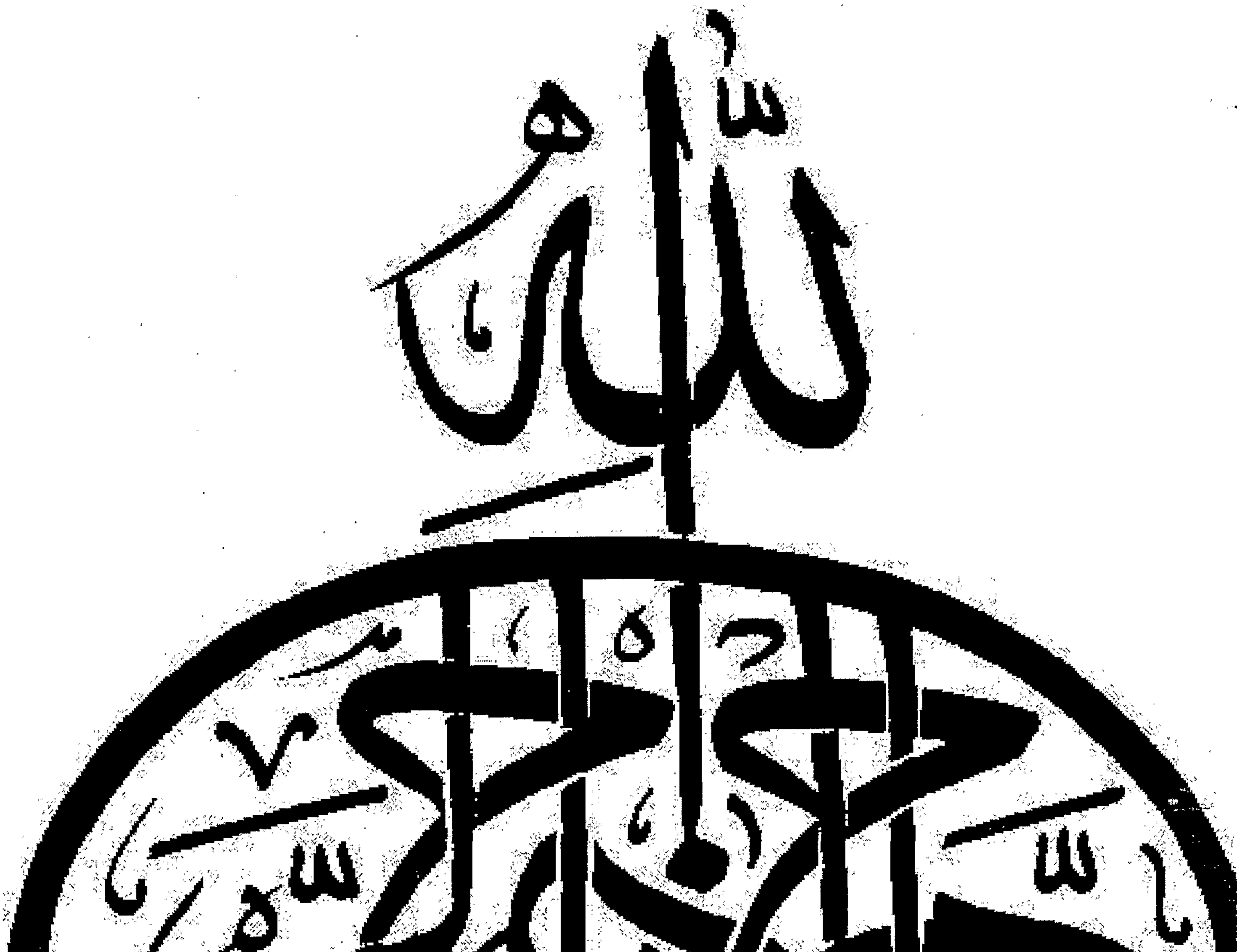

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Razi University

Faculty of Science
Department of Chemistry

M. Sc. Thesis

A Kinetic Investigation of the Oxidative Addition Reactions of [$PtMe_2(Ph_2phen)$] Complex in Different and a Mixture of Solvents

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July 2008

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دانشگاه رازی

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گروه شیمي

پایان نامه جهت اخذ درجه کارشناسي ارشد

در رشته:
شیمي معدني

بررسی سینتیکي واکنش هاي اکسایشي – افزایشي کمپلکس $[PtMe_2(Ph_2phen)]$ در حلال های مختلف و مخلوطی از حلال ها

استاد راهنما:
دکتر ناهید شاه آبادي

نگارش:
سمیرا شجاع پور

۱۰۴۲۱۳

تیر ۱۳۸۷

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July 2008

Dedicated to :

My dear husband

My parents

My husband 's parents

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Abstract

A Kinetic Investigation of the Oxidative Addition Reactions of [$PtMe_2(Ph_2phen)$] Complex in Different and a Mixture of Solvents

By:

Samira Shojapoor

In this thesis the oxidative addition reactions of reagents, ethyl bromide (EtBr), n-propyl bromide (n-PrBr) with [$PtMe_2(Ph_2phen)$] (I) were studied in different solvents such as acetone, benzene and the mixture of acetone and acetonitrile.

Oxidative addition reactions of [$PtMe_2(Ph_2phen)$] with (EtBr) and (n-PrBr) produced the [$PtMe_2Et(Ph_2phen)Br$] (II) and [$PtMe_2$n-Pr(Ph_2phen)Br] (III).

These complexes were characterized by ^{1}H-NMR, UV-Vis spectroscopy and elemental analysis.

The kinetic study of these reactions were proceeded by UV-Vis spectrophotometry . The decrease in MLCT absorption band of starting platinum(II) substrate during the conversion to platinum(IV) product was selected as a criterion for the reaction rate.

The reactions were monitored at different concentrations of excess amounts of reagents in different temperatures. These reactions occurred in acetone, benzene and a mixture of acetone and acetonitrile.

The reaction rate was determined and the effect of solvent and the reagents on reaction rate has been discussed.

The activation parameters were calculated by Arrhenius and Eyring equations and compared with other data previously reported on analogous systems.

With the aid of the kinetic results and other collected results a modified S_N2-type mechanism was suggested for oxidative addition reactions.

It has been concluded that the mechanism is strongly dependent on the solvent and kind of reagent.

The radical scavenger, benzoquinone, and also p-methoxy phenol as inhibitor had no effect on the rate.

These results and also the reproducibility of the kinetic data suggested that the radical pathway had no contribution.

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ABBREVIATIONS

A_0	Absorbance at time 0
A_t	Absorbance at time t
A_∞	Absorbance completion of reaction
bipy	2,2′-bipyridine
Dppm	Bis(diphenyl phosphino) methane
EtBr	bromo ethane
IL	Inter Ligand transition
L	Ligand
LF	Ligand Field transition
LLCT	Ligand to Different Ligand Charge Transfer
LMCT	Ligand to Metal Charge Transfer
M	Metal
Me	Methyl
MLCT	Metal to Ligand Charge Transfer
n-PrBr	1-bromo propane
N N	bidentate ligand
ox.add.	Oxidative addition reaction
Ph_2phen	4,7-diphenyl 1,10-phenanthroline
^{i}Pr	Isopropyl
Py	Pyridine
R	Alkyl group
S	Solvent
UV	Ultra-Violet
X	Halide

CHAPTER ONE

INTRODUCTION

AND

LITERATURE REVIEW

CHAPTER ONE

INTRODUCTION AND LITERATURE REVIEW

1.1 General background:

Organometallic complexes are any compounds containing a metal atom or ion at least one direct metal – carbon bond [1], of which the simplest is the M – C single bond of metal alkyls[2]. The first organometallic compound, tetramethyl diarsine, was synthesized by Cadet and Gassincourt in 1760 [3].

The compound was characterized by Bunsen. Frankland, student of Bunsen's synthesized diethylzinc as liquid [4].

The field of organometallic chemistry began in 1827 when W.C. Zeise, a Danish pharmacist, boiled a solution of potassium hexa chloro platinate (IV) in ethanol and obtained, on cooling, long yellow needles of the very first organometallic complex ever prepared, $K^+[Pt(C_2H_4)Cl_3]^-$. H_2O commonly referred to as zeise's salt [5].

At the first time platinum become known as "white gold"(this term is used to described an Au/Pd alloy) [6].

The name originates from the Spanish word "platina" meaning "silver"[7]. Platinum was discovered by a stronomer, Antonia de Ulloa in 1735 in South America[8].

The platinum group metals (PGM_s), which consist of six elements in group 8-10 of the periodic table are often found collectively in nature. They are ruthenium, rhodium, palladium, osmium, iridium and platinum.

Organometallic and coordination chemistry of platinum is peculiar on two accounts : (i) due to the variety of compounds that this metal forms, and (ii) owing to the wide variety of reactions that these participate in [9].

Platinum with atomic weight 195.08 has several isotopes. These isotopes are of mass 194.0 (32.9%), 195.0 (33.6%), 196.0 (25.3%) and 198.0 (7.2%) [6]. Since ^{195}Pt with

natural abundance 33.6% has a nuclear spin of 1.2 , coupling between the metal and other nuclei creates distinctive patterns in the spectra [10].

Platinum has been an important element in organometallic chemistry because it forms a broad range of organometallic compounds that are kinetically inert to enable them to be isolated and characterized [10].

1.1.1 Application of platinum compounds

Platinum is a basic metal for resistance temperature range and therefore used for wires, glass fiber, optical glasses, special scientific apparatus, electrodes subjected to chemical attack and for making jewellery [11] and for plating. Also it is used in the chemicals as cladding to prevent attack by particularly corrosive materials such as hot hydrofluoric acid, therefore, it is used with rhodium as a hardening agent.

In the chemical industries, platinum or compounds of platinum are used in a wide variety of catalytic applications. For instance decomposition of N_2H_4 to N_2 and NH_3 is catalyzed by platinum. It is used as catalyst in oxidation of ammonia to nitric acid [6], oxidation of hydrocarbons in the fuel cells.

Discovery of the remarkable biological activites of the anticancer platinum drug, cisplatin, cis-$[PtCl_2(NH_3)_2]$, has opened an impressive chapter in the history of bioinorganic chemistry[12]. The platinum diamino complexes cisplatin and carboplatin are highly effective anticancer drugs, but their use is limited by dose-limiting side-effects, by their restricted spectrum of anticancer activity, and by the development of resistance after repeated use in treatment [13]. As an approach to avoid toxic side-effects, we are exploring the use of non-toxic platinum pro-drugs which can be activated by light leading to the release of active antitumour agents directly into the cancer cells. The first crystal structures of the Pt(IV)-diazido complexes are cis,trans,cis-$[Pt(N_3)_2(OH)_2(NH_3)_2]$ and cis,trans-$[Pt(N_3)_2(OH)_2(en)]$ that shown in Fig (1.1). These complexes can be activated by light to give highly reactive platinum(II) species which bind rapidly to nucleotides and ultimately cause damage to the cell that leads to cell death [14].

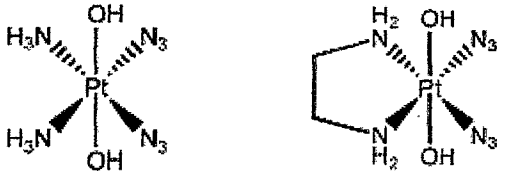

Fig.1.1 Chemical drawings of cis,trans,cis-$[Pt(N_3)_2(OH)_2(NH_3)_2]$ and cis,trans-$[Pt(N_3)_2(OH)_2(en)]$