

**The Chemistry of Tris(phosphino)borate Supported Iron-Nitrogen
Multiply-Bonded Linkages**

Thesis by
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Abstract

The metallation of FeX_2 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) salts with the strong-field $[\text{PhBP}_3]$ ($[\text{PhBP}_3] = \text{PhB}(\text{CH}_2\text{PPh}_2)_3^-$) ligand is presented. The resulting four-coordinate, 14-electron species, $[\text{PhBP}_3]\text{FeX}$, have been thoroughly characterized and feature high-spin ($S = 2$) electronic ground-states. X-ray diffraction analysis of $[\text{PhBP}_3]\text{FeCl}$ establishes a monomeric structure in the solid state.

The one electron reduction of $[\text{PhBP}_3]\text{FeCl}$ in the presence of a triphenylphosphine cap affords a rare example of four-coordinate iron(I). This species, $[\text{PhBP}_3]\text{Fe}(\text{PPh}_3)$, serves as a synthetic surrogate to a low-valent “[PhBP_3] $\text{Fe}(\text{I})$ ” subunit that is readily oxidized in the presence of organic azides. The resulting $S = \frac{1}{2}$ iron(III) imides of general formula $[\text{PhBP}_3]\text{Fe}\equiv\text{NR}$ may be subsequently reduced by one electron to yield the anionic $S = 0$ derivatives. Exposure of the former to an atmosphere of CO results in cleavage of the $\text{Fe}\equiv\text{NR}$ linkage to yield $[\text{PhBP}_3]\text{Fe}(\text{CO})_2$ and free isocyanate ($\text{O}=\text{C}=\text{N}-\text{R}$). Dicarbonyl $[\text{PhBP}_3]\text{Fe}(\text{CO})_2$ is itself an imide precursor and is gradually converted back to $[\text{PhBP}_3]\text{Fe}\equiv\text{NR}$ upon exposure to excess organic azide.

Tolyl imide $[\text{PhBP}_3]\text{Fe}\equiv\text{N}-p\text{-tolyl}$ readily reacts with H_2 under mild conditions to undergo a step-wise $\text{Fe}-\text{N}_x$ bond scission process to ultimately release free p -toluidine. Initially formed is the $S = 2$ iron(II) anilide, $[\text{PhBP}_3]\text{Fe}(\text{N}(\text{H})-p\text{-tolyl})$, which has been independently prepared and shown to release p -toluidine in the presence of H_2 . In benzene solvent the final iron containing product of the hydrogenation process is diamagnetic $[\text{PhBP}_3]\text{Fe}(\eta^5\text{-cyclohexadienyl})$, which is presumably formed from benzene insertion into a low-valent iron-hydride intermediate.

Reduction of the ferromagnetically coupled dimer, $\{[\text{PhBP}_3]\text{Fe}(\text{N}_3)\}_2$, yields the bridging nitride species, $[\{[\text{PhBP}_3]\text{Fe}\}_2(\mu\text{-N})][\text{Na}(\text{THF})_5]$. This compound features two high-spin iron(II) metal centers that are so strongly antiferromagnetically coupled that a diamagnetic $S = 0$ ground-state is exclusively populated at room temperature. X-ray diffraction analysis reveals a bent Fe-N-Fe linkage that quantitatively releases ammonia in the presence of excess protons. Reactivity with CO and H₂ is also presented, and for the latter, complete rupture of the Fe-N-Fe manifold is not observed as the presence of an additional metal center (when compared with the iron(III) imides) favors the formation of the diamagnetic bridging imide-hydride species, $[\{[\text{PhBP}_3]\text{Fe}\}_2(\mu\text{-NH})(\mu\text{-H})][\text{Na}(\text{THF})_5]$.

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List of Abbreviations and Nomenclature

[PhBP ₃]	[PhB(CH ₂ PPh ₂) ₃] ⁻
[PhBP ^{<i>i</i>Pr} ₃]	[PhB(CH ₂ P ^{<i>i</i>Pr} ₂) ₃] ⁻
[BP ₃]	general tris(phosphino)borate ligand
Cp	cyclopentadienyl
Cp [*]	pentamethylcyclopentadienyl
[PhTp ^{<i>t</i>Bu}]	phenyl tris(3- <i>tert</i> -butylpyrazolyl)borate
[Tp]	general hydrotris(pyrazolyl)borate ligand
[Tp ^{Me₂}]	hydrotris(3,5-dimethylpyrazolyl)borate
{ ¹ H}	hydrogen-1 decoupled
°	degrees, in measure of angles
°C	degrees Celcius
¹ H	hydrogen-1
¹¹ B	boron-11
¹⁵ N	nitrogen-15
¹⁹ F	fluorine-19
³¹ P	phosphorus-31
Å	Angstrom, 10 ⁻¹⁰ m
ACN	acetonitrile
Ad	1-adamantyl
Anal. Calcd.	elemental analysis calculated
atm	atmosphere
av	average

A_x	EPR coupling constant where X is the nucleus coupling to the unpaired electron
B3LYP	Becke three-parameter function with Lee-Yang-Parr correlation
br	broad
C_6H_6	benzene
C_6D_6	benzene- d_6
C_3, C_{2v}, C_1	Schoenflies symmetry designations
CCD	charge-coupled device
cm	centimeter(s)
cm^{-1}	inverse centimeters or wavenumbers
cm^3	cubic centimeters
cont.	continued
d	doublet
dbabh	2,3:5,6-dibenzo-7-aza bicycle[2.2.1]hepta-2,5-diene
DC	direct current
D_{calcd}	calculated density
dd	doublet of doublets
d^n	d-electron count of n-electrons for a transition metal
DFT	density functional theory
dt	doublet of triplets
dtbpe	1,2 bis(di- <i>tert</i> -butylphosphino)ethane
E	an atom or functional group forming a metal-ligand multiple bond
EPR	electron paramagnetic resonance

Eq	equation
equiv.	equivalents
ESI/MS	electrospray ionization mass spectrometry
eV	electron volt
<i>fac</i>	<i>facial</i> coordination
Fc/Fc ⁺	ferrocene/ferrocenium
g	gram(s)
G	Gauss
GC/MS	gas chromatography mass spectrometry
GHz	gigahertz
<i>g</i>	<i>g</i> -factor
h	hour(s)
H	applied magnetic field
HOMO	highest occupied molecular orbital
Hz	hertz
I_n	nuclear spin of atom n
IR	infrared
K	degrees in Kelvin
kcal	kilocalories
kHz	kilohertz
L	donative ligand for a transition metal
LACVP	Los Alamos core valence potential
LUMO	lowest unoccupied molecular orbital

m	multiplet
M	general transition metal
mg	milligram(s)
MHz	megahertz, 10^6 Hertz
min	minute(s)
mL	milliliter(s)
mmol	millimole(s)
MO	molecular orbital
mol	mole(s)
MS	mass spectrometry
mT	millitesla(s)
mV	millivolt(s)
mW	milliwatt(s)
${}^nJ_{A-Z}$	in NMR spectroscopy, coupling constant between nuclei A and Z over n bonds (n, A, or Z omitted if not known)
NIR	near-infrared
nm	nanometer(s)
NMR	nuclear magnetic resonance
[nacnac]	general β -diketiminato ligand
OTf	$-\text{OSO}_2\text{CF}_3$
<i>p</i> -	<i>para</i> position of an aryl ring
Ph	phenyl
ppm	parts per million

q	quartet
R	general alkyl or aryl substituents
rt	room temperature
s	second(s)
<i>S</i>	spin
SOMO	singly occupied molecular orbital
SQUID	superconducting quantum interference device
sqrt	square root
t	triplet
T	temperature
THF	tetrahydrofuran
THF- <i>d</i> ₈	tetrahydrofuran- <i>d</i> ₈
tmeda	tetramethylethylenediamine
TMS	trimethylsilyl
tolyl	-C ₆ H ₄ CH ₃
TPP	tetraphenylporphyrinato
triphos	H ₃ CC(CH ₂ PPh ₂) ₃
UV-vis	ultraviolet-visible
V	volume
X	monoanionic atom or group, such as halide
XRD	X-ray diffraction
δ	delta, chemical shift
ε	extinction coefficient in M ⁻¹ cm ⁻¹

η^n	hapticity of order n
λ	wavelength
λ_{\max}	wavelength of maximum absorption
μ	absorption coefficient (XRD)
$\mu\text{-A}$	bridging atom
μ_{B}	Bohr magnetons
μ_{eff}	effective magnetic moment
μL	microliter(s)
ν	frequency
χ	magnetic susceptibility
χ_{M}	molar magnetic susceptibility

Dedication

This work is dedicated to my parents,
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