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Transition Metal-Mediated Dinitrogen Functionalisation with Boron

Antoine Simonneau*

The quest for efficient dinitrogen transformations has continuously attracted interest from the chemical community. Since the advent of dinitrogen coordination chemistry, N_2 complexes have proven valuable platforms for the conversion of dinitrogen into valuable compounds such as ammonia or silylamines. Although less developed, probably as a consequence of challenging implementation into catalysis, functionalization of N_2 with other elements than H or Si does hold great promise in view of the ubiquity of nitrogen-containing compounds and materials in chemistry. The present article focuses on the currently available methods to functionalise dinitrogen activated by transition metal centres with boron reagents resulting in N–B bond formation.

Introduction

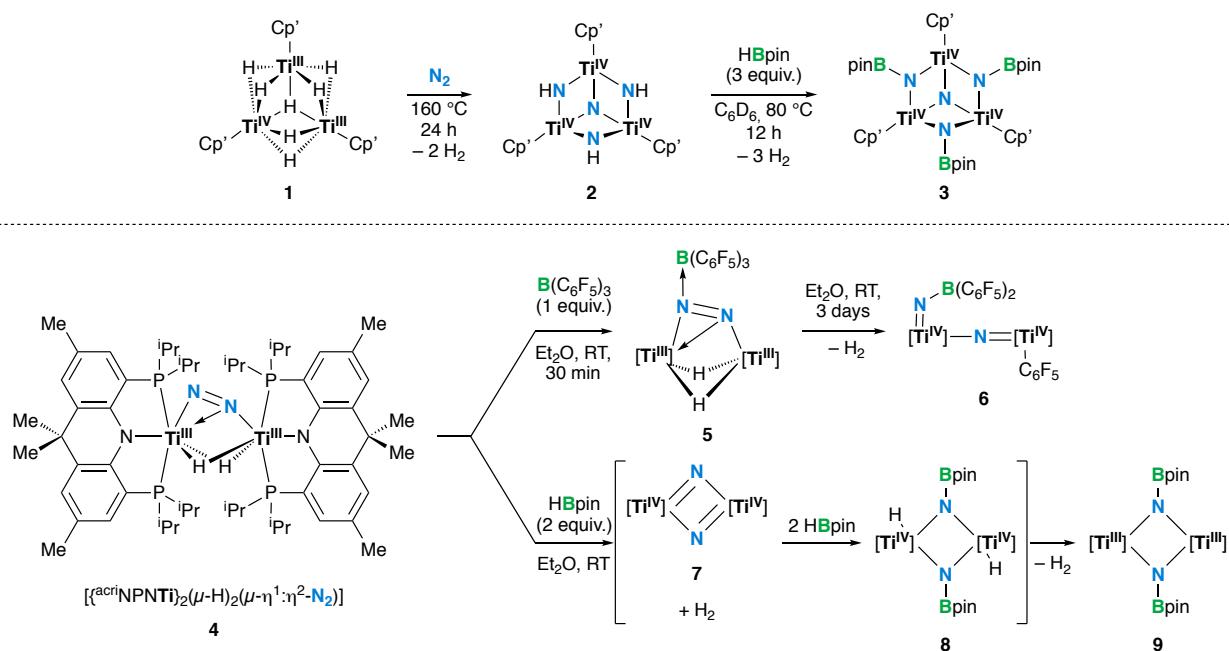
Dinitrogen, N_2 , is commonly considered as an inert molecule. As the primary constituent of our atmosphere, it represents an inexhaustible and unique, widely available source of the element N, which is crucial for all living organisms on Earth. Therefore, its transformation into more reactive sources of nitrogen is of vital importance for life to be sustained. In Nature, some bacteriae express an enzyme, the nitrogenase, which gives them the ability to reduce N_2 into ammonia (NH_3) through a process called nitrogen fixation.¹ The whole biosphere takes advantage of this fixed and reactive nitrogen as it can be easily metabolised. The food crisis that plagued Europe at the advent of the 20th century, due to demographic explosion and shortage of nitrate ore —the nitrogen fertilizer employed at the time— has pushed chemists to find a reliable method to artificially perform nitrogen fixation and provide enough fixed nitrogen to fertilize soils and increase crop yields to sustain a growing population. The Haber-Bosch process was developed for that purpose, and still remains one of the most important industrial processes, more than a century after its discovery. It allows the reduction of N_2 into NH_3 by hydrogenolysis over an heterogeneous iron catalyst and has supplied mankind with sufficient amounts of nitrogen fertilizers to sustain its intensive agriculture.² Although efficient, the sustainability issues posed by the Haber-Bosch process (high energy consumption and large CO_2 emissions) has motivated a quest for greener nitrogen fixation methods. Inspired by the nitrogenases, that features an active site that incorporate an iron-sulfur cluster to which N_2 binds before it is reduced, coordination and organometallic chemists have devised ways to activate and transform dinitrogen using molecular complexes that bind N_2 ,³ eventually achieving catalytic, homogeneous N_2 -to- NH_3 reaction.⁴ But it would be forgetful not to recognise another important and exclusive aspect of dinitrogen coordination complexes, which is their ability to build bonds between N_2 's nitrogen atoms and elements other than H. Thus, amines, silylamines and borylamines have been prepared from dinitrogen complexes by reacting N_2 complexes with carbon, silicon and boron reagents, respectively.^{3a,b} While still in its infancy, the synthesis of

borylamines from N_2 is an attractive goal since such compounds have been employed as molecular precursors *en route* to ordered boron nitride-based materials.⁵ The present article gives an overview of the available methods to create covalent B–N bonds between a dinitrogen (or a N_2 -derived nitrido) ligand and a boron-based reagent, the first elementary step to look at when targeting the preparation of N_2 -sourced borylamines.

Group 4 Metals

N_2 Borylation Relying on Titanium Hydride Complexes

The group of Hou has reported dinitrogen cleavage and hydrogenation using a trinuclear, mixed-valence titanium polyhydride complex **1** leading to a tris-imido/nitrido complex **2** (Scheme 1, top).⁶ The latter was shown to react with 3 equiv. of pinacolborane (HBpin) to give the tris-borylimido/nitrido species **3** through dehydrogenative coupling between the hydroborane and the imido moieties.⁷ The same group has recently documented the reactivity of a side-on, end-on dinitrogen dititanium hydride complex **4** in which the two metal centres are stabilised by an acridine-based PNP pincer ligand (*acri*PNP, see Scheme 1, bottom).⁸ Compared to a similar system from the same group,⁹ the rigidity imparted by the *acri*PNP ligand was key to observe various reactions with main group organometallics. Notably, treatment of **4** with $B(C_6F_5)_3$ led to the rapid formation of the Lewis acid-base adduct **5**. Lewis acid coordination was proposed to trigger N–N bond cleavage over days in Et_2O at room temperature, followed by B–C bond cleavage and covalent B–N bond formation to afford a borylimido/ μ_2 -nitrido Ti^{IV} compound **6**. N-borylation ensuing N–N bond scission was also observed in the reaction of **4** with two equivalents of pinacolborane (HBpin). The authors proposed that, after the loss of H_2 , the N–N bond is cleaved to lead to an intermediate dinuclear $Ti(IV)$ nitride **7**. Double 1,2 addition of B–H bonds across the Ti –N double bonds¹⁰ may then afford the bis(borylimido)-bridged dititanium dihydride species **8** (not observed), which subsequently loses H_2 to afford the dititanium complex **9**.



Scheme 1 N₂ cleavage and hydrogenation promoted by titanium hydrides and their subsequent reactivity with boranes results in B–N bond formation.

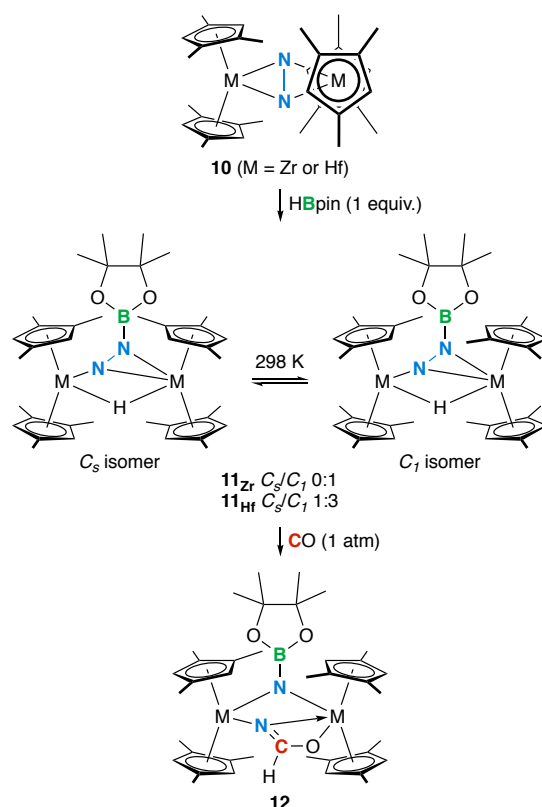
Metalloenes of Zirconium and Hafnium

The group of Chirik has successfully demonstrated that dinuclear, side-on bound dinitrogen metallocene complexes based on Zirconium and Hafnium could engage in a wide array of nitrogen-element bond-forming events.¹¹ Zirconium and hafnium bimetallic N₂ complexes **10** stabilised with the 1,2,4-trimethylcyclopentadienyl ligand reacted with pinacolborane to afford N-borylated compound **11**, obtained as a mixture of C₁ and C_s isomers in the case of hafnium (Scheme 2).^{11p} Other hydroboranes have not been examined. Further reactivity was explored and, in particular, the authors have shown that when exposed to CO, the N–N bond in **11** was cleaved concomitantly with C–N bond formation (**11** → **12**).

Group 5 Metals

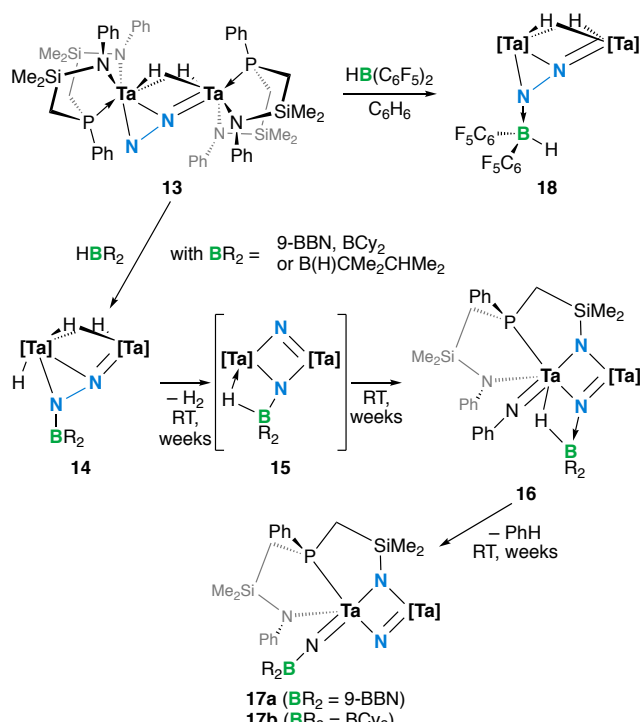
In the 2000s, the group of Fryzuk has extensively studied the reactivity of the side-on, end-on dinitrogen ditantalum hydride complex **13** supported by the NPN ligand (NPN = (PhNSiMe₂CH₂)₂PPh),¹² which core structure resembles those of the dititanium complexes later studied by the group of Hou (*vide supra*).^{8,9} Notably, secondary or primary hydroboranes such as 9-BBN, HBCy₂ or thexylborane reacted with **13** by 1,2-B–H bond addition over one Ta–N bond to afford boryldiazenido complexes **14** (Scheme 3).¹³ By contrast with the report from Hou's team, the Ta complex **13** readily reacted with hydroboranes, while the structurally related dititanium compound **4** (Scheme 1) was proposed to eliminate H₂ and undergo N–N bond cleavage before N-borylation with HBpin. However, the Fryzuk group observed that N-borylation in **14** was followed by H₂ loss, leading presumably to a transient Ta–Ta bonded intermediate (not shown) in which N–N bond scission occurred. Reaction of the thus-formed bridging nitride in intermediate **15** with the NPN ligand backbone then afforded complex **16** showing a square silylimido-nitrido Ta₂N₂ motif. Interestingly, the B–H bond re-formed during that process, the

hydride bridging the B and Ta centres, and the B atom had a weaker interaction with the N atom than in **14** (d_{BN} = 1.517(8) Å in **16** vs. 1.40(2) Å in **14**). In the case of the 9-BBN and BCy₂ derivatives, further reactivity was observed, as the terminal phenylimido in **16**, formed after cleavage of the ligand's N–Si bond, reacted with the proximal coordinated hydroborane to provide a borylimido moiety concomitantly with the release of benzene (**16** → **17a,b**).



Scheme 2 Borylation of the dinitrogen ligand with HBpin in dinuclear Zr and Hf metallocene N₂ complexes.

The authors could not observe a similar rearrangement for the hexyl derivative. The reaction of **13** with Piers' borane $\text{HB}(\text{C}_6\text{F}_5)_2$ did not lead to 1,2-B-H bond addition, instead a stable Lewis acid-base adduct **18** was observed.¹⁴

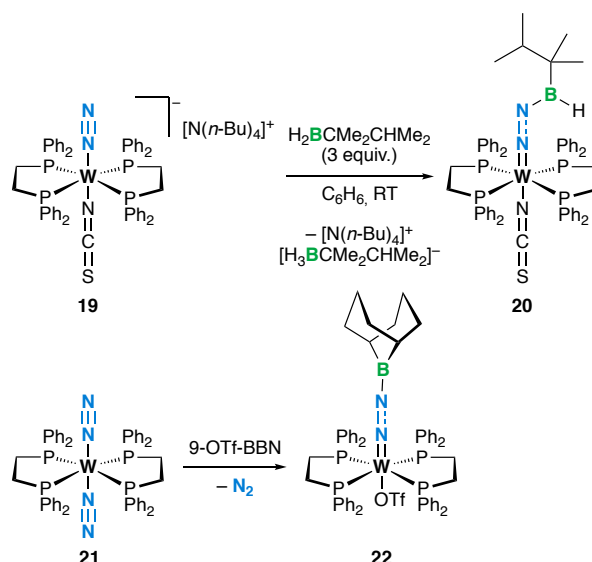


Scheme 3 Reactivity of the dinuclear side-on, end-on dinitrogen Ta complex with hydroboranes.

Group 6 Metals

Early Works

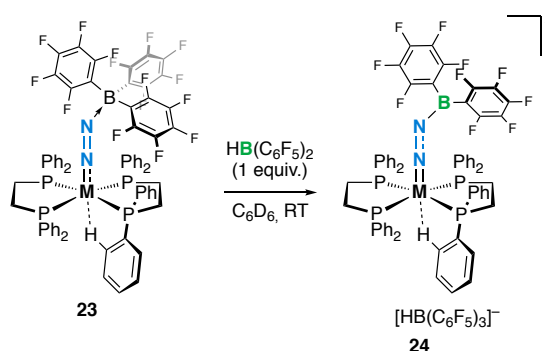
The Hidai group is one of the research team to have pioneered the chemistry of dinitrogen complexes, especially with low-valent group 6 metal-phosphine compounds. It was indeed the first to report the reaction of a dinitrogen complex with boron reagents leading to B-N bond formation. In this seminal publication, the anionic tungsten complex **19** reacted with thexylborane to produce the neutral boryldiazenido compound **20** with the tris-hydridoborate salt $[\text{NBu}_4][\text{H}_3\text{BCMe}_2\text{CHMe}_2]$ as by-product (Scheme 4).¹⁵ Dialkylboranes such as 9-borabicyclo[3.3.1]nonane (9-BBN) and dicyclohexylborane (HBCy_2) reacted more sluggishly (not shown). The authors emphasised the fact that related, neutral dinitrogen complexes remained unreactive towards thexylborane as a result of lower N_2 activation. However, the former were reactive towards more electrophilic boron-pseudohalide reagents, such as 9-borabicyclo[3.3.1]nonyl triflate (9-OTf-BBN). In its presence, N_2 complex **21** was converted to the boryldiazenido triflate compound **22**. Intriguingly, in the solid state structure of **22**, the W-N-N-B array is linear, likely for steric reasons. This contrasts with commonly encountered bent M-N-N-B motifs found in other structures of boryldiazenido complexes.



Scheme 4 Borylation of zero-valent end-on tungsten- N_2 complexes

Frustrated Lewis Pair (FLP)-inspired Borylation and 1,3-B-H bond addition

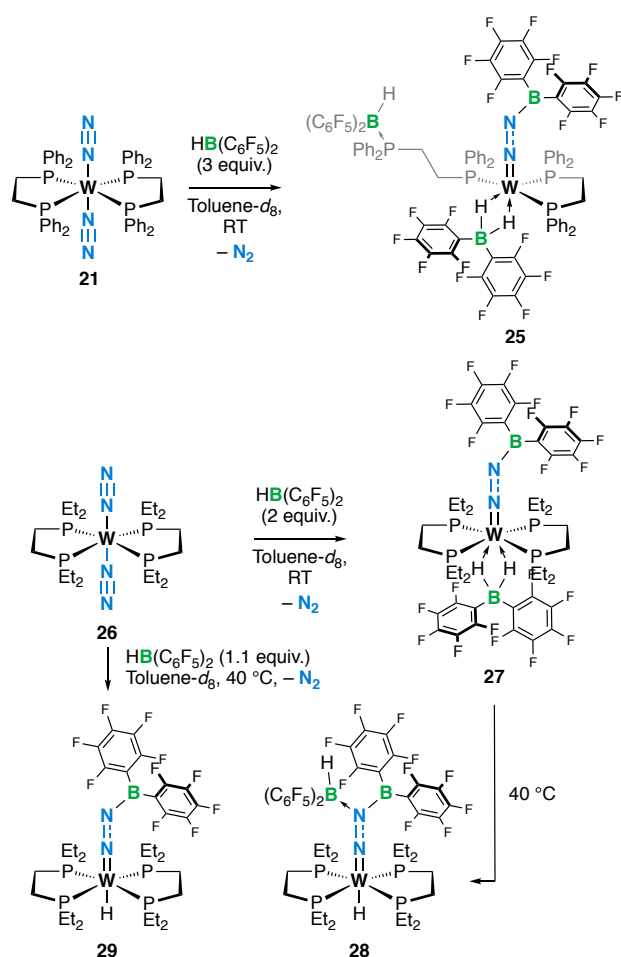
Our group has recently studied the reactivity of Lewis adducts of $\text{B}(\text{C}_6\text{F}_5)_3$ with group 6, zero-valent bis-dinitrogen complexes supported with phosphines, taking inspiration from the frustrated Lewis pair (FLP) chemistry.¹⁶ Especially, we have shown that adducts **23** efficiently performed the heterolytic, FLP-type cleavage of Piers' borane's¹⁷ B-H bond¹⁸ to afford ionic complexes **24** in which the N_2 ligand was borylated (Scheme 5).¹⁹



Scheme 5 FLP-type B-H bond activation by N_2 complex- $\text{B}(\text{C}_6\text{F}_5)_3$ combinations (M = Mo or W).

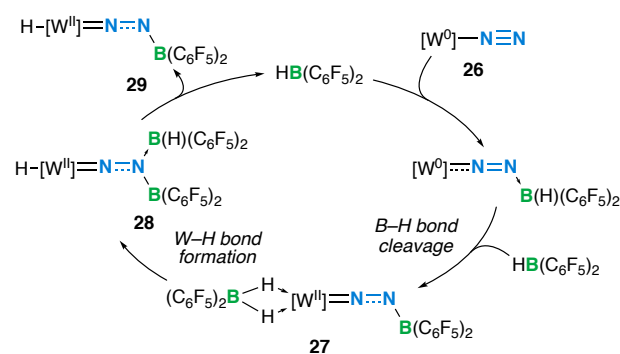
Further investigations on Piers' borane reactivity with N_2 -tungsten complex **21** have shown that it alone is an effective N_2 -borylation agent, leading to boryldiazenido complex **25** (Scheme 6).²⁰ Similar reactivity was observed with the monophosphine N_2 complex $[\text{W}(\text{N}_2)_2(\text{PMe}_2\text{Ph})_4]$ (not shown). Solid-state structures allowed us to differentiate these reactions from the one described in Scheme 5 as Piers' borane demonstrated its ability to easily dissociate a phosphine, a phenomenon that was not observed when the more sterically hindered $\text{B}(\text{C}_6\text{F}_5)_3$ was employed. Heterolytic B-H bond cleavage, similarly to the reaction affording **24**, generates a bis(hydrido) borate anion that was found, according to crystallographic data, to interact with the metallic centre, while in **24** the $[\text{HB}(\text{C}_6\text{F}_5)_3]^-$ anion was clearly separated from the cationic part. Such interaction was possible due to the liberation

of a coordination site after phosphine dissociation as well as the bidenticity and suitable steric demand of $[\text{H}_2\text{B}(\text{C}_6\text{F}_5)_2]^-$. It is likely that the borylation of **19** reported by Hidai and colleagues, producing a tris(hydrido)borate anion (Scheme 4), shares similar mechanistic features (B–H bond cleavage) to our work. A remarkable ligand effect was found when we examined the reactivity of the depe-supported W complex **26** (depe = 1,2-bis(diethylphosphino)ethane). Indeed, thanks to the strong σ -donor ability of the ligand coupled to the chelating effect, Piers' borane was not able to dissociate a phosphorus atoms like in **25**, leading to a different interaction of the $[\text{H}_2\text{B}(\text{C}_6\text{F}_5)_2]^-$ anion with tungsten in complex **27**, now located in trans relationship to the boryldiazenido ligand (Scheme 6). Upon heating at 40 °C or addition of another equivalent of $\text{HB}(\text{C}_6\text{F}_5)_2$, W–H bond formation occurred, leading to the formal 1,3-B–H addition compound **28**. Repeating the experiment with a slight excess of Piers' borane at 40 °C allowed us to obtain the boryldiazenido-hydrido compound **29**.



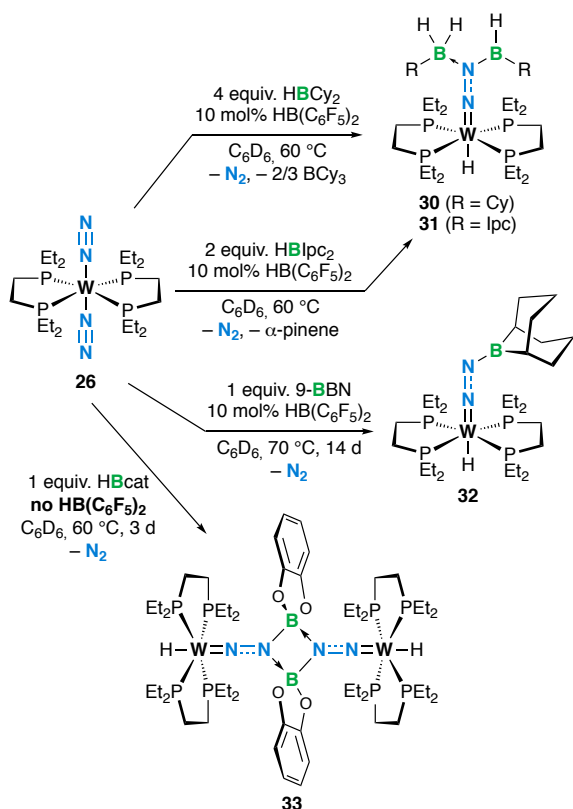
Scheme 6 From borylation of N_2 to 1,3-B–H bond addition over a M– N_2 unit using Piers' borane

This last experiment suggested that in **28**, one equivalent of $\text{HB}(\text{C}_6\text{F}_5)_2$ can dissociate to enter a new 1,3-B–H bond addition process. From this we proposed a catalytic effect for Piers' borane in the **26** → **29** transformation, as visualised in Scheme 7. The boron reagent has three roles: i) borylation agent, ii) B–H bond cleavage and iii) shuttling the hydride to the metal.



Scheme 7 A Piers' borane-driven catalytic cycle for 1,3-B–H bond addition

More recently, we have shown that Piers' borane can be employed as a catalyst to assist 1,3-B–H bond addition over the W– $\text{N} \equiv \text{N}$ unit of **26** of otherwise unreactive boranes (Scheme 8).²¹ Thus, boryldiazenido compounds **30** and **31** have been obtained from treatment of **26** with HCy_2 or HBIpc_2 (Cy = cyclohexyl, Ipc = isopinocampheyl) and catalytic amounts (10 mol%) of Piers' borane. In these reactions, primary alkyl boranes, stemming from retro-hydroboration processes undergone by HCy_2 and HBIpc_2 , are the species reacting with the N_2 -complex. 9-BBN, which was stable towards retro-hydroboration, reacted much more sluggishly under catalytic conditions (**26** → **32**). From additional experiments, we have highlighted the possibility that 1,3-B–H bond addition of Piers' borane onto **26** to give **29**, followed by boron to boron H-transfer in a σ -bond metathesis sequence lead to the formation of the observed boryldiazenido compounds. Surprisingly, catecholborane (HBcat) spontaneously added to the W complex without the need for a catalyst, leading to a dimeric boryldiazenido complex **33**. We have not been able to collect experimental evidence suggesting a similar mechanism than for Piers' borane 1,3-addition, but we believe that the high hydride donor ability of either $\text{L} \cdot \text{HBcat}$ or $[\text{H}_2\text{Bcat}]^-$ as well as the formation of dimers offer a thermodynamic driving force to this process that counter-balance its weak Lewis acidity, whereas the low steric hindrance of HBcat imparts a kinetic advantage.



Scheme 8 Catalysed and uncatalysed 1,3-B-H bond addition with various hydroboranes.

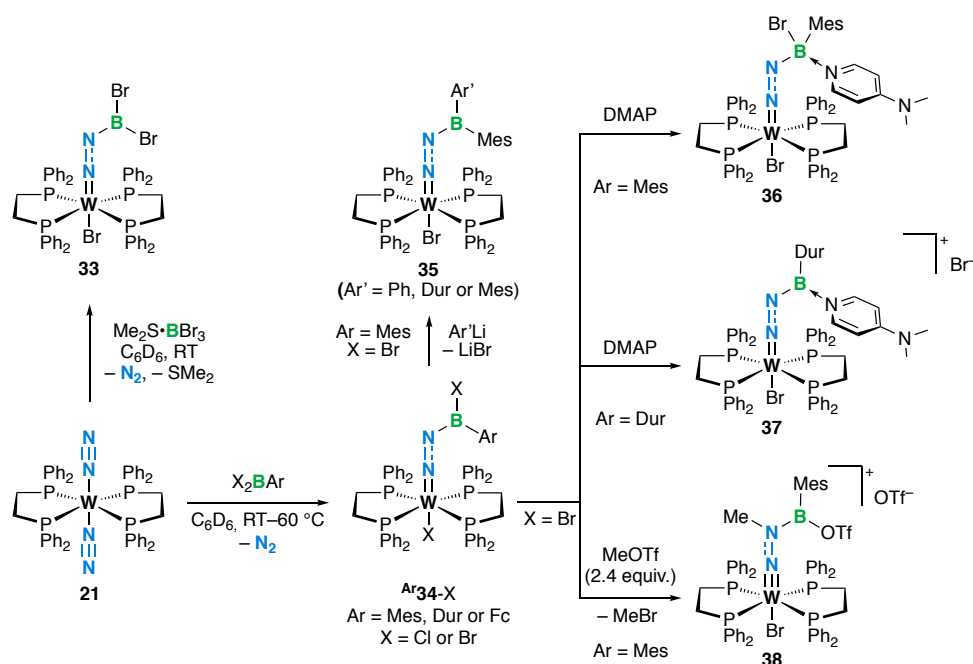
1,3 Haloboration

The group of Braunschweig has recently shown that the W complex **21** is also reactive towards tri- and dihalo(aryl)boranes.²² The latter reacted with **21** through a formal 1,3-haloboration, allowing the preparation of boryldiazenido compounds **33** and Ar^334-X (Scheme 9). Chloroboranes reacted more sluggishly than the bromo derivatives. The authors

suggested that a comparable mechanism than the one we proposed for 1,3-B-H bond addition took place, the halide being shuttled to the metal centre by a second equivalent of borane. Further reactivity of the haloboryldiazenido complexes bearing mesityl and duryl substituents was explored. Bromide substitution at boron with various aryllithium reagents could be achieved ($^{Mes}34-Br \rightarrow 35$), forcing in some instances an almost linear geometry for the W-N-N-BAr₂ motif. Reaction with *N,N*-dimethylaminopyridine (DMAP) resulted either in Lewis acid-base pairing ($^{Mes}34-Br \rightarrow 36$) or bromide substitution to give the borenium compound **37**. When treated with methyl triflate (MeOTf), the mesityl derivative underwent smooth N-alkylation to provide the cationic borylmethylhydrazido complex **38**.

Borylamine synthesis from N₂-derived Molybdenum nitrides

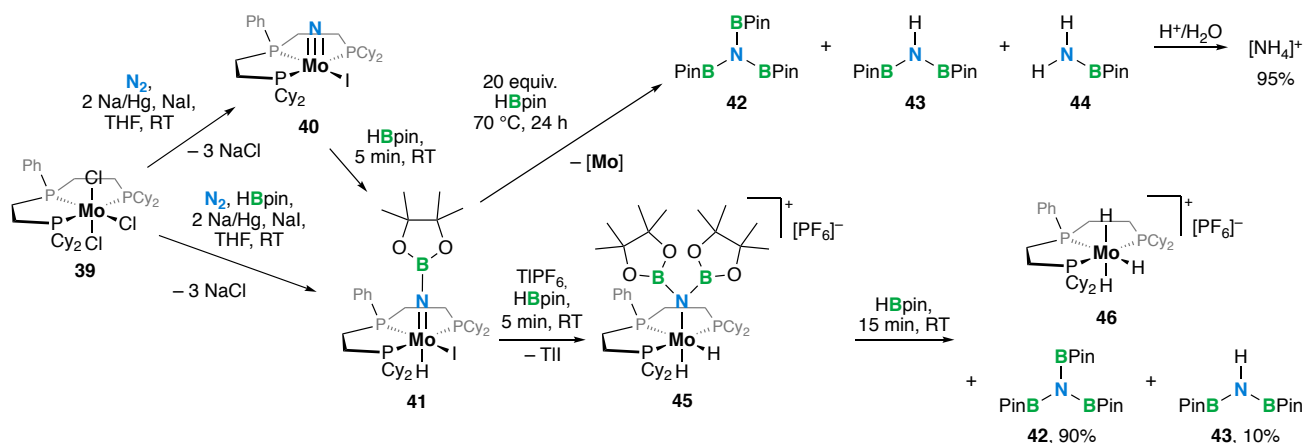
The above described examples all implied the reactivity of a N₂ unit with a boron reagent, but N₂-derived nitrides issued from bimetallic N₂ cleavage by low-valent metal centres are also species to look at for N₂ transformation. While previous reports have shown their ability to react with carbon electrophiles to ultimately lead to the release of nitriles after several chemical steps, the development of catalytic N₂ transformation relying on N₂ cleavage is, like most other examples of nitrogen compound synthesis from N₂ complexes, plagued by incompatibility issues between the functionalising reagent (generally an electrophile) and the strong reducing agent needed to access the low oxidation states to effect N₂ activation. From this appraisal, the group of Mézailles has looked at N-Si and N-B bond formation between the N₂-derived nitrido Mo-complex **40** supported by a triphosphine ligand and hydrosilanes²³ or pinacolborane (HBpin) as mild electrophiles. In the latter case, HBpin was shown to add in a 1,2 fashion over the MoN unit, affording a borylimido complex **41** (Scheme 10).²⁴ The authors have also shown that **41** can also be obtained when the N₂ splitting step, employing the strong Na(Hg) reductant, was performed in the presence of HBpin (**39** \rightarrow **41**).



Scheme 9 1,3-haloboration of [W(N₂)₂(dppe)₂] (**21**) and subsequent reactivity of the (halo)boryldiazenido complexes.

Remarkably, when **41** was treated with a 20-fold excess of borane, a mixture of primary to tertiary borylamines **42–44** and paramagnetic Mo complexes were obtained upon heating, the nitrogen compounds being collected in an almost quantitative yield with respect to **41**, as measured by ammonium formation after acidic hydrolysis of the borylamines mixture. After abstraction of the iodide by Ti^+ to liberate a coordination site in the borylimido complex **41**, the obtained cationic complex showed improved reactivity towards a second equivalent of

HBpin, affording the bis(boryl)amido dihydrido Mo complex **45** in 5 min at RT. After addition of a third equivalent, tris(boryl)amine **42** is obtained in 90% yield, along with small amounts of bis(boryl)amine **43** and the cationic Mo trihydride complex **46**. Closure of a synthetic cycle from the latter back to **40** or **41** has not been unveiled yet; the achievement of such reaction would make a solid basis to next envision the development of a catalytic borylamine synthesis.



Scheme 10 Generation of Mo-nitrido and -borylimido complexes from N_2 and production of borylamines from them.

Conclusion

Various B–N bond formation methods between transition metal-activated dinitrogen and boranes have been disclosed since chemists have started to explore the reactivity of coordinated dinitrogen or N_2 -derived nitrides. However, the examples gathered in this focus show that it is only recently that borane reactivity was systematically explored with dinitrogen complexes when compared to N–C or N–Si bond formation. This might be correlated with the growing interest over the last two decades for inorganic B/N compounds and materials. In addition, the reader may have realized that examples of N_2 borylation are missing with N_2 complexes beyond group 6. Yet, to date, promising routes have been uncovered, where mildly electrophilic hydroboranes were shown to be sufficiently reactive to functionalise dinitrogen (or N_2 -derived nitrido complexes). While in most of the examples discussed above the release of a boron-nitrogen compound was not reported, the recent achievement of stoichiometric borylamine synthesis described in the last section paves the way for catalytic processes to emerge. In addition, it is worth noting that direct borylation of N_2 using low-valent boron species was recently achieved by the group of Braunschweig.²⁵ This presage other exciting developments for dinitrogen borylation.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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