Low spin pseudotetrahedral cobalt tris(phosphino)borate complexes

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 January 31, 2005)

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Acknowledgements

The number of people who have helped me throughout my education is too great for me to acknowledge everyone individually. I would, however, like to single out a few people. Foremost, I want to thank my advisor Jonas Peters for providing advice and encouragement. I will always remember the importance of doing the “best” chemistry in a thorough and accurate manner and of communicating the results in a precise fashion. I would also like to thank my boxmates, who have helped make day-to-day life so much more enjoyable. In particular, B.Q. (Baixin Qian) taught me the ropes of working in an inorganic laboratory and impressed on me the value of “life goals.” Christine Thomas, in addition to her valuable help editing many of my papers, was always supportive in lab and a joy to be around in the office. I would like to thank the Peters’s group in general for making sure life was never dull and, of course, “keepin’ it real.” I would also like to thank Héctor Abruña and Diego Diaz, who introduced me to chemical research at Cornell and for that have my utmost thanks.

There are several other people who helped me in the course of my research at Caltech. Angelo Di Bilio helped immensely with my EPR spectra acquisition and interpretation; Larry Henling and Mike Day provided superb assistance with X-ray crystallography; Mohan Sankaran taught me how to use the SQUID, which was a vital part of my research. Without your collective help, my graduate studies would not have been as fruitful and rewarding. I would also like to thank my graduate committee for their guidance and criticism.

Finally, I would like to thank my parents, William and Vicki Jenkins, for their steadfast love and support throughout my educational endeavors. I also must express my utmost gratitude to Mahogany Paulino, my future wife, for her tenderness and love.

Abstract

A synthetic protocol is developed for the preparation of a thallium complex featuring the tris(phosphino)borate ligand [$PhBP_3$] ([$PhBP_3$] = [$PhB(CH_2PPh_2)_3$]$^-$). The transmetallating reagent, [$PhBP_3$]Tl, is characterized by single crystal X-ray diffraction and solution NMR spectroscopy, and is the first example of a stable homoleptic Tl(I)-phosphine complex.

The synthesis and characterization of [$PhBP_3$]Co-X (X = I, Br or Cl) is discussed. These halide complexes are structurally characterized and magnetic investigations establish that they are low spin when monomeric. The low spin iodide complex is a monomer in solution and in the solid state. The other halides exhibit a monomer/dimer equilibrium that complicates their magnetic behavior. Theoretical calculations help provide a rationale as to why these pseudotetrahedral species are low spin. A classic high spin species supported by [$PhBP_3$] is compared to the low spin complexes.

Spin state control involving pseudotetrahedral [$PhBP_3$]Co(II) complexes is explored. Both high and low spin, as well as spin crossover, complexes are synthesized and structurally characterized. The complexes are discussed in terms of the relationship between local geometry and spin state. Changing the axial or tripodal ligand can cause a different spin state to be favored. Since the energy difference between the states is small, ligand changes at remote positions from the metal center have a significant effect on spin crossover phenomena. Theoretical calculations help illuminate why the low spin state is preferred for many of the complexes.

The first examples of cobalt imide complexes ([$PhBP_3$]Co≡NR (R = aryl or alkyl)) are prepared and they are supported by the [$PhBP_3$] ligand. These diamagnetic species are evaluated by NMR and single crystal X-ray diffraction. Theoretical studies suggest that they have a similar molecular orbital bonding scheme as the previously prepared group 9 imides.

A cobalt μ_2-bridging nitride complex (([PhBP$_3$]Co)$_2$(μ-N)) is synthesized and structurally characterized. This mixed-valence species is evaluated by magnetometry to determine its ground state, which is low spin ($S = \frac{1}{2}$).

Several cobalt diazoalkane complexes are prepared. These diamagnetic species adopt two different bonding modes depending on the nature of the diazoalkane ligand.

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List of Abbreviations and Nomenclature

$[BP_3]$	general abbreviation for $[PhBP_3]$ or $[PhBP^{iPr}_3]$
[Cp]	cyclopentadienyl
[Cp*]	pentamethyl-cyclopentadienyl
$[Me_2NN]$	$[HC(CMeNC_6H_3\text{-}2,6\text{-}Me_2)_2]^-$
$[PhBP_3]$	$[PhB(CH_2PPh_2)_3]^-$
$[PhBP^{iPr}_3]$	$[PhB(CH_2P^iPr_2)_3]^-$
[Tp]	general tris(pyrazolyl)borate
$[Tp^{3,5\text{-}Me2}]$	hydro-tris(3,5-dimethyl-pyrazolyl)borate
[Tp'']	hydro-tris(3-*tert*-butyl-5-methyl-pyrazolyl)borate
$[Tt^{\textit{tert-butyl}}]$	$[PhB(CH_2S^tBu)_3]^-$
$\{^1H\}$	hydrogen-1 decoupled
°	degrees in measure of angles
°C	degrees Celsius
^1H	hydrogen-1
^{11}B	boron-11
^{13}C	carbon-13
^{19}F	fluorine-19
^{31}P	phosphorus-31
^{59}Co	cobalt-59
^{127}I	iodine-127
^{203}Tl	thallium-203
^{205}Tl	thallium-205

Å	Angstrom, 10^{-10} m
Ad	adamantyl
Anal. Calcd	elemental analysis calculated
Ar	general aryl group
av	average
A_X	EPR hyperfine coupling where X is the nucleus coupling to the unpaired electron (also sometimes abbreviated ^{X}A)
B3LYP	Becke three-parameter functional with Lee-Yang-Parr correlation functional
BM	Bohr magnetons
br	broad
Bu	butyl
C_{3v}, C_s	Schoenflies symmetry designations
Calcd	calculated
CCD	charge coupled device
cm	centimeter(s)
cm^{-1}	inverse centimeters or wavenumbers
cm^3	cubic centimeters
cont.	continued
d	doublet
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
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
Et	ethyl
Exptl	experimental
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
HOMO	highest occupied molecular orbital
Hz	hertz
I_n	nuclear spin of atom n
^{i}Pr	*iso*-propyl
IR	infrared

K	degrees in Kelvin
kcal	kilocalories
kHz	kilohertz
L	dative ligand for a transition metal
LACVP	Los Alamos core valence potential
LFT	ligand field theory
LUMO	lowest unoccupied molecular orbital
m	multiplet
M	general metal
Me	methyl
Mes	mesityl
Me_3-tacn	1,4,7-trimethyl-1,4,7-triazocyclononane
mg	milligram(s)
MHz	megahertz, one million Hertz
min	minute(s)
mL	milliliter(s)
mmol	millimoles
MO	molecular orbital
mol	moles
ms	millisecond(s)
MS	mass spectrometry
mT	millitesla(s)
mV	millivolt(s)

mW	milliwatt(s)
NA	not applicable
^{n}Bu	*n*-butyl
near-IR	near-infrared
$^{n}J_{A\text{-}Z}$	in NMR spectroscopy, coupling constant between nuclei A and Z over n bonds (n, A, or Z omitted if not known)
nm	namometer(s)
NMR	nuclear magnetic resonance
np_3	tris(2-diphenylphosphino)ethyl)amine
OTf	$-OSO_2CF_3$
p-	*para* position on an aryl ring
Ph	phenyl
ppm	parts per million
q	quartet
R	general alkyl or aryl substituent
rt	room temperature
s	second(s)
s	solvent peak (in NMR spectrum)
S	spin
SOMO	singly occupied molecular orbital
SQUID	superconducting quantum interference device
S(*G*)	distance (i.e., deviation) of a given molecule from an idealized polyhedron of a symmetry point group defined as *G*

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
tt	triplet of triplets
UV-vis	ultraviolet-visible
V	volume
X	monoanionic atom or group, such as a halide or thiolate
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 n of single ligating atom attachments of a polyatomic ligand
λ	wavelength
λ_{max}	wavelength of maximum absorption
μ	absorption coefficient (X-ray diffraction)

μ-A	bridging atom A
μ_2	atom bridging between two metal centers
μ_B	Bohr magnetons
μ_{eff}	effective magnetic moment, measured 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 father and mother, William and Vicki Jenkins.

I love you dearly.