

In The  
Name of  
God

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Shiraz University  
Faculty of Science

**Ph.D. Dissertation In Inorganic Chemistry**

**Binuclear Organoplatinum and Organopalladium  
Complexes Containing 2-diphenylphosphinopyridine  
Ligands**

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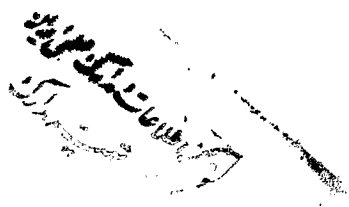
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LIGANDS**

BY:

Bitá Shafaatian

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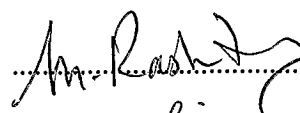
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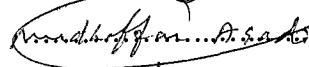
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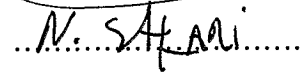
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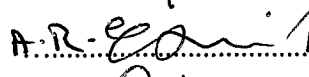
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*Dedicated to:*

*My Dear Son Saeid*

*and*

*My Husband*

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## ABSTRACT

### BINUCLEAR ORGANOPLATINUM AND ORGANOPALLADIUM COMPLEXES CONTAINING 2-DIPHENYLPHOSPHINOPYRIDINE LIGANDS

BY

BITA SHAFATIAN

Using a designed general synthetic method, some unsymmetrical cationic organo-diplatinum complexes each containing two bridging 2-diphenylphosphinopyridine (PN), PPh<sub>2</sub>py, ligands and a platinum-platinum donor-acceptor bond have been synthesized. Thus, reaction of *cis,cis*-[Me<sub>2</sub>Pt(μ-SMe<sub>2</sub>)<sub>2</sub>PtMe<sub>2</sub>], **1**, with 4 equivalent of PN in CH<sub>2</sub>Cl<sub>2</sub> gave *cis*-[PtMe<sub>2</sub>(PN-κ<sup>1</sup>P)<sub>2</sub>], **2**. When complex **2** was reacted with 1 equivalent of HX (X=CF<sub>3</sub>COO) in CH<sub>2</sub>Cl<sub>2</sub>, an approximately 2:1 mixture of *trans*-[PtMeX(PN-κ<sup>1</sup>P)<sub>2</sub>], **3**, and [PtMe(η<sup>2</sup>-PN)(PN-κ<sup>1</sup>P)]X, **4**, was obtained. The reaction of one equivalent of the latter monomeric mixture with one equivalent of *cis*-[Pt(*p*-MeC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>(SMe<sub>2</sub>)<sub>2</sub>] in CH<sub>2</sub>Cl<sub>2</sub> immediately gave a mixture of the head-to-head (*HH*) stereoisomer of diplatinum complex *hh*-[MePt(μ-PN)<sub>2</sub>Pt(*p*-MeC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>]X, **7a**, with (*HT*) stereoisomer *ht*-[MePt(μ-PN)(μ-NP)Pt(*p*-MeC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>]X, **7b**. The conversion of the *HH* isomer **7a** to the *HT* isomer **7b** in CH<sub>2</sub>Cl<sub>2</sub> 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<sup>-</sup> with the N<sub>2</sub>Pt(*p*-MeC<sub>6</sub>H<sub>4</sub>)<sub>2</sub> 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(μ-PN)(μ-NP)Pt(*p*-MeC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>]X, **7b**, in solution gradually isomerizes to *ht*-[(*p*-MeC<sub>6</sub>H<sub>4</sub>)Pt(μ-PN)(μ-NP)PtMe(*p*-MeC<sub>6</sub>H<sub>4</sub>)]X, **7c**, by an aryl ligand transfer. When the complexes have non-coordinating PF<sub>6</sub><sup>-</sup> as the counter anion, no such isomerization would occur. All the complexes were fully characterized using multinuclear (<sup>1</sup>H, <sup>31</sup>P and <sup>195</sup>Pt) NMR spectroscopy and the complex *ht*-[(*p*-MeC<sub>6</sub>H<sub>4</sub>)Pt(μ-PN)(μ-NP)PtMe(*p*-MeC<sub>6</sub>H<sub>4</sub>)]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.

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