Coordination Chemistry from Trigonally Coordinated Iron Platforms:

Chemistry Relevant to Dinitrogen Reduction

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Abstract

The synthesis for a sterically encumbered, strong-field tris(diisopropylphosphino)borate ligand, $[PhBP^{iPr}_3]$ ($[PhBP^{iPr}_3] = [PhB(CH_2P^iPr_2)_3]^-$), is reported to probe aspects of its conformational and electronic characteristics within a host of complexes. To this end, the Tl(I) complex, $[PhBP^{iPr}_3]Tl$, was synthesized and characterized in the solid state by X-ray diffraction analysis. The Tl(I) complex was used to install the $[PhBP^{iPr}_3]$ ligand onto complexes of Fe, Co, and Ru. The spectroscopic, electrochemical, magnetic, and structural features of these complexes are compared with similar, previously described examples.

Trigonally coordinated "$[PhBP^{iPr}_3]M$" platforms (M = Fe, Co) support both π-acidic (N_2) and π-basic (NR) ligands at a fourth binding site. Methylation of monomeric $[M^0(N_2)^-]$ species successfully derivatizes the β-N atom of the N_2 ligand and affords the diazenido product $[M^{II}(N_2Me)]$. $M^I(N_2)M^I$ complexes provide clean access to the chemistry of the "$[PhBP_3]M(I)$" subunit. For example, addition of RN_3 to $M^I(N_2)M^I$ results in oxidative nitrene transfer to generate $[PhBP^{iPr}_3]M{\equiv}NR$ with concomitant N_2 release.

A tetrahedrally coordinated $L_3Fe\text{-}N_x$ platform that accommodates both terminal nitride ($L_3Fe^{IV}{\equiv}N$) and dinitrogen ($L_3Fe^I\text{-}N_2\text{-}Fe^IL_3$) functionalities is described. The diamagnetic $L_3Fe^{IV}{\equiv}N$ species featured has been characterized in solution under ambient conditions by multinuclear NMR (^1H, ^{31}P, and ^{15}N) and infrared spectroscopy. The electronic structure of the title complex has also been explored using DFT. The terminal nitride complex oxidatively couples to generate the previously reported $L_3Fe^I\text{-}N_2\text{-}Fe^IL_3$ species.

The [PhBP$^{iPr}{}_3$] ligand can support a single iron or cobalt center in a pseudo-tetrahedral environment in which dinitrogen is bound in the fourth coordination site. Zero-valent metal-dinitrogen complexes have the general formula, [([PhBP$^{iPr}{}_3$]M(μ-N_2)]$_2$[Mg^{2+}], while bridging structures can also be obtained as neutral [M^I]—N_2—[M^I] or as anionic [$(M)_2(N_2)$]$^-$ species. The nature of the structural distortions observed in both [M](μ-N_2)]$_2$[Mg^{2+}] and [M^n]—N_2—[M^n] complexes are described. Magnetic characterization of the neutral and mixed-valence dimeric complexes reveal the complexes remain ferromagnetically coupled over all temperatures investigated.

The coordination chemistry of group VIII metals featuring the bis(8-quinolinyl)amine (HBQA) ligand is presented. The electrochemical behavior of several Fe, Ru, and Os complexes bearing the BQA ligand is reported and compared to related ligand platforms. Halide and phosphine ligand exchange reactions are examined from complexes of the type (BQA)MX$(PR_3)_2$ (M = Ru, Os). Carbonyl and dinitrogen complexes of Ru and Os are prepared from halide abstraction from divalent Ru and Os precursors. The spectroscopic and structural features of these complexes are compared with similar, previously described examples.

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List of Abbreviations and Nomenclature

[PhBP$_3$]	[PhB(CH$_2$PPh$_2$)$_3$]$^-$
[PhBP$^{i\mathrm{Pr}}{}_3$]	[PhB(CH$_2$P^{i}Pr$_2$)$_3$]$^-$
Cp	cyclopentadienyl
Cp*	pentamethyl-cyclopentadienyl
[Tp]	hydrotris(pyrazolyl)borate
{^{1}H}	hydrogen-1 decoupled
º	degrees in measure of angles
ºC	degrees Celcius
^{1}H	hydrogen-1
^{11}B	boron-11
^{13}C	carbon-13
^{19}F	fluorine-19
^{15}N	nitrogen-15
^{31}P	phosphorous-31
^{203}Tl	thallium-203
^{205}Tl	thallium-203
Å	Angstrom, 10^{-10} m
Ad	adamantyl
Anal. Calcd.	elemental analysis calculated
Ar	aryl group
av	average
B3LYP	Becke three-parameter functional with Lee-Yang-Parr correlation

BM	Bohr magnetons
br	broad
Bu	butyl
BQA	8-bis(quinolinyl)amine
C_{3v}, C_s, S_6	Schoenflies symmetry designations
Calcd	calculated
CCD	charge coupled device
cm	centimeter(s)
cm^{-1}	inverse centimeters or wavenumbers
cm^3	cubic centimeters
cod	1,4-cyclooctadiene
d	doublet
dbabh	2,3:5,6-dibenzo-7-aza bicyclo[2.2.1]hepta-2,5-diene
dd	doublet of doublets
dt	doublet of triplets
DC	direct current
D_{calcd}	calculated density
deg	degrees in measure of angles
d^n	d-electron count of n-electrons for a transition metal
DFT	density functional theory
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
Et	ethyl
EXAFS	extended X-ray absorption fine structure
fac	*facial* coordination
g	gram
G	Gauss
GC/MS	gas chromatography mass spectrometry
GHz	gigahertz
g_{iso}	isotropic g-factor
h	hour(s)
H	applied magnetic field
Hdbabh	1-H-2,3:5,6-dibenzo-7-aza bicyclo[2.2.1]hepta-2,5-diene
HOMO	highest occupied molecular orbital
Hz	hertz
^{i}Pr	isopropyl
IR	infrared
JT	Jahn-Teller
K	degrees in Kelvin
kcal	kilocalories
kHz	kilohertz
L	dative ligand for a transition metal
LAVCP	Los Alamos core valence potential

LFT	ligand field theory
LUMO	lowest unoccupied molecular orbital
m	multiplet
M	general metal
Me	methyl
Mes	mesityl
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)
NA, na	not applicable
^{n}Bu	*n*-butyl
$^{n}J_{A\text{-}Z}$	in NMR spectroscopy, coupling constant between nuclei A and Z over n bonds (n, A, or Z omitted if not known)
nm	nanometer(s)
NMR	nuclear magnetic resonance

OTf	-OSO_2CF_3
p-	*para* position on aryl ring
Ph	phenyl
ppm	parts per million
q	quarted
R	general alkyl or aryl substituents
rt	room temperature
s	second(s)
s	solvent peak in NMR
S	spin
SOMO	singly occupied molecular orbital
SQUID	superconducting quantum interference device
t	triplet
T	temperature
TBA	tetrabutylammonium
^{t}Bu	*tert*-butyl
THF	tetrahydrofuran
tmeda	tetramethylethylenediamine
TMS	trimethylsilyl
tolyl	-$C_6H_4CH_3$
triphos	$H_3CC(CH_2PPh_2)_3$
Ts	-$S(O)_2$-*p*-tolyl
UV-vis	ultraviolet-visible

V	volume
X	monoanionic atom or group, such as halide
XANES	X-ray absorption near-edge spectroscopy
XAS	X-ray absorption spectroscopy
XRD	X-ray diffraction
δ	delta, chemical shift
ε	extinction coefficient in M^{-1} cm^{-1}
η^n	hapticity of order n
κ^n	number of single ligating atom attachments of a polyatomic ligand
λ	wavelength
λ_{max}	wavelength of maximum absorption
μ	absorption coefficient (XRD)
μ^n-A	bridging atom to n metal centers
μ_B	Bohr magnetons
μ_{eff}	effective magnetic moment, measure in Bohr magnetons
μL	microliter(s)
ν	frequency
θ	Weiss constant
χ	magnetic susceptibility
χ_m	molar magnetic susceptibility

Dedication

This work is dedicated to my parents Ted and Maria,

for their encouragement and patience.