

DOCTORAL THESIS

The syntheses and reactivity of polydentate PNNP ligands and macrocyclic polyphosphine ligands

Chen, Yang

Date of Award:
1998

[Link to publication](#)

General rights

Copyright and intellectual property rights for the publications made accessible in HKBU Scholars are retained by the authors and/or other copyright owners. In addition to the restrictions prescribed by the Copyright Ordinance of Hong Kong, all users and readers must also observe the following terms of use:

- Users may download and print one copy of any publication from HKBU Scholars for the purpose of private study or research
- Users cannot further distribute the material or use it for any profit-making activity or commercial gain
- To share publications in HKBU Scholars with others, users are welcome to freely distribute the permanent URL assigned to the publication

**The Syntheses and Reactivity
of
Polydentate PNNP Ligands
and
Macrocyclic Polyphosphine Ligands**

CHEN Yang

A thesis submitted in partial fulfillment of the requirements

For the degree of

Doctor of Philosophy

November 1998

Hong Kong Baptist University

ABSTRACT

A series of novel and chiral diimino-diphosphine (PNNP) ligands were synthesized in good yields *via* the condensation of *o*-(diphenylphosphino)benzaldehyde with the appropriate diamine. The corresponding diamino-diphosphine (PNNP) ligands were synthesized in good yields by the reduction of the diimino-diphosphino ligands with NaBH₄. The reactions of such novel and chiral PNNP ligands with Ru(II), Fe(II), Pd(II), Cu(I) produced bis-chelate/single-bridged dinuclear complexes, tri-dentate and tetra-dentate mononuclear complexes. All of the complexes were characterized by analytical and spectroscopic methods. Some of them were further confirmed by the X-ray crystal structures.

The reactions of *trans*-RuCl₂[P₂N₂H₄], *trans*-RuCl₂[*R,R*-cyclohexyl-P₂N₂] and *trans*-RuCl₂[*R,R*-cyclohexyl-P₂N₂H₄] with Ag⁺, CuCl or [Cu(CH₃CN)₄]⁺ result in *trans*→*cis* isomerization giving *cis* analogues in near quantitative yields which have been isolated and characterized. Photolytical *cis*→*trans* isomerizations of the *cis* species were observed by ³¹P{¹H} NMR monitoring. The pathway of the isomerization has been addressed experimentally.

The first selective-functionalized tritertiary 1,5,9-triphosphacyclododecane Mo complexes with one or three pendant ether functions were prepared from the trisecondary 1,5,9-triphospha-cyclododecane precursor. All the compounds have been characterized analytically and spectroscopically.

TABLE OF CONTENTS

Declaration	i
Abstract	ii
Acknowledgements	iv
Table of Contents	vi
List of Tables	x
List of Figures	xii
List of Schemes	xv
List of Abbreviation	xx
INTRODUCTION	1
CHAPTER 1 PNNP Ligands and Their Transition Metal Complexes	
1.1. Introduction	5
1.1.1. Preparation of PNNP ligands	5
1.1.2. Reactivities of PNNP Ligands Towards Transition Metals	8
1.2. Results and Discussion	17
1.2.1. Preparation of PNNP ligands	17

1.2.2. Electronic and Steric Consideration of PNNP Ligands	19
1.2.2.1. Phosphines as Ligands	20
1.2.2.2. Imines as Ligands	23
1.2.2.3. Amines as Ligands	25
1.2.3. Reactivity of PNNP Ligands Towards Transition Metals	28
1.2.3.1. Mono- and Binuclear Complexes of P_2N_2 and $P_2N_2H_4$ Ligands with The $[(\eta^5-Cp^*)Ru]^+$ Fragment	28
1.2.3.2. Mononuclear Pd(II) Complex of $P_2N_2H_4$ Ligand	41
1.2.3.3. Photochemical Reaction of Cationic Metallocenic Iron-Complexes with P_2N_2 Ligand	45
1.2.3.4. <i>Trans-cis</i> Isomerization of $RuCl_2[P_2N_2H_4]$	51
1.2.3.5. A Proposed Mechanism of $RuCl_2[P_2N_2H_4]$ - Catalyzed Homogeneous Hydrogenation of Olefins	62
1.3. Experimental Section	66
Chapter 2 Chiral PNNP Ligands and Their Transitions Metal Complexes	
2.1. Introduction	73
2.1.1. Chiral Diphosphines	73
2.1.1.1. Diphosphines With At Least One Asymmetric Phosphorus	

2.1.1.2. Diphosphines With A Chiral Group connecting Two Achiral Phosphorus Atoms	
2.1.2. Chiral P-N Ligands	82
2.2. Results and Discussion	90
2.2.1. Preparation of chiral PNNP ligands	89
2.2.2. Reactivity of chiral PNNP ligands	98
2.2.2.1. <i>Trans-cis</i> rearrangement of $\text{RuCl}_2[\text{R,R-cyclohexyl-P}_2\text{N}_2]$ and $\text{RuCl}_2[\text{R,R-cyclohexyl-P}_2\text{N}_2\text{H}_4]$	98
2.2.2.2. Reactivity of <i>R,R</i> -diphenyl- P_2N_2 ligand towards $\text{RuCl}_2(\text{DMSO})_4$ and $\text{PdCl}_2(\text{PhCN})_2$	111
2.2.2.3. Reactivity of <i>R,R</i> -diphenyl- $\text{P}_2\text{N}_2\text{H}_4$ ligand towards $\text{RuCl}_2(\text{DMSO})_4$ and $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$	115
2.2.2.4. Reactivity of <i>S</i> -Binap- P_2N_2 Towards Ag(I), Cu(I) and Pd(II)	118
2.2.2.5. Reactivity of <i>S</i> -Binap- $\text{P}_2\text{N}_2\text{H}_4$ Towards $\text{PdCl}_2(\text{PhCN})_2$, $\text{RuCl}_2(\text{DMSO})_4$ and $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$	123
2.3. Experimental Section	127

CHAPTER 3 Polyphosphine Macrocycles and Transition Metal Complexes

3.1. Introduction	141
3.1.1. The major synthetic categories	143

3.1.1.1. Direct macrocyclic syntheses	143
3.1.1.2. Metal-template macrocyclic syntheses	146
3.1.2. The liberation of free macrocycles from their metal complexes	153
3.1.2.1. The addition of excess acid	153
3.1.2.2. The addition of a strongly competition ligand	154
3.1.2.3. Oxidizing or reducing the complexed metal leads to its spontaneous dissociation from the macrocycle	155
3.1.3. The coordination chemistry of P ₃ -macrocyclic ligands towards transition metals	156
3.2. Results and Discussion	158
3.2.1. The molybdenum (0) complexes of P ₃ -macrocycle with a pendant donor	158
3.2.2. Metal-template synthesis of P ₄ -macrocyclic complexes	172
3.3. Experimental Section	181
CONCLUSION	195
REFERENCES	197
APPENDICES	210
CURRICULUM VITAE	282