

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

Thesis by

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In partial fulfillment of the requirements for the degree of Doctor of Philosophy

California Institute of Technology

Pasadena, California

2005

(Defended May 24, 2005)

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Acknowledgements

It seems surreal that the opportunity for me to acknowledge those individuals who have helped me throughout my graduate experience has finally arrived. First and foremost I must thank my graduate advisor, Professor Jonas C. Peters, whose intensity and passion for inorganic chemistry was apparent from our very first phone conversation. The dedication and standard of excellence that he demanded from me were crucial for achieving my goals of a productive and timely graduate career, and for that I am indebted to him. I also owe a great deal of gratitude to the remaining members of my committee, Professor John E. Bercaw, Professor Brian M. Stoltz, and Professor Harry B. Gray. Each of these individuals played an integral role in keeping me focused on my scientific endeavors—especially during my second year. I would also like to thank Professor Thomas G. Richmond at the University of Utah for exposing me to inorganic chemistry as an undergraduate student, and for personally teaching me the techniques required for the manipulation of air sensitive compounds.

I couldn't have asked for a better group of co-workers than those with whom I have been fortunate enough to share 304 Noyes. Each day with these individuals was always a new adventure in which at least five minutes of my day were guaranteed to be devoted to laughter. To the senior members of the lab, Dr. J. Christopher Thomas, Dr. Cora MacBeth, Dr. Bruce MacKay, and Dr. Mark Mehn, I thank you for sharing your scientific intellect and for providing me with sound advice during my graduate career. Seth "Powder" Harkins, Christine Thomas, and Connie Lu were always a pleasure to be around in the office. To the new group members, Dr. Xile "Exile" Hu, Matt Whited, and Neal Mankad, I have enjoyed getting to know each of you and wish you the best with

your continued studies in the Peters lab. Many thanks go to Kathleen Hand for keeping the day-to-day operations running smoothly and for providing a bottomless candy jar. I want to personally thank Dr. Theodore “T-Bone” Betley for being my best friend over the past five years; rarely does one have the opportunity to befriend an individual with so many common interests and so much character. He is the brother that I wish I always had. It’s hard to believe that our “Boston marriage” is almost over, and I have thoroughly enjoyed sharing an office, dry-box, and apartment with you. I wish you the best of luck in your impending marriage with The Beve, and I hope that the future brings plenty of prosperity for the both of us.

Several individuals have provided technical support and deserve recognition. Larry Henling, Dr. Mike Day, and Dr. Betley were instrumental in assisting with X-ray crystallography. Solid-state magnetic data (SQUID) were collected by Dr. Mehn and Dr. David Jenkins, while EPR spectroscopy would not have been possible if it weren’t for the efforts of Dr. Angel di Bilio. Dr. Scott Ross is gratefully acknowledged for aiding with ¹⁵N NMR experiments.

For constantly reminding me that there is life outside of science, I wish to thank my friends. To Team Justice, I enjoyed our Saturdays and Sundays filled with football and Carl’s Jr. It is imperative that we institute an annual Las Vegas Justice weekend to ensure that our Justice bonds are never broken. My adventures in Old Town with Dr. Bruce Lambert have provided a lifetime of unforgettable, and often entertaining, memories. And finally, I wish to thank my family. There are too many of you to list individually, but know that I love you all and I hope that I continue to make you proud. Your unconditional love and support has molded me into the person that I am today.

Abstract

The metallation of FeX_2 ($\text{X} = \text{Cl, Br, I}$) 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]Fe(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 ^{iPr} ₃]	[PhB(CH ₂ P ^{iPr} ₂) ₃] ⁻
[BP ₃]	general tris(phosphino)borate ligand
Cp	cyclopentadienyl
Cp [*]	pentamethylcyclopentadienyl
[PhTp ^{tBu}]	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 bicyclic[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>I_n</i>	nuclear spin of atom n
IR	infrared
K	degrees in Kelvin
kcal	kilocalories
kHz	kilohertz
L	dative 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 -diketiminate ligand
OTf	-OSO ₂ 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)
S	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	tetr phenylporphyrnato
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,
Steven Jay Brown and Elizabeth Ann Blake.