

AN ELECTROSPRAY STUDY OF RHODIUM (I) WITH BIDENTATE PHOSPHINES  
AND THE PREPARATION AND CHARACTERIZATION OF OTHER LIGANDS

Except where reference is made to the work of others, the work described in this dissertation is my own or was done in collaboration with my advisory committee.

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AN ELECTROSPRAY STUDY OF RHODIUM (I) WITH BIDENTATE PHOSPHINES  
AND THE PREPARATION AND CHARACTERIZATION OF OTHER LIGANDS

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## VITA

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DISSERTATION ABSTRACT

AN ELECTROSPRAY STUDY OF RHODIUM (I) WITH BIDENTATE PHOSPHINES  
AND THE PREPARATION AND CHARACTERIZATION OF OTHER LIGANDS

Kent Lee McCorkle

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Part I: Electrospray mass spectrometry, ESMS, was used to probe the solution chemistry of rhodium(I) complexes of the type  $[\text{Rh}(\text{COD})\{\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\}]_x[\text{BF}_4]_x$  and  $[\text{Rh}(\text{CO})_y\{\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\}]\text{BF}_4$  ( $n = 4, 8, 10, \text{ or } 12$ ;  $x = 1 \text{ or } 2$ ;  $y = 1, 2, \text{ or } 3$ ). Complementary techniques such as  $^{31}\text{P}$  NMR and FAB MS were also used to verify the observations.

Formation of monomer was observed for the short backbone ( $n = 4$ ) and a mixture of monomer and dimer for those with longer backbones ( $n = 8, 10, 12$ ). The amount of monomer vs dimer formed was determined by both ESMS and  $^{31}\text{P}$  NMR and seems to depend largely on reaction conditions. The cyclooctadiene complexes are *cis* while the carbonyls are always *trans*.

By increasing the cone voltage in ESMS, C-H insertion and hydrogen-transfer in these complexes was studied. Loss of hydrogen, formaldehyde, and methanol was observed. Of the three long-chain bis-phosphines ( $n = 8, 10, \text{ and } 12$ ) ease of dehydrogenation increased as chain length decreased. Formation of methanol was also favored as chain length decreased. DPPH underwent only a single dehydrogenation.

Study of DPPB indicated a different process involving the bis-phosphine forming and losing  $\text{HPPH}_2$  and 1,3-butadiene.

Part II: Dodecyl- and octadecyliminodiacetic acid were also synthesized and complexed with a variety of metals to study their potential usefulness in environmental clean-up. However, both ligands were found to primarily form insoluble  $\text{ML}_2$ -type complexes or metal hydroxides rendering them ineffective.

Part III: Synthesis of novel mixed arsine-phosphine ligands were attempted by reacting  $\text{LiAsPh}_2$  with several different phosphonium salts. The novel complex  $[\text{Ph}_3\text{P}(\text{CH}_2)_3\text{AsPh}_2]\text{I}$  was formed, along with  $\text{Ph}_2\text{As}(\text{CH}_2)_3\text{AsPh}_2$ , from reaction of  $\text{LiAsPh}_2$  with  $[\text{Ph}_3\text{P}(\text{CH}_2)_3\text{I}]\text{I}$ .

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## ABBREVIATIONS

acac	$\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{C}(\text{O})\text{CH}_3$	acetylacetonate
amu	atomic mass units	
BDPBZ	$\text{o-Ph}_2\text{PC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{C}_6\text{H}_4\text{PPh}_2\text{-o}$	2,2'-Bis(o-diphenylphosphino)bibenzyl
BDPH	$\text{Ph}_2\text{P}(\text{CH}_2)_2\text{CH}=\text{CH}(\text{CH}_2)_2\text{PPh}_2$	1,6-Bis(diphenylphosphino)- <u>trans</u> -hex-3-ene
bpt	boiling point	
CID	Collisionally induced dissociation	
CMC	Critical micelle concentration	
DCI	Desorption chemical ionization	
DPPM	$\text{Ph}_2\text{P}(\text{CH}_2)_1\text{PPh}_2$	Bis(diphenylphosphino)methane
DPPE	$\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$	1,2-Bis(diphenylphosphino)ethane
DPPP	$\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$	1,3-Bis(diphenylphosphino)propane
DPPB	$\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2$	1,4-Bis(diphenylphosphino)butane
DPPO	$\text{Ph}_2\text{P}(\text{CH}_2)_8\text{PPh}_2$	1,8-Bis(diphenylphosphino)octane
DPPD	$\text{Ph}_2\text{P}(\text{CH}_2)_{10}\text{PPh}_2$	1,10-Bis(diphenylphosphino)decane
DPPDOD	$\text{Ph}_2\text{P}(\text{CH}_2)_{12}\text{PPh}_2$	1,12-Bis(diphenylphosphino)dodecane
DPPHD	$\text{Ph}_2\text{P}(\text{CH}_2)_{16}\text{PPh}_2$	1,16- Bis(diphenylphosphino)hexadecane

dtc	$S_2CNR_2$	Dithiocarbamate
e.e.	enantiomeric excess	
ESI	Electrospray ionization	
ESMS	Electrospray mass spectrometry	
FAB	Fast-atom bombardment	
g	gram	
GC	Gas chromatography	
hr	hour	
kJ	kilojoule	
kV	kilovolt	
L	liter	
mbar	millibar	
mins	minute	
ml	milliliter	
mol	mole	
MS	mass spectrometry	
NBA	$3-NO_2-C_6H_4-CH_2OH$	3-nitrobenzyl alcohol
NBD		bicyclo[2,2,1]heptadiene <i>or</i> norbornadiene
NMR	nuclear magnetic resonance	
PCE	$Cl_2C=CCl_2$	perchloroethylene
POP	$Ph_2P(CH_2)_2O(CH_2)_2PPh_2$	
POOP	$Ph_2P(CH_2)_2(OCH_2CH_2)_2PPh_2$	

POOOP	$\text{Ph}_2\text{P}(\text{CH}_2)_2(\text{OCH}_2\text{CH}_2)_3\text{PPh}_2$	
ppm	parts per million	
TMEDA	$(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$	tetramethylethylenediamine
$\mu\text{l}/\text{min}$	microliters per minute	