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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Abstract

Synthetic methods are presented for the preparation of various substituted bis(phosphino)borates. A relatively general protocol based on the delivery of a nucleophilic phosphine-containing carbanion to a borane electrophile has been developed. Preparative methods for the synthesis of substituted diarylchloroboranes from dimethyl-diaryltin reagents provide the borane electrophiles. Methyldialkyl- or methyldiarylphosphines are selectively deprotonated at the phosphine-methyl using alkyl lithium bases to form the carbanion nucleophiles. The reaction of diverse phosphine-containing carbanions with diarylchloroboranes results in bis(phosphino)borates selectively substituted at the borate, at the phosphine, or at both positions. In addition to the generated lithium salts of the bis(phosphino)borates, cation-exchange protocols provide methods for preparing ammonium and thallium bis(phosphino)borate salts. Structural data for some of these derivatives are presented.

The electronic properties of transition metals coordinated by bis(phosphino)borates are explored through NMR and IR spectroscopies. The spectroscopic features of platinum(II) dimethyl and methyl carbonyl complexes are examined for trends based on the substitution pattern of the (phosphino)borate ligand. These trends indicate that phosphine substituents have a more significant impact than borate substituents on electronics of the metal center. Structural and spectroscopic comparisons of structurally similar platinum(II) dimethyl and methyl carbonyl complexes indicate that the anionic bis(phosphino)borate ligand renders platinum(II) more electron-rich than structurally similar neutral phosphine donors. Related spectroscopic studies of
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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<td>Ph&lt;sub&gt;2&lt;/sub&gt;B(CH&lt;sub&gt;2&lt;/sub&gt;PPh&lt;sub&gt;2&lt;/sub&gt;)&lt;sup&gt;2&lt;/sup&gt;</td>
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<td>[PhBP&lt;sub&gt;3&lt;/sub&gt;]</td>
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<td>[PhBTT&lt;sup&gt;the&lt;/sup&gt;]</td>
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<td>[Tp]</td>
<td>HB(pyrazolyl)&lt;sup&gt;3&lt;/sup&gt;</td>
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<td>Å</td>
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<td>B3LYP</td>
<td>Becke three-parameter functional with Lee-Yang-Parr correlation functional</td>
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<td>C&lt;sub&gt;2v&lt;/sub&gt;, C&lt;sub&gt;3v&lt;/sub&gt;, C&lt;sub&gt;s&lt;/sub&gt;</td>
<td>Schoenflies symmetry designations</td>
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<tr>
<td>CCDC ID</td>
<td>Cambridge crystallographic data centre identification</td>
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<tr>
<td>cm&lt;sup&gt;-1&lt;/sup&gt;</td>
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<tr>
<td>COD</td>
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</tr>
<tr>
<td>Cy</td>
<td>cyclohexyl</td>
</tr>
<tr>
<td>d&lt;sup&gt;n&lt;/sup&gt;</td>
<td>d-electron count of n electrons for a transition metal</td>
</tr>
<tr>
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<td>dd</td>
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<td>ddd</td>
<td>doublet of doublets of doublets</td>
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<tr>
<td>dffepe</td>
<td>di(per-fluoro)ethylphosphinoethane, (CF&lt;sub&gt;3&lt;/sub&gt;CF&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;PCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;P(CF&lt;sub&gt;2&lt;/sub&gt;CF&lt;sub&gt;3&lt;/sub&gt;) &lt;sub&gt;2&lt;/sub&gt;</td>
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<td>dippe</td>
<td>di-iso-propylphosphinoethane, &lt;sup&gt;i&lt;/sup&gt;Pr&lt;sub&gt;2&lt;/sub&gt;PCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;P&lt;sup&gt;i&lt;/sup&gt;Pr&lt;sub&gt;2&lt;/sub&gt;</td>
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<td>dppe</td>
<td>diphenylphosphinoethane, Ph&lt;sub&gt;2&lt;/sub&gt;PCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;PPh&lt;sub&gt;2&lt;/sub&gt;</td>
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</tr>
<tr>
<td>dq</td>
<td>doublet of quartets</td>
</tr>
<tr>
<td>dt</td>
<td>doublet of triplets</td>
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dtbpe  
di-tert-butylphosphinoethane, \(^\text{tBu}_2\text{PCH}_2\text{CH}_2\text{P}^{\text{tBu}_2}\)

E  
an atom or functional group

E\text{1/2}  
halfwave potential

E\text{1 MS}  
electrospray ionization mass spectrometry

eq  
equation

E\text{S MS}  
electrospray mass spectrometry

Et  
ethyl

Et-tripod  
CH\(_3\)CH\(_2\)C(CH\(_2\)PPh\(_2\))\(_3\)

Fc  
ferrocene, bis(cyclopentadienyl)iron

Fc\(^+\)  
ferrocenium, [bis(cyclopentadienyl)iron]\(^+\)

\(g\)  
gram

GC\text{ 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

\(^{\text{iPr}}\)  
isopropyl

IR  
infrared

\(L\)  
daative ligand for a transition metal

LACVP  
Los Alamos core valence potential

LUMO  
lowest unoccupied molecular orbital

\(m\)  
multiplet

\(m^-\)  
meta position on an aryI ring

M  
general metal

md  
medium (intensity)

Me  
methyl

Mes  
mesityl, 2,4,6-trimethylphenyl

Me-tripod  
CH\(_3\)C(CH\(_2\)PPh\(_2\))\(_3\)

mg  
milligram

MHz  
Megahertz, one million Hertz

\(\text{min}\)  
minute(s)

\(\text{mL}\)  
milliliter(s)

\(\text{mmol}\)  
millimoles

MO  
molecular orbital

mol  
moles

MS  
mass spectrometry

\(\text{mV/s}\)  
millivolts per second

\(n^-\)  
normal, as in \(n\)-butyl

\(n\)\text{ K}\  
n Kelvin

\(n\)\text{ M}\  
n molar solution

\(n\)\text{ mV}\  
n millivolts

\(n\)\text{ V}\  
n volts

\(^{\text{aBu}}\)  
\(n\)-butyl

\(^{\text{aJ}_{A-Z}}\)  
in NMR spectroscopy, coupling constant between nuclei A and Z over \(n\) bonds (\(n\), A, or Z omitted if not known)

\(\text{nm}\)  
nanometer
NMR  nuclear magnetic resonance
 orthogonal, *o*-  ortho position on an aryl ring
 parallel, *p*-  para position on an aryl ring
 pet.  petroleum
 Ph  phenyl
 Ph\(_2\)SiP\(_2\)  Ph\(_2\)Si(CH\(_3\)PPh\(_2\))\(_2\)
 ppm  parts per million
 q  quartet
 R  general alkyl or aryl substituent
 ref.  reference
 s  singlet
 S  spin
 \(^3\)Bu  sec-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 \(n\)-butyl ammonium
 \(^t\)Bu  tert-butyl
 td  triplet of doublets
 TEA  tetra ethyl ammonium
 Tf  triflate, -S(O)\(_2\)CF\(_3\)
 THF  tetrahydrofuran
 TMEDA  \(N,N,N',N'\)-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\(^{-1}\)
 n\(^a\)  hapticity of order n
 λ (Å)  wavelength in Angstroms
 λ\(_{\text{max}}\)  wavelength of maximum absorption
 κ\(^a\)  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\(_{\text{eff}}\)  effective magnetic moment
 µL  microliter(s)
 µmol  micromoles
 ν\(_{\text{AZ}}\)  stretching frequency of A-Z bond
DEDICATION

Ecce enim veritatem dilexisti:
incerta et occulta sapientiae
 tuae 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.