ALKYLATION OF $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ WITH BORONIC ACID DERIVATIVES BY PRESSURIZED SAMPLE INFUSION ELECTROSPRAY IONIZATION MASS SPECTROMETRY (PSI-ESI-MS) TECHNIQUE

BY

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DEPARTMENT OF PURE AND INDUSTRIAL CHEMISTRY

FACULTY OF PHYSICAL SCIENCES
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A RESEARCH PROJECT SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF THE DEGREE OF MASTER OF SCIENCE IN INORGANIC CHEMISTRY.

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AUGUST, 2016

CERTIFICATION

This is to certify that, OFFIE, OGOCHUKWU ETHEL, a postgraduate student in the Department of Pure and Industrial Chemistry and with the Reg. No. PG/M.Sc/13/65212 has satisfactorily completed the requirements for course and research work for the degree of Master of Science (M.Sc.) in Inorganic Chemistry. The work embodied in this project report is original and has not been submitted in part or full for any other diploma or degree of this or any other university.

---------- ----------
Dr. Oguejiofo T. Ujam Date
Supervisor

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Prof.Uchechukwu C. Okoro Date
Head of Department

---------- ----------External
Examiner Date

DECLARATION

I, OFFIE Ogochukwu E. declare that this project was carried out by me under the supervision of Dr. Oguejiofo T. Ujam and it has not been presented for the award of diploma or a degree elsewhere.

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Offie, Ogochukwu Ethel Date

DEDICATION

To my husband Nnamdi and my parents Engr. and Mrs Innocent Uchechukwu Offie.

ACKNOWLEDGEMENT

This work would not have been possible without the effort and support of many individuals.I am grateful to my supervisor, Dr. Oguejiofo T. Ujam for his guidance, constant supervision and support to make this work worthwhile, and its completion a reality.

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I highly appreciate my husband for his support, unfailing effort, contribution and understanding through the period of this research. Many thanks to my parent and siblings. They never ceased showing me love and support throughout the period of this work.

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I also acknowledge my fellow students for their assistance and occasional seemingly disturbing laboratory jokes. My thanks goes to Journal of Coordination Chemistry who find this work of mine worthy for publication in their journal.

ABSTRACT

This project work present the alkylating reaction of $[Pt_2(\varepsilon\text{-}S)_2(PPh_3)_4]$ with boronic acid alkylating agents.The reactivity of the metalloligand $[Pt_2(\varepsilon\text{-}S)_2(PPh_3)_4]$ with the boron-functionalized alkylating agents $BrCH_2(C_6H_4)B(OR)_2$ (R = H or $C(CH_3)_2$) was investigated by electrospray ionization mass spectrometry (ESI-MS) in real time using the pressurized sample infusion (PSI). The macroscopic reaction of $[Pt_2(\varepsilon\text{-}S)_2(PPh_3)_4]$ with one mole equivalent of alkylating agents $BrCH_2(C_6H_4)B\{OC(CH_3)_2\}_2$and $BrCH_2(C_6H_4)B(OH)_2$ gave the dinuclear monocationic μ-sulfide thiolate complexes $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2(C_6H_4)B\{OC(CH_3)_2\}_2\}(PPh_3)_4]^+$ and $[Pt_2(\mu\text{-}S)\{\mu\text{-}S^+CH_2(C_6H_4)B(OH)(O^-)\}(PPh_3)_4]$. The products were isolated as the $[PF_6]^-$ salts and zwitterion respectively, and fully characterized by ESI-MS, IR, ^1H and ^{31}P NMR spectroscopy and single crystal X-ray structure determinations. The alkylation reaction of $BrCH_2(C_6H_4)B\{OC(CH_3)_2\}_2$ with $[Pt_2(\mu\text{-}S)_2(PPh_3)_4 + H]^+$was determined via kinetic analysis by PSI-ESI-MS to be second order consistent with the expected S_N2 mechanism for an alkylation reaction. The PSI-ESI-MS microscale synthesis showed that$[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$disappeared rapidly with consequent formation of onlymonoalkylated cationic product, $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2(C_6H_4)B\{OC(CH_3)_2\}_2\}(PPh_3)_4]^+$. This was indicated by the immediate appearance of the monoalkylated product peak at *m/z* 1720.6.The reaction came to completion within 6 minutes after injection and no trace of any other product or dialkylated species. The desk top synthesis observed after further stirring for six hours also show the formation of no other product. The reaction of$BrCH_2(C_6H_4)B(OH)_2$, with($\{[Pt_2(\mu\text{-}S)_2(PPh_3)_4] + H\}^+$)within same time interval yielded three monocationic species that were detected by ESI-MS and assignable to the three alkylated products: $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2C_6H_5)(PPh_3)_4]^+$, *m/z* 1593.4 from the loss of $B(OH)_2$ moiety; a hemiketal-like species $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2(C_6H_4)B(OH)(OCH_3)\}(PPh_3)_4]^+$, *m/z* 1651.5 and $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2(C_6H_4)OH\}(PPh_3)_4]^+$, *m/z* 1609.5. The laboratory scale synthesis indicated the same products.The masses were identified by comparing the experimental isotope patterns with calculated ones. No peak was observed in the mass spectrum that was attributable to the formation of the expected product $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2(C_6H_4)B(OH)_2\}(PPh_3)_4]^+$. The structural determination by X-ray diffraction showed that the compound formed was a zwitter ion (neutral complex) $[Pt_2(\mu\text{-}S)\{\mu\text{-}S^+CH_2(C_6H_4)B(OH)(O^-)\}(PPh_3)_4]$. $[Pt_2(\mu\text{-}S)\{\mu\text{-}S^+CH_2(C_6H_4)B(OH)(O^-)\}(PPh_3)_4]$ is a neutral species and not detectable in ESI-MS. ^1H NMR spectra showed a complicated set of resonances in the aromatic region due to the terminal triphenylphosphine ligands and were broadly assigned as such. However, SCH_2 hydrogen atoms were easily identified as broad peaks at ŭ 3.59 ppm and 3.60 ppm for $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2(C_6H_4)B\{OC(CH_3)_2\}_2\}(PPh_3)_4]^+PF_6$ and $[Pt_2(\mu\text{-}S)\{\mu\text{-}S^+CH_2(C_6H_4)B(OH)(O^-)\}(PPh_3)_4]$, respectively. The monoalkylated products shows IR and $^{31}P\{^1H\}$ NMR spectra expected of the complexes. The OH vibration (3336 cm^{-1}) in **2.1** shifted to 3435 cm^{-1} in **2.1a.** The absorption bands of the B-O bond in **2.2** (1355 cm^{-1}) and **2.1** (1350 cm^{-1}) shifted to 1360 cm^{-1} and 1367 cm^{-1} in **2.2a·(PF_6)** and **2.1a** respectively. The $^{31}P\{^1H\}$ NMR spectra showed nearly superimposed central resonances and clearly separated satellite peaks due to ^{195}Pt coupling. The $^1J(PtP)$ coupling constants showed the differences due to the *trans* influences of the substituted and the unsubstituted sulfide centers. The *trans* influence of the unsubstituted sulfide is greater than the thiolate (substituted) species demonstrated by the coupling constants at (2628 and 3291 Hz) for **2.2a·(PF_6)** and (2632 and 3272 Hz) **2.1a**,respectively.

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CHAPTER ONE

1.0 Introduction

1.1 Background of Study

The diverse study on platinum and sulfur element has been possible due to their rich individual chemistries.Their compounds have been extensively studied due to their wide range of applications in both biology and industry[1]. Platinum was first discovered in 1735 by Don Antonio de Ulloa. It has high melting point and good resistance to corrosion and chemical attack[2]. Consequence to its resistance to wear and tarnish and its beautiful looks, it is employed in jewellery production[3,4]. It is also used in laboratory equipment, electrical contacts, catalytic converters, dentistry equipment, electrodes, antioxidation processes, catalysis, biomedical applications and hard disk[4,5,6,7, 8-11]. Platinum compounds like cisplatin, carboplatin and oxaliplatin are used in cancer treatments[12,13,14]. The use of cisplatin in cancer chemotherapy is limited by ototoxicity, emetogenesis effect, neurotoxicity, and nephrotoxicity of the drug[15-18]. It has been suggested that the toxicity of the drug is as a result of bonding between platinum and protein sulfur atoms[19].

Platinum exists in different oxidation states, 0 to +6, due to its vacant *d orbitals*. The most common oxidation state is +2 including non-even[20] with +1 and +3 found in dinuclear Pt-Pt bonded complexes. These properties make platinum form coordination compounds easily.

Sulfur is commonly used in the manufacturing of important chemical like sulfuric acid. It is also used to refine oil and in processing ores[11]. It is an essential element in most biochemical processes. Sulfur compounds serve as substrates in biochemical process (serving as an electron acceptor in anaerobic respiration of

sulfate-sulfur eubacteria), fuels (electron donors) and respiratory (oxygen alternative) in metabolism[22]. Vitamins such as thiamine and biotin, antioxidants like thioredoxin and glutathiones, and myriads of enzymes contain organic sulfur[23]. Organic sulfur has an anti-neoplastic effect and used in oral and other cancers treatment[24].

Sulfur ligands coordinate with most transition metals in different oxidation states[25]. The chemical properties of sulfur as a versatile coordination ligand is illustrated by its tendency to extend its coordination from terminal groups example ($[Mo_2S_{10}]^{2-}$)[26] to ε-sulfido group e.g. $[Pt_2(\mu\text{-}S)_2(PPh_2Py)_4]$[27] 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 cluster[28]. It has the propensity to catenate and give rise to polysulfide ligands (S_n^{2-}) with n ranging from 1 to 8. Sulfur ligands coordination chemistry is widely manifested in the variety of structures it forms with most of the transition metals[25]. The important roles of metal sulfide compounds are seen in catalysis[29], bioinorganic and rich solid-state chemistry [30]. The metal-sulfur bonding serves as key part of the active site component in reactivity of the biological macromolecule[31-35].

$\{Pt_2S_2\}$ chemistry is dated back to 1903 when Hofmann and Hochlen reported a work on isolation of the first platinum-sulfur complex $[(NH_4)_2[Pt(\eta^2\text{-}S_5)_3]$[36]. Platinum sulfido complexes are classified as homometallic sulfido complexes and heterometallic sulfido complexes. The homometallic sulfido complex of platinum was further classified into groups consisting of the platinum atom metal-metal bond bridged by single sulfur, and that in which the two non-bonded platinum atoms are held together by two sulfur ligands. The sulfur atoms, in both complexes have the capability of bonding further to other metals or ligands. Following the development reported by Hofmann and Hochlen in 1903, a metal-metal bond bridged by single

sulfur complex $[Pt_2(\mu\text{-}S)(CO)_2(PPh_3)_3]$ was reported by Baird and Wilkinson as a product of the reaction of $[Pt(PPh_3)_3]$ with COS[37]. On heating in chloroform, the intermediate $[Pt(PPh_3)_2(COS)]$ gave an orange air-stable compound which was identified using infra-red spectroscopy and elemental analysis technique[38]. X-ray crystallography showed that the compound had only one CO ligand and the structure was reported by Skapski and Troughton[39].

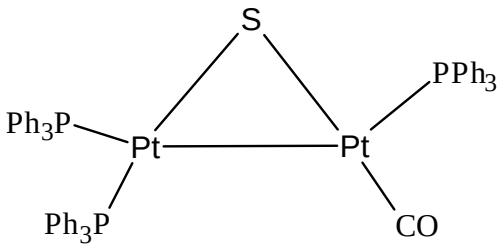


Figure 1.1: Structure of$[Pt(PPh_3)_2(COS)]$ formed by the reaction of $[Pt(PPh_3)_3]$ with COS.

A related synthesis which uses CS_2 instead of COS was also reported[40]. The reaction of $[Pt(dppe)(CS_2)]$ with $[Pt(PPh_3)_2(C_2H_4)]$ is a typical example of the synthetic reaction and gives the complex in Figure 1.2.

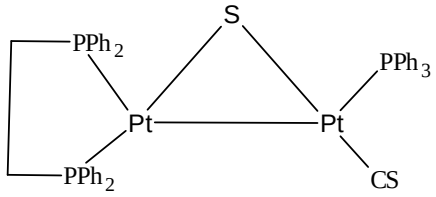


Figure 1.2: Product for the reaction of $[Pt(dppe)(CS_2)]$ with $[Pt(PPh_3)_2(C_2H_4)]$

Chatt and Mingos[41] in 1970 reported a related complex $[Pt_2(PMe_2Ph)(\varepsilon\text{-}S)_2]_4^-$ having two non-bonded platinum atoms held together by two sulfur ligands so-called $\{Pt_2(\varepsilon\text{-}S)_2\}$. Ugo *et al*[26] followed almost immediately in a study of the reaction of zerovalent platinum phosphine complexes with H_2S and or elemental sulfur to give di-ε-

sulfidotetrakis-(triphenylphosphine) diplatinum(II) $[Pt_2(\varepsilon\text{-}S)_2(PPh_3)_4]$ **1.0**. Similar complexes having different terminal ligands that have been reported also include: 2-(diphenylphosphino)pyridine $[Pt_2(\varepsilon\text{-}S)_2(PPh_2Py)_4]$[27] **1.2**, Redox active 1,1ô-bis(diphenyiphosphino) ferrocene $[Pt_2(\varepsilon\text{-}S)_2(dppf)_2]$[36] **1.3**, 1,2-bis (diphenylphosphino)$[Pt_2(\varepsilon\text{-}S)_2(dppe)_2]$[42] **1.4**, dimethylphenylphosphane $[Pt_2(PMe_2Ph)_4(\varepsilon\text{-}S)_2]$[43] **1.5** , 1,3-bis(diphenylphosphino) propane $[Pt_2(\varepsilon\text{-}S)_2(dppp)_2]$ **1.6**[44], $[Pt_2(\varepsilon\text{-}S)_2(Ptolyl_3)_2]$[45] **1.7**, diphosphines such as $(Ph_2P(CH_{2S})_nPPh_2)_2$[46] (n = 2,3). Chiral phosphine such as *O*-Isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane (DIOP)[47] have also been studied but to a lesser extent. $[Pt_2(\varepsilon\text{-}S)_2(PPh_3)_4]$ is the most widely studied of the complexes due to its ease of preparation, from air-stable starting materials, and its tendency to produce crystalline derivatives which was highlighted in an excellent review by Fong and Hor[48]. González-Duarte[46] and co-workers also worked on the development of other sulfide-bridged complexes with the $\{Pt_2(\varepsilon\text{-}S)_2\}$ core, as well as the synthesis of its derivatives, structure, and reactivities**.** They also synthesized series of di-ε-thiolate complexes with the $\{M_2(\varepsilon\text{-}S)_2\}$ core (where M = Ni, Pd or Pt),[49,50,51] provided the molecular orbital study of the hinge distortion of the $\{Pt_2(\varepsilon\text{-}S)_2\}$ ring[52] and used chelating diphosphines as terminal ligands[53].

1.2 Statement of Problem

Sulfide alkylation chemistry of di-ε-sulfidotetrakis-(triphenylphosphine) diplatinum(II) $[Pt_2(\varepsilon\text{-}S)_2(PPh_3)_4]$ **(1.0)** using alkyl, aryl, and functionalised organic electrophiles[46,54] to form thiolate[55] ligands has been a subject of researchers interest. However, no derivatives of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ containing boronic acid electrophiles, 4-bromomethyl phenyl boronic acid pinacolester, $BrCH_2(C_6H_4)B\{OC(CH_3)_2\}_2$ and 4-bromomethylphenylboronic acid, $BrCH_2(C_6H_4)B(OH)_2$ or any metalloid

functionalized thiolate ligands has been synthesised using sulfide alkylation. Kinetic analysis has not been previously applied in the investigation of the synthetic complexities surrounding the alkylation of $\{Pt_2S_2\}$. Boronic acid derivatives have been used in the synthesis of bi- and polyaryl compounds via the Suzukiï Miyaura coupling reactions[56-60]. To date, no derivatives of **1.0** containing boron or any metalloid functionalized thiolate ligands have been synthesized using sulfide alkylation. We present in this report the first experimental kinetic analysis of alkylation of **1.0**, and the first synthesis and characterization of boronic acid derivatives of **1.0**. The isolation and crystallographic identification of the dinuclear structures incorporating boron thiolate substituents suggests that useful synthetic precursor groups can be incorporated into **1.0**, and in particular open up avenues for preparing larger multinuclear assemblies on the nanometer scale. Therefore there is a need to further develop the alkylation chemistry of this system by investigation the reactivity of other potentially synthetic precursor groups. Detailed investigation of the reaction kinetics by careful monitoring of the reaction in real time using Pressurized Sample Infusion Electrospray Ionization Mass Spectrometry (PSI-ESI-MS) has never been reported.

1.3 Justification of Study

Despite the fact that much work has been reported on **1.0** complex, no derivatives of **1.0** containing boron has been used to generate coordinated functionalized thiolate ligands (-SR) on **1.0**. In view of this, this research work will investigate the incorporation of new functionalized organic electrophiles of boronic acid derivatives and monitor the reaction kinetics with the aid of Pressurized Sample Infusion Electrospray Ionization Mass Spectrometry (PSI-ESI-MS). This work will present the first study on the monoalkylation chemistry of **1.0** towards organic electrophiles

$BrCH_2(C_6H_4)B\{OC(CH_3)_2\}_2$ and $BrCH_2(C_6H_4)B(OH)_2$.The chemistry of this system is of great interest due to the reactivity of **1.0** with different electrophiles as observed in the ESI-MS, NMR and IR spectroscopic result.

1.4 Aims and Objectives of the Study

The objectives of this study are:

1. To design, synthesize and characterise functionalized monoalkylated derivatives of **1.0**; acquire and analyze the kinetic data of the monoalkylation reaction between boronic acid derivatives $BrCH_2(C_6H_4)B\{OC(CH_3)_2\}_2$ and $BrCH_2(C_6H_4)B(OH)_2$.
2. Use the data obtained from (1) to incorporate the boronic acid derivatives in the desktop/laboratory scale synthesis.
3. Characterize the isolated products using conventional spectroscopic technique: NMR, IR, and X-ray crystallography.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Brief Summary of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$.

The binuclear platinum chalcogenide complexes $[Pt_2(\varepsilon\text{-}S)_2(PPh_3)_4]$ **1.0**, was synthesized by Chatt & Mingos in 1970 from the metathesis of *cis*-$[PtCl_2(PPh_3)_2]$ in the presence of excess Na_2S[41]and also by Ugo *et al.* in 1971 from the oxidation of $Pt(PPh_3)_4$ with stoichiometric amount of sulphur or hydrogen sulfide[26]. The method by Chatt & Mingos is the best method for the preparation of **1.0**. Other synthetic routes introduce impurities which are not easily removed.Optimum reaction precautions taken to obtain $[Pt_2(\varepsilon\text{-}S)_2(PPh_3)_4]$ complex from $[PtCl_2(PPh_3)_4]$ and $Na_2S{\cdot}9H_2O$[20] include elimination of chlorinated compounds like CH_2Cl_2 as they lead to the decomposition of the complex[43]. The use of an inert solvent like benzene is important to avoid coordination of the solvent to the high nucleophilic sulfide ligands. Protic acids that may cause protonation and disintegration of the $\{Pt_2(\varepsilon\text{-}S)_2\}$ core in the final product should be avoided[44]. Complex **1.0** is a fine orange powder insoluble in common solvents and water but sparingly soluble in methanol, so it cannot be easily characterized by normal techniques. The sulfide centers in **1.0** can react with a wide range of electrophiles and metal centers. Alkylation reactions of **1.0** were among the earliest notable reactions demonstrated on $Pt_2(\varepsilon\text{-}S)_2$ system. Mild electrophiles such as CH_2Cl_2 and $CHCl_3$ are able to alkylate one of the sulfido ligands[61], converting it to coordinated thiolate (SR) ligands. The nucleophilicity of the sulfide centers towards metal centers was first discovered by Mingos and co-workers in 1983 by reacting **1.0** with Ag^+ ion[62,63]. Since then, reactions of **1.0** towards range of metals

species have been greatly explored and used as a building block for multimetallic (homo-[64], hetero-[65] and intermetallic[66]) sulfido complexes.

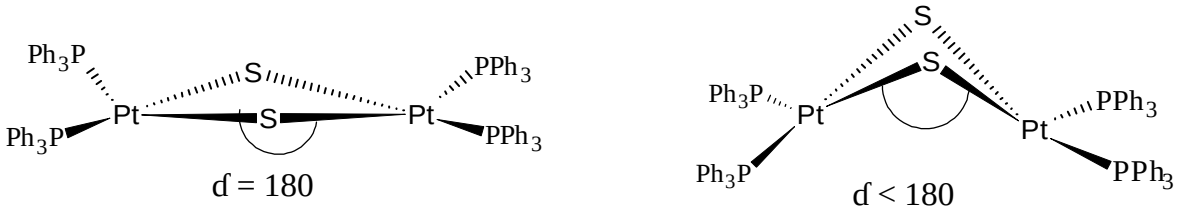
2.2 Electronic and Molecular Features of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$

$[Pt_2(\varepsilon\text{-}S)_2(PPh_3)_4]$ **1.0** is made up of a four-membered $\{Pt_2(\varepsilon\text{-}S)_2\}$ ring core. Its main geometry is characterized by a square planar arrangement of the platinum(II) centers. The flexible hing central core of $\{Pt_2(\varepsilon\text{-}S)_2\}$is measured by the dihedral angle (d) between the two PtS_2 planes, and the variable Pté Pt and Sé S nonbonding distances.

$\{Pt_2(\varepsilon\text{-}S)_2\}$core adopt either of two structural preferences:

(1) Planar geometry when the dihedral angle is 180^o,

(2) Bent geometry when the dihedral angle is less than 180^o.



Scheme 2.2: The two possible geometrical forms adopted by the $\{Pt_2(\varepsilon\text{-}S)_2\}$ ring.

Theoretical and structural studies by Aullón *et al* [67] and Capdevila *et al* [53]on S^{2-} and SR^- bridging ligands of complexes $[M_2(\varepsilon\text{-}Z)_2(L)_4]$ and $[M_2(\varepsilon\text{-}ZR)_2(L)_4]$ complex (where Z representS, Se, Te; óMô a metal; óLô a terminal ligand) showed that there are factors that account for the degree of ring bending or hinging of the complex. The bending is as a result of attractive metal...metal interactions between an occupied dz^2 orbital and an empty pz orbital of the two metal atoms. Degree of bending is controlled by the nature of the metal atom, the terminal ligand and the

bridging atom. In most cases, the degree of bending of the bridging atoms decreases down the chalcogen group (S, Se and Te). Therefore, bending is more favourable in complexes with bridged S^{2-} atom compared to heavier elements of the group such as Se^{2-} and Te^{2-} due to their larger atomic size[46].

Bending is more propitious in heavier metal (that is, down the group in the other: Pt > Pd > Ni), and in complexes with terminal ligands having favourable ů donor ability (like CO, PR_3) as well as PPh_3 and PPh_2Py provided that no important steric hindrance occurs. When the bridging atoms are less electronegative, bent geometry is likely to occur except in the case of the bulkiest bridging atom. This is because bulky terminal ligands and bulkiest bridging atom disfavours bending.

Analogues complex of **1.0** with related chemistry but different terminal ligands include: $[Pt_2(\varepsilon\text{-}S)_2(PPh_2Py)_4]$[27]**1.2**, $[Pt_2(\varepsilon\text{-}S)_2(dppf)_2]$[36] **1.3**, $[Pt_2(\varepsilon\text{-}S)_2(dppe)_2]$[33] **1.4**, $[Pt_2(\varepsilon\text{-}S)_2(PMe_2Ph)_4]$[43] **1.5**, $[Pt_2(\varepsilon\text{-}S)_2(dppp)_2]$[44] **1.6,** $[Pt_2(\varepsilon\text{-}Se)_2(PPh_3)_4]$[68]**1.1** and $[Pt_2(\varepsilon\text{-}Te)_2(PPh_3)_4]$[69]**1.8**. Table 2.1 outlines the effect on the main geometrical parameters of $[Pt_2(\varepsilon\text{-}Z)_2(L)_4]$ due to different terminal phosphine ligands and bridging (ε-Z) atom.

Table **2.1**: Main Geometrical Parameters of $[Pt_2(\varepsilon\text{-}X)_2]$ Complexes[46] (Z = S, Se and Te).

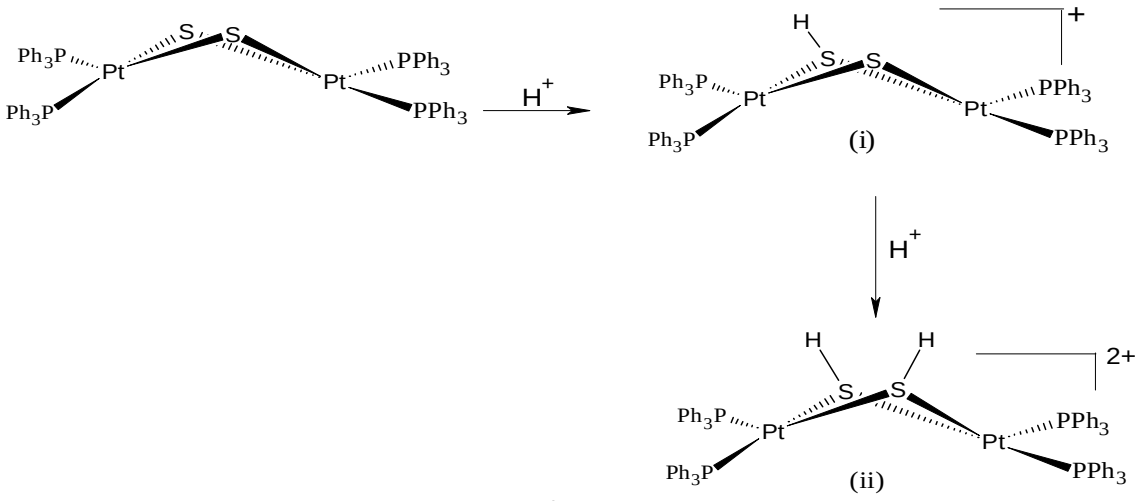
Ref	Complexes	d(º)	Pt---Pt (Å)	Z---Z (Å)	Pt-Z-Pt(º)
25	$[Pt_2(\varepsilon\text{-}S)_2(PPh_3)_4]$	168	3.17	2.89	99.0
36	$[Pt_2(\varepsilon\text{-}S)_2(PPh_2Py)_4]$	180	3.55	3.01	99.6
37	$[Pt_2(\varepsilon\text{-}S)_2(dppp)_2]$	135	3.23	3.10	87.4
38	$[Pt_2(\varepsilon\text{-}S)_2(PMe_2Ph)_4]$	121	3.17	-	85.5
39	$[Pt_2(\varepsilon\text{-}S)_2(dppe)_2]$	140	3.29	3.13	88.9
46	$[Pt_2(\varepsilon\text{-}Se)_2(PPh_3)_4]$	180	3.76	3.13	100.4

70	$[Pt_2(\varepsilon\text{-}Te)_2(PPh_3)_4]$	180	4.10	3.25	102.7

The initial assumed structure of **1.0**[71] was erroneous and was later found to be $[Pt_2(\varepsilon\text{-}OH)_2(PPh_3)_4]^{2+}$ [72]. The real structure of free **1.0** is not known. However, the alcohol solvates of **1.0** through a hydrogen bond with ethanol, n-butanol, methanol and hexafluoropropan-2-ol[73] are known.

2.3 Protonation of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$

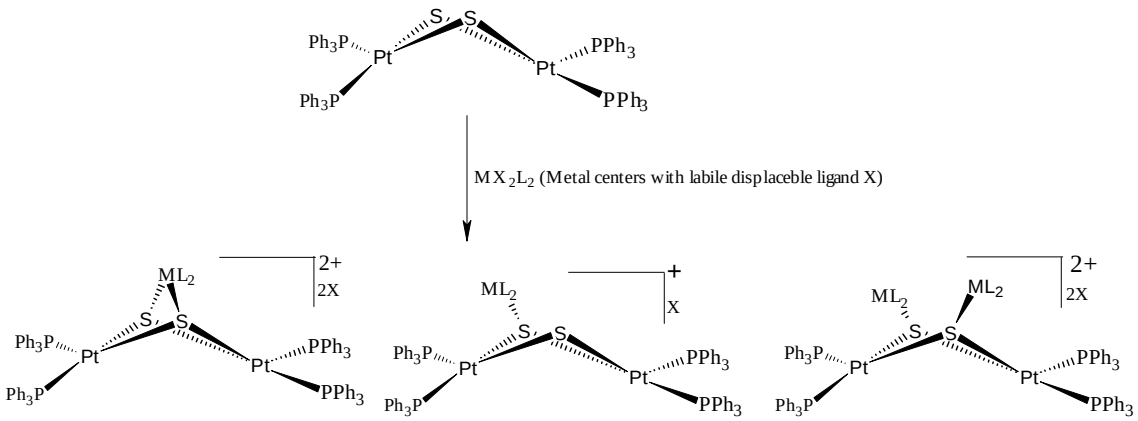
The sulfide centers of **1.0** has extraordinary capability to react with any positive species including proton (H^+)[74]. The reactions of **1.0** with H^+ to form either a monoprotonated or diprotonated species $[Pt_2(\varepsilon\text{-}S)(\varepsilon\text{-}SH)(PPh_3)_4]^+$ and $[Pt_2(\varepsilon\text{-}SH)_2(PPh_3)_4]^{2+}$ (áiô and áiiô respectively as in Scheme 2.3) has been reported and characterised by X-ray crystallography[75]. The diprotonated specie $[Pt_2(\varepsilon\text{-}SH)_2(PPh_3)_4]^{2+}$ has only been detected under Electrospray Ionisation Mass Spectrometry (ESI-MS) conditions but eluded isolation[76].



Scheme 2.3: Single and double protonation of $[Pt_2(\varepsilon\text{-}S)_2(PPh_3)_4]$.

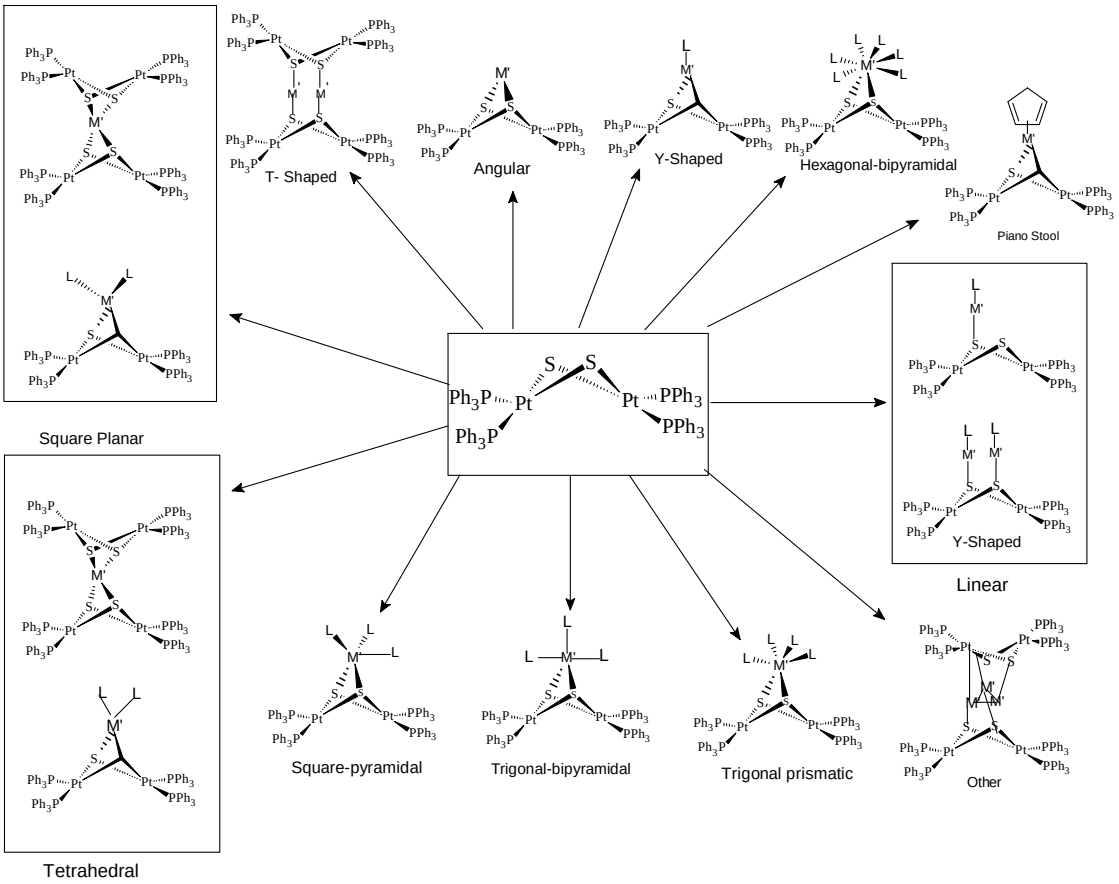
2.4 $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ as a Metalloligand for Metal Centers.

The use of **1.0** as a metalloligand for metal centres could be traced back to early 1980s when first reported in the pioneering work of Mingos[43,62,76-79]. This initiated the emergence of **1.0** as the best building block for polynuclear metallic aggregates. Research into the use of **1.0** and its selenide analogue $[Pt_2(\varepsilon\text{-}Se)_2(PPh_3)_4]$ **1.1** as a metalloligand towards a wide range of transition and main group metal fragments has been extensively reported[48,70,74,80-87]. Any metal compound with Lewis acidic (electrophile) character can be incorporated into **1.0** through the sulfide centres. Scheme **2.4** shows multimetallic aggregates formed by $[Pt_2(\varepsilon\text{-}S)_2(PPh_3)_2]$, with metal fragment bridging the two sulfur atoms or coordinating through one of the sulfur centers of the complex.



Scheme 2.4: Reaction of $[Pt_2(\varepsilon\text{-}S)_2(PPh_3)_4]$ with metal-halide to form multimetallic aggregates.

The reaction **Scheme 2.4** involves the addition of one or two (in rarer case) metal fragment to the $\{Pt_2S_2\}$ core of **1.0**, giving compounds $\{Pt_2S_2M\}$ (homotrimetallic) or $\{Pt_2S_2M_2\}$ (hetrotrimetallic) complexes. Some homotrimetallic complexes of **1.0,** $[Pt_3(PPh_3)_6(\varepsilon_3\text{-}S)_2]^{+}$[64], $[Pt_3Cl_2(PPh_3)_6(\varepsilon_3\text{-}S)_2]$[64] and $[Pt_3(C_6F_5)_2(PPh_3)_4(\varepsilon_3\text{-}S)_2]$[88] formed by the reaction of $[PtCl_2(MeCN)_2]$, $[Pt(MeCN)_2(PPh_3)_2]^{2+}$ and $[Pt(C_6F_6)_2(PhCN)_2]$ with **1.0** are known. The coordinated metal centers are tightly heldby the sulfide ligands[48].They form diverse structural geometries of the derivatives (**Scheme 2.5**): linear[62,89,90], angular[66], Tshaped[62,90], Y-shaped[91], tetrahedral[78,52,92,64], square planar[78,79,82,92], square pyramidal[93], distorted trigonal prismatic[94], trigonal bipyramidal[95], hexagonal bipyramidal,[80] ñpiano stoolò[83] and others[96,97].

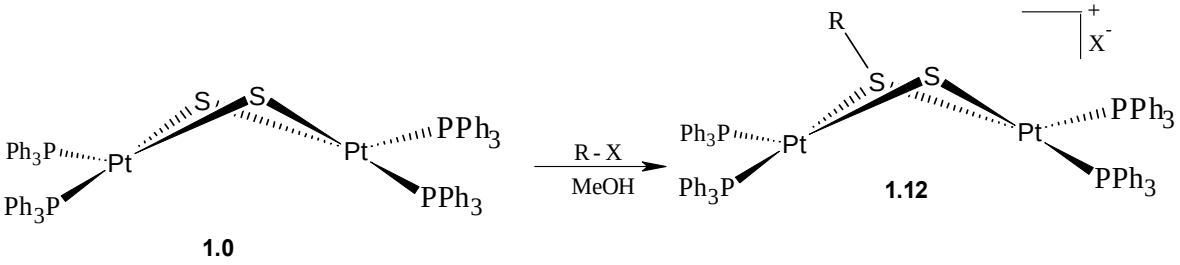


Scheme 2.5: Coordination geometry of the two sulfur centers of $[Pt_2(\varepsilon\text{-}S)_2(PPh_3)_4]$ at metal centers M[46].

2.5 Mono-, Homodi- and Heterodi Alkylation Reactions of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$.

The reactions of $[Pt_2(\varepsilon\text{-}S)_2(PPh_3)_4]$ has been extended to non-metallic centers through alkylation with electrophiles[46, 54,11]. This is due to its potential application for the syntheses of organochalcogen materials[23]. Monoalkylation reaction of **1.0** is usually facile and occurs rapidly to attach functionalized substituent on one of the sulfide centers[98].

Monoalkylated derivative $[Pt_2(\varepsilon\text{-}S)(\varepsilon\text{-}SR)(PPh_3)_4]^+$ can be prepared with any suitable electrophilic[76,99,54]. Many of the alkylation reactions of **1.0** primarily results in the conversion of one of the sulfide ligands to a thiolate ligand[54], as in **Scheme 2.5**.

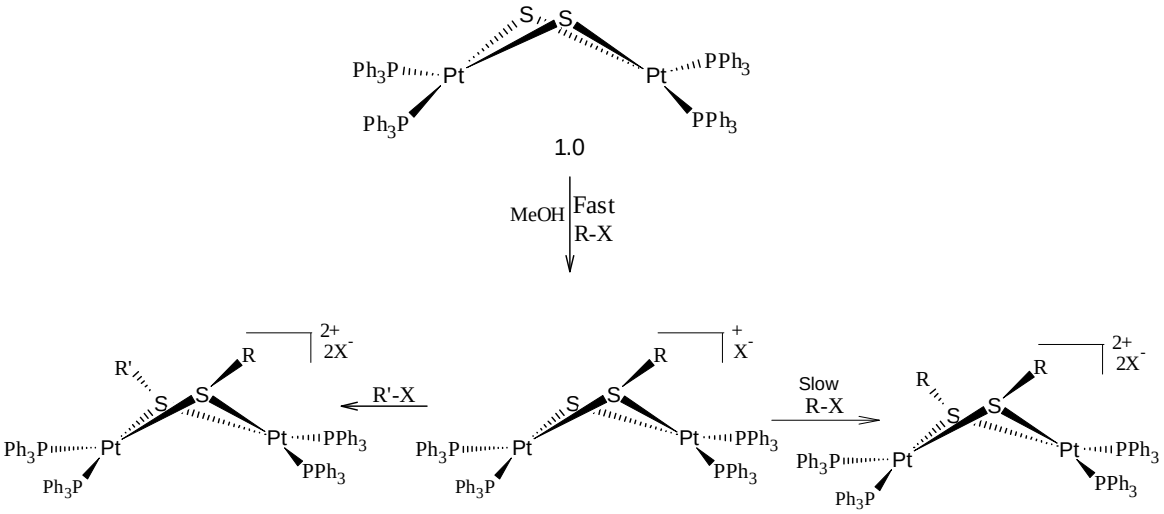


Scheme 2.5 Reaction of **1.0** with mono-halide leads to the formation of a stable mono-alkylated product $[Pt_2(\varepsilon\text{-}S)(\varepsilon\text{-}SR)(PPh_3)_4]^+$.

Dialkylation synthesis of **1.0** is not common and yet to be deeply understood. Homodialkylation of **1.0** is not easily achieved. The methylation product of **1.0** with methyl iodide which gave $[Pt_2(\varepsilon\text{-}S)(\varepsilon\text{-}SCH_3)(PPh_3)_4]I$ was initially thought to be a dialkylated complex $[Pt_2(\varepsilon\text{-}SCH_3)_2(PPh_3)_4]I_2$[26]. Although the sulfur atoms in the $\{Pt_2(\varepsilon\text{-}S)_2\}$ core are highly nucleophilic, incorporation of R on one of the sulfur atom leads to the formation of a positively charged monocation therefore discouraging further alkylation of the unsubstituted sulfur atom. This could be attributed to the exceptionally high stability of the monoalkylated complex formed and successive electronic changes[100]. Reaction with a powerful methylating agent, dimethyl sulfate

(Me_2SO_4), favours a second alkylation and gives $[Pt_2(\varepsilon\text{-}SCH_3)_2(PPh_3)_4]^{2+}$. Furthermore, the free sulfide in a monoalkylated derivative $[Pt_2(\varepsilon\text{-}S)(\varepsilon\text{-}SCH_3)(PPh_3)_4]^{+}$ can further react with Me_2SO_4 to give hetero-dialkylation product $[Pt_2(\varepsilon\text{-}SR)(\varepsilon\text{-}SCH_3)(PPh_3)_4]^{2+}$ **1.9** as in (**Scheme 2.6**).

The use of organo-chloro compounds often result in incomplete dialkylation. Triphenylphosphine displacement has been observed by the use of organo-bromide or iodide alkylating agents. In some of the reactions, using organo-bromo compounds lead to the displacement of the terminal PPh_3 ligands, to give $[Pt_2(\varepsilon\text{-}SR)(\varepsilon\text{-}SCH_3)(PPh_3)_3Br]^{+}$[98].



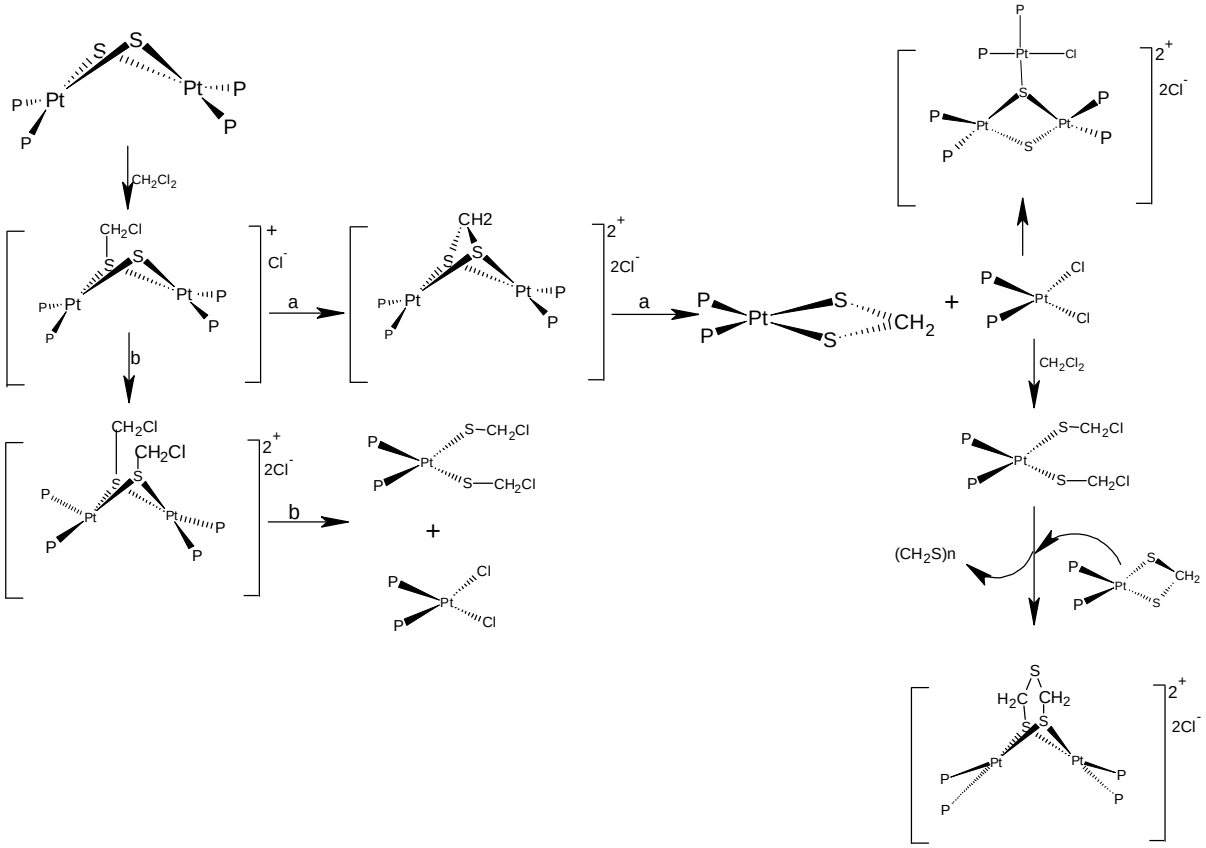
Scheme 2.6 Two stage homo- or heterodialkylation of $[Pt_2(\varepsilon\text{-}S)_2(PPh_3)_4]$ with suitable electrophiles (where X= attached halide group) .

The overall developments of the dialkylation chemistry of 1.0 are yet to be determined. Hence, a detailed study of the reaction conditions that influence the dialkylation of **1.0** and the stability of the resulting alkylated products is important.

Nevertheless, Chong *et al*[101] report suggested that alkylating agents with conjugated aromatic residual encourages homodialkylation. On the other hand, reaction of **1.0** with excess conjugated aromatic electrophiles like $ClCH_2Ph$[54] and $ClCH_2C(O)Ph$[99] form monoalkylated derivatives. This is a strong suggestion that the

conjugated residual part of an electrophile is not the only determining factor to the formation of homo- and hetero-dialkylated derivatives. Therefore, the absence of a detailed study of the factors influencing homo- and hetero-dialkylation has hindered the design and synthesis of the products and the overall development of the dialkylation chemistry of **1.0**.

Dialkylation reaction of **1.0** and other analogous complexes $[Pt_2(\varepsilon\text{-}S)_2(PPh_2Py)_4]$[27] **1.2**, $[Pt_2(\varepsilon\text{-}S)_2(dppf)_2]$[36] **1.3**, $[Pt_2(\varepsilon\text{-}S)_2(dppe)_2]$[42] **1.4**, $[Pt_2(PMe_2Ph)_4(\varepsilon\text{-}S)_2]$[43] **1.5** and $[Pt_2(\varepsilon\text{-}S)_2(dppp)_2]$[44] **1.6** with organic electrophiles in chlorinated solvent (CH_2Cl_2) leads to rapid decomposition of the $\{Pt_2(\varepsilon\text{-}S)_2\}$ core[76]. The reason for the collapse to a mixture of mononuclear complexes (**Scheme 2.7**) is attributed to the powerful nucleophilicity of the $[Pt_2(\varepsilon\text{-}S)_2(PP)_4]$ complex (where PP represent phosphine ligands). The dialkylated intermediates, $[Pt_2(\varepsilon\text{-}S_2CH_2)]^{2+}$ **1.10** and $[Pt_2(\varepsilon\text{-}SCH_2Cl)_2]^{2+}$ **1.11** are highly unstable and eluded isolation and disintegrate but remain the most likely intermediates en route the mononuclear product óaô and óbô (**Scheme 2.7**).



Scheme 2.7: Mechanistic pathway of the evolution of reaction of $[Pt_2(\varepsilon\text{-}S)_2(PPh_3)_2]$ with CH_2Cl_2.

The nature of the terminal ligand has an effect on the extent of reaction development and the nature of the product that will be formed in the reaction of $\{Pt_2(\varepsilon\text{-}S)_2\}$ in CH_2Cl_2. Complex with terminal phosphine ligands (PP) as dppy **1.2**, dppe **1.4** and PMe_2Ph **1.5** terminates after the formation of $[Pt(S_2CH_2)(PP)_2]$ **1.10** and $[PtCl_2(PP)]$ **1.12** (route 'a' in **Scheme 2.7**), but terminal ligand (PPh_3) **1.0** route óa(i)ô and dppp **1.6** route óa(ii)ô reacted further to give $[\{Pt(S_2CH_2)(PPh_3)_2\}Pt(PPh_3)_2Cl]Cl$ **1.13** through condensation of $[Pt(S_2CH_2)(PPh_3)_2]$ **1.10** and $[PtCl_2(PPh_3)_4]$ **1.13** and $[Pt_2\{\varepsilon\text{-}[S_3(CH_2)_2]\}(dppp)_2](Cl)_2$ **1.14** respectively. Complex **1.14** is formed as a result of a greater nucleophilicity of the sulfur atoms in $[Pt(S_2CH_2)(dppp)]$ **1.15** which enable it to pick up another molecule of CH_2Cl_2 to yield $[Pt(SCH_2Cl)_2(dppp)]$ **1.16**; and in doing so, has undergone subsequent C-Cl bond activation by the sulfur atoms in **1.15**.

Reaction of $[Pt_2(\mu\text{-}S)_2(dppf)_2]$ **1.3** with CH_2Cl_2 (route đbô **Scheme 2.7**) results in the isolation of mononuclear complexes, $[Pt(SCH_2Cl)_2(dppf)]$ **1.17** and $[PtCl_2(dppf)]$ **1.18** when the dialkylated intermediate $[Pt_2(\mu\text{-}SCH_2Cl)_2(dppf)_2]^{2+}$ **1.17** disintegrates. The compound $[PtCl_2(PP)_2]$ has wide range of terminal ligands according to literatures and can be recycled by reacting with sodium sulfide to obtain the starting complex. The formation of $\{Pt_2(\mu\text{-}SCH_2Cl)_2\}$ as an intermediate homodialkylated species to mononuclear end products, even though it eluded isolation, is one of the earliest significance that dialkylation of **1.0** may be achieved under appropriate conditions.

The length of the alkylating agent does not appear to affect the rate of alkylation. Halides with long alkyl chain react as quickly as ones with shorter chain length. This was observed by comparing of the reaction between 3-bromopropionitrile and bromoacetonitrile with **1.0**, respectively. The reaction completed within 10 minutes for 3-bromopropionitrile, as well as in the reaction of **1.0** with bromoacetonitrile, which has one carbon chain shorter. Similar observation was made and reported in the comparison of ethyl 3-bromopropionate and ethyl 6-bromohexanoate, where an increase in the alkyl chain length by three carbons in the latter does not slow down the reaction.

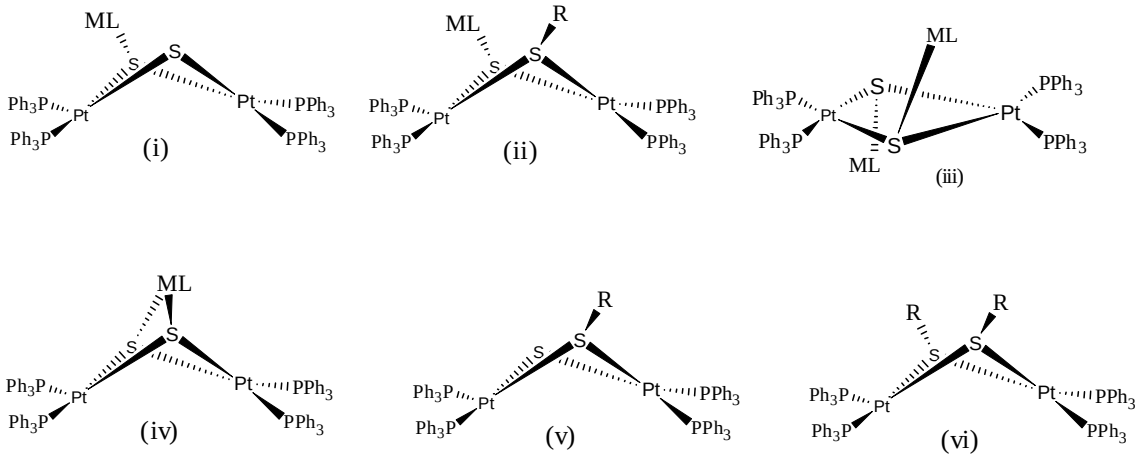
Complex **1.0** reacts with alkyl halides (like CH_3I and $ClCH_2C_6H_4CH_2Cl$) to give a homodialkylated derivative. The reaction might go through a secondary process which leads to the terminal PPh_3 ligands dissociation by the resulting halide (iodide) ion[55,54] to produce asymmetric products $[Pt_2(\mu\text{-}SRS)(PPh_3)_3X]^+$, $[Pt_2(\mu\text{-}SR)_2(PPh_3)_3I]^+$ and $[Pt_2(\mu\text{-}SR)(\mu\text{-}SR)(PPh_3)_3I]^+$. The choice of dihalides affects the product. The propensity of the halide ion from the organohalide electrophile to displace the terminal PPh_3 ligand increases in this following trend $I^- > Br^- > Cl^- > F^-$ within the halogen group. Organo iodides have the highest displacement tendency while organo

fluorides have the least tendency to displace the terminal PPh_3 ligand. On account of higher stability of the alkylated product owing to conjugation, electron resonance and greater steric shielding of the platinum atoms, the displacement of the terminal ligand has not been observed with bulky aromatic conjugated electrophiles[97]. Displacement of the terminal ligand is more likely to attack from the less shielded or unevenly shielded side of the atom. This explains the fact that displacement of the PPh_3 by the halide ion was due to the deshielded or unevenly shielded platinum atoms. This was expounded using the synthesis of $[Pt_2(\varepsilon\text{-}SC_{10}H_{10}N)_2(PPh_3)_4](PF_6)_2$ and $[Pt_2(\varepsilon\text{-}SCH_2C(O)C_6H_4C_6H_5)_2(PPh_3)_4](PF_6)_2$[101] and with the proof that there was no trace of displaced PPh_3.

2.6 Effect of Alkylation/Metellation on $\{Pt_2(\mu\text{-}S)_2\}$ Geometry

Incorporation of groups to $\{Pt_2(\varepsilon\text{-}S)_2\}$ core through metallation or alkylation, affects the $\{Pt_2(\varepsilon\text{-}S)_2\}$ geometry. The $\{Pt_2(\varepsilon\text{-}S)_2\}$ ring in monoalkylated derivatives is affected by the electronic factor[53] but not affected by the nature of the incorporated organic group R attached to the sulfur lone pair. The attaching position and size of the metal fragment or the incorporated thiolate group (SR) determines the conformation of the complex causing it to take either a bent or planer structures (**Scheme 2.8**). The incorporation of an alkylated derivative in one or both of the bridging (ε-S) atoms of complex **1.0** is taken into consideration due to steric repulsion between the bridge substituents and the terminal PPh_3 ligands, as well as repulsion between the bridge substituents[53].The attached groups could be on the opposite side of the $\{Pt_2(\varepsilon\text{-}S)_2\}$ ring adopting an *anti*- conformation [**Scheme 2.8** (**iii**)] or at the (ε-S) bridge pointing away (exo) from the PPh_3 adopting a *syn* conformation (**Scheme 2.8** á, ii, iv-viô) in order to minimise steric repulsion between the incorporated group and the terminal ligands therefore resulting in the hinged geometry and reduced dihedral angle.

Complexes with planer geometry have hinge angle å180º while bent structured complexes have hinge angle <180º. Complexes that have planar geometry when one or both sulfur atoms of the $\{Pt_2(\varepsilon\text{-}S)_2\}$ core are metallated or alkylated include $[Pt(\varepsilon\text{-}SAuCl)_2(PPh_3)_4]$[89] (**1.19**), $[Pt(\varepsilon\text{-}SAgCl)_2(PPh_3)_4]$[102] (**1.20**) and $\{[(dppp)Pt\{\varepsilon\text{-}S(CH_2)_2NHC(=O)NHEt\}]_2\}^{2+}$ [103] (**1.21**). Complexes with planer geometry adopt the anti-conformation as in complexes (**1.19**), (**1.20**), (**1.21**). Complexes with bent structures have their incorporated group attached on the same sides therefore adopting a *syn*- conformation such complexes include $[Pt_2(\varepsilon\text{-}SC_{10}H_{10}N_2)_2(PPh_3)_4]^{2+}$[101] (**1.22**), $[Pt_2(\varepsilon_3\text{-}S)_2(PPh_3)_4HgPPh_3]$ (**1.23**), $[Pt_2(\varepsilon_3\text{-}S)_2(PPh_3)_4]Au(pap\text{-}C^1,N)]$ (**1.24**). Most complexes adopt bent conformation; there are predominantly more reported examples of complexes with bent conformations among the metallated and alkylated $\{Pt_2(\varepsilon\text{-}S)_2\}$ complexes (**Scheme 2.8**) than the planar complexes.



Scheme 2.8: Conformational preference of the metallated and alkylated $[\{Pt_2(\varepsilon\text{-}S)_2(PPh_3)_4\}M]^{n+}$ complexes.

Geometrical isomerism arises from the arrangement of the terminal ligands in cis[43, 104,105] and trans[106-108] positions, giving rise to molecular structures (**Scheme 2.8**) for the alkylated diplatinum complexes containing the molecular cores $\{Pt_2(\varepsilon\text{-}S)(\varepsilon\text{-}SR)\}$

and $\{Pt_2(\varepsilon\text{-}SR)_2\}$. Bidentate ligands like 1,2-diaminoethane[51] and 1,2-bis(diphenylphosphino)ethane[50] result in series of doubly substituted $(\varepsilon\text{-}S)_2$ complexes containing a planar central $\{Pt_2(\varepsilon\text{-}X)_2\}$ ring when used in place of unidentate phosphines.

In conjunction with the variation in dihedral angle in bent complexes, the Pté Pt and Sé S non-bonding distances change as the molecular structure deviates

from planar to bent geometry. Pté Pt bond distance shortens with Sé S axis folds. Some examples of complexes and the effect of bent geometry on their Pté Pt bonding distance include: the bent cis-$[Pt_2(\varepsilon\text{-}SMe)_2(NO_2)_2(PPh_3)_2]$[43](**1.25**) with Pté Pt bonding distance of 3.342 A, and the planar complex trans-$[Pt_2(\varepsilon\text{-}S(CH_2)_2CMe{=}CH_2)_2(I)_2(PPh_3)_2]$[107] (**1.29**) with Pté Pt bonding distance of 3.539 A. The Sé S distance is shorter in bent structures compared to its planer geometry. For example, $[Pt_2(\varepsilon\text{-}SC_5H_9NMe)_2(dppe)_2]$[50] has an Sé S (3.040 A) in the bent (**1.25**) [43], compared to that in the planar (3.210 A) (1.47). Pt-S-Pt angles ɗ reduce from 95^o in planar structures to approximately 90^o in bent structures (hinge distortion).

2.7 Effect of Leaving Group (Halogens) in Alkylation Reactions

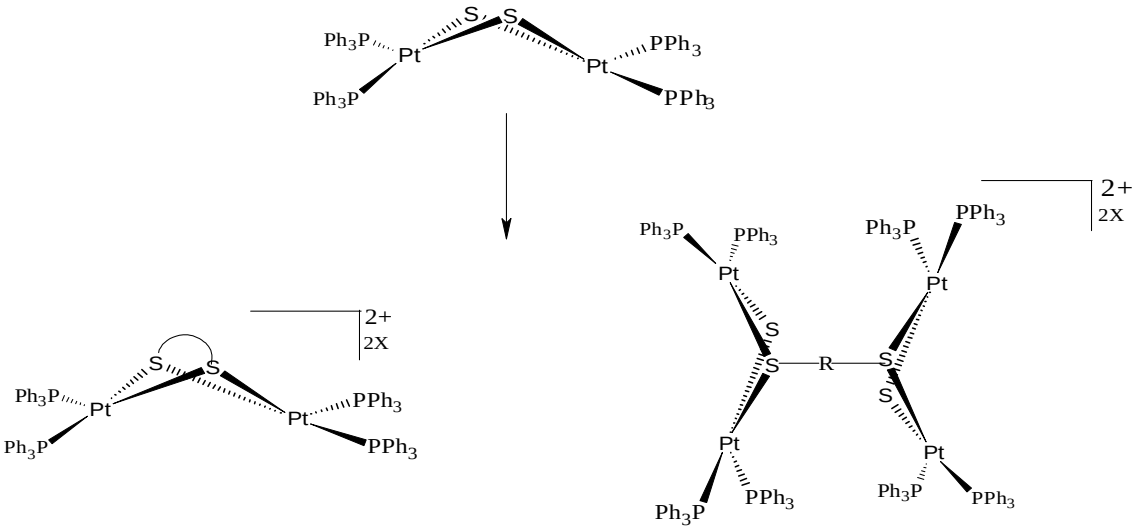
The use of organohalide electrophiles in alkylation reactions of **1.0** involves incorporation of the alkyl group electrophile into the $\{Pt_2(\varepsilon\text{-}S)_2\}$ core of the complex and the labile halide ions (X = F^-, Cl^-, Br^- and I^-) departs with a pair of the electron from the reacting carbon halogen covalent bond[109]. The rate at which the halogen leaves in the alkylation reaction depends on the C-X bond strength and have been reported to follow the electronegativity trend in the order of increasing lability of the leaving group F > Cl > Br > I. In nucleophilic substitution process, the energy barrier that is essential for carbon-halogen bond activation also follows the same trend[110]. Hence, less electronegative halogen forms weak carbon-halogen covalent bond and it

will require less energy for the electrophile to leave and vice versa. Therefore, organo-flouride electrophiles have the least tendency to alkylate **1.0** than other halogens while organo-iodo has the highest alkylating power. However, low nucleophilicity of Cl^- and F^- will minimise side reactions involving loss of coordinated phosphine ligands that may occur with iodide and bromide ion leading to the formation of a secondary product as observed in the ESI-MS survey of the alkylation chemistry of **1.0**[111,100]. $[Pt_2(\varepsilon\text{-}SR)_2(PPh_3)_3I]^+$and $[Pt_2(\varepsilon\text{-}SR)(\varepsilon\text{-}SR')(PPh_3)_3I]^{2+}$ are the secondary products formed by displacement of the terminal PPh_3 by iodide ion in the reaction of **1.0** with alkyl iodide. This secondary reaction is mostly observed in reactions where the platinum atom in the dialkylated product is sterically susceptible to the leaving halide ions. The reaction is much more likely to occur with dialkylated dication than with a monoalkylated monocation while organo-flouride and organo-chloride halide have lesser tendency to effect dialkylation. The reason for the dication formation could be as a result of the generation of dication which is more electrophilic towards anionic iodide ions (I^-). $[Pt_2(\varepsilon\text{-}S)_2(PPh_3)_4]$ has low affinity for halide ions because it is neutrally charged. However, the affinity of halide ions towards Pt(II) is increased by the formation of alkylated cationic derivative of **1.0** and follows the order; $I^- > Br^- > Cl^- > F^-$[112]. I^- ion is therefore a better nucleophile than Br^- and Cl^- ions and more likely to displace PPh_3[100, 112].

2.8 Formation of Inter- and Intramolecular Bridging Di-Alkylated Derivatives of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$.

Reactions of $[Pt_2(\varepsilon\text{-}S)_2(PPh_3)_4]$ with a wide range of Ŭ,ɤ-dialkylating electrophiles result in the formation of two forms of alkylated derivatives: the intra and the intermolecular bridged complex (**Scheme 2.9**). Dialkylation of **1.0** by flexible Ŭ,ɤ-dialkylating electrophiles with the appropriate number of alkyl chain length

atoms (spacer) results in bridging of the two sulfur atoms by the electrophile to give the product $[Pt_2(\varepsilon\text{-S-R-S})(PPh_3)_4]^{2+}$ **1.26**. The product formed is strongly dependent on the length of the alkyl chain and the reaction conditions. The alkyl chain length appears to have a core direction on the nature of the alkylated product formed[54]. Intramolecular bridging of the two sulfur atoms can be achieved by using the appropriate organo dihalides with fewer than six atoms to dialkylate **1.0** while dihalides having more than six alkyl chain length atoms tend to form bridged Pt_4 aggregates with two molecule of **1.0**; with each **1.0** attaching to one end of the dihalide electrophile. The number of spacer atoms restriction could be expected due to steric hindrance as a result of repulsion between the bulky electron rich terminal PPh_3 ligand of the Pt_2S_2 complex. Albeit, this effect is reduced with longer electrophile with more spacer atoms.

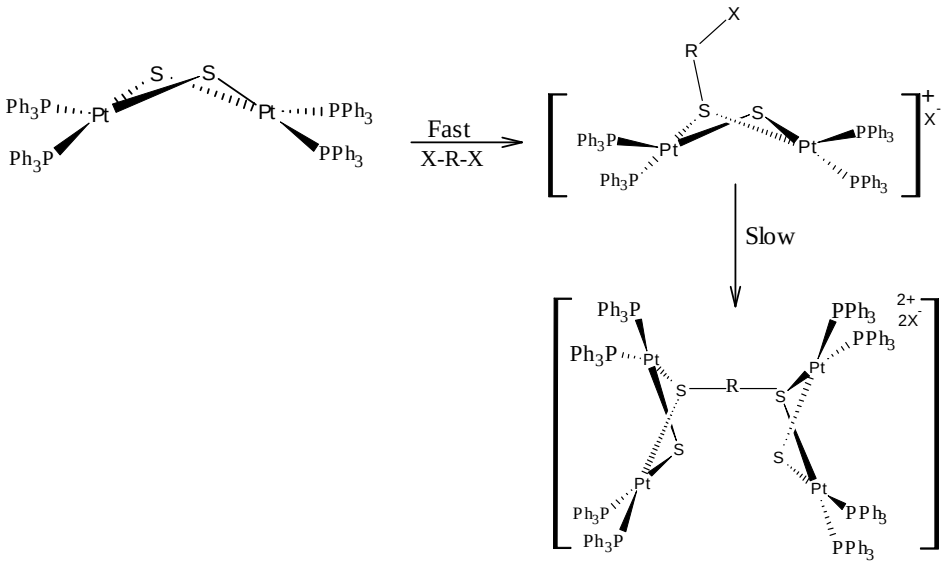


Scheme 2.9: Inter and intramolecular products formed from the alkylation of $[Pt_2(\varepsilon\text{-}S)_2(PPh_3)_4]$ depending on the length of the Ŭ,ɣ -alkylating electrophile and the reaction ratio.

Reaction of $[Pt_2(\varepsilon\text{-}S)_2(PPh_3)_4]$ with monofunctional Ŭ,ɣ -dialkylating agents with general formula XRX (example 1,4-dibromobutane) gives a monoalkylated product $[Pt_2(\varepsilon\text{-}S)\{\varepsilon\text{-}S(CH_2)_4Br\}(PPh_3)_4]^+$ initially, which subsequently converts into

the dithiolate derivative $[Pt_2\{\varepsilon\text{-}S(CH_2)_4S\}(PPh_3)_4]^{2+}$. However, in a reaction of **1.0** with another similar XRX electrophile (i.e 1,5-dibromopentyl), the reaction gives a monoalkylated $[Pt_2(\varepsilon\text{-}S)\{\varepsilon\text{-}S(CH_2)_5Br\}(PPh_3)_4]^{+}$ which seems to be the effective complex of the reaction as the longer alkyl chain length slows down the rate of the second intramolecular alkylation step to form the analogous dication was slow, due to the longer alkyl chain length[113].

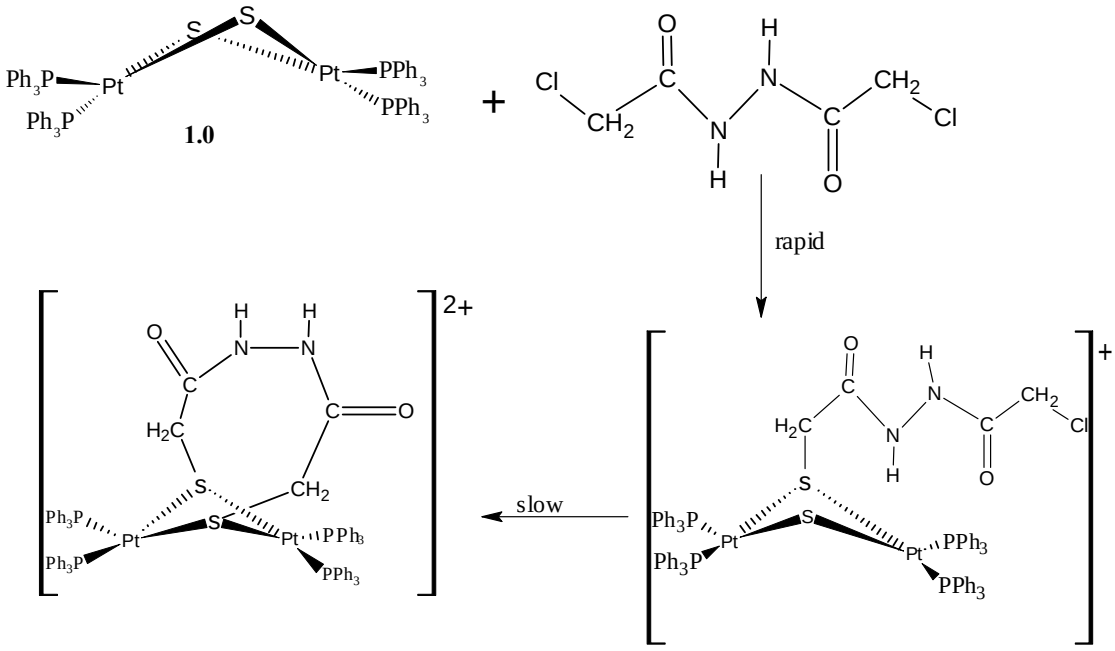
Ŭ,ɣ-Dialkylating agents with strong electrophilic groups (e.g: $ClCH_2C(=NNAr)CH_2Cl$) near the two alkylating carbons give dialkylated complex with **1.0** by bridging the sulfide centres. However, intramolecular rearrangement may occur upon dialkylation depending on the type of alkylating agent. The loss of H^+ from one of the methylene hydrogen atoms ($-CH_2-S-$) bonded to sulfur atoms was ascribed to be the likely cause of the intramolecular rearrangement by the preliminary studies. This lead to opening of the four membered $\{Pt_2(\varepsilon\text{-}S_2\}$ ring into a five membered ring followed by the loss of one PPh_3 ligand[99].



Scheme 2.10: The formation of an intermolecular bridged Pt_4 aggregates from the reaction of $[Pt_2(\varepsilon\text{-}S)_2(PPh_3)_4]$ with dialkylating agent[54].

Interest in the alkylation chemistry of $[Pt_2(\varepsilon\text{-}S)_2(PPh_3)_4]$ and analogous complexes, owing to the high nucleophilicity of the sulfide centers, has led to more studies on their reactivity towards different multifunctional dihalides[115] and organohalides[111, 54]. Through theoretical studies on the reaction mechanism of the complexes with organodihalides[112], it is found that dihalides of the type XRX reactions followed an SN_2 mechanism and the sulfide replaces the halide ion. Studies also show that the presence of excess halides reduces the activation energy barrier for the alkylation reaction. These above explain why excess organo halide helps to achieve alkylation and the bridging sulfide centres in **1.0**. An exception is the formation of bridged alkylated products where stoichiometric control of the reactants is required.

The reaction of $[Pt_2(\varepsilon\text{-}S)_2(PPh_3)_4]$ towards difunctional chloroacetamide alkylating agents and formation of cyclized or bridged products has been reported[100]. In a reported reaction of **1.0** with the hydrazine derived compound (e.g $ClCH_2C(O)NHNHC(O)CH_2Cl$), the formed $[Pt_2\{SCH_2C(O)NHNHC(O)CH_2S\}(PPh_3)_4]^{2+}$ showed two different PPh_3 environments in the NMR spectrum, which was thought to be as a result of non-fluxional behaviour of the dithiolate ligand in solution. Reactions of **1.0** with the ortho and para isomers of the phenylene diamine derived bis(chloroacetamides) such as ($ClCH_2C(O)NHC_6H_4NHC(O)CH_2Cl$), give tetrametallic complexes containing two $\{Pt_2S_2\}$ moieties spanned by the $CH_2C(O)NHC_6H_4NHC(O)CH_2$ group. Crystallographic characterisation of the ortho isomer showed there was an intermolecular C=Oé Hï N and Sé Hï N hydrogen bonding involving the two amide groups (**Scheme 2.12**)[114].



Scheme 2.1: Step wise formation of intramolecular bridged dithiolate derivative $[Pt_2\{\varepsilon\text{-}SCH_2C(O)NHNHC(O)CH_2S\}(PPh_3)_4]^{2+}$ [114].

The long alkyl chain length of $ClCH_2C(O)NHNHC(O)CH_2Cl$ is attributed the cause of its slow conversion to $[Pt_2(\varepsilon\text{-}SCH_2C(O)NHNHC(O)CH_2S)(PPh_3)_4]^{2+}$, which slows down the cyclization reaction due to entropy considerations[100]. Thus, the type of alkyl halide used will determine the product formed upon alkylation of $[Pt_2(\varepsilon\text{-}S)_2(PPh_3)_4]$ for both monoalkylated $[Pt_2(\varepsilon\text{-}S)(\varepsilon\text{-}SR)(PPh_3)_4]^{+}$ and dialkylated $[Pt_2(\varepsilon\text{-}SR)(\varepsilon\text{-}SR)(PPh_3)_4]^{2+}$ products which can be obtained industrially through appropriate choice of alkylating agent[115,36,111].

2.9 Spectroscopic Methods for Structural Characterization

2.9.1 Electrospray Ionisation Mass Spectrometry (ESI-MS)

Electrospray Ionization (ESI) is a technique used in the generation of ions in mass spectrometry by applying high voltage to a liquid and creation of aerosol using an electrospray. It is very useful in ion production from macromolecules because it overcomes the tendency of these molecules to fragment when ionized. Electrospray

process has been known for more than a hundred years ago[116] but its first use with mass spectrometry was reported by Dole M. in the 1960s [117,118] when he was trying to characterize the size and mass distribution of some synthetic polymers.

ESI technique was developed and reported by J. B. Fenn in the year 1984[119]. The technique involves electrospray ionization source coupled to a single quadrupole mass spectrometer. New applications and uses of ESI technique continue to grow at an unprecedented rate after its discovery and the instrument continued to advance as fast as the need. J. B. Fenn was recognized and awarded the 2002 Noble Price in Chemistry for the development of electrospray ionization mass spectrometry in the late 1980s[120].

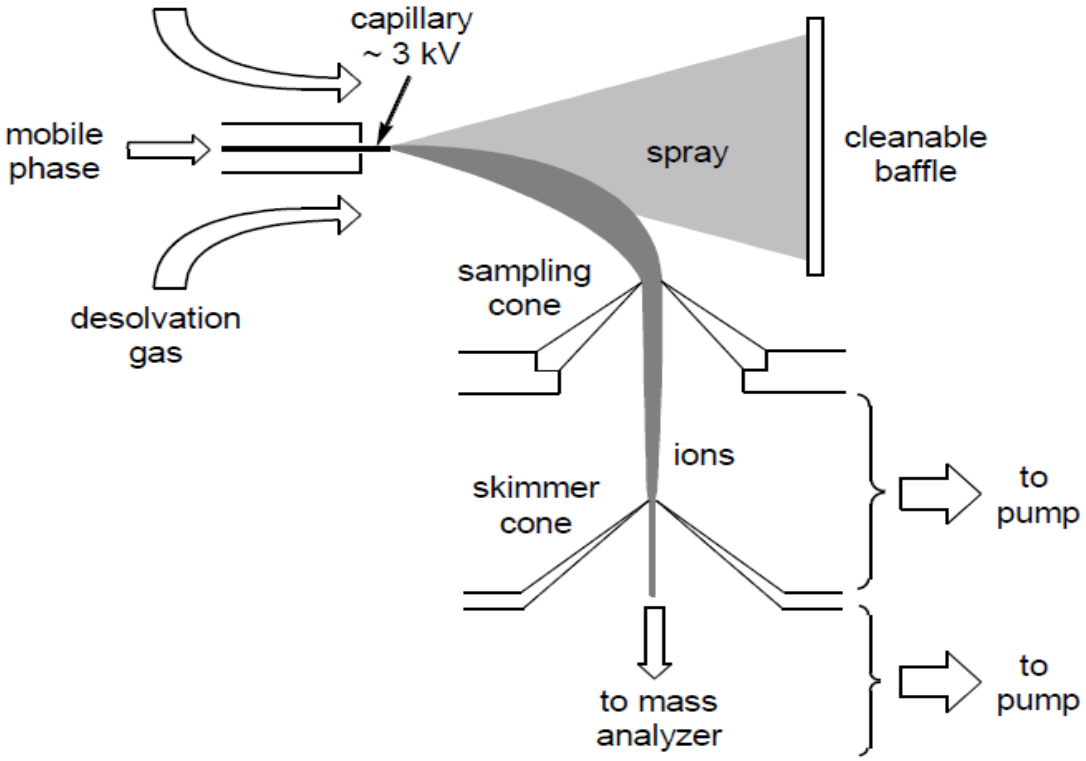


Figure 2.1 A schematic diagram of ESI-MS coupled to a mass analyser. Adopted from Ref[121].

ESI-MS is a highly efficient ionization process and useful in the generation of multiply charged ions. ESI-MS provides a sensitive, robust, and reliable tool for analysing large, polar, non-volatile and thermally labile molecules in solution. The mobile phase is a polar solvent, mainly methanol. ESI makes use of electrical energy in assisting the transfer of ions from solution to the gaseous phase before being subjected to mass spectrometric analysis. ESI-MS analyses ionic species in solution, with increased sensitivity. Neutral compounds can be converted to ionic compounds in solution or gaseous phase by protonation to enable the compound to be studied by ESI-MS. ESI-mass spectrometer compose of three basic components: the ion source, mass analyzer, and the detector.

Water is mixed with volatile organic compounds (like ethanol, chloroform, acetonitrile, methanol, dichloromethane etc) to prepare solvent for electrospray ionization. Compounds that enhance conductivity, like acetic acid, are usually added to the solution to decrease the initial droplet size and to serve as a source of protons that aid in facilitating the ionization process. A mechanical syringe pump is used in introducing the analyte solution at low flow rate (typically 1εL/min to 2εL/min) via a stainless steel capillary (with a bore between ~0.1mm to ~0.2mm in diameter) or a hypodermic needle. High voltage of 2kV to 6kV is then applied across the tip of the stainless steel capillary and the surrounding source-sampling cone or heated capillary (usually positioned at 1cm to 3cm from the spray needle tip). A fine spray of charge droplets dispersion occurs as the analyte solution flows through the tip of the stainless steel capillary under the applied very high voltage and pressure (**Figure 2.2**).This fine spray of highly charged droplets generated has the same polarity as the capillary voltage. A nebulising gas (e.g. nitrogen) is applied to increase sample flow rate as it shears around the eluted sample solution, and also to help direct the charged mist

dispersing from the capillary tip towards the mass spectrometer. The charged droplets generated pass down a potential and a pressure gradients toward the analyser region of the mass spectrometer. With the aid of an elevated ESI-source temperature and/or another stream dry nitrogen gas, the size of the charged droplets is continuously reduced thereby decreasing the charged droplets radii (its Rayleigh limit) and thus increasing the surface charge density of the droplets. At this juncture, the droplet undergoes Coulomb fission in which the electric field strength within the charged droplet (as a result of increased surface charge density and decreased droplet size) reaches a critical point at which it is energetically and kinetically possible for the charged droplets to fragment and ions at its surface to be evaporated into the gaseous phase. A sampling skimmer cone samples the ejected ions which are then accelerated into the mass analyser for measurement of ion intensity and analysis of molecular mass.

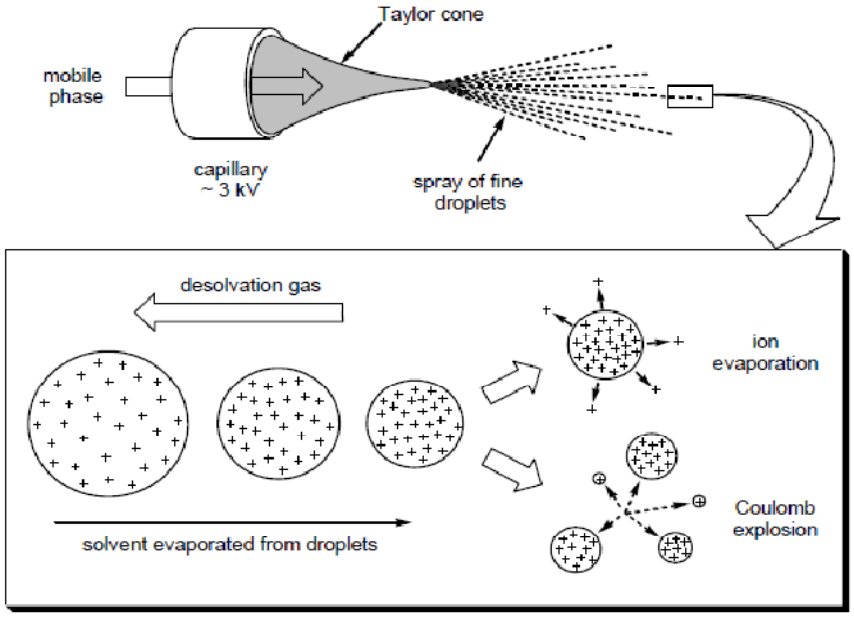


Figure 2.2 A schematic diagram of the mechanism of ion formation in ESI-MS. Adopted from Ref[1121].

2.9.1.1 Application of ESI-MS in Chemical Analysis

Single and multiple charged ions generated by electrospray processare typically identified using ESI-MS if the analyte remains unaltered when suitable instrumental conditions are applied. ESI-MS is suitable for ionization system which generates molecular ions (without altering their structures) in the gas phase from the highly non-volatile synthetic polymers. It is also an appropriate detector system that can probe the appearance of the large molecular ions with high m/z value[122]. ESI is a soft ionization technique extensively used for the generation of gas phase ions of thermally labile large supramolecules with very little or no fragmentation. It is applied in clinical biochemistry to determine the amount of metabolitesin biological specimens[124]. Electrospray ionization was first used in the analysis of biological macromolecules to observe mass spectra of ionizing biopolymers like proteins[100]. ESI-MS helps researchers to identify the molecular species present in a solution during the process of a chemical transformation. ESI-MS is typically useful for investigations of metal catalysis or organic reactions that involve ionic intermediates. Researchers are increasingly using ESI-MS in mechanistic and synthetic studies, and catalyst development. The quantitative and qualitative properties of solution, and the processes occurring in it correlate very well with the established data of gas-phase of their ions obtained by researchers lately through ESI-MS measurements. In this context, counter ion effects, concentration series, and time dependences can serve as criteria that help researchers assess if there are linkages between the gas-phase measurements and the situation in the solution[123]. It is simple, highly sensitive and affords rapid determination of molecular mass accurately; thus large number of samples can be analysed within a short period of time.

2.9.1.2 Electrospray Ionization Mass Spectrometry - An Indispensable Tool for the Preliminary Screening of $[Pt_2(\mu\text{-}S)_2(PPh_3)_2]$ Chemistry.

Electrospray Ionization Mass Spectrometry (ESI-MS) is an effective technique in probing the initial screening of $[Pt_2(\varepsilon\text{-}S)_2(PPh_3)_4]$ reactions[74,126,55,54,125] towards metal halides, organo halides and related compounds. When compounds are mixed in solution, ESI-MS is helpful in observing and identifying the species present in the solution and the promising reactions can be identified for further macroscopic study of potentially stable products[70]. The established studies are supported by the synthesis and characterization of the observed species. This correlation between the synthesis-scale reactions and the mass spectroscopic data, alongside the exceptional capability of $[Pt_2(\varepsilon\text{-}S)_2(PPh_3)_4]$ complexes to act as a powerful nucleophile to almost any metallic and non-metallic electron-acceptor species, lead to the successful isolation of a large number of derivatives based on the $\{Pt_2(\varepsilon\text{-}S)_2\}$ core. Apart from being economical solution based, convenient and rapid, this method is also very soft and causes minimal fragmentation. Therefore, an in debt information about the fundamental reaction steps in the reaction of $[Pt_2(\varepsilon\text{-}S)_2(PPh_3)_4]$ with fully intact coordination spheres of the formed aggregates can readily be ascertained[70,80,82,126].

Neutral molecules are detected by ESI-MS after $[Pt_2(\varepsilon\text{-}S)_2(PPh_3)_4]$ is ionised by protonation in methanol solution to give the ESI-MS the protonated specie $[Pt_2(\varepsilon\text{-}S)_2(PPh_3)_4 + H]^+$ which has a mass/charge (*m/z*) ratio of 1503. On account of its usefulness in higher molecular masses detection, it is therefore suitable for studying complex **1.0**. Metallated and/or alkylated complexes of $[Pt_2(\varepsilon\text{-}S)_2(PPh_3)_4]$ are already charged and makes it very easy for detection in ESI-MS. In the absence of side reactions and decomposition, the alkylation or metallation product is readily detectable. Most recent reports on $[Pt_2(\varepsilon\text{-}S)_2(PPh_3)_4]$ involves the application of this

technique to accurately predict and monitor the outcome of promising reactions of **1.0** with metal centres or electrophiles.

ESI-MS is useful in predicting the reaction mechanisms and structures of the resulting products[74, 54] making it an invaluable technique in cases where there is a side reaction as observed in the displacement of PPh_3 by halogen ion or rearrangement in the product formed[98]. It is useful in detecting decomposition of the products. Ionisation technique in ESI-MS is soft and an adjustment of the cone voltage gives strong parent ions with very little or no fragmentation. ESI-MS detects single and multiply charged ions, thus, one or both sulfur atoms in **1.0** are readily detectable when incorporated with metal and/or organic groups to give a monocationic or dicationic product.

The experimental molecular ion isotope patterns which are comparable with the theoretical computer generated pattern that is used in monitoring the synthesis of chemical products and in correct specie identification are generated with ESI-MS[127]. A classic example was reported by Ujam O. T. where the reaction of $[Pt_2(\varepsilon\text{-}S)_2(PPh_3)_4]$ with $ClCH_2C(O)CH_2Cl$ in MeOH yielded $[Pt_2(\varepsilon\text{-}SCH_2C(O)CHS)(PPh_3)_4]^+$ as the positive ion in ESI-MS (**Figure 2.3)**.

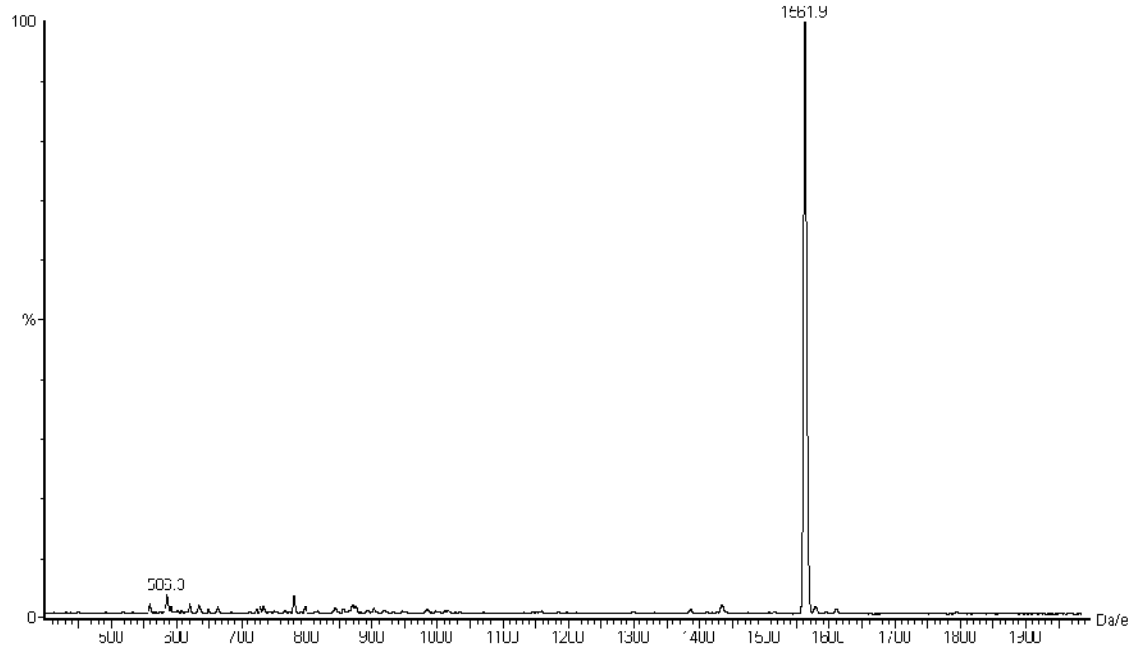


Figure 2.3 ESI-MS of the reaction mixture of $ClCH_2C(O)CH_2Cl$ and **1.0** after the addition of 1 mL 0.1 mol L^{-1} NaOH solution. The inset shows the theoretical isotope patterns of $[Pt_2(\varepsilon\text{-}SCH_2C(O)CHS)(PPh_3)_4]^{+}$ [125].

ESI-MS is efficient in determining the ionizability of different or similar charged molecule in same solution by showing their different peak intensities. The peak intensities in the ionization spectrum correspond to the quantities of molecules in solution. Since monocationic species do not just give indication of the species contained inside but also their relative quantities, ESI-MS spectra is suitable technique for monitoring the possible side reactions in alkylation reactions of **1.0**. It is unknown if it will be quantitatively relevant for mixture of dicationic and monocationic solutions derivatives. ESI-MS peaks intensities will likely depend on the ionisation formation of each species and perhaps represent the actual quantities in solution. Equimolar solution of different monocationic derivatives of **1.1** shows approximately equal peak intensities in ESI-MS spectra (**Figure 2.4**). The spectrum from the reports of ujam *et al*[125] show the spectra of an equimolar solutions of $[Pt_2(\varepsilon\text{-}$

S)(ε-S)(PPh_3)$_4$] and [Pt_2(ε- S)(ε-SCH_2Ph)(PPh_3)$_4$]$^+$.Both dicationic and monocationic derivatives are the two products observed as a result of alkylation reactions of **1.0**[54]. It is not yet known if the number of charges on the species in solution has an effect on the ionisation process.

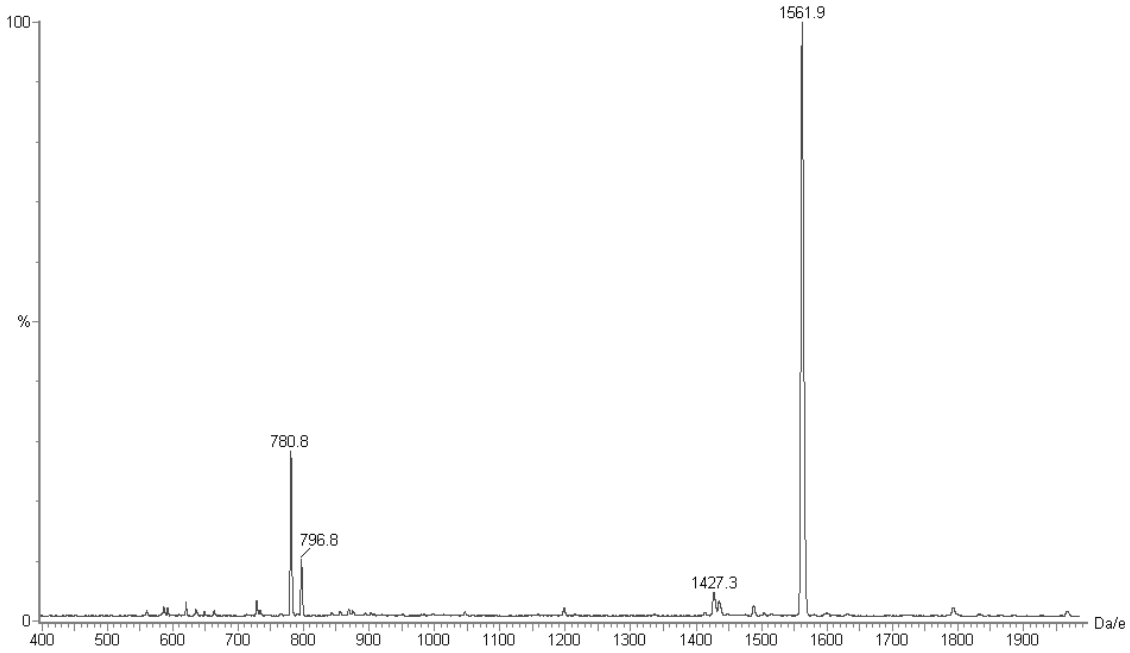


Figure 2.4: ESI-MS peak for equimolar solution [Pt_2(ε-S)(ε-S)(PPh_3)$_4$] and [Pt_2(ε-$SCH_2C(O)CHS$)(PPh_3)$_4$]$^+$ showing similar ionisation efficiencies.

CHAPTER THREE

3.0 Experimental

3.1 General Reagent Information

All reagents used were of analytical standard. The alkylating agents $BrCH_2(C_6H_4)B(OH)_2$ **2.1**, $BrCH_2(C_6H_4)B\{OC(CH_3)_2\}_2$ **2.2** were purchased from Sigma Aldrich chemical Co. Germany in sure-seal bottles and were used without further purification (Sigma-Aldrich; CAUTIONï highly toxic, potent lachrymator and vesicant and should be handled using appropriate safety precautions). $[PtCl_2(PPh_3)_2]$, $Na_2S{\cdot}9H_2O$ and NH_4PF_6 were supplied by Sigma-Aldrich. Reaction solvents: Benzene (Sigma-Aldrich), methanol (Caledon Chemicals), dichloromethane (Sigma-Aldrich) and diethyl ether (EMD Chemicals) were of laboratory reagent grade and used without further purification. The distilled water, methanol and diethyl ether were purchase from Joechem Ventures Co. Nsukka, Enugu state Nigeria and were used as received. $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ **1.0** was synthesized according to reported literature procedure by the metathesis reaction of *cis*-$PtCl_2(PPh_3)_2$ with excess $Na_2S{\cdot}9H_2O$ in benzene[26,73].

3.2 General Analytical Information

Elemental analyses were performed using vacuum dried samples on a Perkin-Elmer 2400 CHN elemental analyzer. NMR spectra were recorded in $CDCl_3$ solution, unless otherwise stated. ^1H and $^{31}P\{^1H\}$ spectra referenced to TMS for ^1H and to 85% phosphoric acid for ^{31}P were recorded on Bruker Avance 300 MHz spectrometer. IR spectra were obtained as KBr disks with a Perkin Elmer Spectrum FTIR Spectrometer, version 10.4.3. Melting points of the compounds were determined with a Gallenkamp melting point apparatus and are uncorrected. ESI-MS of solid products

were obtained by dissolving a small quantity of the material in 1ï 2 drops of dichloromethane, followed by dilution to ca. 2 mL using methanol. ESI-MS kinetic profile of the reactions was analyzed by the Pressurised Sample Infusion (PSI) technique. Mass Spectral data were recorded on a Waters Micromass Q-TOF II Mass Spectrometer in positive ion mode using pneumatically assisted electrospray ionization: capillary voltage, 2900 V; sample cone voltage, 15 V; extraction voltage, 1 V; source temperature, 80 °C; desolvation temperature, 160 °C; cone gas flow, 100 L $h^{\bar{1}1}$; desolvation gas flow, 100 L $h^{\bar{1}1}$; collision voltage, 2 V; MCP voltage, 2400 V. No smoothing of the data was performed and comparison of observed and calculated isotope patterns [128,129] was used in the ion assignment.

3.3 Synthesis of the Alkylated Derivatives of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$

3.3.1 Pre-Synthetic Kinetic Profile of the Reaction of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ With $BrCH_2(C_6H_4)B\{OC(CH_3)_2\}_2$.

Minuscule amounts of the two reactants $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (7 mg, 0.0047mmol) and $BrCH_2(C_6H_4)B\{OC(CH_3)_2\}_2$ **2.2** (1.4 mg, 0.0047mmol, 1.2 mol equiv.) were used for Pressurized Sample Infusion Electrospray Ionization mass Spectrometry (PSI-ESI-MS) investigations. The reaction solvent (methanol) was sparged with nitrogen on the Schlenk line for 2 h to remove oxygen. The $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ **1.0** was added to the Schlenk flask and purged with argon for 30 min. The electrophile, $BrCH_2(C_6H_4)B\{OC(CH_3)_2\}_2$ **2.2** in a sample vial capped with a septum was sparged with nitrogen on the Schlenk line for 30 min. A methanolic solution of **1.0** was initially injected by PSI into ESI-MS. Once the signal for [**1.0** + H]$^+$ at *m/z* 1503 reached a stable intensity, a 1 mL methanol solution of 1.4 mg $BrCH_2(C_6H_4)B\{OC(CH_3)_2\}_2$ **2.2** was added to the reaction mixture by string injection into the reaction flask and reaction data recorded by the mass spectrometer.

3.3.2 Synthesis of $[Pt_2(\mu\text{-}S)\{\mu\text{-}CH_2(C_6H_4)B\{OC(CH_3)_2\}_2\}(PPh_3)_4](PF_6)$, **2.2a·($PF_6$)**

To an orange suspension of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (50 mg, 0.033 mmol) in methanol (25 mL) was added an excess of $BrCH_2(C_6H_4)B\{OC(CH_3)_2\}_2$ (10 mg 0.037 mmol, 1.1 mole equiv.) and the solution stirred for 45 min at room temperature. Complete formation of the monoalkylated product was confirmed by ESI-MS which showed only $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2(C_6H_4)B\ \{OC(CH_3)_2\}_2\}(PPh_3)_4]^+$ at *m/z* 1720.57. The solution was filtered and excess NH_4PF_6 (25 mg, 0.15 mmol) added to the clear filtrate. The resulting yellow precipitate was filtered, washed with water (4 x 10 mL) and diethyl ether (4 x 10 mL) and dried in air, giving **2.2a·(PF_6)** (54 mg, 87%). Crystals suitable for X-ray structure determination were isolated by slow diffusion of diethyl ether into a dichloromethane solution of **2.2a·(PF_6)**.

EA: C, 54.3; H, 4.4. $C_{85}H_{78}BF_6O_2P_5Pt_2S_2$ requires C, 54.6; H, 4.4%.

M.p. : 168ï 170 ºC.

IR: 840, 1096, 1144, 1360, 1436, 1481, 1610, 3054, 3441 cm^{-1}.

$^{31}P\{^1H\}$ NMR ($CDCl_3$): ŭ 23.31 [br, s, $^1J(PtP_B)$, 3291], 22.88 [br, s, $^1J(PtP_A)$, 2628.19].

^1H NMR ($CDCl_3$, 300 MHz): ŭ 7.43ï 6.54 (64H, m, 17Ph), 3.52 (2H, t, SCH_2) 1.26 (12H, s, CH_3)

ESI-MS (*m/z*): ($[M]^+$ 100%). 1720.57

3.3.3 Synthesis of $[Pt_2(\mu\text{-}S)\{\mu\text{-}S^+CH_2(C_6H_4)B(OH)(O^-)\}(PPh_3)_4]$,2.1a

To a suspension of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (50 mg, 0.033 mmol) in methanol (25 mL) was added an excess of $BrCH_2CH_2(C_6H_4)B(OH)_2$ (7.9 mg, 0.037 mmol, 1.1 mole equiv.) and the solution stirred for 30 min at room temperature. Complete formation of the monoalkylated products was confirmed by ESI-MS which showed $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2C_6H_5)(PPh_3)_4]^+$, *m/z* 1593.44, $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2(C_6H_4)OH\}(PPh_3)_4]^+$, *m/z* 1609.45 and $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2(C_6H_4)\ B(OH)(OCH_3)\}(PPh_3)_4]^+$, *m/z* 1651.49. The solution was filtered and NH_4PF_6 (25 mg, 0.15 mmol) added to the clear filtrate. The resulting yellow precipitate was filtered, washed with water (4 x 10 mL) and diethyl ether (4 x 10 mL) and dried in air, giving (52 mg, 87%) of the product. Recrystallisation by vapour diffusion of hexane into a chloroform solution of **2.1a** gave pure crystals of $[Pt_2(\mu\text{-}S)\{\mu\text{-}S^+CH_2(C_6H_4)B(OH)(O^-)\}(PPh_3)_4]$ suitable for X-ray structure determination and spectroscopic characterisations.

EA: C, 58.1; H, 4.5. $C_{76}H_{67}BO_2P_4Pt_2S_2$requires C, 57.8; H, 4.4%.

M.p.: 158ï 160 ºC.

IR: 1096, 1186, 1367, 1435, 1481, 1608, 3052, 3435 cm^{-1}.

$^{31}P\{^1H\}$ NMR ($CDCl_3$): ŭ 23.50 [br, s, $^1J(PtP_B)$ 3272.51], 23.05 [br, s, $^1J(PtP_A)$ 2632.04].

^1H NMR ($CDCl_3$, 300 MHz): ŭ 7.55ï 6.61 (64H, m, 17Ph), 3.60 (2H, t, SCH_2), 1.58 (H, s, OH)

ESI-MS (*m/z*): ($[M]^+$ 100%) 1593.44; ($[M]^+$ 45%) 1609.45; ($[M]^+$ 75%) 1651.49

CHAPTER FOUR

4.0 Results And Discussion

The products, rates of product formation, reaction

completion time, and the rate of consumption of the starting materials was monitored utilizing the Pressurized Sample Infusion Electrospray Ionization Mass Spectrometry (PSI-ESI-MS) technique[130,131]. The reaction mixture is prepared in a Schlenk flask into which a length of PEEK tubing attached to the source of the mass spectrometer is inserted. An overpressure of 2 - 4 psi is applied displacing the reacting solution into the MS. This allows for real-time observation of all charged species and how they behave over the course of the reaction[132-135], and providing a better understanding of mechanism and optimization of synthetic protocols. For this report speciation and dynamic behavior in the reaction of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ **1.0** with 4-(bromomethyl)phenylboronic acid pinacol ester, $BrCH_2(C_6H_4)B\{OC(CH_3)_2\}_2$, **2.2** was monitored.

The alkylation reaction of $BrCH_2(C_6H_4)B\{OC(CH_3)_2\}_2$ **2.2** with **1.0** was determined to be second order (Figure 1), consistent with the expected S_N2 mechanism for an alkylation reaction. **1.0** disappeared rapidly with consequent formation of the monoalkylated cationic product, $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2(C_6H_4)B\{OC(CH_3)_2\}_2\}(PPh_3)_4]^+$, **2.2a**. This was indicated by the immediate appearance of the monoalkylated product peak at *m/z* 1720.6. The reaction was complete 6 minutes after injection. The two species $(\{[Pt_2(\mu\text{-}S)_2(PPh_3)_4] + H\}^+$ and $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2(C_6H_4)B\{OC(CH_3)_2\}_2\}(PPh_3)_4]^+$, **2.2a** have dramatically different ESI-MS responses due to the difference in their electrospray ionization efficiencies. $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ produces weak $[\mathbf{1} + H]^+$ ions in methanol, but is immediately outcompeted by the appearance of the inherently charged alkylated product, which

provides a much stronger ESI-MS response in addition to consuming $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ **1.0**.

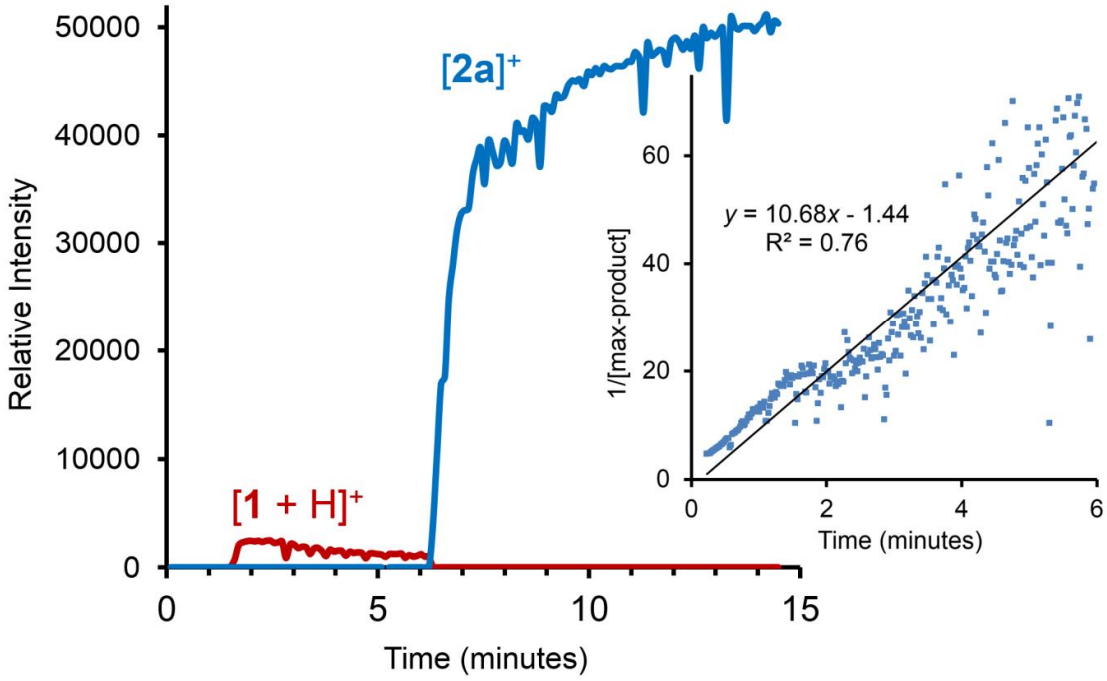


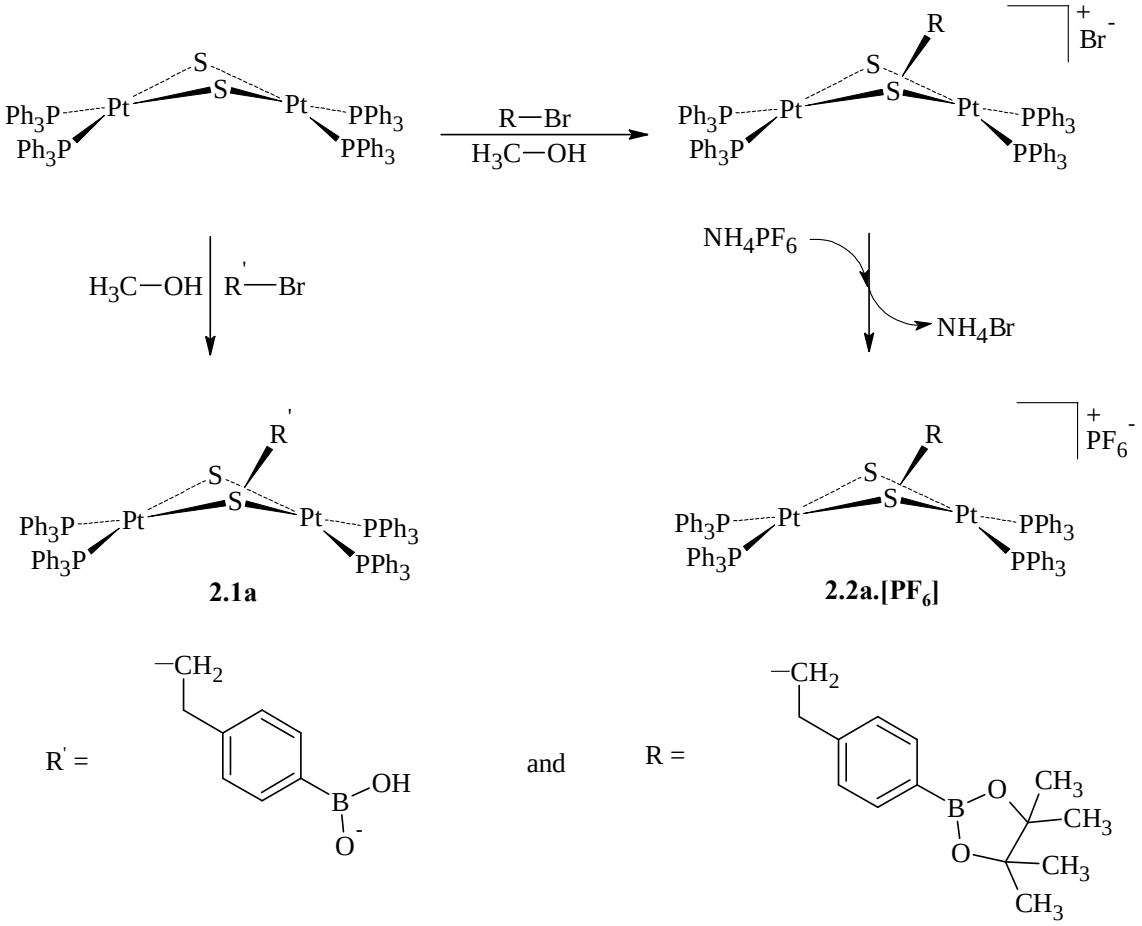
Figure 4.1. Intensities versus time for reaction of **1** and $BrCH_2(C_6H_4)B\{OC(CH_3)_2\}_2$ (injected at t = 6 minutes), measured using positive ion PSI-ESI-MS in methanol. Reaction is second order. Insert: plot of 1/[maximum intensity ï product intensity] vs time since addition demonstrating that the production of [**2.2a**]$^+$ follows second order kinetics.

4.1 Synthesis and Spectroscopic Characterization

Weak electrophiles, halogeno-boronic acid compounds containing bromoalkyl ($BrCH_2$-) groups were selected for the synthesis due to the better leaving ability of bromide than chloride and their lesser tendency to form dialkylated species. The laboratory scale reactions were monitored by ESI-MS[121] which has been previously found to be a valuable technique in the investigation of the alkylation chemistry of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$[54]. **1.0** is a neutral species but is mono-protonated in methanol and

detected in ESI-MS as [**1.0** + H]$^+$, at *m/z* 1503.5. {[$Pt_2(\mu\text{-}S)_2(PPh_3)_4$] + H}$^+$ has been previously synthesized by reacting dilute HCl with **1.0**, isolated and characterized by single crystal X-ray crystallography[136]. The gradual change in color from an orange methanolic suspension of **1.0** to a clear yellow solution indicated alkylation upon the addition of an electrophile. When a weaker electrophile is used monoakylation of **1.0** occurs generating the monocation [$Pt_2(\mu\text{-}S)(\mu\text{-}SR)(PPh_3)_4$]$^+$. The alkylating agent **2.2** reacted with **1.0** in methanol, within 6 min to give only the monoalkylated product [$Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2(C_6H_4)(OC(CH_3)_2)_2\}(PPh_3)_4$]$^+$, **2.2a** (Scheme 4.1**)** which was isolated as the PF_6^- salt following the addition of excess NH_4PF_6. No trace of any other product or dialkylated species were observed after further stirring for six hours. The reaction of $BrCH_2(C_6H_4)B(OH)_2$, **2.1** with **1.0** within same time interval yielded three monocationic species that were detected by ESI-MS and assignable to the three alkylated products: [$Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2C_6H_5)(PPh_3)_4$]$^+$, *m/z* 1593.4 from the loss of $B(OH)_2$ moiety; a hemiketal-like species [$Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2(C_6H_4)B(OH)(OCH_3)\}(PPh_3)_4$]$^+$, *m/z* 1651.5 and [$Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2(C_6H_4)OH\}(PPh_3)_4$]$^+$, *m/z* 1609.5. The minor peak at *m/z* 538.3 is [$N(PPh_3)_2$]$^+$, bis(triphenylphosphoranylidene)ammonium, which is the internal standard (**Figure 4.2**). The masses were identified by comparing the experimental isotope patterns with calculated ones[128]. No peak was observed in the mass spectrum that was attributable to the formation of the expected product [$Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2(C_6H_4)B(OH)_2\}(PPh_3)_4$]$^+$. The ESI-MS of the products isolated as $[PF_6]^{ï}$ salts also gave the same *m/z* species in the positive ion mode. Purification by vapor diffusion of diethyl ether into the dichloromethane solution of the products yielded crystals suitable for single crystal X-ray structure determination and further spectroscopic characterization. The structural determination showed that the compound formed was a zwitterion (neutral complex)

$[Pt_2(\mu\text{-}S)\{\mu\text{-}S^+CH_2(C_6H_4)B(OH)(O^{\ddot{}})\}(PPh_3)_4]$; accordingly, $[PF_6]^{\ddot{}}$ was not observed in the crystal structure. $[Pt_2(\mu\text{-}S)\{\mu\text{-}S^+CH_2(C_6H_4)B(OH)(O^{\ddot{}})\}(PPh_3)_4]$ is a neutral species and as such not detectable by ESI-MS.



Scheme 4.1: The synthesis of monoalkylated complexes $[Pt_2(\varepsilon\text{-}S)(\varepsilon\text{-}SR)(PPh_3)_4]^+$, **2.2a·(PF$_6$)** and $[Pt_2(\varepsilon\text{-}S)(\varepsilon\text{-}SR')(PPh_3)_4]^+$, **2.1a**. R and R' = boronic acid pinacole ester and boronic acid moiety respectively.

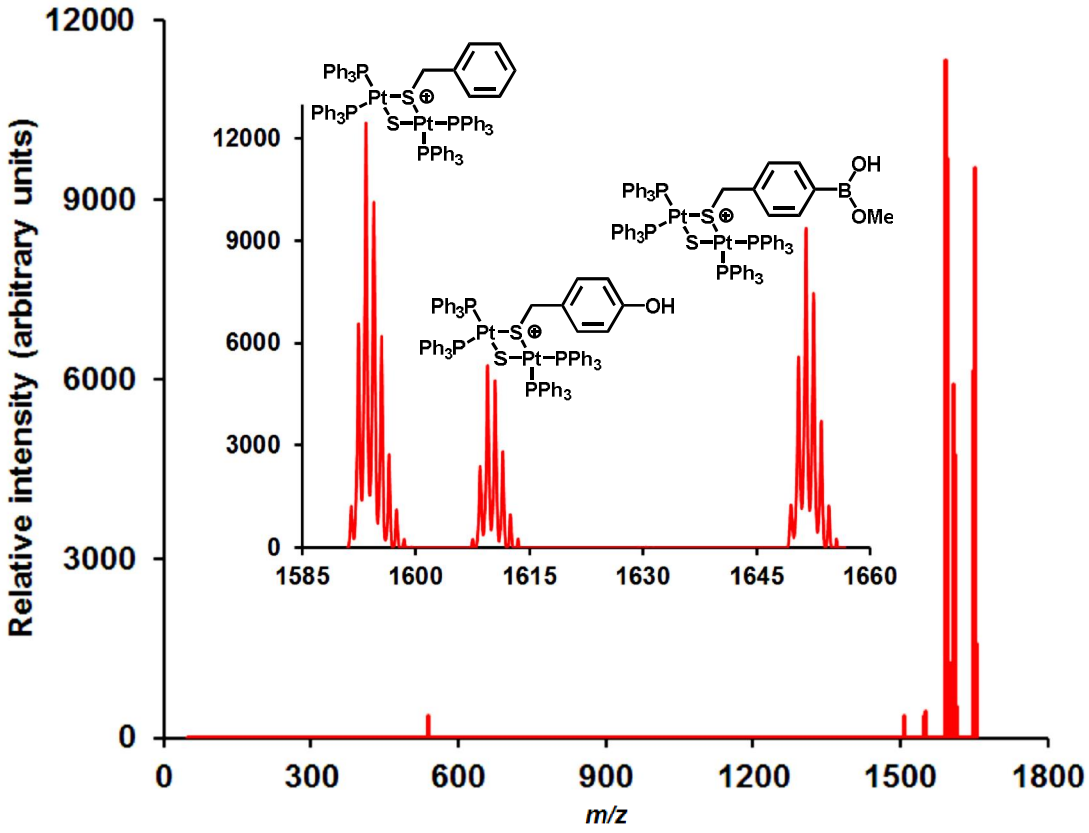


Figure 4.2. ESI-MS of the reaction of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with $BrCH_2(C_6H_4)B(OH)_2$. Insert is an expansion of the region of interest showing $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2C_6H_5)(PPh_3)_4]^+$, *m/z* = 1593.4; $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2(C_6H_4)OH\}(PPh_3)_4]^+$, *m/z* = 1609.5 and $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2(C_6H_4)B(OH)(OCH_3)\}(PPh_3)_4]^+$, *m/z* 1651.5.

The monoalkylated complexes, **2.2a·(PF$_6$)** and **2.1a** show IR, ^{1}H and ^{31}P{1H} NMR spectroscopic features expected for these type of complexes. The differences between the IR absorption bands of the reactants {$[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ **1.0**, alkylating agents **2.2** ,**2.1**} and the products **2.2a·(PF$_6$)** and **2.1a** clearly indicate the incorporation of the boronic acid electrophile into **1.0**. The assignment of the IR bands is comparable with those reported in the literature[137]. In the IR spectrum, the

OH vibration (3336 cm^{-1}) in **2.1** shifted to 3435 cm^{-1} in **2.1a.** The absorption bands of the B-O bond in **2.2** (1355 cm^{-1}) and **2.1** (1350 cm^{-1}) shifted to 1360 cm^{-1} and 1367 cm^{-1} in **2.2a·(PF_6)** and **2.1a** respectively.

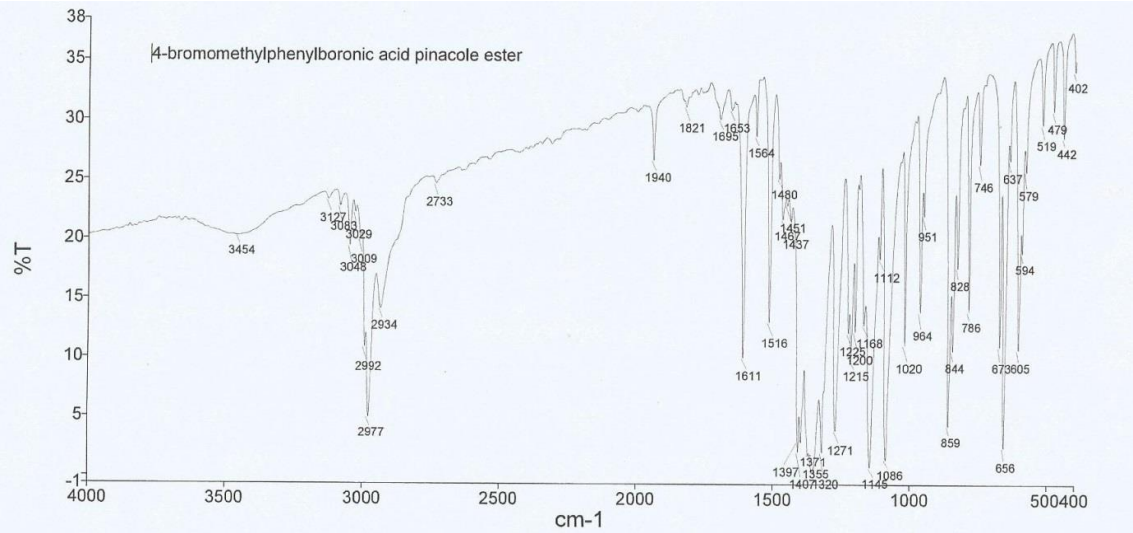


Figure 4.3: IR Spectra for the 4-bromomethylphenylboronic acid pinacole ester (2.2).

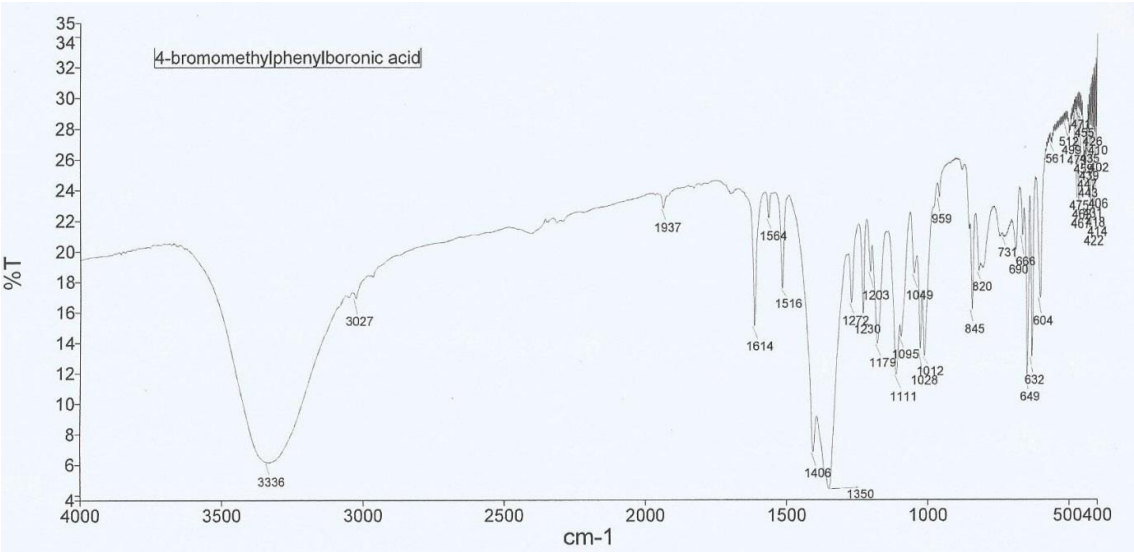


Figure 4.4: IR spectrum of 4-bromomethylphenylboronic acid (2.1).

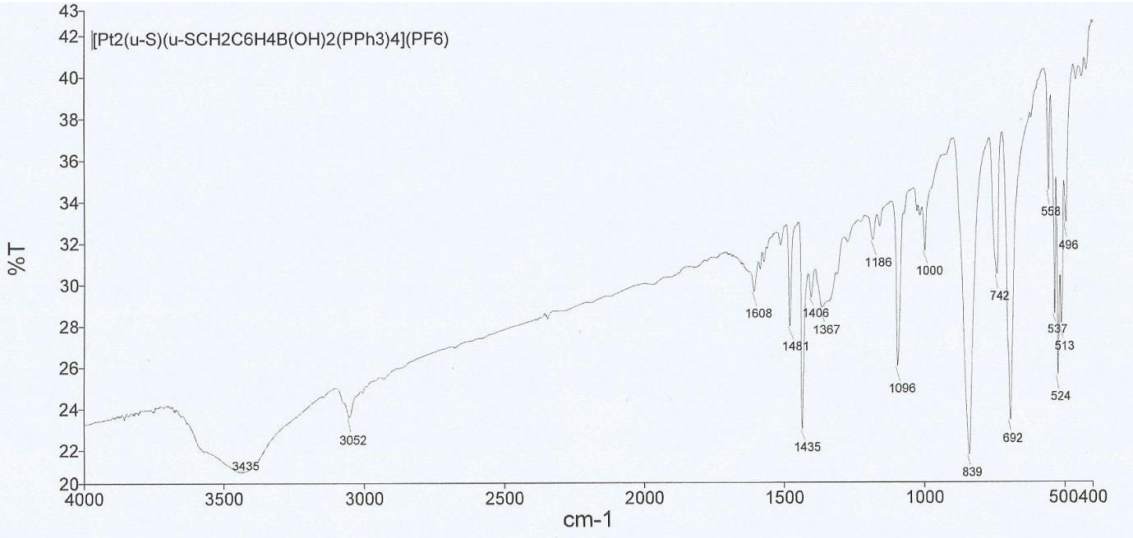


Figure 4.5: IR spectra for the reaction of 1.0 with alkylating agent 2.1 to give the product 2.1a.

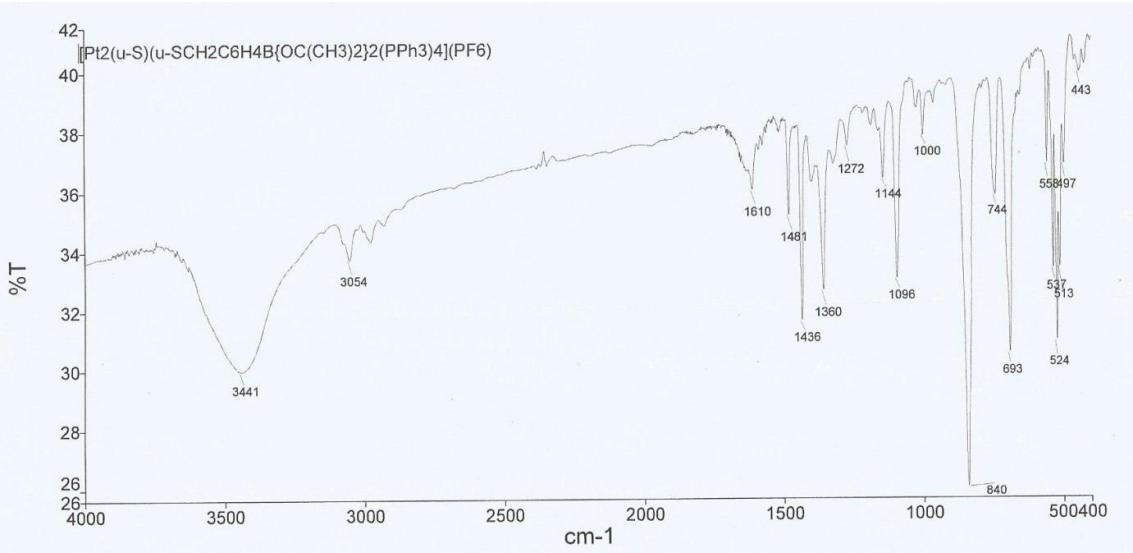


Figure 4.6: IR spectra for the product of the reaction of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (**1.0**) with alkylating agent $BrCH_2(C_6H_4)B\{OC(CH_3)_2\}_2$ **(2.2)** to give the product $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2(C_6H_4)B\{OC(CH_3)_2\}_2\}(PPh_3)_4]^+$, **2.2a.**

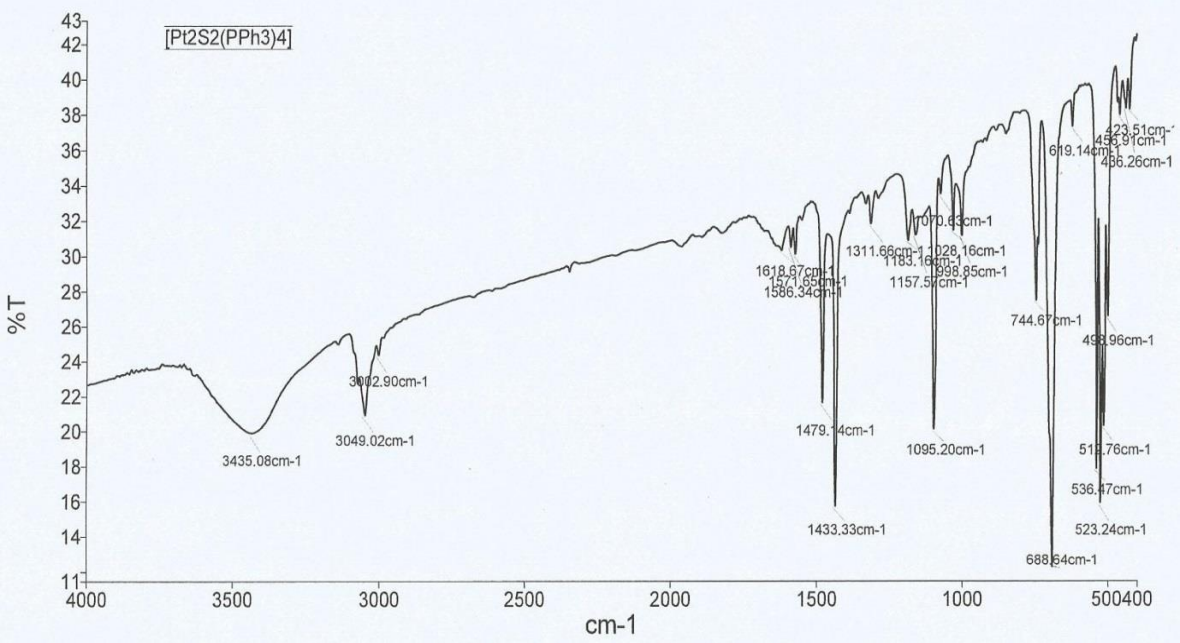


Figure 4.7. IR spectra for complex $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$(**1.0**)

Predictably, the ^{1}H NMR spectra showed a complicated set of resonances in the aromatic region due to the terminal triphenylphosphine ligands and were broadly assigned as such. However, SCH_2 hydrogen atoms were easily identified as broad peaks at ŭ 3.59 ppm and 3.60 ppm for **2.2a·(PF_6)** and **2.1a**, respectively. The observation of this resonance is further indication of sulfide alkylation. In both complexes, there are two inequivalent phosphorus centers: the phosphorus *trans* to the thiolate (-SR) or and the phosphorus *trans* to the sulfide (-S-) atom. The $^{31}P\{^1H\}$ NMR spectra showed nearly superimposed central resonances and clearly separated satellite peaks due to ^{195}Pt coupling (Figure 4.7). The ^{1}J(PtP) coupling constants showed the differences due to the *trans* influences of the substituted and the unsubstituted sulfide centers[136]. The *trans* influence of the unsubstituted sulfide is greater than the thiolate (substituted) species demonstrated by the coupling constants at (2628 and 3291 Hz) for **2.2a·(PF_6)** and (2632 and 3272 Hz) **2.1a**,respectively.

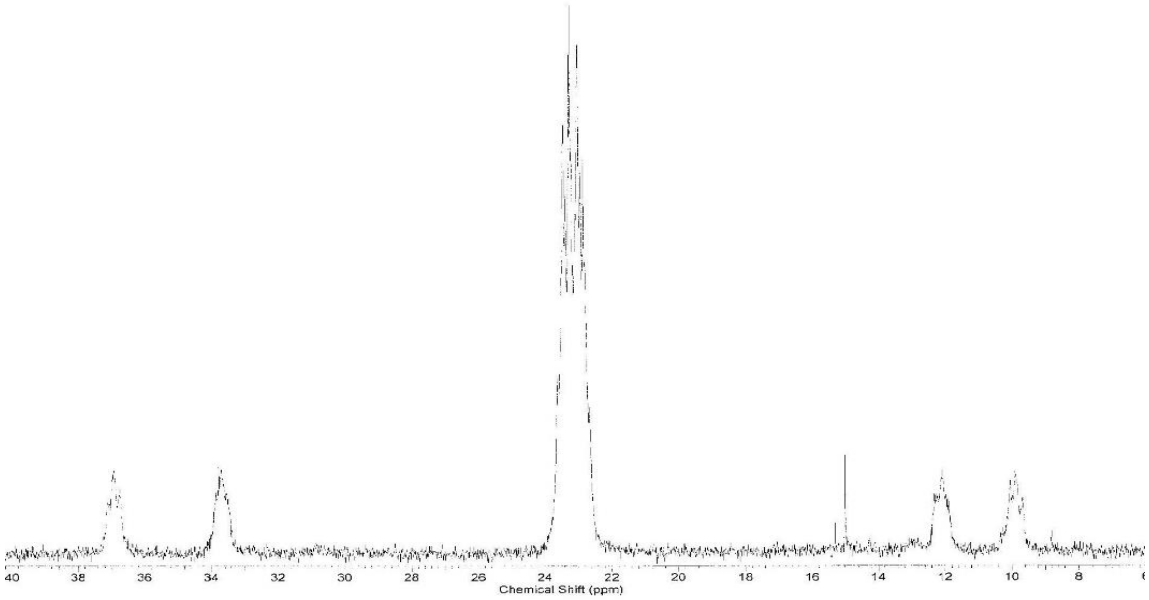


Figure 4.8. The $^{31}P\{^{1}H\}$ NMR spectrum of $[Pt_2(\mu\text{-}S)\{\mu\text{-}CH_2(C_6H_4)B\{OC(CH_3)_2\}_2\}(PPh_3)_4]$ (PF_6), **2a·(PF$_6$)** showing the almost equivalence of the central peaks, with two sets of satellites due to different ^{195}Pt coupling constants.

4.2 X-Ray Crystal Structures

X-ray structures of the complexes $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2(C_6H_4)B\{OC(CH_3)_2\}_2\}(PPh_3)_4]$ (PF_6), **2.2a·(PF$_6$)** and $[Pt_2(\mu\text{-}S)\{\mu\text{-}S^{+}CH_2(C_6H_4)B(OH)(O^{-})\}(PPh_3)_4]$, **2.1a** were determined to confirm the identity of complexes and to allow for structural comparison with related monoalkylated molecules previously reported. Selected bond lengths and angles are presented in Tables 4.1and 4.2. The molecular structures and atom numbering schemes for **2.2a·(PF$_6$)** and **2.1a** are shown in **Figures 4.8** and **4.9** respectively. The structures show both complexes **2.2a·(PF$_6$)** and **2.1a** have the typical hinged conformation of the $\{Pt_2(\mu\text{-}S)_2\}$ core dihedral angles formed by the two PtS_2 planes in each of

2.2a·(PF_6) and **2.1a** of 136.66° and 134.40°, respectively. A comparison of the important structural parameters of **2.2a·(PF_6)** and **2.1a** with those of structurally-related monoalkylated compounds $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2C(O)Ph\}(PPh_3)_4](BPh_4)$[111] **4a·($BPh_4$)**, $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2C(=NNHC(O)NH_2)Ph\}(PPh_3)_4](PF_6)$[111] **5a·($PF_6$)** and $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2CH_2\,NHC(O)N(CH_2CH_2)_2S\}(PPh_3)_4](PF_6)$[113] **6a·($PF_6$)** are shown in Table 4.3. The structural parameters are comparable across the series of compounds.

Table 4.1. Selected bond lengths (Å) and angles (°) for $[Pt_2(\mu\text{-}S)\{\mu\text{-}CH_2(C_6H_4)B\{OC(CH_3)_2\}_2\}(PPh_3)_4](PF_6)$, **2.2a·($PF_6$)**

Bond lengths (Å)			
Pt(1)-P(1)	2.3056(11)	Pt(1)-P(2)	2.2843(11)
Pt(2)-P(3)	2.3002(11)	Pt(2)-P(4)	2.2779(11)
Pt(1)-S(1)	2.3603(10)	Pt(1)-S(2)	2.3313(10)
Pt(2)-S(1)	2.3858(10)	Pt(2)-S(2)	2.3284(10)
S(1)-C(1)	1.829(5)	C(1)-C(2)	1.493(6)
O(1)-B(1)	1.365(7)	O(2)-B(1)	1.356(7)
Bond angles (°)			
P(1)-Pt(1)-S(2)	172.41(4)	P(2)-Pt(1)-S(1)	167.00(4)
P(4)-Pt(2)-S(1)	172.53(4)	P(3)-Pt(2)-S(2)	166.94(4)
S(1)-Pt(1)-S(2)	81.41(4)	S(2)-Pt(2)-S(1)	80.93(4)
C(1)-S(1)-Pt(1)	106.85(15)	C(1)-S(1)-Pt(2)	100.17(15)
Pt(2)-S(2)-Pt(1)	90.83(4)	Pt(1)-S(1)-Pt(2)	88.73(3)

Table 4.2. Selected bond lengths (Å) and angles (°) for $[Pt_2(\mu\text{-}S)\{\mu\text{-}S^+CH_2(C_6H_4)B(OH)(O^-)\}(PPh_3)_4]$, **2.1a**

Bond lengths (Å)			
Pt(1)-P(1)	2.296(2)	Pt(1)-P(2)	2.271(2)
Pt(2)-P(3)	2.282(2)	Pt(2)-P(4)	2.290(2)
Pt(1)-S(1)	2.366(2)	Pt(1)-S(2)	2.325(2)
Pt(2)-S(1)	2.346(2)	Pt(2)-S(2)	2.342(2)
S(1)-C(1)	1.836(10)	C(1)-C(2)	1.507(13)
Bond angles (°)			
P(1)-Pt(1)-S(2)	167.76(8)	P(2)-Pt(1)-S(1)	173.68(8)
P(4)-Pt(2)-S(1)	166.90(8)	P(3)-Pt(2)-S(2)	175.49(8)
S(1)-Pt(1)-S(2)	81.18(7)	S(2)-Pt(2)-S(1)	81.24(7)
C(1)-S(1)-Pt(1)	99.3(3)	C(1)-S(1)-Pt(2)	106.6(4)
Pt(2)-S(2)-Pt(1)	89.38(7)	Pt(1)-S(1)-Pt(2)	88.29(7)

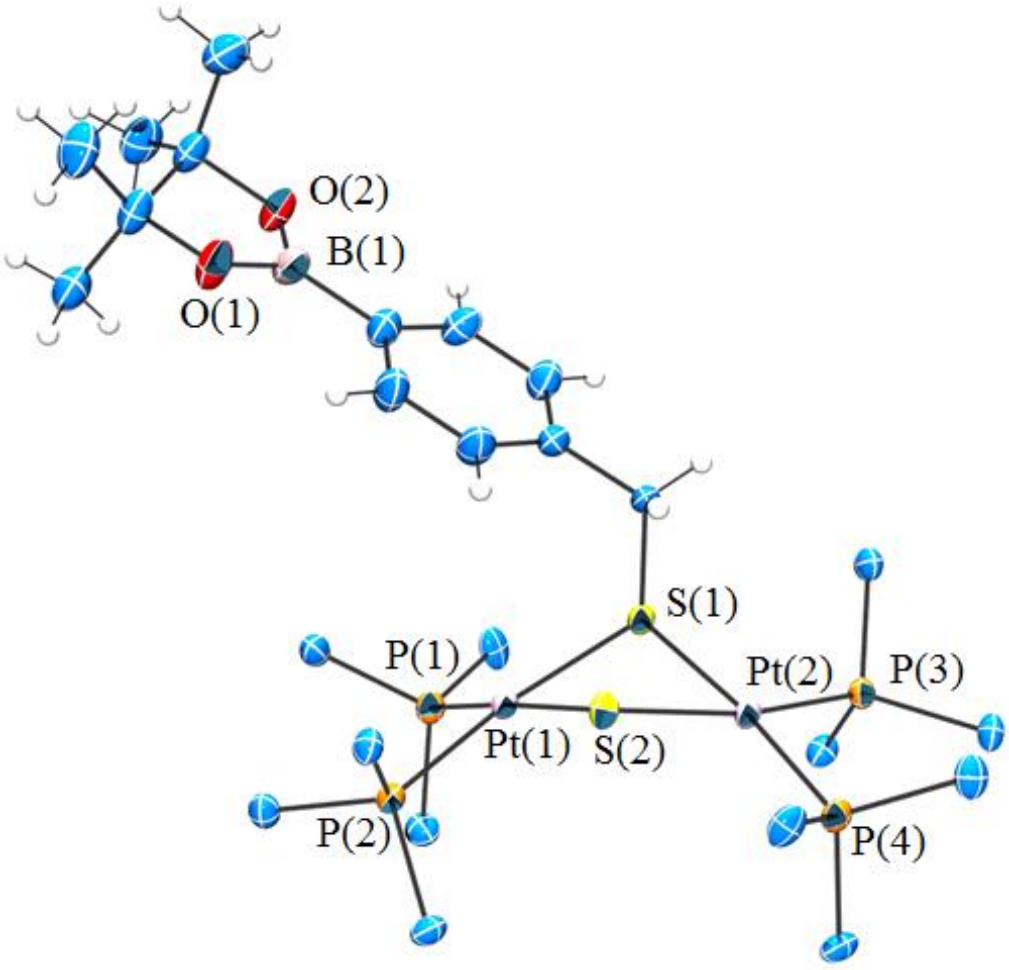


Figure 4.9: Molecular structure of the core of the complex $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2(C_6H_4)B\{OC(CH_3)_2\}_2\}(PPh_3)_4]^+$, **2.2a**, with only the ipso carbon atoms of the PPh_3 ligands shown.

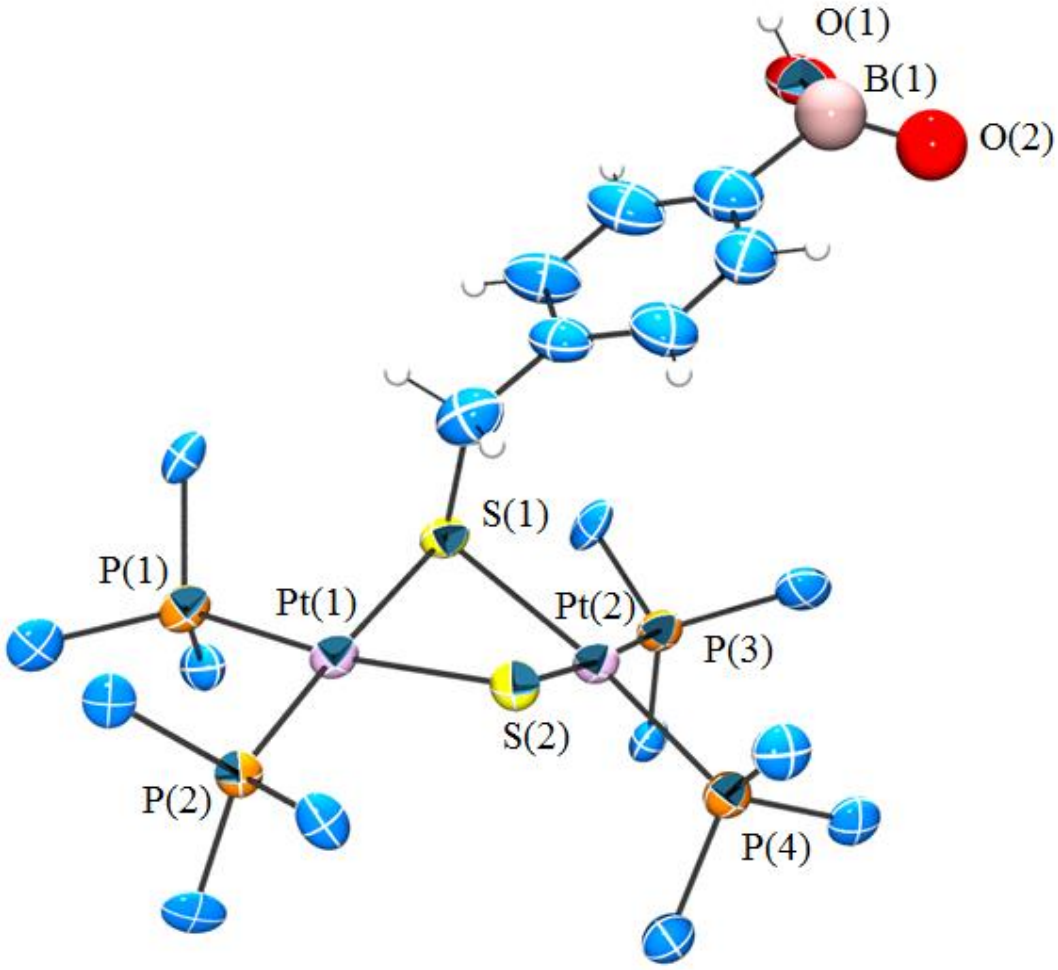


Figure 4.10: Molecular structure of the core of the complex $[Pt_2(\mu\text{-}S)\{\mu\text{-}S^+CH_2(C_6H_4)B(OH)(O^-)\}(PPh_3)_4]$, **2.1a**, with only the *ipso* carbon atoms of the PPh_3 ligands shown.

Table 4.3. A Comparison of the Geometric Parameters [Distances (Å) and Angles (°)] for the Complexes **2.2a·(PF_6), 2.1a, 4a·(BPh_4) and 5a·(PF_6) and 6a·(PF_6)** Together with (Estimated Standard Deviations are in Parentheses where Reported).

Parameter	**2.1a·(PF_6)**	**2.1a**	**4a·(BPh_4)**	**5a·(PF_6)**	**6a·(PF_6)**
Mean Ptï S	2.3299(10)	2.356(2)	2.3380(7)	2.339(3)	2.3343(17)

Mean Ptï SR	2.3731(10)	2.3335(2)	2.3716(7)	2.390(3)	2.3671(17)
Pt---Pt	3.319	3.282	3.282	3.297	3.325
S---S	3.060	3.052	3.087	3.071	3.077
Mean Ptï Sï Pt	89.78(4)	88.84(7)	88.39(2)	88.44(8)	90.03(6)
Mean Sï Ptï S	81.17(4)	81.21(7)	81.90(3)	81.02(9)	81.76(6)
Dihedral angle[a]	136.66	134.40	133.8	133.1	138.6

[a]Dihedral angle = angle between the S(1)ï Pt(1)ï S(2) and S(1)ï Pt(2)ï S(2) planes.

4.3 X-Ray Structure Determinations of 2.2a·(PF_6) and 2.1a

An appropriately sized crystal of **2.2a·(PF_6)** or **2.1a** was selected from a bulk sample under Paratone-N oil and mounted on a MiTeGen loop. The loop was transferred to a Bruker APEX-II diffractometer equipped with a CCD area detector under a cold gaseous nitrogen stream. An arbitrary sphere of data was recorded, using Mo-KŬ radiation (ə 0.71073 Å) and a combination of ɤ - and ű-scans of 0.5°[138]. Data were corrected for absorption and polarization effects and analyzed for space group determination[139]. The structures were solved by intrinsic phasing methods and expanded routinely[140]. The models were refined by full-matrix least-squares analysis of F^2 against all reflections. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Unless otherwise noted, hydrogen atoms were included in calculated positions. Atomic displacement parameters for the hydrogens were tied to the U_{eq} parameter of the atom to which they are bonded (1.5 × for methyl, 1.2 × for all others). Crystallographic data are summarized in Tables 4.4 and 4.5.

Table 4.4: Crystallographic data for complex **2.2a·(PF_6)**.

Empirical formula	$C_{88}H_{84}BCl_6F_6O_2P_5Pt_2S_2$
Formula weight	2120.21
Temperature	120(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	*a* = 22.1024(15) Å Ŭ= 90°
	b = 15.4058(11) Å ɓ = 104.8170(10)°
	c = 26.9561(19) Å ɔ = 90°
Volume	8873.5(11) $Å^3$
Z	4
Density (calculated)	1.587 $g.cm^{-3}$
Absorption coefficient (ε)	3.526 mm^{-1}
F(000)	4208
Crystal color, habit	Yellow, block
Crystal size	0.232 × 0.120 × 0.106 mm^3
ɗ range for data collection	1.535 to 27.122°
Index ranges	-28 Òh Ò28, -19 Òk Ò19, -34 Òl Ò34
Reflections collected	158923
Independent reflections	19626 [R_{int} = 0.0371]
Completeness to ɗ = 25.242°	100.0 %
Absorption correction	Numerical

Max. and min. transmission	0.8210 and 0.5351
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	19626 / 42 / 1049
Goodness-of-fit on F^2	1.012
Final R indices [I>2ů(I)]	R_1 = 0.0346, wR_2 = 0.0885
R indices (all data)	R_1 = 0.0436, wR_2 = 0.0949
Largest diff. peak and hole	2.132 and -1.489 $e^{ï}.Å^{-3}$

Table 4.5. Crystallographic data for complex **2.1a**

Empirical formula	$C_{79}H_{68}BO_2P_4Pt_2S_2$	
Formula weight	1638.32	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_ı/n$	
Unit cell dimensions	*a* = 17.6538(16) Å	Ŭ= 90°
	b = 23.694(2) Å	ɓ = 92.7640(10)°
	c = 20.1360(19) Å	ɔ = 90°
Volume	8412.7(13) $Å^3$	
Z	4	
Density (calculated)	1.294 $g.cm^{-3}$	
Absorption coefficient (ε)	3.486 mm^{-1}	
F(000)	3240	
Crystal color, habit	Yellow, rod	
Crystal size	0.185 × 0.061 × 0.035 mm^3	

ɗ range for data collection	1.499 to 23.256°
Index ranges	-19 Òh Ò19, -26 Òk Ò26, -22 Òl Ò22
Reflections collected	107001
Independent reflections	12089 [R_{int} = 0.0765]
Completeness to ɗ = 23.256°	100%
Absorption correction	Numerical
Max. and min. transmission	0.09292 and 0.5336
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	12089 / 0 / 805
Goodness-of-fit on F^2	1.091
Final R indices [I>2ů(I)]	R_1 = 0.0468, wR_2 = 0.0958
R indices (all data)	R_1 = 0.0730, wR_2 = 0.1054
Largest diff. peak and hole	1.689 and -1.291 $e^{ï}.Å^{-3}$

4.4 $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2(C_6H_4)B\{OC(CH_3)_2\}_2\}(PPh_3)_4](PF_6)$, **2.2a·(PF$_6$)**

The complex crystallizes as colorless block-like crystals from vapour diffusion of diethyl ether into a dichloromethane solution at room temperature. There are four molecules of the $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2(C_6H_4)B\{OC(CH_3)_2\}_2\}(PPh_3)_4]^+$ cation, four associated PF_6^- anions and twelve dichloromethane molecules of crystallization in the unit cell of the primitive, centrosymmetric, monoclinic and are uncorrected $P2_1/c$. The structure of **2.2a·(PF$_6$)** complex is as expected. The cation consists of two, four-coordinate, square planar Pt centers; each is coordinated by two triphenylphosphine ligands and bridged by a sulfide sulfur and the thiol sulfur of the dioxaborolane phenyl methanethiol ligand (Figures 4.8 and Table 4.1). One of the three independent dichloromethane molecules located within the asymmetric unit is disordered. Two

sites were observed for this molecule. Refinement of the occupancy of the two sites yielded an effective 50:50 occupancy. In the final model, the occupancies of the two sites were set to 50%. Further, one of the chlorine atoms is additionally disordered over two sites and was refined with 25% occupancy at each site.

4.5 $[Pt_2(\mu\text{-}S)\{\mu\text{-}S^+CH_2(C_6H_4)B(OH)(O^-)\}(PPh_3)_4]$, 2.1a

The compound $[Pt_2(\mu\text{-}S)\{\mu\text{-}S^+CH_2(C_6H_4)B(OH)(O^-)\}(PPh_3)_4]$, 2.1a crystallizes as colorless block-like crystals from a chloroform/hexanes solution. There are four molecules of the complex in the unit cell of the primitive, centrosymmetric, monoclinic space group $P2_1/n$ (**Figure 4.11** below). Also present was diffuse, disordered solvent. After several attempts at modeling this electron density it was elected that the solvent contribution to the model be accounted for using the SQUEEZE routine in PLATON[141]. The routine located two voids (**Figure 4.12**), of 1182 $Å^{-3}$, each contributing 305 electrons to the intensities. These additional factors were omitted from the final model and no interpretation of the solvent content (likely to be less than unitary values for various combinations of solvents present from crystallization) made. The solvent content has not been added to the chemical formula.

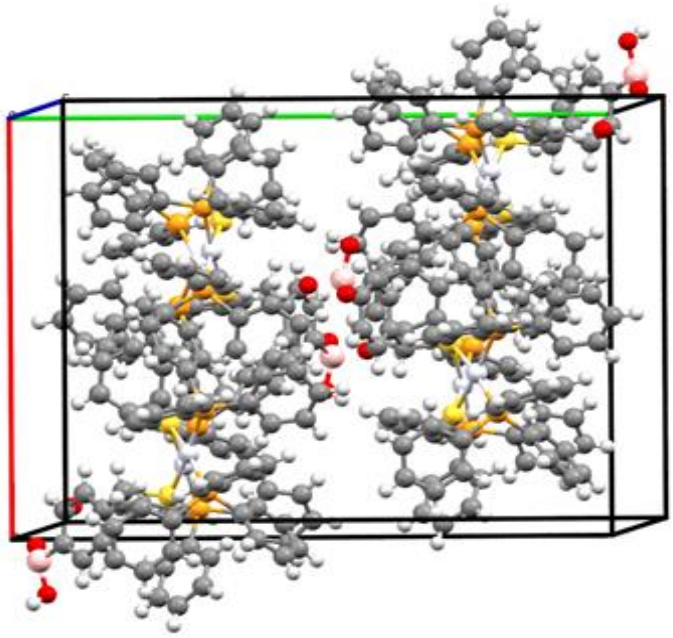


Figure 4.11: Packing diagram of 2.1 showing the foru molecules in the unit cell.

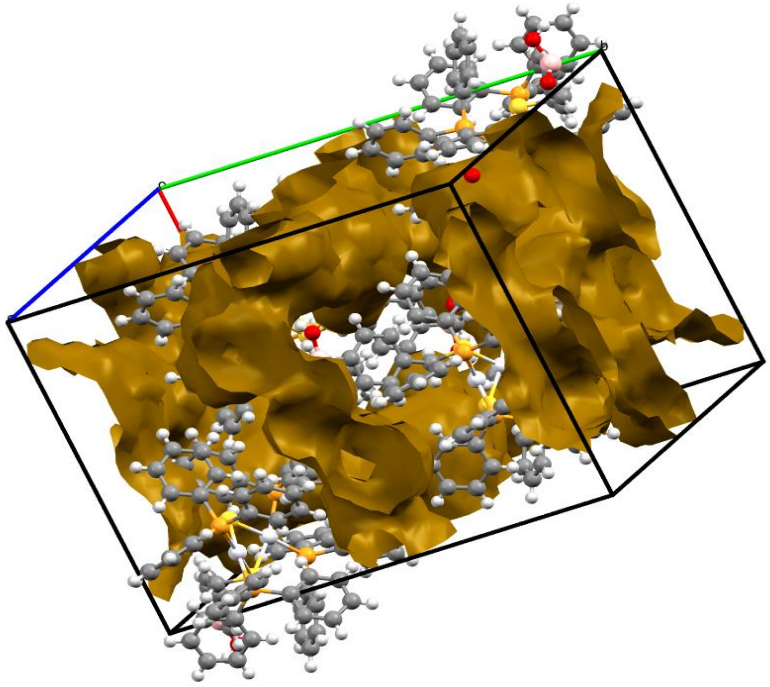


Figure 4.12: Packing diagram of 2.1 showing the solvent accessible voids.

The structure of **2.1a** is as expected (Figure 4.9, Table 4.2). The core consists of two Pt atoms each coordinated in a square-planar fashion. The coordination environment about each Pt center is two, *cis*, triphenylphosphine ligands, a bridging sulfur and the bridging sulfur of the thiolate ligand. There is some disorder present in

the borate moiety that has been modeled with one fully occupied oxygen and two partial occupancy oxygen atoms. The boron is modelled with isotropic atomic displacement parameters. It is also slightly disordered, but not well defined in its disorder. Thus a reasonable model could not be obtained.

The disordered boronate appears to consist of $B(OH)(O^-)$. Despite the disorder present in this group, the ordered oxygen, O1, has a slightly longer bond distance (B1-O1 = 1.446(18) Å) than the oxygen that is disordered over two sites (B1-O2/O2A = 1.29(2)/1.38(2) Å). This would support the negative charge for a zwitterionic species residing on this peripheral group, balancing the core positive (+) charge (from the two Pt centres, bridging S and bridging thiolate SR).

CONCLUSIONS

This study has demonstrated the successful incorporation of two organo-boron moieties on to $\{Pt_2(\mu\text{-}S)_2\}$ core yielding dinuclear platinum complexes of the type $[Pt_2(\mu\text{-}S)(\mu\text{-}SR)(PPh_3)_4]^+$. Potentially, any boron group can be incorporated into $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ **1.0** through a suitable electrophile and the unsubstituted sulfide center can be capped with a suitable group. In the future, we also intend to investigate alkylated boron derivatives in the synthetic design of diverse bi- and poly aryl compounds of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ moiety.

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