

Chapter 1: Introduction and Background to Tris(phosphino)borate

Iron Chemistry

1.1 Tris(phosphino)borates

Since their inception in 1999,¹ the family of (phosphino)borate ligands has emerged as a versatile class of strong-field ligands for both coordination chemistry² and catalysis.³ In general, these ligands feature one, two, or three phosphine donor arms linked to an anionic borate center. As a result of their modular synthesis, a variety of ligand architectures with varying steric and electronic properties may be achieved through substitutions at both the borate and phosphine functionalities.⁴ Selected examples of (phosphino)borates are shown in Figure 1.1.

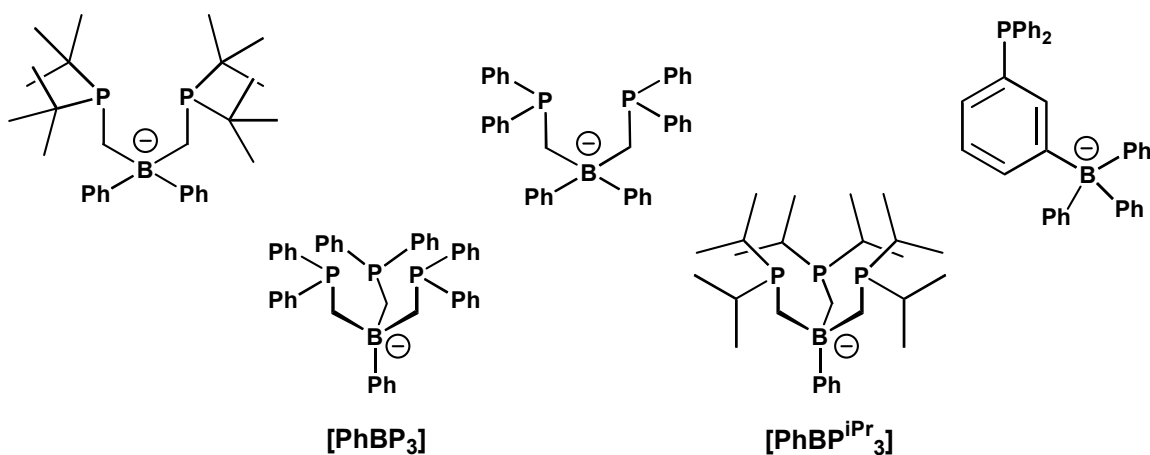


Figure 1.1. Examples of mono, bis, and tris(phosphino)borates.

The tris(phosphino)borates, first generation $[\text{PhBP}_3]$ ($[\text{PhBP}_3] = [\text{PhB}(\text{CH}_2\text{PPh}_2)_3]$) and second generation $[\text{PhBP}^{\text{iPr}}_3]$ ($[\text{PhBP}^{\text{iPr}}_3] = [\text{PhB}(\text{CH}_2\text{P}^{\text{iPr}}_2)_3]$), are isolobal to the *facially* coordinating L_2X architectures that include the well-known families of tris(pyrazolyl)borate ($[\text{Tp}]$), tris(thioether)borate,⁵ cyclopentadienyl (Cp), and pentamethylcyclopentadienyl (Cp^*) ligands. Comparative structural and electronic studies from the Tilley group between Cp^* , Tp^{Me_2} ($\text{Tp}^{\text{Me}_2} = \text{hydrotris}(3,5\text{-dimethylpyrazolyl})\text{borate}$), and $[\text{PhBP}_3]$ suggest that of these three ligands, $[\text{PhBP}_3]$ is the most electron rich and sterically encumbering.⁶ Additionally, the anionic charge of

[PhBP₃] likely renders a more electron-rich scaffold than that of the structurally similar, but charge-neutral triphos ligand (triphos = CH₃C(CH₂PPh₂)₃).⁷ Recent studies with [PhBP^{iPr}₃] suggest that it is even more electron rich than [PhBP₃].^{2f}

From a molecular orbital perspective, the tris(phosphino)borates preserve a threefold symmetric environment about a ligated metal center. The resulting *e* set of orbitals with π -symmetry along the borate-metal vector is therefore well suited for the formation of two energetically equivalent π -bonds with a ligand in the fourth coordination site of the metal center.^{8,9} As long as the resulting π^* orbitals remain vacant (*i.e.*, no more than 6 d-electrons), terminal M \equiv E (E = electronegative element) linkages with these auxiliary scaffolds are anticipated to be stable.^{2c} Indeed a brief survey of the literature demonstrates that threefold symmetry has been exploited for the synthesis of a variety of M \equiv E linkages.¹⁰

The potential for the tris(phosphino)borate framework to engender novel properties at a transition metal center was demonstrated in dramatic fashion with the report of [PhBP₃]CoI, an unprecedented example of *low-spin*, pseudotetrahedral Co(II).¹¹ Of additional interest was the installation of an imido ligand (NR²⁻) onto this [PhBP₃]Co platform.¹² The resulting 4-coordinate, terminal Co(III) imide is diamagnetic and features a triple bond (1 σ + 2 π) between the Co-N linkage. This chemistry is in contrast to what is typically observed for low-coordinate (4-coordinate or lower), late-transition metal ions of the first-row: an increased preference for the population of high-spin electronic ground-states (and thus π^* orbitals),^{13,14} and the formation of bridging species with electronegative elements.¹⁵ Ensuing work by the groups of Meyer¹⁶ and Theopold¹⁷ established the ability for tris(carbene) and tris(pyrazolyl)borate ligands, respectively, to

also facilitate the formation of 4-coordinate, Co(III) imides. Of the three systems, however, the tris(phosphino)borate-supported is the most stable.

Electronically, the typical 3 over 2 molecular orbital diagram anticipated for a 4-coordinate tetrahedral species does not provide for an accurate description of the $[\text{PhBP}_3]\text{Co}(\text{III})$ imides. More consistent is a 2 over 3 splitting diagram, similar to that obtained for a d^6 sandwich compound.¹⁸ Consequently, it was hypothesized that a *low-spin*, $[\text{PhBP}_3]$ supported terminal Fe(III) imide should be stable, considering the relatively non-bonding nature of the anticipated SOMO (Figure 1.2). Furthermore, the inherent metalloradical character of this system may yield enhanced chemical reactivity when compared with its closed shell Co(III) congener.

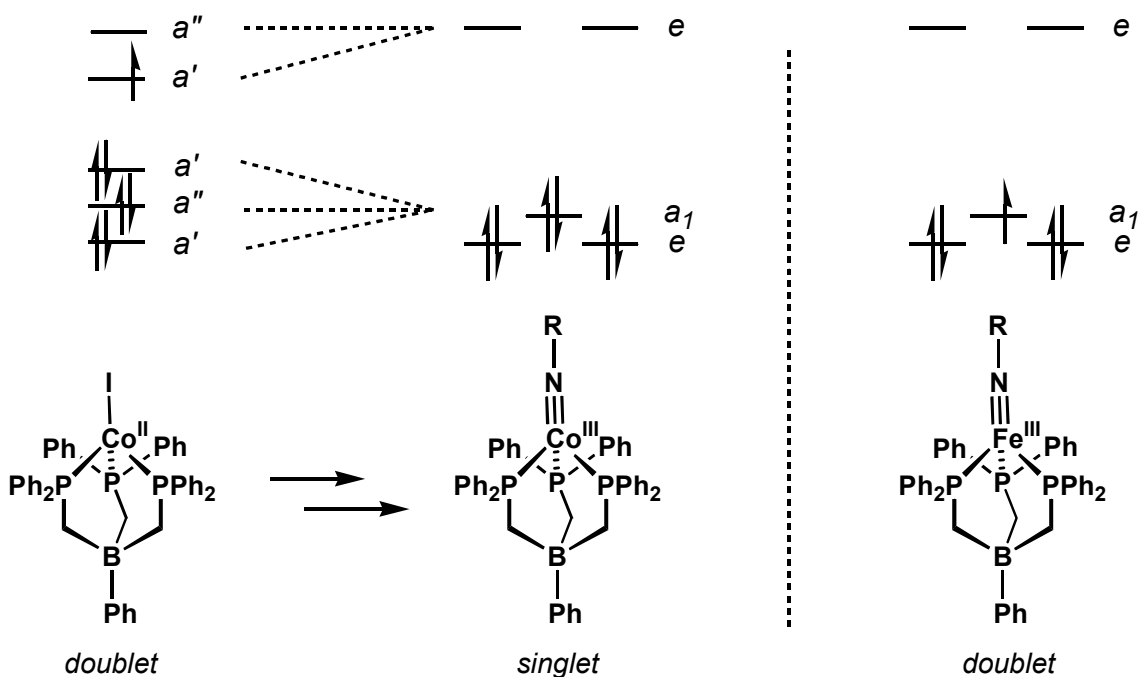


Figure 1.2. (left) Qualitative molecular orbital splitting diagram deduced for the $[\text{PhBP}_3]\text{Co}$ platform. Adapted from reference ¹². (right) Anticipated electronic structure of a $[\text{PhBP}_3]\text{Fe}^{\text{III}}(\text{NR})$ species.

1.2 Iron Imides and Iron Nitrides

As alluded to above, the [PhBP₃] ligand has the potential to serve as an ideal scaffold for the preparation and reactivity studies of iron-nitrogen multiply bonded linkages. The importance of such linkages is highlighted by their implicated intermediacy in both biological¹⁹ and industrial²⁰ nitrogen fixation processes. Establishing their reactivity patterns and spectroscopic signatures in well-defined synthetic systems is therefore of considerable interest. Additionally, any catalytic group-transfer processes with these linkages, such as aziridination,^{21,22} would be of practical importance as iron is an abundant and inexpensive transition metal.²³

Holland's work with low-coordinate iron has established N₂ binding and activation,²⁴ in addition to both N=N²⁵ and N-N²⁶ hydrazine bond cleavage processes.²⁷ Missing from these "[nacnac]Fe" platforms, however, are examples of compounds featuring multiply-bonded iron-nitrogen linkages (nacnac = general β -diketiminato ligand²⁸). Similarly, multiply-bonded intermediates have yet to be characterized during iron-facilitated N₂ binding, activation, and protonation processes that ultimately yield hydrazine and ammonia.²⁹ Precedence for a 4-coordinate iron center featuring a terminal NR²⁻ linkage was provided in 2000 with Lee's report of [Fe₄(μ ₃-N^tBu)₄(N^tBu)Cl₃].³⁰ Obtained in very low yields (~ 1 – 2%), a detailed magnetic study was not forwarded although it was assumed that three iron(III) centers and one iron(IV) center were present on the basis of charge balance. Prior to this work, azide decomposition with [Fe(salen)] units (salen = *N,N'*-ethane-1,2-diylbis(salicylaldiminato)) was reported to yield bridging iron(III) imides. Magnetic studies with these linkages established the presence of antiferromagnetically coupled, *high-spin* iron(III) centers,³¹ similar to what has been

reported for $[\text{Fe}(\text{salen})]_2\text{O}$ ³² and $[\text{Fe}(\text{salen})]_2\text{S}$.³³ The preparation of well-defined $[\text{PhBP}_3]\text{Fe}\equiv\text{NR}$ imides would therefore be of considerable interest as they would provide the first examples of mononuclear, terminal iron imides. Additionally, their anticipated *low-spin* electronic configurations would be unprecedented for pseudotetrahedral Fe(III).

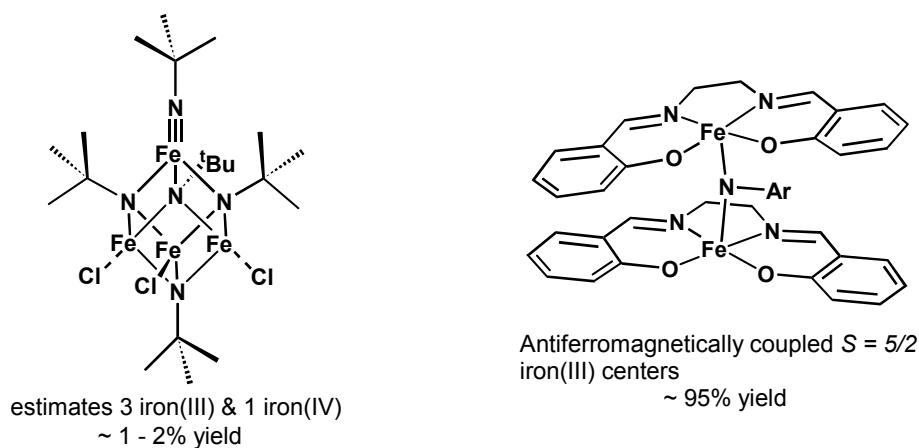


Figure 1.3. Examples of known iron imides.

The chemistry of the iron-nitride (N^{3-}) linkage is similarly underdeveloped. When considering terminal linkages, solid-state structural data is not yet available as these systems are typically generated at low temperature (~ 30 K) via photolysis of the corresponding azide and decompose upon warming.³⁴ Alternatively, the thermal decomposition of a $[\text{PhBP}^{\text{iPr}}_3]\text{Fe}(\text{II})$ amide was recently reported by Betley and Peters to yield a terminal iron(IV) nitride that is stable at 0°C .³⁵ However, efforts to obtain a solid-state structure are hampered by a bimetallic reduction process to form N_2 , although ammonia production was noted in the presence of excess protons and electrons. Bridging iron nitrides, which have been characterized in the solid state, typically feature five- or six-coordinate iron centers in mid- to high-valent oxidation states (*i.e.*, Fe(III) and Fe(IV)).³⁶ Although these systems are well characterized, little data has been forwarded concerning their reactivity.

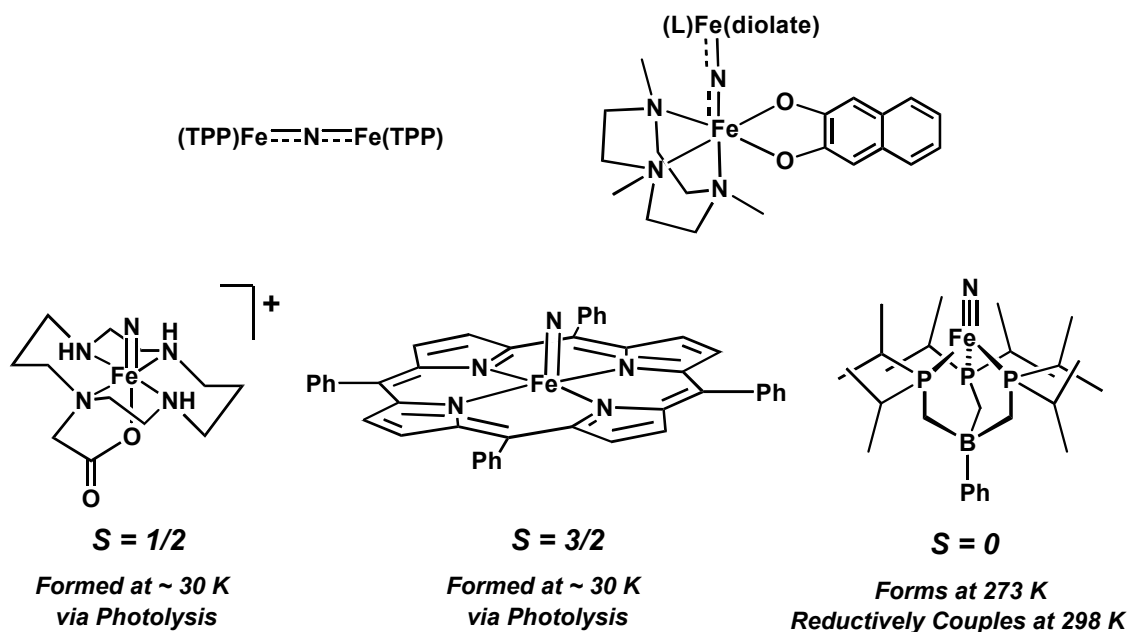


Figure 1.4. Examples of known iron nitrides (TPP = tetraphenylporphyrinato).

The preparation and investigation into the chemical reactivity of [PhBP₃] supported iron nitrides is therefore of considerable interest. Of immediate concern is to assess whether this scaffold is capable of supporting a terminal nitride that may be characterized in the solid state. Bridging systems, which are anticipated to be more stable, may also facilitate unique reaction chemistry with small molecules as a consequence of the coordinatively unsaturated nature of each metal center. Indeed, the recent discovery of an interstitial atom, presumably a nitride, within the active site of nitrogenase enzymes highlights the potential biological importance of low-coordinate “Fe-(μ-N)-Fe” linkages.³⁷ Reactivity with H₂ is also of interest, as no iron nitride (or iron imide) has been shown to react directly with H₂, which is presumably a key mechanistic step in the Haber-Bosch synthesis of ammonia.²⁰

The following chapters demonstrate that through the use of an anionic, strong-field tris(phosphino)borate ligand, several unique features concerning the chemistry of

Fe-N_x linkages are revealed. Foremost among these is the isolation and characterization of stable, mononuclear low-spin iron(III) imides that may be hydrogenated under mild conditions to promote a complete Fe-N_x bond scission process. Also presented is the first 4-coordinate, low-valent bridging nitride of iron, [$\{\text{PhBP}_3\text{Fe}\}_2(\mu\text{-N})\text{][Na(THF)}_5\text{]}$. This species features two high-spin antiferromagnetically coupled iron(II) centers and reacts with H₂ under mild conditions to generate an unprecedented L₃Fe^{II}-(μ-NH)(μ-H)-Fe^{II}L₃ manifold.³⁸

1.3 Chapter Summaries

Chapter 2 introduces the [PhBP₃]Fe framework and presents characterization data for a number of four-coordinate Fe(I), Fe(II), and Fe(III) compounds. Of particular interest is the preparation of [PhBP₃]Fe(PPh₃), which reacts with organic azides to yield terminal Fe(III) imides. Initial reactivity studies with the imides demonstrate their enhanced reactivity in group transfer processes when compared with their closed-shell cobalt(III) congeners. Whether this is in fact a reflection of the metalloradical character of the iron system is worth considering. Density functional theory calculations and solid state studies corroborate the assignment of a triple bond between the iron-nitrogen linkages.

Chapter 3 presents the room temperature hydrogenation chemistry of [PhBP₃]Fe≡N-*p*-tolyl. Surprisingly, a complete Fe-N bond scission process is observed to yield free amine and a solvent-activated product as the final iron containing species. The reaction appears to proceed in a stepwise fashion, as an independently prepared iron(II) anilide, [PhBP₃]Fe(N(H)-*p*-tolyl), is observed during the course of the hydrogenation reaction. Mechanistically, the rate-limiting step for the disappearance of the iron(III)

imide is consistent with a high degree of H-H bond-breaking character as a kinetic isotope effect (k_H/k_D) of 5.6 is observed for this process.

Chapter 4 discusses the preparation and characterization of ground-state singlet $L_3Fe-(\mu-N)-FeL_3$ and $L_3Fe(NR)$ complexes featuring pseudotetrahedral iron(II) centers. In contrast to the *low-spin* mononuclear iron(II) imide, spectroscopic data suggests that the anionic bridging nitride is best described as two *high-spin* iron(II) centers that are sufficiently antiferromagnetically coupled at room temperature to yield a singlet-ground state. Protonation of the $L_3Fe-(\mu-N)-FeL_3$ linkage with an excess of acid liberates ammonia in isolated yields greater than 80%.

Chapter 5 describes the hydrogenation and oxidation chemistry of the $L_3Fe-(\mu-N)-FeL_3$ linkage presented in Chapter 4. In contrast to $[PhBP_3]Fe\equiv N-p\text{-tolyl}$, a complete Fe-N bond scission process is not observed when $[\{[PhBP_3]Fe\}_2(\mu-N)][Na(THF)_5]$ is exposed to an atmosphere of H_2 . Rather, the presence of an additional metal center favors the formation of the bridging imide-hydride species, $[\{[PhBP_3]Fe\}_2(\mu-NH)(\mu-H)][Na(THF)_5]$. This compound may be chemically oxidized by one electron to yield $\{[PhBP_3]Fe\}_2(\mu-NH)(\mu-H)$, which may independently be prepared from the hydrogenation of $\{[PhBP_3]Fe\}_2(\mu-N)$.

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