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Metallaboratranes

Terminal Iron Dinitrogen and Iron Imide Complexes Supported by a Tris(phosphino)borane Ligand[**]

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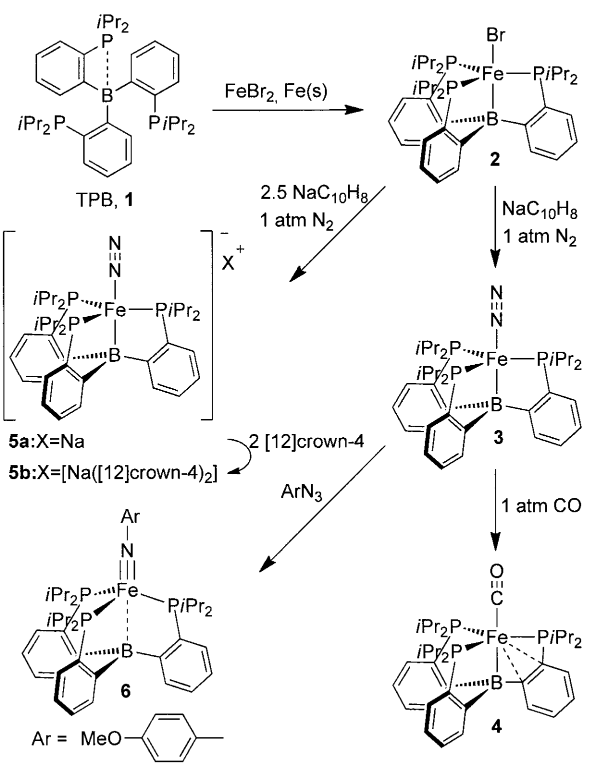
Our currently limited understanding of the mechanism of biological dinitrogen fixation[1]—that is, reduction of N_2 to two equivalents of ammonia by addition of protons and electrons—motivates a sustained effort to prepare functional models of the nitrogenase MoFe cofactor. One plausible mechanism for N_2 reduction is a so-called distal or Chatt-type cycle,[2] in which successive addition of three hydrogen-atom equivalents to the distal N atom of a metal-bound dinitrogen molecule ($M{-}N{\equiv}N$) results in elimination of one equivalent of NH_3 to yield an intermediate nitrido complex ($M{\equiv}N$). The latter is in turn converted to ammonia by reaction with three additional protons and electrons. Indeed, such a cycle has been suggested as operative for a mononuclear, molybdenum-based catalyst.[3] The increasing evidence for substrate coordination at iron in the MoFe cofactor[1b] warrants the continued investigation of iron-based models in a related context.[4]

A Chatt-type cycle at an iron center would require a single ligand scaffold to stabilize low-valent complexes with a π-acidic dinitrogen molecule as well as high-valent complexes with a π-basic nitride ligand. We have investigated this chemistry in two different ligand-imposed geometries that model the local trigonal symmetry of the coordination environment of iron in the MoFe cofactor. The pseudotetrahedral geometry was successfully used to stabilize terminal imide[5,6] and nitride[7,8] ligands, because the π-antibonding d orbitals of e parentage are empty, but most of the N_2 complexes in this geometry are dinuclear, bridged species rather than terminal ones due to the difficulty of implementing sufficient steric protection.[9,10] On the other hand, the trigonal-bipyramidal geometry enforced by tetradentate tris(phosphino)silyl ligands has been shown to stabilize terminal N_2 complexes of iron in three different oxidation states,[11] but is less well suited for accommodating Fe−N multiple bonds because of the presence of low-lying π-antibonding orbitals.[12]

Both the trigonal-bipyramidal and tetrahedral geometries can be accessed with a single NL_3-type scaffold (L = phosphine,[13] N-heterocyclic carbene[8c]) in which the nitrogen donor is labile. We reasoned that a similar behavior could be accessed with a Lewis acidic borane in the apical position and therefore turned our attention to tris(phosphino)borane (TPB) ligand **1** (Scheme 1), which was introduced recently by Bourissou and co-workers.[14] Ligand **1** forms a range of C_3-symmetrical metallaboratranes with an $(M{-}B)^{10}$ configuration,[15] in which variation of the B−M distance from 2.168 Å in [(TPB)Ni] to 2.540 Å in [(TPB)AgCl] points to some flexibility in adapting the metal–boron interaction to the Lewis basicity of the metal atom.[14b,c] Herein we explore the iron chemistry of ligand **1**, showing that the (TPB)Fe fragment accommodates both terminal N_2 complexes in low oxidation states and an imido iron complex in the iron(II) state.



Scheme 1. Synthesis and reactivity of ferraboratranes derived from tris(phosphino)borane (TPB) ligand **1**.

A convenient entry into the iron chemistry of the TPB ligand was provided by iron bromide complex **2** (Scheme 1),

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which was obtained as a greenish brown powder by comproportionation of iron(II) bromide and iron powder in the presence of TPB (THF, 90 °C, 66 h). Broad ^{1}H NMR resonances ranging from $\delta = -23.1$ to 92.5 ppm and the solution magnetic moment of 4.1 μ_B (Evans method) indicate an $S = 3/2$ ground state. The XRD crystal structure[16] of **2** (Figure 1) exhibits a slightly distorted trigonal-bipyramidal geometry, with rather long Fe–Br (2.4138(7) Å) and Fe–P (2.3832(13)–2.4351(11) Å) distances, as expected for a high-spin complex. The (M–B)^7 electron configuration of **2** is, to our knowledge, unprecedented in metallaboratrane chemistry.

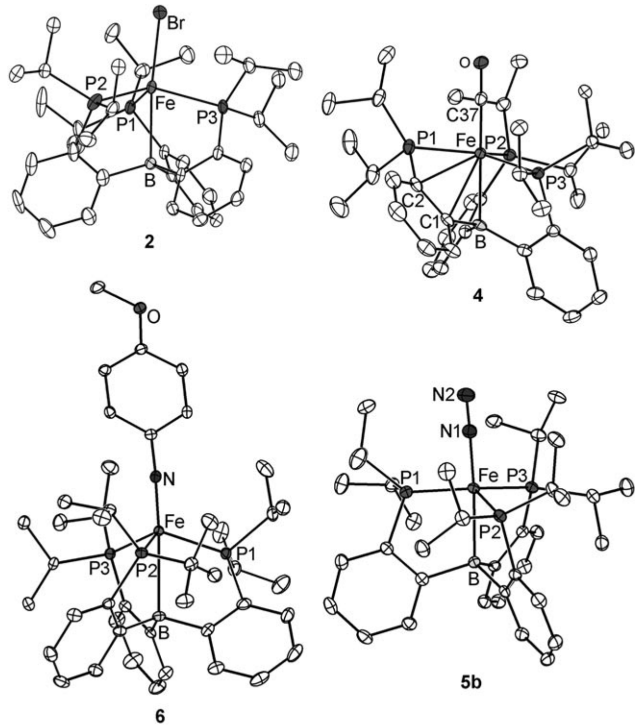

Figure 1. Solid-state structures of **2**, **4**, **5b**, and **6.** Thermal ellipsoids set at 50%. For clarity, hydrogen atoms, the [Na([12]crown-4)$_2$]$^+$ counterion, and an unbound diethyl ether molecule in structure **5b** are omitted. Only the main component of a disordered isopropyl group in **2** and only one of the two independent molecules of **6** are plotted.

Reduction of **2** with a slight excess of sodium naphthalide (THF, −60 °C to RT) afforded a brown compound that exhibits a strong IR absorption at 2011 cm^{-1} and a solution magnetic moment of 2.8 μ_B. These data are consistent with its formulation as the terminal (Fe–B)^8 dinitrogen complex **3** with an $S = 1$ ground state. Exposure of a yellowish brown solution of **3** to vacuum results in a reversible color change to dark reddish brown accompanied by major changes in the ^{1}H NMR spectrum, indicative of a labile N_2 ligand. Crystals of **3** invariably suffered from severe twinning that prevented an unequivocal structure determination, but its monomeric nature was confirmed by a DOSY experiment showing that **2** and **3** have virtually equal diffusion coefficients.

The nature of complex **3** was further confirmed by its reaction with one atmosphere of CO to afford a brown compound that exhibits a single IR absorption at 1857 cm^{-1} and is consequently formulated as [(TPB)Fe(CO)] (**4**). Despite the isoelectronic nature of N_2 and CO, compound **4** does not have the expected spin-triplet ground state, but is diamagnetic. The ^{1}H NMR spectrum of **4** resembles that of a C_3-symmetrical species, but a broad ^{31}P resonance at $\delta = 87$ ppm suggests fluxionality. On cooling to −90 °C, this signal splits into three mutually coupled resonances at $\delta = 94$, 87.5, and 16.7 ppm, indicating an asymmetric geometry. This was confirmed by the XRD crystal structure[16] (Figure 1), which reveals an additional interaction of the iron center with two carbon atoms of an aromatic ring of the TPB ligand (Fe–C1 2.337(2), Fe–C2 2.321(2) Å), resulting in overall η^4 coordination of one arm. Partial dearomatization of the iron-bound ring is evident from C–C bond-length alternation (see Supporting Information). There are a few examples of related η^3-coordinated phenylborane moieties,[17] but incorporation of this motif in a metallaboratrane cage structure was, to the best of our knowledge, unknown.

A quasireversible wave at −2.19 V versus Fc/Fc$^+$ in the cyclic voltammogram (CV) of **3** suggested accessibility of the anionic N_2 complex **5**, which could indeed be isolated as its sodium salt **5a** from the reaction of **2** with 2.5 equiv of sodium naphthalide (THF, −60 °C to RT). The paramagnetic compound **5a** has an $S = 1/2$ ground state, as shown by its solution magnetic moment of 1.6 μ_B and a quasi-axial EPR signal (X-band, toluene/THF glass, 20 K) with $g_1 = 2.23$, $g_2 = 2.09$, $g_3 = 2.05$. The IR spectrum of **5a** in THF solution exhibits two intense bands at 1918 and 1877 cm^{-1}, which are attributed to the N–N stretch of the free anion Fe–N≡N$^-$ and tight ion pair Fe–N≡N$^-$•••Na$^+$, respectively. In accord with this assignment, only the second band is observed in the less-coordinating solvent diethyl ether (1862 cm^{-1}) and in the solid state (1879 cm^{-1}). This was additionally confirmed by treating **5a** with two equivalents of [12]crown-4 to afford complex salt **5b**, which exhibits only the free-anion band at 1918 cm^{-1} in THF and at 1905 cm^{-1} in the solid state. X-ray crystal structures[16] were obtained for both **5a** (Supporting Information) and **5b** (Figure 1). Both exhibit a distorted trigonal-bipyramidal geometry with P-Fe-P angles of 107.3, 110.3, and 134.6° in **5a** and 105.4, 112.3, and 135.0° in **5b**, consistent with a Jahn–Teller distortion arising from having three electrons in degenerate orbitals of d_{xy}, and $d_{x^2-y^2}$ character. The main difference between **5a** and **5b** is that the sodium counterion in **5a** is terminally bound to the N_2 unit, while the complexed cation [Na[12]crown-4)$_2$]$^+$ is isolated in **5b**, which appears to have little effect on the N–N distance (1.149(2) in **5a** versus 1.144(3) in **5b**).

To test the ability of the (TPB)Fe platform to support a two-electron redox process, compound **3** was treated with *p*-methoxyphenyl azide (benzene, room temperature) to yield the stable diamagnetic imido complex **6** (Scheme 1), which has the unusual (Fe–B)^6 configuration. Compound **6** was thoroughly characterized by multinuclear NMR spectroscopy, UV/Vis spectroscopy, and XRD.[16] Two independent molecules were found in the asymmetric unit of **6**, with an average Fe–N distance (1.668 Å) only marginally longer than that of 1.651 Å found in the pseudotetrahedral iron(II) imide [(BP$_3$)Fe≡N(1-Ad)][nBu$_4$N] ((BP$_3$) = [PhB(CH$_2$PPh$_2$)$_3$]$^-$, 1-Ad = 1-adamantyl).[5c] The large Fe-N-C angle (170.2°) additionally supports the description of the Fe–N linkage as a triple bond. The very long Fe–B distance (2.608 Å) causes us to describe the coordination geometry as derived from pseudotetrahedral, as confirmed by a sum of P-Fe-P angles (333.0°) close to the value of 328.4° for a regular tetrahedron.

More insight into the electronic structure of **6** is gained by considering the frontier Kohn–Sham orbitals (Figure 2) obtained from DFT calculations[18] on the closely related compound [(TPB)Fe≡NPh]. The HOMO is of d_{z^2} parentage but still has some Fe–B σ-bonding character arising from a stabilizing interaction with the empty boron-centered orbital. Two orbitals of d_{xy} and $d_{x^2-y^2}$ parentage, respectively, lie within a 0.4 eV interval of the HOMO. Accordingly, the two orbitals of π-antibonding character derived from d_{xz} and d_{yz} are unoccupied, consistent with the presence of an Fe≡NAr triple bond.

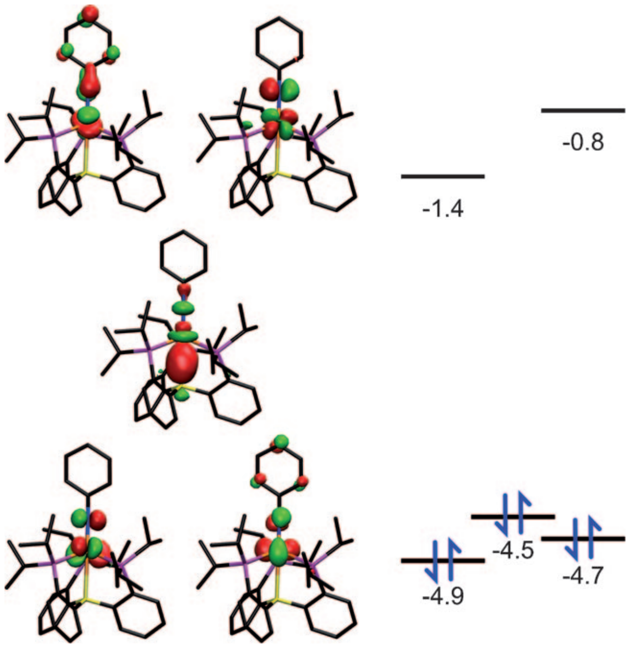

Figure 2. Frontier Kohn–Sham orbitals of [(TPB)Fe≡NPh] calculated at the B3LYP/6-31G(d) level. Energies in electron volts.

While metallaboratranes have now been isolated for all transition metals from groups 8 to 11,[20] examples of metal-based reactivity in such compounds are scarce. These include oxidative cleavage of Fe–B[21] and Ni–B[22] bonds, as well as reversible B–H bond formation.[23] To our knowledge, the only previously known redox reactions that preserve the metal–boron bond are deprotonation of the $(\text{Pt–B})^8$ cation $[\{\text{B(mim}^{\text{Me}})_3\}\text{Pt(H)(PPh}_3)]^+$ (mim^{Me} = 2-mercapto-1-methylimazolyl) and oxidative additions to the resulting $(\text{Pt–B})^{10}$ complex $[\{\text{B(mim}^{\text{Me}})_3\}\text{Pt(PPh}_3)]$.[24] The series of compounds described herein is unique in that they span four different electronic configurations ($(\text{Fe–B})^6$ in **6** to $(\text{Fe–B})^9$ in **5a,b**) that can be interconverted by formal one- or two-electron processes.

This property largely stems from the ability of the Fe–B interaction to respond to changes in the electronic properties of the metal center, as is evident from the structural properties summarized in Table 1 and the schematic orbital correlation diagram depicted in Figure 3. In the highly reduced compound **5a**, the short Fe–B distance (2.311(2) Å) and strong pyramidalization of the boron atom ($\Sigma\sphericalangle$(C-B-C) = 329.8°) indicate a strong metal–boron interaction that pulls the iron center into the P_3 plane ($\Sigma\sphericalangle$(P-Fe-P) = 352.2°). As a result, the σ(Fe–B) bonding orbital is expected to be lower in energy than the d orbitals, and the electronic structure of **5a,b** parallels that of a d^7 metal in a trigonal-bipyramidal geometry. This is in accord with the covalent bond classification (CBC) system,[19] in which all σ-bonding electrons are subtracted from the d-electron count. In contrast, the Fe–B distance of 2.608 Å in imido iron(II) complex **6** points to a weak interaction resulting in a pseudotetrahedral geometry ($\Sigma\sphericalangle$(P-Fe-P) = 333.0°) in which the two sets of d orbitals of e parentage are inverted as compared to **5a,b**. The similarity between this orbital diagram and that previously obtained for the related pseudotetrahedral iron(II) imide $[(\text{BP}_3)\text{Fe≡N-(1-Ad)}]n\text{Bu}_4\text{N}$[5c] suggests that **6** closely resembles a low-spin d^6 compound, even though the d_{z^2} orbital has some σ-bonding character. The geometry of **2**—and presumably **3**—is intermediate between the trigonal-bipyramidal and pseudotetra-

Table 1: Geometrical features of **2**, **4**, **5a,b**, and **6** relevant to the Fe–B interaction.

Compound	*d*(Fe–B) [Å]	$\Sigma\sphericalangle$(C-B-C) [°]	$\Sigma\sphericalangle$(P-Fe-P) [°]
2	2.459	341.9	341.9
4	2.227	352.0	357.4
5a	2.311	329.8	352.2
5b	2.293	331.0	352.7
6	2.608[a]	338.3[a]	333.0[a]

[a] Averaged over two independent molecules.

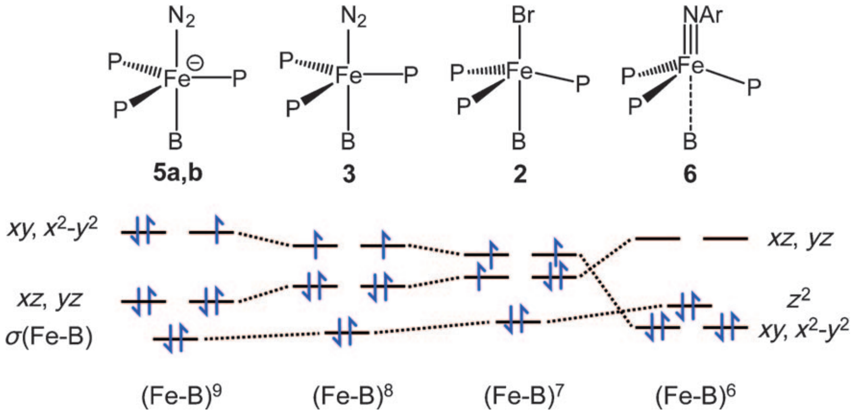

Figure 3. Schematic orbital correlation diagram for **2**, **3**, **5a,b**, and **6**.

hedral extremes, and the consequent energetic proximity of the two sets of degenerate orbitals is consistent with the $S = 3/2$ ground state of **2.** Finally, neutral carbonyl complex **4** adds another twist with η^4-BCCP coordination that results in an Fe–B distance (2.227(2) Å) even shorter than that in **5a**,**b**. It is noteworthy that all observed Fe–B bond lengths are significantly longer than that of 2.108 Å in the octahedral complex [{B(mim^{tBu})$_3$}Fe(CO)$_2$] (mim^{tBu} = 2-mercapto-1-*tert*-butylimidazolyl).[21] This can be attributed to the lower angular flexibility of the tertiary phosphine donors of TPB (av C(Ar)-P-Fe = 107.5° in **5a**) as compared to the terminal thione (av C-S-Fe = 99.2° in the B(mim^{tBu})$_3$ ligand of [{B(mim^{tBu})$_3$}Fe(CO)$_2$].

It is of interest to compare the chemistry of the neutral TPB ligand with that of the closely related anionic SiP$^{iPr}{}_3$ (SiP$^{iPr}{}_3$ = [2-(iPr$_2$P)C$_6$H$_4$]$_3$Si$^-$).[11] Both ligands are able to stabilize low-valent iron N$_2$ compounds in a trigonal-bipyramidal geometry, and the degree of activation of N$_2$ is similar for compounds having the same electrical charge: $\tilde{\nu}_{NN} = 2011$ and $1905\ cm^{-1}$ for **3** and **5b** versus 2008 and $1920\ cm^{-1}$ for [(SiP$^{iPr}{}_3$)Fe(N$_2$)] and [(SiP$^{iPr}{}_3$)Fe(N$_2$)][Na[12]crown-4)$_2$], respectively. This observation may at first appear surprising, because the SiP$^{iPr}{}_3$ complexes have one more valence electron than their TPB counterparts, but it can be easily understood by considering that the additional electron lies in an orbital of d_{xy} or $d_{x^2-y^2}$ parentage that has no overlap with the σ and π orbitals of N$_2$. A major difference between TPB and SiP$^{iPr}{}_3$ resides in the greater flexibility of the Fe–B bond length compared to Fe–Si,[11] which explains why the triply bonded imido complex **6** is stable, while imido iron complexes of SiP$^{iPr}{}_3$ are short-lived intermediates in the formation of azo compounds from aryl azides.[12,25]

In summary, the TPB ligand has been shown to stabilize both low-valent iron dinitrogen complexes and a mid-valent imido species with an Fe≡NAr triple bond, thanks to its ability to shuttle between trigonal-bipyramidal and pseudotetrahedral geometries by elongation of the apical iron-boron bond. The adaptability of the coordination environment in ferraboratranes derived from tris(phosphino)borane ligands makes them promising candidates as functional models for biological N$_2$ fixation, which will be the subject of further investigation.

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Keywords: iron · metallaboratranes · multiple bonds · nitrogen fixation · phosphinoborane ligands

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