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

Thesis by

John Christopher Thomas

In Partial Fulfillment of the Requirements

for the Degree of

Doctor of Philosophy

California Institute of Technology

Pasadena, California

2004

(Defended May 28, 2004)

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.

Several teachers in particular deserve to be acknowledged: Mrs. Jacobs, Mrs. (nee) Goodyear, Mrs. Hamline, Mr. Spreeman, Ms. (nee) Dieter, Rex and Bob (Mr.'s Martin and Peters), Mr. Symalla, Mrs. Aubineau, and particularly Mr. Jeff Ranta and Dr. Erik (Doc) Christiansen. Mr. Ranta was a true science inspiration with his passion for biology and earth sciences and his expectation of excellence. How many other teachers would encourage high school students to undertake below-freezing camping on the lake behind their house? On the contrary side, Dr. Christiansen, as my choir conductor inspired a passion for singing through his unwavering demands for his students to achieve beyond themselves. I wouldn't even recognize the version of myself that had not been touched by his influence.

As this is a dissertation on inorganic chemistry, it is fitting that I acknowledge Professor Christopher Cummins for piquing both my academic and research interests. I grew my first crystals for X-ray diffraction in his labs, and they remain among the best

and most memorable to date. Working in his group also introduced me to my future Ph.D. advisor, Professor Jonas Peters. While our relationship has not always been the smoothest of interactions, it has led me this far. I've learned a bit about organometallic chemistry under his guidance, not to mention a thing or two about myself. Thanks for your patience, persistence, and focus, Jonas. I also want to thank several other professors, some of whom have served on my committee, for their time and effort in trying to make me a better scientist: John Bercaw, Dave MacMillan, Jackie Barton, Brian Stoltz, and Harry Gray have all had a hand in helping me reach this point. Professors Jennifer Love and Pierre Kennepohl also graced me with their advice and wisdom. Dr. Gregory Kubas at Los Alamos National Laboratories was very friendly and helpful during the preparation of one of our manuscripts.

Some people who made it easier to get chemistry done include Dian Buchness, Tom Dunn, Rick Gerhart, Mike Roy, Tony "the pump guy" Solyom, Chris Smith, Steve Gould, Anne Penney, Silva Stepanian, and, more recently, Scott Ross. These people are definitely underpaid and undervalued for their contributions. Larry Henling and Dr. Mike Day deserve special thanks for all of their assistance with X-ray crystallography. Larry, in particular, has been wonderfully patient over the years with various members of the Peters group impinging upon his domain. All the while, he has passed on some of his wisdom about the solution and refinement of X-ray diffraction patterns.

The Peters research group has been an adventure. I had the unique experience of starting with the group twice, as everyone left the first time around. Brian Johnson made some of those late nights the first year more enjoyable. Connie Lu, my box-mate of four years, was all I could hope for. I'm sure we weren't always perfect, but it worked out amazingly well. I leave you in the capable hands of two post docs, Connie. Ted Betley and Steve Brown, who can't be mentioned separately, almost managed to turn me into an adequate, if not more polite, bowler. Dave Jenkins was always ready with advice, and Seth Harkins was often good for a beer afterwards. Christine Thomas, Claire Jacobs, and Erin Daida represent the future of the Peters group - best wishes! Mother hen Dr. Cora MacBeth has a great attitude and fine tastes both of which she shared generously. The upheaval of the Peters group begins again as I leave and Drs. Mark Mehn, Eric Rivard, and Bruce MacKay enter stage left, pursued by furies. A special thanks to Dr. MacKay who had the misfortune to be placed in the same office with me just as I entered the writing phase of my graduate experience. Some part of this thesis is probably his as a result of all of the editing and advice he gave, for which I am very grateful. The other member of the Peters group who has been here through it all, Kathleen Hand, has been a dear friend and trusted associate. She is always ready with her bowl of candy and a kind ear and will be greatly missed.

A few other people at Caltech also need to be acknowledged. Smith Nielsen of the Goddard group has been amazingly patient, prompt, and helpful in teaching me about computational methods, and he was always a willing and enjoyable competitor on the softball diamond. Dr. Charlene Ahn, Dr. Theresa Lynn, and Peter Freddolino have been valued singing companions for many years now. We may never have made it as professionals, but it was a lot of fun. Darren Beene, Dr. Oren Scherman, and E. Joseph Nemanick were good friends and good roommates. There were some good times in apartment #103, including (but not limited to) rug burns, candidacy writing, painting, fantasy sports, real sports, late night pie, and some great abstract discussions. As we scatter to the ends of the globe, I hope we manage to stay in touch.

Finally, I want to acknowledge my family. The support of my parents has been tremendous over the years. Home has always been a welcome place to be, however long I have been gone. The soon-to-be newest member of my family, my future wife, and my friend Ann Polsenberg, has made these last two and a half years worthwhile. We're perfect for each other, and I look forward to our long years together.

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 dimethyldiaryltin 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.

Table of Contents

List of Figures

Chapter 1. Background and context for the development of (phosphino)borate ligands

Chapter 2. Bis(phosphino)borates: a new family of monoanionic chelating phosphine ligands

Chapter 3. Electronic studies of bis(phosphino)borate ligands on transition metals

Chapter 4. Zwitterionic and cationic bis(phosphine) platinum(II) complexes: comparative studies relevant to ligand exchange and benzene C-H activation processes

Chapter 5. Platinum-alkyl and hydride complexes supported by the monoanionic tris(phosphino)borate ligand $[PhB(CH_2PPh_2)_3]^-$

Chapter 6. Ni(II), Ni(I), and Ni(0) complexes supported by the isopropyl-substituted tris(phosphino)borate, $[PhB(CH_2P^iPr_2)_3]^-$

Chapter 7. Three-coordinate copper(I) supported by bis(phosphino)borate ligands

List of Tables

Chapter 2. Bis(phosphino)borates: a new family of monoanionic chelating phosphine ligands

Chapter 3. Electronic studies of bis(phosphino)borate ligands on transition metals

Chapter 4. Zwitterionic and cationic bis(phosphine) platinum(II) complexes: comparative studies relevant to ligand exchange and benzene C-H activation processes

Chapter 5. Platinum-alkyl and hydride complexes supported by the monoanionic tris(phosphino)borate ligand $[PhB(CH_2PPh_2)_3]^-$

Chapter 6. Ni(II), Ni(I), and Ni(0) complexes supported by the isopropyl-substituted tris(phosphino)borate, $[PhB(CH_2P^iPr_2)_3]^-$

Chapter 7. Three-coordinate copper(I) supported by bis(phosphino)borate ligands

List of Abbreviations and Nomenclature

Term	Definition
$[Ph_2BP_2]$	$Ph_2B(CH_2PPh_2)_2^-$
$[PhBP_3]$	$PhB(CH_2PPh_2)_3^-$
$[PhBP^{iPr}{}_3]$	$PhB(CH_2P^iPr_2)_3^-$
$[PhBTt^{tBu}]$	$PhB(CH_2S_tBu)_3^-$
[Tp]	$HB(pyrazolyl)_3^-$
$[Tp^{Me_2}]$	$HB(3,5\text{-dimethylpyrazolyl})_3^-$
$\{^1H\}$	hydrogen-1 decoupled
°	degrees in measure of angles
°C	degrees Celsius
^1H	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$^+$, $\{(CH_2CH_2)_2\}_2N^+$
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, $Cy_2PCH_2CH_2PCy_2$
dd	doublet of doublets
ddd	doublet of doublets of doublets
dfepe	di(*per*-fluoro)ethylphosphinoethane, $(CF_3CF_2)_2PCH_2CH_2P(CF_2CF_3)_2$
DFT	density functional theory
dippe	di-*iso*-propylphosphinoethane, $^iPr_2PCH_2CH_2P\,^iPr_2$
DME	1,2-dimethoxyethane
dppe	diphenylphosphinoethane, $Ph_2PCH_2CH_2PPh_2$
dppp	diphenylphosphinopropane, $Ph_2PCH_2CH_2CH_2PPh_2$
dq	doublet of quartets
dt	doublet of triplets

dtbpe	di-*tert*-butylphosphinoethane, $^tBu_2PCH_2CH_2P^tBu_2$
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	$CH_3CH_2C(CH_2PPh_2)_3$
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
^iPr	*iso*-propyl
IR	infrared
L	dative ligand for a transition metal
LACVP	Los Alamos core valence potential
LUMO	lowest unoccupied molecular orbital
m	multiplet
m-	*meta* position on an aryl ring
M	general metal
md	medium (intensity)
Me	methyl
Mes	mesityl, 2,4,6-trimethylphenyl
Me-tripod	$CH_3C(CH_2PPh_2)_3$
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
n-	normal, as in *n*-butyl
n K	n Kelvin
n M	n molar solution
n mV	n millivolts
n V	n volts
^nBu	*n*-butyl
$^nJ_{A-Z}$	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
o-	*ortho* position on an aryl ring
p-	*para* position on an aryl ring
pet.	petroleum
Ph	phenyl
Ph_2SiP_2	$Ph_2Si(CH_2PPh_2)_2$
ppm	parts per million
q	quartet
R	general alkyl or aryl substituent
ref.	reference
s	singlet
S	spin
^{s}Bu	*sec*-butyl
SCE	saturated calomel electrode
SCF	self-consistent field
sec	second(s)
st	strong (intensity)
t	triplet
T (ºC)	temperature in degrees Celsius
TBA	tetra *n*-butyl ammonium
^{t}Bu	*tert*-butyl
td	triplet of doublets
TEA	tetra ethyl ammonium
Tf	triflate, $-S(O)_2CF_3$
THF	tetrahydrofuran
TMEDA	*N,N,N′,N′*-tetramethylethylenediamine
tripod	$HC(CH_2PPh_2)_3$
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.