCl ₂	1870	-	^d
[CrCl ₃ (THF) ₃]	1890	-	1:1
[MoCl ₃ (THF) ₃]	1850	-	^d
FeCl ₂ (THF) _{1.5}	1860	1795	^d
CoCl ₂ (THF) _{1.5}	1855	1795	^d
[Pt ₂ Cl ₄ (PEt ₃) ₂]	1890	1825	^d

Later studies: ^a Adducts of TiCl₄ are formed; ^b Ratio established in reference 118; ^c Mo^v species are formed. ^d Unknown ratio.

This comparison across the d-block revealed two classes of LAs, characterized by the magnitude of the $\nu(\text{N}_2)$ bathochromic shift. Activation of N₂ is stronger when the LA has vacant *d* orbitals able to receive electronic density *via* π -bonding, such is the case for the early TMs that demonstrate large $\Delta\nu(\text{N}_2)$ (< -100 cm⁻¹, down to -292 cm⁻¹). LAs with occupied (such as Cr^{III}Cl₃ or Fe^{II}Cl₂) or energetically inaccessible *d* orbitals (such as group 13 elements) tend to provide a much smaller $\Delta\nu(\text{N}_2)$ (> -70 cm⁻¹, up to -32 cm⁻¹). These results can be rationalized through the push-pull mechanism of N₂ activation: a lesser “pull” of electronic density to the LA will cause a lesser “push” of electronic density from the metal center to the N₂ π -antibonding orbital. Evidently, the N₂ ligand act as a rather hard base with increased activation going up in the periodic table (HfCl₄ to ZrCl₄: $\nu(\text{N}_2) = -34$ cm⁻¹; TaCl₅ to NbCl₅: $\nu(\text{N}_2) = -65$ cm⁻¹). Adducts obtained by the addition of MoCl₄(L) (L = Et₂O, THF, phosphines) displayed very little influence of the L ligand. After careful investigation of the Mo adducts, the authors reformulated (**11**), (**12**) and the new Mo adducts as [(PMe₂Ph)₄ClRe(μ -N₂)MoOCl₃L] species. The formation of adducts with 1:2 (**7**):LA ratio, which they proposed to be of the form [(PMe₂Ph)₄ClRe(μ -N₂)Mo₂OCl₅L], was accompanied by shifts of the N₂ vibration exceeding 100 cm⁻¹. Despite the lack of definitive characterizations, complicated by the extreme instability of some of these adducts (less than half could be isolated), the presence of the Re–N≡N–M motif was conclusively demonstrated by selective decomposition of the adducts to recover (**7**) and comparative reactions with *trans*-[ReCl(CO)(PMe₂Ph)₄].

These findings have then been expanded upon by several groups, with complete characterizations of some of the complexes described and considerable examination of the $\text{Re}^I\text{-N}_2/\text{Group 6}$ adducts.

3.2. *trans*-[$\text{ReCl}(\text{N}_2)(\text{PMe}_2\text{Ph})_4$] adducts of group 6 halides complexes.

Chatt *et al* proceeded in the characterization of the aforementioned $[\text{Cl}(\text{PMe}_2\text{Ph})_4\text{Re}(\mu\text{-N}_2)\text{CrCl}_3(\text{THF})_2]$ (**9**), obtained from the reaction of (**7**) with $\text{CrCl}_3(\text{THF})_3$ in dichloromethane.⁵⁶ While no solid-state structure could be obtained, the nature of the complex has been confirmed by elemental analysis, decompositions experiments and the magnetic moment corresponding to a chromium(III) (d^3) and rhenium(I) (low-spin d^6) complex. On exposure to air, (**9**) readily convert to a mixture of (**7**) and the Re^{II} complex $[\text{ReCl}(\text{N}_2)(\text{PMe}_2\text{Ph})_4]^+$ (**13**). Oxidation to Re^{II} is facilitated by the $\text{Re-N}_2\text{-Cr}$ bridge providing a path for rapid $\text{Re}\rightarrow\text{O}$ electron transfer when dioxygen attacks the chromium atom. The electronic spectrum of the adduct features an intense absorption band at 537 nm which has been considered through the qualitative depiction of the four-center π molecular orbital in Figure 4 (transition metals d_{xz} and nitrogen p_x orbitals, an equivalent set oriented at 90° , are not represented).

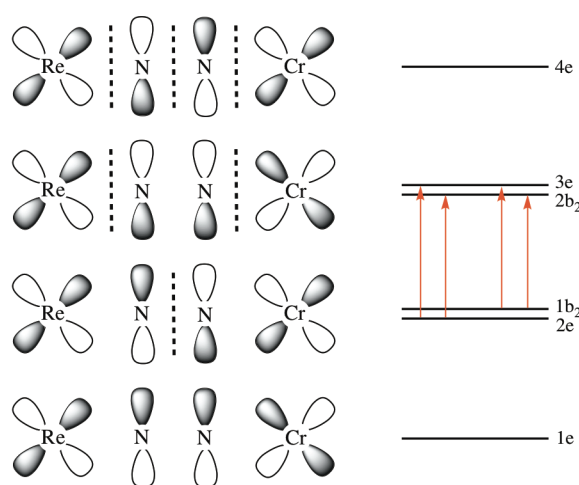


Figure 4. Molecular orbital diagram for **9**. In red: allowed electronic transitions.

The energy of the molecular orbitals (1e to 4e in idealized C_{4v} symmetry) increases with the number of nodes, with 1e and 4e orbitals having mainly $\pi(\text{N}_2)$ and $\pi^*(\text{N}_2)$ characters, respectively. The intense absorption band can be assigned to a $\text{Re}\rightarrow\text{Cr}$ charge transfer as allowed transition occurs from orbitals that are mainly rhenium in character (2e: d_{xz} , d_{yz} ; 1b₂: δ bonding d_{xy}) to orbitals that are mainly chromium in character (3e: d_{xz} , d_{yz} ; 2b₂: δ bonding d_{xy}). These orbital considerations are applicable to all $\text{Re}^I\text{-N}_2$ adducts of TM LAs, that all display significant charge-transfer bands. Moreover, the orbital 2e is $\pi^*(\text{N}_2)$ in character while 3e is $\pi(\text{N}_2)$, 2e is completely filled in $\text{Re-N}\equiv\text{N-M}$ complexes but the population of 3e will depend on the electronic configuration of the LA. This electronic interpretation fits nicely with the separation in two classes of LAs uncovered empirically in previous studies from the group of Chatt: LAs with d^0 , d^1 or d^2 configurations lead to a vacant or singly occupied 3e orbital which gives rise to a higher N_2 activation than with LAs with higher d electrons count (3e doubly occupied and more).

In a series of publications, Mercer and Cradwick tackled on the structural characterizations by X-ray diffraction of adducts formed by the reaction of (**7**) and $\text{MoCl}_4(\text{L})_2$ (Figure 5). Reaction of a twofold excess amount of $\text{MoCl}_4(\text{THF})_2$ with (**7**) in a $\text{CH}_2\text{Cl}_2/\text{MeOH}$ mixture allowed for the formation over a period of days of the Re^I/Mo^V adduct $[(\text{PMe}_2\text{Ph})_4\text{ClRe}(\mu\text{-N}_2)\text{MoCl}_4(\text{OMe})]$ (**11**).^{110,111} The $\text{Re-N}_2\text{-Mo}$ core is effectively linear, with Re-N (1.82 Å), N-N (1.18 Å) and N-Mo (1.90 Å) distances denoting a significant activation of the N_2 ligand. The N-N distance is elongated but fall short of formal $[\text{N}_2]^{2-}$ dimensions

(1.25 Å),¹¹² the metal nitrogen bonds lengths are intermediate of single and double M-N bonds. This strong N₂ activation is highlighted by a low $\nu(\text{N}_2)$ of 1660 cm⁻¹. Two equivalents of (7) can react in dichloromethane with MCl₄(PPh₃)₂ to yield the trinuclear complexes [MCl₄{(μ-N₂)ReCl(PMe₂Ph)₄}₂] (M = Mo {13}, W {14}) by phosphine elimination.^{113,114} The solid-state structure of (13) could be resolved by X-ray diffraction analysis, showing that (13) displays a linear Re-N₂-Mo-N₂-Re motif, analogous to Re^I/Ti^{IV} trinuclear complexes discussed hereunder. Dinitrogen activation is lower than in the related dinuclear complex (11) as manifested by shorter N-N distances (1.154 Å), longer N-M distances (Re-N = 1.89 Å; Mo-N = 1.98 Å) and higher $\nu(\text{N}_2)$ (1800 cm⁻¹). The tungsten analogue (14) displays a similar N₂ activation with $\nu(\text{N}_2) = 1795\text{cm}^{-1}$.¹¹⁵

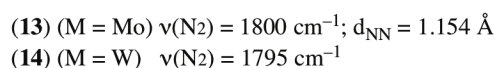
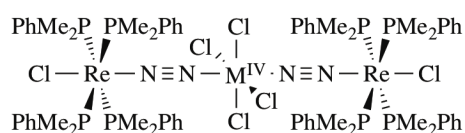
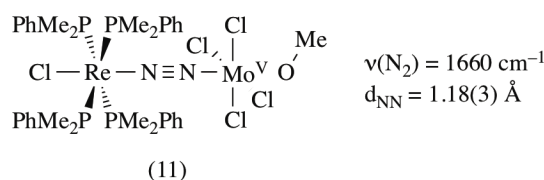
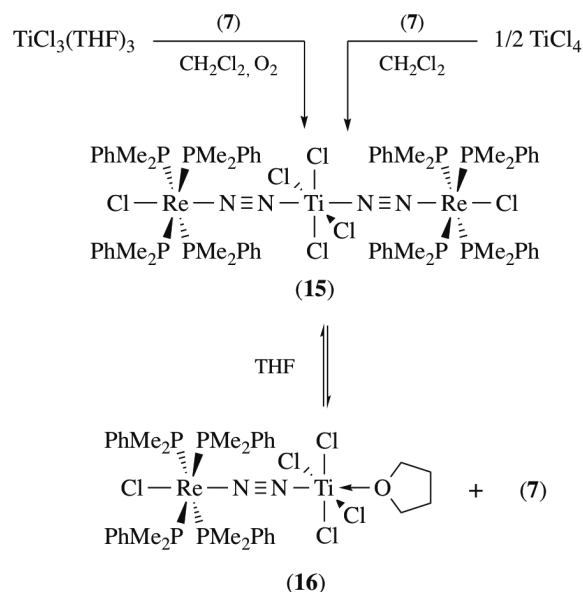


Figure 5. Structurally characterized Mo and W adducts of Re dinitrogen complexes.

The molybdenum center acts as a ($\delta + \pi$) acceptor, whose properties can be altered by several factors such as oxidation states. The Mo^{III}Cl₃(THF)₂ adduct (10) displays a relatively high $\nu(\text{N}_2)$ value (1858 cm⁻¹) and the Mo^VCl₄(OMe) adduct (11) has a much lower $\nu(\text{N}_2)$ value (1660 cm⁻¹). Intermediate values are achieved with Mo^{IV}Cl₄(PR₃) (1805–1810 cm⁻¹) or W^{IV}Cl₄(PMe₂Ph) (1740 cm⁻¹). These adducts have essentially the same molecular orbitals bonding schemes than the analogous Cr^{III} adduct (9) (Figure 4). Contrary to (9) and (10), the Mo^V d¹ configuration of (11) leaves the two 3e orbitals vacant, resulting in an elongation of the N–N bond. Because of the singly occupied 3e orbitals in the d² Mo^{IV} and W^{IV} adducts, intermediate N–N bond lengths are observed.

3.3. *trans*-[ReCl(N₂)(PMe₂Ph)₄] adducts of early TMs halides complexes

The coordination between (7) and TiCl₃ derivatives were reexamined by Robson.¹¹⁶ No adducts could be isolated from the reaction of (7) and TiCl₃(THF)₃ in dichloromethane, however, admission of oxygen into the mixture allowed for the isolation of the TiCl₄ derived trinuclear adduct [TiCl₄{(μ-N₂)ReCl(PMe₂Ph)₄}₂](CH₂Cl₂)₂ (15)·(CH₂Cl₂)₂. The color and the $\nu(\text{N}_2)$ (1812 cm⁻¹) of (15) were virtually identical to adducts reported by Chatt and mistakenly identified as resulting from the coordination of TiCl₃(L)₂ (see Table 1). While no solid-state structure could be determined, the Ti^{IV} oxidation state was confirmed by the diamagnetism of the sample. A high yield preparation of (15) was achieved by reacting a two-fold excess of (7) with TiCl₄ in dichloromethane. THF can compete with (7) for the coordination to TiCl₄, solubilization of (15) in THF induced an equilibrium between (15) and [(PMe₂Ph)₄ClRe(μ-N₂)TiCl₄(THF)] (16) [$\nu(\text{N}_2) = 1755\text{cm}^{-1}$ (THF); 1740 cm⁻¹ (Nujol)] (Scheme 3).



Scheme 3. Formation of (7)/TiCl₄ adducts.

Contrary to what was observed in Chatt's study, complex (7) was found to be resistant to oxidation in the presence of excess TiCl₄. Under these conditions, a new adduct with a $\nu(\text{N}_2) = 1635 \text{ cm}^{-1}$ was formed. It remained unidentified but decomposition experiments suggested that it resulted from coordination of two TiCl₄. Treatment of this adduct with Et₂O led to the isolation of [(PMe₂Ph)₄ClRe(μ -N₂)(Ti₂Cl₆O)(Et₂O)] (17) with a $\nu(\text{N}_2)$ of 1622 cm^{-1} . It is unclear whether (17) is formed by partial hydrolysis of TiCl₄ or activation of the C–O bond as such reaction is known to occur between TiCl₄ and ethers.¹¹⁷ Two possibilities have been considered for the structure of (17) (not shown): an arrangement with two bridged inequivalent titanium centers in which only one is coordinated to the N₂ ligand or a symmetrical arrangement with two TiCl₃ bridged by the terminal nitrogen and oxygen atoms. While the structure has not been categorically identified, the second hypothesis is favored in light of the single type of titanium environment observed by X-ray photoelectron spectroscopy (XPS). In agreement with the electronic considerations discussed above for Re–N₂–M bridges, the coordination to (7) of a d⁰ metal center induces a strong N₂ activation in (16) and (17) along with intense charge transfer bands.

In a later study by Donovan-Mtunzi and his team, adducts of (7) with group 4 and group 5 halides have been isolated and the N₂ ligand properties characterized by ¹⁵N NMR.¹¹⁸ Adducts [(PMe₂Ph)₄ClRe(μ -N₂)MCl₅] (M = Nb {18}, Ta {19}) have been isolated from equimolar mixtures of (7) and the corresponding MCl₅ in dichloromethane. The Zr analogue of (15), the trinuclear adduct [ZrCl₄{(μ -N₂)ReCl(PMe₂Ph)₄]₂·C₆H₁₄ (20) has been isolated in the same manner from the hexane solvate of ZrCl₄. Owing to the poor solubility of HfCl₄ and stability issues, [HfCl₄{(μ -N₂)ReCl(PMe₂Ph)₄]₂ (21) could only be observed in solution within uncharacterized mixtures of compounds. Their ¹⁵N₂ analogues were obtained from [ClRe(¹⁵N₂)(PMe₂Ph)₄], the chemical shifts of the ¹⁵N₂ ligand (noted as Re–N _{α} ≡N _{β} –M) are reported along $\nu(^{14}\text{N}_2)$ for adducts (15), (16) and (18)–(21) in Table 2.

Table 2. Spectroscopic properties of selected early TMs adducts of (7).

Compound	$\nu(\text{N}_2)$ cm ⁻¹	$\delta(^{15}\text{N}_\alpha)$ ppm	$\delta(^{15}\text{N}_\beta)$ ppm
ClRe(N ₂)(PMe ₂ Ph) ₄ (7)	1923	-87.2	-63.9
(7)-TiCl ₄ (THF) 1:1 (16)	1740	-68.1	-19

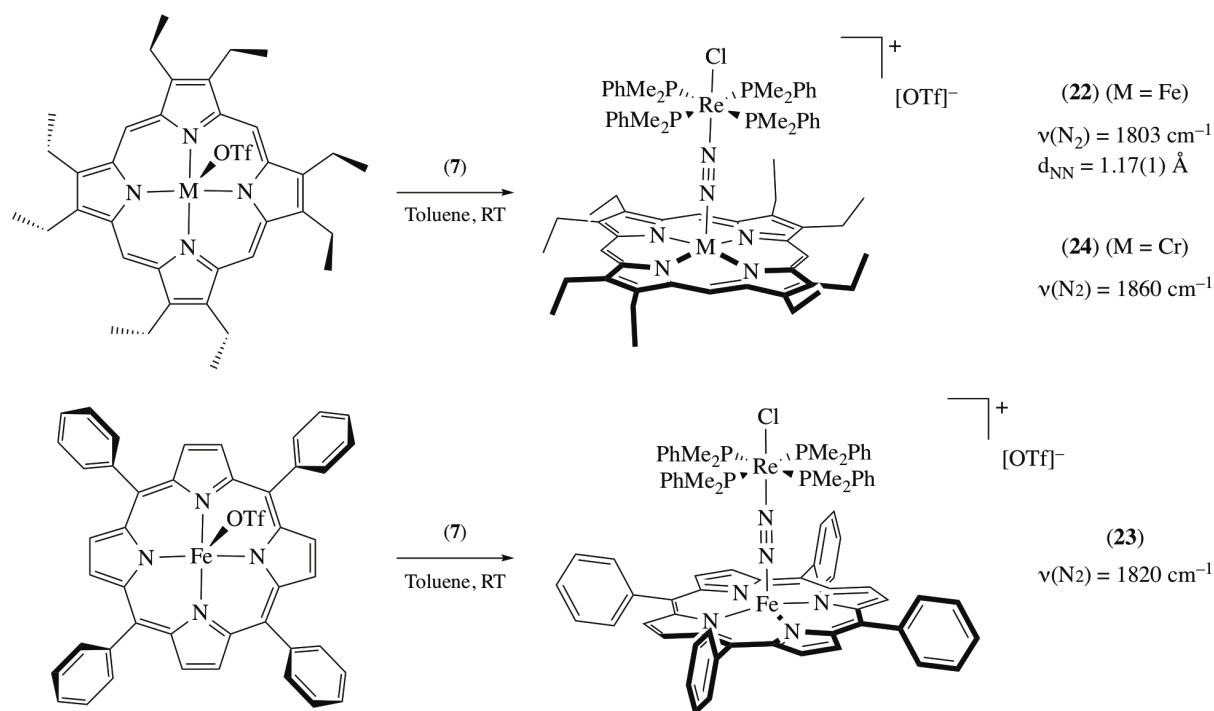
(7)-NbCl ₅ 1:1 (18)	1630	-74.3	-8
(7)-TaCl ₅ 1:1 (19)	1695	-76.7	-24.2
(7)-TiCl ₄ 2:1 (15)	1812	-76.7	-53.2
(7)-ZrCl ₄ 2:1 (20)	1825	-75.9	-95.0
(7)-HfCl ₄ 2:1 (21)	1824	-75.4	-96.8

In addition to the clarification of the structures of these already reported complexes,⁵⁴ this work addressed the effect of LA coordination to the N₂ ligand on the ¹⁵N NMR chemical shifts. In a prior study exploring the ¹⁵N NMR of a series of end-on N₂ complexes, the authors observed that the shielding of both nitrogen increased gradually with the atomic number of the transition metal with an expectedly more pronounced effect on N_α than N_β.¹¹⁹

In the adducts, both signals are deshielded upon coordination of the LAs and the same periodic dependence is then observed for N_β with shielding increasing along the LA atomic number. There is however little influence of the LA identity on the N_α chemical shift apart from the deshielding caused by the formation of the Lewis pair. From an orbital standpoint, the shielding is related to the splitting of the nitrogen orbitals of the π type. The splitting is larger in ReN₂MN₂Re complex than ReN₂M and the increased shielding from the Ti to the Zr complex reflects the increase in orbital splitting from the first to the second TM series.

3.4. *trans*-[ReCl(N₂)(PMe₂Ph)₄] adducts of non-halide TM complexes

In light of previous reports of a diruthenium species bearing a diporphyrin ligand able to oxidize ammonia to form N₂ bridged homometallic complex,^{120,121} Zhang *et al.* set out to study the properties of bridged dinitrogen complexes of metalloporphyrins.¹²² Because of the *de facto* use of *trans*-[ReCl(N₂)(PMe₂Ph)₄] as a model for N₂ complexes coordination to TM LAs, they explored the coordination of (**7**) to iron(III) and chromium(III) porphyrins (Scheme 4). Complexes [Fe(por)(OTf)] (por = octaethylporphyrinate, OEP or tetra(*p*-tolyl)porphyrinate, TTP) react with one equivalent of (**7**) in toluene to afford the bridged heterobimetallic adducts [(PMe₂Ph)₄ClRe(μ-N₂)Fe(por)][OTf] (por = OEP {**22**}, TTP {**23**}) in moderate yields. Dissociation of the (OTf)⁻ ligand is necessary to the coordination of N₂ as no reaction is observed with the less labile chloride derivatives. Similarly, (**7**) react with one equivalent of [Cr(OEP)(OTf)] in toluene to yield [(PMe₂Ph)₄ClRe(μ-N₂)Cr(OEP)][OTf] (**24**).

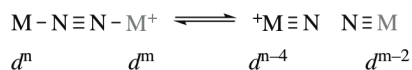


Scheme 4. Formation of bridged N_2 complexes with metalloporphyrins.

The N_2 ligand is moderately activated by the iron complexes with $\nu(\text{N}_2) = 1803$ and 1820 cm^{-1} for **(22)** and **(23)**, respectively. These values for $d^5 \text{Fe}^{\text{III}}$ adducts are expectedly lower than the previously reported $d^6 \text{Fe}^{\text{II}}$ adduct $\{[(\text{PMe}_2\text{Ph})_4\text{ClRe}(\mu\text{-N}_2)\text{FeCl}_2(\text{THF})] \nu(\text{N}_2) = 1860 \text{ cm}^{-1}\}$.⁵⁵ The slightly lower N_2 activation by **(23)** is mirrored by a lower formation constant of $240 \pm 25 \text{ M}^{-1}$ [vs. $410 \pm 40 \text{ M}^{-1}$ for **(22)**] and is related to the larger steric bulk and lower basicity of TTP compared to OEP. Complex **(24)** displays an even lower formation constant ($140 \pm 15 \text{ M}^{-1}$) as well as a quite weak N_2 activation [$\nu(\text{N}_2) = 1887 \text{ cm}^{-1}$], which is comparable to $[\text{Cl}(\text{PMe}_2\text{Ph})_4\text{Re}(\mu\text{-N}_2)\text{CrCl}_3(\text{THF})_2]$ [$\nu(\text{N}_2) = 1860 \text{ cm}^{-1}$].⁵⁶ In porphyrin complex **(22)** the iron center displays an admixed intermediate spin state ($S = 3/2, 5/2$) and an upfield pyrrolic resonant signal in ^1H NMR, diagnostic of a weakly coordinating weak-field ligand in metalloporphyrins.¹²³ The solid-state structure of **(22)** exhibits an essentially linear $\text{Re-N}_2\text{-Fe}$ motif with an elongated N-N distance of $1.17(1) \text{ \AA}$. The Re-N distance is longer and the N-N one shorter by *ca.* 0.1 \AA than in $[(\text{PMe}_2\text{Ph})_4\text{ClRe}(\mu\text{-N}_2)\text{MoCl}_4(\text{OMe})]$ **(11)**, which is coherent with a lower N_2 activation [$\Delta\nu(\text{N}_2) = +143 \text{ cm}^{-1}$ vs **(11)**]. The difference of N_2 activation between the isostructural Fe^{III} and Cr^{III} metalloporphyrins indicates that the relative strength of N_2 acceptors is an interplay of several factors beyond d electrons count. Taking into consideration the molecular orbital diagram discussed above (Figure 4), the relatively strong activation for a d^5 LA seen with **(22)** could be related to its intermediate spin state. In the high-spin configuration, two of the d orbitals that are occupied are not implicated in the bonding to N_2 and thus the $3e$ orbital, $\pi(\text{N}_2)$ in character, is less populated than with low spin d^5 LAs.

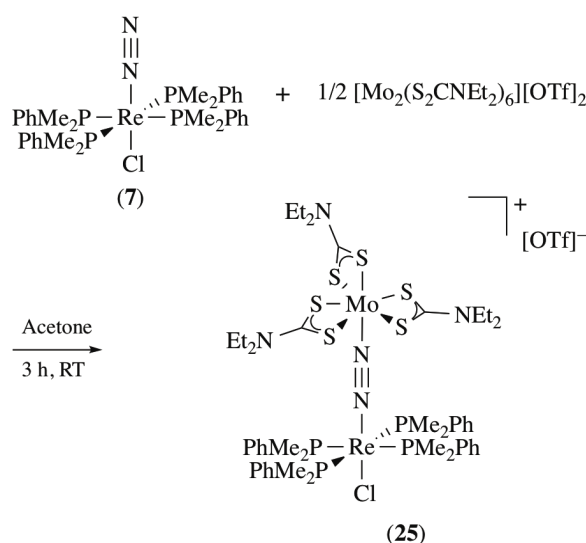
The discovery by Cummins of a molybdenum(III) complex able to spontaneously cleave the triple N-N bond of dinitrogen to form metal nitrides has driven an intense curiosity over the possible use of such reactivity in catalytic reduction of N_2 .¹⁰¹ A study of the microscopic reverse of N_2 cleavage, nitride coupling, has been performed by Seymore *et al.* Notably, they observed that the osmium nitride complex $[\text{TpOs}(\text{N})\text{Cl}_2]$ reacted with the molybdenum nitride complex $[(\text{R}_2\text{NCS}_2)_3\text{Mo}(\text{N})]$ faster than in self-coupling reactions owing to polar effects.¹²⁴ In subsequent research, they proposed that such effects could also lower the barrier for N_2 cleavage. To explore this hypothesis, they prepared adducts

of rhenium(I) dinitrogen complexes with the molybdenum(IV) cation $[\text{Mo}(\text{S}_2\text{CNEt}_2)_3]^+$ and assessed whether such adducts could undergo unsymmetrical, “heterolytic” N_2 cleavage (Scheme 5) to form the known molybdenum(VI) $[(\text{Et}_2\text{NCS}_2)_3\text{Mo}(\text{N})]$ and rhenium(V) $[(\text{PMe}_2\text{Ph})_4\text{ClReN}]^+$ nitrido complexes.¹²⁵



Scheme 5. Unsymmetrical nitride cleavage.

Complex **(7)** reacts in acetone with half an equivalent of $[\text{Mo}_2(\text{S}_2\text{CNEt}_2)_6][\text{OTf}]_2$ in three hours to afford the adduct $[(\text{PMe}_2\text{Ph})_4\text{ClRe}(\mu\text{-N}_2)\text{Mo}(\text{S}_2\text{CNEt}_2)_3][\text{OTf}]\cdot\text{Et}_2\text{O}$ (**25**), isolated in 55 % yield (Scheme 6). The same reaction carried out with *mer*- $[\text{ReCl}(\text{N}_2)(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{CNEt}_2)]$ results in the adduct $[(\text{S}_2\text{CNEt}_2)(\text{PMe}_2\text{Ph})_2\text{ClRe}(\mu\text{-N}_2)\text{Mo}(\text{S}_2\text{CNEt}_2)_3][\text{OTf}]$ (**26**), which is stable in solution but decomposes upon isolation. The complex $[\text{ReCl}(\text{N}_2)(\text{dppe})_2]$ also reacts with $[\text{Mo}_2(\text{S}_2\text{CNEt}_2)_6][\text{OTf}]_2$ but the putative adduct $[(\text{dppe})_2\text{ClRe}(\mu\text{-N}_2)\text{Mo}(\text{S}_2\text{CNEt}_2)_3][\text{OTf}]$ is too unstable to be characterized.



Scheme 6. Synthesis of adduct **(25)**.

The lowering of the $\nu(\text{N}_2)$ frequencies to 1818 cm^{-1} (**25**) and 1829 cm^{-1} (**26**) induced by coordination of $[\text{Mo}(\text{S}_2\text{CNEt}_2)_3]^+$ is comparable to other examples of dinuclear $\text{Re}^{\text{I}}/\text{Mo}^{\text{IV}}$ bridged complexes (e.g. the series of $\text{MoCl}_4(\text{PR}_3)$ adducts, see section 3.2). Accordingly, the solid-state structure of **(25)** is very similar to other reported dinuclear adducts (Table 3) with a linear $\text{Re}-\text{N}_2-\text{Mo}$ motif, an elongated $\text{N}-\text{N}$ distance (1.167 \AA) and a shortened $\text{Re}-\text{N}$ distance ($\text{Re}-\text{N}: 1.858\text{ \AA}$). The Lewis pair nature of **(25)** has been demonstrated by the abstraction of $[\text{Mo}(\text{S}_2\text{CNEt}_2)_3][\text{OTf}]$ by PPh_3 to recover **(7)** and $[\text{Mo}(\text{PPh}_3)(\text{S}_2\text{CNEt}_2)_3][\text{OTf}]$ after 3 h at RT. The instability of **(26)** toward isolation precluded the determination of its solid-state structure but **(26)** is likely to adopt a *mer* geometry according to NMR data.

Table 3. Bond distances of structurally characterized adducts of **(7)**.

Compound	Re-N Å	N-N Å	N-M Å
(7)	1.87 ^a	1.126 ^a	-
$[(\text{7})_2\text{MoCl}_4]$ (13)	1.888	1.154	1.975
$[(\text{7})\text{-Mo}(\text{S}_2\text{CNEt}_2)_3]^+$ (25)	1.858	1.167	1.998
$[(\text{7})\text{-Fe}(\text{OEP})]^+$ (22)	1.832	1.17	1.93

Heating or photolysis of (25) and (26) did not result in N₂ cleavage but led to decomposition in mixtures of products. (7) and [ReCl₃(PMe₂Ph)₃] were identified in minor quantities when (25) degraded. Likewise, reduction of (25) by electrochemistry or chemical reactants did not induce N₂ cleavage but allowed for the recovery of (7). Attempts to react [(Et₂NCS₂)₃Mo(N)] and [ReCl(N)(PMe₂Ph)₄][OTf] to form (25) by nitride coupling were also unsuccessful. These results led to the conclusions that kinetic factors govern the stability of N₂ in this system and the use of polar effects to kinetically favor the cleavage of N₂ will also tend to make it thermodynamically inaccessible.

3.5. Adducts of Mo and Fe N₂ complexes with Fe^{II} Lewis Acids.

There are very few studies of formal TM LAs coordination to dinitrogen complexes of other metallic center than rhenium(I). Unsurprisingly, these examples concern molybdenum and iron centers, whose coordination properties to N₂ have been explored thoroughly owing to their role in nitrogen fixation in both nitrogenase and Haber-Bosch processes.^{126,127}

In their seminal work on the chemistry of arene Mo⁰ complexes of N₂, Green *et al* were able to isolate a series of Mo⁰-N₂ complexes [(Mo(PR₃)(η⁶-Ar)(N₂)] that could also form N₂-bridged dinuclear complexes [(Mo{PR₃}(η⁶-Ar))₂(μ-N₂)] (Ar = benzene, toluene, mesitylene; PR₃ = PPh₃, PMePh₂, PMe₂Ph).¹²⁸ While unstable and prone to release the N₂ ligand by reaction with CO or H₂, they remarked that the dinuclear complexes were closely related to the previously isolated N₂-bridged dinuclear complex of Fe^{II} [(Cp){dmpe}Fe]₂(μ-N₂)[BF₄]₂ (27) (dmpe = 1,2-bis(dimethylphosphino)ethane)¹²⁹ Given the possible involvement of Mo-N₂-Fe bridged species in the nitrogenase mechanism (which has been later ruled out), they set out to pioneer the characterization of such complexes (Figure 6). Treatment of [Fe(Cp)(dmpe)(Me₂CO)][BF₄] with [Mo(toluene)(N₂)(PPh₃)₂] (28) was carried out in acetone under argon to afford in 50% yield the Mo⁰/Fe^{II} heterobimetallic complex [(toluene)(PPh₃)₂Mo(μ-N₂)Fe(Cp)(dmpe)][BF₄] (29).

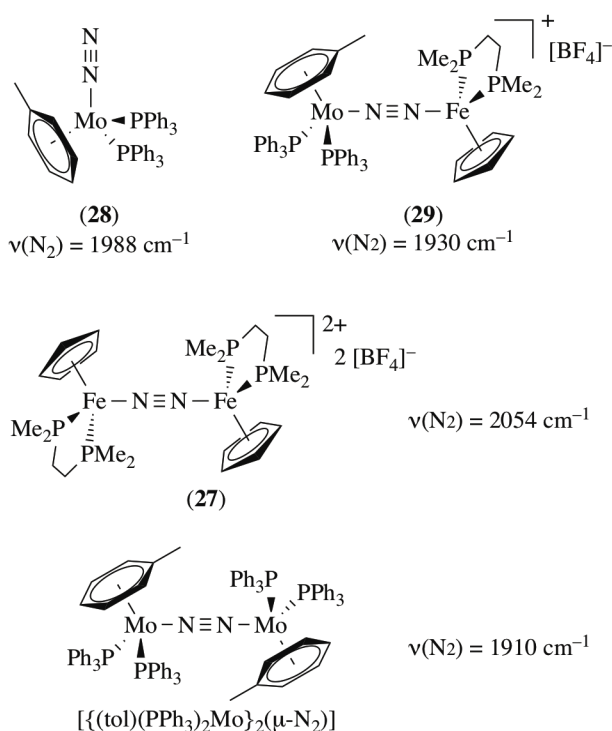


Figure 6. Dinitrogen bridged dinuclear complexes of Mo⁰, Fe^{II} and Mo⁰/Fe^{II}.

The bridging N₂ is characterized by two bands at 1945 and 1930 cm⁻¹ whose relative intensity depend on the solvent used for recrystallisation, acetone-light petroleum ether affording almost exclusively the 1930 cm⁻¹ band. The coordination of the Fe^{II} cation resulted in a modest N₂ activation with $\Delta\nu(\text{N}_2) = -58 \text{ cm}^{-1}$ compared to **(28)** (1988 cm⁻¹), which is similar to the effect of FeCl₂(THF) coordination to the rhenium(I) complex **(7)** [$\Delta\nu(\text{N}_2) = -63 \text{ cm}^{-1}$]. The structure of **(29)** is expected to be closely related to the respective homometallic dinuclear adducts of Fe^{II} and Mo⁰ with the same ligand system. Due to the symmetry of these dinuclear complexes the bridged N₂ ligand is silent in IR spectroscopy, the Raman vibrations of 1910 cm⁻¹ (Mo dimer) and 2054 cm⁻¹ (Fe dimer) would infer that the activation level of N₂ ligand in **(29)** is about midway between these homobimetallic complexes.

The group of Schrock has also reported a tetranuclear FeMo₃ complex that can formally be depicted as an adduct of an Fe(II) neutral complex with a neutral Mo(III) end-on dinitrogen complex.⁸³ By the reaction of $\{[\text{N}_3\text{N}]\text{Mo}(\text{N}_2)\}_2\text{Mg}(\text{THF})_2$ (**30**) ($[\text{N}_3\text{N}]^{3-} = [(\text{Me}_3\text{SiNCH}_2\text{CH}_2)_3\text{N}]^{3-}$) with FeCl₂, they were able to isolate a trigonal planar iron complex $\{[\text{N}_3\text{N}]\text{Mo}(\text{N}_2)\}_3\text{Fe}$ (**31**), formed under a quite unclear mechanism (Figure 7). The solid-state structure reveals that one of the N-N-Fe arrangement is bent, suggesting an iron(II) center stabilized by two anionic $\{[\text{N}_3\text{N}]\text{Mo}(\text{N}_2)\}^-$ and one neutral $[\text{N}_3\text{N}]\text{Mo}(\text{N}_2)$ ligands. The N₂ ligand embedded in the bent Mo^{III}-N₂-Fe^{II} arrangement shows a comparatively short N-N distance (1.20 Å) against the two other N₂ units (*ca.* 1.26 Å). The lability of one of the Fe-N linkages has been evidenced by treating **(31)** with an excess of THF, leading to equilibrated mixtures of **(31)**, $\{[\text{N}_3\text{N}]\text{Mo}(\text{N}_2)\}_2\text{Fe}(\text{THF})_n$ and $[\text{N}_3\text{N}]\text{Mo}(\text{N}_2)$. The latter complex could be prepared separately and analyzed by X-ray diffraction and IR spectroscopy. It is characterized by an N-N distance of 1.09 Å and a $\nu(\text{N}_2)$ of 1934 cm⁻¹ in pentane. The coordination of the Fe^{II} fragment to this neutral complex, which could not be realized experimentally but formally accomplished in complex **(31)**, results in a remarkable bathochromic shift for $\nu(\text{N}_2)$ (-231 cm⁻¹) and significant N-N bond elongation (+0.11 Å). Such push-pull activation cannot be accounted for using the model proposed by Chatt and his team (Figure 4) because of the particular geometry of the iron fragment as well as the bent geometry, but trigonal planar Fe^{II}L₃ complexes possess a set of 2 vacant antibonding e' orbitals, one of which has the requisite geometry to overlap with a π orbital of the neutral N₂ ligand. Thus, the conditions for strong push-pull activation like those found with d⁰⁻² metal complexes (section 3.2) may be met in this case.

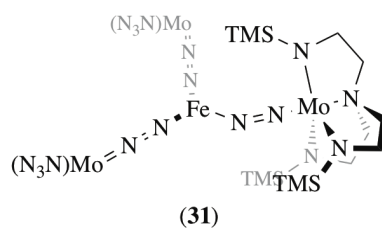
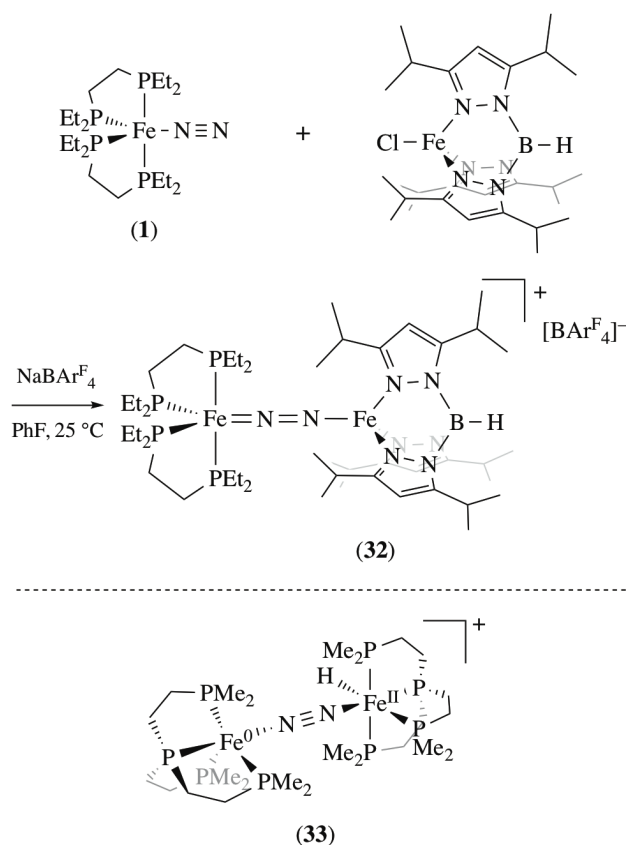


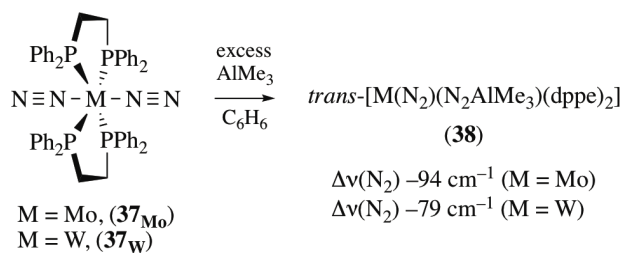
Figure 7. Schrock's tetranuclear FeMo₃ dinitrogen complex **(31)** (TMS = trimethylsilyl).

Szymczak and coll. have achieved the synthesis of a mixed-valence Fe⁰/Fe^{II} complex showing a bridging dinitrogen between the two metallic centers. As part of their study of the interaction between $[\text{Fe}(\text{N}_2)(\text{depe})_2]$ (**1**) and various LAs (see sections 2.2 and 4.3.1), they have reacted **(1)** with the sterically accessible high spin d⁶ Fe^{II} cation $[\text{Fe}(\text{Pr}_2\text{Tp})]^+$ bearing the hydrotris(3,5-iso-propyl-pyrazolyl) borate ligand (Pr₂Tp). The N₂-bridged adduct $[(\text{depe})_2\text{Fe}(\mu\text{-N}_2)\text{Fe}(\text{Pr}_2\text{Tp})][\text{BAr}^{\text{F}}_4]$ (**32**, Ar^F = 3,5-(CF₃)₂C₆H₃) was obtained in excellent yield from the reaction in fluorobenzene of **(1)** with one equivalent of $[\text{FeCl}(\text{Pr}_2\text{Tp})]$ in presence of NaBAr^F₄ (Scheme 7).⁶¹ Complex **(32)** contains two structurally distinct iron centers and displays a high energy charge transfer band at 910 nm consistent with a mixed-valence complex containing localized Fe⁰/Fe^{II} centers. The N₂ ligand is well activated as demonstrated by a lengthening of the N-N distance in the solid-state structure [1.177 Å vs. 1.142 for **(1)**] and the bathochromic shift of the N-N stretching vibration [$\Delta\nu(\text{N}_2) = -134 \text{ cm}^{-1}$]. This activation is almost

identical than the activation provided by the coordination of $\text{B}(\text{C}_6\text{F}_5)_3$ [$\Delta\nu(\text{N}_2) = -129 \text{ cm}^{-1}$, see section 4.3.1] even though the interaction of these two LAs with N_2 are occurring *via* different orbitals interplay. The orbital situation in **(32)** is comparable to the previously discussed $\text{Re}^{\text{I}}/\text{Cr}^{\text{III}}$ adduct and contrasts strongly with the coordination of $\text{B}(\text{C}_6\text{F}_5)_3$ whose interaction between boron's vacant p orbital with one of the lobes of the $\pi^*(\text{N}_2)$ results in a bent N-N-B geometry (137.0°) and an activation occurring through the lowering of the homo $\pi^*(\text{N}_2)$ orbital energy (see section 4.3.1). It is worth mentioning here that the team of Field had previously managed to prepare a cationic dinitrogen-bridged, mixed valence $\text{Fe}^0/\text{Fe}^{\text{II}}$ complex $[\{(\text{PP}_3)\text{FeH}\}(\mu\text{-N}_2)\{\text{Fe}(\text{PP}_3)\}][\text{BPh}_4]$ **(33)** bearing the tetra phosphine ligand $\text{P}(\text{CH}_2\text{CH}_2\text{PMe}_2)_3$ (PP_3) (Scheme 7) by selective reduction of an iron(II) hydride center with KO^tBu in the dinuclear end-on bridging dinitrogen $\text{Fe}^{\text{II}}/\text{Fe}^{\text{II}}$ complex $[(\text{FeH}\{\text{PP}_3\})_2(\mu\text{-N}_2)][\text{BPh}_4]_2$ **(34)** (not shown).¹³⁰ By contrast with the $\text{Fe}^0/\text{Fe}^{\text{II}}$ complex **(32)** prepared by the Szymczak group, structural data point to the absence of further N_2 activation by the reduction of the Fe^{II} center in **(34)**: the linear $\text{Fe-N}_2\text{-Fe}$ motif displays an N-N distance of 1.127 \AA , almost identical to the parent complex (1.129 \AA) or the related Fe^0 homobimetallic complex $[(\text{Fe}\{\text{dmpe}\})_2(\mu\text{-N}_2)]$ (1.144 \AA).¹³¹ The different level of activation provided by the coordination of an Fe^{II} center to a $\text{Fe}^0\text{-N}_2$ complex between **(32)** and **(33)** appears to be the result of two parameters. Contrary to **(32)**, **(33)** displays two nearly identical coordination spheres which will diminish any structurally related polarization of the central N_2 ligand. The difference in ligand field strength results in a low spin Fe^{II} center in **(33)** and a high spin Fe^{II} center in **(32)**, considering that the dx^2-y^2 and the dz^2 are not taking part in the M- N_2 interaction, a high spin system in d^6 transition metal will result in a less populated $3e$ MO (see Figure 4), which is $\pi(\text{N}_2)$ in character.



Scheme 7. Formation of complex **(32)** and the mixed-valence $\text{Fe}^0/\text{Fe}^{\text{II}}$ complex **(33)**.



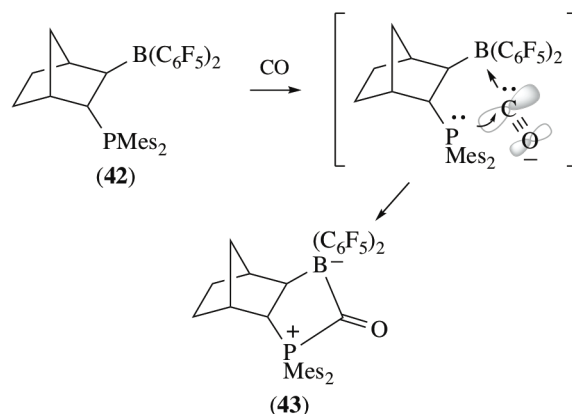
Scheme 9. Adducts of bis-dinitrogen group 6 complexes with AlMe₃.

More recently, the team of Tuzek have studied the reaction of trimethylaluminum with a molybdenum complex supported by a tripodal MeSi(CH₂PMe₂)₃ (SiP₃) ligand and dpmm (dpmm = bis(diphenylphosphino)methane).¹³² The naked complex [Mo(N₂)(SiP₃)(dpmm)] (**39**) exhibited a decent level of N₂ activation as judged by IR spectroscopy [$\nu(\text{N}_2) = 1952 \text{ cm}^{-1}$ in the solid or 1988 cm^{-1} in benzene], but unfruitful reactions with strong Brønsted acids have led them to consider Lewis acid coordination as a mean to assess basicity of the terminal nitrogen atom. The AlMe₃ adduct (**40**) was characterized by solution IR spectroscopy [$\Delta\nu(\text{N}_2) = -107 \text{ cm}^{-1}$] and by ³¹P NMR: the spectrum showed an upfield resonance for the PMe₂ group in *trans* position to N₂ [shifted from $\delta -0.4 \text{ ppm}$ for the parent complex **39** to $\delta -12.1 \text{ ppm}$ for the LA adduct (**40**)]. The equatorial phosphines were only slightly affected by the adduct formation [$\Delta\delta(\text{PPh}_2) = -0.3 \text{ ppm}$ and $\Delta\delta(\text{PMe}_3) = -1.4 \text{ ppm}$].

4.2. Adducts of group 6 end-on dinitrogen complexes with fluorinated aryl boranes: N₂ functionalization inspired by the Frustrated Lewis Pair chemistry

In 2017, the team of Simonneau reported the formation of 1:1 adducts between group 6 N₂ complexes [M(N₂)₂(dppe)₂] (**37**) [dppe = 1,2-bis(diphenylphosphino)ethane] and B(C₆F₅)₃ (**41**). This study was conducted to assess the push-pull effect using a highly electrophilic borane as LA, in the context of the frustrated Lewis pairs (FLPs) chemistry, but also to devise original reactivities for these metal/main group combinations that activate N₂.

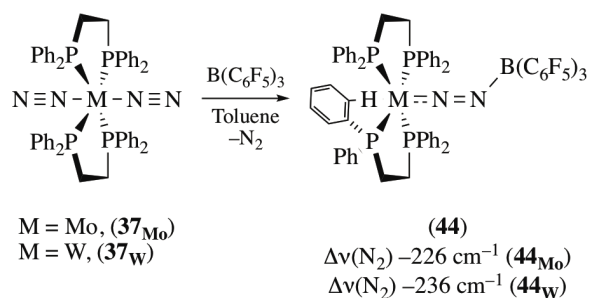
The now mature field of FLPs chemistry exploits the simultaneous action of a LA and a Lewis base (LB), prevented from forming a classical LA–LB adduct by steric interactions, for the activation of a vast array of molecules.^{133–136} In a seminal paper by Stephan and coworkers, H₂ could be heterolytically and reversibly cleaved by a simple phosphine-borane,¹³⁷ paving the way for the development of metal-free hydrogenation reactions.^{138–142} Interestingly, related FLP systems were reported to activate carbon monoxide (CO), which is isoelectronic to N₂. The Erker research group reported that phosphine borane (**42**) reacts with CO¹⁴³ to form a five-membered heterocyclic carbonyl compound (**43**) as the result of the following orbital interactions: the non-bonding 3σ orbital localized on carbon mixes with the vacant *p* orbital of the boron atom, while the non-bonding doublet on the phosphorus atom combines with the antibonding π* of the diatomic molecule, largely developed on the C atom (Scheme 10).



Scheme 10. Activation of CO by an FLP.

The team of Simonneau has been able to quantitatively prepare adducts (**44**) in solution in aromatic solvents (Scheme 11).¹⁴⁴ Their formation was ascertained by several NMR spectroscopy indicators: loss of symmetry in the ¹H NMR spectrum, downfield shift of the ³¹P resonance, upfield shift of the *meta* fluorine signals of (**41**) in ¹⁹F NMR and sharpening of the ¹¹B signal and its displacement towards negative chemical shifts, which were strong indicators of boron pyramidalization. The X-ray structures of (**44**) have the following particular features:

- i) one of the N₂ ligand in the starting complexes (**37**) has been lost upon coordination of the strong Lewis acid (**41**), leaving one apical site vacant for an agostic interaction between the metal center and an *ortho* hydrogen of one of the phenyl group of the ligand to take place;
- ii) the N–N bond is significantly elongated (*ca.* +0.1 Å) compared to the starting complex in which activation of N₂ is weak. This is also corroborated by bathochromic shifts of the $\nu(\text{N}_2)$ stretching frequency ($\Delta\nu(\text{N}_2)$ *ca.* 230 cm⁻¹) in IR spectroscopy;
- iii) the NNB arrangement is bent (*ca.* 140 °).

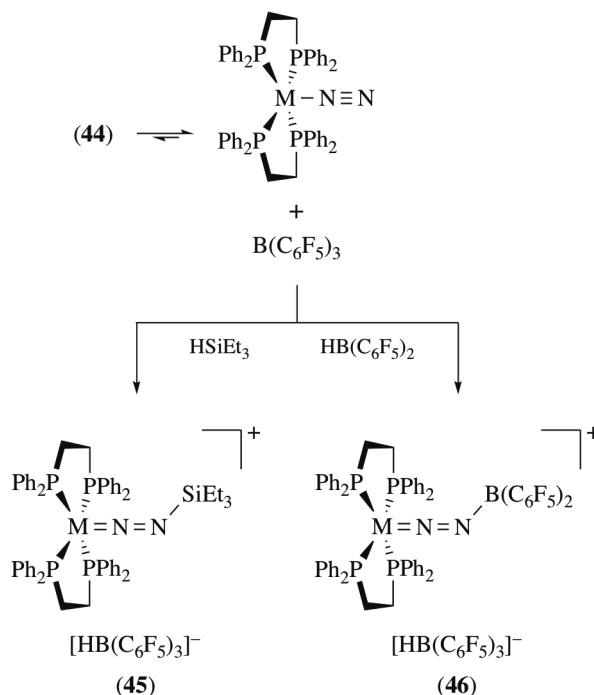


Scheme 11. Adducts of Mo- and W-N₂ complexes with B(C₆F₅)₃.

The push-pull activation of N₂ in these systems can be paralleled to the FLP chemistry since the electron-rich transition metal center injects more electron density from its filled *d* orbitals into the antibonding ones of N₂ upon coordination of the borane. However, unlike the “conventional” FLPs that activate CO, adduct formation does not occur through interaction of the lone pair on the terminal nitrogen between the vacancy at boron. Instead, the boron *p* orbital mixes with a π^* orbital of N₂, accounting for the observed bent N–N–B arrangement observed in the solid-state structure. Such orbital mixing was confirmed by theoretical calculations on related complexes of iron(0) (*vide infra*).

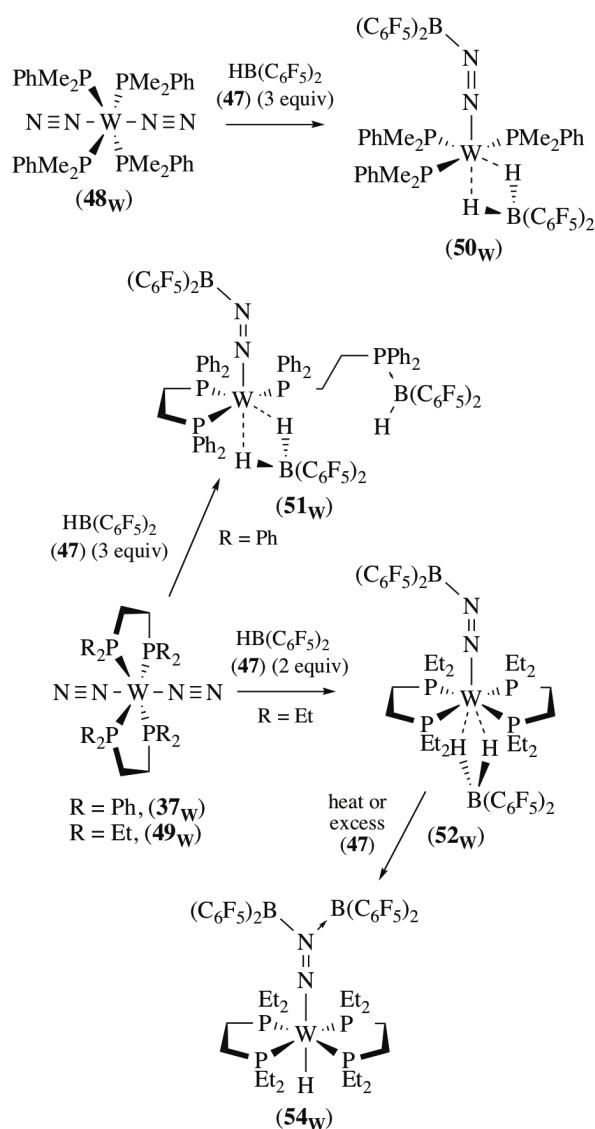
The same team demonstrated that their dinitrogen complexes/borane combinations were reactive towards Et₃SiH and HB(C₆F₅)₂, resulting in the functionalization of the terminal N with the triethylsilyl

(45) and bis(pentafluorophenyl)boryl (46) groups, respectively (Scheme 12). The mechanisms of these transformations were proposed on the basis of already existing data on Si–H^{145–147} and B–H¹⁴⁴ bond activation with FLP systems and implies prior dissociation of Lewis pairs (44).



Scheme 12. Functionalization of N₂ based on the FLP-type splitting of B–H and a Si–H bonds.

As a continuation of this work, the team of Simonneau has explored the ability of HB(C₆F₅)₂ (47), which is a strong Lewis acid as well as a good hydride donor,¹⁴⁸ to form adducts with a family of tungsten(0) dinitrogen complexes (37_w), (48_w) and (49_w).¹⁴⁴ While equimolar mixtures of a tungsten complex with (47) have systematically led to mixtures of compounds, adding an excess of (47) (2–3 fold) has led to the formation of single compounds that had all in common the borylation of the terminal nitrogen of one of the N₂ ligands, the other being lost during the reaction. A remarkable ligand effect was noticed by the authors: with dinitrogen complexes (37_w) and (48_w), one equivalent of (47) dissociates a phosphine, and the vacant coordination sites are occupied by a dihydridobis(pentafluorophenyl)borate anion in compounds (50_w) and (51_w); however, with the depe-supported [depe = 1,2-bis(diethylphosphino)ethane] complex (49_w), no phosphine dissociation was observed upon treatment with 2 equivalent of (47) and complex (52_w) was obtained (Scheme 13).



Scheme 13. Reactions of various W-N_2 complexes with $\text{HB}(\text{C}_6\text{F}_5)_2$ (**47**).

Monitoring of the reaction of **(49_w)** with one equivalent of **(47)** revealed a mixture of several compounds among which the adduct of **(49_w)** with **(47)** (**53**) could be partially characterized but not isolated. Notably, in IR spectroscopy, two previously unobserved bands were attributed to **(53)**: a red-shifted $\nu(\text{N}_2)$ ($\Delta\nu(\text{N}_2) = -132 \text{ cm}^{-1}$) corresponding to the bridging N_2 (Figure 8). This remarkable shift reflects the high Lewis acidity of **(47)**. A high energy $\nu(\text{N}_2)$ stretching frequency (2051 cm^{-1} in THF) was also observed, attesting that the other N_2 ligand was retained at this stage. In complexes **(50_w)**–**(52_w)**, borylation of the N_2 ligand was proposed to operate through a similar mechanism than the one accounting for the formation of **(46)**: B–H bond activation in **(53)** mediated by free **(47)** leads to the formation of the dihydridobis(pentafluorophenyl)borate anion and complexes **(50_w)**–**(52_w)**. Notably, when **(52_w)** was heated or treated with a slight excess of **(47)**, net hydride transfer was observed, leading to **(54_w)** (Scheme 13).

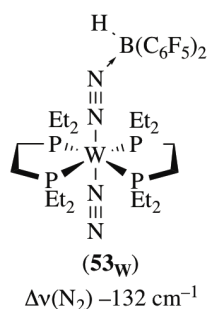


Figure 8. Adduct (53) observed during the reaction of (47) with (49_w).

4.3. Adducts of end-on dinitrogen iron complexes with strong main-group electrophiles: insights into catalysis

4.3.1. With boranes

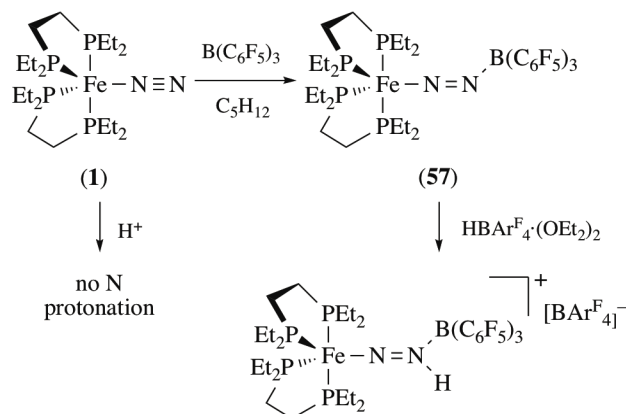
As part of a study already mentioned above and aiming at testing the "push-pull hypothesis" concerning the mechanism of the nitrogenases,¹³ Szymczak and his team have investigated the spectroscopic and electrochemical properties as well as electronic structures of Lewis pairs made of the end-on iron-dinitrogen complex [Fe(depe)₂(N₂)] (**1**) and various LAs.⁶¹ To evaluate the generality of the observed augmented N₂ activation induced by s-block (section 2.2) and d-block (section 3.5) LAs complexation, a set of boranes BR₃ (R = 2,6-F₂Ph, 2,4,6-F₃Ph, C₆F₅, F, OC₆F₅) of variable Lewis acidities [quantified by the acceptor number (AN)⁸⁹] were also reacted with (**1**). The [Fe(depe)₂(N₂-BR₃)] adducts (**55**)–(**59**) were obtained in quantitative yields and characterized by IR and NMR spectroscopy. The IR spectra revealed that the dinitrogen bond was considerably weakened as judged by the significant red-shift of the ν(N₂) stretching frequency, with Δν(N₂) ranging from -101 to -172 cm⁻¹, tracking to the AN of the boranes (Table 4).

Table 4. Key parameters of the [Fe(depe)₂(N₂-BR₃)] adducts showing dependency to LAs' ANs.

[(depe) ₂ Fe(N ₂ BR ₃)]	AN of LA	Δν(N ₂) (cm ⁻¹)	E _{HOMO} (eV)	N _β charge (e ⁻)	π*(N ₂) population (e ⁻)	E _{pa} (V) vs Fc ⁺ /Fc
(1) (no BR ₃)	/	0	-3.73	-0.215	0.169	-1.72
R = 2,6-C ₆ H ₃ F ₂ , (55)	67.42	-101	-4.298	-0.252	0.217	-1.24
R = 2,4,6-C ₆ H ₂ F ₃ , (56)	69.07	-115	-4.38	-0.264	0.218	-1.05
R = C ₆ F ₅ , (57)	79.37	-143	-4.597	-0.296	0.222	-0.89
R = F, (58)	81.37	-146	-4.758	-0.377	0.220	n.c.
R = OC ₆ F ₅ , (59)	89.46	-172	-4.867	-0.369	0.228	-0.73

An X-ray structure was reported for the B(C₆F₅)₃ adduct (**57**), showing an elongated N–N bond (+0.04 Å) and a bent N–N–B arrangement. DFT calculations were performed in order to shed light on the electronic structure and bonding situation. Mixing of the vacant *p* orbital at boron and π*(N₂) is responsible for the dative N–B bonding, accounting for the bent geometry. Energetically, LA complexation leads to the stabilization of the HOMO of the complex, which is a combination of *d* orbitals and π*(N₂), giving it greater π*(N₂) character and therefore facilitating back-donation from the metal. The magnitude of stabilization and electron delocalization were found to track closely with the AN of the LAs. Counterintuitively, since LA coordination would be expected to quench the basicity of the terminal N (N_β), charges issued from NBO (Natural Bond Orbital) calculations were in line with increased negative charge. Several experimental facts came to support the computations:

- i) in cyclic voltammetry, oxidation of the boron adducts occurred at more anodic potentials than **(1)** with differences consistent with the calculated stabilization energies.
- ii) The ^{15}N isotopologue ^{15}N -**(57)** has a significantly shielded signal for the boron-bound nitrogen atom compared to the parent complex [$N_{\beta} \delta = -40.5$ ppm for ^{15}N -**(1)**; -119.8 ppm for ^{15}N -**(57)**]. This confirms the polarization of the dinitrogen moiety induced by LA complexation, electron density being localized on the terminal nitrogen atom.
- iii) the increased negative charge on the terminal N makes it prone to react with electrophiles, reactions that are quite complicated with **(1)** owing to the occurrence of redox events. Treated with HBAr^{F}_4 ($\text{Ar}^{\text{F}} = 3,5\text{-(F}_3\text{C)}_2\text{C}_6\text{H}_3$), **(57)** underwent clean and selective protonation at N_{β} (Scheme 14).



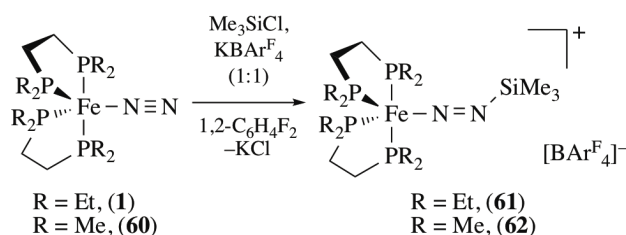
Scheme 14. Formation of adduct **(57)** and its selective protonation.

This body of work is remarkable in the way that the postulated influence of acidic residues within the active site of the nitrogenases on N_2 activation, that would be otherwise difficult to assess, has been verified using simple models. This illustrates well how synthetic N_2 complexes can help understand the functioning of the very complex nitrogenase enzymes. The same team has later reported push-pull activation of dinitrogen using H-bond donors.⁶²

4.3.2. With Silicon cations

In biological as well as in homogeneous catalyses, characterization of intermediates is of primary importance to understand their mechanisms. In the previous section, characterization of a mono-protonated species by Geri *et al.* (Scheme 14) offers a snapshot of what may resemble elusive MN_2H intermediates formed after the first protonation step in catalytic N_2 reductions.^{17,23} Facing difficulties to isolate such species, 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.¹⁴⁹ Treatment of **(1)** or $[\text{Fe}(\text{dmpe})_2(\text{N}_2)]$ [**(60)**, $\text{dmpe} = 1,2\text{-bis}(\text{dimethylphosphino})\text{ethane}$] with $\text{Me}_3\text{SiCl}/\text{KBAr}^{\text{F}}_4$ afforded the ionic compounds **(61)** and **(62)** also bearing a bent N-N-Si arrangement (Scheme 15). IR data were in line with a notable weakening of the N–N bond. As expected with the strong LA Me_3Si^+ , the $\nu(\text{N}_2)$ was dramatically shifted towards lower energies ($\Delta\nu(\text{N}_2) = -224 \text{ cm}^{-1}$). The X-ray diffraction structures of complexes **(61)** and **(62)** 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 **(1)** or **(60)**. DFT calculations performed on the silyldiazenido complexes were in line with those run by Szymczak and co-workers regarding orbital interactions (*vide supra*). According to their diamagnetic character, trigonal bipyramid geometry and *d* orbital-centered HOMOs, the complexes were best described as Fe(0), d^8 , rather than Fe(II), high spin d^6 species, although Mössbauer experiment were missing to support this proposition. This contrasts with the neutral silyldiazenido complexes prepared by the

reactions of silyl halides or pseudohalides with low valent iron N₂ complexes: in these cases, formal oxidation of the metal center was systematically observed.^{81,150–153}

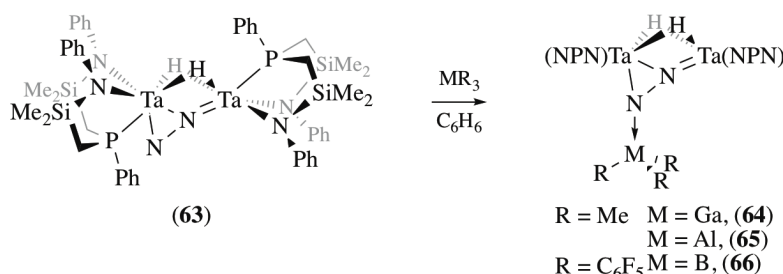


Scheme 15. Formal adducts of iron(0) dinitrogen complexes with silylium ions.

4.4. Adducts of p-block Lewis acids with end-on, side-on bimetallic dinitrogen complexes

4.4.1. Adducts with end-on, side-on dinitrogen tantalum complexes

In 2005, Fryzuk, Tuzek and coworkers jointly reported an in-depth study on the interaction of the tantalum end-on, side-on dinitrogen complex $[(\text{NPN})\text{Ta}]_2(\mu\text{-H})_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-N}_2)$ (**63**) ($\text{NPN} = (\text{PhNSiMe}_2\text{CH}_2)_2\text{PPh}$), with various p-block LAs.¹⁵⁴ They had previously demonstrated by orbital analysis¹⁵⁵ a possible increased reactivity of the terminal nitrogen atom of (**63**) towards electrophiles and later showed that these reactions divided into two broad classes: addition reactions^{156,157} or Lewis acid-base interactions. In order to better apprehend the reactivity of the N₂ ligand in (**63**), the interaction with group 13 LAs $[\text{GaMe}_3, \text{AlMe}_3 \text{ and } \text{B}(\text{C}_6\text{F}_5)_3]$ was explored. The 1:1 reaction of these LAs with (**63**) resulted in the immediate formation of the clean adducts $[(\text{NPN})\text{Ta}]_2(\mu\text{-H})_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-NNGaMe}_3)$ (**64**), $[(\text{NPN})\text{Ta}]_2(\mu\text{-H})_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-NNAI Me}_3)$ (**65**) and $[(\text{NPN})\text{Ta}]_2(\mu\text{-H})_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-NNB}(\text{C}_6\text{F}_5)_3)$ (**66**) (Scheme 16). By contrast, attempts to prepare adducts with BMe_3 and BEt_3 were unsuccessful.



Scheme 16. Adducts of a side-on, end-on (NPN)Ta complex with GaMe_3 , AlMe_3 and $\text{B}(\text{C}_6\text{F}_5)_3$.

The irreversibility of Lewis acid-base pairs formation was demonstrated by treating a solution of (**65**) with one equivalent of labelled [¹⁵N]-(**63**), resulting in no reaction. Solid-state molecular structures of (**64**)–(**66**) were determined by X-ray crystallography. The Ta₂N₂ moiety show increased N–N distances ranging from 1.319(4) Å in the parent complex to 1.356(18), 1.363(7) and 1.393(7) Å in adducts (**64**)–(**66**), respectively. The level of N₂ activation correlates to the Lewis acidity of the group 13 electrophiles employed [quantified by the acceptor number (AN),⁸⁹ $\text{GaMe}_3 < \text{AlMe}_3$ (57.0) < $\text{B}(\text{C}_6\text{F}_5)_3$ (77.6)]. The M–N bond distances (M = Ga, Al or B) in (**64**)–(**66**) are 2.101(12), 1.993(5) and 1.584(9) Å, respectively. This observed shortening along the series is the result of decreasing covalent radii ($R_{\text{Ga}} = 1.22(3)$ Å, $R_{\text{Al}} = 1.21(4)$ Å, $R_{\text{B}} = 0.84(3)$ Å) but also increasing Lewis acidity. These distances are in accordance with the formation of Lewis pairs, with B–N distances being in the range of the B–N bonds of tetracoordinated boron [average B–N bonds lengths in tetracoordinated boron species = 1.624 Å (SD = 0.0422 Å) gathered from 1161 structures of the SCD database]. ¹⁵N NMR spectra of labelled [¹⁵N]-

(64)–(66) exhibited two resonances; an upfield resonance corresponding to the shielded bridging N (N_{α}) and a downfield resonance assigned to the terminal N (N_{β}). The vibrational properties of (64)–(66) were measured by IR and resonance Raman spectroscopy (not shown) and found to be close to those of the parent complex (63), showing a slight decrease in the N–N stretching frequency in agreement with the observed elongation of the N–N bond (Table 5). The bonding situation in a model complex, $[\{\text{PH}_3(\text{NH}_2)_2\text{Ta}\}_2(\mu\text{-H})_2(\mu\text{-}\eta^1:\eta^2\text{-N}_2\text{-BH}_3)]$, was investigated by means of DFT calculations. Dative bonding between boron and the terminal nitrogen occurs through mixing of a hybrid of the p_{σ} and a π bond of the N_2 fragment and the empty p orbital at boron. This leads to a decrease of the HOMO's energy, which 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 charge donation from the metal centers' filled d_{π} orbitals into the antibonding π^* orbitals of the dinitrogen ligand is increased, resulting in a net negative charge accumulation at the terminal N. Related to this work, the same team have explored the feasibility of a catalytic sequence to produce a functionalized hydrazine moiety (N_2B_4) from hydroboranes, N_2 and the Ta complex by examining the reaction of (63) with various hydroboranes.¹⁵⁷ No catalytic cycle could be completed but they discovered that with the hydroboranes 9-BBN, C_2BH and $\text{H}_2\text{BCMe}_2\text{CHMe}_2$, a new type of N–N bond cleavage proceeded subsequently to functionalization of the coordinated N_2 by B–H 1,2-addition over the Ta–N bond. Contrastingly, the reaction between (63) and the more Lewis acidic bis(pentafluorophenyl)borane (47) afforded the stable adduct (67) (not shown). Metric parameters collected by X-ray diffraction analysis as well as ^{15}N NMR data were close to those reported for the $\text{B}(\text{C}_6\text{F}_5)_3$ adduct (66).

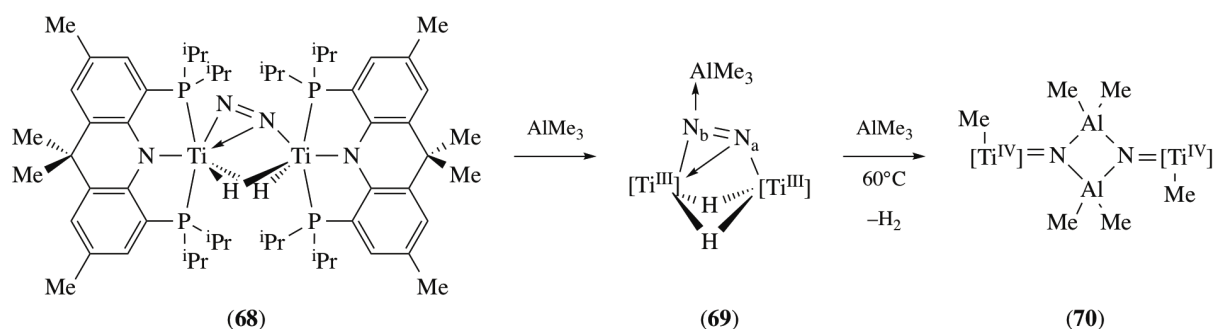
Table 5. Selected metrical and spectroscopic parameters of complexes (63)–(66).

	63	64	65	66
d_{NN} (Å)	1.319(4)	1.356(18)	1.363(7)	1.393(7)
d_{MN} (Å)	n. a.	2.101(12)	1.993(5)	1.584(9)
^{15}N NMR (ppm)				
N_{α}	-20.4	-29.9	-33.1	-21.2
N_{β}	163.6	79.9	54.6	2.4
$\nu(\text{N}_2)$ (cm^{-1})	1165	1131	1132	1145

4.4.2. Adducts with end-on, side-on titanium dinitrogen complexes

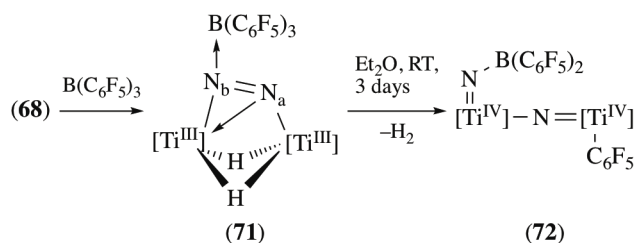
The team of Hou has reported the synthesis of a new end-on, side-on dinitrogen dititanium hydride complex (68) that reacts with a variety of organometallic compounds such as ZnMe_2 , MgMe_2 , AlMe_3 , $\text{B}(\text{C}_6\text{F}_5)_3$, PinBH and PhSiH_3 .¹⁵⁸ Relevant to the present review is the reaction of complex (68) with one equivalent of AlMe_3 that leads to the formation of adduct (69) (Scheme 17). The ^{15}N NMR spectrum of the ^{15}N -labelled analogue ^{15}N -(69) exhibits two resonances; an upfield resonance corresponding to the shielded bridging nitrogen nuclei (N_{α} : 46.6 ppm, slightly downfield shifted compared to ^{15}N -(68): 43.2 ppm) and a downfield resonance assigned to the terminal N (N_{β} : 197.9 ppm, significantly upfield shifted compared to ^{15}N -(68): 354.6 ppm). Solid-state molecular structure of (69) was determined by X-ray crystallography, which revealed an increase of the N–N distance from 1.296(3) Å in the parent complex (68) to 1.339(3) Å in (69), delineating the significant influence of LA coordination on the dinitrogen moiety. When a second equivalent of AlMe_3 was added and the reaction mixture heated at 60 °C, a new complex (70) containing a four-membered dialuminum dinitrido metallacycle was obtained. This structure was confirmed by an X-ray diffraction study and revealed shorter Al–N bond lengths than in adduct (69) [(70): 1.930(2) and 1.942(2) Å vs. (69): 1.982(2) Å]. The ^{15}N NMR spectrum of the ^{15}N -labelled analogue of (70) shows one singlet at δ 194.5 ppm, suggesting that the two nitride

units are equivalent on the NMR time scale. The detection of possible intermediates of the reaction from (69) to (70) failed but the authors suggested that the addition of the second equivalent of AlMe₃ led to the formation of a dinitride/AlMe₃ adduct accompanied by H₂ loss and followed by Al–Me addition across the Ti=N unit.



Scheme 17. Reaction of complex (68) with AlMe₃.

The reaction of B(C₆F₅)₃ with complex (68) was also performed and resulted in adduct (71) (Scheme 18). The ¹⁵N NMR spectrum of the [¹⁵N]-labelled analogue of (71) exhibited two doublets (N_α: 15.3 ppm and N_β: 93.9 ppm) shifted upfield compared to [¹⁵N]-(68). Solid-state molecular structure of (71) was determined by X-ray crystallography and features an elongated N–N bond (1.343(3) Å) compared to (68); the B–N distance remained within the range of those observed in the case of tetracoordinated boron species (d_{B–Nβ} = 1.578(4) Å), similarly to what was observed with the tantalum complex (63) (*vide supra*). When a diethyl ether solution of (71) was left at room temperature for 3 days, H₂ release was observed as well as a borylimido/μ₂-nitrido titanium complex (72), resulting from the splitting of the dinitrogen moiety and the migration of a C₆F₅ group from the boron to a titanium center. This body of work is a remarkable illustration of main-group LA coordination induced-N₂ splitting and that push-pull activation can trigger original reactivities for ligating dinitrogen.



Scheme 18. Reaction of complex (68) with B(C₆F₅)₃.

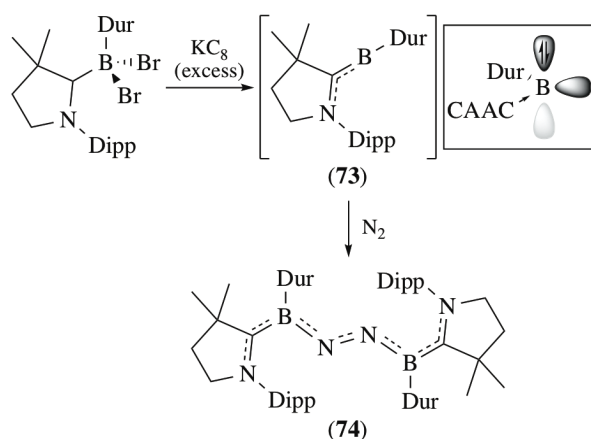
5. P-BLOCK-ONLY SYSTEMS FOR PUSH-PULL ACTIVATION OF N₂

Although transition metals clearly dominate dinitrogen chemistry, the cost, scarcity, toxicity and environmental issues associated with them have pushed molecular chemists to find more sustainable alternative for N₂ activation. Argon matrix,^{159–161} gas-phase¹⁶² and in silico^{163,164} studies have already demonstrated the ability of very reactive main group species to bind N₂. Recently, p-block metallomimetics, and borylenes in particular have emerged as effective N₂ fixation entities, while condensed and gas-phase models for FLP-type N₂ activation have also been proposed.

5.1. Borylenes for N₂ activation

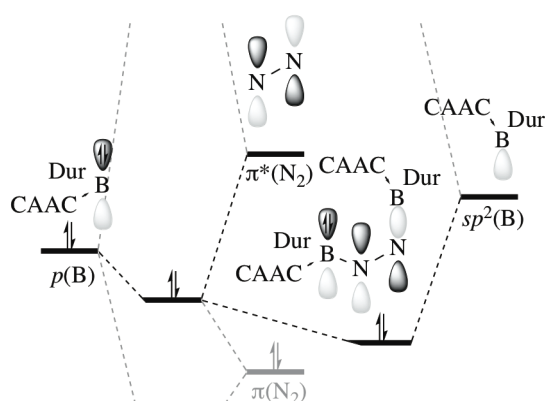
In a remarkable article published in 2018, Braunschweig and co-workers have reported the first example of N₂ activation with a main group element, boron, in the condensed phase.^{165,166} This was achieved thanks to the transient generation of a very reactive borylene species (73), in which a filled *p*

orbital and an orthogonal empty sp^2 orbital on the boron atom were proposed to play the role of the d orbitals of transition metals that are responsible for N_2 binding in dinitrogen complexes (Scheme 19). The solid-state structure of the N_2 activation product (**74**) reveals that two borylene moieties are implied with the dinitrogen molecule bridging them in a $\mu\text{-}\eta^1\text{:}\eta^1$ fashion. The BNNB arrangement is bent with a B-N-N-B dihedral angle of ca. 110° , which contrasts with bimetallic end-on bridging N_2 complexes that show a linear M-N-N-M motif. The N-N bond is in the range of double N-N bonds ($1.248(4)$ Å).



Scheme 19. Dinitrogen activation by borylene species (Dur = duryl, Dipp = 2,6-diisopropylphenyl, CAAC = cyclic alkyl amino carbene).

DFT calculations by the team of Mo with the use of block localized wavefunctions on a simplified model have shed light on this particular bonding.¹⁶⁷ They have shown that it is the result of two opposite and perpendicular push-pull channels and interactions with the orbitals of N_2 with π geometry only, as well as the uniqueness of borylenes for acting both as a Lewis acid and Lewis base. As with transition metals, N_2 activation in (**74**) is mainly the result of electron delocalization from the filled p orbital of the boron atoms into the π^* antibonding orbitals of the diatomic molecule. Pauli repulsion due to the filled p orbital on the boron atoms pushes the electrons populating the π/π^* orbitals of N_2 into the empty sp^2 orbital of the opposite borylene. This interaction differs from what is encountered in end-on, mono- and bi-metallic complexes of N_2 where the σ -type bonding occurs through N_2 's lone pair overlap with the empty dz^2 of the metal (Scheme 20).

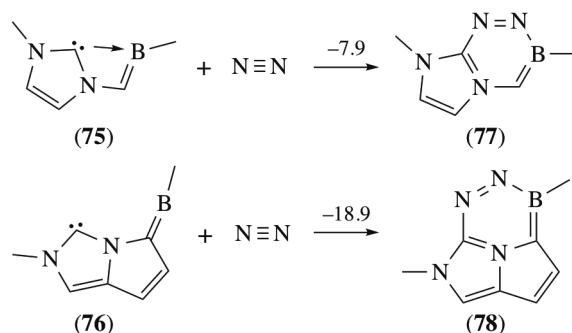


Scheme 20. Simplified molecular orbital showing one push-pull channel for N_2 activation in (**74**).

5.2. Boron-carbon FLP models for N₂ activation

5.2.1. *In silico* models: NHC-tethered borylenes

Zhu proposed in 2019 two theoretical examples of metal-free compounds that can activate dinitrogen with favorable thermodynamics and kinetics.¹⁶⁸ They examined the ability of intramolecular FLP consisting of either *sp*²-hybridized, dicoordinated phosphorus, nitrogen or carbon as the Lewis basic site and *sp*-hybridized, dicoordinated boron as the Lewis acidic site. Thermodynamic calculations have shown that among the tested theoretical models, compounds **(75)** and **(76)** that both feature an N-heterocyclic carbene (NHC) can bind dinitrogen exergonically, thanks to the strength of the C–N bond formed in the N₂ activation products **(77)** and **(78)** as well as to their aromatic nature (Scheme 21).



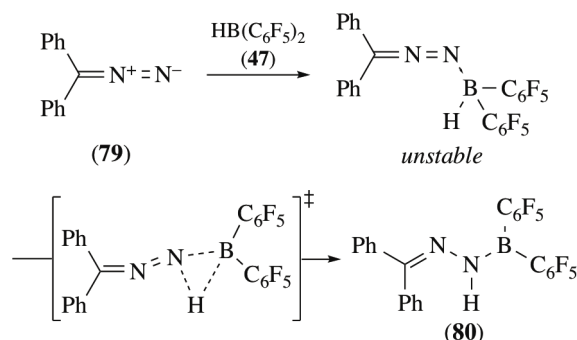
Scheme 21. Carbon-boron FLP systems for N₂ activation. ΔG given in kcal mol⁻¹.

The superiority of **(75)** over **(76)** for N₂ activation was established on both thermodynamic and kinetic grounds. First, after N₂ activation, greater delocalization of the π electrons gives greater aromaticity to **(78)** and therefore greater stabilization. This was highlighted by nucleus-independent chemical shift (NICS) calculations, as well as by the replacement of the *sp*-hybridized boron by an *sp*²-hybridized one, resulting in significantly endergonic N₂ activation ($\Delta G = 40.8$ kcal.mol⁻¹). Secondly, the significant donor-acceptor interaction between the boron atom and the carbene moiety in **(75)** imparts a kinetic disadvantage to the first elementary step of the transformation, which is the binding of N₂ to the *sp*-hybridized boron Lewis acid —the pull effect [activation barrier is 18.9 kcal.mol⁻¹ for **(75)** and 8.3 kcal.mol⁻¹ for **(76)**]. The Gibbs free energy of the second transition state of this transformation by which ring closure occurs through C–N bond formation is also reduced with enhanced aromaticity [11.3 kcal.mol⁻¹ for **(75)** vs. 8.3 kcal.mol⁻¹ for **(76)**].

5.2.2. Condensed phase models using diazo compounds

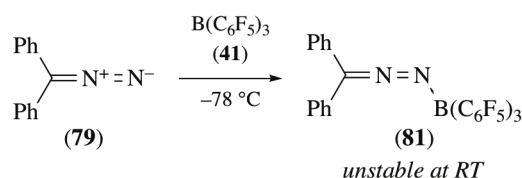
The team of Stephan recently published studies on diazo compounds that move the metal-free, FLP-type activation of dinitrogen a step closer to its realization.¹⁶⁹ Indeed, diazo compounds can be viewed as the products of N₂ binding over carbenes. In a previous report, they showed that diazomethanes liberate N₂ in the presence of boranes and insertion of the formally divalent carbon into a B–C bond was observed.¹⁷⁰ In 2017, they continued to explore the reactivity of diazomethane with strongly Lewis acidic boranes such as HB(C₆F₅)₂ (**(47)**) and B(C₆F₅)₃ (**(41)**).¹⁷¹ The reaction of diphenyldiazomethane Ph₂CN₂ (**(79)**) with **(47)** resulted in the rapid formation of compound **(80)** (Scheme 22). It was identified by NMR spectra analysis as the product of 1,1-hydroboration of the terminal nitrogen atom by **(47)**. The ¹H NMR displayed a peak at 8.77 ppm assignable to a single NH proton. An X-ray diffraction study revealed the double and single bond characters of the C–N and N–N linkages, respectively. DFT calculation showed that the reaction proceeds first by adduct formation between **(47)** and **(79)** followed by a 3-center, 2-electron-bond B–H–N transition state that allows the migration of the H atom from the boron to the proximal nitrogen. Two other synthetic pathways were found for the formation of **(80)** both implying the initial formation of an adduct between either **(47)** or **(41)** and benzophenone

hydrazone. Upon heating, these adducts released H₂ [with (47)] or HC₆F₅ [with (41)] leading to the formation of the covalent B–N bond in (80).



Scheme 22. 1,1-hydroboration of diphenyldiazomethane (79) by borane (47).

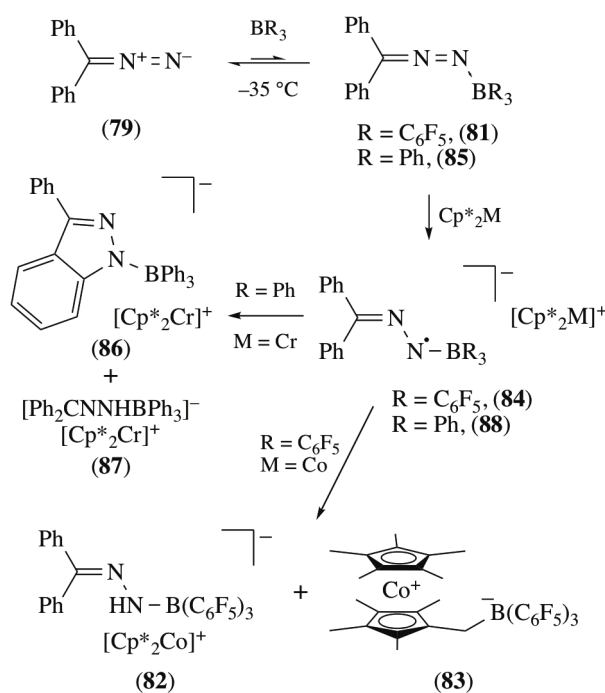
A thermally unstable adduct (81) could be isolated from the reaction between (79) and B(C₆F₅)₃ at –78 °C (Scheme 23). It was characterized by NMR spectroscopy analysis: upfield ¹¹B NMR shift and the reduced *meta-para* gap of the fluorine resonances compared to those of free B(C₆F₅)₃ were consistent with the formation of an adduct. IR data displayed absorption bands characteristic of C–N and N–N double bonds. Despite the sensitivity of (81), an X-ray diffraction study could be performed and confirmed the spectroscopic data (*d*_{CN} = 1.278(8) Å, *d*_{NN} = 1.177(7) Å, *d*_{BN} = 1.65(1) Å). Compared to the above-discussed “hybrid” metal boron templates (44) and (57) (sections 4.2 and 4.3.1) reported by the teams of Szymczak and Simonneau, the N–N bond length is shorter in (81), while the B–N linkage is significantly longer. The N–N–B arrangement is also bent, however, in (81) the N–N–B angle is much smaller [125 ° vs ca. 140 ° for (44) and (57)], most probably as the result of reduced steric repulsion between the boron and carbene substituents than with the phosphine ligands in (44) and (57). As the temperature is raised, (81) evolves dinitrogen. The authors have proposed, on the basis of partial characterization data, that the adduct of diphenylcarbene with (41), Ph₂C(B(C₆F₅)₃), was formed (not shown).



Scheme 23. Reaction of diphenyldiazomethane (79) with B(C₆F₅)₃ (41).

The successful isolation of (81) foreshadowed the possibility of FLP-N₂ chemistry. In a parallel study, the Stephan research group recently showed that weak Lewis acid-base adducts can be stabilized by one electron reduction promoted by decamethylferrocene, which afforded novel anions and a new strategy for small molecule activation.¹⁷² They next explored the possibility of stabilizing the weak B⋯N interaction of diazomethane-borane adducts by single electron transfer (SET) (Scheme 24).¹⁷³ The adduct between diphenyldiazomethane (79) and B(C₆F₅)₃ (41) was reacted at –35 °C with one equivalent of decamethylcobaltocene to readily give two new compounds (82) and (83) containing a tetracoordinated boron atom according to ¹¹B NMR. The ¹H NMR spectrum also revealed the formation of an N–H bond and the presence of a CH₂ fragment. These compounds could be separated by fractional recrystallization and were characterized by X-ray diffraction. Compound (82) was identified as a salt where the anionic part is a hydrazide-borane adduct with a significantly shorter B–N bond compared to (81) (*d*_{BN} = 1.539(7) Å vs. 1.65(1) Å). The H atom on compound (82) originates from the abstraction of one hydrogen of a Cp* methyl group which led to formation of compound (83) where

the hydrogen abstracted is replaced by the $[B(C_6F_5)_3]^-$ group. The reaction proceeded first by the formation of the unstable adduct **(81)** which is then reduced by Cp^*_2Co to give the transient diazomethane-borane adduct radical anion $[Ph_2CN_2B(C_6F_5)_3]^-$ (**84**). This species is then able to abstract a hydrogen atom from the metallocene to form **(82)** and **(83)**. Strong support to this mechanism was brought by the absence of reaction between **(79)** and the $[HB(C_6F_5)_3]^-$ anion that would form after C–H activation by the $[B(C_6F_5)_3]^-$ radical-anion. Although attempts to observe this transient radical adduct were unsuccessful, the reaction between the fluorenyl analogue of **(79)**, Cp^*_2Fe and $Al(C_6F_5)_3$ afforded a long-lived N-based radical (not shown) that was characterized by EPR spectroscopy. When the weaker Lewis acid BPh_3 was used, adduct **(85)** could not be observed but addition of Cp^*_2Cr resulted in a color change. Fractional crystallization allowed for the isolation of two new compounds **(86)** and **(87)** (Scheme 24). While the latter is comparable to **(82)**, in this case, the H atom carried by the terminal nitrogen originates from an intermolecular H atom transfer. Indeed, **(86)** results from an intramolecular cyclization of **(88)** that issues a 5-membered ring upon addition of the nitrogen radical to an *ortho* aromatic position. The delocalized aryl radical intermediate generated after the addition transfers an H atom to free **(79)** that eventually delivers **(87)** by reduction by Cp^*_2Cr and reaction with BPh_3 .



Scheme 24. Reactivity of diazomethanes-boranes adducts upon one electron reduction.

Although this body of work employs compounds not made from dinitrogen, they offer a view of what could be the reactivity of push-pull, FLP-type N_2 activation compounds. Especially, the one electron reduction of borane-diazomethanes adducts demonstrates that highly reactive N centered radicals can be generated using these systems.

6. CONCLUSIONS

We hope we have offered with the present article a concise but as exhaustive as possible view on the activation of N_2 through a push-pull mechanism. The population of N_2 antibonding orbitals, key to N_2 activation by an electron-rich element, can be greatly enhanced if a second, comparatively electron-poorer element, interacts concomitantly with the diatomic. Although the level of N_2 activation is significantly lower than those reached with homobimetallic systems using reducing metals, push-pull

activation is generally achieved through redox-neutral processes and grants dinitrogen a high level of polarization, which has, in some instances, allowed the discovery of original reactivities. With the emergence of strongly Lewis acidic compounds, we are confident that new systems will be examined that will permit to expand the scope of reactivities known for coordinated N₂.

7. ACKNOWLEDGEMENTS

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8. ABBREVIATIONS AND ACRONYMS

AN	acceptor number
Ar ^F	3,5-bis(trifluoromethyl)phenyl
BBN	borabicyclononane
CAAC	cyclic alkyl amino carbene
depe	1,2-bis(diethylphosphino)ethane
Dipp	2,6-diisopropylphenyl
dmpe	1,2-bis(dimethylphosphino)ethane
dppe	1,2-bis(diphenylphosphino)ethane
Dur	duryl,
FLP	frustrated Lewis pair
LA	Lewis acid
NC	Natural Charges
NMR	Nuclear magnetic resonance
NPA	Natural Population Analysis
OEP	octaethylporphyrinate
SET	single electron transfer
TM	transition metal
TMS	trimethylsilyl
TTP	tetra(<i>p</i> -tolyl)porphyrinate

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