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

Thesis by

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Abstract

The metallation of FeX_2 (X = Cl, Br, I) salts with the strong-field $[PhBP_3]$ ($[PhBP_3] = PhB(CH_2PPh_2)_3^-$) ligand is presented. The resulting four-coordinate, 14-electron species, $[PhBP_3]FeX$, have been thoroughly characterized and feature high-spin ($S = 2$) electronic ground-states. X-ray diffraction analysis of $[PhBP_3]FeCl$ establishes a monomeric structure in the solid state.

The one electron reduction of $[PhBP_3]FeCl$ in the presence of a triphenylphosphine cap affords a rare example of four-coordinate iron(I). This species, $[PhBP_3]Fe(PPh_3)$, 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 $S = ½$ iron(III) imides of general formula $[PhBP_3]Fe{\equiv}NR$ 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 $Fe{\equiv}NR$ linkage to yield $[PhBP_3]Fe(CO)_2$ and free isocyanate (O=C=N-R). Dicarbonyl $[PhBP_3]Fe(CO)_2$ is itself an imide precursor and is gradually converted back to $[PhBP_3]Fe{\equiv}NR$ upon exposure to excess organic azide.

Tolyl imide $[PhBP_3]Fe{\equiv}N$-*p*-tolyl readily reacts with H_2 under mild conditions to undergo a step-wise $Fe-N_x$ bond scission process to ultimately release free *p*-toluidine. Initially formed is the $S = 2$ iron(II) anilide, $[PhBP_3]Fe(N(H)$-*p*-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 $[PhBP_3]Fe(\eta^5$-cyclohexadienyl), which is presumably formed from benzene insertion into a low-valent iron-hydride intermediate.

Reduction of the ferromagnetically coupled dimer, $\{[PhBP_3]Fe(N_3)\}_2$, yields the bridging nitride species, $[\{[PhBP_3]Fe\}_2(\mu\text{-}N)][Na(THF)_5]$. 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 H_2 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, $[\{[PhBP_3]Fe\}_2(\mu\text{-}NH)(\mu\text{-}H)][Na(THF)_5]$.

Table of Contents

List of Figures

Chapter 1.

Chapter 2.

Chapter 3.

Chapter 4.

Chapter 5.

List of Tables

Chapter 2.

Chapter 3.

Chapter 4.

Chapter 5.

List of Abbreviations and Nomenclature

[$PhBP_3$]	[$PhB(CH_2PPh_2)_3]^-$
[$PhBP^{iPr}{}_3$]	[$PhB(CH_2P^{iPr}{}_2)_3]^-$
[BP_3]	general tris(phosphino)borate ligand
Cp	cyclopentadienyl
Cp^*	pentamethylcyclopentadienyl
[$PhTp^{tBu}$]	phenyl tris(3-*tert*-butylpyrazolyl)borate
[Tp]	general hydrotris(pyrazolyl)borate ligand
[Tp^{Me2}]	hydrotris(3,5-dimethylpyrazolyl)borate
$\{^1H\}$	hydrogen-1 decoupled
°	degrees, in measure of angles
°C	degrees Celcius
^1H	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-*tert*-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
fac	*facial* coordination
Fc/Fc^+	ferrocene/ferrocenium
g	gram(s)
G	Gauss
GC/MS	gas chromatography mass spectrometry
GHz	gigahertz
g	g-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	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	$-OSO_2CF_3$
p-	*para* 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-d_8	tetrahydrofuran-d_8
tmeda	tetramethylethylenediamine
TMS	trimethylsilyl
tolyl	-$C_6H_4CH_3$
TPP	tetraphenylporphyrnato
triphos	$H_3CC(CH_2PPh_2)_3$
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)
μ-A	bridging atom
μ_B	Bohr magnetons
μ_{eff}	effective magnetic moment
μL	microliter(s)
υ	frequency
χ	magnetic susceptibility
χ_M	molar magnetic susceptibility

Dedication

This work is dedicated to my parents,

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