

Ligand design, coordination chemistry, and mechanistic studies of
(phosphino)borates and their platinum, nickel, and copper complexes

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Acknowledgments

Twenty-two years ago, when I was just beginning my trek through the academic ranks of the American education system, I was convinced that I was going to attend either Harvard or Yale. Apparently the education I was blessed with did a proper job, as I ended up attending neither of those fine universities. Instead, I have had the good fortune of having been through two of the world's greatest institutes of science and technology. Hopefully this document is a testament to many jobs well done by every teacher and mentor that I have had along the way. From my kindergarten teacher Mrs. Madison, who to this day inquires about my doings, to my Ph.D. advisor Professor Jonas Peters, I have had the advantage of being led by many people for whom their job was a passion.

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anionic and neutral molybdenum(0) tetracarbonyl complexes provide results analogous to those found when comparing neutral and cationic platinum(II) systems.

Comparative studies on the ligand exchange and benzene C-H activation chemistry of structurally similar platinum(II) complexes convey the similarities and differences between zwitterionic and cationic systems. Examination of THF ligand self-exchange by magnetization transfer shows a change in mechanism between the neutral and cationic species. Both bis(phosphino)borate-ligated and neutral bis(phosphine) platinum methyl solvento complexes undergo a benzene C-H activation to form the corresponding phenyl solvento complex; however, the rates of reaction and ultimate products differ. Extensive isotopic studies indicate that the zwitterionic system forms observable intermediates prior to benzene C-H activation, some of which are attributable to ligand metalation processes.

Structural and spectroscopic studies of a phenyl-substituted tris(phosphino)borate on platinum are presented. Alkyl- and hydride-containing platinum(II) and platinum(IV) species have been synthesized. The structural and spectroscopic features of these complexes are compared to related tris(pyrazolyl)borate systems on platinum.

Coordination and reaction chemistry of an isopropyl-substituted tris(phosphino)borate on nickel are discussed. Complexes in the Ni(II), Ni(I), and Ni(0) oxidation states have been prepared. This system is compared through structural, spectroscopic, and electrochemical methods to related phenyl-substituted tris(phosphino)borate chemistry on nickel. Reactivity studies aimed at preparing Ni(III) and Ni(IV) complexes containing metal-ligand multiple bonds through group-transfer

reactions are presented. Theoretical studies using density functional methods are used to probe several target species containing multiply-bonded ligands.

The coordination chemistry of copper(I) is explored using bis(phosphino)borates. Both aryl- and alkyl-substituted bis(phosphino)borates provide access to copper(I) complexes. A *tert*-butyl-substituted bis(phosphino)borate is particularly useful for preparing a family of three-coordinate compounds. The spectroscopic and structural features of these complexes are compared with similar, previously described examples.

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List of Abbreviations and Nomenclature

<u>Term</u>	<u>Definition</u>
[Ph ₂ BP ₂]	Ph ₂ B(CH ₂ PPh ₂) ₂ ⁻
[PhBP ₃]	PhB(CH ₂ PPh ₂) ₃ ⁻
[PhBP ^{iPr} ₃]	PhB(CH ₂ P ^{iPr} ₂) ₃ ⁻
[PhBTt ^{tBu}]	PhB(CH ₂ S ^{tBu}) ₃ ⁻
[Tp]	HB(pyrazolyl) ₃ ⁻
[Tp ^{Me} ₂]	HB(3,5-dimethylpyrazolyl) ₃ ⁻
{ ¹ H}	hydrogen-1 decoupled
°	degrees in measure of angles
°C	degrees Celsius
¹ H	hydrogen-1, proton
¹¹ B	boron-11
¹³ C	carbon-13
¹⁹ F	fluorine-19
²⁹ Si	silicon-29
³¹ P	phosphorus-31
¹⁹⁵ Pt	platinum-195
9-BBN	9-borabicyclo[3.3.1]nonane
[ASN]	5-azonia-spiro[4.4]nonane ⁺ , {(CH ₂ CH ₂) ₂ } ₂ N ⁺
Å	Angstrom, 10 ⁻¹⁰ m
Anal. Calcd.	elemental analysis calculated
B3LYP	Becke three-parameter functional with Lee-Yang-Parr correlation functional
br	broad
C _{2v} , C _{3v} , C _s	Schoenflies symmetry designations
CCD	charge coupled device
CCDC ID	Cambridge crystallographic data centre identification
cm ⁻¹	inverse centimeters
COD	1,5-cyclooctadiene
Cy	cyclohexyl
d ⁿ	d-electron count of n electrons for a transition metal
d	doublet
DABCO	1,4-diazabicyclo[2.2.2]octane
dcype	dicyclohexylphosphinoethane, Cy ₂ PCH ₂ CH ₂ PCy ₂
dd	doublet of doublets
ddd	doublet of doublets of doublets
dfep	di(<i>per</i> -fluoro)ethylphosphinoethane, (CF ₃ CF ₂) ₂ PCH ₂ CH ₂ P(CF ₂ CF ₃) ₂
DFT	density functional theory
dippe	di- <i>iso</i> -propylphosphinoethane, ^{iPr} ₂ PCH ₂ CH ₂ P ^{iPr} ₂
DME	1,2-dimethoxyethane
dppe	diphenylphosphinoethane, Ph ₂ PCH ₂ CH ₂ PPh ₂
dppp	diphenylphosphinopropane, Ph ₂ PCH ₂ CH ₂ CH ₂ PPh ₂
dq	doublet of quartets
dt	doublet of triplets

dtbpe	di- <i>tert</i> -butylphosphinoethane, ${}^t\text{Bu}_2\text{PCH}_2\text{CH}_2\text{P}{}^t\text{Bu}_2$
E	an atom or functional group
$E_{1/2}$	halfwave potential
EI MS	electrospray ionization mass spectrometry
eq	equation
ES MS	electrospray mass spectrometry
Et	ethyl
Et-tripod	$\text{CH}_3\text{CH}_2\text{C}(\text{CH}_2\text{PPh}_2)_3$
Fc	ferrocene, bis(cyclopentadienyl)iron
Fc^+	ferrocenium, [bis(cyclopentadienyl)iron] $^+$
g	gram
GC MS	gas chromatography mass spectrometry
h	hour(s)
Hdbabh	2,3:5,6-dibenzo-7-azabicyclo[2.2.1]hepta-2,5-diene
HOMO	highest occupied molecular orbital
Hz	Hertz
${}^i\text{Pr}$	<i>iso</i> -propyl
IR	infrared
L	dative ligand for a transition metal
LACVP	Los Alamos core valence potential
LUMO	lowest unoccupied molecular orbital
m	multiplet
<i>m</i> -	<i>meta</i> position on an aryl ring
M	general metal
md	medium (intensity)
Me	methyl
Mes	mesityl, 2,4,6-trimethylphenyl
Me-tripod	$\text{CH}_3\text{C}(\text{CH}_2\text{PPh}_2)_3$
mg	milligram
MHz	Megahertz, one million Hertz
min	minute(s)
mL	milliliter(s)
mmol	millimoles
MO	molecular orbital
mol	moles
MS	mass spectrometry
mV/s	millivolts per second
<i>n</i> -	normal, as in <i>n</i> -butyl
n K	n Kelvin
n M	n molar solution
n mV	n millivolts
n V	n volts
${}^n\text{Bu}$	<i>n</i> -butyl
${}^nJ_{\text{A-Z}}$	in NMR spectroscopy, coupling constant between nuclei A and Z over n bonds (n, A, or Z omitted if not known)
nm	nanometer

NMR	nuclear magnetic resonance
<i>o</i> -	<i>ortho</i> position on an aryl ring
<i>p</i> -	<i>para</i> position on an aryl ring
pet.	petroleum
Ph	phenyl
Ph ₂ SiP ₂	Ph ₂ Si(CH ₂ PPh ₂) ₂
ppm	parts per million
q	quartet
R	general alkyl or aryl substituent
ref.	reference
s	singlet
<i>S</i>	spin
^s Bu	<i>sec</i> -butyl
SCE	saturated calomel electrode
SCF	self-consistent field
sec	second(s)
st	strong (intensity)
t	triplet
T (°C)	temperature in degrees Celsius
TBA	tetra <i>n</i> -butyl ammonium
^t Bu	<i>tert</i> -butyl
td	triplet of doublets
TEA	tetra ethyl ammonium
Tf	triflate, -S(O) ₂ CF ₃
THF	tetrahydrofuran
TMEDA	<i>N,N,N',N'</i> -tetramethylethylenediamine
tripod	HC(CH ₂ PPh ₂) ₃
UV-Vis	ultraviolet-visible
V (Å ³)	volume in cubic Angstroms
vt	virtual triplet
w	weak (intensity)
X	monoanionic atom or group, such as a halide or alkyl
δ	delta, chemical shift
ε	extinction coefficient in M ⁻¹ cm ⁻¹
η ⁿ	hapticity of order n
λ (Å)	wavelength in Angstroms
λ _{max}	wavelength of maximum absorption
κ ⁿ	number n of single ligating atom attachments of a polyatomic ligand
μ	absorption coefficient (X-ray diffraction)
μ-A	bridging atom A
μ _B	Bohr magnetons
μ _{eff}	effective magnetic moment
μL	microliter(s)
μmol	micromoles
ν _{AZ}	stretching frequency of A-Z bond

DEDICATION

*Ecce enim veritatem dilexisti:
incerta et occulta sapientiæ
tuæ manifestasti mihi.*

For behold, you have loved the truth:
the obscure and hidden elements of your wisdom
you have made known to me.

Psalm 51, verse 6

This work is dedicated to my family and friends who I love
and from whom I have been hidden for too long.