

**SYNTHESIS AND CHARACTERISATION OF ALKYLATED
ISOCYANATE DERIVATIVES OF $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$**

BY

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**DEPARTMENT OF PURE AND INDUSTRIAL CHEMISTRY
UNIVERSITY OF NIGERIA, NSUKKA**

DECEMBER, 2015

TITLE PAGE

**SYNTHESIS AND CHARACTERISATION OF ALKYLATED ISOCYANATE
DERIVATIVES OF $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$**

**A PROJECT REPORT SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENT FOR THE DEGREE OF MASTER OF SCIENCE (M.Sc) IN
INORGANIC CHEMISTRY, UNIVERSITY OF NIGERIA, NSUKKA**

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APPROVAL PAGE

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(Head of Department)

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Date _____

External Examiner

CERTIFICATION

This is to certify that the research work titled Synthesis and Characterisation of Alkylated Isocyanate Derivatives of $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$ was carried out by Ozoemena, Chimezie Peter (PG/M.Sc/12/61786) , and has been approved by the undersigned of the Department of Pure and Industrial chemistry, University of Nigeria, Nsukka, submitted in partial fulfilment for the requirement of the award of Master of Science (M.Sc.) in Inorganic Chemistry.

Dr. Oguejiofo T. Ujam
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DEDICATION

I dedicate this research work to the almighty God for his enabling grace and ability, and to my beloved parent Mr. and Mrs. Christopher and Patience Ozoemena.

ACKNOWLEDGEMENTS

I wish to express my profound gratitude to God for his infinite mercies and protection over my life during my academic pursuit. My very special appreciation goes to my project supervisor, Dr. Oguejiofo T. Ujam, our collaborators Prof. Pius Ukoha, Prof. Allen Oliver, Prof. Bill Henderson, and Prof. Scott .J. McIndoe and the entire staff of the Department of Pure and Industrial chemistry, University of Nigeria, whose encouragements immensely contributed to the success of this work. In addition to my supervisor, a large number of other scientific professionals and institutions played important roles in this project. Their contributions of time and experiences added immeasurably to the relevance and accuracy of the outcome of this research. I highly appreciate Dr. Obasi and Mrs Ukwueze for their moral advice to continue in this research. I am indebted to my lovely wife Mary Ozoemena, my sister-in-laws, nephews, niece, friends; Ebube, Dorathy, David, Grace and my classmates for their support towards the successful completion of this project work. My family members were most supportive during this research. Finally, I am thankfully grateful to my parents for their encouragement and support; my brothers and my sisters, Osita, Emeka, Chinasa and Ngozi for their supportive concerns.

ABSTRACT

The highly nucleophilic bridging sulfide centers in bis(ϵ -sulfido)tetrakis(triphenylphosphine) diplatinum(II), $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$ enables the incorporation of any organic functionality (R) through facile monoalkylation to form cationic complex $[\text{Pt}_2(\mu\text{-S})(\mu\text{-SR})(\text{PPh}_3)_4]^+$. The organic electrophiles; N,N $\hat{\text{o}}$ -(2-dichloroethyl) piperazine-4-carboxi-amine, N-(2-chloroethyl) morpholine-4-carboxi-amine, and N-(2-chloroethyl)-1-methylpiperazine-4-carboxi-amine derived from isocyanate were synthesised by the reactions of piperazine, morpholine and methyl piperazine respectively with 2-chloroethyl isocyanate in diethyl ether. This potentially formed highly functionalised organic electrophiles N-(2-chloroethyl) morpholine-4-carboxi-amine, and N-(2-chloroethyl)-1-methylpiperazine-4-carboxi-amine was incorporated into $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$ in methanol to yield the corresponding monoalkylated derivatives $[\text{Pt}_2(\epsilon\text{-S})(\epsilon\text{-SCH}_2\text{CH}_2\text{NHC}(\text{O})\text{N}(\text{CH}_2\text{CH}_2)_2\text{O})(\text{PPh}_3)_4]^+$ and $[\text{Pt}_2(\epsilon\text{-S})(\epsilon\text{-SCH}_2\text{CH}_2\text{NHC}(\text{O})\text{N}(\text{CH}_2\text{CH}_2)_2\text{NCH}_3)(\text{PPh}_3)_4]^+$. The reaction of $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ with the functionalised dialkylating agent $\text{ClCH}_2\text{CH}_2\text{NHC}(\text{O})\text{N}(\text{CH}_2\text{CH}_2)_2\text{NC}(\text{O})\text{HNCH}_2\text{CH}_2\text{Cl}$ proceeded in two stages in a 2:1 mole ratio. The first stage is the monoalkylation of $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ to give the monocation $[\text{Pt}_2(\epsilon\text{-S})(\epsilon\text{-SCH}_2\text{CH}_2\text{NHC}(\text{O})\text{N}(\text{CH}_2\text{CH}_2)_2\text{NC}(\text{O})\text{HNCH}_2\text{CH}_2\text{Cl})(\text{PPh}_3)_4]^+$. The monoalkylated derivative provided the enabling condition for a second intermolecular nucleophilic attack by another molecule of $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ yielding the bridging Pt_4 aggregate spanned by $\text{SCH}_2\text{CH}_2\text{NHC}(\text{O})\text{N}(\text{CH}_2\text{CH}_2)_2\text{NC}(\text{O})\text{HNCH}_2\text{CH}_2\text{S}$. The resulting products was isolated as the tetraphenyl borate (BPh_4^-) salts and characterized by Electrospray Ionization Mass Spectrometry (ESI-MS), FT-IR, ^1H , ^{13}C and ^{31}P {H} NMR.

TABLE OF CONTENTS

Title Page	i
Approval Page	ii
Certification	iii
Dedication	iv
Acknowledgements	v
Abstract	vi
Table of Contents	vii
List of Tables	x
List of Figures	xi
List of Schemes	xii
List of General Abbreviations	xiv
List of Chemical Abbreviations	xv

CHAPTER ONE

1.0	Introduction	1
1.1	Background of Study	1
1.2	Statement of Problem	4
1.3	Justification of Study	5
1.4	Aims of Study	5
1.5	Objectives of Study	5

CHAPTER TWO

2.0	Literature Review	6
2.1	Synthesis of $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$	6
2.2	The Main Geometrical and Electronic Features of $\{\text{Pt}_2(\epsilon\text{-S})_2\}$ Complexes	8

2.3	Protonation and Monoalkylation of $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$	10
2.4	Reaction of $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ with U_{X} -Dialkylating Agent	12
2.5	Spectroscopic Methods for Structural Elucidation	15
2.5.1	Mass Spectrometry	15
2.5.1.1	Soft Ionisation Techniques	17
2.7.1.2	Description of Electrospray Ionisation Mass Spectrometry	17
2.7.1.3	Electrospray Ionisation Mass Spectrometry-As a Technique in Probing the Reactivity of $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$	20
CHAPTER THREE		
3.0	Experimental	23
3.1	General Reagent Information	23
3.2	General Analytical Informatio	23
3.3	Synthesis of the Alkylating Agent	24
3.4	Synthesis of the Alkylated Derivatives of $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$	26
CHAPTER FOUR		
4.0	Result and Discussion	28
4.1	Synthesis	28
4.1.1	Synthesis and Characterisation of the Alkylating Agents	30
4.1.2	General Procedure	30
4.1.3	Mass Spectrometric and Spectroscopic Characterisation	32
4.1.4	IR Spectroscopic of the Alkylating Agents	33
4.2	Synthesis and Spectroscopic Characterisation of the Alkylated Derivatives of $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$	34
4.2.1	General Procedure	34
4.2.2	Mass Spectrometric and Spectroscopic Characterisation	35
4.2.2.1	^{31}P {H} NMR Spectroscopy	40

4.3	Intermolecular Bridging Alkylation	42
4.3.1	IR Spectroscopy	44
4.3.1.1	Comparison of the IR Spectral of $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ and the Complexes	45
4.4	Conclusion	46
	Reference	47
	Appendixes	54

List of Tables

Table 2.0	Comparison of some structural parameters of compounds with $\{\text{Pt}_2(\epsilon\text{-X})_2\}$ cores.	9
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List of Figures

Figure 2.0	Schematic diagram of a mass spectrometer	16
Figure 2.1	A schematic diagram of ESI-MS coupled to a mass analyser	18
Figure 2.2	The schematic diagram of the mechanism of the mechanism of the formation of ions during electrospray ionisation	19
Figure 2.3	Positive ion electrospray mass spectrum of a 1:1 mixture of $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ and $\text{ClCH}_2\text{C}(\text{O})\text{NHC}(\text{O})\text{CH}_2\text{Cl}$ in methanol	22
Figure 4.0	Positive ion electrospray mass spectrum of a mixture of $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ with $\text{ClCH}_2\text{CH}_2\text{NHC}(\text{O})\text{N}(\text{CH}_2\text{CH}_2)_2\text{O}$	36
Figure 4.1	Positive ion electrospray mass spectrum of a mixture of $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ With $\text{ClCH}_2\text{CH}_2\text{NHC}(\text{O})\text{N}(\text{CH}_2\text{CH}_2)_2\text{CH}_3$	39
Figure 4.2	Shows the ^1H NMR Spectrum of $[\text{Pt}_2(\epsilon\text{-S})(\epsilon\text{-SCH}_2\text{CH}_2\text{NHC}(\text{O})\text{N}(\text{CH}_2\text{CH}_2)_2\text{CH}_3)(\text{PPh}_3)_4]^+$ complex	40
Figure 4.3	^{31}P {H} NMR of $[\text{Pt}_2(\epsilon\text{-S})(\epsilon\text{-SCH}_2\text{CH}_2\text{NHC}(\text{O})\text{N}(\text{CH}_2\text{CH}_2)_2\text{O})(\text{PPh}_3)_4]^+$ Showing the two chemically inequivalent P_A and P_B environment	41

List of Schemes

Scheme 1.0	The formation of different multimetallic aggregates	3
Scheme 1.1	The structure of monoalkylation, Homo-, Hetero and Bridging dialkylation Containing thiolate and dithiolate ligand.	4
Scheme 2.0	Synthetic routes to $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ complex starting from platinum metal	7
Scheme 2.1	Optimum reaction conditions for obtaining $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ complexes from $[\text{Pt}_2\text{Cl}_2(\text{PPh}_3)_4]$ and $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$	8
Scheme 2.2	The two possible geometries for complexes with a $\{\text{Pt}_2(\epsilon\text{-S})_2\}$ core	9
Scheme 2.3	Single and double protonation of $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$	10
Scheme 2.4	Formation of monoalkylated cations from mild electrophiles	11
Scheme 2.5	Formation of thiolate derivative via alkylation of a single sulphur atom in $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$	11
Scheme 2.6	Step wise formation of intramolecular bridged dithiolate derivative $[\text{Pt}_2(\text{SCH}_2\text{C}(\text{O})\text{NHNHC}(\text{O})\text{CH}_2\text{S})(\text{PPh}_3)_4]$	13
Scheme 2.7	The formation of an intermolecular bridged Pt_4 aggregates from the reaction of $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ with dialkylating agent	14
Scheme 4.0	Formation of both monoalkylated derivatives $[\text{Pt}_2(\epsilon\text{-S})(\text{SCH}_2\text{CH}_2\text{R})(\text{PPh}_3)_4]^+$ and the intermolecular dialkylated Pt_4 aggregate	29
Scheme 4.1	General procedure for the synthesis of 4.1a, 4.2a and 4.3a electrophiles	31
Scheme 4.2	Formation of the monoalkylated derivatives $[\text{Pt}_2(\epsilon\text{-S})(\epsilon\text{-SCH}_2\text{CH}_2\text{NHC}(\text{O})\text{N}(\text{CH}_2\text{CH}_2)_2\text{O})(\text{PPh}_3)_4]^+$	36
Scheme 4.3	Protonation of $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ in the solvent	38
Scheme 4.4	Formation of the monoalkylated derivatives $[\text{Pt}_2(\epsilon\text{-S})(\epsilon\text{-SCH}_2\text{CH}_2\text{NHC}(\text{O})\text{N}(\text{CH}_2\text{CH}_2)_2\text{CH}_3)(\text{PPh}_3)_4]^+$	38

Scheme 4.5	The numbering scheme of the phosphorus environment P _B trans- to S ²⁻ and P _A cis- to the thiolate SR	40
Scheme 4.6	The formation of intermolecular dialkylated Pt ₄ aggregate via bridging dialkylation of two molecules of [Pt ₂ (ε-S) ₂ (PPh ₃) ₄]	44

List of General Abbreviations

Å	Angstrom
ESI-MS	Electrospray ionisation mass spectrometry
IR	infrared spectroscopy
NMR	nuclear magnetic resonance
M	metal species
$[M]^{n+}$	molecular ion (ESI-MS)
m.p	melting point
m/z	mass to charge ratio
ppm	part per million
s	singlet
d	doublet
t	triplet
m	multiplet
J	coupling constant (NMR)
X	halide
ν	stretch (IR)
ϵ	bridging ligand

List of Chemical Abbreviations

Dmso	dimethylsulfoxide
Ph	phenyl
Me	methyl
Cod	cycloocta-1,5-diene

CHAPTER ONE

1.0 Introduction

1.1 Background of Study

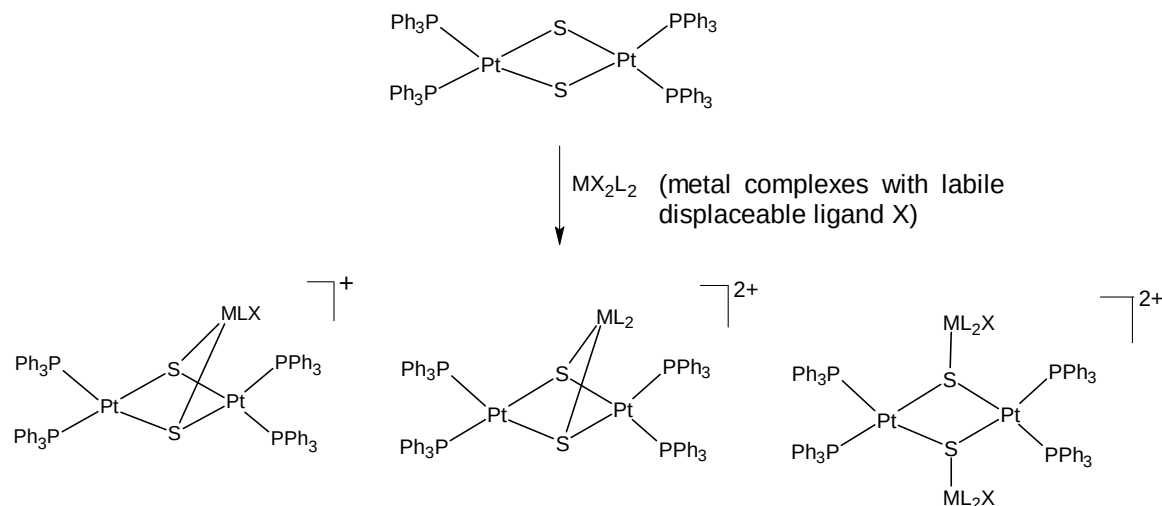
Investigation of the chemistry of platinum and sulphur has attracted considerable attention in recent years due to the broad applications of the two elements and their compounds, in biological systems¹, applied catalysis^{2,3} and to the chemistry of novel molecular systems⁴. Other main areas of application are in the design of homo- and hetero-polynuclear clusters⁵, fine wires^{6,7}, jewellery, antitumor drugs⁸, the self-assembly of supramolecular structures, and the photophysical properties of new luminescent and mesogenic phases⁹. Platinum, however has six naturally occurring isotopes, ¹⁹⁰Pt, ¹⁹²Pt, ¹⁹⁴Pt, ¹⁹⁵Pt, ¹⁹⁶Pt and ¹⁹⁸Pt with a maximum oxidation state of +6, the oxidation states of +2 and +4 being the most stable^{10,11} and the rare odd number form of +1 and +3 oxidation states are found in dinuclear Pt-Pt bonded complexes¹².

Sulphur also exhibits an important chemical properties especially as a versatile coordinating ligand which is illustrated by its ability to catenate forming polysulfide ligands (S_n^{2-}) with n ranging from 1 to 8. It also has the ability to expand its coordination from terminal groups example $([Mo_2S_{10}]^{2-})^{13}$, to ϵ -sulfido group e.g. $[Pt_2(l-S)_2(PPh_3)_4]^{14}$ and to an encapsulated form e.g. $[Rh_{17}(S)_2(CO)_{32}]^{3-}$ consisting of a S-Rh-S moiety in the cavity of a rhodium-carbonyl cluster¹⁵. The coordination chemistry of sulfur ligands has been reviewed and has shown a unique variety of structure in its reactions with most transition metals in different oxidation states¹⁶.

The outstanding ability of sulphur to bind to heavy metals is not only evidenced by the enormous variety of the metal sulfide minerals found in nature but also by the appearance of platinum group metals in mineral ores different from the naturally occurring ores^{17,18}. examples are Cooperite ($\text{Pt}_{0.6}\text{Pd}_{0.3}\text{Ni}_{0.1}\text{S}$)^{17,18}, and Braggite ($\text{Pt}_{0.38}\text{Pd}_{0.50}\text{Ni}_{0.10}\text{S}_{1.02}$)¹⁷.

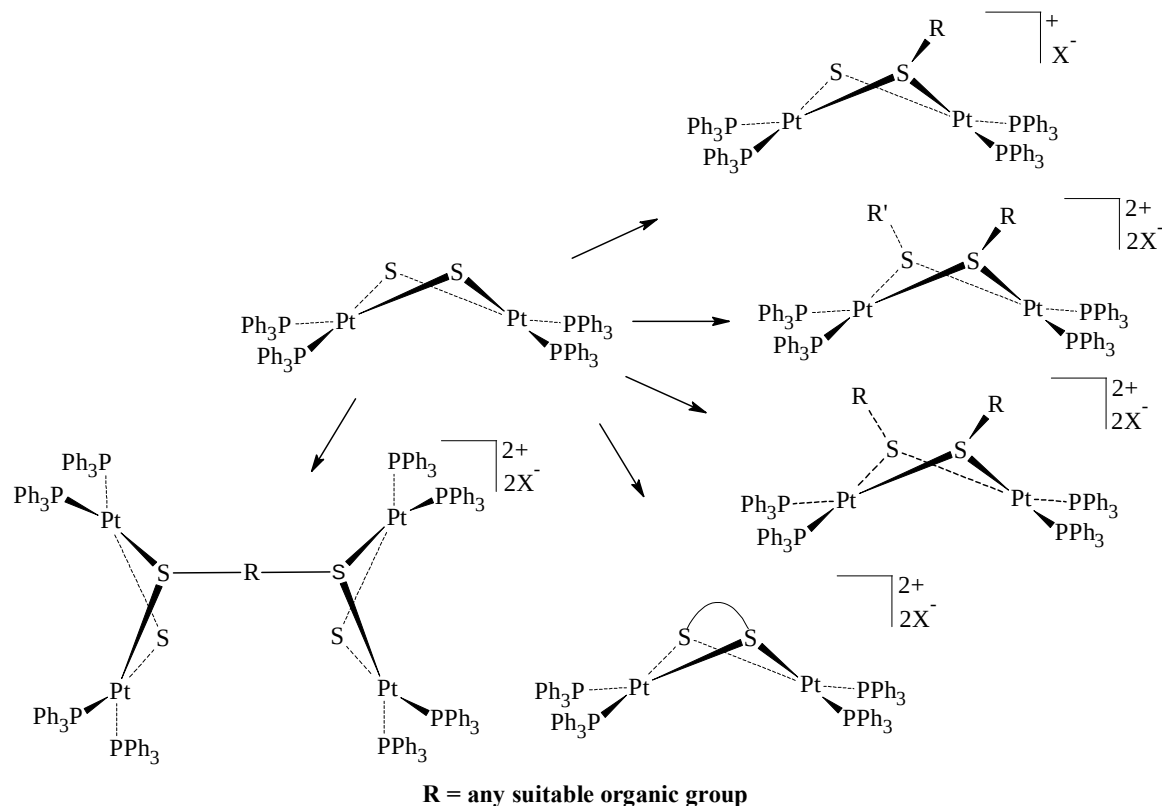
The development of platinum sulfide complexes has received much less attention for many years after the first platinum-sulfur complex, $(\text{NH}_4)_2[\text{Pt}(\text{d}_2\text{-S}_5)_3]$, was isolated in 1903¹⁹. However the main features in the field of platinum(II)sulfur chemistry was established by Chatt and Mingos in 1970, who obtained several complexes of various nuclearities and structures²⁰. Among them, $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PMe}_2\text{Ph})_4]$ followed by $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ ¹⁴ {bis(ϵ -sulfido)tetrakis (triphenylphosphine) diplatinum (II)} reported by Ugo *et al*¹⁴ a year later, constitutes the first examples of platinum(II)sulphide complexes containing the $\{\text{Pt}_2(\epsilon\text{-S})_2\}$ core²¹. The compound is a fine orange powder, insoluble in hydrocarbon solvents and water but sparingly soluble in methanol. It is soluble by reaction with mild alkylating agents, e.g CH_2Cl_2 , CH_3Cl which indicates the high nucleophilicity of the sulfide centres.

The exceptional nucleophilicity of the sulfido ligands in $\{\text{Pt}_2(\epsilon\text{-S})_2\}$ core accounts for their ability to act as potent metalloligands towards a diverse range of metal centres, including main group²¹⁻²³ and transition metals²³⁻²⁸, as well as the actinide uranium⁹ and also enhances the development of homo-, hetero- and inter-metallic sulfide complexes²³ (Scheme 1.1). The advancement in the chemistry of $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ and the other sulfide-bridged complexes with the $\{\text{Pt}_2(\epsilon\text{-S})_2\}$ core, as well as the improvement made in their synthesis, structures, and reactivity have been exceptionally reviewed by Fong and Hor, who have made important contributions to this field²³. However, the overall ability of the sulfido ligands in the $\{\text{Pt}_2(\epsilon\text{-S})_2\}$ core to extend their coordination mode from $\epsilon\text{-S}$ to $\epsilon_3\text{-S}$ give rise to the behaviour of $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ ¹⁴ as building blocks for the synthesis of multimetallic sulfide bridged aggregates. Scheme 1.0 shows the different formation of multimetallic aggregates^{23,25}. It involves the bridging of the two sulfur atoms in a molecule of $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ by a metal fragment.



Scheme 1.0 The formation of different multimetallic aggregates

It is a clear fact from literature sources that alkylation of metalⁱ sulfido complexes is potentially a very general means of synthesising metalⁱ thiolate complexes^{29,30}. It has continued to be developed as a versatile means of synthesising dinuclear platinum thiolate complexes³¹ resulting in its ability to generate a wide variety of functionalised thiolate ligands at platinum by appropriate choice of alkylating agent and the reaction conditions (Scheme 1.1). In some cases it may be possible to obtain thiolate ligands not easily accessible by other methodologies. This methodology has been employed in the synthesis of thiolate ligands containing, for example, fluorinated substituents³², semicarbazone, urea, oxime and other groups³³. The use of a dialkylating agent allows extension of the methodology to generate complexes containing a dithiolate ligand, and its investigation under electrospray mass spectrometry (ESI-MS) conditions indicates that the outcome of dialkylation indeed depends on the strength of the electrophile and the spectral study however provides an effective means of screening the electrophiles and their activities towards $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]^{34}$.



Scheme 1.1 The structure of Monoalkylation, Homo-, Hetero- and Bridging dialkylation containing thiolate and dithiolate ligand

1.2 Statement of Problem

Previous study on alkylation of $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ was narrowed to simple alkyl, aryl and very few functionalised organic electrophiles²⁹. There are still many functionalised organic substrate whose reactivity with $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ are not yet known. The current research on the synthesis and characterisation of novel functionalised organic electrophiles and their complexes was informed by the interest to explore the other areas of these complexes. The chemistry of this investigation will be of great interest considering the observed variable reactivity of $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ with different electrophiles as these can lead to unexpected reactions like displacement of the terminal PPh_3 through coordination of donor atoms of the incorporated groups.

1.3 Justification of Study

In view of the aforementioned problems, this research is justified by exploring the other areas of new functionalised organic electrophiles involving derivatives of isocyanate. Isocyanate derivatives of good ligating properties towards metal centers, for examples Piperazine ($\text{HN}(\text{X})_2\text{NH}$), Morpholine ($\text{HN}(\text{X})_2\text{O}$) and 1-methylpiperazine ($\text{HN}(\text{X})_2\text{NCH}_3$) are carefully incorporated by reacting with 2-Chloroethylisocyanate ($\text{Cl}(\text{X})_2\text{NCO}$) ($\text{X} = \text{CH}_2\text{CH}_2$) into suitable electrophiles for $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$.

1.4 Aim of Study

The aim of the study was to synthesize and characterise the alkylated isocyanate derivatives of $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$.

1.5 Objectives of Study

The specific objectives of the study were:

1. To synthesize multifunctional electrophiles derived from isocyanate morpholine, piperazine, and 1-methylpiperazine.
2. To Study their reactivities towards $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$
3. To Incorporate the alkylating agents in $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ forming monoalkylated and intermolecular dialkylated complexes
4. To characterise the resulting new functionalised electrophiles and their $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ alkylated derivatives by IR, ^1H , ^{13}C and ^{31}P {H} NMR spectroscopy.

CHAPTER TWO

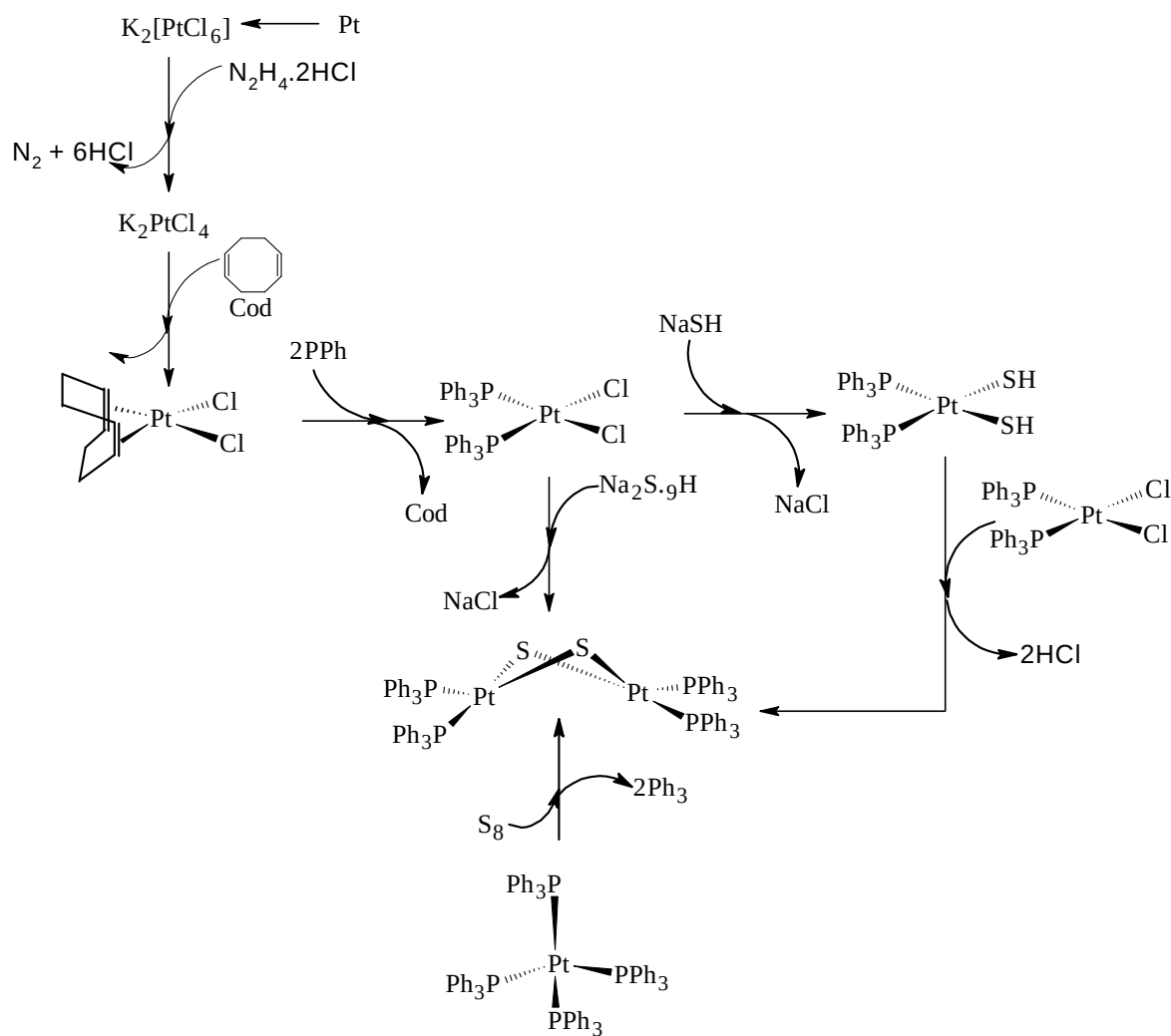
2.0 Literature Review

2.1 Synthesis of $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$

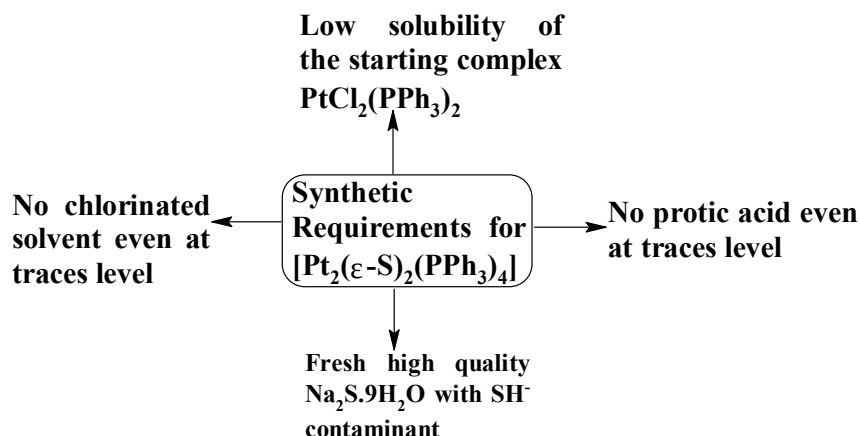
$[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ and other related complexes, can be prepared through a variety of techniques as shown in Scheme 2.0, although the synthesis routes for complexes containing $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ are not straight forward, despite their apparent simplicity, often leading to a mixture of products¹². The best method of synthesising pure $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ is the metathesis reactions between *cis*- $[\text{PtCl}_2(\text{PPh}_3)_2]$ and $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ in benzene for at least 48 hours^{12,18}. Chlorinated compounds like CH_2Cl_2 are strictly avoided in the synthesis as they react to decompose $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ through alkylation of the sulfides. *Cis*- $[\text{PtCl}_2(\text{PPh}_3)_2]$ is synthesised by replacing the 1,5-cyclooctadiene (cod) in $[\text{PtCl}_2(\text{cod})]$ by the corresponding phosphane. $[\text{PtCl}_2(\text{cod})]$ is prepared by metathesis reaction between K_2PtCl_4 and 1,5-cyclooctadiene. K_2PtCl_4 can be made by the reaction of 2 mole equivalent of potassium hexachloroplatinate(IV) ($\text{K}_2[\text{PtCl}_6]$) and hydrazine dihydrochloride ($\text{N}_2\text{H}_4\cdot 2\text{HCl}$) in water²³.

Other less direct routes of preparing $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ entail the oxidation reaction of $\text{Pt}(\text{PPh}_3)_4$ with S_8 Which affords phosphane sulfide (Ph_3PS) as secondary product in $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ ¹⁴. Alternatively, the synthesis is achieved through an initial reaction between *cis*- $[\text{PtCl}_2(\text{PPh}_3)_2]$ and NaSH ^{12,23}. This involves the initial formation of $\text{Pt}(\text{SH})_2(\text{PPh}_3)_2$ which is further reacted with a second equivalent of *cis*- $[\text{PtCl}_2(\text{PPh}_3)_2]$, thus yielding $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ and two equivalent of HCl . The resulting HCl reacts with $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ to give a secondary product $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4\cdot \text{HCl}]$ ²³. The presence of HCl in $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ exist as an impurity in the final product which may not be easily separated and therefore it is not a convenient by-product in the reaction as it may cause the decomposition of $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ through the $\{\text{Pt}_2\text{S}_2\}$ core^{12,29}. For this reason the alternative method can not be efficiently used in the

preparation of $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$. Scheme 2.1 shows the synthetic conditions required to obtain $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ from $[\text{PtCl}_2(\text{PPh}_3)_4]$ and $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$



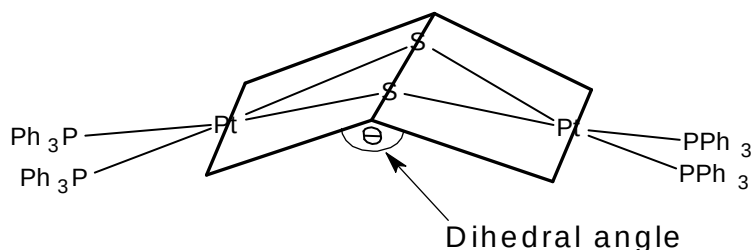
Scheme 2.0. Synthetic routes to $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ complex starting from platinum metal.



Scheme 2.1. Optimum reaction conditions for obtaining $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ complexes from $[\text{PtCl}_2(\text{PPh}_3)_4]$ and $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ ¹².

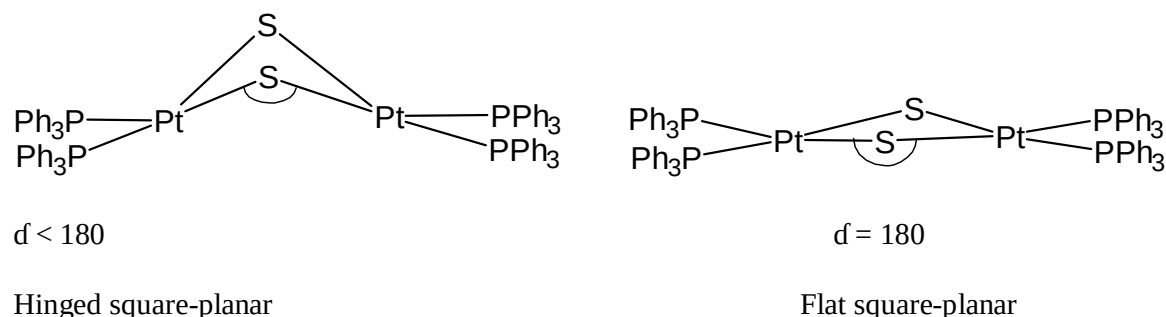
2.2 The Main Geometrical and Electronic Features of $\{\text{Pt}_2(\mu\text{-S})_2\}$ Complexes.

The geometrical features of the $\{\text{Pt}_2\text{S}_2\}$ core is the flexible hinge angle (θ) of the central $\{\text{Pt}_2\text{S}_2\}$ ring and the coordination planes along the S---S axis regulates the dihedral angle (θ). Generally the core of $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ consists of four membered $\{\text{Pt}_2(\epsilon\text{-S})_2\}$ ring with the platinum(II) centres in a square-planar arrangement¹².



However, the two possible structural patterns formed, depending on the geometry of the central Pt_2S_2 ring and the distances of separation of the Pt---Pt and S---S, are hinged geometry and planar geometry. The planar geometry occurs when the dihedral angle between the local coordination planes Pt_1SS and Pt_2SS is 180° . The hinged geometry occurs when the dihedral angle is less than 180° (Scheme 2.2)³⁶. Complexes with two S^{2-} , or with one S^{2-} and one RS^- ,

bridging ligands are hinged; the decrease of the through-ring antibonding interaction between the in-plane sulfur p orbitals with folding appears to be the determinant for hinging. Complexes with two RS^- bridging ligands can be planar or hinged depending on the relative orientation, either *syn* or *anti*, of the R groups and the nature of the terminal PPh_3 ligands, and also their disposition, either *cis* or *trans*. On the other hand, the aromatic or aliphatic nature of bridging thiolates does not influence the geometry of the Pt_2S_2 ring significantly³⁶.



Scheme 2.2. The two possible geometries for complexes with a $\{\text{Pt}_2(\epsilon\text{-S}_2)\}$ core.

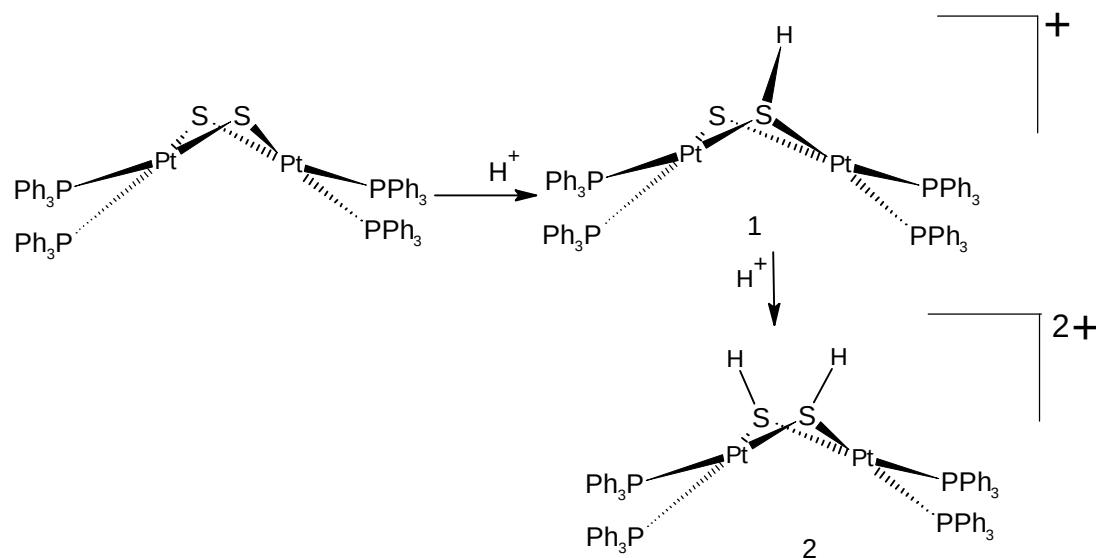
The comparison of some structural parameters are summarised in Table 2.0 showing variations in the dihedral angles and other parameters due to different terminal ligands and non-rigid PtS_2 planes.

Table 2.0 Comparison of some structural parameters of Compounds with $\{\text{Pt}_2(\mu\text{-S})_2\}$ cores .

Complex	Pt-S (Å)	Pt-Pt Å	S-S (Å)	Pt-S-Pt (°)	S-Pt-S (°)	$\bar{U}$ (°)	Ref.
$[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_2\text{Py})_4]$	2.33	3.55	3.01	99.6	80.4	180.0	14
$[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$	2.11	3.17	2.69	99.0	80.3	168.2	16
$[\text{Pt}_2(\epsilon\text{-S})_2(\text{dppe})_2]$	2.35	3.29	3.13	88.9	83.7	140.2	15
$[\text{Pt}_2(\epsilon\text{-S})_2(\text{PMe}_2\text{Ph})_4]$	2.34	3.17	3.06	85.5	81.6	121.0	17

2.3 Protonation and Monoalkylation of $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$

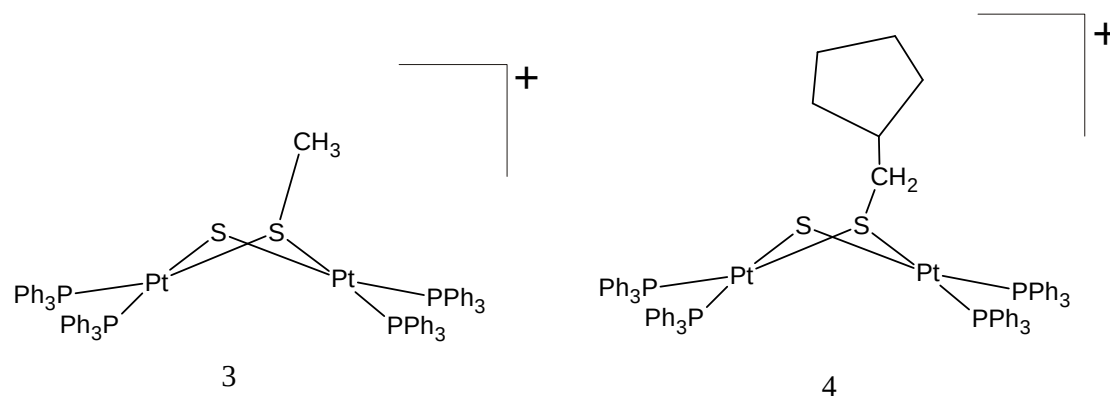
The exceptional nucleophilicity of the sulfide centres in $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ is clearly shown by its ability to incorporate virtually any form of positive species even the smallest known positive species, the proton (hydrogen ion)³⁷. The first evidence was provided by Hor *et al*³⁸, who fully characterized the $[\text{Pt}_2(\epsilon\text{-S})(\epsilon\text{-SH})(\text{PPh}_3)_4]^+$ cation produced by the reaction of $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ with H^+ to form a single or diprotonated species as shown in Scheme 2.3, which have been identified by Electrospray Ionisation Mass Spectrometry (ESI-MS)⁹ and the monoprotonated species are stable and are therefore isolated and characterised by X-ray crystallography². The corresponding diprotonated $[\text{Pt}_2(\epsilon\text{-SH})_2(\text{PPh}_3)_4]^{2+}$ complexes are unstable in solution and therefore not isolated³⁶. $[\text{Pt}_2(\epsilon\text{-SeH})_2(\text{PPh}_3)_4]^{2+}$ is the only analogue species reported as a result of the protonation of the $\{\text{Pt}_2(\epsilon\text{-Se})_2\}$ core³⁷ opposed to the reluctance of the $\{\text{Pt}_2(\epsilon\text{-S})_2\}$ core to afford $[\text{Pt}_2(\epsilon\text{-SH})_2(\text{PPh}_3)_4]^{2+}$ complexes.



Scheme 2.3. Single and double protonation of $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$.

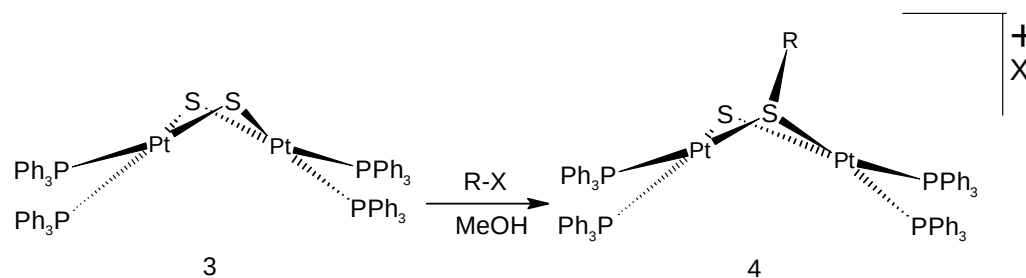
The alkylation reactions of $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ with organic electrophiles were among the first set of rudimentary reactions to be established. This included the reactions of $[\text{Pt}_2(\epsilon\text{-$

$S)_2(PPh_3)_4]$ with mild electrophiles like CH_3I , $PhCH_2Br$ and CH_2Cl_2 which led to the corresponding monoalkylated cations derivatives $[Pt_2(\epsilon-S)(\epsilon-SCH_2Ph)(PPh_3)_4]^+$, $[Pt_2(\epsilon-S)(\epsilon-SCH_3)(PPh_3)_4]^+$ ³⁷ and $[Pt_2(\epsilon-S)(\epsilon-SCH_2Cl)(PPh_3)_4]^+$ ³⁸ as shown scheme 2.4, even if stoichiometric excess of the alkyl halide was present. These provide the initial evidence for the reactivity of $[Pt_2(\epsilon-S)_2(PPh_3)_4]$ towards organic electrophiles. amazingly, this attractive feature has not been fully utilized as a synthetic route to functionalised metal bonded thiolate derivatives of $[Pt_2(\epsilon-S)_2(PPh_3)_4]$.



Scheme 2.4. Formation of monoalkylated cations from mild electrophiles

It is very simple to prepare monoalkylated $[Pt_2(\epsilon-S)(\epsilon-SR)(PPh_3)_4]^+$ cations with almost any appropriate electrophilic aliphatic or aromatic halide⁴³. In fact most alkylation and arylation reactions of $[Pt_2(\epsilon-S)_2(PPh_3)_4]$ result in predominant conversion of only one of the sulphido ligands to a thiolate ligands⁴³ as shown in Scheme 2.5.

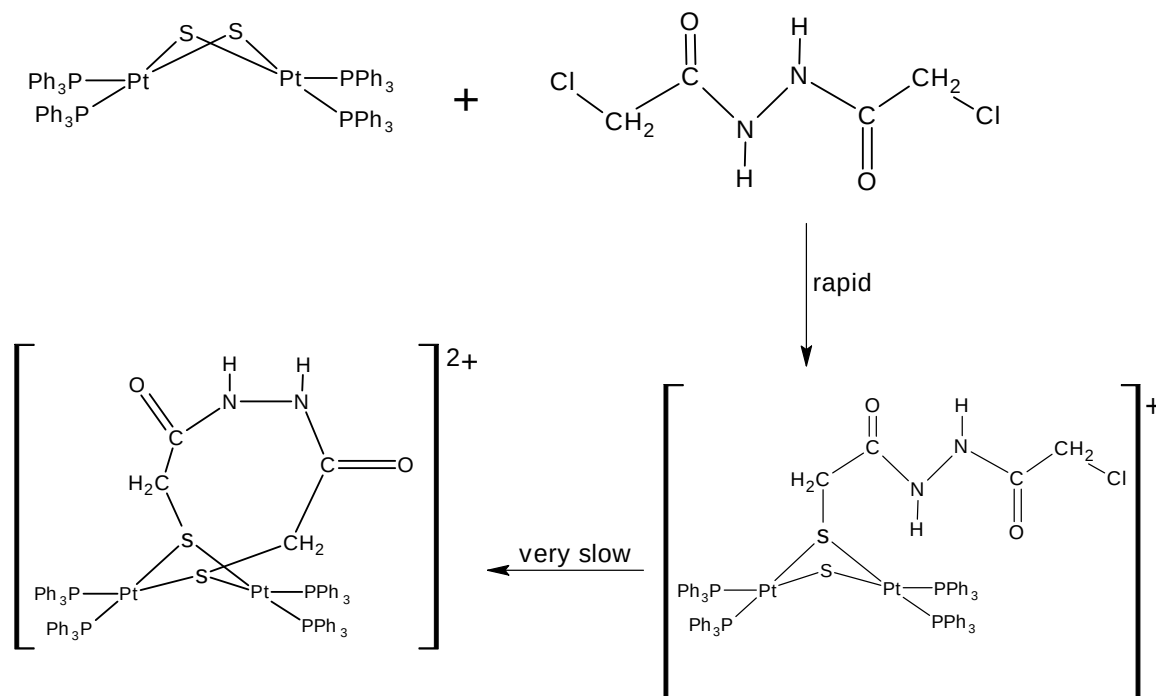


Scheme 2.5. Formation of thiolate derivative via alkylation of a single sulphur atom in $[Pt_2(\epsilon-$

S)₂(PPh₃)₄]

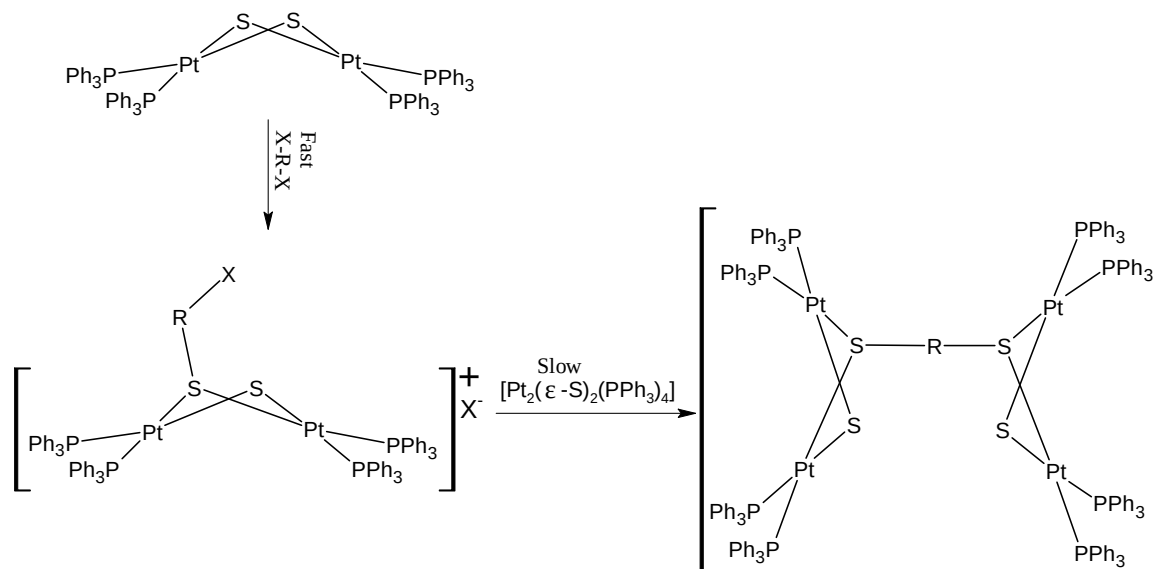
2.4 Reaction of [Pt₂(μ-S)₂(PPh₃)₄] with α,ω-Dialkylating Agent

The reactivity of a difunctional alkylating agent is strongly dependent on the length of the spacer between the two dihalides groups which dialkylate [Pt₂(ε-S)₂(PPh₃)₄] by bridging the two sulphur atoms to give [Pt₂(ε-S-R-S)(PPh₃)₄]²⁺,⁴⁴. The two different alkylated derivatives that can be formed by $\ddot{X}$ - electrophiles are the intra- and intermolecular bridging dialkylated products of [Pt₂(ε-S)₂(PPh₃)₄]. Formation of this type of dialkylated derivative is limited by the number of spacer atoms in the electrophile. Appropriate organo-dihalides with short spacer length can dialkylate [Pt₂(ε-S)₂(PPh₃)₄] by intramolecular bridging of the two sulfur atoms while dihalides with long spacer length tends to form an intermolecular bridged Pt₄ aggregates with two molecule of [Pt₂(ε-S)₂(PPh₃)₄], each attached to one end of the dihalide electrophile as shown in scheme 2.8, with R = dihalide electrophile with more than six spacer atoms⁴⁴. However, ESI-MS are used to determine the relative reactivities of different alkyl halides, and the tendency towards mono- or dialkylation. for example, in the reaction of [Pt₂(ε-S)₂(PPh₃)₄] with ClCH₂CH₂Cl. The disappearance of the starting material occurs with concomitant formation of the dicationic [Pt₂(ε-SCH₂CH₂S)(PPh₃)₄]²⁺ and a small quantity of the intermediate monoalkylated species [Pt₂(ε-S)(ε-SCH₂CH₂Cl)(PPh₃)₄]⁺. Rapid conversion to [Pt₂(ε-SCH₂CH₂S)(PPh₃)₄]²⁺ occurs, indicating that the initial monoalkylated species undergoes a rapid intramolecular reaction which is attributed to the short spacer length of ClCH₂CH₂Cl⁴⁴ but in the reaction of [Pt₂(ε-S)₂(PPh₃)₄] with ClCH₂C(O)NHNHC(O)CH₂Cl a fast initial monoalkylation of [Pt₂(ε-S)₂(PPh₃)₄] occurred followed by a much slower intramolecular reaction to form a cyclized product of [Pt₂(l-SCH₂C(O)NHNHC(O)CH₂S)(PPh₃)₄]²⁺, as reported by Ujam *et al.*⁴⁵ shown in scheme 2.9.



Scheme 2.6. step wise formation of intramolecular bridged dithiolate derivative $[\text{Pt}_2\{\text{SCH}_2\text{C}(\text{O})\text{NHNHC}(\text{O})\text{CH}_2\text{S}\}(\text{PPh}_3)_4]^{2+}$

The slow conversion to $[\text{Pt}_2(\epsilon\text{-SCH}_2\text{C}(\text{O})\text{NHNHC}(\text{O})\text{CH}_2\text{S})(\text{PPh}_3)_4]^{2+}$ is attributed to the long spacer length of $\text{ClCH}_2\text{C}(\text{O})\text{NHNHC}(\text{O})\text{CH}_2\text{Cl}$, which slows down the cyclization reaction due to entropy considerations⁴⁵. Thus, the product formed upon alkylation of $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ are strongly dependent on the alkyl halide with both monoalkylated $[\text{Pt}_2(\epsilon\text{-S})(\epsilon\text{-SR})(\text{PPh}_3)_4]^+$ and dialkylated $[\text{Pt}_2(\epsilon\text{-SR})(\epsilon\text{-SR})(\text{PPh}_3)_4]^{2+}$ products being accessible through appropriate choice of alkylating agent³³. The limitation imposed by the number of spacer atoms give rise to steric hindrance due to repulsion between the bulky terminal electron rich PPh_3 of $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ and is reduced with longer electrophile of more spacer atoms⁴⁶.



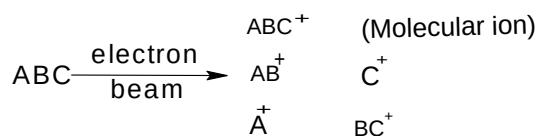
Scheme 2.7. The formation of an intermolecular bridged Pt_4 aggregates from the reaction of $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ with dialkylating agent⁴⁵.

Monofunctional $\text{X}\text{-R-X}$ dialkylating agents with general formula XRX with rigid spacers groups e.g. XX -dibromo-*p*-xylene and 4,4'-bis(chloromethyl)-1,1'-biphenyl react with $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ to give Pt_4 aggregate frameworks with overhead dithiolate bridges, $[\text{PPh}_3]_4\text{Pt}_2(\epsilon\text{-S})(\epsilon\text{-S-R-S})(\epsilon\text{-S})\text{Pt}_2(\text{PPh}_3)_4]^{2+}$ ⁴⁶. This type of aggregate is also limited by the type of the alkylating agent especially when the rigidity is imposed by spacer atoms within a phenyl groups. $\text{X}\text{-R-X}$ Dialkylating agents with strong electron-withdrawing groups (e.g. $\text{ClCH}_2\text{C}(=\text{NNAr})\text{CH}_2\text{Cl}$) close to the two alkylating carbons dialkylate $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ by bridging the sulfide centres. However, intramolecular rearrangement may occur upon dialkylation with this type of alkylation agent. Preliminary studies attributed this to the loss of H^+ from one of the methylene hydrogen atoms ($-\text{CH}_2\text{-S}-$) bonded to sulfur atoms which lead to opening of the four membered $\{\text{Pt}_2(\epsilon\text{-S}_2)\}$ ring into a five membered ring followed by the loss of one PPh_3 ligand⁴⁷.

2.5 Spectroscopic Methods for Structural Elucidation

2.5.1 Mass Spectrometry

Mass spectrometry (MS) has been in existence for the past 20 years with its various applications invading every discipline within the life and health sciences⁴⁸⁻⁵¹. It is an analytical technique that measures the mass-to-charge ratio of charged particles. Mass spectrometry (MS) is used for determining masses of particles, for determining the elemental composition of a sample or molecule⁵¹. The mass spectrometer uses electric and magnetic fields to measure the mass of the charged particles. There are many different kinds of mass spectrometers, but all use magnetic or electric fields to exert forces on the charged particles produced from the chemical to be analyzed. A basic mass spectrometer consists of three parts: A source in which ions are produced from the chemical substance, an analyzer in which ions are separated according to mass, and a detector, which produces a signal from the separated ions. The MS principle consists of ionizing chemical compounds to generate charged molecules or molecule fragments and measurement of their mass-to-charge ratios by using the one of a variety of techniques (e.g. EI/CI/FAB/ESI/MALDI)⁵². In a mass spectrometer, organic and inorganic molecules are vapourised and bombarded with a beam of very high energy electrons and the resulting collisions impart considerable energy to the molecules which in turn emit electrons to produce positively charged ions. These ions possess so much energy that they often fragment through various bond cleavages to produce new positively charged ions^{53,54}.



The positive ions are accelerated toward a negatively charged plate by passing them through a magnetic field which deflects the ions. The ions of lighter mass are deflected more

than heavier ions. Each kind of ion has a particular mass to charge (m/e) ratio. For most ions produced in the fragmentation of the molecule, the charge is +1 such that m/e usually represents the mass of the ion.

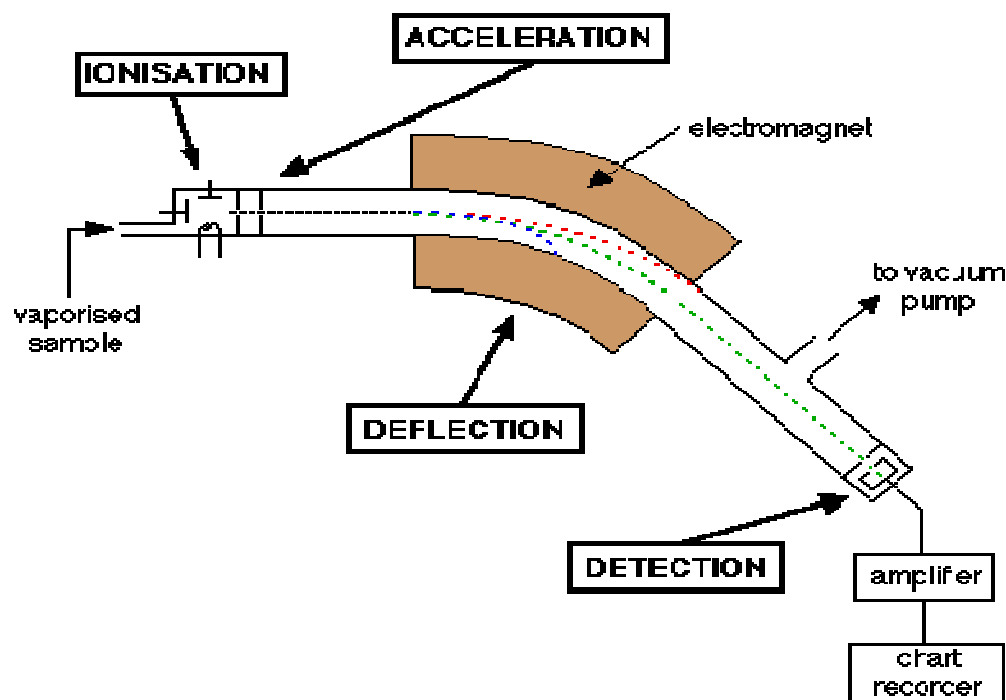


Figure 2.0. Schematic diagram of a mass spectrometer

Mass spectrometric analysis can provide important information about the analyte, including their structure, purity, and composition. The largest peak found in a mass spectrum that is the highest intensity is called the *base peak* and is given the numerical value of 100. the intensities of all other peaks are expressed relative to the height of the base peak. A mass spectrum is highly characteristic of a particular compound and the ion formed by removing one electron from the parent molecule is called *molecular ion or parent ion*. The molecular ion peak is usually represented as M^{+53-55} . Mass spectrometers are used for all kinds of chemical analyses, ranging from environmental analysis (e.g. detection of poisons such as dioxin) to the analysis of petroleum products, trace metals and biological materials (including the products of genetic engineering)⁵⁵. We have two types of mass spectrometry based on

their ionisation techniques which are hard and soft ionisation mass spectrometer and the current research uses the soft ionisation techniques.

2.5.1.1 Soft Ionisation Techniques

Soft ionisation techniques are techniques in which minimum amount of internal energy are absorbed by the analytes during ionisation process. Irrespective of the method by which a sample is introduced into a mass spectrometer (i.e., GC, HPLC, direct injection), the ion source is the compartment where charged species are produced and is the ñgated to other sections of the instrument namely the analyzer and the detector. Various ionization techniques are currently used with mass spectrometric instrumentations which include the traditional ionization method namely electron impart (EI) and chemical ionisation method, plasma desorption (PD) technique, fast atom bombardment (FAB)⁵⁶⁻⁵⁷, liquid secondary ion mass spectrometry (LSIMS)⁵⁸, matrix-assisted laser desorption ionization (MALDI)⁵⁹⁻⁶⁰ and electrospray ionization (ESI)⁵⁹⁻⁶². The last two ionization techniques in particular have revolutionized the usage of mass spectrometers and enabled researchers to easily study biological substances which are usually soluble in polar solvent but relatively difficult to vaporise in the solid state, such as glycoconjugates, proteins, and DNA. This last two ionisation techniques tends to lead to less fragmentation of molecular ion than EI.

2.5.1.2 Description of Electrospray Ionisation Mass Spectrometry (ESI-MS)

The development of electrospray ionization started in the late 1960s with the work of Dole and coworkers who successfully introduced a polystyrene polymer with average molecular weight of 51,000 Da into the gas phase as a charged species⁶¹. Surprisingly, this ionization technique is by far one of the most simplest to understand. Samples are usually dissolved in a buffer or solvent that is introduced into the mass spectrometer in the form of a fine spray of highly charged droplets of a solution. The technique was extensively developed

by M. Yamashita and J. B. Fenn in the 1980s who linked an electrospray source to a quadrupole mass analyser making it easier for use as an analytical instrument in chemical analysis⁶²⁻⁶³. ESI-MS is currently used for qualitative and quantitative studies of a wide variety of nonvolatile and thermally labile simple inorganic chemicals as well as complex biological structures⁶³.

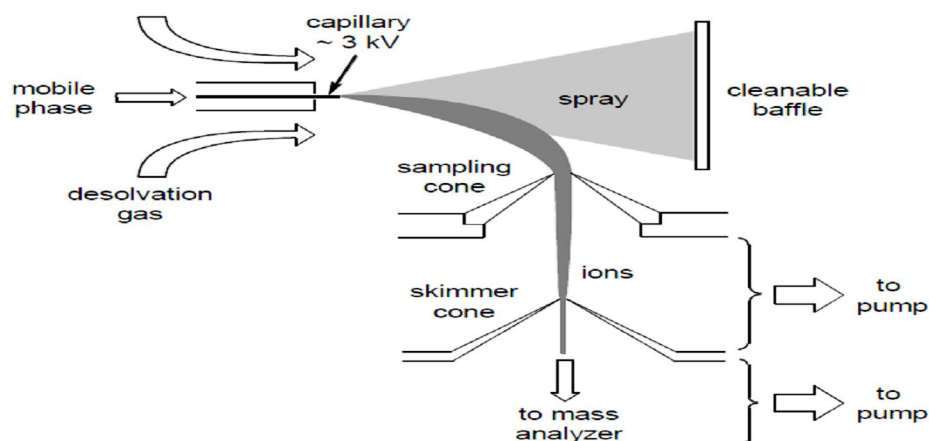


Figure 2.1. A schematic diagram of ESI-MS coupled to a mass analyser.

A schematic diagram of the basic features of ESI-MS is shown in Figure 2.0. ESI-MS is vigorous and employs a gentle ionisation technique that allows the analysis of large, in volatile and also sensitive molecules in solution. During preparation the mobile phase is a polar solvent, usually methanol. A very dilute solution of the analyte is prepared with suitable solvent such as water, methanol, ethanol, acetonitrile, dichloromethane, chloroform etc or in combination of one with the other.

In ESI-MS, the solution is infused, under atmospheric pressure, into the ionization source via a thin needle (figure 2.0). As the sample is being constantly sprayed, a high electrical potential is applied at the needle (about 3i 4 Kv), resulting in the formation of highly charged droplets (i.e., nebulization). These droplets are then driven electrically and are

vaporized with the aid of a warm neutral gas (usually nitrogen). Under these conditions, the droplets break down and, while shifting inside the source, their size is continuously being reduced. Eventually, the repulsive forces, also known as the *coulombic* forces, among the ions on the surface of the shrinking droplets become very high. These forces will ultimately exceed the surface tension of the solvent, resulting in ions that desorb into the gas phase. This theory of ESI ion formation is known as the *ion evaporation method*⁶⁴⁻⁶⁵, and is believed to favor ions with relatively low m/z values⁶⁶. ESI can produce singly or multiply charged ions. The number of charges retained by a particular analyte depends on several factors such as the size, chemical composition, and higher order structure of the analyte molecule, the solvent composition, the presence of co-solutes, and the instrument parameters. For small molecules (< 2000 Da) ESI typically generates singly, doubly, or triply charged ions, while for large molecules (> 2000 Da) ESI can produce a series of multiply charged ions. Figure 2.2 illustrates the proposed mechanisms for the formation of ions during the ESI process. This is a very soft ionisation process as minimum internal energy is absorbed by the analytes during ionisation process⁶⁶.

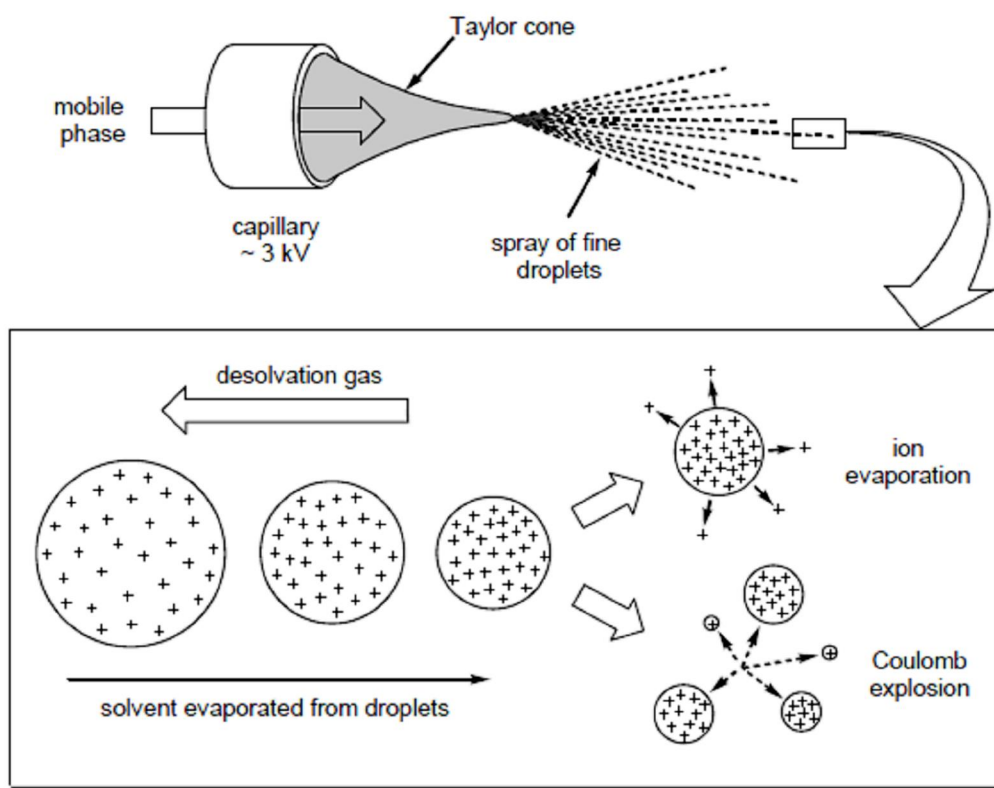


Figure 2.2. The schematic diagram of the mechanism of The formation of ions during electrospray ionization.

2.5.1.3 Electrospray Ionisation Mass Spectrometry-As a Technique in probing the Reactivity of $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$

Electrospray ionisation mass spectrometry (ESI-MS) provides a rapid and convenient technique for probing the nucleophilicity of the $\{\text{Pt}_2\text{S}_2\}$ core. It is effectively applied in determination of electrospray mass spectra of Positive-ion resulting in a wide array of aggregates incorporating various metallo-fragments into the $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ moiety. The development of electrospray ionisation mass spectrometry (ESI-MS) by Yamashita and Fenn⁶² has provided a powerful technique for analyzing multiply charged ions, primarily applied to large biomolecules such as proteins and oligonucleotides and later to various charged inorganic and organometallic species in solution³⁰. Recently, ESMS was also applied in the characterization of thiometal complexes and thiolate-capped chalcogenide

cadmium clusters⁶⁷. In contrast to conventional MS methods, which spawn a lot of undesirable fragment ions in the mass spectra, the ESMS technique is very sensitive and as a result it detects compounds in solutions of very low concentration. Small amounts of material can therefore be used in micro synthesis and analysis. It affords rapid determination of molecular mass accurately with high sensitivity and therefore well suited for the studies of polar, high molecular weight molecules. The formation of cationic complexes from $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ is ideally suited for this form of ESMS probe. consequently, in screening of chemical synthesis it is capable of identifying single or multiple charged species that may result from variable combination of the reactants and the products formed.

The efficient reactivity of $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ was previously hindered by its low solubility in a wide variety of solvents. The ESMS technique requirement for only very dilute solutions for analysis is especially advantageous for the analysis of compounds where other techniques requiring greater solubility, *e.g.* NMR, is not possible. $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ is neutral and cannot be detected by ESI-MS but is ionised by protonation on dissolution in methanol to give in the ESI-MS the ion $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4 + \text{H}]^+$ which has a mass/charge ratio of m/z 1504. Metallation and/or alkylation reactions of $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ invariably involve the formation of charged products which makes it easy for detection in ESI-MS. In the absence of decomposition and side reactions the alkylation or metallation product is usually detected. Most of the recently reported work on $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ involves the use of this technique to monitor and accurately predict the outcome of promising reactions of $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ with metal centres or electrophiles. The inherent softness of the ESMS ionization technique have been successfully modified to provide a preliminary screening of the reactivity of a reactant with a large variety of transition metal complexes to ascertain if a particular reaction is indeed feasible prior to a lab-scale synthesis. the monocations or dications resulting from incorporation of metal and organic groups on one or both sulfur atoms in $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ can easily be detected Because the ESI-MS detects single and multiple charged ions. ESI-MS

has proved its effectiveness in predicting the reaction mechanisms and structures of the resulting products in situations where there is a side reaction like the displacement of PPh_3 by halogen ion leaving the group and rearrangement of the products or decomposition^{18,23,45}.

ESI-MS allows the generation of experimental molecular ion isotope patterns as applied to monitor synthesis used in the correct identification of the species since the experimental isotope pattern can be compared with the expected theoretical computer generated isotope pattern⁶⁰. A typical example is the positive ESI-MS of the product $[\text{Pt}_2(\text{SCH}_2\text{C}(\text{O})\text{NHC}(\text{O})\text{CH}_2\text{S})(\text{PPh}_3)_4]^{2+}$ drive from a 1:1 mixture of $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ and $\text{ClCH}_2\text{C}(\text{O})\text{NHC}(\text{O})\text{CH}_2\text{Cl}$ in Methanol reported by ujam *et al*⁴⁵ as shown in Figure 2.3. Such mixtures often give a suspension in Methanol due to the insolubility of $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$. The mass spectrum consists of peaks due to $[\text{Pt}_2(\text{SCH}_2\text{C}(\text{O})\text{NHC}(\text{O})\text{CH}_2\text{S})(\text{PPh}_3)_4]^{2+}$ (m/z 808), and $[\text{Pt}_2(\epsilon\text{-S})(\text{SCH}_2\text{C}(\text{O})\text{NHC}(\text{O})\text{CH}_2\text{Cl})(\text{PPh}_3)_4]^+$ (m/z 1652).

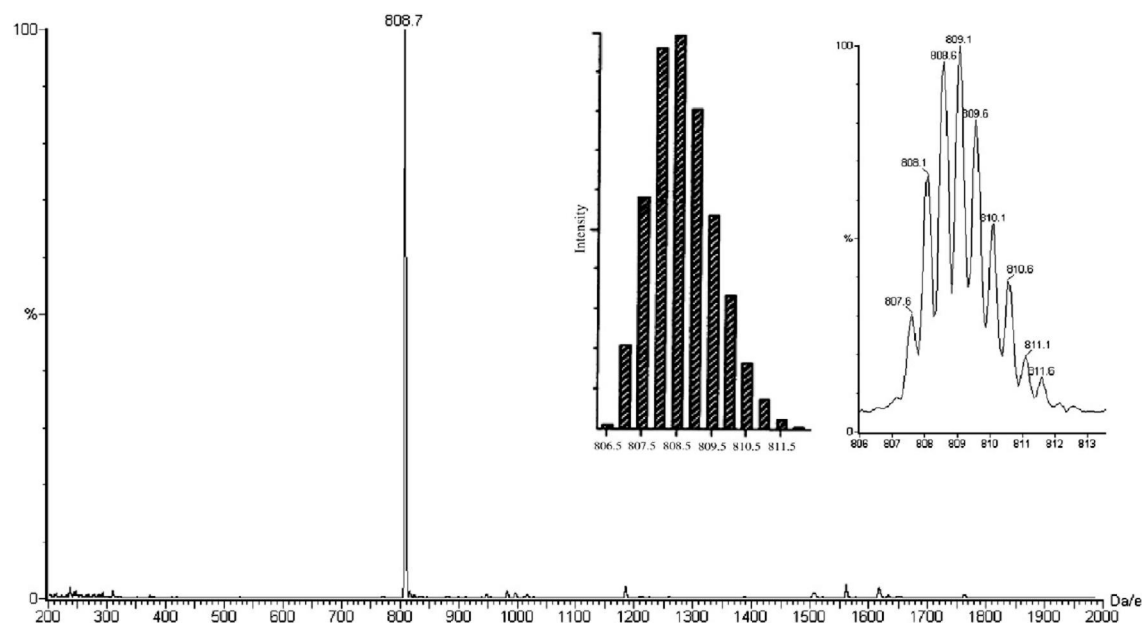


Figure 2.3. Positive ion electrospray mass spectrum of a 1:1 mixture of $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ and $\text{ClCH}_2\text{C}(\text{O})\text{NHC}(\text{O})\text{CH}_2\text{Cl}$ in Methanol recorded at a cone voltage of 20 V. The insets show the theoretical (left) and experimental (right) isotope distribution patterns for the dication $[\text{Pt}_2(\text{SCH}_2\text{C}(\text{O})\text{NHC}(\text{O})\text{CH}_2\text{S})(\text{PPh}_3)_4]^{2+}$.

CHAPTER THREE

4.0 Experimental

3.1 General Reagent Information

All reactions were carried out under normal laboratory conditions. $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ was synthesised by the metathesis reaction of $\text{cis-PtCl}_2(\text{PPh}_3)_2$ with $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ in benzene¹². The alkylating agents N,N-(2-dichloroethyl) piperazine-4 carboxi-amine, N-(2-chloroethyl) morpholine-4 carboxi-amine, and N-(2-chloroethyl) 1-methylpiperazine-4 carboxi-amine were synthesised following the literature procedure⁸. The analytical grade chemicals, 2-Chloroethyl isocyanate, Piperazine, Morpholine, 1-Methylpiperazine, and Sodium tetraphenylborate (NaBPh_4) were purchased from Sigma Aldrich chemical Co. Germany in sure-seal bottles and were used without further purification.

3.2 General Analytical Information

Melting points of the compounds was taken using Fisher-Johns melting point apparatus and were uncorrected. Compounds were characterized by ^1H NMR, ^{13}C NMR, IR spectroscopy and ESI-MS. IR spectra were recorded on 8400s Fourier Transform Infrared (FTIR) spectrophotometer using KBr disc and absorption were reported in cm^{-1} . IR analysis was done at National Research Institute for Chemical Technology (NARICT), Zaria, Kaduna. Nuclear Magnetic Resonance (^1H NMR ^{13}C NMR and ^{31}P NMR) were determined using Jeol 400MHz at Strathclyde University, Scotland and at the University of Victoria, Canada on Advance 300MHz. the chemical shift were reported in (̈́). Mass spectrometry data were collected on a Waters Micro mass Q-TOF II mass spectrometer in positive ion mode using pneumatically assisted electrospray ionization and methanol as the mobile phase and solvent (University of Victoria, Canada) and on MicroTof (University of Waikato, New

Zealand). No smoothing of the data was performed and comparison of observed and calculated isotope patterns was used in the ion assignment.

3.3 Synthesis of the Alkylating Agent

The alkylating agents N,N'-(2-dichloroethyl) piperazine-4 carboxi-amine, N-(2-chloroethyl) morpholine-4 carboxi-amine, and $\text{ClCH}_2\text{CH}_2\text{NHC(O)N}(\text{CH}_2\text{CH}_2)_2\text{NCH}_3$ were synthesised following the literature procedure.

Synthesis of N,N'-(2-dichloroethyl) piperazine-4 carboxi-amine

$\text{HN}(\text{CH}_2\text{CH}_2)_2\text{NH}$, Piperazine (200 mg, 2 mmol) and $\text{ClCH}_2\text{CH}_2\text{NCO}$ (211mg, 2mmol, 2 mol equiv.,) in diethyl ether (30mL) in a 100 mL round bottomed flask was stirred for 5 min. A quantitative precipitate of the product $\text{ClCH}_2\text{CH}_2\text{NHC(O)N}(\text{CH}_2\text{CH}_2)_2\text{NC(O)HNCH}_2\text{CH}_2\text{Cl}$ (164mg, 40%) was formed. The product was filtered and washed with ether (20mL) and dried under air.

Melting Point: 190 - 195°C.

IR (KBr): $\nu(\text{C-H})$ 2943.47 cm^{-1} , $\nu(\text{C=O})$ 1700 - 1630 cm^{-1} , $\nu(\text{NH})$ 3417.98 cm^{-1} , $\nu(\text{C-Cl})$ 1450 cm^{-1} , $\nu(\text{NCO})$ 2134.31 cm^{-1} .

^1H NMR (400MHz, DMSO): $\delta_{\text{H}} = 4.81$ (m, 2H, CH_2), 3.88 (m, 2H, CH_2), 7.01 (t, 1H, NH), 6.87 (t, 1H, NH) 3.25 δ 3.10 (s, 8H, 4 CH_2).

ESI-MS: m/z 225, ($[\text{M}]^{2+}$ 100%).

Synthesis of N-(2-chloroethyl) morpholine-4 carboxi-amine

$\text{HN}(\text{CH}_2\text{CH}_2)_2\text{O}$, Morpholine (200 mg, 2.3 mmol,) and $\text{ClCH}_2\text{CH}_2\text{NCO}$ (243mg, 2.3mmol, 1 mol equiv.,) in diethyl ether (30 mL) in a 100 mL round bottomed flask was stirred for 5 min. A quantitative precipitate of the product $\text{ClCH}_2\text{CH}_2\text{NHC(O)N}(\text{CH}_2\text{CH}_2)_2\text{O}$ (160mg, 36%) was formed. The product was filtered and washed with ether (20 mL) and dried

under air.

Melting Point 185 - 182°C,

IR (KBr): $\nu(\text{C-H})$ 2930.93 cm^{-1} , $\nu(\text{C=O})$ 1693.56 cm^{-1} , $\nu(\text{NH})$ 3408.33 cm^{-1} , $\nu(\text{C-Cl})$ 1450 cm^{-1} , $\nu(\text{NCO})$ 2115.02 cm^{-1} .

^1H NMR (400MHz, DMSO): $\delta_{\text{H}} = 3.26 - 3.23$ (t, 2H, CH_2), 3.42 (m, 2H, CH_2), 4.80 (t, J = 8.56Hz, 1H, NH), 3.86 (t, J = 8.44Hz, 2H, CH_2), 3.62 δ 3.59 (t, 2H, CH_2)

^{13}C NMR: 46.54 δ 43.88 C_1 , 42.75 C_2 , 158.39 δ 157.96 (C=O), 66.49 δ 66.45 (C_4 δ C_5), 71.93 (C_6 δ C_7).

ESI-MS: m/z 157, ($[\text{M}]^+$ 100%).

Synthesis of N-(2-chloroethyl) 1-methylpiperazin-4 carboxi-amine

$\text{HN}(\text{CH}_2\text{CH}_2)_2\text{NCH}_3$, 1-methylpiperazin (200 mg, 2mmol,) and $\text{ClCH}_2\text{CH}_2\text{NCO}$ (211mg, 2mmol, 1mol equiv.) in diethyl ether (30 mL) in a 100 mL round bottomed flask was stirred for 5 min. A quantitative precipitate of the product $\text{ClCH}_2\text{CH}_2\text{NHC(O)N}(\text{CH}_2\text{CH}_2)_2\text{NCH}_3$ (110mg, 29%) was formed immediately. The product was filtered and washed with ether (20 mL) and dried under air.

Melting Point: 160 - 165°C,

ESI-MS: m/z 170, ($[\text{M}]^+$ 100%).

3.4 Synthesis of the Alkylated Derivatives of $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$

Synthesis of $[(\text{PPh}_3)_4\text{Pt}_2(\mu\text{-S})(\mu\text{-SCH}_2\text{CH}_2\text{NHC(O)N}(\text{CH}_2\text{CH}_2)_2\text{N(O)HNCH}_2\text{CH}_2\text{S})(\mu\text{-S})\text{Pt}_2(\text{PPh}_3)_4]$ (BPh_4)₂

$[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$ (200mg, 0.0665mmol) and $\text{ClCH}_2\text{CH}_2\text{NHC(O)N}(\text{CH}_2\text{CH}_2)_2\text{N(O)HNCH}_2\text{CH}_2\text{Cl}$ (19.8mg, 0.0667mmol, 0.5 mol equiv.) in methanol (25 mL) in a 100 mL round bottomed flask was stirred at room temperature for 120 hours to give a pale yellow solution. the solution was filtered to remove traces of solid matter and excess NaBPh_4 was added followed by distilled water (40mL) to complete

precipitation of the product from solution. A pale yellow powder of $[(PPh_3)_4Pt_2(\mu-S)(\mu-SCH_2CH_2NHC(O)N(CH_2CH_2)_2N(O)HNCH_2CH_2S)(\mu-S)Pt_2(PPh_3)_4](BF_4)_2$

(90mg, 35%) was obtained after washing with deionised water (40 mL) followed by diethyl ether (40mL) using whatman no 1 filter paper and air dried.

Melting Point: 268-270°C

IR (KBr): $\nu(C=O)$ 1641.48 cm^{-1} , $\nu(NH)$ 3420.87 cm^{-1}

^1H NMR (400MHz, DMSO): δ_H = 7.60 (m, 60H, 12Ph), 3.04 (t, J = 5.25Hz, 2H, SCH₂), 6.79 (t, J = 7.20Hz, 1H, NH), 2.22 (s, 8H, 4CH₂).

Synthesis of $[Pt_2(\mu-S)(\mu-SCH_2CH_2NHC(O)N(CH_2CH_2)_2O)(PPh_3)_4](BPh_4)$

$[Pt_2(\mu-S)_2(PPh_3)_4]$ (200 mg, 0.1331mmol) and $ClCH_2CH_2NHC(O)N(CH_2CH_2)_2O$ (25.6mg, 0.1330mmol, 1.2 mol equiv.) in methanol (25 mL) in a 100 mL round bottomed flask was stirred at room temperature for 24 hours to give a pale yellow solution. the solution was filtered to remove traces of solid matter and excess $NaBPh_4$ (100 mg) was added followed by distilled water (40 mL) to complete precipitation of the product from solution. A pale yellow powder of $[Pt_2(\mu-S)(\mu-SCH_2CH_2NHC(O)N(CH_2CH_2)_2O)(PPh_3)_4](BF_4)$ (130mg, 49%) was obtained after washing with deionised water (40 mL) followed by diethyl ether (40 mL) using whatman no 1 filter paper and air dried.

Melting Point: 280-282°C

IR (KBr): $\nu(C=O)$ 1645.33 cm^{-1} , $\nu(NH)$ 3418.94 cm^{-1}

^1H NMR (400MHz, DMSO): δ_H = 7.35 (m, 60H, 12ph), 2.31 (t, 2H, SCH₂), 7.03-7.07

(t, 1H, NH), 6.51 (t, 4H, CH₂), 6.88 (t, 4H, CH₂),

$^{31}P\{^1H\}$ NMR: δ_P = 24.45 ppm (*br, s*, $^1J(Pt-P_A)$ 2603.97 Hz) and 24.84 ppm $^1J(Pt-P_B)$

3223.61 Hz)

ESI-MS m/z 1660, ($[M]^+$ 100%).

Synthesis of [Pt₂(μ-S)(μ-

SCH₂CH₂NHC(O)N(CH₂CH₂)₂NCH₃)(PPh₃)₄](BPh₄)

[Pt₂(μ-S)₂(PPh₃)₄] (200 mg, 0.331mmol) and ClCH₂CH₂NHC(O)N(CH₂CH₂)₂NCH₃ (27.4mg, 0.1333mmol, 1.2 mol equiv.) in methanol (25 mL) in a 100 mL round bottomed flask was stirred at room temperature for 24 hours to give a pale yellow solution. the solution was filtered to remove traces of solid matter and excess NaBPh₄ (100 mg) was added followed by distilled water (40 mL) to complete precipitation of the product from solution. A pale yellow powder of [Pt₂(μ-S)(μ-SCH₂CH₂NHC(O)N(CH₂CH₂)₂NCH₃)(PPh₃)₄](BPh₄) (70mg, 26%) was obtained after washing with deionised water (40 mL) followed by diethyl ether (40 mL) using whatman no 1 filter paper and air dried.

Melting Point: 265-267°C

IR (KBr): ν(C=O) 1661.73 cm⁻¹, ν(NH) 3438.23 cm⁻¹

¹H NMR (400MHz, DMSO): δ_H = 7.37 (m, 60H, 12ph), 2.75 (t, 2H, SCH₂), 3.97 (m, 4H, CH₂), 6.89 (t, 1H, NH), 2.96 (s, 8H, 4CH₂), 2.25 (s, 3H, CH₃),

³¹P{¹H} NMR: δ_P = 24.36 ppm (*br, s*, ¹J(Pt-P_A) 2603.97 Hz) and 24.76 ppm ¹J(Pt-P_B) 3245.31 Hz)

ESI-MS m/z 1673, ([M]⁺ 100%).

The percentage yield of the compounds above were calculated using the formular as follows:

$$\text{Percentage yield} = \frac{\text{Practical Yield} \times 100}{\text{Theoretical Yield}}$$

CHAPTER FOUR

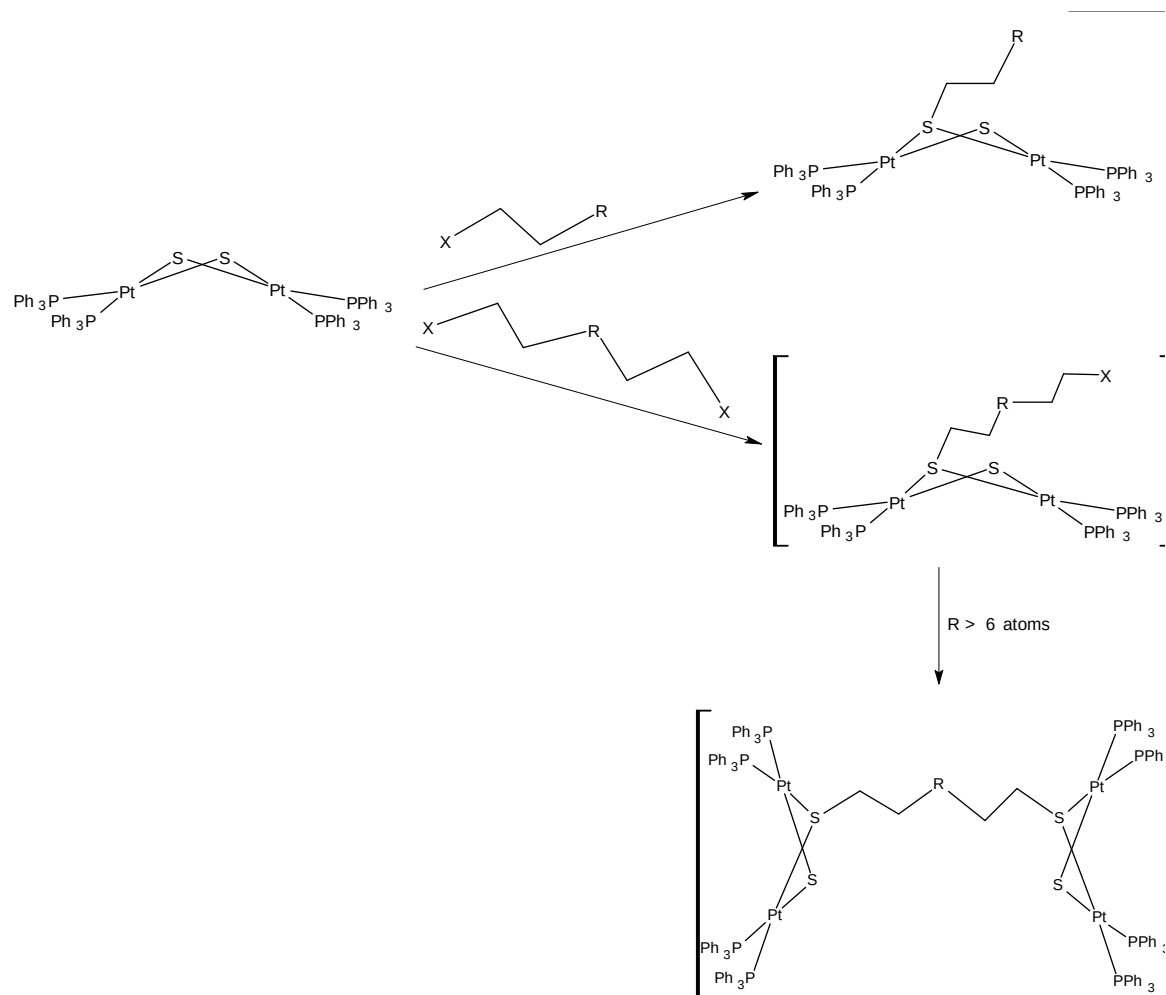
4.0 Results and Discussion

4.1 Synthesis

This chapter describes the synthesis and characterisation of a highly functionalised electrophiles of the derivatives of isocyanates $\text{ClCH}_2\text{CH}_2\text{NHC(O)N(CH}_2\text{CH}_2)_2\text{O}$, $\text{ClCH}_2\text{CH}_2\text{NHC(O)N(CH}_2\text{CH}_2)_2\text{N}$ CH_3 and $\text{ClCH}_2\text{CH}_2\text{NHC(O)N(CH}_2\text{CH}_2)_2\text{NC(O)NHCH}_2\text{CH}_2\text{Cl}$, and the study of their reactions with $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ to yield the monoalkylated derivatives of $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$. Furthermore, this sections also include the studies of the reactivity of $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ towards the highly functionalised dihalide electrophile. This is aimed at the synthesis of intermolecular bridged derivatives of the two sulfide groups in $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$. This was informed by the interest to further develop the use of the alkylated derivatives as precursor for constructing multimetallic molecules⁴³ in which the metal centres are attached to the donor atoms of the incorporated group⁴³.

In reactions with organic electrophiles, monoalkylation of the sulfide centres dominates unless with an electrophile strong enough to dialkylate the two sulfides. An exception to the above common reactivity of **1.1** towards organic electrophiles has been observed with the use of appropriate $\check{\text{Y}}_{\text{X}}$ -dialkylating electrophiles (Scheme 4.0). However, amine containing substrates, which are particularly abundant and widely commercially available, can be converted into alkylating agents of high functionality by chloroacetylation and other derivatisation method. This potentially formed highly functionalised organic electrophiles which include $\text{RCH}_2\text{CH}_2\text{X}$ and $\text{XCH}_2\text{CH}_2\text{RCH}_2\text{CH}_2\text{X}$ with R having spacer length of more than six atoms can be incorporated into $\{\text{Pt}_2\text{S}_2\}$ core to yield a monoalkylated derivatives $[\text{Pt}_2(\epsilon\text{-S})(\epsilon\text{-S}-\text{CH}_2\text{CH}_2\text{R})(\text{PPh}_3)_4]^+$ and $\check{\text{Y}}_{\text{X}}$ -dialkylated derivatives or intermolecular dithiolate bridged Pt_4 aggregate $[(\text{PPh}_3)_4\text{Pt}_2(\epsilon\text{-S})(\text{SCH}_2\text{CH}_2\text{RCH}_2\text{CH}_2\text{S})(\epsilon\text{-S})\text{Pt}_2(\text{PPh}_3)_4]^{2+}$ as shown in scheme 4.0. the later involve a two step reaction, first is the

monoalkylation of $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ to yield $[\text{Pt}_2(\epsilon\text{-S})(\epsilon\text{-SCH}_2\text{CH}_2\text{RCH}_2\text{CH}_2\text{X})(\text{PPh}_3)_4]^+$ and then the alkylation of one molecule $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ at each end of the $\text{X}-\text{R}-\text{X}$ electrophile (scheme 4.0). (R = alkyl or aryl or combination of both, X = halide).

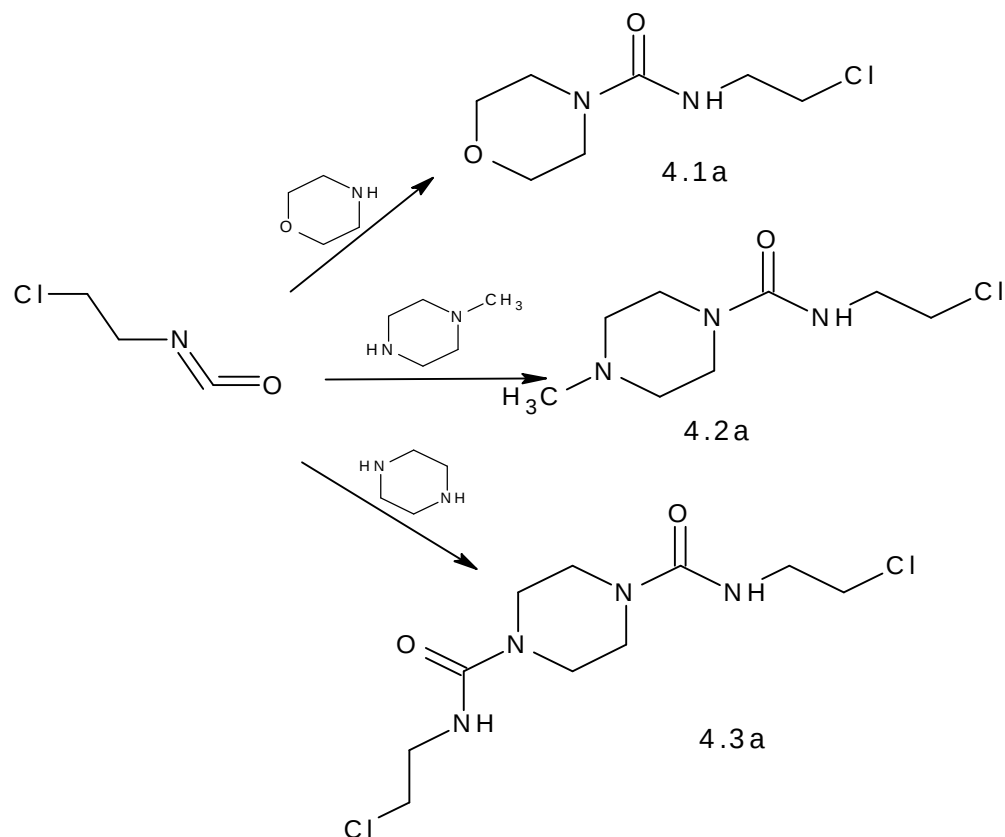


Scheme 4.0. Formation of both monoalkylated derivatives $[\text{Pt}_2(\epsilon\text{-S})(\epsilon\text{-SCH}_2\text{CH}_2\text{R})(\text{PPh}_3)_4]^+$ and the intermolecular dialkylated Pt_4 aggregate via bridging dialkylation of two molecules of $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$

4.1.1 Synthesis and Characterisation of the Alkylating Agents

4.1.2 General Procedure

The same reactions procedure were used in this study for the synthesis of the alkylating agents with the same reaction time and temperature. The reaction of morpholine ($\text{HN}(\text{CH}_2\text{CH}_2)_2\text{O}$), 1-methyl piperazines ($\text{HN}(\text{CH}_2\text{CH}_2)_2\text{NCH}_3$), and piperazine ($\text{HN}(\text{CH}_2\text{CH}_2)_2\text{NH}$) with 2-Chloroethyl isocyanate $\text{ClCH}_2\text{CH}_2\text{NCO}$ proceeded very quickly to give the corresponding derivatives of isocyanates 4.1a, 4.2a and 4.3a in within 5 minutes of stirring at room temperature respectively. The ESI-MS of each reaction mixture indicated a simple spectrum with peaks at m/z 157, 170 and 225 respectively due to the presence of $[\text{M}]^+$ cations for 4.1a and 4.2a, and $[\text{M}]^{2+}$ cation for 4.3a. further characterisation by IR and NMR confirmed the products to be 4.1a, 4.2a and 4.3a derivatives of isocyanates. The general reaction sequences are shown in scheme 4.1. However, this synthesis focused on compounds containing chloroalkyl groups rather than bromo- or iodo-derivatives because of their lesser tendency to effect dialkylation reactions, and the low nucleophilicity of chloride will minimise side reactions involving the displacement of coordinated phosphine ligands which can occur with iodide³³



Scheme 4.1. General procedure for the synthesis of 4.1a, 4.2a and 4.3a electrophiles.

Wide range of functionalised alkylating agents containing urea functional group which include $\text{ClCH}_2\text{CH}_2\text{NHC(O)NHPy}$, $\text{ClCH}_2\text{CH}_2\text{NHC(O)N}(\text{CH}_2\text{CH}_2)_2\text{S}$, $\text{ClCH}_2\text{C(O)NHC(O)NHCH}_2\text{CH}_3$ and $\text{ClCH}_2\text{C(O)NHNHC(O)CH}_2\text{Cl}$ have been previously reported^{8,20} but the more highly functionalised electrophile 4.1a, 4.2a and 4.3a are the first analogues to be reported in this study.

4.1.3 Mass Spectrometric and Spectroscopic Characterisation

N-(2-chloroethyl) morpholine-4 carboxi-amine

The reaction of $\text{ClCH}_2\text{CH}_2\text{NCO}$ (1) and $\text{HN}(\text{CH}_2\text{CH}_2)\text{O}$ (2) in a 1:1 mole ratio indicated only the formation of $\text{ClCH}_2\text{CH}_2\text{NHC}(\text{O})\text{N}(\text{CH}_2\text{CH}_2)_2\text{O}$ (4.1a) after stirring for 5 minutes in diethyl ether. The product was analysed by ESI - MS which gave m/z 157 as the base peak in the spectrum.

The ^1H NMR spectra of 4.1a organic electrophiles gave complicated overlapping signals in the aliphatic region which could not be easily assigned. This can be attributed to the presence of heteroatoms (Cl, O, N) of different electronegativities. However the CH_2 protons are easily identified as triplet between δ 3.26 and 3.23 due to the ClCH_2 protons adjacent to the electronegative chlorine and NH proton, a multiplet at δ 3.42 with 8.44 Hz coupling constant occur for ClCH_2CH_2 and a triplet at δ 4.80 for NH with 8.56 Hz coupling constant. The increase in downfield of NH can be attributed to the presence of the carbonyl group adjacent to it. The two CH_2 protons in the morpholine ring adjacent to the nitrogen atom are chemically equivalent and the two CH_2 protons in the same cyclic ring adjacent to the oxygen atom are also chemically equivalent and are identified as triplet between δ 3.62 and 3.59 due to $\text{CH}_2\text{CH}_2\text{N}$ and δ 3.86 due to $\text{CH}_2\text{CH}_2\text{O}$ with 8.44 Hz coupling constant $\text{CH}_2\text{CH}_2\text{O}$ is more deshielded due to the presence of oxygen atom of more electronegativity than nitrogen atom.

The ^{13}C NMR spectra of 4.1a also showed complicated signals around the aliphatic region. The observed signals due to ClCH_2 , CH_2 , $\text{C}=\text{O}$ and any other carbon atoms in the ring are easily identifiable.

N-(2-chloroethyl) 1-methylpiperazine-4 carboxi-amine

The reaction of $\text{ClCH}_2\text{CH}_2\text{NCO}$ (1) and $\text{HN}(\text{CH}_2\text{CH}_2)_2\text{NCH}_3$ (2) in a 1:1 mole ratio indicated only the formation of $\text{ClCH}_2\text{CH}_2\text{NHC}(\text{O})\text{N}(\text{CH}_2\text{CH}_2)_2\text{NCH}_3$ (4.2a) after stirring for 5 minutes in diethyl ether. The product was analysed by ESI - MS which gave m/z 170 as the

base peak in the spectrum. Further characterisation of this compound could not be achieved because of its inability to withstand certain room temperature.

N,N'-(2-dichloroethyl) piperazine-4 carboxi-amine

The reaction of $\text{ClCH}_2\text{CH}_2\text{NCO}$ (1) and $\text{HN}(\text{CH}_2\text{CH}_2)_2\text{NH}$ (2) in a 2:1 mole ratio indicated only the formation of $\text{ClCH}_2\text{CH}_2\text{NHC}(\text{O})\text{N}(\text{CH}_2\text{CH}_2)_2\text{NC}(\text{O})\text{HNCH}_2\text{CH}_2\text{Cl}$ (4.3a) after stirring for 5 minutes in diethyl ether. The product was analysed by ESI - MS which gave m/z 225 as the base peak in the spectrum.

Analysis of 4.3a by ^1H NMR spectroscopy yielded two multiplets due to the two CH_2 groups and one complicated overlapping singlet due to the cyclic CH_2 protons in the aliphatic region which could not be easily assigned and two triplets in the aromatic region, due to the two NH groups present. The central CH_2 protons on both sides of the chain appear as a multiplet at δ 3.88, while the ClCH_2 protons are most deshielded at δ 4.81 with 8.62 Hz coupling constant due to the ClCH_2 protons adjacent to the electronegative chlorine. All the CH_2 protons in the piperazine ring appear as a singlet between δ 3.25 and 3.10. This is because all the protons in the ring are chemically equivalent and therefore do not split each other. The NH protons appear as triplets and are most deshielded, at δ 7.01 and 6.87 which can be attributed to the presence of the carbonyl groups adjacent to NH. The ^1H NMR spectrum of 4.3a is consistent with the assigned structure.

The ^{13}C NMR spectrum, shows that all the carbon atom peaks of 4.3a alkylating agent are weakly absorbed and are therefore hidden in the instrumental background noise.

4.1.4 IR Spectroscopic of the Alkylating Agents

The infrared spectra of the alkylating agents show bands attributed to the characteristic functionalities of the derivatives of isocyanates. Variable IR absorptions attributable to C-H between 3000 and 2900cm^{-1} , 1700 to 1630cm^{-1} due to C=O, and between 3500 and 3350cm^{-1} due to NH were observed in all the functionalised electrophiles. The

weakly absorbed IR bands due to NCO were also observed in all the electrophiles between 2150 and 2100 cm^{-1} . The IR absorptions between 1400 and 700 cm^{-1} in all the electrophiles were due to strong overlapping stretching absorptions from C-Cl which occur in the most crowded region and makes assignment difficult.

4.2 Synthesis and Characterisation of the Alkylated Derivatives of $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$

A similar method was used in the reactions between $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ and the electrophiles to prepare the monoalkylated and α,α' -dialkylated derivatives (scheme 4.2, 4.4 and 4.5). Slight variations in the reaction time and temperature were required to effect complete reaction and formation of the product. Complete alkylation was often indicated by the changing of the original orange suspension of $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ in methanol to a clear, pale yellow solution. As soon as complete alkylation was achieved, the solution was filtered to remove traces of solid impurity and ESI-MS was used in the confirmation of the product indicated by the disappearance of $[\text{M} + \text{H}]^+$ peak of $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ in the reaction mixture. The alkylated product was precipitated from the filtrate as its tetraphenyl borate salt by the addition of excess NaBPh_4 to the reaction mixture. The results from the reactions showed that all the electrophiles selectively alkylate one of the sulfide centres in $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$. Further characterisations by IR, and NMR spectroscopic also confirmed the product to be monoalkylated and α,α' -dialkylated derivatives of $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$.

4.2.1 General Procedure

The reactions of the derivatives of isocyanates with $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ in methanol proceeded with the dissolution of the Pt complex and the change of the orange colour of $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ into a clear pale yellow solution to give the corresponding monoalkylated derivatives 4.1b. BPh_4 and 4.2b. BPh_4 and the intermolecular dialkylated derivative 4.3b. $(\text{BPh}_4)_2$ in within 24 hours and 120 hours of stirring at room temperature respectively.

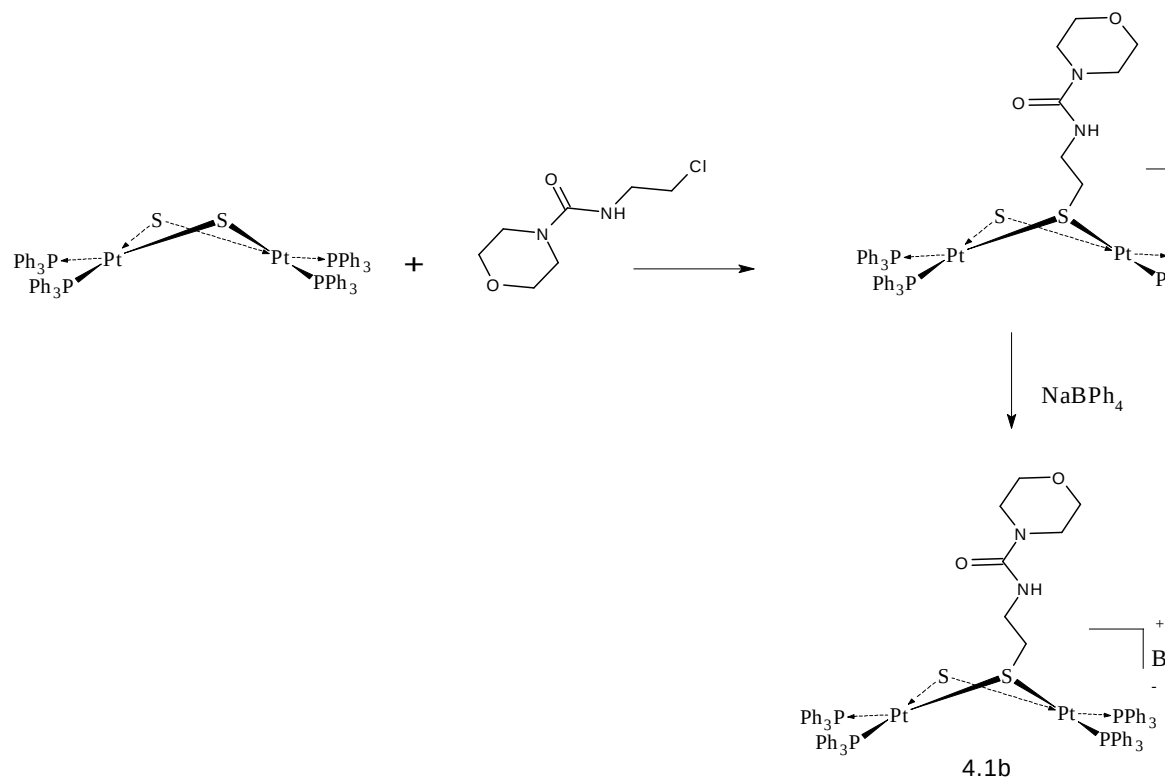
The ESI-MS of each reaction mixture indicated a simple spectrum with peaks at m/z 1660 and 1673 due to the presence of $[M]^+$ cations.

Monoalkylated derivatives containing $\text{ClCH}_2\text{CH}_2\text{NHC(O)N(CH}_2\text{CH}_2)_2\text{S}$ and $\text{ClCH}_2\text{C(O)NHC(O)NHCH}_2\text{CH}_3$ functionalised electrophiles have been reported^{8,20} and complexes containing monoalkylated $[\text{Pt}_2\text{S}_2]$ core bridged by dichloro-organic compound derived from a flexible aromatic backbone which include $o\text{-CH}_2\text{C(O)NHC}_6\text{H}_4\text{NHC(O)CH}_2\text{Cl}$ readily prepared by derivatisation of ortho-phenylene diamines with chloroacetyl chloride have also been previously reported^{8,20} but complexes 4.1b, 4.2b and 4.3b are the first analogues to be reported in this studies.

4.2.2 Mass Spectrometric and Spectroscopic Characterisation

$[\text{Pt}_2(\mu\text{-S})(\mu\text{-SCH}_2\text{CH}_2\text{NHC(O)N(CH}_2\text{CH}_2)_2\text{O})(\text{PPh}_3)_4]$ (BPh_4)

The reaction of $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ with the $\text{ClCH}_2\text{CH}_2\text{NHC(O)N(CH}_2\text{CH}_2)_2\text{O}$ derivatives of $\text{ClCH}_2\text{CH}_2\text{NCO}$ in methanol yielded purely a monoalkylated derivative $[\text{Pt}_2(\epsilon\text{-S})(\epsilon\text{-SCH}_2\text{CH}_2\text{NHC(O)N(CH}_2\text{CH}_2)_2\text{O})(\text{PPh}_3)_4]^+$ as shown in scheme 4.2., after 24 hours of stirring. From the resulting solution, the product was isolated as its tetraphenyl borate salt $[\text{Pt}_2(\epsilon\text{-S})(\epsilon\text{-SCH}_2\text{CH}_2\text{NHC(O)N(CH}_2\text{CH}_2)_2\text{O})(\text{PPh}_3)_4] \text{BPh}_4$ (4.1b. BPh_4) by the addition of excess NaBPh_4 to the reaction mixture. The positive ion ESI-MS spectra of the alkylated derivatives of isocyanate 4.1b. BPh_4 give single ion at m/z 1660 suggesting the formation of pure product as shown in fig 1.



Scheme 4.2. Formation of the monoalkylated derivative $[\text{Pt}_2(\epsilon\text{-S})(\epsilon\text{-SCH}_2\text{CH}_2\text{NHC}(\text{O})\text{N}(\text{CH}_2\text{CH}_2)_2\text{O})(\text{PPh}_3)_4]^+$

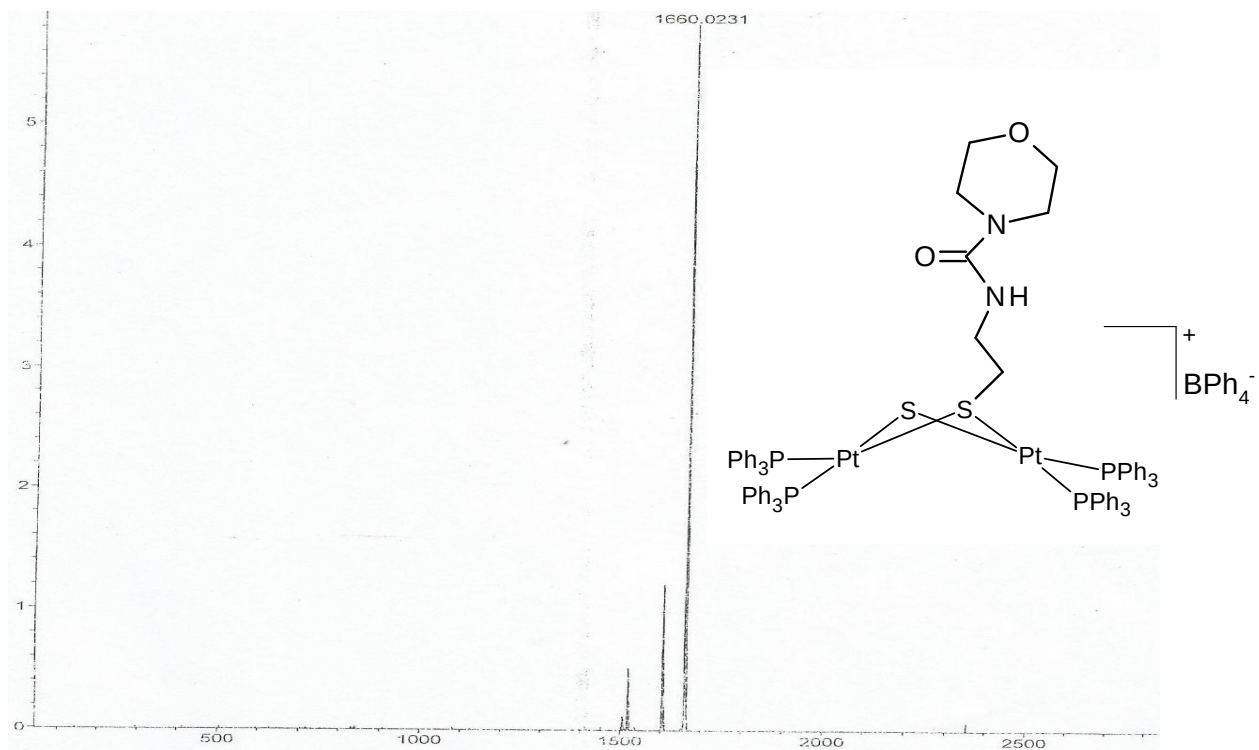
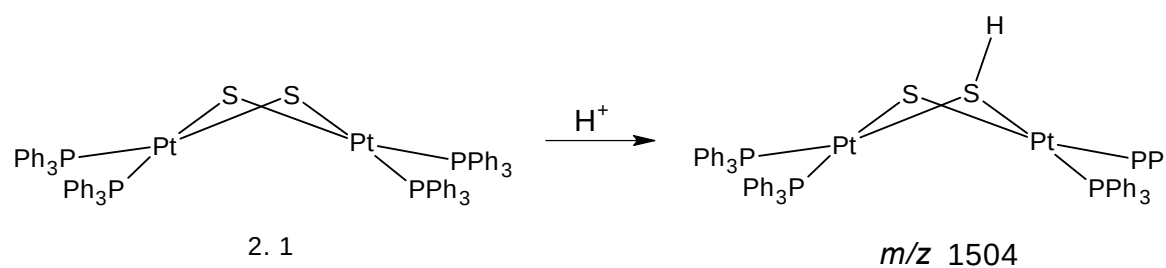


Figure 4.0. Positive ion electrospray mass spectrum of a mixture of $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ with $\text{ClCH}_2\text{CH}_2\text{NHC}(\text{O})\text{N}(\text{CH}_2\text{CH}_2)_2\text{O}$, showing the exclusive formation of $[\text{Pt}_2(\epsilon\text{-S})(\epsilon\text{-SCH}_2\text{CH}_2\text{NHC}(\text{O})\text{N}(\text{CH}_2\text{CH}_2)_2\text{O})(\text{PPh}_3)_4]^+$.

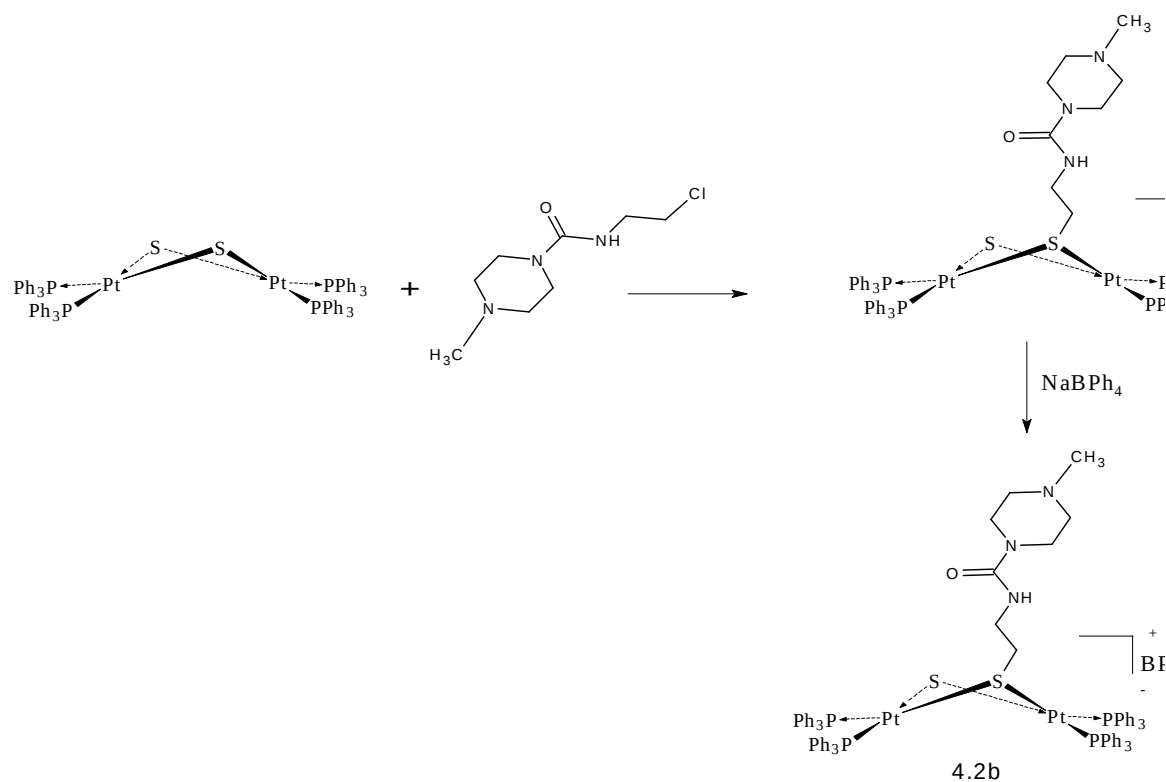
Analysis of 4.1b by ^1H NMR spectroscopic gave complicated signal in the aromatic region which could not be easily assigned. This is attributable to the large number of phenyl rings in the complexes. However, the NMR spectra of PPh_3 ligands and the counter ion BPh_4^- were observed as multiplets at δ 7.35. The signals due to SCH_2 protons in the monoalkylated complex occurred as triplet at δ 2.31. the methylene SCH_2 protons were weakly absorbed and therefore does not occurred as the expected broad satellite peaks which can be attributed to the presence of poorly ^{31}P and ^{195}Pt coupling. The central CH_2 protons expected to occurred as multiplet were weakly absorbed and were therefore hidden in the instrumental background noise. The four CH_2 protons of the morpholine ring are chemically non equivalent due to the presence of oxygen and nitrogen atom adjacent to them. The two CH_2 protons adjacent to nitrogen occur as triplet at δ 6.51 while the two CH_2 protons adjacent to oxygen also appears as triplet and were most deshielded at δ 6.88. The NH proton were observed as triplet between δ 7.07 and 7.03.

$[\text{Pt}_2(\mu\text{-S})(\mu\text{-SCH}_2\text{CH}_2\text{NHC(O)N(CH}_2\text{CH}_2)_2\text{NCH}_3)(\text{PPh}_3)_4](\text{BPh}_4)$

The reaction of $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ with $\text{ClCH}_2\text{CH}_2\text{NHC(O)N(CH}_2\text{CH}_2)_2\text{NCH}_3$ in methanol yielded a monoalkylated derivative $[\text{Pt}_2(\epsilon\text{-S})(\epsilon\text{-SCH}_2\text{CH}_2\text{NHC(O)N(CH}_2\text{CH}_2)_2\text{NCH}_3)(\text{PPh}_3)_4]^+$ as shown in scheme 4.4., after stirring for 24hours. The product was isolated as the triphenyl borate salt $[\text{Pt}_2(\epsilon\text{-S})(\epsilon\text{-SCH}_2\text{CH}_2\text{NHC(O)N(CH}_2\text{CH}_2)_2\text{NCH}_3)(\text{PPh}_3)_4](\text{BPh}_4)$ (4.2b. BPh_4) by the addition of excess NaBPh_4 to the reaction mixture . The positive ion ESI-MS spectra of the alkylated derivatives of isocyanate 4.2b. BPh_4 gave purely an $[\text{M}]^+$ ion at m/z 1673 suggesting the exclusive formation of the products as shown in fig 4.2. The inset shows the observed isotope distribution patterns for $[2.1 + \text{H}]^+$ ion at m/z 1504 which can be attributed to the protonation of $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ 2.1 shown in scheme 4.3.



Scheme 4.3. Protonation of $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ in the solvent



Scheme 4.4. Formation of monoalkylated derivative $[\text{Pt}_2(\epsilon\text{-S})(\epsilon\text{-SCH}_2\text{CH}_2\text{NHC(O)N}(\text{CH}_2\text{CH}_2)_2\text{N CH}_3)(\text{PPh}_3)_4]^+$.

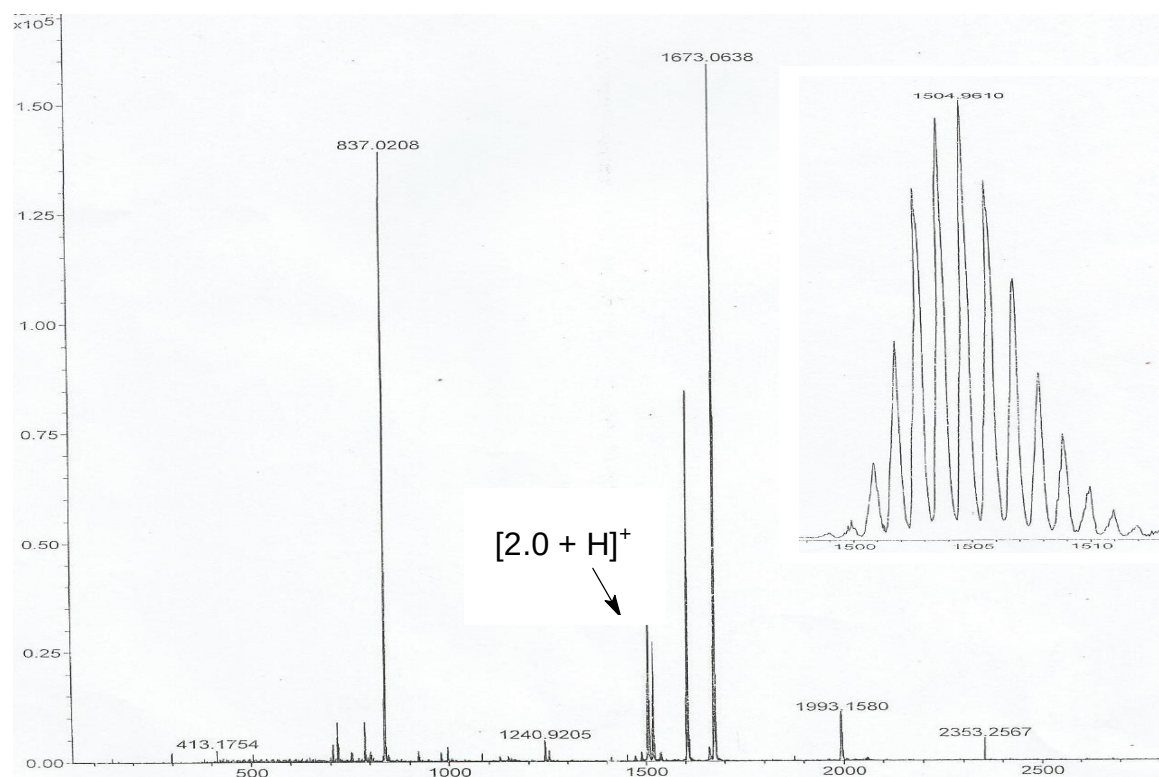


Figure 4.1. Positive ion electrospray mass spectrum of the reaction mixture of $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ with $\text{ClCH}_2\text{CH}_2\text{NHC}(\text{O})\text{N}(\text{CH}_2\text{CH}_2)_2\text{NCH}_3$. The inset shows the observed isotope distribution pattern for $[2.0 + \text{H}]^+$ ion.

Analysis of 4.2b by ^1H NMR spectra gave complicated signals in the aromatic region which can not be easily assigned due to the large number of phenyl rings in the complex. However, the signals which are consistent with the non phenyl hydrogen atoms of the incorporated group are identifiable except in cases where the hydrogen possess an unusual features that prevent it signal from being clearly observed. The NMR spectra of PPh_3 ligands and the counter ions BPh_4^- were identified as multiplet at δ 7.37. in addition to the typical complex of PPh_3 resonances, three unique resonances occurred in the aliphatic region, a broad satellite peaks due to SCH_2 protons occurred as triplet at δ 2.75, a singlet due to CH_3 protons at δ 2.25, and a singlet for the four CH_2 protons of the piperazine ring at δ 2.96. The presence of singlet in the aliphatic region is consistent with the CH_2 protons of the piperazine ring which are chemically equivalent. The most deshielded central CH_2 protons in the aliphatic region occurred as multiplets at δ 3.97 due to the adjacent NH group. The NH proton signal were observed as overlapping and complicated triplets at δ 6.89. the increase in downfield of

NH can be attributed to the presence of adjacent carbonyl groups. Figure 4.2. shows the ^1H NMR spectrum.

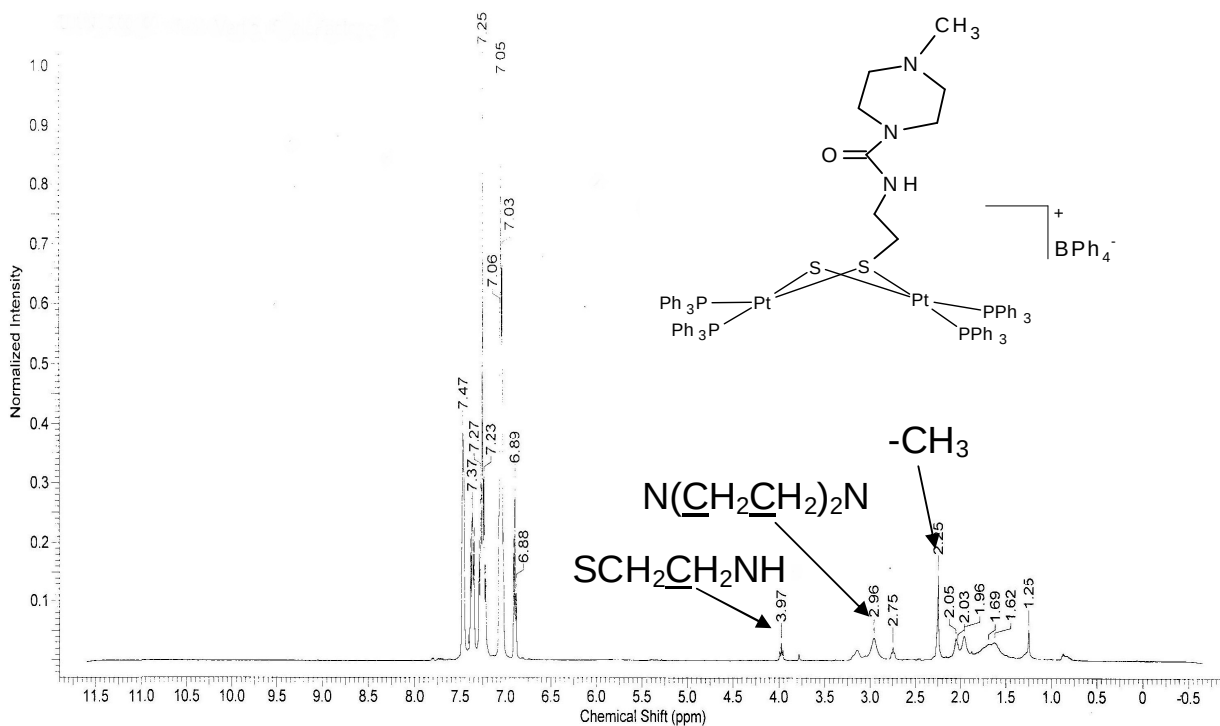
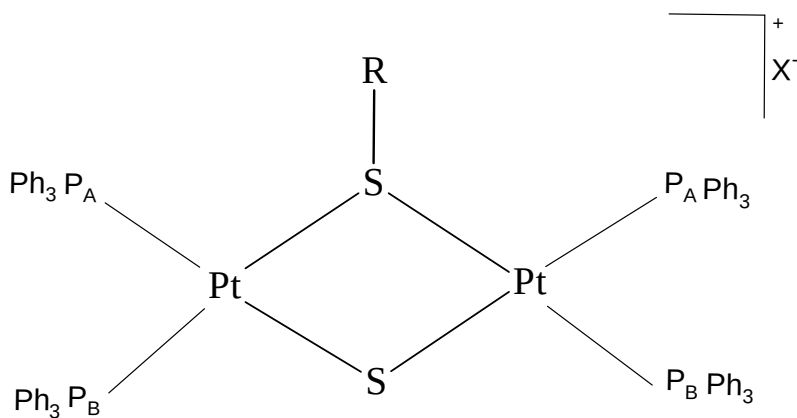


Figure 4.2. Shows the ^1H NMR spectrum of $[\text{Pt}_2(\epsilon\text{-S})(\epsilon\text{-SCH}_2\text{CH}_2\text{NHC(O)N}(\text{CH}_2\text{CH}_2)_2\text{NCH}_3)(\text{PPh}_3)_4]^+ \text{BPh}_4^-$ complex

4.2.2.1 ^{31}P NMR Spectroscopy

The ^{31}P $\{^1\text{H}\}$ NMR spectra of all the complexes show common features. The spectra of the complexes yielded the expected two overlapping resonances due to two different triphenyl phosphine environments P_A and P_B , each giving rise to a doublet. The two signals were however, distinguished by their different $^1\text{J}(\text{Pt-P})$ coupling constant as shown in scheme 4.6. An example is the ^{31}P $\{^1\text{H}\}$ NMR of 4.1b.BPh₄ in figure 4.3.



Scheme 4.5. The numbering scheme of the phosphorus environment P_B *trans*- to S^{2-} and P_A *cis*- to the thiolate SR

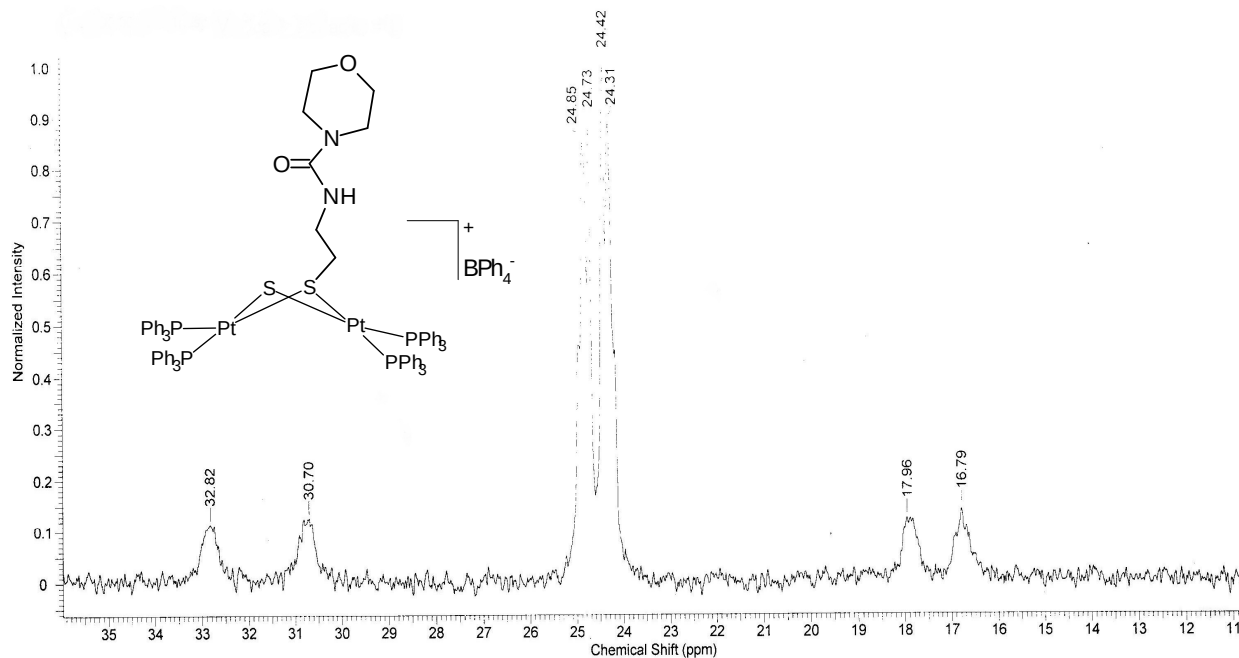


Figure 4.3. ^{31}P NMR of $[\text{Pt}_2(\epsilon\text{-S})(\epsilon\text{-SCH}_2\text{CH}_2\text{NHC(O)N(CH}_2\text{CH}_2)_2\text{O})(\text{PPh}_3)_4]^+$ showing the two chemically inequivalent P_A and P_B environment.

The two different phosphorus groups have different coupling constants to ^{195}Pt , with the phosphines *cis* to the SR ligand, P_A and P_B *trans* to the S^{2-} . The two phosphorus atoms *cis* to SR are expected to give rise to the smaller $1J(\text{Pt-P})$ coupling constant. This is because the higher *trans* influence of S^{2-} , relative to SR, lengthens the Pt- P_A bond, resulting in a smaller

$^1J(\text{Pt-P})$ value. The two chemically inequivalent ^{31}P nuclei were confirmed by ^{31}P NMR spectra of the complexes. The spectra showed that the signals for both P_A and P_B were flanked by two satellite peaks, one on each side. Hence, the $^{31}\text{P}\{\text{H}\}$ NMR spectrum of complexes 4.1b (BPh_4) and 4.2b (BPh_4) showed the same coupling constant around 2603.97 Hz with similar resonances at δ 24.45 and δ 24.36 respectively, due to the phosphorus atoms *trans*- to the S^{2-} ligand and the large coupling constants 3223.63 Hz and 3245.31 Hz showing similar resonance at δ 24.84 and δ 24.76 respectively for the phosphorus atoms *trans*- to the thiolate SR. Similar spectrum has been previously observed in the ^{31}P NMR spectrum of $[\text{Pt}_2(\epsilon\text{-S})(\epsilon\text{-SCH}_2\text{CH}_2\text{NHC}(\text{O})\text{N}(\text{CH}_2\text{CH}_2)_2\text{S})(\text{PPh}_3)_4](\text{PF}_6)^{32}$.

4.3 Intermolecular Bridging Alkylation

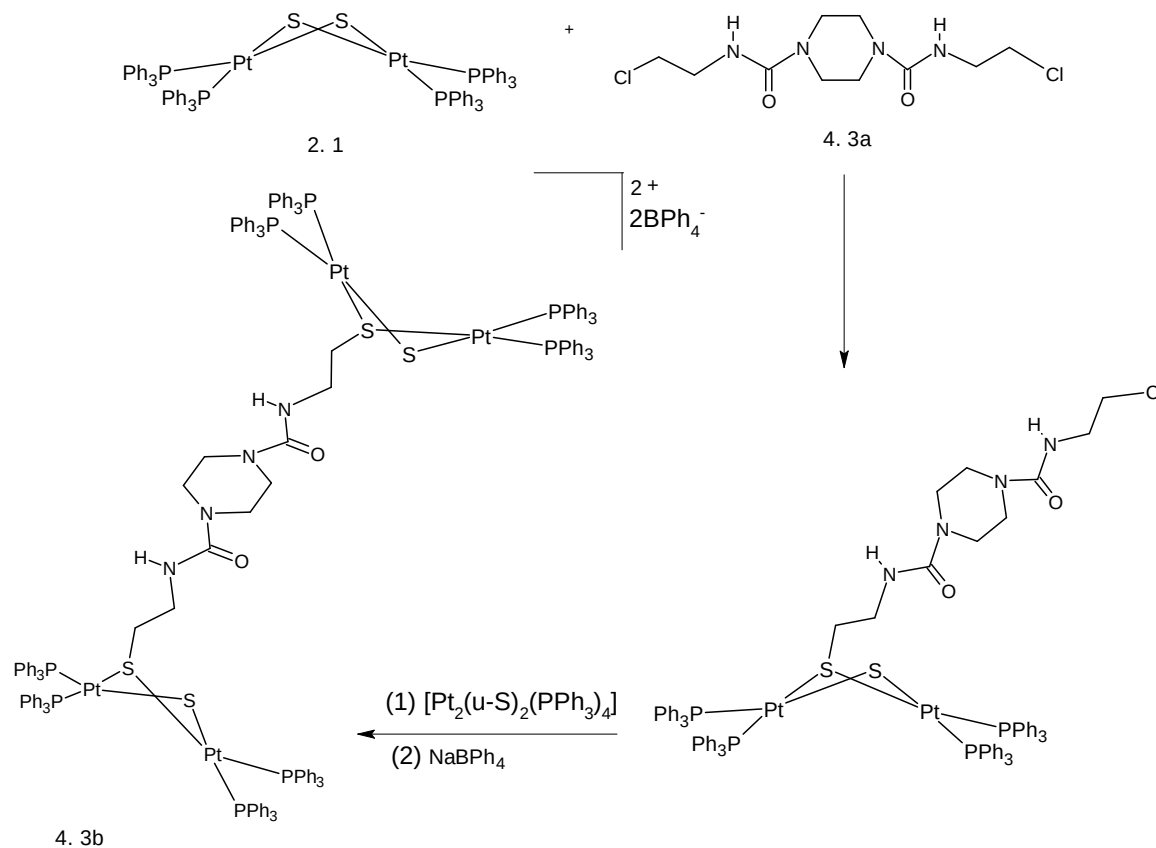
$[(\text{PPh}_3)_4\text{Pt}_2(\mu\text{-S})(\mu\text{-SCH}_2\text{CH}_2\text{NHC}(\text{O})\text{N}(\text{CH}_2\text{CH}_2)_2\text{NC}(\text{O})\text{HNCH}_2\text{CH}_2\text{S})(\mu\text{-S})\text{Pt}_2(\text{PPh}_3)_4](\text{BPh}_4)_2$

The highly functionalised $\ddot{\text{X}}_\text{R}$ -dialkylating agent with R having length of more than six spacer atoms between the two halide groups encourages the formation of intermolecular dialkylated Pt_4 aggregate as aforementioned in section 4.0. In addition, the formation of the monoalkylated alkyl halide derivative of $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ enhances its ability to act as an electrophile and therefore makes it possible to incorporate another molecule of $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ through the C-X bond of $[\text{Pt}_2(\epsilon\text{-S})(\epsilon\text{-SCH}_2\text{CH}_2\text{RCH}_2\text{CH}_2\text{X})(\text{PPh}_3)_4]^+$ where R can be alkyl or aryl group or combination of both, and X is the halide resulting from the initial monoalkylation.

The reaction of $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ with the 0.5 mole equivalent of functionalised dialkylating agent $\text{ClCH}_2\text{CH}_2\text{NHC}(\text{O})\text{N}(\text{CH}_2\text{CH}_2)_2\text{NC}(\text{O})\text{HNCH}_2\text{CH}_2\text{Cl}$ of the derivative of isocyanate proceeded in two stages in a 2:1 mole ratio. The first stage is the monoalkylation of $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ to give the monocation $[\text{Pt}_2(\epsilon\text{-S})(\epsilon\text{-SCH}_2\text{CH}_2\text{NHC}(\text{O})\text{N}(\text{CH}_2\text{CH}_2)_2\text{NC}(\text{O})\text{HNCH}_2\text{CH}_2\text{Cl})(\text{PPh}_3)_4]^+$. The monoalkylated

derivative provided the enabling condition for a second intermolecular nucleophilic attack by another molecule of $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ yielding the bridging Pt_4 aggregate spanned by $\text{SCH}_2\text{CH}_2\text{NHC}(\text{O})\text{N}(\text{CH}_2\text{CH}_2)_2\text{NC}(\text{O})\text{HNCH}_2\text{CH}_2\text{S}$ as shown in scheme 4.5. the reaction of $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$ and 4.3a in a 2:1 mole ratio was completed after 120 hours of stirring at room temperature yielding Pt_4 overhead bridged aggregates of two molecules of $[\text{Pt}_2(\epsilon\text{-S})_2(\text{PPh}_3)_4]$. The product was isolated as $[(\text{PPh}_3)_4\text{Pt}_2(\epsilon\text{-S})(\epsilon\text{-SCH}_2\text{CH}_2\text{NHC}(\text{O})\text{N}(\text{CH}_2\text{CH}_2)_2\text{NC}(\text{O})\text{HNCH}_2\text{CH}_2\text{S})(\epsilon\text{-S})\text{Pt}_2(\text{PPh}_3)_4](\text{BPh}_4)_2$ with the addition of excess NaBPh_4 . The long time required for the complete reaction can be attributed to the long spacer length of the $\check{\text{U}}\chi$ -dialkylating agent having more than six atoms which slows down the reaction process.

Analysis of 4.3b by ^1H NMR spectrum gave two distinct signals in the aliphatic region and five complicated signals in the aromatic region which could not be easily assigned due to the large number of phenyl rings in the complex. The NMR spectra of PPh_3 ligands and the counter ions $(\text{BPh}_4)_2^-$ were the most deshielded and therefore occurred as multiplet at $\check{\text{u}}$ 7.60. However the non phenyl hydrogen atoms of the attached group can be easily identified except in the case of the central CH_2 protons which was not observed due to weak absorption. The SCH_2 protons in the $\check{\text{U}}\chi$ -dialkylated complex were easily identified as a broad triplet signal at $\check{\text{u}}$ 3.04, with broad satellite peaks produced by coupling to the ^{31}P and ^{195}Pt atoms respectively³⁰. The four CH_2 protons of the piperazine ring are chemically equivalent and therefore appears as singlet at $\check{\text{u}}$ 2.22. the signals due to NH protons in the $\check{\text{U}}\chi$ -dialkylated complex occurred as triplet between $\check{\text{u}}$ 6.92 and 6.79 with 7.20 Hz coupling constant. The increase in downfield of NH can be attributed to the presence of carbonyl groups on the adjacent side.



Scheme 4.6. The formation of intermolecular dialkylated Pt_4 aggregate via bridging dialkylation of two molecules of $[Pt_2(\epsilon-S)_2(PPh_3)_4]$.

4.3.1 IR Spectroscopy

The infrared (IR) spectra of the complexes were assigned in most cases for the complete characterisation of the alkylated complexes and to confirmed the presence of the functional groups due to the incorporated electrophiles but did not give structural information about the complexes³². the IR adsorption bands attributable to C=O groups in all the complexes were observed between 1700 and 1640 cm^{-1} and the absorption due to NH was also observed in all the complexes between 3500 and 3410 cm^{-1} .

4.3.1.1 Comparison of the IR Spectral of $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$ and the Complexes

Different IR absorptions attributable to C-H, C=O and NH were observed in all the functionalised electrophiles and their complexes. However the IR spectral of $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$ gives a distinguishable characteristics when compared with that of the various electrophiles and their corresponding complexes. It shows the absence of NH and CO which are most dominant in the complexes but indicates the presence of complicating signals which could not be easily assigned. This is attributable to the large number of phenyl rings in the complexes. The IR spectral absorptions attributable to C-H in the phenyl rings occurred between 3050 and 3000cm^{-1} and between 1480 and 1450cm^{-1} for C-H scissoring while the region between 1200 and 700cm^{-1} are referred to as the finger print region which includes C-C single bond stretches and C-H bending vibrations. The finger print region is often the most complex and confusing region to interpret and is usually the last section of the spectrum to be interpreted.

4.4 Conclusion

The incorporation of functionalised alkylating agents N-(2-chloroethyl) morpholine-4-carboxi-amine, N-(2-chloroethyl)-1-methyl piperazen-4-carboxi-amine, and N,N-(2-dichloroethyl) piperazine-4-carboxi-amine into $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$ was achieved forming a new set of novel functionalised monoalkylated and dialkylated complexes and the resulting products successfully characterised. The isolated complexes have unreacted sulfide centers which can be used to further functionalise them with say, metal fragments and powerful electrophiles. The multifunctional cationic ligand systems offer a potential template that could mediate the synthesis of diverse compounds tailored towards specific applications. The overall outcome of this study indicates that any suitable functional group can be incorporated into a suitable electrophile and incorporated into $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$. The ESI-MS technique is a very convenient and efficient screening and monitoring tool in the study of alkylation reactions between the electrophiles and $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$. The application of this technique in monitoring the laboratory scale syntheses of promising reactions between the electrophiles and $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$ and the ability of the instrument to detect charged species in the reaction mixtures successfully aided the synthesis and isolation of the monoalkylated derivatives of $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$. The isolated derivatives which were further characterised by NMR and IR perfectly correlated the ESI-MS data. However, the electrophiles used in this synthesis selectively monoalkylated one of the sulfide centres in $[\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]$ even when used in a large excess and the possibilities of synthesising dialkylated derivatives depends on the appropriate choice of alkylating agent.

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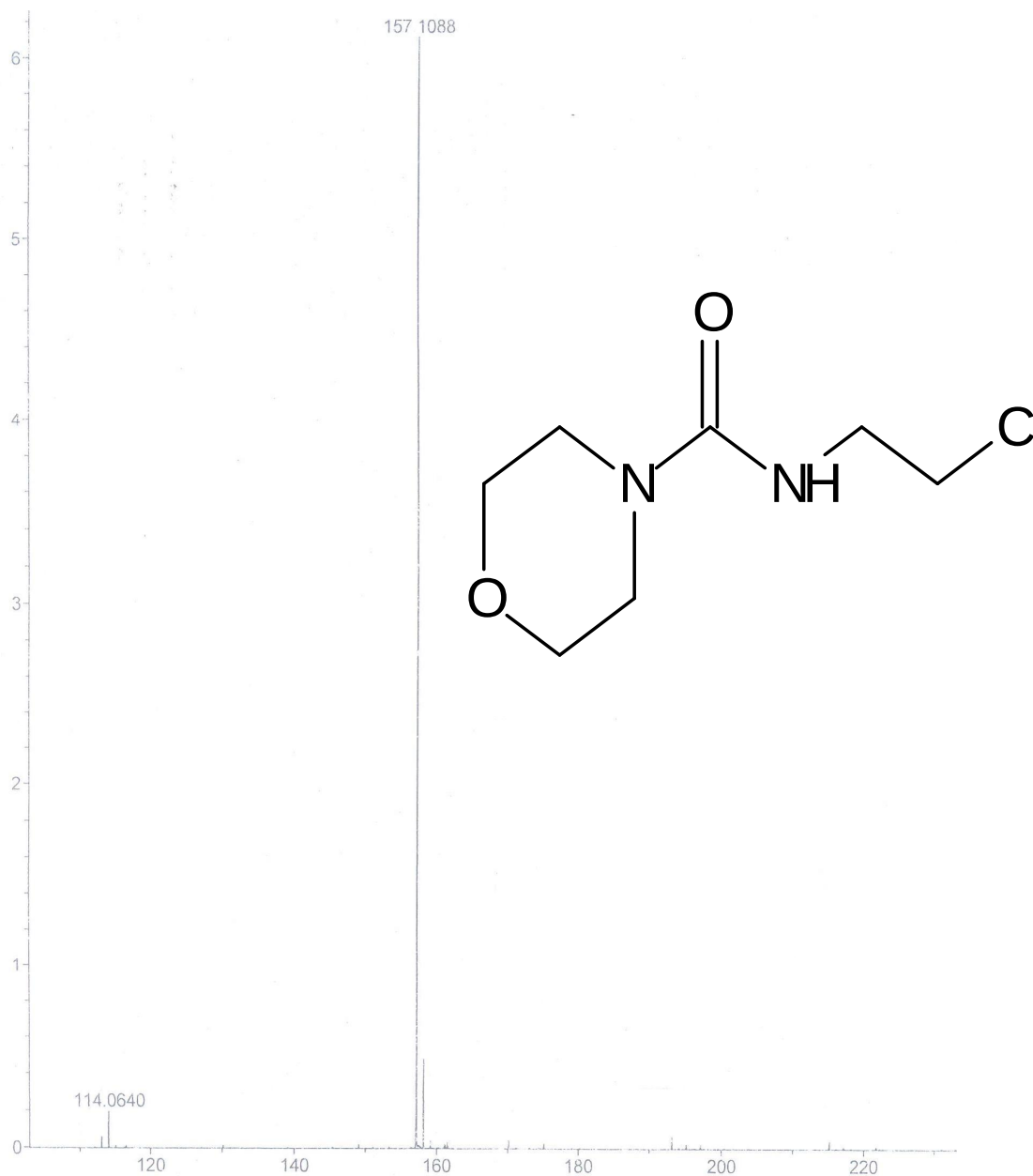
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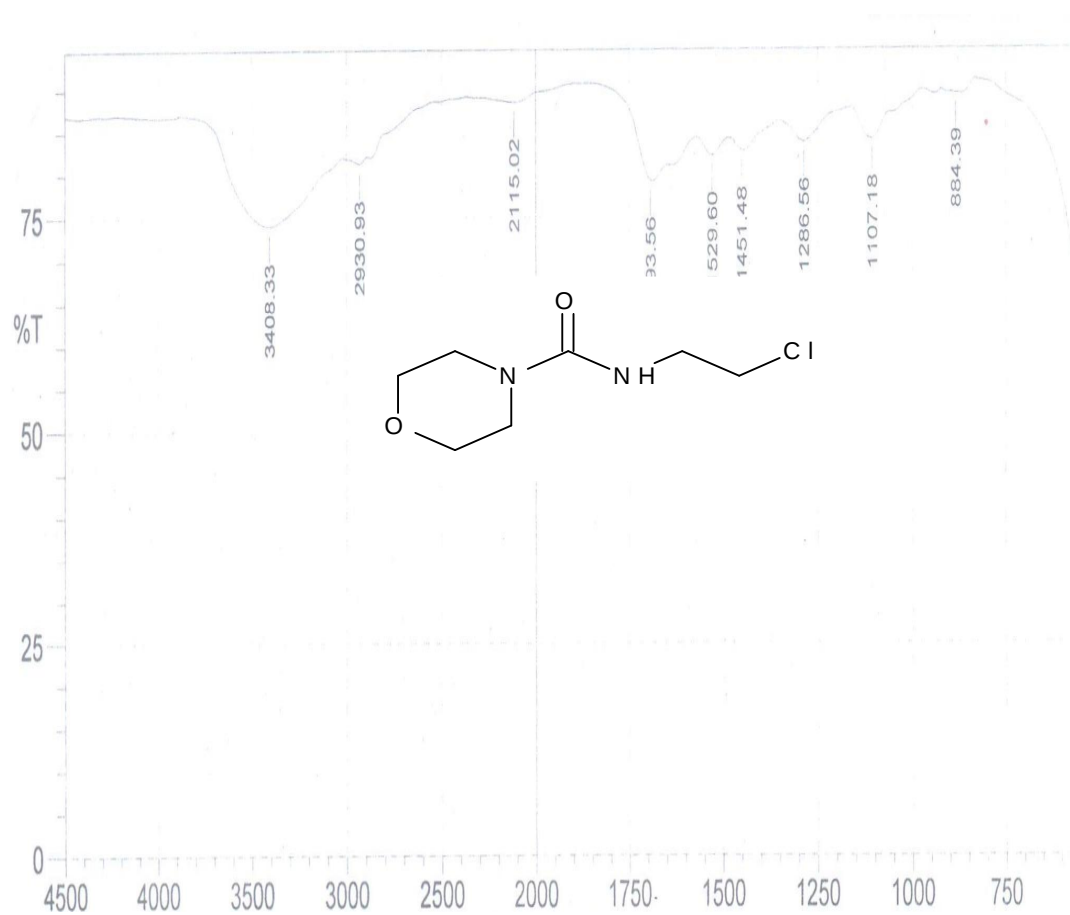
Appendixes

General Spectroscopy Result of the Alkylating Agent and their Complexes

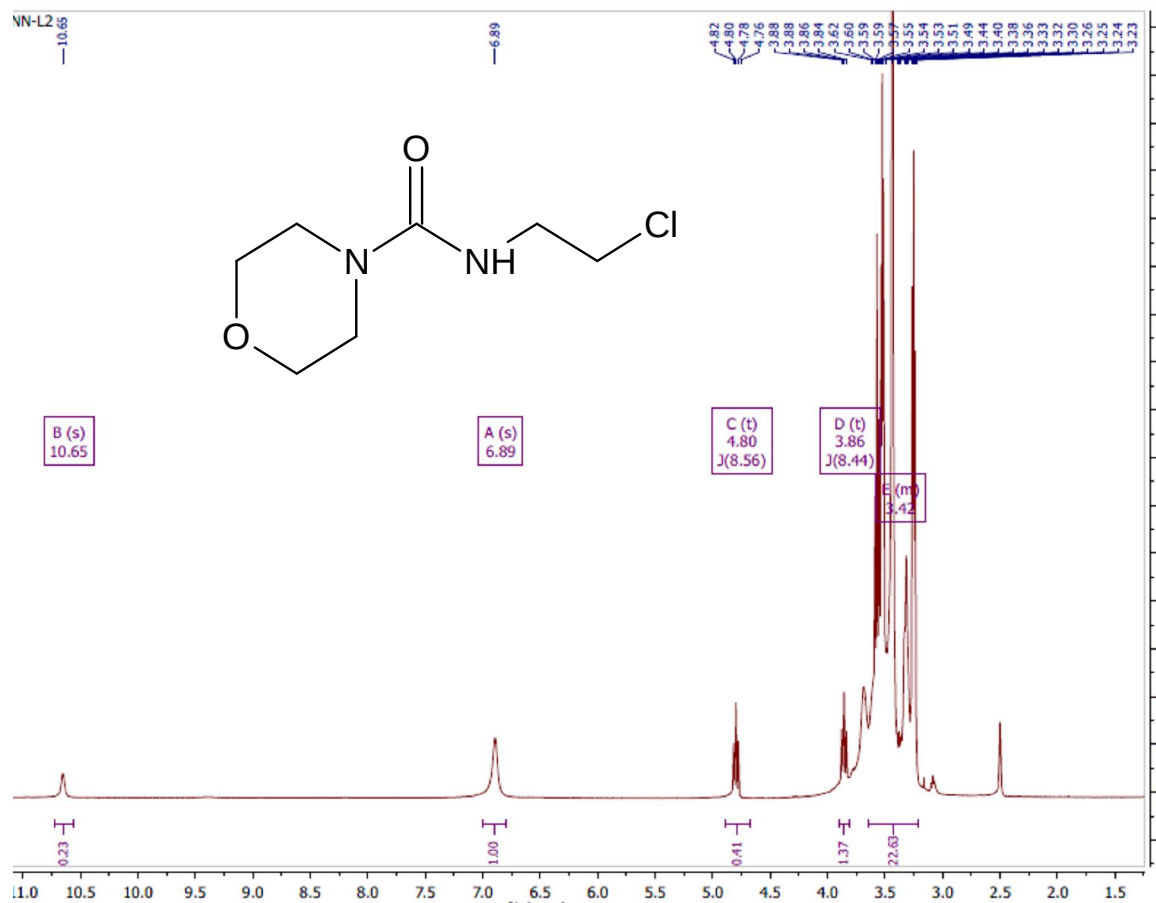
Appendix One: ESI-Mass Spectrum of N-(2-dichloroethyl) morpholine-4 carboxi-amine



Appendix Two: IR Spectrum of N-(2-dichloroethyl) morpholine-4 carboxi-amine

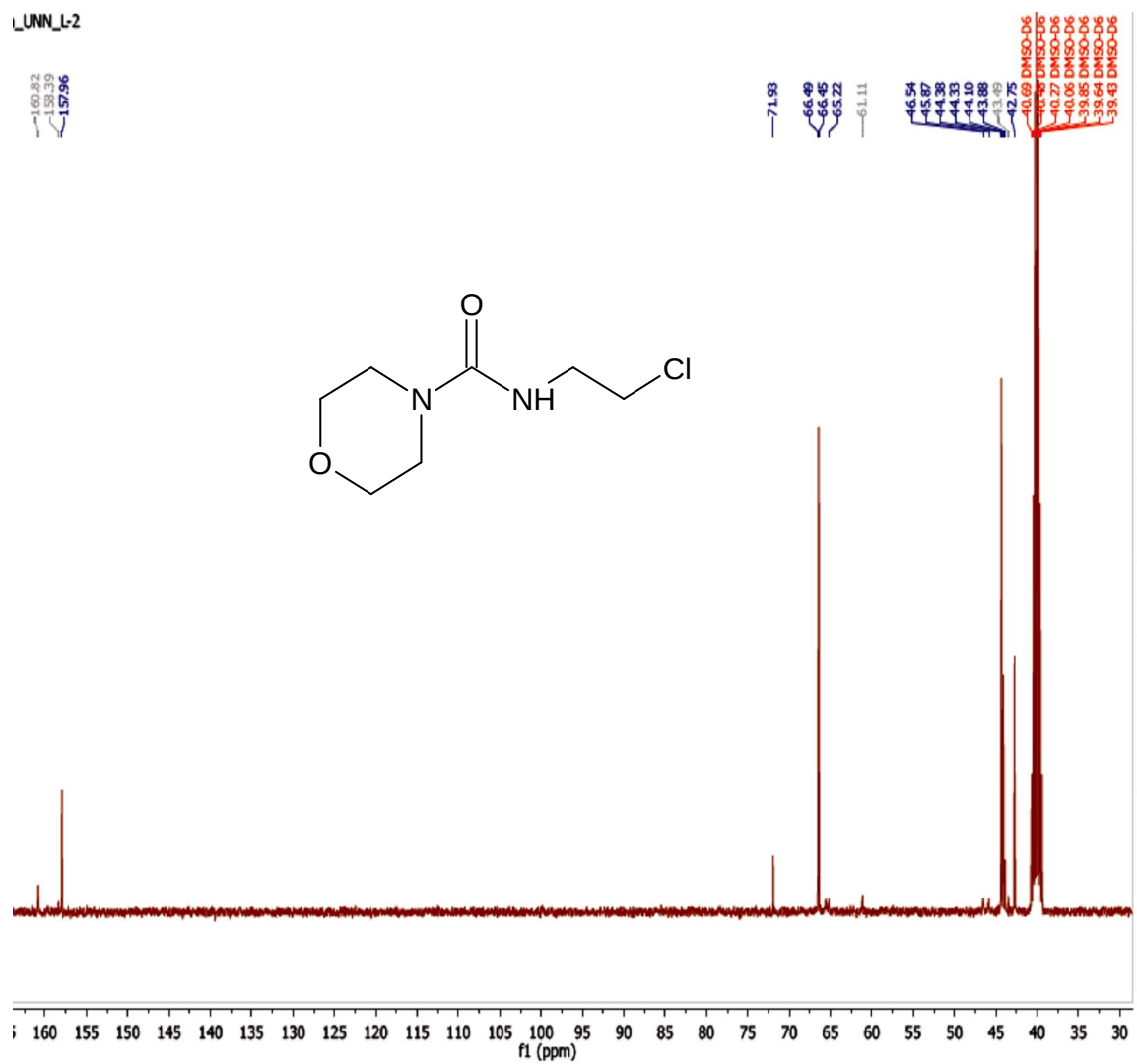


Appendix Three: ^1H NMR Spectrum of N-(2-dichloroethyl) morpholine-4 carboxi-amine

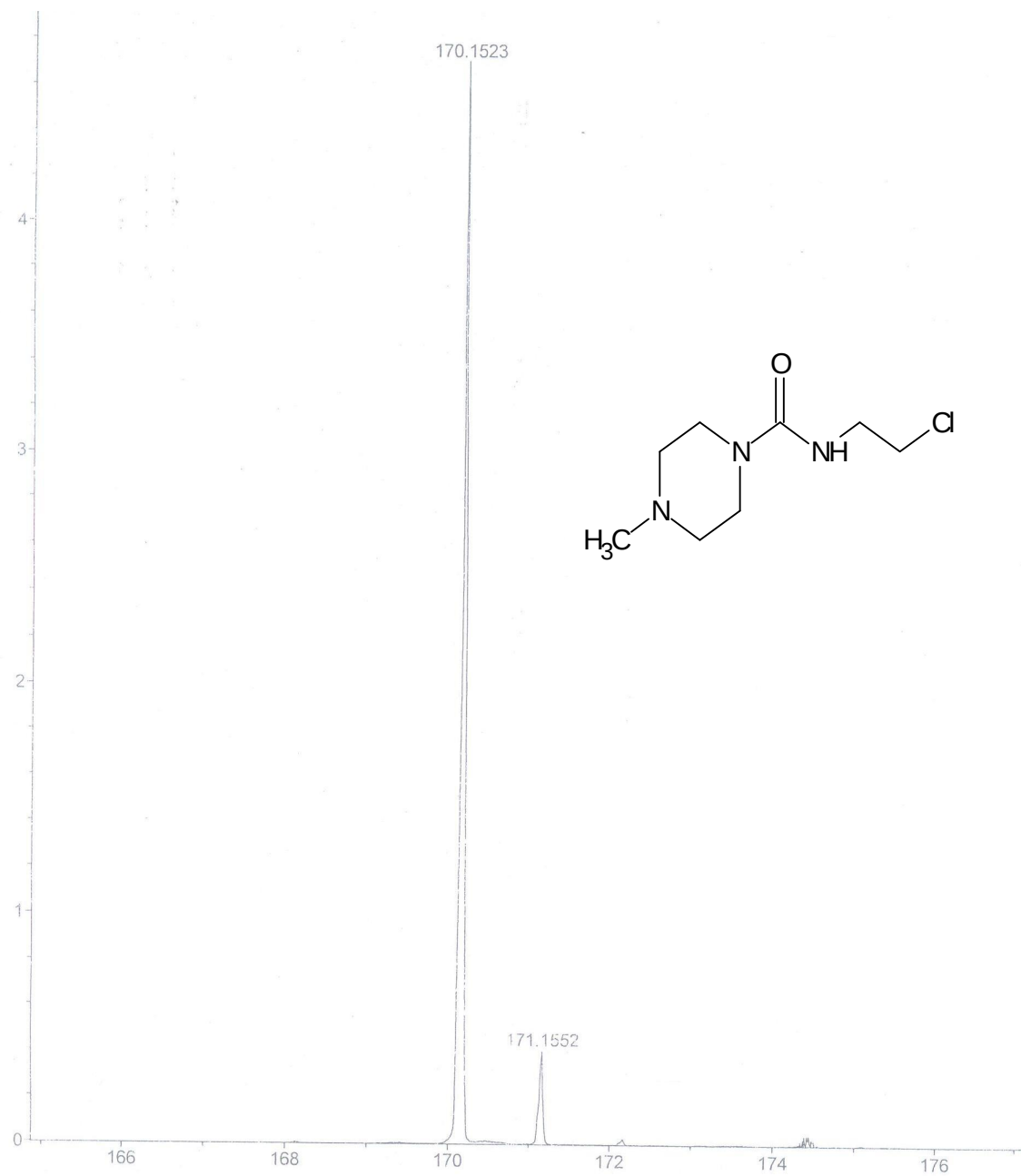


AppendixFour:¹³CNMR of N-(2-dichloroethyl) morpholine-4carboxi-amine

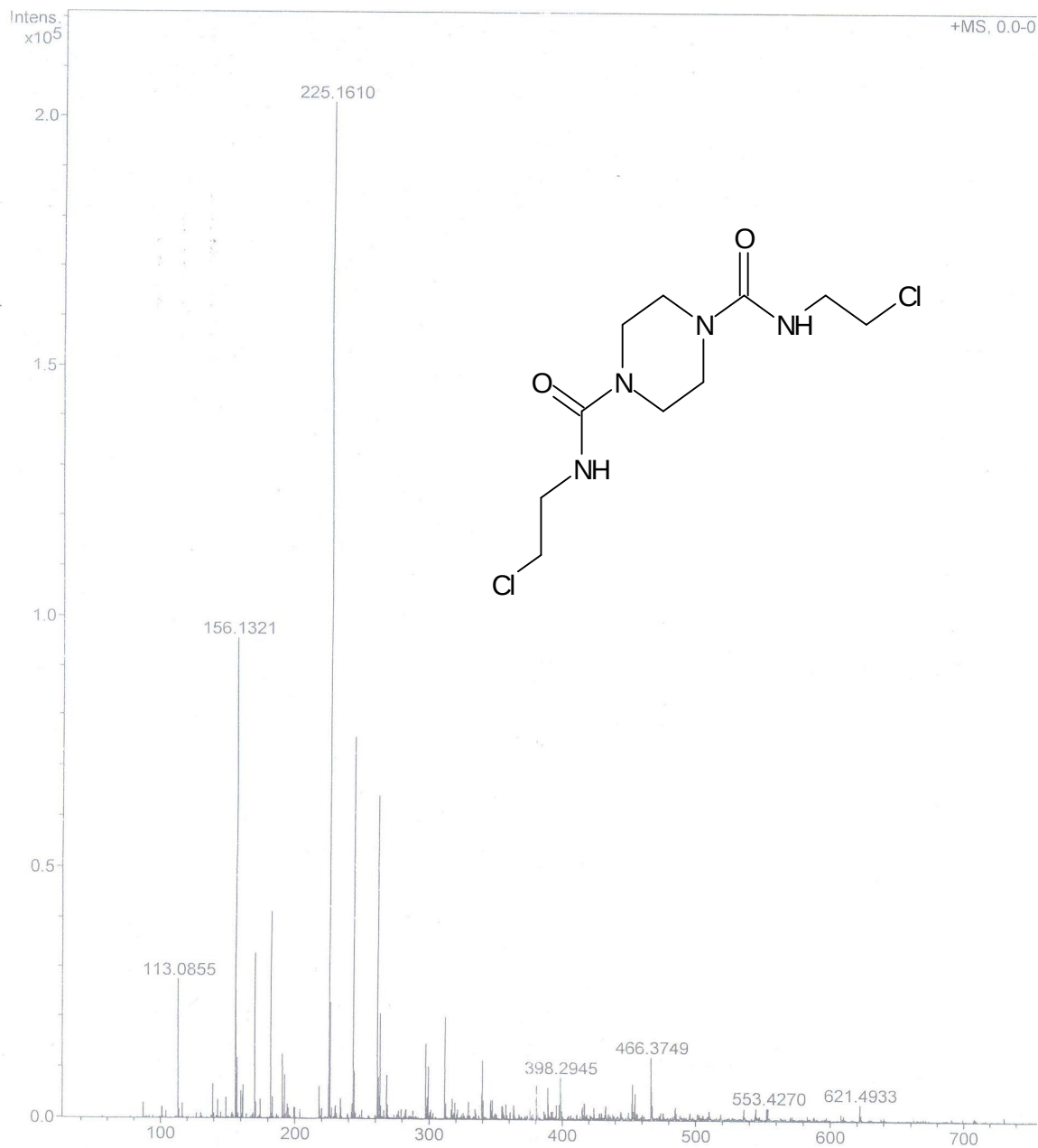
LUNN_L-2



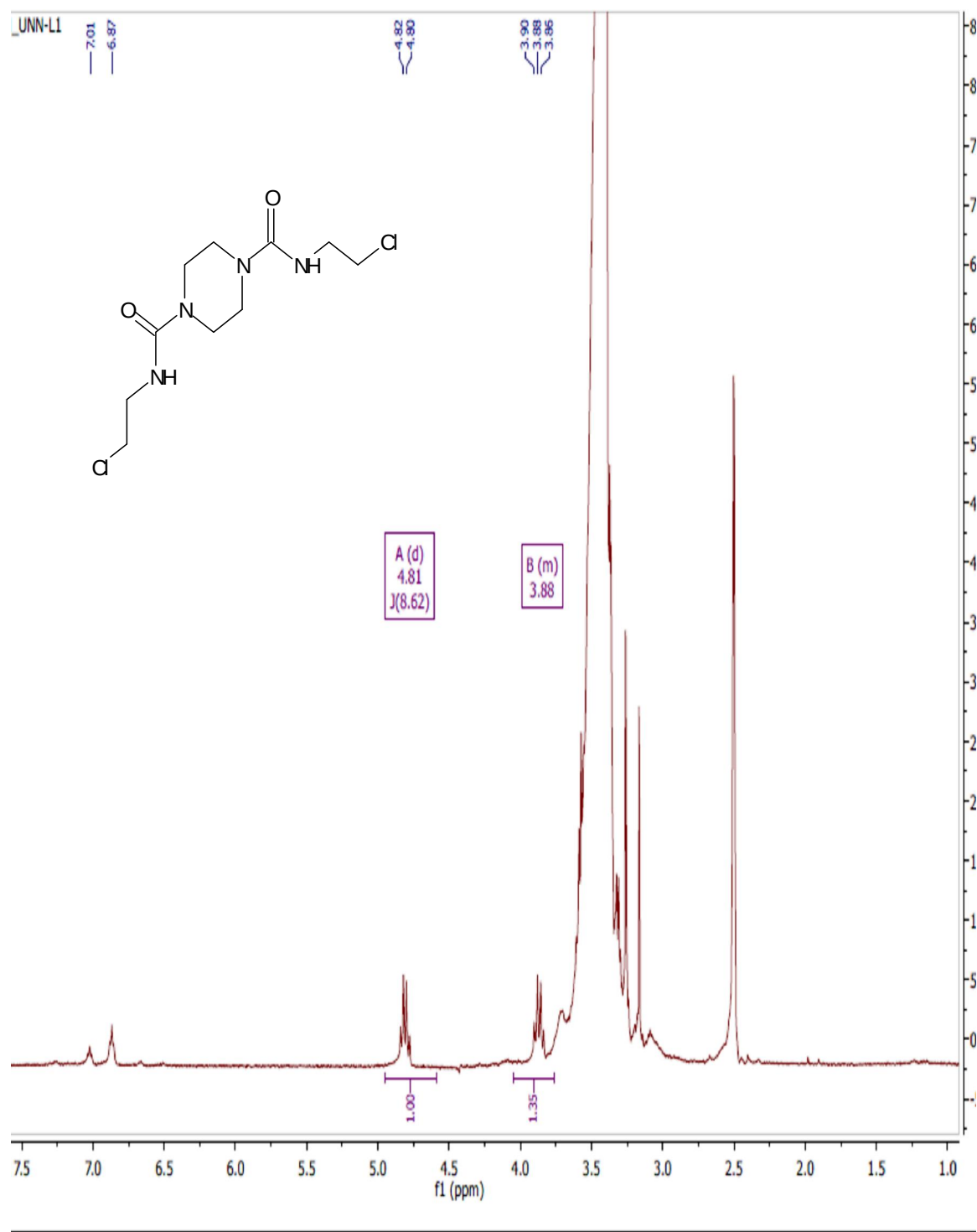
Appendix Five: ESI-Mass Spectrum of N-(2-dichloroethyl) methylpiperazine-4 carboxi-amine



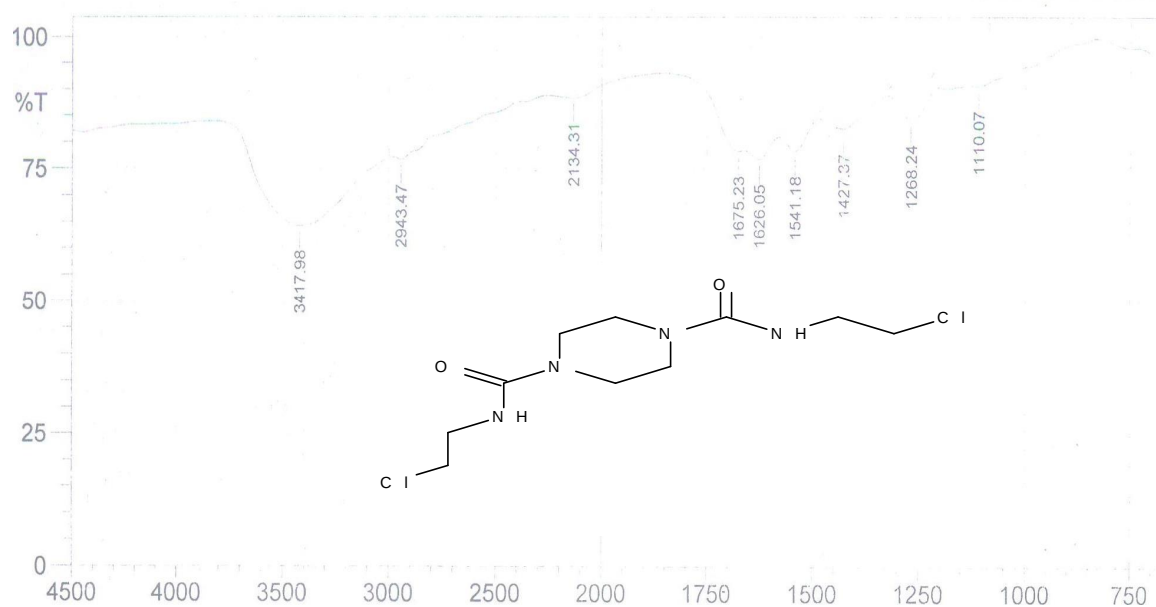
Appendix Six: ESI-Mass Spectrum of N,N-bis(2-dichloroethyl) piperazine-4 carboxi-amine



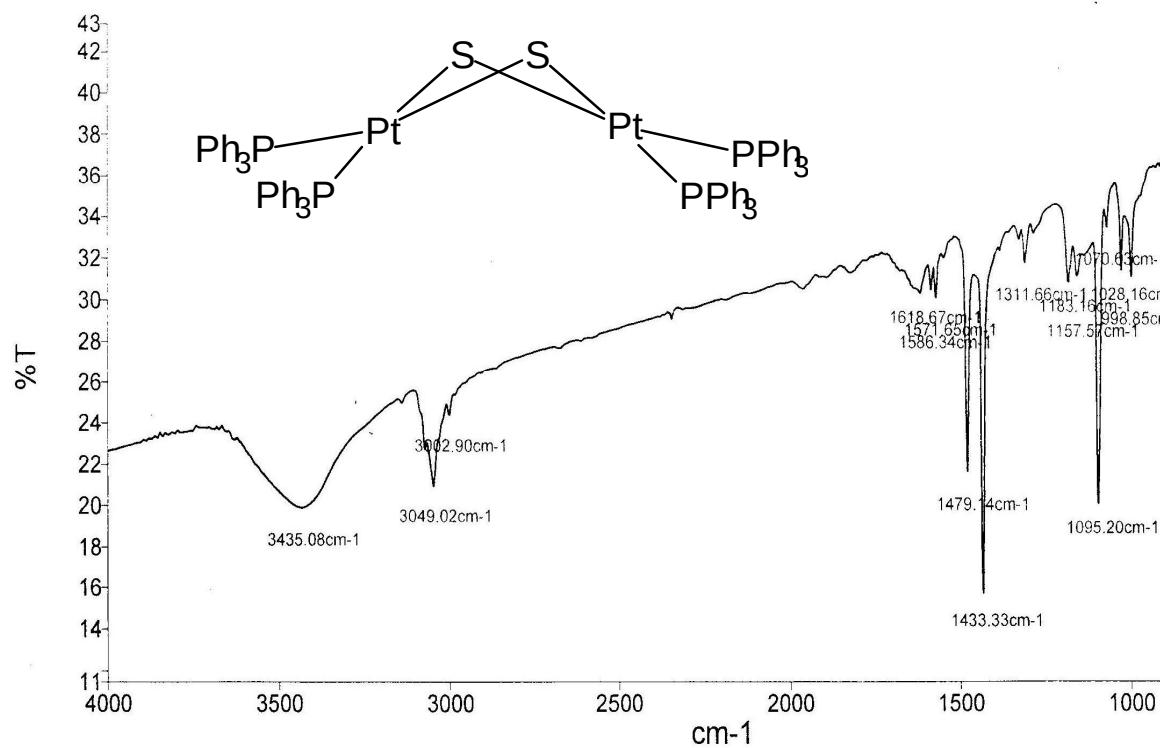
Appendix Seven: ^1NMR Spectrum of N,N'-2-dichloroethyl piperazine-4 carboxi-amine



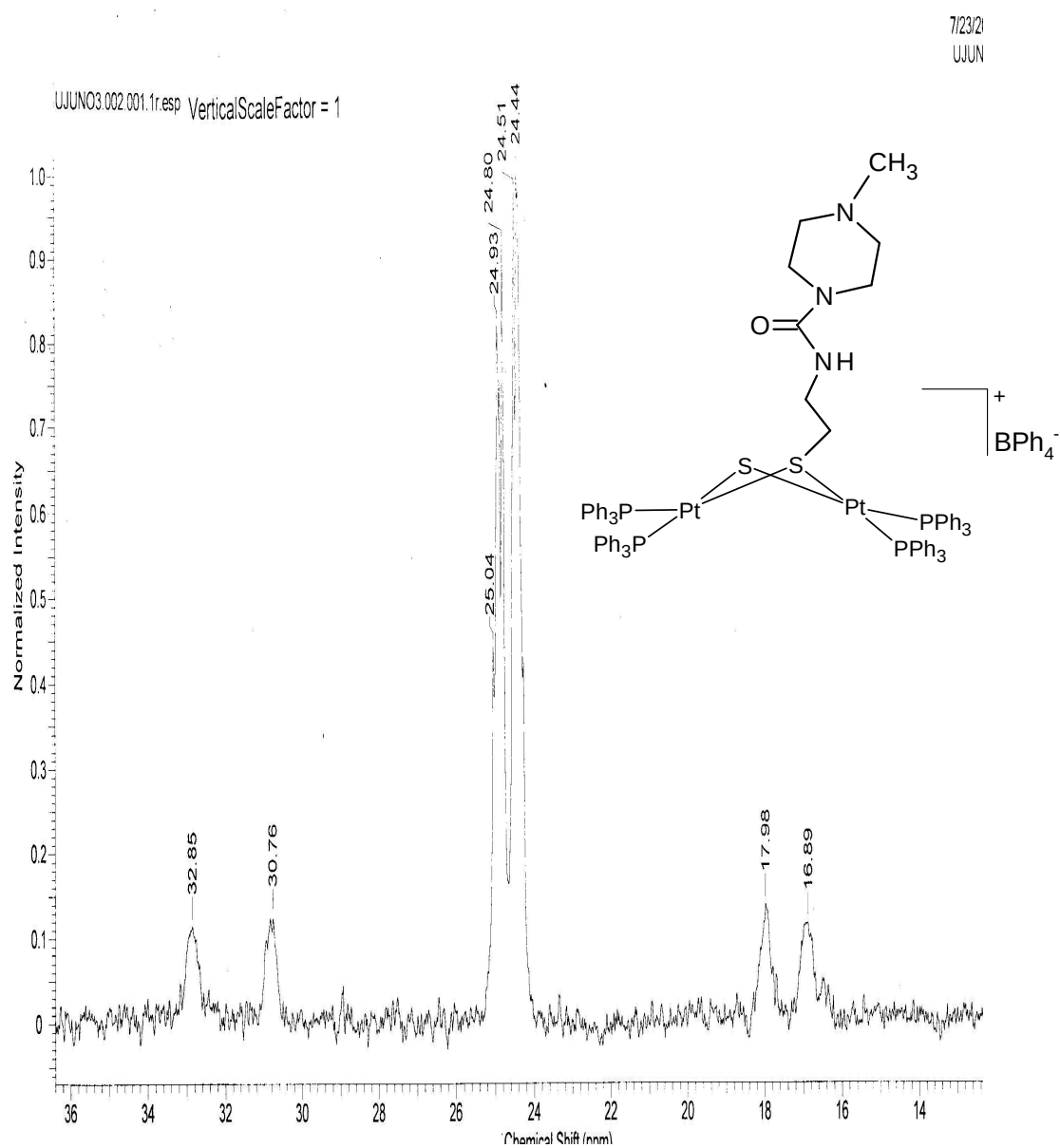
Appendix Eight: IR Spectrum of N,N-(2-dichloroethyl) piperazine-4 carboxi-amine



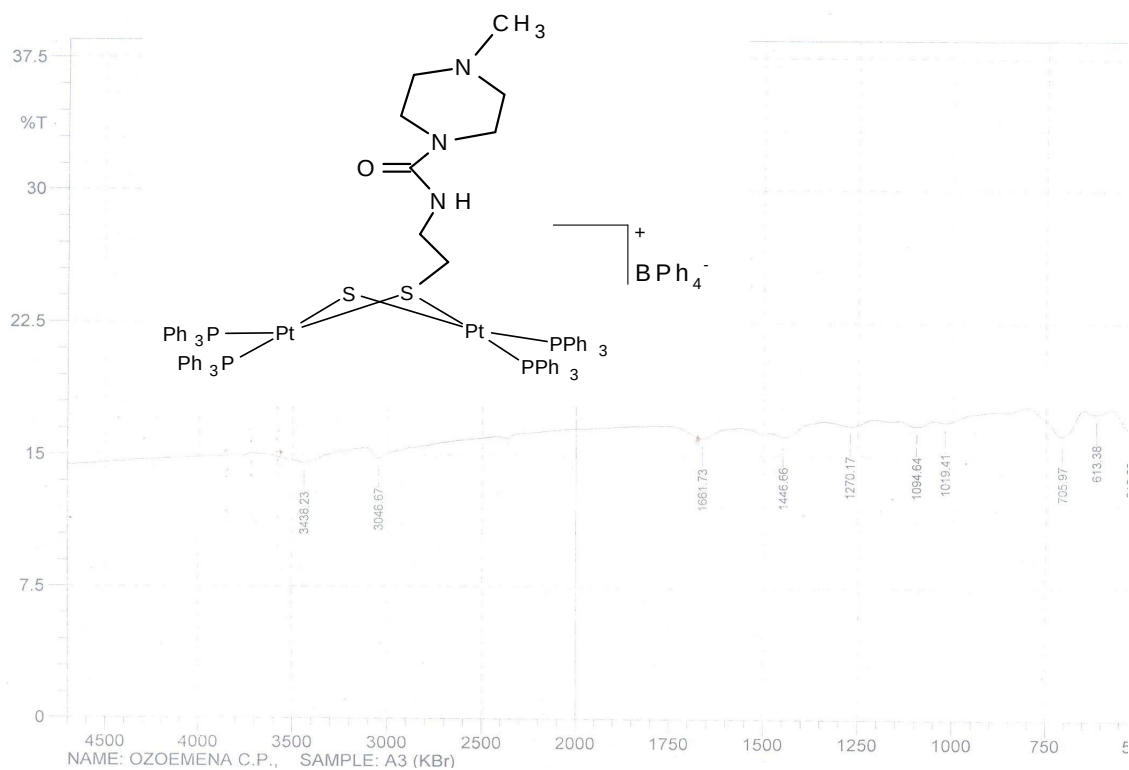
Appendix Nine: IR Spectrum of [Pt₂(ε-S)₂(PPh₃)₄]



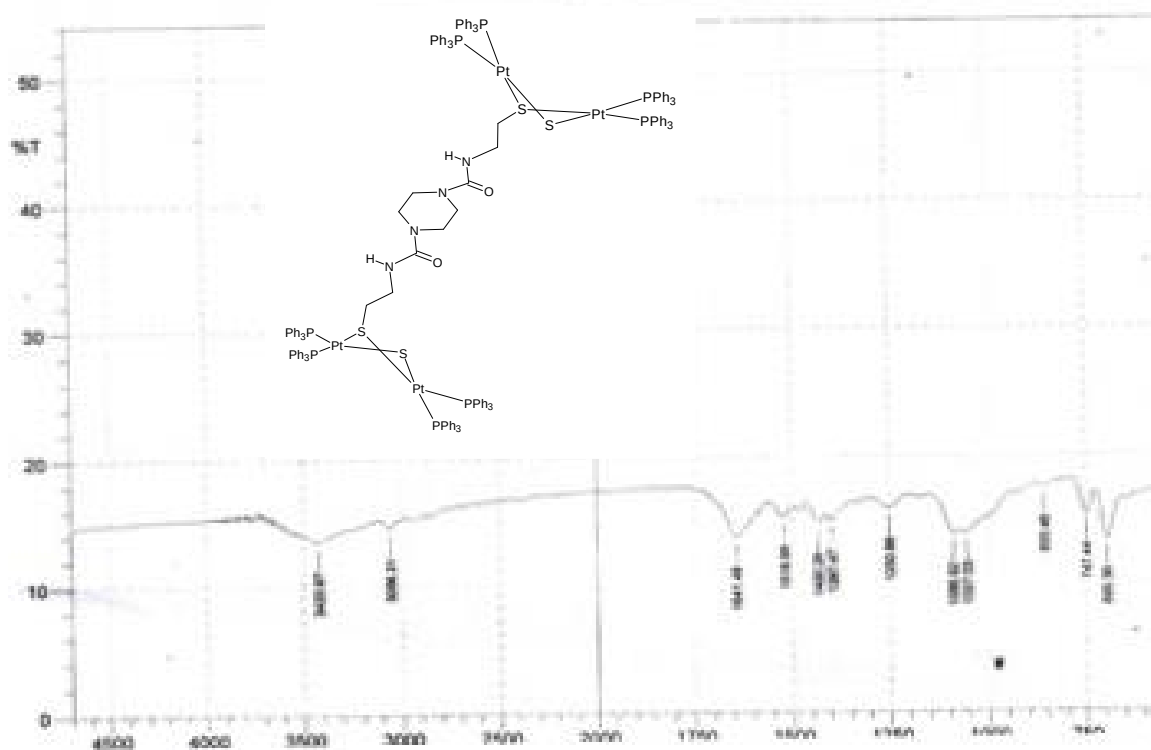
Appendix 10: ^{31}P NMR Spectrum of $[\text{Pt}_2(\epsilon\text{-S})(\epsilon\text{-SCH}_2\text{CH}_2\text{NHC(O)N}(\text{CH}_2\text{CH}_2)_2\text{CH}_3)(\text{PPh}_3)_4]^+$



Appendix 11: IR Spectrum of $[\text{Pt}_2(\epsilon\text{-S})(\epsilon\text{-SCH}_2\text{CH}_2\text{NHC(O)N}(\text{CH}_2\text{CH}_2)_2\text{CH}_3)(\text{PPh}_3)_4]^+$.



Appendix 12: IR Spectrum of $[(\text{PPh}_3)_4\text{Pt}_2(\epsilon\text{-S})(\epsilon\text{-SCH}_2\text{CH}_2\text{NHC(O)N}(\text{CH}_2\text{CH}_2)_2\text{NC(O)HNCH}_2\text{CH}_2\text{S})(\epsilon\text{-S})\text{Pt}_2(\text{PPh}_3)_4]^+$



Appendix 13: IR Spectrum of $[\text{Pt}_2(\epsilon\text{-S})(\epsilon\text{-SCH}_2\text{CH}_2\text{NHC(O)N}(\text{CH}_2\text{CH}_2)_2\text{O})(\text{PPh}_3)_4]^+$.

