In The Name of God

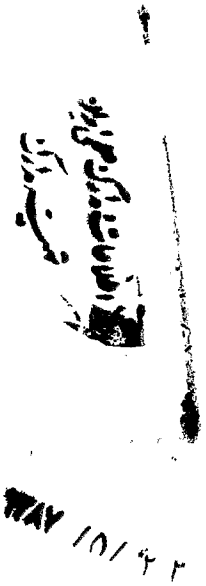
Shiraz University
Faculty of Science

Ph.D. Dissertation In Inorganic Chemistry

Binuclear Organoplatinum and Organopalladium Complexes Containing 2-diphenylphosphinopyridine Ligands

By

Bita Shafaatian



Supervised by

Mehdi Rashidi Ph.D

November 2007

دانشگاه شیراز

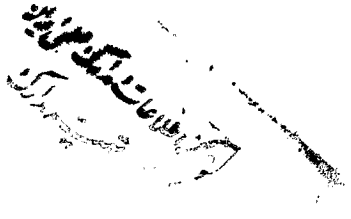
دانشکده علوم

پایان‌نامه دکتری در رشته شیمی (معدنی)

کمپلکسهای دو هسته ای آلی پلاتین و پالادیم حاوی دو لیگاند ۲-دی فنیل فسفینو پیریدین

توسط:

بیتا شفاعتیان



استاد راهنما:

دکتر مهدی رشیدی

آذر ماه ۱۳۸۶

IN THE NAME OF GOD

BINUCLEAR ORGANOPLATINUM AND ORGANOPALLADIUM COMPLEXES CONTAINING 2-DIPHENYLPHOSPHINOPYRIDINE LIGANDS

BY:

Bita Shafaatian

THESIS

SUBMITTED TO THE SCHOOL OF GRADUATE STUDIES IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY (Ph.D.)

IN

INORGANIC CHEMISTRY

SHIRAZ UNIVERSITY

SHIRAZ

ISLAMIC REPUBLIC OF IRAN

EVALUATED AND APPROVED BY THE THESIS COMMITTEE AS: **EXCELLENT**

.....M. Rashidi, Ph.D., Prof. of Chemistry (Chairman)

.....D. Mohajer, Ph.D., Prof. of Chemistry

.....M. Asadi, Ph.D., Prof. of Chemistry

.....N. Safari, Ph.D., Prof. of Chemistry

.....A. R. Esmaeilbeig, Ph.D., Assis. Prof. of Chemistry

.....S. M. Nabavizadeh, Ph.D., Assis. Prof. of Chemistry

November 2007

Dedicated to:

My Dear Son Saeid

and

My Husband

ACKNOWLEDGEMENT

I would like to express my sincere gratitude to my research director Dr. M. Rashidi and for his excellent constructive and supervision during my research.

I would like to express my appreciation to the members of the thesis committee for their valuable suggestions.

I express my gratitude to my husband and my little Son for their kindness, patience and encouragement during the study.

Deep appriciation is expressed to my mother and my father for their encouragement during my education.

ABSTRACT

BINUCLEAR ORGANOPLATINUM AND ORGANOPALLADIUM COMPLEXES CONTAINING 2-DIPHENYLPHOSPHINOPYRIDINE LIGANDS

BY

BITA SHAFAATIAN

Using a designed general synthetic method, some unsymmetrical cationic organo-diplatinum complexes each containing two bridging 2-diphenylphosphinopyridine (PN), PPh_2py, ligands and a platinum-platinum donor-acceptor bond have been synthesized. Thus, reaction of *cis,cis*-[$Me_2Pt(\mu\text{-}SMe_2)_2PtMe_2$], **1**, with 4 equivalent of PN in CH_2Cl_2 gave *cis*-[$PtMe_2(PN\text{-}\kappa^1P)_2$], **2**. When complex **2** was reacted with 1 equivalent of HX (X=CF_3COO) in CH_2Cl_2, an approximately 2:1 mixture of *trans*-[$PtMeX(PN\text{-}\kappa^1P)_2$], **3**, and [$PtMe(\eta^2\text{-}PN)(PN\text{-}\kappa^1P)$]X, **4**, was obtained. The reaction of one equivalent of the latter monomeric mixture with one equivalent of *cis*-[$Pt(p\text{-}MeC_6H_4)_2(SMe_2)_2$] in CH_2Cl_2 immediately gave a mixture of the head-to-head (*HH*) stereoisomer of diplatinum complex *hh*-[$MePt(\mu\text{-}PN)_2Pt(p\text{-}MeC_6H_4)_2$]X, **7a**, with (*HT*) stereoisomer *ht*-[$MePt(\mu\text{-}PN)(\mu\text{-}NP)Pt(p\text{-}MeC_6H_4)_2$]X, **7b**. The conversion of the *HH* isomer **7a** to the *HT* isomer **7b** in CH_2Cl_2 took place during 14 h. Based on the observations, a mechanism for the conversion of the kinetic *HH* stereoisomer to the thermodynamic *HT* stereoisomer is suggested which involves association of X^- with the $N_2Pt(p\text{-}MeC_6H_4)_2$ center following by one-arm dissociation of one of the PN bridging ligands from the nitrogen terminal in the *HH* isomer, and subsequent exchange of the ligating atom and reformation of the *HT* arrangement. The methyl-di *p*-tolyl dimer *ht*-[$MePt(\mu\text{-}PN)(\mu\text{-}NP)Pt(p\text{-}MeC_6H_4)_2$]X, **7b**, in solution gradually isomerizes to *ht*-[$(p\text{-}MeC_6H_4)Pt(\mu\text{-}PN)(\mu\text{-}NP)PtMe(p\text{-}MeC_6H_4)$]X, **7c**, by an aryl ligand transfer. When the complexes have non-coordinating PF_6^- as the counter anion, no such isomerization would occur. All the complexes were fully characterized using multinuclear (^1H, ^{31}P and ^{195}Pt) NMR spectroscopy and the complex *ht*-[$(p\text{-}MeC_6H_4)Pt(\mu\text{-}PN)(\mu\text{-}NP)PtMe(p\text{-}MeC_6H_4)$]X, **7c**, was further characterized by single crystal X-ray crystallography. The possibility of formation of the corresponding Pt-Pd analogue has also been investigated.

LIST OF CONTENTS

Content Page

Content Page

Content Page

Content **Page**

Content **Page**

Content **Page**

List of Tables

Tables **Page**

List of Figures

Figure **Page**

Figure **Page**

Figure **Page**

Figure **Page**

Figure **Page**