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.

_____

Kent Lee McCorkle

Certificate of Approval:

_____	_____
Thomas R. Webb Associate Professor Chemistry	William E. Hill, Chair Professor Chemistry
_____	_____
Curtis G. Shannon Associate Professor Chemistry	Michael L. McKee Professor Chemistry

_____

Stephen L. McFarland
Dean
Graduate School

Computer software used:

Word Processor:	WordPerfect 9.0 (for Windows)
Graphs:	Excel 2002 (for Windows)
Molecules:	ChemDraw 4.0.1 (for Windows) and ChemWindow 6.5 Spectroscopy (for Windows)

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

Kent Lee McCorkle

A Dissertation

Submitted to

the Graduate Faculty of

Auburn University

in Partial Fulfillment of the

Requirements for the

Degree of

Doctor of Philosophy

Auburn, Alabama

August 4, 2003

VITA

Kent Lee McCorkle, son of Lyndon Kent and Lorena Marcum McCorkle, and Joyce Prather and Kenneth Wayne Graham, Jr., was born on May 23, 1969 in Tipton, Indiana. He graduated from Tri-Central High School in 1987. In the spring of 1991 he graduated from Rose-Hulman Institute of Technology in Terre Haute, Indiana with a Bachelor of Science degree in Chemistry. He attended graduate school for two years at Kansas State University before entering the Graduate School, Auburn University, Auburn Alabama, in September, 1994. He is a member of the Phi Lambda Upsilon chemistry honor society.

DISSERTATION ABSTRACT

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

Kent Lee McCorkle

Doctor of Philosophy, August 4, 2003
(B.S. Chemistry, Rose-Hulman Institute of Technology)

246 Typed pages

Directed by William E. Hill

Part I: Electrospray mass spectrometry, ESMS, was used to probe the solution chemistry of rhodium(I) complexes of the type $[Rh(COD)\{Ph_2P(CH_2)_nPPh_2\}]_x[BF_4]_x$ and $[Rh(CO)_y\{Ph_2P(CH_2)_nPPh_2\}]BF_4$ (n = 4, 8, 10, or 12; x = 1 or 2; y = 1, 2, or 3). Complementary techniques such as ^{31}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}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, 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 $HPPh_2$ 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 ML_2-type complexes or metal hydroxides rendering them ineffective.

Part III: Synthesis of novel mixed arsine-phosphine ligands were attempted by reacting $LiAsPh_2$ with several different phosphonium salts. The novel complex $[Ph_3P(CH_2)_3AsPh_2]I$ was formed, along with $Ph_2As(CH_2)_3AsPh_2$, from reaction of $LiAsPh_2$ with $[Ph_3P(CH_2)_3I]I$.

ACKNOWLEDGMENTS

The author would like to express his deepest and most sincere appreciation to Dr. William E. Hill for his support, guidance, and patience, without which this work would not have been possible. He also wishes to thank his committee members; Dr. Michael L. McKee, Dr. Curtis G. Shannon, and Dr. Thomas R. Webb for their time, discussions, and helpful suggestions. Special thanks also to Dr. Christopher B. Roberts for assistance and input in his role as outside reader. Finally, the author would like to thank the members of the 'Hill group' for their friendship and assistance in the laboratory, especially Dr. Paul D. Norgaard.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABBREVIATIONS

acac	$CH_3C(O)CH_2C(O)CH_3$	acetylacetonate
amu	atomic mass units	
BDPBZ	o-$Ph_2PC_6H_4CH_2CH_2C_6H_4PPh_2$-o	2,2'-Bis(o-diphenylphosphino)bibenzyl
BDPH	$Ph_2P(CH_2)_2CH{=}CH(CH_2)_2PPh_2$	1,6-Bis(diphenylphosphino)-trans-hex-3-ene
bpt	boiling point	
CID	Collisionally induced dissociation	
CMC	Critical micelle concentration	
DCI	Desorption chemical ionization	
DPPM	$Ph_2P(CH_2)_1PPh_2$	Bis(diphenylphosphino)methane
DPPE	$Ph_2P(CH_2)_2PPh_2$	1,2-Bis(diphenylphosphino)ethane
DPPP	$Ph_2P(CH_2)_3PPh_2$	1,3-Bis(diphenylphosphino)propane
DPPB	$Ph_2P(CH_2)_4PPh_2$	1,4-Bis(diphenylphosphino)butane
DPPO	$Ph_2P(CH_2)_8PPh_2$	1,8-Bis(diphenylphosphino)octane
DPPD	$Ph_2P(CH_2)_{10}PPh_2$	1,10-Bis(diphenylphosphino)decane
DPPDOD	$Ph_2P(CH_2)_{12}PPh_2$	1,12-Bis(diphenylphosphino)dodecane
DPPHD	$Ph_2P(CH_2)_{16}PPh_2$	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 chromotography	
hr	hour	
kJ	kilojoule	
kV	kilovolt	
L	liter	
mbar	millibar	
mins	minute	
ml	milliter	
mol	mole	
MS	mass spectrometry	
NBA	$3\text{-}NO_2\text{-}C_6H_4\text{-}CH_2OH$	3-nitrobenzyl alcohol
NBD		bicyclo[2,2,1]heptadiene *or* 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	$Ph_2P(CH_2)_2(OCH_2CH_2)_3PPh_2$	
ppm	parts per million	
TMEDA	$(CH_3)_2NCH_2CH_2N(CH_3)_2$	tetramethylethylenediamine
µl/min	microliters per minute	