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Tripodal $P_3^XFe-N_2$ Complexes ($X = B, Al, Ga$): Effect of the Apical Atom on Bonding, Electronic Structure, and Catalytic N_2 -to- NH_3 Conversion

Javier Fajardo Jr., Jonas C. Peters

Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, United States

Abstract

Terminal dinitrogen complexes of iron ligated by tripodal, tetradentate P_3^X ligands ($X = B, C, Si$) have previously been shown to mediate catalytic N_2 -to- NH_3 conversion (N_2RR) with external proton and electron sources. From this set of compounds, the tris(phosphino)borane (P_3^B) system is most active under all conditions canvassed thus far. To further probe the effects of the apical Lewis acidic atom on structure, bonding, and N_2RR activity, $Fe-N_2$ complexes supported by analogous group 13 tris(phosphino)alane (P_3^{Al}) and tris(phosphino)gallane (P_3^{Ga}) ligands are synthesized. The series of $P_3^XFe-N_2^{[0/1-]}$ compounds ($X = B, Al, Ga$) possess similar electronic structures, degrees of N_2 activation, and geometric flexibility as determined from spectroscopic, structural, electrochemical, and computational (DFT) studies. However, treatment of $[Na(12-crown-4)_2][P_3^XFe-N_2]$ ($X = Al, Ga$) with excess acid/reductant in the form of $HBAr^F_4/KC_8$ generates only 2.5 ± 0.1 and 2.7 ± 0.2 equiv of NH_3 per Fe , respectively. Similarly, the use of $[H_2NPh_2][OTf]/Cp^*_2Co$ leads to the production of 4.1 ± 0.9 ($X = Al$) and 3.6 ± 0.3 ($X = Ga$) equiv of NH_3 . Preliminary reactivity studies confirming P_3^XFe framework stability under pseudocatalytic conditions suggest that a greater selectivity for hydrogen evolution versus N_2RR may be responsible for the attenuated yields of NH_3 observed for $P_3^{Al}Fe$ and $P_3^{Ga}Fe$ relative to P_3^BFe .

Graphical Abstract

Corresponding Author: Jonas C. Peters – *Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, United States*; jpeters@caltech.edu.

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c03354>.

Experimental details, synthetic procedures, and compound characterization data, including NMR spectra, EPR spectra, IR spectra, cyclic voltammograms, XRD structures, XRD tables, and DFT optimized coordinates (PDF)

Accession Codes

CCDC 2043743–2043748 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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INTRODUCTION

While it was not long ago that well-defined molecular N₂-to-NH₃ conversion (N₂RR) catalysts were scarce and limited to Fe- and Mo-based transition metal complexes,^{1–3} significant progress in the development of N₂RR catalysts in recent years has resulted in their increase in number, diversity, and efficiency.⁴ These advancements have largely been made possible by a combination of systematic reactivity studies, in-depth mechanistic investigations, and structure–activity surveys. Notably, the latter have been instrumental in improving the performance of Fe and Mo N₂RR catalysts, as well as in the discovery of new catalytic systems based on other metals. For instance, building upon their first report on (PNP)Mo-mediated N₂RR,² Nishibayashi and co-workers have performed systematic pincer ligand variations to develop a number of related (PXP)Mo complexes (X = N, P, C) capable of catalyzing N₂RR with more mild proton and electron sources, higher turnover numbers, and/or greater selectivities.⁵ Similarly, metal center substitution of known Fe N₂-to-NH₃ conversion catalysts by V⁶ or the nonbiologically relevant metals Co,⁷ Ru,⁸ and Os⁸ has led to new catalytic systems supported by the same ligand platforms and featuring comparable N₂RR efficiencies. These systematic comparative studies (see Chart 1 for group 8 systems) are a critical component to gaining a better understanding of key N₂RR catalyst design principles.

In this context, extensive investigations carried out by our group on the dinitrogen coordination chemistry and N₂RR catalysis by tripodal P₃^X-ligated Fe complexes ($\text{P}_3^{\text{B}} = (\text{o-}^i\text{Pr}_2\text{PC}_6\text{H}_4)_3\text{B}$; $\text{P}_3^{\text{C}} = [(\text{o-}^i\text{Pr}_2\text{PC}_6\text{H}_4)_3\text{C}]^-$; $\text{P}_3^{\text{Si}} = [(\text{o-}^i\text{Pr}_2\text{PC}_6\text{H}_4)_3\text{Si}]^-$) have established that the identity of the apical atom (X) influences the observed N₂RR versus HER (hydrogen evolution reaction) selectivity.^{3,9–13} Notably, from this series, the $\text{P}_3^{\text{B}}\text{Fe}$ system is the most efficient N₂RR catalyst under all conditions canvassed thus far, highlighting the privileged role of the group 13 Lewis acidic borane. This enhanced efficacy is in part attributed to the electron-accepting nature and geometric flexibility of the $\text{Fe} \rightarrow \text{B}$ interaction, which helps stabilize both low-valent and Fe–N multiply bonded species proposed to be intermediates of a $\text{P}_3^{\text{B}}\text{Fe}$ -mediated N₂ fixation cycle.^{14–20}

Given the importance of the boron center, a common question that has surfaced concerns the effect of X(III) apical atom substitution in the P_3^XFe framework, with respect to bonding, electronic structure, and N_2RR activity (Chart 1). To address this issue, herein we report the synthesis and characterization of a series of P_3^XFe-Br and $P_3^XFe-N_2^{[0/1-]}$ compounds supported by analogous group 13 tris(phosphino)alane ($P_3^{Al} = (o\text{-}iPr_2PC_6H_4)_3Al$)²¹ and tris(phosphino)gallane ($P_3^{Ga} = (o\text{-}iPr_2PC_6H_4)_3Ga$)²² ligands. Structural, spectroscopic, electrochemical, and computational studies reveal that all three P_3^XFe systems ($X = B, Al, Ga$) possess similar electronic structures, degrees of N_2 activation, and geometric flexibility. However, $P_3^{Al}Fe$ and $P_3^{Ga}Fe$ display significantly lower N_2RR efficiencies than P_3^BFe . Preliminary reactivity studies show that all P_3^XFe frameworks are robust under the catalytic conditions employed, suggesting that a greater selectivity for competing HER may be responsible for the attenuated NH_3 yields observed for the former.

RESULTS AND DISCUSSION

Synthesis and Characterization of $P_3^XFe-N_2^{[0/1-]}$ Complexes.

As an entry point into the desired P_3^XFe dinitrogen chemistry, we sought to prepare an Fe(I) halide precursor similar to our approach in the related P_3^BFe system. Whereas P_3^BFe-Br (**2a**) can readily be prepared by heating a mixture of P_3^B (**1a**), Fe(0), and $FeBr_2$ to 90 °C in THF,¹⁴ P_3^{Al} (**1b**) and P_3^{Ga} (**1c**) proved thermally unstable under these conditions. Instead, stirring **1b** and **1c** with $FeBr_2$ in benzene, followed by one-electron reduction with sodium amalgam (Na(Hg)), afforded the corresponding P_3^XFe-Br complexes **2b** and **2c** as bright green solids in moderate isolated yield (Scheme 1). Like P_3^BFe-Br , both P_3^XFe-Br derivatives feature paramagnetically shifted 1H NMR resonances, solution magnetic moments of 4.3 μ_B (**2b**) and 4.2 μ_B (**2c**), and low-temperature rhombic EPR spectra (toluene glass, 10 K), consistent with an $S = 3/2$ ground state.

The long Fe–P bond lengths in the solid-state structures of **2b** (2.4603(3) Å) and **2c** (2.4690(3) Å) are also consistent with this high-spin configuration assignment (Figure 1). It is noteworthy that the Fe–Br bond in **2b** and **2c** remains intact, as previous examples of P_3^{Al} and P_3^{Ga} coordination to CuCl and AuCl(SMe₂) have instead yielded the zwitterionic complexes $P_3^{Al-Cl}Cu$ and $P_3^{X-Cl}Au$ ($X = Al, Ga$) resulting from halide abstraction by the apical X atom.^{21,22} For comparison, reaction of P_3^B with these metal precursors instead yields P_3^BCu-Cl and P_3^BAu-Cl .²³ These differences in reactivity suggest that Al(III) and Ga(III) are stronger Lewis acids than B(III) within the P_3^X framework.

Reduction of **2b** and **2c** with Na(Hg) in benzene under a nitrogen atmosphere results in the formation of mononuclear dinitrogen complexes of the form $P_3^XFe-N_2$ ($X = Al$ (**3b**), $X = Ga$ (**3c**)) (Scheme 1). **3b** and **3c** display intense, diagnostic infrared (IR) absorption bands at $\nu(NN) = 2003$ and 1997 cm^{-1} , respectively, where the end-on N_2 ligand is only slightly more activated than in the related $P_3^BFe-N_2$ (**3a**, 2011 cm^{-1})¹⁴ and iron alumatrane (AltraPhos)Fe– N_2 (**6**, 2010 cm^{-1} , AltraPhos = $Al[N(o\text{-}C_6H_4NCH_2P^iPr_2)_3]$)²⁴ complexes and is moderately labile under vacuum.

The terminal nature of the N_2 moiety was further corroborated by X-ray diffraction (XRD) analysis of single crystals of **3b** and **3c** (Figure 1). The dinitrogen ligand in **3b** and **3c**

exhibits a $d(\text{N-N})$ of 1.0616(17) and 1.118(6) Å, respectively, consistent with minimal N_2 activation. In the solid state, **3b** and **3c** feature two short (**3b**: 2.3781(4), 2.3843(4) Å; **3c**: 2.3898(5), 2.3969(3) Å) and one comparable (**3b**: 2.4220(4) Å; **3c**: 2.4342(5) Å) Fe–P contact compared to **2b** and **2c**. This contraction in the Fe–P bonds is in line with increased π -backdonation from the Fe center to the phosphines upon reduction, as well as the $S = 1$ ground state adopted by **3b** (3.1 μ_{B}) and **3c** (2.8 μ_{B}) in room temperature C_6D_6 solutions. XRD characterization of **3b** and **3c** allows for a structural comparison across the series of compounds **2–4** (*vide infra*) that span the formal oxidation states Fe(I) to Fe(–I). This contrasts with the $\text{P}_3^{\text{B}}\text{Fe}$ system, where the XRD structure of **3a** could not be authenticated due to severe twinning.¹⁴

Treatment of $\text{P}_3^{\text{X}}\text{Fe-Br}$ or $\text{P}_3^{\text{X}}\text{Fe-N}_2$ with excess Na(Hg) in the more polar solvent THF leads exclusively to the anionic $S = 1/2$ complex $[\text{Na}(\text{THF})_3][\text{P}_3^{\text{X}}\text{Fe-N}_2]$ ($\text{X} = \text{Al}$ (**4b**), $\text{X} = \text{Ga}$ (**4c**)) (Scheme 1). Like $[\text{Na}(\text{THF})_3][\text{P}_3^{\text{B}}\text{Fe-N}_2]$ (**4a**), **4b** and **4c** feature a phase-dependent Lewis acid–base interaction between N_β and the Na^+ counterion that can be monitored by IR spectroscopy.

Whereas in the solid state **4b** and **4c** exhibit a single $\nu(\text{NN})$ at 1883 and 1879 cm^{-1} , in THF two bands (**4b**: 1879, 1922 cm^{-1} ; **4c**: 1878, 1920 cm^{-1}) are observed as a result of solvation of the Na^+ ion to yield some population of the free anion $\text{P}_3^{\text{X}}\text{Fe-N}_2^-$. Encapsulation of Na^+ by treatment of **4b** and **4c** with two equivalents of 12-crown-4 (12-c-4) yields $[\text{Na}(12\text{-c-4})_2][\text{P}_3^{\text{Al}}\text{Fe-N}_2]$ (**5b**) and $[\text{Na}(12\text{-c-4})_2][\text{P}_3^{\text{Ga}}\text{Fe-N}_2]$ (**5c**), respectively, which give rise to only the higher energy vibration. Compound **4a** (1877, 1918 cm^{-1}),¹⁴ compound **5a** (1918 cm^{-1}),¹⁴ and the reduced iron alumatrane, $[\text{K}(18\text{-crown-6})][(\text{AltraPhos})\text{Fe-N}_2]$ (**7**, 1925 cm^{-1}),²⁵ display similar degrees of N_2 activation to **5b** and **5c**.

The intimate ion pair in salts **4b** and **4c** was also authenticated by their corresponding solid-state structure, where the capping Na^+ is coordinated by three additional THF molecules (Figure 1). As was the case in going from the formally Fe(I) to Fe(0) complexes, the Fe–P bond lengths in **4b** (2.2751(6) Å) and **4c** (2.2824(5) Å) are significantly contracted from those of **3b** and **3c**, respectively. Increased π -backbonding into the N_2 unit also leads to shorter Fe–N (**4b**: 1.769(3) Å; **4c**: 1.759(5) Å) and longer N–N (**4b**: 1.134(4) Å; **4c**: 1.141(4) Å) distances in **4b** and **4c**. Complexes **4a** ($d(\text{Fe-N}) = 1.775$ Å; $d(\text{N-N}) = 1.149$ Å) and **7** ($d(\text{Fe-N}) = 1.783$ Å; $d(\text{N-N}) = 1.135$ Å) possess comparable Fe– N_2 bond metrics, in line with their similar IR profiles.

Electronic Structure and Bonding in $\text{P}_3^{\text{X}}\text{Fe}$ Systems.

While isostructural alkyl ($\text{X} = \text{C}$),^{9,10} silyl ($\text{X} = \text{Si}$),¹⁰ and borane ($\text{X} = \text{B}$)^{3,10,11,13} $\text{P}_3^{\text{X}}\text{Fe-N}_2^-$ complexes have all demonstrated the capacity to facilitate catalytic N_2RR , the $\text{P}_3^{\text{B}}\text{Fe}$ system affords the highest efficiencies under all conditions canvassed. This can be attributed, in part, to the greater electronic and geometric flexibility of the dative $\text{Fe} \rightarrow \text{B}$ interaction, which allows access to both reduced Fe– N_2 and Fe–N multiply bonded species that may be traversed along an Fe-mediated nitrogen fixation cycle. Storage of additional electron density in the Fe–B manifold stabilizes the low-valent states, and shuttling of the iron center between trigonal bipyramidal and pseudotetrahedral geometries affords access to

intermediates with different electronic structures.^{14–20} Accordingly, the catalytically relevant species $\text{Fe-N}_2^{[0/1-2-]}$,^{14,18} $\text{Fe=NN}_2\text{H}_2^{[1+/0]}$,^{17–19} and $\text{Fe}\equiv\text{N}^{[1+]}$ ¹⁸ have proven accessible on the P_3^{B} scaffold. Given the significant role of the $\text{Fe} \rightarrow \text{B}$ interaction in this respect, we sought to determine whether the $\text{Fe} \rightarrow \text{Al}$ and $\text{Fe} \rightarrow \text{Ga}$ bonds would behave similarly.

The bonding and electronic structures of $\text{P}_3^{\text{B}}\text{Fe-N}_2^{[0/1-]}$ and $(\text{AltraPhos})\text{Fe-N}_2^{[0/1-]}$ have previously been elucidated through spectroscopic and computational methods.^{14,24–26} In short, the bonding in these complexes is best described as involving an $\text{Fe} \rightarrow \text{X(III)}$ dative interaction where the apical Lewis acidic atom serves to lower the energy of the $\sigma(\text{Fe-X})$ orbital of Fe d_{z^2} and X p_z parentage below that of the d_{xy} , $x^2 - y^2$ set in a typical trigonal bipyramidal orbital scheme. Therefore, reduction of **3** to **4a/5a** and **6** to **7** is primarily Fe centered, giving rise to formally $\text{Fe}(-\text{I})$ species with electronic configurations $(d_{xz}, yz)^4(\sigma(\text{Fe-X}))^2(d_{xy}, x^2 - y^2)^3$ and a substantial Fe-to-X backbond.²⁷

A consequence of having three electrons in a set of degenerate orbitals of d_{xy} and $d_{x^2 - y^2}$ parentage is a Jahn–Teller active state. Distortion from C_3 symmetry is clearly reflected by the asymmetry of the P–Fe–P angles in the solid-state structures of **4a** (two independent molecules present in asymmetric unit; 107.3°, 110.3°, 134.6° and 113.4°, 114.1°, 124.7°), **5a** (105.4°, 112.3°, 135.0°), and **7** (107.1°, 111.9°, 131.1°). In contrast, **4b** and **4c** crystallize in the trigonal space group $R\bar{3}$, being 3-fold symmetric about the apical axis defined by the X–Fe– N_2 unit. While this may suggest that **4b** and **4c** possess an electronic structure that differs from that of **4a/5a**, density functional theory (DFT) geometry optimization and single-point energy calculations on the anions $\text{P}_3^{\text{Al}}\text{Fe-N}_2^-$ and $\text{P}_3^{\text{Ga}}\text{Fe-N}_2^-$ reveal a relaxation to a Jahn–Teller distorted configuration with computed P–Fe–P angles of 111°, 112°, 125° and 111°, 112°, 126°, respectively. Corresponding spin density plots show that this distortion also arises from localization of the unpaired electron in an Fe-based d-orbital of xy symmetry (Figure 2; Mulliken spin density on Fe: X = B = 1.08; X = Al = 1.09; X = Ga = 1.10). X-band EPR spectra of **4b** and **4c** collected in 2-methyltetrahydrofuran glass (77 K) display axial signals with no discernible hyperfine coupling to ^{27}Al or $^{69/71}\text{Ga}$ nuclei. Negligible spin leakage onto the B, Al, and Ga atoms is detected computationally. In conjunction with the measured solution magnetic susceptibilities and computed frontier molecular orbital schemes (Figure 2), these data indicate that $\text{P}_3^{\text{X}}\text{Fe-N}_2^{[0/1-]}$ (X = Al, Ga) possess electronic structures similar to those of $\text{P}_3^{\text{B}}\text{Fe-N}_2^{[0/1-]}$ and $(\text{AltraPhos})\text{Fe-N}_2^{[0/1-]}$.^{14,24–26} The perfect trigonal symmetry exhibited by **4b** and **4c** in the solid state is likely the result of crystal packing effects.²⁸

Having concluded that significant $\text{Fe} \rightarrow \text{X}$ σ -backdonation is operative in $\text{P}_3^{\text{Al}}\text{Fe-N}_2^{[0/1-]}$ and $\text{P}_3^{\text{Ga}}\text{Fe-N}_2^{[0/1-]}$, we next sought to determine the strength of this interaction relative to that in $\text{P}_3^{\text{B}}\text{Fe-N}_2^{[0/1-]}$.²⁷ To do so, we explored the redox behavior of **3b** and **3c** by cyclic voltammetry. **3b** and **3c** display reversible $\text{Fe-N}_2^{[0/1-]}$ redox couples centered at –1.97 V and –1.99 V vs $\text{Fc}^{[1+/0]}$ (Fc = ferrocene), respectively (Figure 3). Under identical conditions, the analogous reduction event for **3a** occurs at the slightly more negative potential of –2.19 V.¹⁴ The scan rate dependence of all three couples is consistent with a diffusion-controlled process. For comparison, the observed trend in the $\text{P}_3^{\text{X}}\text{Fe-N}_2^{[0/1-]}$ redox potentials is also in

accordance with the theoretically^{29,30} and experimentally³¹ determined acceptor ability of XPh_3 according to the order $X = Al > Ga > B$.

The ca. 200 mV anodic shift in the $Fe-N_2^{[0/1-]}$ reduction potential for **3b** and **3c** relative to **3a** suggests that exchange of the apical Lewis acidic element in the P_3^X scaffold results in only modest electronic perturbations at the iron center. This is in line with the $\nu(NN)$ vibrational data for $P_3^XFe-N_2^{[0/1-]}$ complexes, which reveal similar degrees of N_2 activation, as well as with electronic structure calculations, which show that the $Fe \rightarrow X$ interaction directly lowers the energy of the $Fe\ d_{z^2}$ orbital but only indirectly influences the energy of the singly occupied molecular orbital (SOMO) through σ -inductive withdrawal of electron density from the Fe center. Interestingly, the reversible (AltraPhos) $Fe-N_2^{[0/1-]}$ reduction wave occurs at $-2.08\ V$ vs $Fe^{[1+/0]}$,²⁴ suggestive of a weaker $Fe \rightarrow Al$ interaction than that in **3b**. We attribute this difference to competition between both Fe and N_{apical} for donation into the empty $Al\ p_z$ orbital in the former.

To determine whether geometric flexibility is also conserved in the $P_3^{Al}Fe$ and $P_3^{Ga}Fe$ platforms, we turned our attention to the XRD structures of **2–4**. With the exception of the $Fe \rightarrow X$ interaction, all isostructural complexes exhibit comparable bond distances and angles, irrespective of the identity of the apical Lewis acidic atom (Table S3). However, inspection of the $Fe-X$ distances reveals that all three systems possess similar degrees of flexibility (Table 1). The overall changes in these axial bond lengths upon reduction of P_3^XFe-Br to $[Na(THF)_3][P_3^XFe-N_2]$ are $0.149\ \text{\AA}$ ($X = B$), $0.177\ \text{\AA}$ ($X = Al$), and $0.177\ \text{\AA}$ ($X = Ga$). Moreover, the value calculated for the ratio (r) of the $Fe-X$ bond length to the sum of the respective covalent radii,^{32,33} which accounts for the differing sizes of B , Al , and Ga , bares an overall net difference of $r = 0.07$ in each case, suggesting that the $Fe-X$ bond is equally flexible in all three systems.

The decreasing values of r in the order **2** > **3** > **4** are also indicative of a stronger $Fe-X$ bond upon reduction.³⁴ As expected, such an increase in the dative interaction is accompanied by a greater pyramidalization at the $X(III)$ apical atom and more trigonal planar geometry about Fe (Table 1). Interestingly, while the r values of $P_3^{Al}Fe$ and $P_3^{Ga}Fe$ are consistently lower than those of P_3^BFe , alluding to a stronger $Fe \rightarrow Al$ and $Fe \rightarrow Ga$ interaction relative to $Fe \rightarrow B$, the slightly more pyramidalized geometry about boron across the series would seem to imply it forms the strongest $Fe-X$ bond. This discrepancy likely stems from the difference in atomic sizes between B , Al , and Ga , as well as steric constraints imposed by the cage structure. This has also been observed in related P_3^XPd compounds ($X = B, In$), where the larger size of In prevents pyramidalization that accurately reflects the strength of the donor–acceptor interaction. While computations and the smaller $r = 0.93$ value for $P_3^{In}Pd$ indicate it has a stronger $Pd \rightarrow X$ interaction than P_3^BPd ($r = 1.01$), the indium center resides in a less pyramidalized environment than boron ($\angle C-In-C = 354.9^\circ$; $\angle C-B-C = 341.8^\circ$).^{23,35} Therefore, in accord with the electrochemical data, we favor a bonding scheme where the $Fe \rightarrow X$ donor–acceptor interaction is stronger for $X = Al, Ga$ than for $X = B$. This assignment is also validated computationally, where normalized Löwdin bond orders (with respect to the corresponding $Fe-B$ bond) of 1.08, 1.05, 1.05, and 1.02 are calculated for **3b**, **3c**, $P_3^{Al}Fe-N_2^-$, and $P_3^{Ga}Fe-N_2^-$, respectively.

N₂RR Activity.

Having concluded that the P₃^XFe platforms (X = B, Al, Ga) exhibit similar electronic structures, flexibility, and degrees of N₂ activation, we reasoned that **5b** and **5c** might function as competent catalysts for N₂RR. Thus, we subjected these compounds to the catalytic conditions that have proved most fruitful for the P₃^BFe system, namely, treatment with excess [H(OEt)₂][BAr^F₄] (HBar^F₄, BAr^F₄[−] = tetrakis(3,5-bis(trifluoromethyl)phenyl)borate)/KC₈^{3,10} or [H₂NPh₂][OTf]/Cp*₂Co¹¹ as the acid/reductant source at −78 °C in diethyl ether (Et₂O). Under the former conditions, **5b** and **5c** generate 2.5 ± 0.1 (17 ± 1% selectivity based on H⁺) and 2.7 ± 0.2 (17 ± 1% efficiency) equiv of NH₃ per Fe, respectively (Table 2, entries 2 and 3). Moving to the [H₂NPh₂][OTf]/Cp*₂Co combination, which is in the activity regime with the highest N₂-to-NH₃ selectivity observed for P₃^BFe,¹³ results in only modest improvements, with **5b** and **5c** producing 4.1 ± 0.9 (27 ± 6% based on acid) and 3.6 ± 0.3 (24 ± 2% efficiency) equiv of NH₃ per Fe (Table 2, entries 5 and 6). Hydrazine is not detected under either set of conditions. These efficiencies are appreciably lower than those of P₃^BFe under similar conditions (Table 2, entries 1 and 4),^{3,11} and suggest that, in addition to the extent of N₂ activation and flexibility of the Fe–X linkage, other factors associated with the identity of the apical atom in the P₃^X scaffold play an influential role in the nitrogen fixation process.

In order to discern whether the divergent N₂RR catalytic profiles of **5a–c** are a consequence of catalyst deactivation/decomposition, the Fe speciation present after exposure of the complexes to 10 equiv of acid and 12 equiv of reductant was examined. P₃^BFe is known to be rather robust under both sets of catalytic conditions, with substantial active (pre)catalyst remaining at the conclusion of reactions as evidenced by Mössbauer spectroscopic studies and substrate reloading experiments.^{10,11} Indeed, NMR and IR analysis of the postreaction of **5a** with HBar^F₄/KC₈ reveals [M(solv)_x][P₃^BFe–N₂] (solv = solvent) and (P₃^B)(μ–H)Fe(L)(H) (L = H₂, N₂) as the major Fe-containing products. Similarly, P₃^BFe–N₂ and (P₃^B)(μ–H)Fe(N₂)(H) are obtained when [H₂NPh₂][OTf]/Cp*₂Co are employed (see Supporting Information for full procedures). Free or decomposed P₃^B is not observed in either instance. It is worth noting that while the hydride-borohydride complex (P₃^B)(μ–H)Fe(L)(H) is an off-path species of P₃^BFe-mediated N₂RR catalysis, in the presence of protons and electrons it can revert back to P₃^BFe–N₃[−] and serve as a competent precatalyst.¹⁰

Analogous experiments utilizing **5b** and **5c** yield slightly different results depending on the conditions. In the case of reaction with 10 equiv of HBar^F₄ and 12 equiv of KC₈, [M(solv)_x][P₃^XFe–N₂] (X = Al, Ga) is the major terminal Fe-containing product, with very little ligand decomposition observed by ³¹P{¹H} NMR spectroscopy. On the other hand, use of [H₂NPh₂][OTf] and Cp*₂Co yields a mixture of compounds that includes P₃^XFe–N₂ (X = Al, Ga) and products of P₃^XFe decomposition. The latter is evidenced by the presence of an intense ³¹P{¹H} NMR signal consistent with uncoordinated phosphine (see Supporting Information).

While the observation of substantially more decomposition when **5b** and **5c** are reacted with [H₂NPh₂][OTf]/Cp*₂Co appears to be at odds with the milder nature of these reagents, and the higher NH₃ yields obtained relative to HBar^F₄/KC₈ in catalytic reactions, this can be

rationalized by the differing strength of the reductants and reactivity of $P_3^XFe-N_2$ species with H_2 . Because of the highly reducing nature of KC_8 ($E = -3.0$ V vs $Fc^{[1+/0]}$), and its slight excess in the reactions, after complete acid consumption, any residual KC_8 is anticipated to reduce $P_3^XFe-N_2$ to $P_3^XFe-N_2^-$, which is unreactive toward H_2 . Additionally, conversion of $(P_3^B)(\mu-H)Fe(L)(H)$ to $P_3^BFe-N_2^-$ is viable under the $HBArF_4/KC_8$ conditions.¹⁰ In contrast, the reduction potential of Cp^*_2Co ($E = -1.96$ V vs $Fc^{[1+/0]}$) is very close to that of the $P_3^XFe-N_2^{[0/1-]}$ couples ($X = B, Al, Ga$). While Cp^*_2Co is capable of reducing $P_3^BFe-N_2$ to $P_3^BFe-N_2^-$ at -78 °C,¹¹ reaction of $P_3^BFe-N_2$ with excess Cp^*_2Co at room temperature does not produce $P_3^BFe-N_3^-$ (as judged by IR spectroscopy). Such observations are consistent with a temperature-dependent redox equilibrium analogous to that reported for $P_3^{Si}Os-N_2^{[0/1-]}$ ($E = -1.97$ V vs $Fc^{[1+/0]}$).⁸ As a consequence, upon allowing the catalyst speciation reactions to warm and stir at room temperature, $P_3^XFe-N_2$ (rather than $[M(solvent)_x][P_3^XFe-N_2]$) is expected to be the dominant species in solution when Cp^*_2Co is employed as the reductant. Reaction of $P_3^XFe-N_2$ with H_2 formed from background and/or catalyzed HER may therefore account for the remaining terminal products observed in the reaction of **5a–c** with $[H_2NPh_2][OTf]/Cp^*_2Co$. $P_3^BFe-N_2$ is known to react with H_2 to cleanly generate $(P_3^B)(\mu-H)Fe(L)(H)$ ($L = H_2, N_2$).³⁶ In turn, treatment of $P_3^{Al}Fe-N_2$ and $P_3^{Ga}Fe-N_2$ with H_2 gives rise to product profiles that match those observed at the end of catalysis model reactions (see Supporting Information).

The above results suggest that $P_3^{Al}Fe$ and $P_3^{Ga}Fe$ platforms are relatively robust under both sets of N_2RR catalytic conditions explored. Although minor catalyst decomposition/deactivation does occur (and is anticipated to be slower at -78 °C), this does not correlate well with the dramatically lower N_2RR efficiencies of $P_3^{Al}Fe$ and $P_3^{Ga}Fe$ versus P_3^BFe , or with the higher NH_3 yields obtained with the $[H_2NPh_2][OTf]/Cp^*_2Co$ conditions. Instead, our findings are suggestive that $P_3^{Al}Fe$ and $P_3^{Ga}Fe$ exhibit a greater selectivity for HER versus N_2RR . Bimolecular coupling of $Fe=NNH_2^{[1+/0]}$ N_2RR intermediates featuring weak N–H bonds is predicted to be an operative unproductive HER pathway for the P_3^BFe system.¹² In this respect, it is worth noting that Fe-imido ($Fe=N-R$; $R = \text{adamantyl}$,¹⁷ *p*-methoxyphenyl¹⁴) and Fe-disilylhydrazido ($Fe=NNSi_2$)^{15,25} complexes that are accessible and stable on the P_3^BFe and (AltraPhos)Fe platforms could not be isolated on the $P_3^{Al}Fe$ and $P_3^{Ga}Fe$ scaffolds despite our attempts to do so.

CONCLUSION

In summary, the series of $P_3^{Al}Fe$ and $P_3^{Ga}Fe$ complexes **2–4** spanning the formal oxidation states $Fe(I)$ to $Fe(-I)$ have been synthesized, isolated, and thoroughly characterized. These complexes expand upon and complement known P_3^XFe ($X = B, C, Si$) N_2RR catalysts. While $P_3^{Al}Fe-N_2^{[0/1-]}$ and $P_3^{Ga}Fe-N_2^{[0/1-]}$ compounds exhibit degrees of N_2 activation, flexibility in their $Fe \rightarrow X$ interactions, and overall electronic structures similar to those of the P_3^BFe system, **5b** and **5c** display significantly attenuated yields of ammonia under analogous N_2RR catalytic conditions. Preliminary reactivity studies confirm that $P_3^{Al}Fe$ and $P_3^{Ga}Fe$ are relatively robust under these conditions, suggesting that the lower NH_3 turnover numbers observed are likely the result of greater HER versus N_2RR selectivity, as opposed to differences in core–framework stability.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

Solid-state structures of **2b**, **3b**, and **4b** with thermal ellipsoids set at 50% probability.

Hydrogen atoms and cocrystallized solvents are omitted for clarity. The XRD structures of **2c**, **3c**, and **4c** are analogous and are provided in the Supporting Information. See Table 1 for select structural data.

Figure 2. DFT-computed molecular orbital diagram (α -manifold, isovalue = 0.06 au) for $P_3^{Al}Fe-N_2^-$ (top) and spin density plots (isovalue = 0.003 au) for $P_3^{Al}Fe-N_2^-$ (bottom left) and $P_3^{Ga}Fe-N_2^-$ (bottom right). Hydrogen atoms are omitted for clarity. The calculated frontier molecular orbitals for $P_3^{Ga}Fe-N_2^-$ are analogous.

Figure 3. Cyclic voltammograms depicting the $\text{P}_3\text{XFe-N}_2^{[0/1-]}$ redox couple of **3a** (red), **3b** (blue), and **3c** (green) at a scan rate of 40 mV/s in THF with 0.1 M $[\text{Bu}_4\text{N}][\text{PF}_6]$ supporting electrolyte.

Scheme 1.
 Synthesis of $\text{P}_3\text{XFe-N}_2^{[0/1-]}$ Complexes

Catalytic N_2 -to- NH_3 conversion (N_2RR) **Chart 1.**Group 8 Metallotrans Systems for Exploring Factors That Impact Catalytic N_2RR Efficacy

Table 1.

Select Structural Data for Complexes 2–4, 6, and 7

	Fe–X ^a	C–X–C ^b	P–Fe–P ^b	r ^c
2a ^d	2.458	341.8	342.7	1.14 ^h
3a ^e	2.417	332.8	345.8	1.12
4a ^d	2.309	330.1	352.3	1.07
2b	2.662	340.8	344.8	1.05 ^h
3b	2.539	336.2	347.8	1.00
4b	2.485	334.8	349.6	0.98
2c	2.666	341.9	345.8	1.05 ^h
3c	2.544	337.8	348.7	1.00
4c	2.489	335.8	350.4	0.98
6 ^f	2.809	351.6	335.0	1.11
7 ^g	2.574	344.4	350.1	1.02

^aUnits of angstroms (Å).^bUnits of degrees (°).^cRatio of the Fe–X bond length to the sum of the covalent radii (Fe: 1.32 Å; B: 0.84 Å; Al: 1.21 Å; Ga: 1.22 Å; from ref 32).^dFrom ref 14. For **4a**, values are an average of two independent molecules in the asymmetric unit.^eValues obtained from a DFT geometry optimized structure.^fFrom ref 24. In solution, the terminal dinitrogen species (AltraPhos)Fe–N₂ is believed to be in equilibrium with its dinitrogen-bridged analogue, [(AltraPhos)Fe]₂(μ–N₂). The structural data presented here is for the latter complex.^gFrom ref 25.^hSee footnote in ref 33.

Table 2.N₂RR Mediated by [Na(12-c-4)₂][P₃^XFe–N₂] Complexes^a

	cat	acid (equiv)	reductant (equiv)	NH ₃ /Fe (equiv)	Yield NH ₃ /H ⁺ (%)
1 ^b	5a	46 ^d	50 ^e	7.0 ± 1.0	46 ± 7
2	5b	46 ^d	50 ^e	2.5 ± 0.1	17 ± 1
3	5c	46 ^d	50 ^e	2.7 ± 0.2	17 ± 1
4 ^c	-	54 ^f	108 ^g	12.8 ± 0.5	72 ± 3
5	5b	46 ^f	50 ^g	4.1 ± 0.9	27 ± 6
6	5c	46 ^f	50 ^g	3.6 ± 0.3	24 ± 2

^aCatalyst, acid, reductant, and Et₂O sealed in a Schlenk tube at –196 °C under an N₂ atmosphere, warmed to –78 °C, and stirred. For runs utilizing HBAr^F₄, reactions were stirred at –78 °C for 1 h, followed by stirring at room temperature for 45 min. For other runs, reactions were allowed to stir and warm to room temperature overnight. Yields are reported as an average of three runs.

^bFrom ref 3.

^cFrom ref 11. P₃BFe⁺ was used as the precatalyst.

^dHBAr^F₄.

^eKC₈.

^f[H₂NPh₂][OTf].

^gCp*₂Co.