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Reactivity of Dimethylplatinum(II) Complexes with Peroxides

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Graduate Program in Chemistry
A thesis submitted in partial fulfillment of the requirements for the degree in Master of Science

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REACTIVITY OF DIMETHYLPLATINUM(II) COMPLEXES WITH PEROXIDES

(Thesis format: Monograph)

by

Kyle R. Pellarin

Department of Chemistry

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science

The School of Graduate and Postdoctoral Studies
The University of Western Ontario
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THE UNIVERSITY OF WESTERN ONTARIO
School of Graduate and Postdoctoral Studies

CERTIFICATE OF EXAMINATION

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The thesis by

Kyle Richard Pellarin

entitled:

Reactivity of Dimethylplatinum(II) Complexes with Peroxides

is accepted in partial fulfillment of the
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Date

Chair of the Thesis Examination Board

Abstract

This thesis describes a study of dimethylplatinum(II) complexes containing bidentate nitrogen donor ligands. This work deals with the oxidative addition of peroxides and focuses on synthesis, characterization and reaction mechanisms of these complexes.

Dimethylplatinum(II) complexes were reacted with oxidants dimethyldioxirane (DMDO), *meta*-chloroperbenzoic acid (*m*-CPBA) and phthaloyl peroxide. The use of these oxidants has allowed for the synthesis of novel platinum(IV) complexes by oxidative addition and the formation of unique supramolecular networks. The formation of both *trans*- and *cis*-oxidative addition products was controlled by the type of oxidant utilized. By varying the ligand design of the platinum(II) complexes, the formation of the multiple platinum(IV) complexes have been obtained, each demonstrating their own unique chemistry.

In other interests, low temperature ^{1}H NMR spectroscopy has been utilized to follow the reaction pathway of the oxidative addition of iodine at [$PtMe_2$(bpy)]. This technique allowed for the observation of intermediates formed within this reaction. The formation of intermediates shows solvent dependence following the trend; acetone >CD_2Cl_2 > toluene, suggesting there is stabilization of these intermediates by more polar solvents.

Keywords: Platinum complexes, oxidative addition, bidentate nitrogen donor ligands, peroxides, dimethyldioxirane, *meta*-chloroperbenozic acid, phthaloyl peroxide, iodine, supramolecular chemistry.

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The most important people that I would like to thank would be my family. They have been very supportive, patience and understanding throughout my entire course of study and for that I am extremely grateful. If it was not for their support, none of this would be possible.

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Abbreviations

a, b, c, α, β, γ	unit cell parameters
Å	angstroms
acac	pentane-2,4-dione
Anal. Calc.	analysis calculated
bpy	2,2'-bipyridine
bu$_2$bpy	4,4'-di-tert-butyl-2,2'-dipyridyl
COSY	correlation spectroscopy
°C	degrees centigrade
δ	chemical shift (NMR)
d	doublet (NMR)
dd	doublet of doublets (NMR)
ddd	doublet of doublets of doublets (NMR)
DMDO	dimethyldioxirane
DECBP	4,4'-diethoxycarbonyl-2,2'-bipyridine
dpa	di-2-pyridyl amine
dpk	di-2-pyridyl ketone
ESI	electrospray ionization
fac	facial
g	grams
hal	halogen
In·	radical initiator
IR	infrared
J	coupling constant
^{x}J(AB)	coupling constant between nuclei A and B through X bonds
Hz	hertz
^{i}Pr	*iso*-propyl
L	ligand
μ	absorption coefficient
m	multiplet (NMR)
m-CPBA	*meta*-chloroperbenzoic acid

Me	methyl
mg	milligrams
mL	millilitres
mol	mole
m/z	mass to charge ratio
MIM	1,1-bis(1-methylimidazloe-2-yl)
MHz	mega-hertz
MS	mass spectrometry
NN	chelating nitrogen donor ligand
NMR	nuclear magnetic resonance
π	pi
phen	1,10-phenanthroline
ppm	parts per million (NMR)
R·	radical chain
r.t.	room temperature
R-X	alkyl halide
σ	sigma
σ*	antibonding sigma
SEM	scanning electron microscopy
S_N2	bimolecular nucleophilic substitution
υ	frequency (cm^{-1})
VT-NMR	variable temperature-NMR
Z	formula units in unit cell

To my family and friends

Chapter 1

General Introduction

1.1 The History of Platinum

Platinum was first discovered in the sixteenth century in the Choco district of Colombia.[1] Observed by Ulloa in 1736, its present name derives from the term “platina del pinto” or “little silver of the Pinto River”.[2] The first sample of platinum was brought to Europe in 1741 by Charles Wood, an Assay Master of Jamaica. The metals within this platina species are platinum, palladium, rhodium, iridium, osmium, and ruthenium. The platinum group metals are amongst approximately 90 elements that comprise less than 2% of the earth’s crust.[1] The main areas from which platinum is extracted are ores in South Africa, Canada, Russia, Colombia, China and Australia. The ores consist of the six platinum metals, with palladium and platinum being the most abundant. The metals are obtained from the metallic phase of the sulphide matte or the anode slime from electrolytic refining of nickel where they fall to the bottom of the electrolytic cell and are recovered by filtration.[2] Platinum has been utilized for many different things, from jewellery due to its beautiful, silvery white colour, to using it for lining of crucibles in the manufacturing of high grade optical glass due to its high corrosion resistant properties and high melting point (1772°C).[2]

1.2 Platinum in Organometallic Chemistry

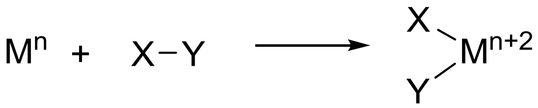
The chemistry of platinum has been studied for over 200 years and has lead to many advances in the fields of organometallic and coordination chemistry. Organometallic chemistry has been established as an exchange between inorganic and organic chemistry. Organometallic complexes are characterized by direct, more or less polar bonds between compounds which contain at least one chemical bond between a carbon and metal atom.[3] The introduction of a metal center and an organic fragment into a single molecule has shown to induce modified properties to each component. Main group organometallics are typically characterized as stoichiometric reagents, however, transition metal organometallics typically act as catalysts.[4] The first and possibly most important discovery in the field of organometallic chemistry was the synthesis of Zeise's Salt in 1827, by W.C. Zeise. The compound of $K[Pt(C_2H_4)Cl_3]\cdot H_2O$ was obtained as yellow, needle-like crystals after refluxing a mixture of $PtCl_4$ and $PtCl_2$ in ethanol, followed by the addition of KCl. This proved to be the first compound containing an organic molecule attached to a metal using the π electrons of the organic ligand.[5] The formation of this first organometallic complex has lead to the discovery of various other platinum coordination complexes, including the first metal carbonyl-compound $[PtCl_2(CO)_2]$ by Schützenberger in 1868, one of the first alkyl transition metal compounds $[PtMe_3I]_4$ by Pope in 1907, and an antitumor chemotherapeutic agent *cis*-$[PtCl_2(NH_3)_2]$, known as cis-platin.[6,7,8]

The development of this type of organometallic chemistry has occurred rapidly, largely due to the versatility of platinum in the formation of a wide range of organometallic complexes. This versatility can be attributed to the formation of various coordination compounds of platinum with varying oxidation states, ranging from 0 to +6. The most common oxidation states of platinum are 0, +2 and +4, with platinum(II) forming d^8 complexes with square planar geometry and platinum(IV) forming d^6 complexes which exhibit octahedral geometry.[9] The ease in ability of organometallic complexes to undergo two electron oxidation and reductions through their three main oxidation states makes these types of complexes promising catalytic species.[10]

Platinum has thirty nine known isotopes to date, with six of these occurring naturally. Three of the six naturally occurring isotopes are ^{194}Pt, ^{195}Pt, and ^{196}Pt, which have the greatest abundance of 32.965%, 33.832% and 25.142%, respectively.[11] The most abundant of these naturally occurring isotopes, ^{195}Pt exhibits a nuclear spin of ½. This NMR active isotope allows for spectroscopic observation of species in solution, especially pertaining to ^{195}Pt NMR as well as ^{195}Pt-H coupling in ^{1}H NMR.[12] The spectroscopic handle allows for platinum species to be characterized much easier than other metals in group 10 of the periodic table. It is also known that the reactivity of group 10, trends from bottom to top. This leads to slower reactions for platinum compared to the first and second row transition metals, which also makes platinum complexes ideal species for probing the reaction pathways and mechanisms, not possible with faster reacting metals.[10]

1.3 Oxidative Addition

Oxidative addition reactions are some of the most fundamentally important reactions in transition metal chemistry in both synthesis and catalysis.[13] They typically consist of a metal of relatively low oxidation state being formally oxidized by the addition of an XY substrate, and complete dissociation of the X-Y bond, as illustrated in scheme 1.1.[4,10] This oxidation process typically results in the oxidation state, coordination number and the electron count increasing by two units.[5] Oxidative additions proceed by a variety of mechanisms, but the fact the electron count increases by two units means that a vacant two electron site is required on the metal. The change in oxidation state of the metal complexes means that they must be able to take on a stable oxidation state two units higher than before the oxidative addition process.[13] Oxidative addition reactions typically occur on transition metal complexes having counts of 16 electrons or fewer. However, addition is possible to an 18 electrons species but loss of ligand is required for this to occur.[5] Based on these parameters and requirements, coordinatively unsaturated organoplatinum(II) complexes are viable candidates for the oxidative addition process, due to the 16 electron configuration.[10] Changes in the nature of the metal, substrate and ligands can often dramatically alter the pathway for oxidative addition and thus several types of mechanism have been proposed and these are discussed in the subsequent sections.



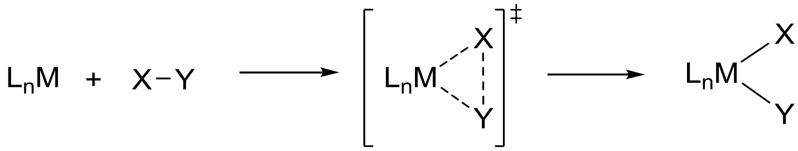
Scheme 1.1: General oxidative addition reactions of a substrate to a metal center

1.3.1 Two Electron Oxidative Addition Pathways

There are two main two electron pathways for the oxidative addition of an X-Y bond at a metal center. The substrates can be classified as class A or class B each varying in the type of molecule involved in the oxidative addition reactions. The first of these two mechanisms is known as three-center or *cis*-concerted oxidative addition and the second is classified as a bimolecular S_N2 mechanism.

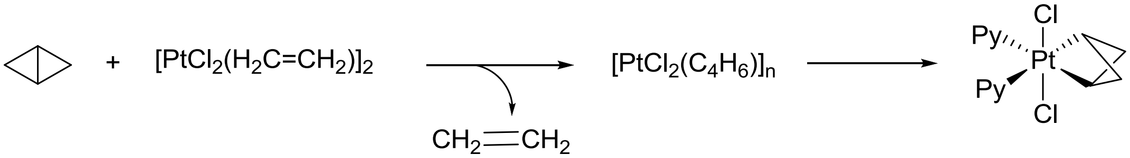
1.3.2 Three-Center Concerted Mechanism

Class A substrates typically are formed by non-polar species such as H_2, R_3Si-H and R-H.[14] This oxidative addition tends to take place by the incoming ligand binding as a σ-complex and then undergoing bond breaking due to strong back donation from the metal into the σ* orbital. This concerted mechanism, depicted in scheme 1.2, typically results in a product with *cis* geometry.[13] A requirement for the *cis*-addition process is the utilization of unsaturation at the metal center, with the reaction proceeding with retention of configuration at a chiral carbon in the substrate.



Scheme 1.2: Three centered or *cis*-concerted oxidative addition mechanism

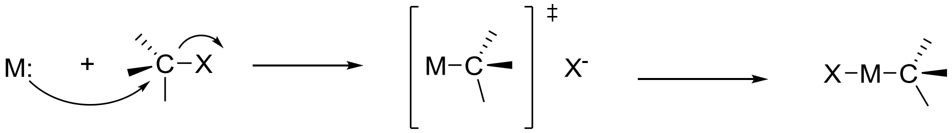
There are few examples of the oxidative addition of class A substrates to platinum(II) centers as these substrates tend to be difficult to activate.[14] One example illustrates the activation of a C-C bond, which can be utilized for catalytic activation of C-C bonds to provide low energy, efficient routes to production of compounds useful in gasoline refining. Most prominent examples of C-C oxidative addition involve the reaction of cyclic hydrocarbons with one strained and weak C-C bond. In the example of Ziese's dimer, $[PtCl_2(H_2C=CH_2)]_2$ with bicyclobutane, the relief of ring strain gives the complex platinabicyclopentane, as a stable complex illustrated in scheme 1.3.[15]



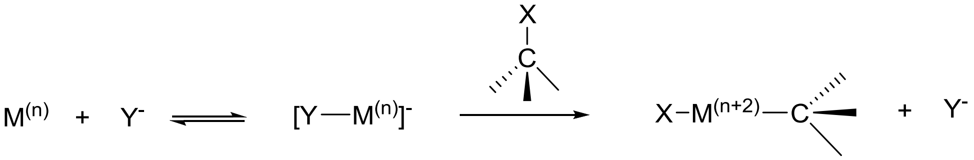
Scheme 1.3: Example of C-C bond activation by platinum complex

1.3.3 S_N2 Bimolecular Mechanism

The second major two electron oxidative addition pathway is termed bimolecular S_N2 oxidative addition. This pathway has been adopted for polarized electrophilic species such as alkyl halides and halogens.[14] The S_N2 pathway typically involves the metal center acting as a nucleophile, where the metal electron pair directly attacks the σ* orbital at the least electronegative atom of the substrate, breaking the bond. The formation of a cationic intermediate occurs, followed by coordination of the anionic ligand to the metal center, as depicted in scheme 1.4.[13] Numerous types of this S_N2 oxidative addition involve reactions that require coordination of an anion to the metal complex, generating a highly nucleophilic complex, illustrated in scheme 1.5.



Scheme 1.4: Bimolecular S_N2 oxidative addition mechanism

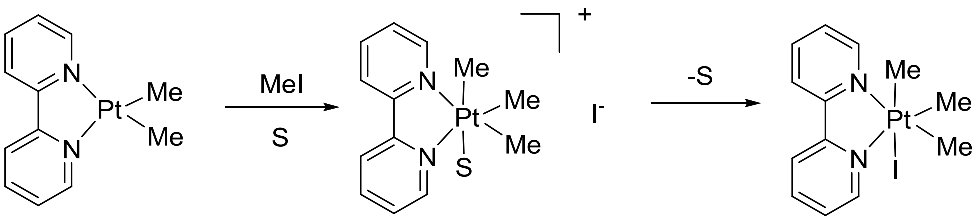


Scheme 1.5: S_N2 oxidative addition forming highly nucleophilic complex

The S_N2 reaction pathway typically invokes a *trans*-oxidative addition product. This reaction displays a characteristic inversion of configuration at a chiral carbon of the substrates, accelerated reaction rates in polar solvents and shows a large negative entropy of activation consistent with the polar transition state, which are all consistent with an S_N2-type mechanism.[13,14]

As opposed to the three center concerted mechanism, there has been much more evidence to illustrate the formation of this *trans*-oxidative addition species by the S_N2 oxidative addition mechanism. Strong evidence for the mechanism of the S_N2 pathway has been illustrated in numerous cases, one utilizing a reaction of Me-I with

[$PtMe_2$(bpy)], where the cationic intermediate was detected by low-temperature NMR spectroscopy, found in scheme 1.6. The cationic intermediate was observed in polar solvents such as CD_3CN and acetone-d_6, with the oxidation step occurring along with coordination of solvent, to help contribute to the large negative entropy of activation. The solvent can then be displaced by the coordination of the anionic species formed, and the *trans*-species is formed due to the high *trans*-effect induced by the methyl ligand.[16]



Scheme 1.6: *Trans*-oxidative addition showing cationic intermediate (S = CD_3CN, acetone-d_6)

1.3.4 Formal One-Electron Oxidative Addition Pathways

Radical mechanisms that are involved in oxidative additions are less desired as they are usually less easily controlled. Issues tend to arise within these systems if there are subtle changes in the structure of the substrate, the complex or in impurities present within the reagent or solvents, leading to possible changes in the rate and the overall mechanism in which the reaction is being carried out.[13] Metal complexes that contain an odd number of *d* electrons, such as Co(II) and Rh(II), tend to act as suitable candidates for these radical type oxidative additions. This is not however to say that complexes with even number of *d* electrons cannot also react via the same radical mechanism, such as the often studied d^8 Vaska's complex.[5] There are two main proposed mechanisms that have been well investigated and are now distinguished as the nonchain and chain radical oxidative addition pathways.[13]

1.3.5 Free-Radical Nonchain Mechanism

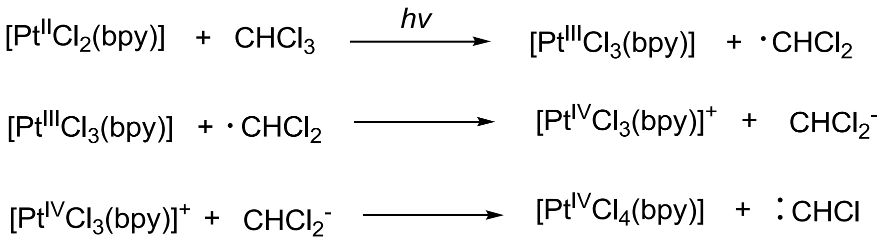
Typically the free-radical nonchain mechanism requires the presence of an alkyl halide (R-X) as the substrate. This mechanism operates by the coordination of the RX via a lone pair on the X, leading to a one electron transfer from the metal to the RX σ* orbital. This causes the formation of a pair of radicals, which recombine rapidly to form the desired product before either can escape the solvent cage, as depicted in Scheme 1.7.[13]

$$ML_2 \quad + \quad RX \xrightarrow{\text{slow}} \cdot MXL_2 \quad + \quad R\cdot \xrightarrow{\text{fast}} RMXL_2$$

Scheme 1.7: Free-radical non chain mechanism

In stark contrast to the S_N2 reaction pathways described in the above section, racemisation instead of inversion is found at the chiral carbon of the substrate. This select difference is the only change in the overall reaction, otherwise the oxidative addition products are the same. There are other features that classify this mechanism, including a bond reactivity of order R-I > R-Br > R-Cl, demonstrating the ability of R-X to be reduced by the metal. The reaction also tends to slow down upon X acting as a good leaving group and the reaction rate increases as the alkyl radical R, becomes more stable. The stability induced in this respect leads to an ordering of R group reactivity of tertiary > secondary > primary > Me[13,14]

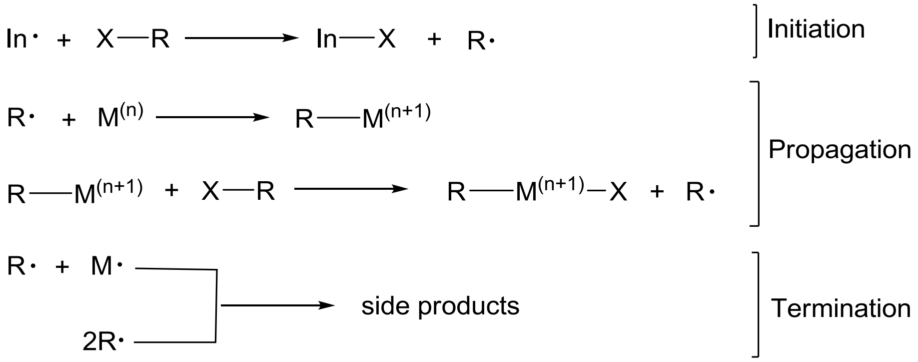
There is a great example illustrated in 1982 that demonstrates the nature of this one-electron, free-radical nonchain mechanism involving a platinum(II) complex. The reaction of [PtCl$_2$(bpy)] with CHCl$_3$ utilizing UV light, illustrates and supports the proposed mechanism for this process and has been shown in scheme 1.8.[17]



Scheme 1.8: Example of one-electron, free-radical nonchain mechanism

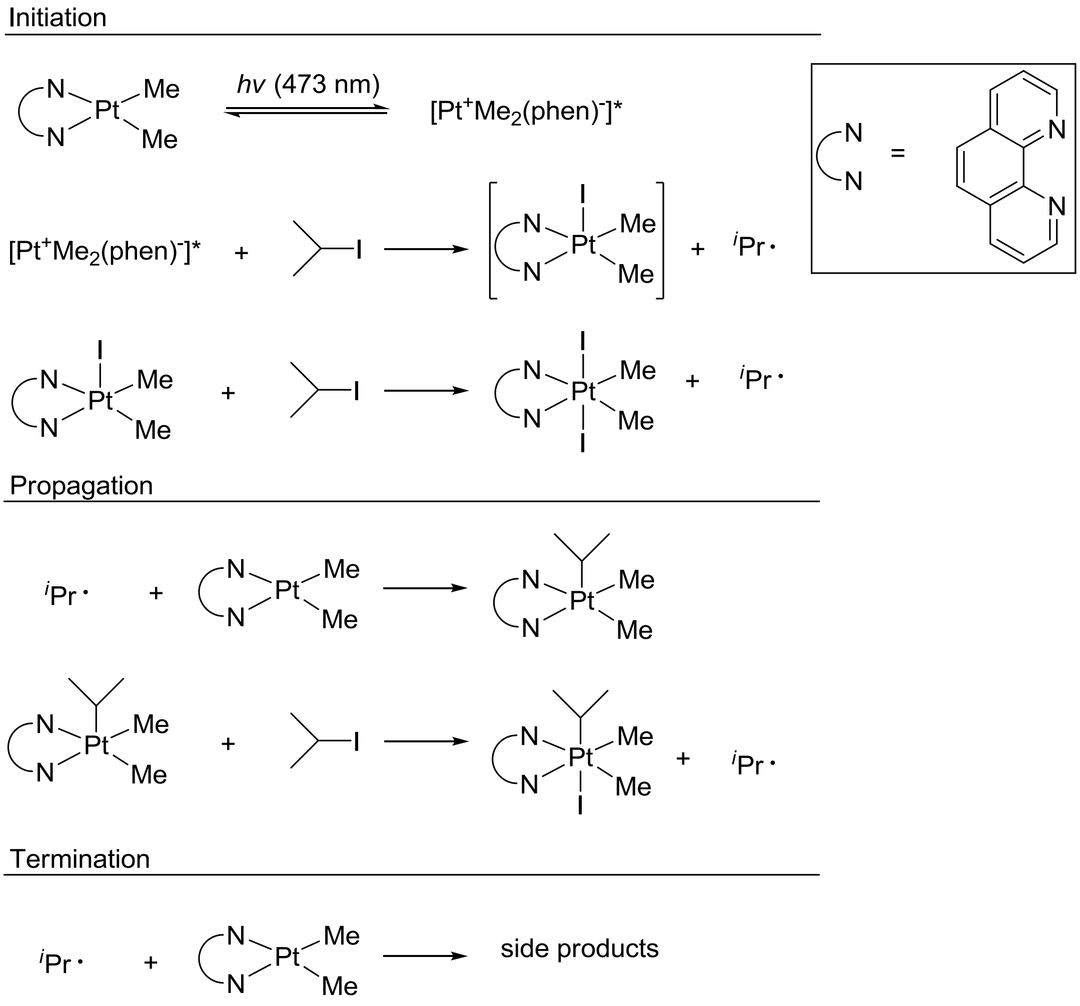
1.3.6 Free-Radical Chain Mechanism

Opposite the radical nonchain mechanism is another type of oxidative addition known as the free-radical chain mechanism. This radical chain mechanism also invokes the use of a organic halide (R-X) and typically involves an induction period, a number of atom-abstraction steps and a source of initiator radicals.[13] This type of mechanism can be initiated two ways. Formed radicals can escape the solvent cage without recombination or a radical initiator, In· (eg. trace of air) may be necessary to set the process in motion. A period of time occurs before the reaction starts, known as the induction period, which is then followed by propagation of the chain be a metal-centered radical abstracting X· from the halide, forming the carrier chain R·, which may react with itself to terminate the chain. This sequence is illustrated in scheme 1.9.[14]



Scheme 1.9: Free-Radical Chain Mechanism

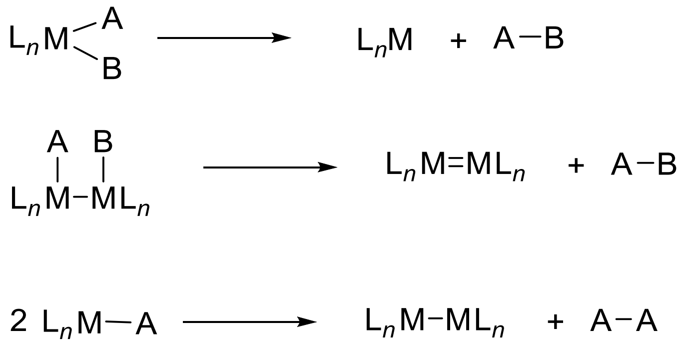
The radical chain pathway can be distinguished by observations of increased reaction rates by radical initiators (such as oxygen or peroxides) and the presence of UV light. This pathway also demonstrates a characteristic retardation of reaction rate upon introduction of radical inhibitors due to quenching of the chain carrier. Literature examples of this type of mechanism have been illustrated, one example being a kinetic study of the photochemically initiated oxidative addition of ^{i}PrI to [PtMe$_2$(phen)]. The reaction is initiated by photochemical MLCT to form the radical initiator [Pt$^+$Me$_2$(phen)]*, which has been utilized for the abstraction of an iodide atom from the isopropyl iodide, forming ^{i}Pr· radical acting as the chain carriers.[18]



Scheme 1.10: Photochemically initiated oxidative addition of ^{i}PrI to [PtMe$_2$(phen)]

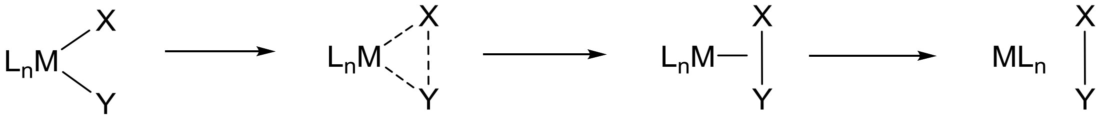
1.4 Reductive Elimination

Reductive elimination, the reverse of oxidative addition, involves the oxidation state, coordination number and electron count all decreasing by two units. This reaction has been demonstrated to be efficient for both d^8 metals Ni(II), Pd(II), and Au(III) and for d^6 metals Pt(IV), Pd(IV), Ir(III) and Rh(III). The elimination reaction is believed to be analogous to the concerted oxidative addition reaction as they are believed to be eliminated by a non-polar, non-radical three center transition state. Retention of stereochemistry is a key characteristic of this type of reduction reaction.[13] This reaction tends to occurs as a result of coupling from two covalent ligands at a single transition metal or two ligands from two different metal centers, shown in scheme 1.11.[19]



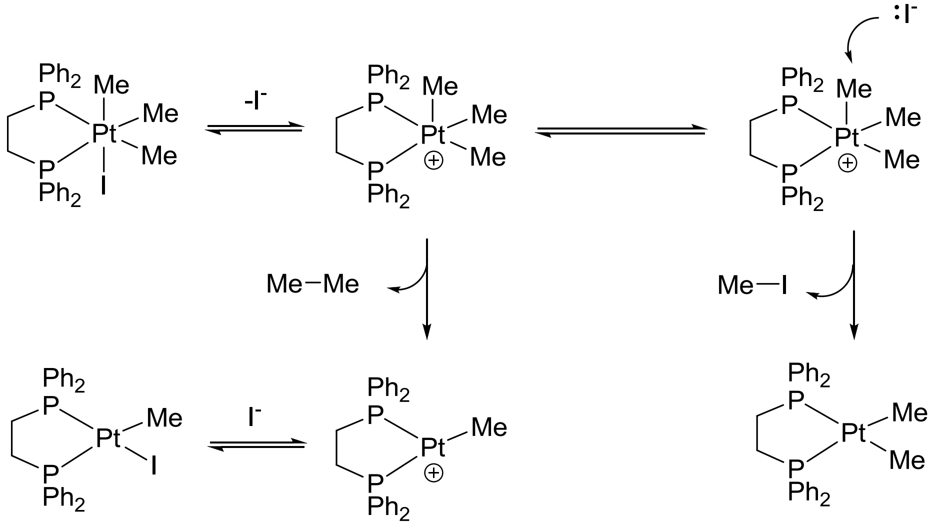
Scheme 1.11: Reductive elimination reactions of single and two metal centers

In most cases, at least those involving synthetically useful reductive elimination reactions, the reactions occur by a concerted three-centered process as outlined in scheme 1.12. This mechanism requires the two leaving groups be attached to the metal in a *cis*-nature and there is a retention of stereochemistry occurring at the leaving group atoms.[5]



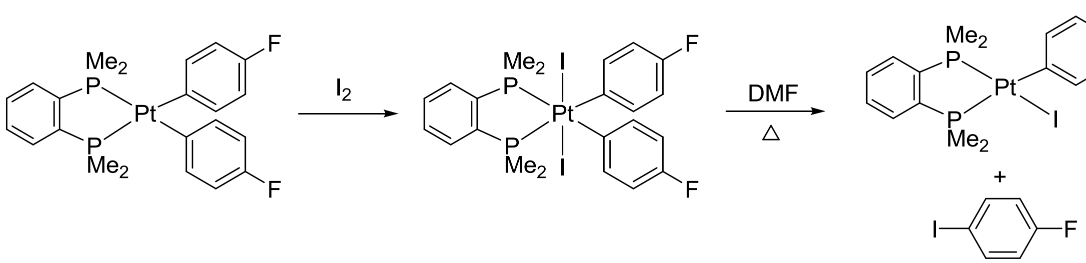
Scheme 1.12: Reductive elimination by a concerted three-centered process

When utilizing octahedral d^6 complexes such as Pt(IV), Pd(IV), Ir(III) and Rh(III), reductive elimination readily occurs with initial loss of a ligand to generate a 5-coordinate intermediate, which tends to be much more reactive than the former 6-coordinate species. Studies carried out involving the six coordination octahedral complex [$PtMe_3I(PPh_2$-CH_2-$PPh_2)$] has illustrated the reductive elimination of alkyl halides and has been illustrated in scheme 1.13. In this example, there is attack of the iodide at the coordinated methyl *trans* to the open side and displaces the platinum complex, which acts as a good leaving group. It has been shown that the reactive 5-coordiante intermediate can undergo concerted reductive elimination of ethane, when concentrations of I^- are low.[20]



Scheme 1.13: Mechanism for reductive elimination forming C-C and C-Hal bonds

More recently, a reductive elimination reaction has been reported involving a Pt(IV) species, bearing two aryl and two iodo ligands, with the iodo ligands being mutually trans to each other. In the presence of polar solvents, products of C-I reductive elimination were the result. The formation of a 5-coordinate intermediate was concluded with implications of stabilization of the transition state by the presence of the polar solvents. The reaction pathway has been illustrated in scheme 1.14.

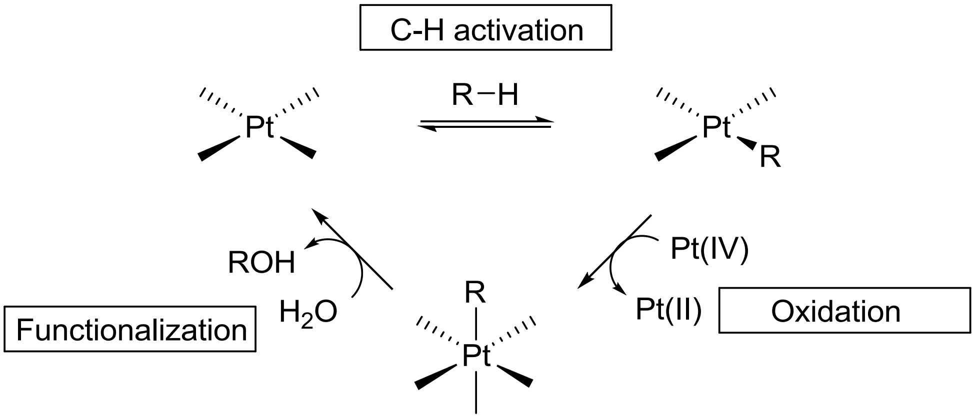


Scheme 1.14: Recent example of reductive elimination utilizing a Pt(IV) complex

1.5 Activation of Inert Bonds

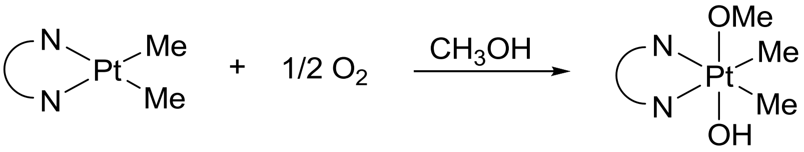
In recent years, there has been intense research into the selective functionalization of alkanes by transition metal complexes. The fact that hydrocarbons are the most abundant and least expensive chemical feedstock available, we need to find a way to make alkanes suitable starting materials for the chemical industry.[21] With this in mind it becomes obvious that transformations of saturated, as well as aromatic, olefinic, and acetylenic hydrocarbons, play an extremely vital role in contemporary chemistry. It is known that there is a chemical inertness associated with alkanes, as reflected by their old names, paraffins, from the Latin *parum affinis* (without affinity). New routes towards the synthesis from hydrocarbons to more valuable products such as alcohols, ketones, acids and peroxides are becoming of the utmost importance to the development of this area. The transformation of hydrocarbons by utilizing metal complexes seems to be a very promising field, especially when the complexes can act as catalysts. By utilizing metal catalysts, increase in reactivity of these generally inert molecules can be achieved by coordination to a metal center.[22]

Strong indications that platinum complexes act as viable sources of C-H bond activation have been prevalent since the early 1950 and 1960’s.[23] Research conducted by Shilov in the late 1960’s, involves the incorporation of aqueous platinum salts in the conversion of various hydrocarbons to their corresponding alcohols or alkyl chlorides, shown in scheme 1.15. The catalytic cycle is typically described in 3 steps; C-H activation, oxidation of Pt(II) to Pt(IV) and reductive elimination of the functionalized hydrocarbon.[24] The discovery by Shilov has attracted much interest aimed at the understanding and improvement of the catalytic system by the use of platinum complexes with a variety of ligands due to the mild reaction conditions and stability of these systems to air. It is the ultimate goal to find a system that operates efficiently under conditions that are not detrimental and involve the use of oxidation without costly platinum salts. This is plausible due to the fact the oxidation step is a an electron transfer rather than alkyl-group transfer.[23]



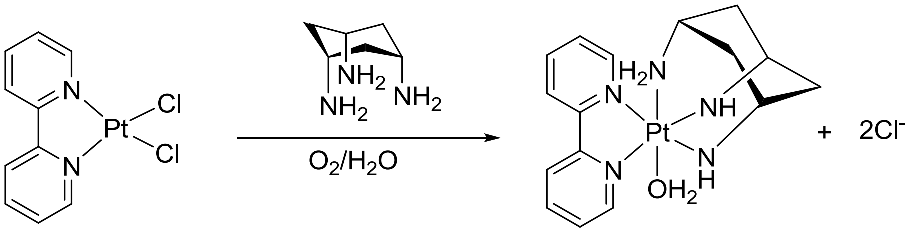
Scheme 1.15: Shilov's catalytic system

The need to replace expensive oxidants with relatively inexpensive and more practical materials is a desired avenue being pursued by researchers. It has been shown that molecular oxygen, O_2, is capable of being used as a suitable oxidant for the oxidation of platinum(II) complexes, shown in scheme 1.16.[25]

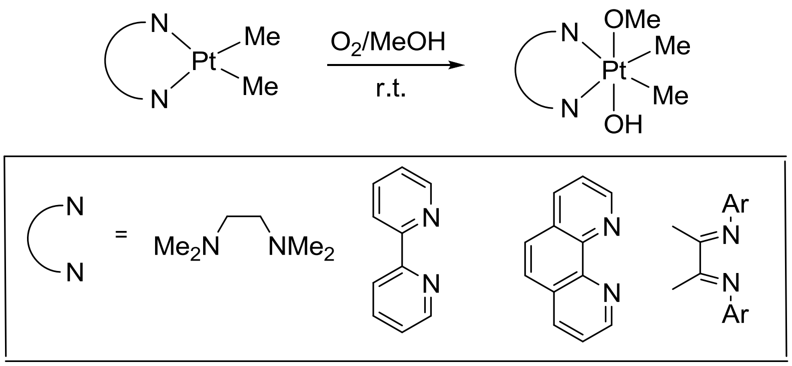


Scheme 1.16: Successful oxidation of platinum(II) complexes by O_2, under mild conditions

With these findings, it is possible to imagine a synthetic route in which the use of a platinum(II) complex is stabilized against reduction to platinum metal by strongly bound ligands and can be capable of activating alkanes to functionalized groups via O_2.[26] Recent articles have been published that shows oxidation by complexes containing O-O bonds in an attempt to replace the expensive platinum(IV) salts.[27,28,29] Some of the reactions of platinum(II) complexes have been illustrated below. Work by Sarneski et al.[30] in 1977, Wieghardt et al.[31] in 1983 and research by Bercaw, Labinger and Goldberg,[26,33] has lead to interest and development in the oxidation of platinum(II) complexes by the benign oxidant, O_2.



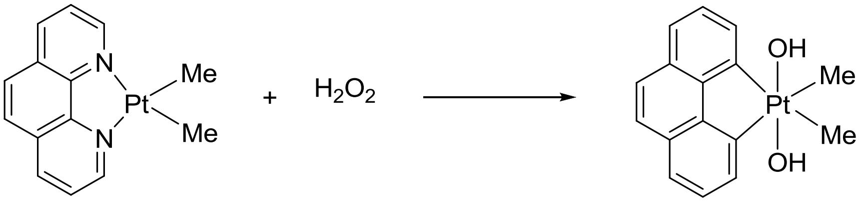
Scheme 1.17: Oxidation of a platinum complex by O_2.Sarneski et al. (1997)



Scheme 1.18: Oxidation of platinum by O_2. Bercaw, Labinger, Goldberg (1998-2002)

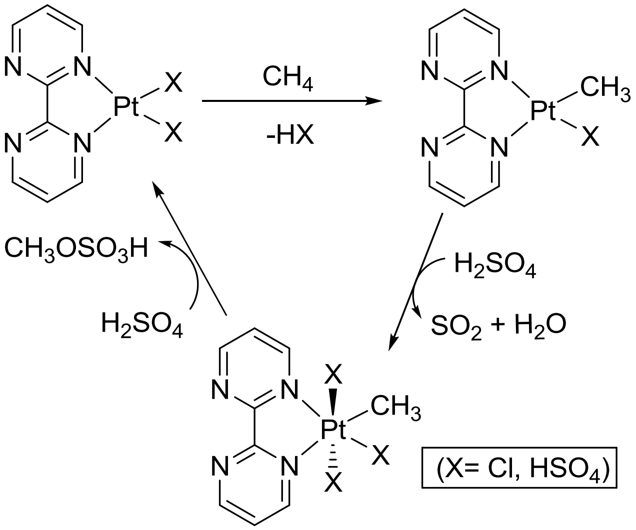
Along these lines there has been work published by Monaghan and Puddephatt, which illustrates the activation of alcohols and water through oxidative addition reactions via interactions with transition metal complexes. This paper involved the use of the complexes [$PtMe_2$(bpy)] and [$PtMe_2$(phen)] in reactions involving water and alcohols. The reactions showed very interesting results in which these were the first examples of oxidation of platinum(II) complexes by alcohols and gave the first stable alkoxoplatinum(IV) complex. $[PtMe_2(OR)(NN)(OH_2)]^+[OH]^-$, was formed through these reactions, with the R group dependent on which type of alcohol was being utilized, or in the case of water R=H.[33]

Oxidative addition chemistry has also been examined utilizing peroxides in the presence of platinum(II) species. Typically electron rich platinum(II) species are utilized containing nitrogen based ligands that act as good sources of electron donation towards the platinum center. It has been shown in studies by both Puddephatt et al. and Tilset et al. that reactions of platinum(II) speices with hydrogen peroxide typically lead to the formation of a single platinum(IV) species containing dihydroxy groups in a *trans*-arrangement.[34,35] One example can be seen for the oxidative addition of the O-O peroxo bond to the complex [$PtMe_2$(phen)], leading to the formation of [$PtMe_2(OH)_2$(phen)], as shown in scheme 1.19.[35]



Scheme 1.19: Example of an oxidative addition of hydrogen peroxide

Promise has been shown with Pt(II) complexes containing bidentate nitrogen donor ligands in the presence of a weakly coordinating solvent. One of the most successful proposals to date has been the oxidation of methane to methyl bisulphate by sulphuric acid, catalyzed by a platinum(II) complex, illustrated in scheme 1.20 It is found that the organometallic compound used in this system is remarkably stable under reactions conditions as the ligand is not oxidized, nor is platinum metal formed. The product formed is of little direct use but has the capabilities of being converted into more useful compounds, such as methanol.[36] This example provides insight into the potential for this type of chemistry in developing catalytic activation of an inert compound.



Scheme 1.20: Proposed mechanism for oxidation of methane by sulfuric acid, catalyzed by Pt(II)

1.6 Supramolecular Chemistry

Supramolecular chemistry may be defined as the chemistry of multicomponent molecular assemblies in which the individual structural units are held together by a variety of non-covalent interactions.[37] This field of supramolecular chemistry has been developed rapidly over recent years, since the seminal discovery by Lehn et al. and their new ideas of molecular recognition and host-guest chemistry added new dimensions to the field of intermolecular interactions.[38] Lehn's description of this supramolecular chemistry refers to the designed chemistry of the intermolecular bond and chemistry beyond the molecule and of the non covalent bond. [37]

This type of chemistry can also be referred to as host-guest chemistry, in which a molecule (host) binds another molecule (guest) producing a supermolecule. The host-guest relationship has been defined by Donald Cram as complexes that are composed of two or more molecules or ions held together by electrostatic forces such as hydrogen bonding, ion pairing, π-acid to π-base interactions, metal to ligand binding, and van der Waals attractive forces.[39] It is found that the relative inertness of organoplatinum complexes makes them viable candidates for secondary bonding interactions, such as hydrogen bonding and there has been formation of complex organometallic complexes using alkylplatinum compounds as building blocks. Recent examples involving platinum complexes and their ability to form supramolecular polymers through hydrogen bonding interactions of amides and carboxylic acids have been demonstrated.[40]

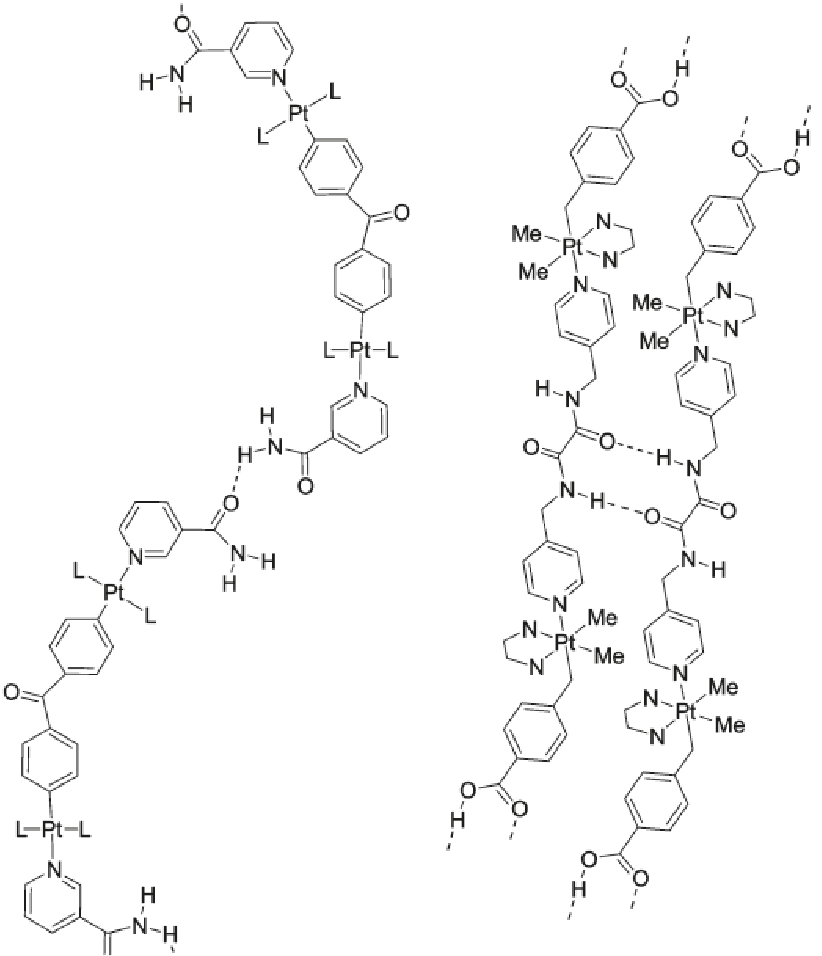


Figure 1.1: Supramolecular chemistry of platinum complexes

Hydrogen bonding interactions deserve special consideration as they are considered a unique type of electrostatic intermolecular interaction.[38] Pauling's description of the chemical bond was the first instance in which it was cited as an atom of hydrogen, under certain conditions being attracted by rather strong forces to two atoms instead of only one, thus acting as a bond between them.[41] A simple definition of this is that there is an attractive interaction between a proton donor and a proton acceptor. Pimentel and McClellan go on further to state that a hydrogen bond exists between a functional group (A-H) and an atom (B) when there is evidence of bond formation or that there is evidence that this new bond linking A-H and B specifically involves the hydrogen atom already bonded to A.[38] Hydrogen bonds are formed when the electronegetivity of A relative to H in an A-H covalent bond, withdraws electrons and leaves the proton partially unshielded, which can then interact with the acceptor B, which has lone pairs or polarziable π-electrons.[41] The usual convention for the representation of a hydrogen bond is denoted as A-H···B (A= donor, B= acceptor) and the length (D,*d*) and angles (θ,ϕ) for the hydrogen bond are described as such, illustrated in figure 1.2.[42]

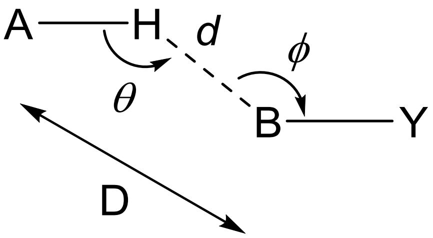


Figure 1.2: Hydrogen bonded bridge between A and B showing representation of lengths and angles

The most common hydrogen bond donor groups are C-H, N-H, O-H, S-H, P-H, F-H, Cl-H, Br-H and I-H, while the acceptor groups involved are commonly N, O, P, S, F, Cl, Br, I, alkenes, alkynes, aromatic π-clouds and transition metals. There are many common arrangements for hydrogen bonding that have been discovered and these are summarized in figure 1.3.[37] Along with the various arrangements for these hydrogen bonds, there are also various strengths of hydrogen bonding, which have been summarized in table 1.1.[41]

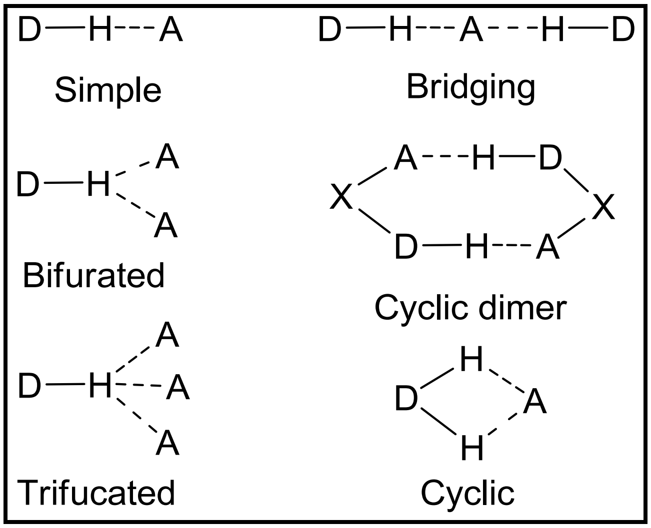
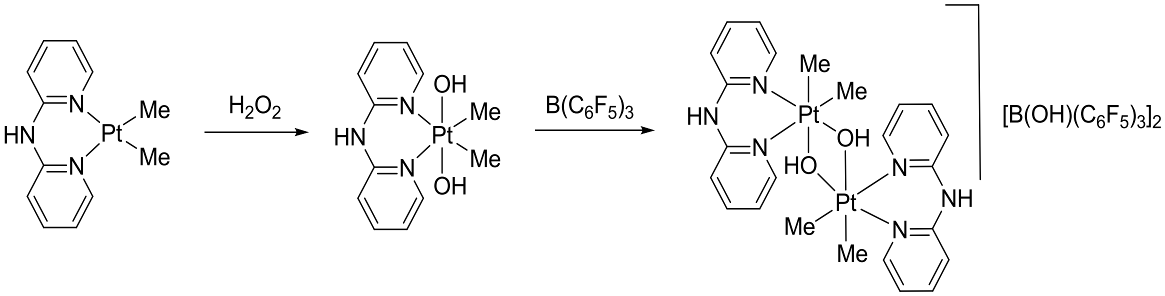


Figure 1.3: Common Arrangements for Hydrogen Bond Types

Table 1.1: Properties of strong, moderate and weak hydrogen bonds

	Strong	**Moderate**	**Weak**
A-H···B	Mostly covalent	Mostly electrostatic	Electrostatic
Bond Lengths	A-H ≈ B···H	A-H < B···H	A-H << B···H
H···B (Å) (d)	~ 1.2-1.5	~ 1.5-2.2	~ 2.2-3.2
A···B (Å) (D)	2.2-2.5	2.5-3.2	3.2-4.2
Bond Angles	175-180	130-180	90-150
Bond Energy (kcal/mol)	14-40	4-15	< 4
Examples	Acid salts	Alcohols	C-H···O/N bonds

A recent example has been published illustrating the use of hydrogen peroxide with a platinum(II) complex, forming an organometallic molecular material through self assembly by hydrogen bonding.[43] It has been found that $[Pt(OH)_2Me_2(dpa)]$ undergoes a remarkable form of self assembly through hydrogen bonding in the solid state, forming what appears to be the first organometallic zeolite. This new structure contains two bridging hydroxyl groups and two NH groups which have hydrogen bonding potential. The reaction is illustrated in scheme 1.21 and this has lead to the formation of a structure containing a network of hydrogen bonding interactions.



Scheme 1.21: Self Assembly to form a complex network structure, the first organometallic zeolite.

1.7 Peroxides

Compounds containing the O-O bond linkages act as key species in carrying out oxidation reactions.[44] The first synthesis of an organic peroxide was that of benzoyl peroxide reported by Brodie in 1858. Since that time, there has been synthesis and isolation of a large number of peroxo species. Today, organic peroxides are being utilized as initiators in the manufacturing of major polymers such as polyethylene, poly(vinyl) chloride, polystyrene and many others.[45] It has been found that the O_2 moiety in peroxides contains two more electrons than neutral dioxygen. These two additional electrons being placed in the π^*_{2p} molecular orbitals, results in a bonding order of one for the peroxo species and the formation of a diamagnetic species. The single bond character within peroxides is indicated by the longer bond length (1.49 Å) as well as the rotation barrier of the peroxide bond.[46] The bond energy within O-O bonds is 34 kcal/mol, which is much lower than any X-O or X-X bond where X is H, C, N or F. This can be explained in the case of the X-O bond by increasing ionic character with difference in electronegativities, and in the case of the X-X bond, where there is weakening of the bond due to lone pair-lone pair repulsion.[44]

The characteristic feature of all organic peroxides is the presence of the O-O bond, however they can be further classified by the number and type of functional group attached to the oxygen atoms. A variety of classes are established and illustrated in figure 1.4. The degree of reactivity of various peroxides tends to vary dependent upon the nature of the functional group attached to the O-O moiety. It has been found that peroxides with lower electron density on the O-O bond, generally act as stronger oxidants. It can be seen that the order of decreasing reactivity is peroxy acids > diacylperoxides > H_2O_2 or hydroperoxides > peroxy esters > dialkyl peroxides. Another factor that influences reactivity is degree of steric hinderence, where more hindered peroxides are non-reactive towards bulky substrates.[45,46]

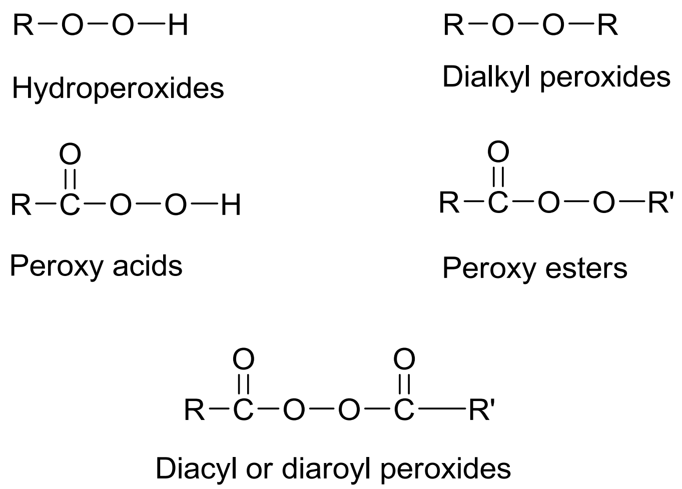


Figure 1.4: Structure and nomenclature of various organic peroxides

Organic peroxides are capable of undergoing numerous reaction pathways, depending on the reaction conditions of the individual reaction. Reaction pathways result typically from either homolytic or heterolytic cleavage of the O-O bond or redox reactions involving metal ions or other redox reagents.[39] Reactions of peroxides mediated by metals can be divided into two groups demonstrating different mechanisms. The first group involves a homolytic, one electron process, in which free radicals are intermediates. The second group involves heterolytic, two electron processes. The formation of a cation and an anion occurs in this scenario, with the more electronegative fragment taking on both electrons. These two types of reactions are illustrated in scheme 1.22.[47] Stabilization of the radicals tends to make homolysis reactions more favourable and also helps lower activation barriers for these reactions.

$$A{-}B \longrightarrow A^{\bullet} + B^{\bullet} \qquad \text{Homolysis}$$

$$A{-}B \longrightarrow A^{+} + B^{-} \qquad \text{Heterolysis}$$

Scheme 1.22: Homolysis and Heterolysis mechanism illustrated for A-B bonds

1.8 Research Objective

In today's society, there is an inherent need for the production of energy resources that will help to reduce the reliance on our current energy sources. Alkanes are the least expensive and most abundant hydrocarbon resource and represent great potential for the formation of petrochemically useful components.[21] Efficient and direct functionalization of hydrocarbons is one of the difficult obstacles facing chemists today. An approach to remedy this issue, involves the use of transition metals to help promote C-H bond activation, leading to the production of these desired functionalized hydrocarbons. Research conducted by Shilov in the late 1960's, involves the incorporation of aqueous platinum salts in the conversion of various hydrocarbons to their corresponding alcohols or alkyl chlorides. This research is focused on the oxidation of the platinum(II) complexes forming platinum(IV) oxidative addition producta. Previous research has illustrated promising results involving reactions of hydrogen peroxide with platinum(II) complexes leading to the formation of Pt(IV) oxidative addition products.[24] In an extension of these studies, the main goal of this research is to better understand the nature of the oxidation at a Pt(II) metal center by peroxides and peroxy acids.

Platinum(II) species containing bidentate nitrogen donor ligands have been chosen as suitable candidates for this project. These nitrogen donor ligands tend to demonstrate good σ donating/weak π accepting capabilities, leading to enhanced nucleophilicity of the metal center, which can be used to promote oxidative addition reactions.[14] A wide range of nitrogen-donor platinum(II) complexes were selected for this project and are illustrated in figure 1.5.

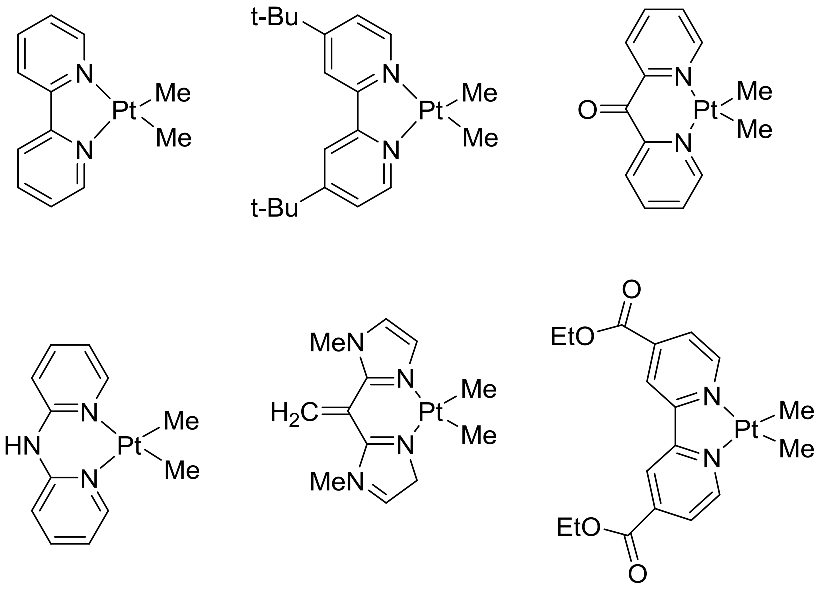


Figure 1.5: Platinum(II) bidentate nitrogen donor complexes

Encouraged by the idea that metal oxo-complexes are key intermediates in biological, homogeneous and heterogeneous catalytic processes.[14,48] Chapter 2 focuses on reactions of platinum(II) complexes with dimethyldioxirane (DMDO) and *meta*-chloroperbenozic acid (*m*-CPBA). Examples are rare for the formation of oxo-platinum complexes, but a recent example has been published in which there is formation of a oxoplatinum(IV) complex.[49] With this result, further study on platinum(II) complexes with DMDO and *m*-CPBA are carried out, resulting in the formation of platinum(IV) complexes via oxidative addition of these benign oxidants.

Chapter 3 focuses on the exploration of the reactivity of phthaloyl peroxide at platinum(II) centers. As opposed to non-cyclic peroxides, where after cleavage of the O-O bond, there exists two separate species, the connectedness of the phthaloyl peroxide group would lead to a relatively close proximity of the oxygen atoms, even after cleavage has occurred. The cyclic nature of this peroxide has shown to form both *cis*- and *trans*-oxidative addition products, converting platinum(II) complexes to platinum(IV) complexes. The structure of this peroxide has shown in some cases to favor the *cis*-oxidative addition products and this has been illustrated through X-ray structure analysis in this chapter.

Chapter 4 is concerned with the mechanism of oxidative addition. Since halogens tend to react in the same manner as these peroxide complexes to platinum(II) complexes, the mechanism of oxidative addition is attempting to be elucidated. Utilizing ^1H low temperature NMR spectroscopy, the detection of intermediates in the reaction of iodine with $[PtMe_2(bpy)]$ was carried out. The results indicate the formation of intermediate species held at low temperature and have been helpful in the determination of oxidative addition by halogen systems.

There are vital techniques that have been utilized that have helped distinguish and characterize the multiple products formed throughout this work. ^1H NMR spectroscopy had been particularly useful in the characterization of all complexes, in that ^1H and ^{195}Pt of spin active isotopes with abundance 100% and 33.7% respectively.[11] Mass spectrometry, elemental analysis and scanning electron microscopy (SEM) have all proved to be useful techniques in characterizing the elemental makeup of the products formed. Finally, single crystal X-ray diffraction was utilized in forming structures of some difficult to characterize complexes, giving confirmation of the complexes formed.

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Chapter 2

Reactivity of Platinum(II) Complexes with Dimethyldioxirane and *Meta*-chloroperbenzoic Acid

A version of some of the material in this chapter has been submitted; Pellarin, K.R.; McCready, M.S.; Puddephatt, R.J. *Organometallics*. **DOI:** 10.1021/om300616x.

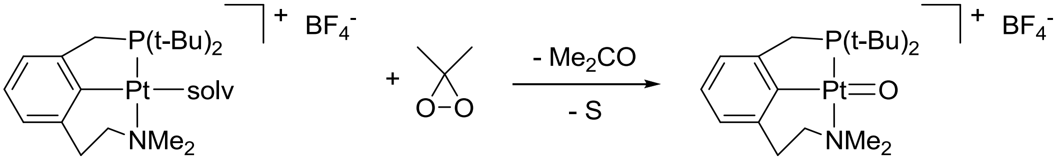
2.1 Introduction

The oxidative addition reaction represents one of the most fundamental processes in transition metal chemistry, involved in such processes such as synthesis and catalysis. Organoplatinum complexes have significant interest due to their capabilities to form a wide range of stable complexes, allowing their reactivity to be studied.[1] These two electron oxidation and reduction reactions involving platinum are successful due to the ability of platinum to transfer between three oxidation states (0, +2, and +4), with the oxidative addition processes dominating the reactions of the metal in its lower oxidation state.[2] Selective functionalization of alkanes has proven to be an attractive process, but it poses major hurdles for chemists to overcome. There has been some progress in this field made in the last decade. However, only few processes are known for oxidizing methane to more value-added products.[3,4]

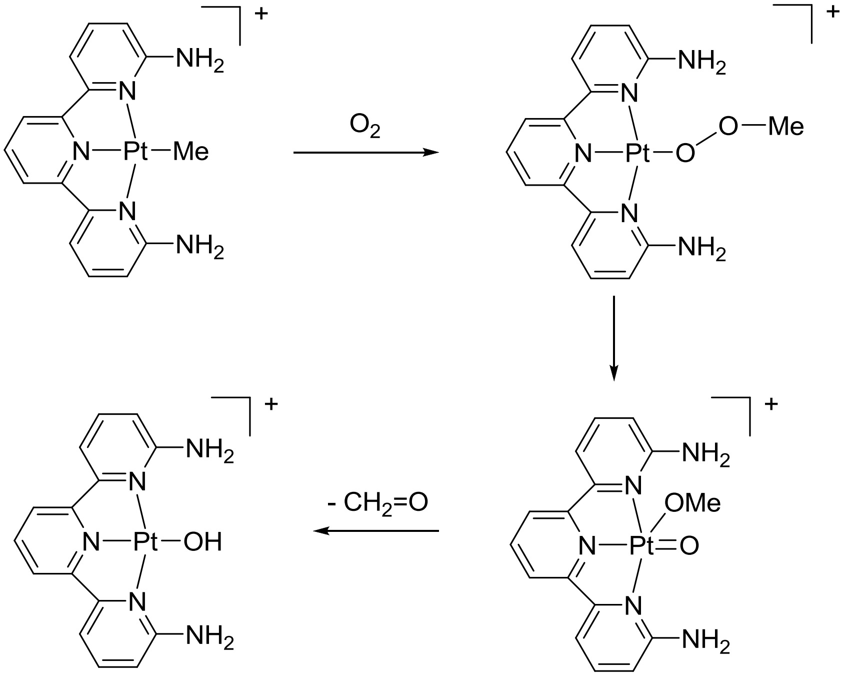
As discussed in section 1.5, the Shilov system represents one of the seminal discoveries in the functionalization of alkanes. It comprises aqueous platinum salts that can be used to convert hydrocarbons to their corresponding alcohols or alkyl halides.[3] It is significant as a proof of concept, but the process is inefficient due to the use of stoichiometric amounts of platinum(IV) oxidant, required for catalytic action to proceed.[5] With the issue in oxidant selection, there has been much interest in the replacement of the impractical platinum(IV) salts used in the original study. Research has been conducted utilizing alternatives, such as dioxygen,[6,7] chlorine,[8] and peroxydisulfate,[9] however all have proven to be ineffective due to low turnover numbers. Relevant to the oxidation step in the Shilov system, studies have been carried out utilizing environmentally friendly oxidants, O_2 and hydrogen peroxide with varying success.[3,10,11]

It is known that terminal metal oxo complexes are invoked as key intermediates in various biological, homogenous, and heterogeneous catalytic process in which oxygen atom transfer takes place, as well as oxygen activation or generation on transition metal surfaces. It has been discovered that terminal oxo-complexes of metals with no more than four *d* electrons are quite stable and common. Until recently, there had been few reports of late transition metal oxo-complexes with *d* electron counts above four.[12] This is due inpart to the instability these complexes have arising from π-antibonding, playing a critical role in these electron rich complexes.[13,14] The π* orbital becomes occupied in d^2 octahedral and d^4 square planar complexes, where reduction of the excess electron density by π-backdonation strengthens the transition metal oxo-bond.[15]

There are rare examples of d^6 transition metal oxo complexes as expected because theory predicts that M=O bonds cannot exist in octahedral metal complexes if the metal ion has a d^6 or higher electron configuration.[16,17,18,19] However, recently an oxoplatinum(IV) complex has been discovered and is illustrated in scheme 2.1.[16] Another example has been proposed utilizing dioxygen with [Pt(6,6'-diaminoterpyridine)Me][SbF_6], in which there is insertion of the dixoxygen into the methylplatinum bond. It has been theorized that there is formation of an intermediate platinum-oxo bond in oxidation reaction, as illustrated in scheme 2.2.[20] These results have lead to research into the possibility that oxoplatinum(IV) complexes may act as intermediates in the chemistry of platinum-catalyzed oxidation reactions. Platinum oxides, hydroxides and peroxides are considered important intermediates in other catalytic reactions and so there is general interest in the synthesis, structure and reactivity of complexes of these types.[12-20]

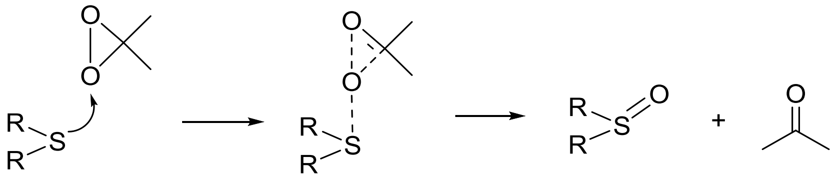


Scheme 2.1: Synthesis of the oxoplatinum(IV) complex (S = solvent).

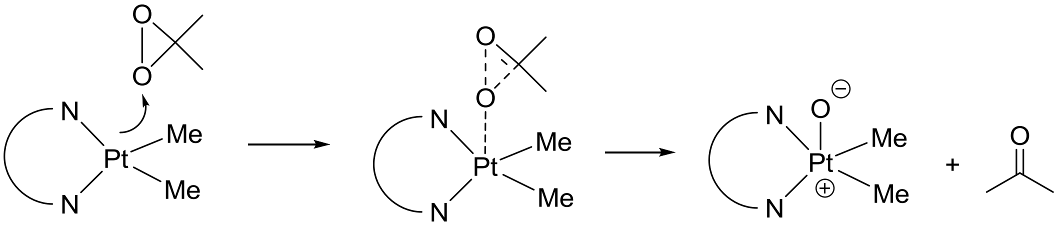


Scheme 2.2: Reaction of dioxygen with a platinum complex, showing possible oxoplatinum(IV) intermediate.

Dimethyldioxirane (DMDO) and *meta*-chloroperbenzoic acid (*m*-CPBA) are both utilized as very common oxidants, typically playing a role in oxidizing alkenes to epoxides, alcohols to aldehydes and ketones and a large variety of other reactions.[21] The reagents are considered equivalent in their reactivities, with DMDO being slightly favoured over the peroxyacid in many cases.[22] Dimethyldioxirane, in particular, has been of interest due to its capabilities as an ideal oxidant in efficient oxygen atom transfer, high chemo- and regioselectivity, mild reactivity towards substrates and can act catalytically.[23] It is noted that the characteristic and distinctive features of dioxiranes consists in their propensity for easy O-atom transfer to a variety of donor substrates and forming new double bond derivatives, as shown in scheme 2.3.[21] Based on this mechanism, it can be seen that the formation of an oxoplatinum(IV) complex may be formed as a reactive intermediate, as shown in scheme 2.4.



Scheme 2.3: General mechanism of oxidation of substrate (S) by DMDO



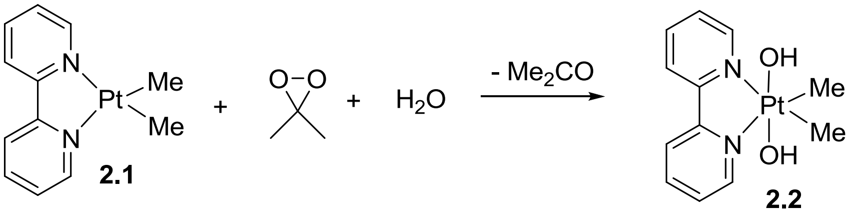
Scheme 2.4: Oxidation of a platinum(II) complex with DMDO, with the potential formation of an oxoplatinum(IV) complex (NN = chelating nitrogen-donor ligand).

Organoplatinum(II) complexes containing nitrogen-donor ligands are known to be very reactive in oxidative addition reactions.[1] The high reactivity exhibited by these types of complexes can prove to be of importance in the activation of normally inert chemical bonds.[24] Desired insight into the oxidation step of the Shilov system has lead this research in the direction of utilizing O-O bond containing species in the oxidation of various platinum(II) complexes. In this chapter, the various reactions of both DMDO and *m*-CPBA with platinum(II) species have been carried out. Starting with a simple bidentate nitrogen donor ligand, 2,2'-bipyridine, adding various groups to the bipyridine rings to vary their solubility as well as reactivity, and finally changing the chelate ring size and function for bonding, the oxidation reactions of these oxidants, DMDO and *m*-CPBA towards platinum(II) complexes have been studied.

2.2 Results and Discussion

2.2.1 Reaction of [PtMe$_2$(bpy)] with DMDO

The synthesis of complex **2.1**, [PtMe$_2$(bpy)] was previously reported and ^{1}H NMR data can be found in appendix **2.2.2**.[25] The synthesis of dimethyldioxirane was carried out by a variation of the procedure reported by Murray et al.[26] Complex **2.2**, [PtMe$_2$(OH)$_2$(bpy)] was prepared by a dropwise addition of DMDO to a stirring solution of [PtMe$_2$(bpy)] in acetone. Upon addition, the initial bright red colour of the platinum complex in solution dissipated, the solution gradually becoming clear and within seconds there was formation of a white precipitate. After isolating the product in *vacuo* and washing with pentane, complex **2.2** was obtained as a solid white powder, with the overall reaction illustrated in Scheme 2.5.



Scheme 2.5: Synthesis of complex **2.2**, by reaction of DMDO with [PtMe$_2$(bpy)].

The product was identical to the complex prepared by oxidation of [PtMe$_2$(bpy)] with H_2O_2 and this has been identified via ^{1}H NMR spectroscopy.[16] The ^{1}H NMR spectrum, indicates a clean reaction with the formation of only one *trans*-addition product as shown in figure 2.1.

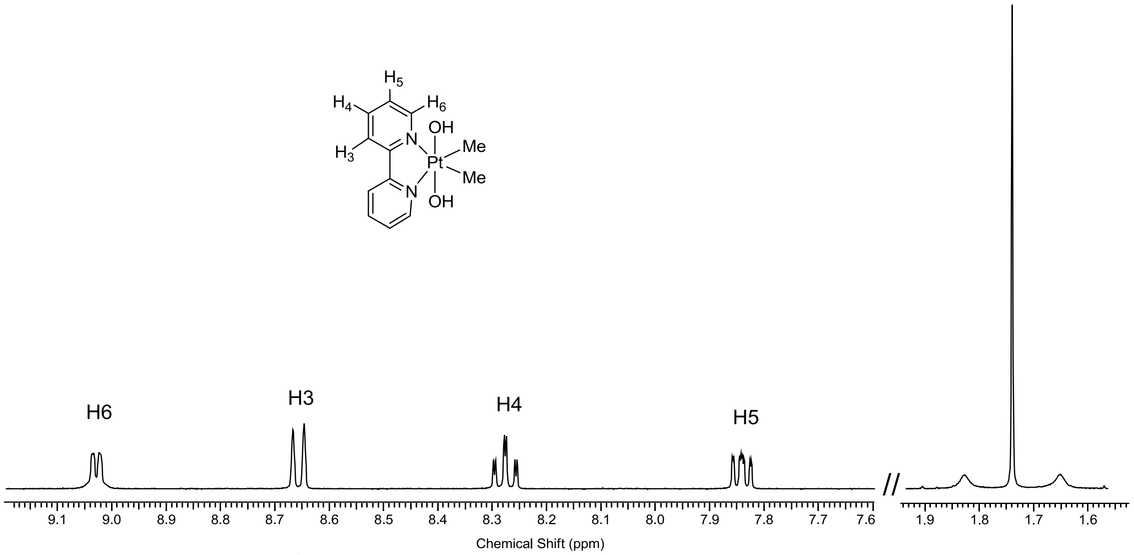


Figure 2.1: ^{1}H NMR spectrum of complex **2.2**, [PtMe$_2$(OH)$_2$(bpy)]

The ^{1}H NMR showed a single methyl platinum resonance at δ =1.74 ppm, with broad satellites indicative of proton coupling to the platinum center with coupling constant of ^2J(PtH) = 72 Hz, indicating the formation of a platinum(IV) octahedral complex, with methyl groups *trans* to nitrogen. The presence of only one methyl platinum resonance indicates that the complex is symmetric, which is only consistent with the formation of the *trans* product. The aromatic region exhibited only four resonances, with each peak integrating to two protons, providing further evidence of the *trans*-oxidative addition product.

Complex **2.2** has been previously prepared via reactions with of complex **2.1** with hydrogen peroxide,[28,29] but a crystal structure had never been obtained. Single, colourless crystals of complex **2.2** suitable for analysis were grown by a slow diffusion of pentane into a solution of complex **2.2** in dichloromethane. The single crystal X-ray structure supported the formation of the dihydroxyplatinum(IV) compound, as illustrated in Figure 2.2.

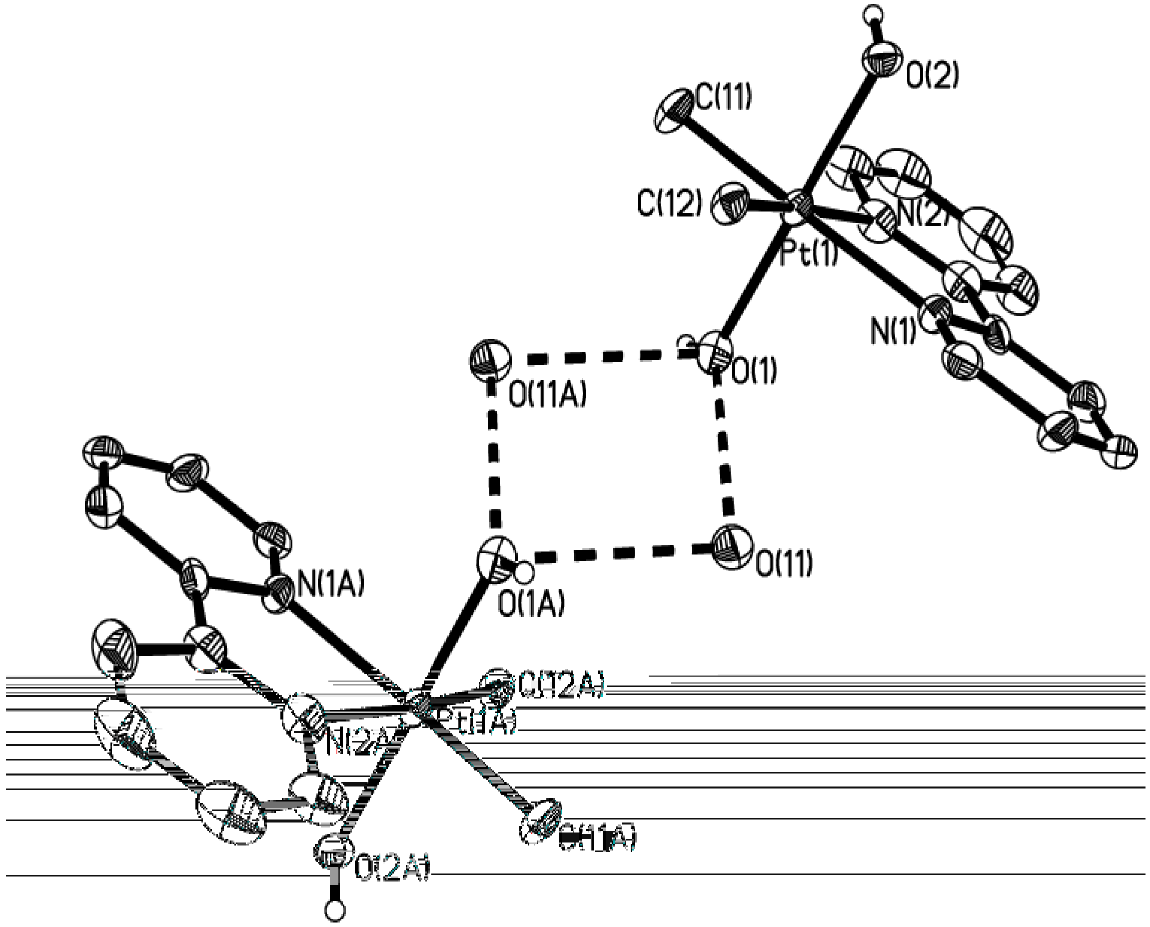


Figure 2.2: Crystal Structure of Complex **2.2**·7H_2O. Selected bond parameters; Bond parameters: Pt(1)-O(1) = 2.019(5), Pt(1)-O(2) = 2.031(5), O(1)-O(11) = 2.925(6).
]

Table 2.1: Bond lengths [Å] and angles [deg] for complex 2.2·7H_2O

Pt(1)-O(1)	2.019(5)	Pt(1)-N(2)	2.178(6)
Pt(1)-O(2)	2.031(5)	O(2)-H(30)	0.8400
Pt(1)-C(12)	2.036(7)	O(1)-H(29)	0.8400
Pt(1)-C(11)	2.045(7)	O(1)-O(11)	2.925(6)
Pt(1)-N(1)	2.170(5)		
O(1)-Pt(1)-O(2)	179.4(2)	C(11)-Pt(1)-N(1)	174.6(3)
O(1)-Pt(1)-C(12)	88.3(3)	O(1)-Pt(1)-N(2)	92.6(2)
O(2)-Pt(1)-C(12)	91.4(3)	O(2)-Pt(1)-N(2)	87.7(2)
O(1)-Pt(1)-C(11)	90.9(3)	C(12)-Pt(1)-N(2)	173.5(3)
O(2)-Pt(1)-C(11)	89.6(3)	C(11)-Pt(1)-N(2)	98.7(3)
C(12)-Pt(1)-C(11)	87.7(3)	N(1)-Pt(1)-N(2)	76.0(2)
O(1)-Pt(1)-N(1)	89.0(2)	Pt(1)-O(2)-H(30)	109.5
O(2)-Pt(1)-N(1)	90.5(2)	Pt(1)-O(1)-H(29)	109.5
C(12)-Pt(1)-N(1)	97.6(3)		

The presence of water in the dichloromethane solution seems to have aided in the stabilization and formation of single crystals for complex **2.2,** which crystallized as the hydrate $[Pt(OH)_2Me_2(bpy)]\cdot 7H_2O$, one of the most hydrated organometallic compounds known.[27] There are two non-equivalent platinum complexes in the structure and fourteen independent water molecules. The hydrogen bonds could not all be located in the structure determination and thus the nature of the hydrogen bonding is deduced from the position of the oxygen atoms. The bond distance between the hydroxyl oxygen and the solvating water molecules, O(1)-O(11) and symmetry equivalents, are in the region representing O-H···O hydrogen bond interaction which have been exemplified in previous literature, justifying the hydrogen bonding interactions of this system.[18] Some of the distances represent weak hydrogen bonds, but if all are counted, the propagation of this motif leads to the formation of a supramolecular double stranded polymer of Pt(1) molecules linked by bridging water molecules.

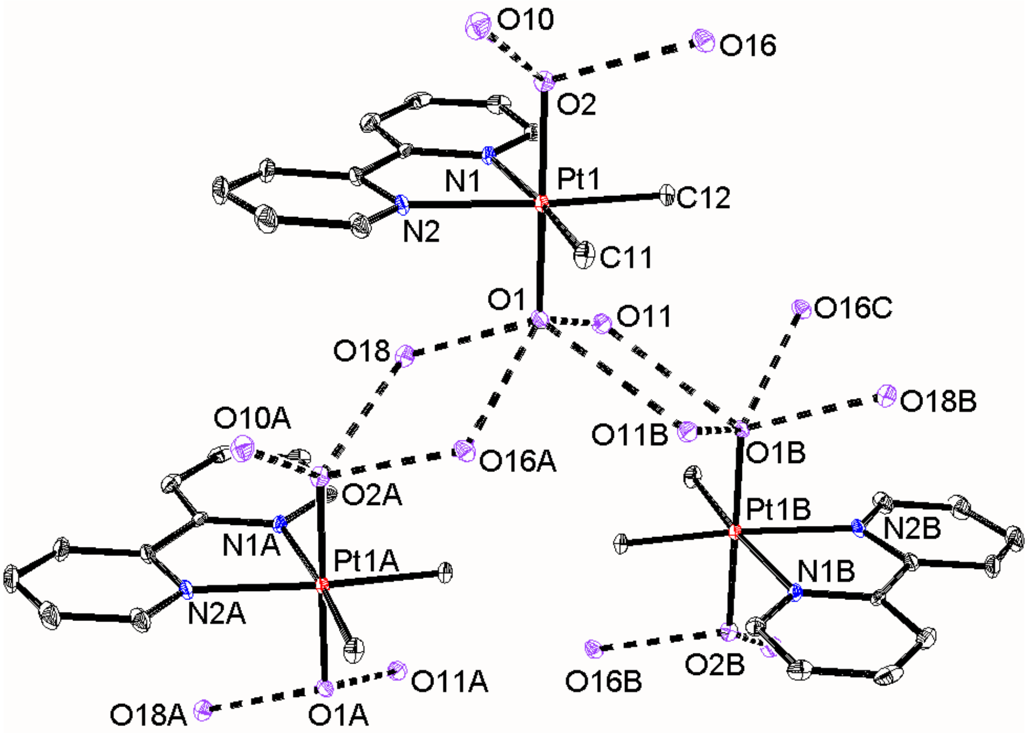
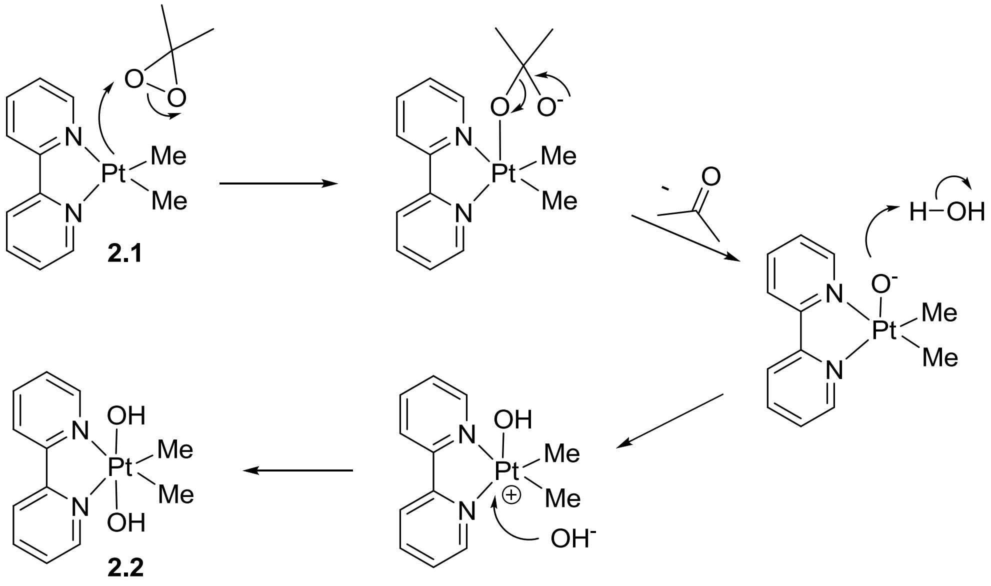


Figure 2.3: Supramolecular double stranded polymer of Pt(1) molecules linked by bridging water molecules.

With this X-ray structure, it can be verified that the dihydroxy-platinum(IV) complex was indeed the product formed, in the reaction of DMDO with complex **2.1**. The most likely mechanism of formation for complex **2.2**, would be a bimolecular S_N2 oxidative addition, resulting in the *trans*-oxidative addition product, which is illustrated in scheme 2.6.



Scheme 2.6: S_N2 mechanism of oxidative addition for the reaction of $[PtMe_2(bpy)]$ with DMDO and H_2O

2.2.2 Reactions of $[PtMe_2(bpy)]$ with *m*-CPBA

Meta-chloroperoxybenzoic acid is a widely used oxidant in organic chemistry due to the relative ease of handling of this peroxycarboxylic acid.[22] An NMR experiment was conducted, involving the addition of *m*-CPBA to complex **2.1**, $[PtMe_2(bpy)]$ in acetone-d_6, affording a cloudy white solution. ^1H NMR data found in shown in Figure 2.4 show the formation of a *cis*-product as a result of the oxidative addition process.

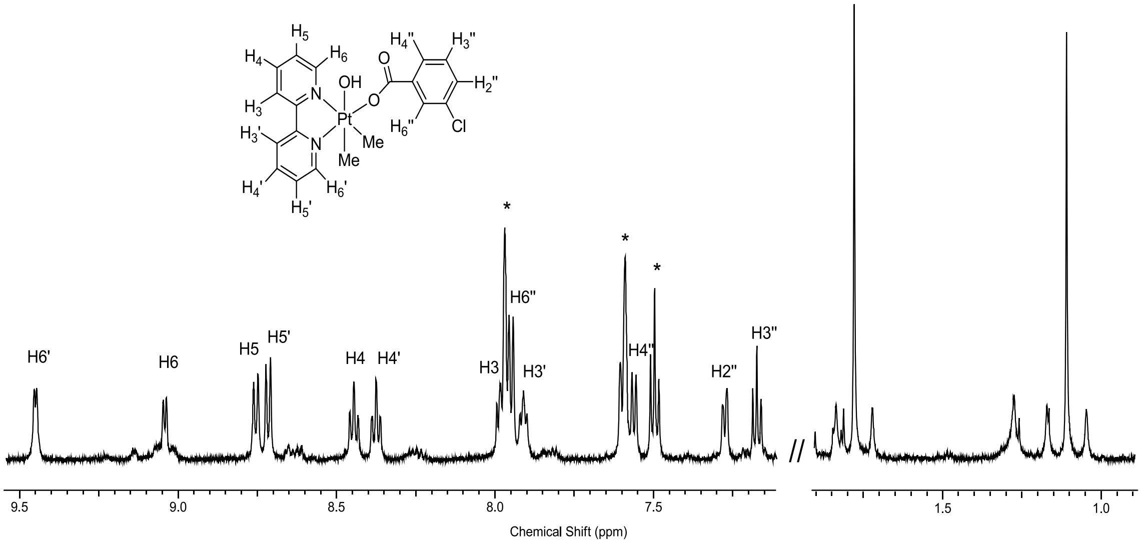
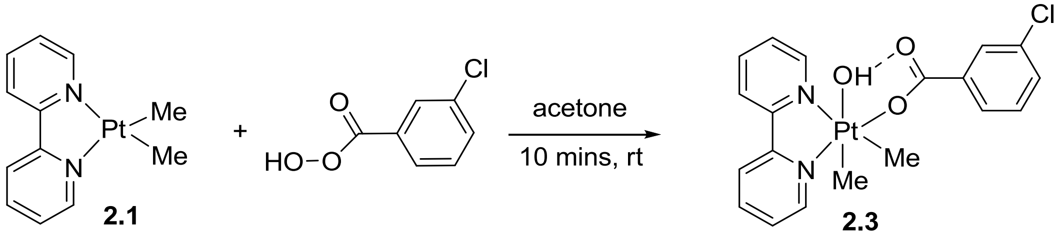


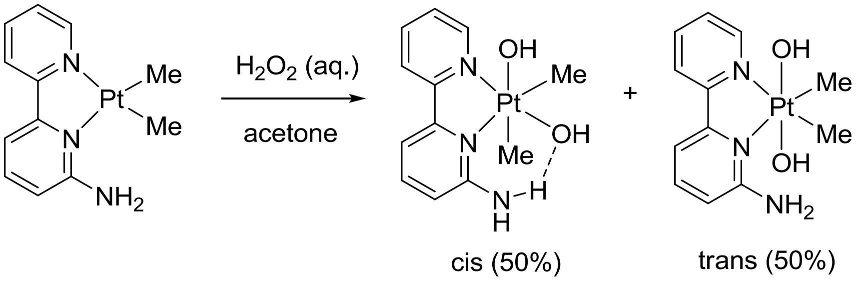
Figure 2.4: ^{1}H NMR spectrum of Complex **2.3**, *cis*-**[PtMe$_2$(OH)(C$_7$H$_4$O$_2$Cl)(bpy)]**. (* = free m-CPBA)

The loss of symmetry of this compound results in the presence of two methyl platinum peaks, one *trans* to the oxygen at δ = 1.12 ppm, with a coupling constant of ^2J(PtMe) = 75 Hz, and one *trans* to the nitrogen shifted further downfield at 1.80 ppm with a smaller coupling of ^2J(PtMe) = 69Hz. In the ^{1}H NMR spectrum, there are resonances from the 3-chlorobenzoate group shifted further upfield from those for free *m*-CPBA. This suggests that this 3-chlorobenzoate group, formed after the loss of the hydroxyl group, has been coordinated to the platinum center along with the hydroxyl group, forming a *cis*-oxidative addition product. With these results a proposed species of complex **2.3,** [PtMe$_2$(OH)(C$_7$H$_4$O$_2$Cl)(bpy)], is illustrated in scheme 2.7.



Scheme 2.7: Proposed *cis*-oxidation species of complex **2.3**, $[PtMe_2(OH)(C_7H_4O_2Cl)(bpy)]$

The reasoning for this proposed structure relies on the ability of the carbonyl group from 3-chlorobenzoate to hydrogen bond with the hydroxyl group on the platinum center driving the formation of this product. This lends itself towards allowing an oxidative addition reaction to take place in which the product is formed in the *cis*-geometry instead of the typical *trans* products seen for other peroxides.[6,9,25,28] Mass spectrometry results have helped in the determination, displaying a m/z ratio of 554.1g/mol which is indicative of the formation of the proposed species, complex **[2.3-H]**$^+$. Crystals of complex **2.3** suitable for X-ray analysis could not be grown, although many attempts were made. Although this result is unusual, it is not unprecedented as there has been literature reported in which there has been *cis*-directed oxidative addition of hydrogen peroxide through hydrogen bonding interactions, shown in scheme 2.8.[30]



Scheme 2.8: *Cis*-oxidative addition directed by hydrogen bonding.

It was found over time, that in the acetone-d_6 reaction mixture, a white precipitate began to form and settle to the bottom of the NMR tube. This lead to interest in whether this precipitate was the same as what was formed in complex **2.3** or a new complex. The reaction of *m*-CPBA and complex **2.1,** [PtMe$_2$(bpy)], was then carried out in acetone and on a larger scale. The two reactants were added and stirred for 10 minutes. The mixture was subsequently layered with pentane to afford a white precipitate. This product was washed and then dried *in vacuo*. The ^{1}H NMR data illustrated in figure 2.5, demonstrates the formation of a *trans*-oxidative addition product, of which a similar product has been reported by Tilset et al. however was never fully characterized.[17]

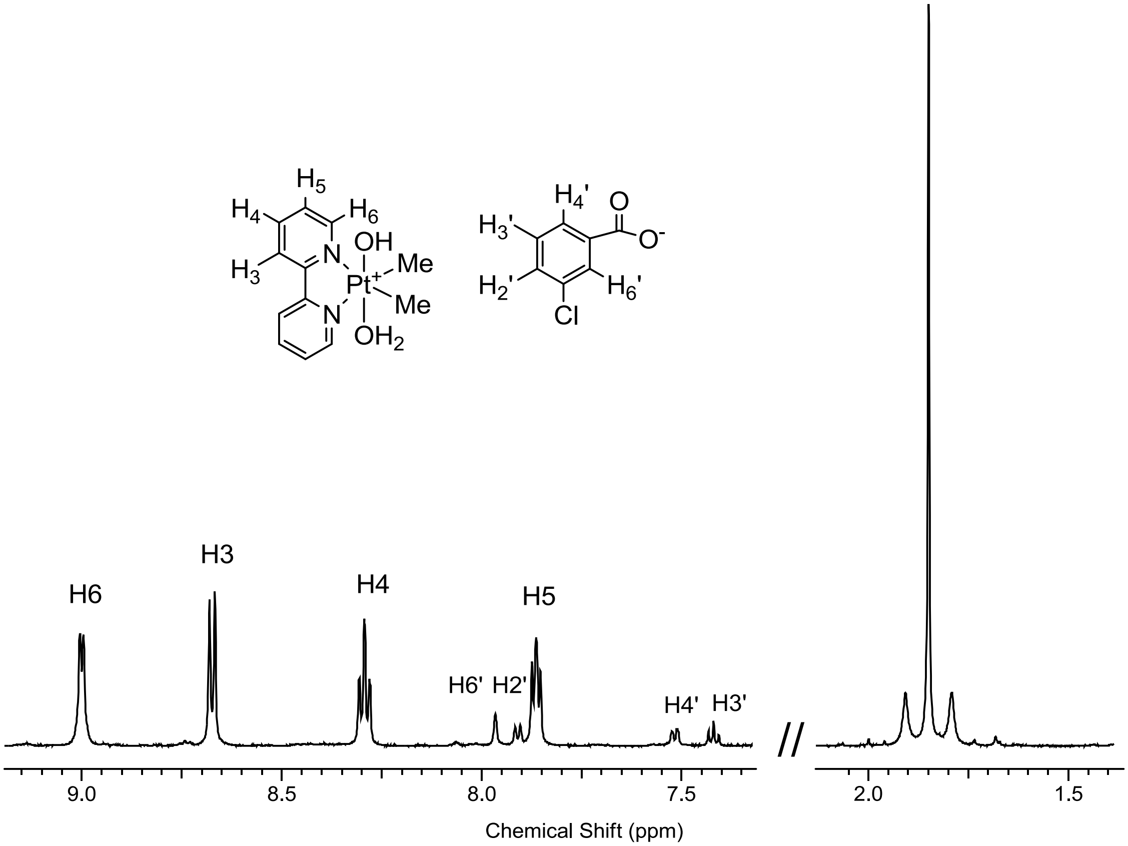
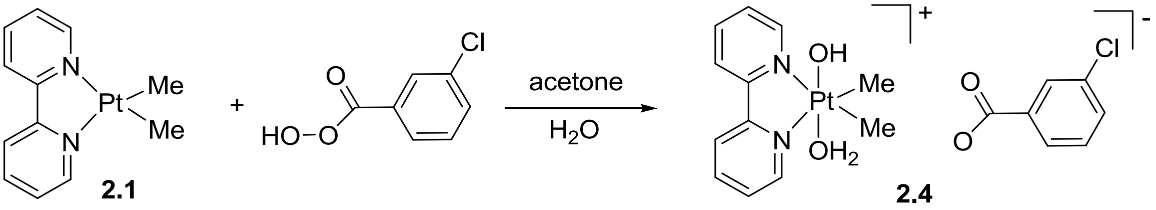


Figure 2.5: ^{1}H NMR spectrum of complex **2.4**, [PtMe$_2$(OH)(OH$_2$)(bpy)]$^+$[*m*-C$_6$H$_4$Cl(COO)]$^-$

The ^{1}H NMR spectrum illustrates the *trans*-addition product by the single methyl platinum resonance at 1.85 ppm with a coupling of $^2J(PtH) = 70Hz$, indicative of an octahedral Pt(IV) complex formed by *trans*-oxidative addition. The product has been washed vigorously, but the ^{1}H NMR spectrum still shows the presence of *m*-CPBA, with resonances ranging from 7.4-8.0 ppm, which are shifted from that of free *m*-CPBA. These results, coupled with the crystal structure data, allow for the determination of complex **2.4**, which has been illustrated in scheme 2.9.



Scheme 2.9: *Trans*-oxidative addition product of complex **2.4**, $[PtMe_2(OH)(OH_2)(bpy)]^+$ $[m\text{-}C_6H_4Cl(COO)]^-$

Single, clear, crystals suitable for X-ray analysis were grown by a slow diffusion of pentane into a dichloromethane solution of complex **2.4**. The results of single crystal X-ray analysis, with the structure illustrated in figure 2.6, indicates the formation of the proposed species.

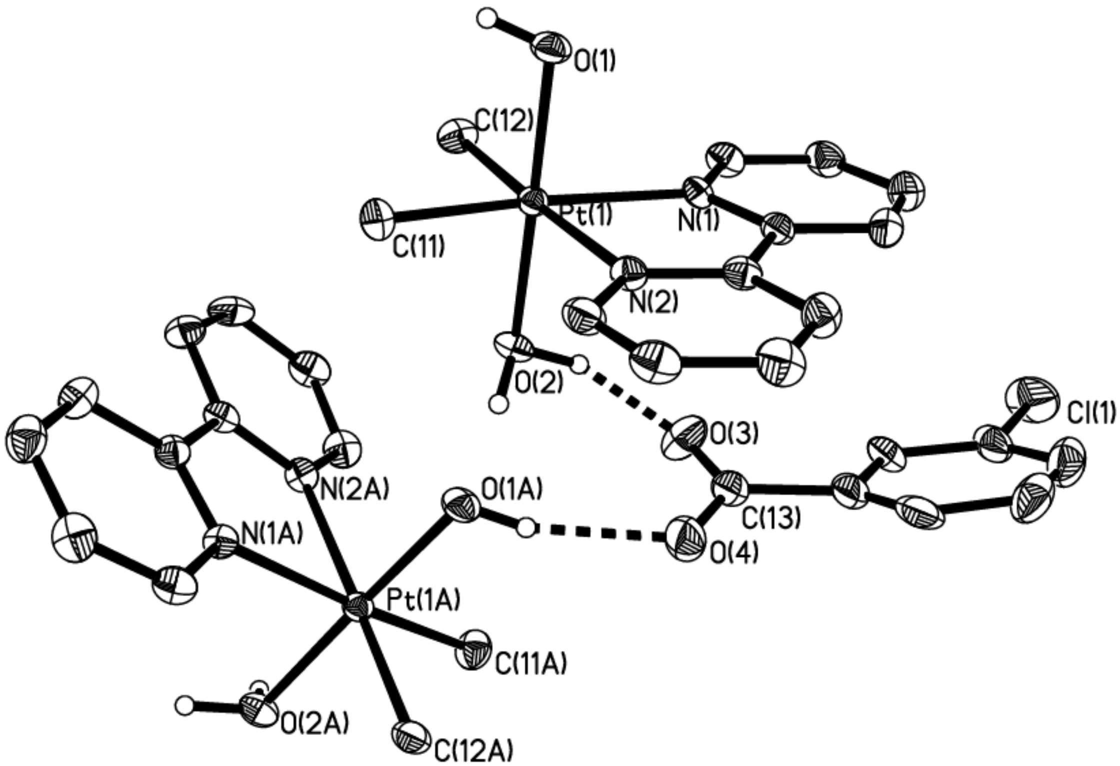


Figure 2.6: Crystal structure of Complex **2.4**, $[PtMe_2(OH)(OH_2)(bpy)]^+[m\text{-}C_6H_4Cl(COO)]^-$. Selected bond parameters: Pt(1)-O(1) = 2.001(4), Pt(1)-O(2): 2.041(4), O(3)-C(13) = 1.259(7), O(4)-C(13) = 1.247(7), O(2)-O(3) = 2.597(5), O(1A)-O(4) = 2.597(5), O(2)-O(1A) = 2.485(6) Å.

Table 2.2: Bond lengths [Å] and angles [deg] for complex 2.4.

Pt(1)-O(1)	2.001(4)	O(4)-C(13)	1.247(7)
Pt(1)-O(2)	2.041(4)	O(2)-H(25B)	0.9807
Pt(1)-C(12)	2.044(5)	O(2)-H(25C)	0.9830
Pt(1)-C(11)	2.048(5)	O(1)-H(1)	0.8400
Pt(1)-N(2)	2.168(4)	O(2)-O(3)	2.597(5)
Pt(1)-N(1)	2.169(4)	O(1)-O(4)	2.791(3)
O(3)-C(13)	1.259(7)	O(2)-O(1)	2.485(6)
O(4)-C(13)	1.247(7)		
O(1)-Pt(1)-O(2)	177.99(15)	C(12)-Pt(1)-N(2)	177.09(19)
O(1)-Pt(1)-C(12)	89.16(19)	C(11)-Pt(1)-N(2)	96.6(2)
O(2)-Pt(1)-C(12)	88.87(19)	O(1)-Pt(1)-N(1)	88.45(16)
O(1)-Pt(1)-C(11)	91.9(2)	O(2)-Pt(1)-N(1)	91.60(16)
O(2)-Pt(1)-C(11)	88.3(2)	C(12)-Pt(1)-N(1)	101.0(2)
C(12)-Pt(1)-C(11)	86.1(2)	C(11)-Pt(1)-N(1)	172.9(2)
O(1)-Pt(1)-N(2)	89.85(16)	N(2)-Pt(1)-N(1)	76.24(16)
O(2)-Pt(1)-N(2)	92.11(16)		

The single crystal X-ray analysis demonstrates the formation of complex **2.4**, illustrating interactions of the octahedral platinum(IV) complex with 3-chlorobenzoate anion which is formed by loss of the hydroxyl group. There appears to have been a transfer of the hydroxyl group of the *m*-CPBA, followed by uptake of water into the vacant site on the platinum center. There are also hydrogen bonding interactions shown between the hydroxo and aqua ligands of the newly formed platinum(IV) molecule with the 3-chlorobenzoate anion. The main problem in the determination of this structure is whether there are two hydroxyl groups on the platinum center and 3-chlorobenozoic acid or if a water molecule has coordinated to the platinum and the hydrogen bonded species is 3-chlorobenzoate. Comparison of bond lengths between C(13)-O(3) and C(13)-O(4), illustrates similar distances, which would suggest that this species exists as a carboxylate. This would suggest the formation of $[PtMe_2(OH)(OH_2)(bpy)]^+$ and $[m\text{-}C_6H_4Cl(COO)]^-$. There is also a strong hydrogen bonding interactions of type O-H···O, between O(1A)-

O(2) with bond distance of 2.485(6) Å, indicating that the third hydrogen is bridging between neighboring platinum complexes $[PtMe_2(OH)(OH_2)(bpy)]^+$. Complex **2.4**, also exhibits hydrogen bonding interactions between the ion pairs; from the hydroxo or aqua groups on the platinum center and the carboxylate group of the 3-chlorobenzoate. This is determined by the short bond distances between O(1)-O(4) and O(2)-O(3) of 2.791(3) and 2.597(5) Å, respectively, which fall within the range typically observed for hydrogen bonding interactions.[31] The hydrogen bonding interaction found between platinum complex and *m*-CPBA, leads to the formation of a polymeric species, as illustrated in figure 2.7.

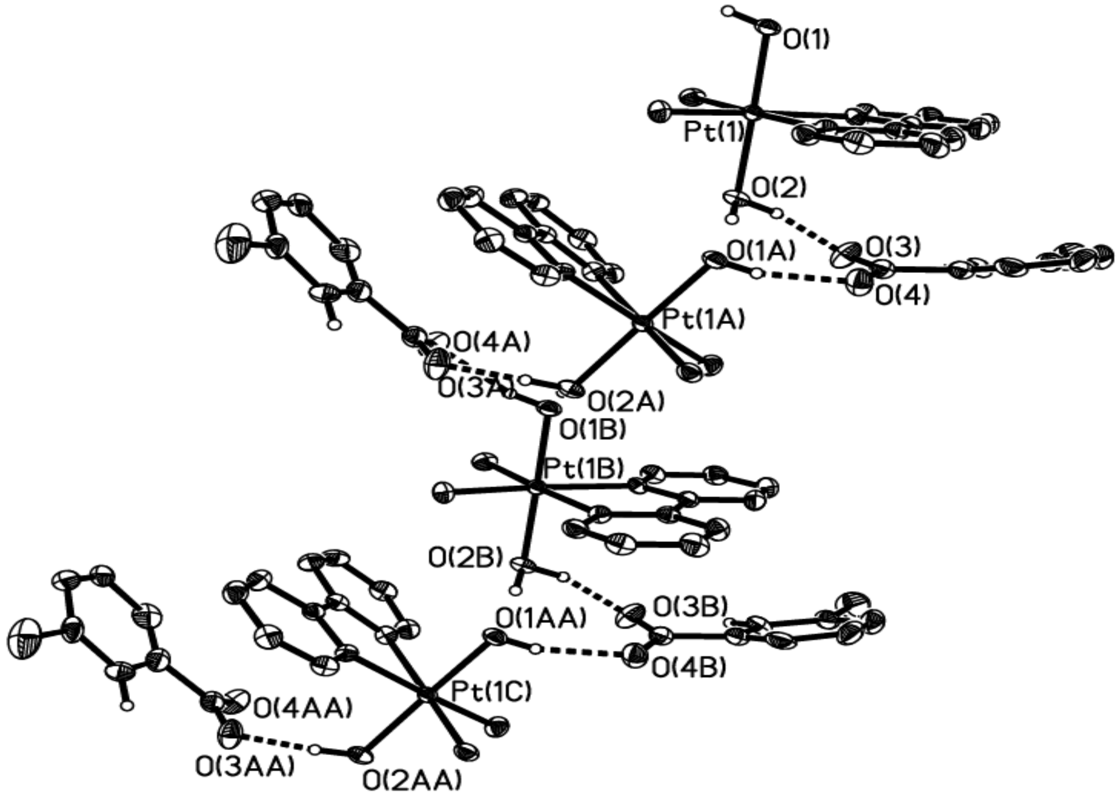
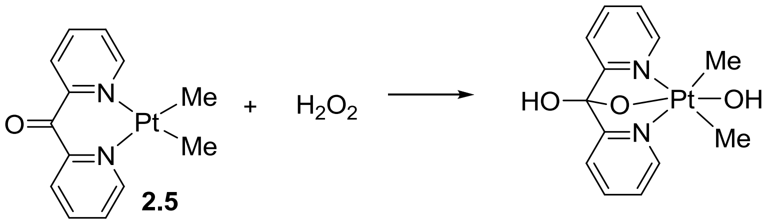


Figure 2.7: Polymeric species of $[PtMe_2(OH)(OH)_2(bpy)]^+$ and $[m\text{-}C_6H_4Cl(COO)]^-$ connected through hydrogen bonded interactions.

2.2.3 Reactions of 6-Membered Chelate Rings, [PtMe$_2$(dpk)] and [PtMe$_2$(dpa)] with Dimethyldioxirane

Following experimental results of Zhang et al.[24] utilizing hydrogen peroxide in reactions with the complex **2.5**, [PtMe$_2$(dpk)], a reaction with DMDO was carried out.



Scheme 2.10: Reaction of complex **2.5** with hydrogen peroxide.

Complex **2.5**, [PtMe$_2$(dpk)] was prepared according to the literature and ^{1}H NMR data can be found in Appendix 2.2.3.[32] To a stirring solution of [PtMe$_2$(dpk)] in acetone was added DMDO until the inital red colour disappeared and the product was immediately bleached. A precipitate formed within the reaction mixture and this was isolated and characterized by ^{1}H NMR spectroscopy, which is illustrated in figure 2.8.

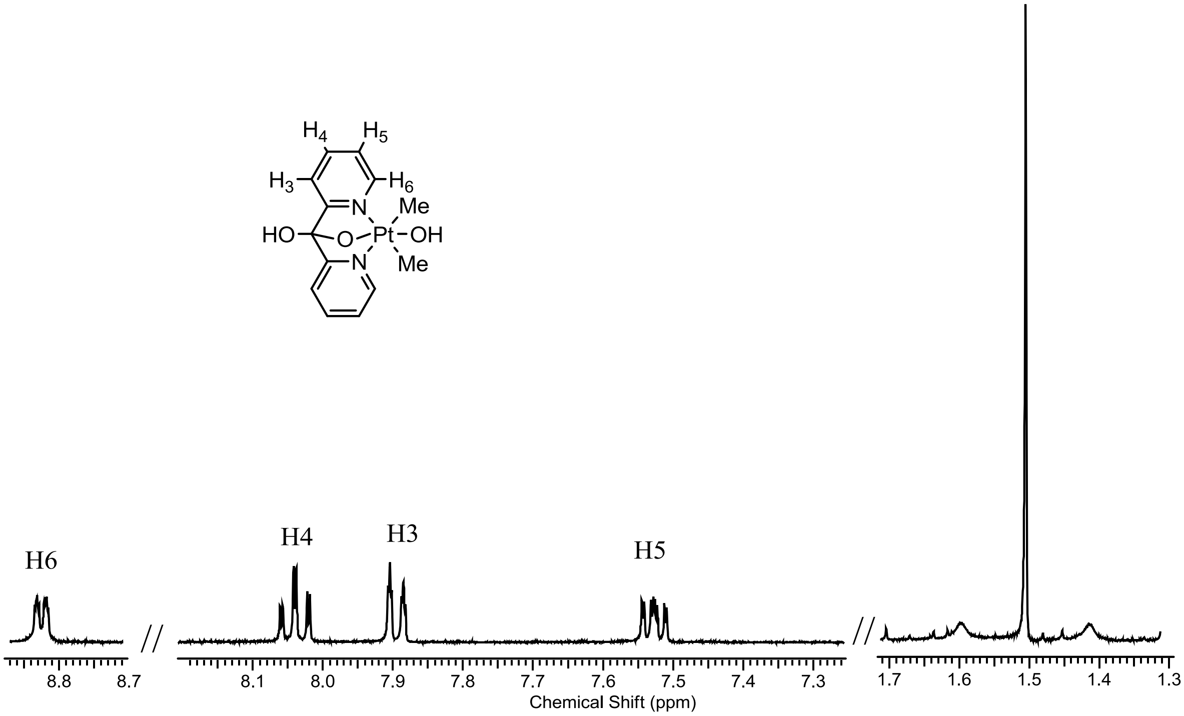
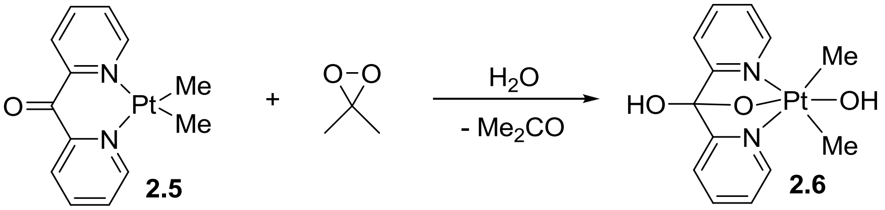


Figure 2.8: ^1H NMR spectrum of complex **2.6**, [Pt(OH)Me_2(dpkOH)]

The results of the ^1H NMR illustrate the formation of a clean product, showing a single platinum(IV) species based on the single resonance representing the six methyl protons on the platinum center with coupling of ^2J(PtH) = 73 Hz. The aromatic region of the spectrum is easy to distinguish as there are only four resonances representing the eight aromatic protons from the bipyridyl ring system, representing symmetry within this molecule. When comparing these results to that of the results obtained by Zhang et al.[32] it can be seen that this spectrum is identical except for the fact that the peaks in the spectra are slightly shifted upfield due to solvent effects. It can be said definitively that the product formed in this reaction is complex **2.6**, [Pt(OH)Me_2(dpkOH)], forming a platinum(IV) involving a *fac*-tridentate ligand with the reaction illustrated in scheme 2.11.



Scheme 2.11: Synthesis of complex **2.6**, [Pt(OH)Me_2(dpkOH)]

Furthering the study of six-coordinate platinum(II) complexes, complex **2.7**, [PtMe_2(dpa)] was synthesized according to the literature and ^{1}H NMR data can be found in Appendix 2.2.4.[33] Carrying out a reaction similar to all other platinum(II) complexes, the use of DMDO in a reaction with complex **2.7**, was completed, however the results were not as conclusive as seen with the other platinum(II) species previously discussed. Typically in these reactions, a stoichiometric volume of DMDO is difficult to measure as the exact concentration of the DMDO solution is hard to determine. For previous reactions, reliance on the bleaching of the acetone solution forming a clear or white mixture is typically how to gauge the end point of this reaction. Initially, DMDO was added dropwise to a stirring solution of complex **2.7**, [PtMe_2(dpa)], however there appeared to be very little change from the yellow solution even with a large amount of DMDO being added. In a final attempt to gather information about this product a large excess of DMDO was added to a stirring solution of [PtMe_2(dpa)], the product was purified leaving an orange-brown solid. The product complex **2.8**, [PtMe_2(dpa)$(OH)_2$] was characterized by ^{1}H NMR spectroscopy which is illustrated in figure 2.9.

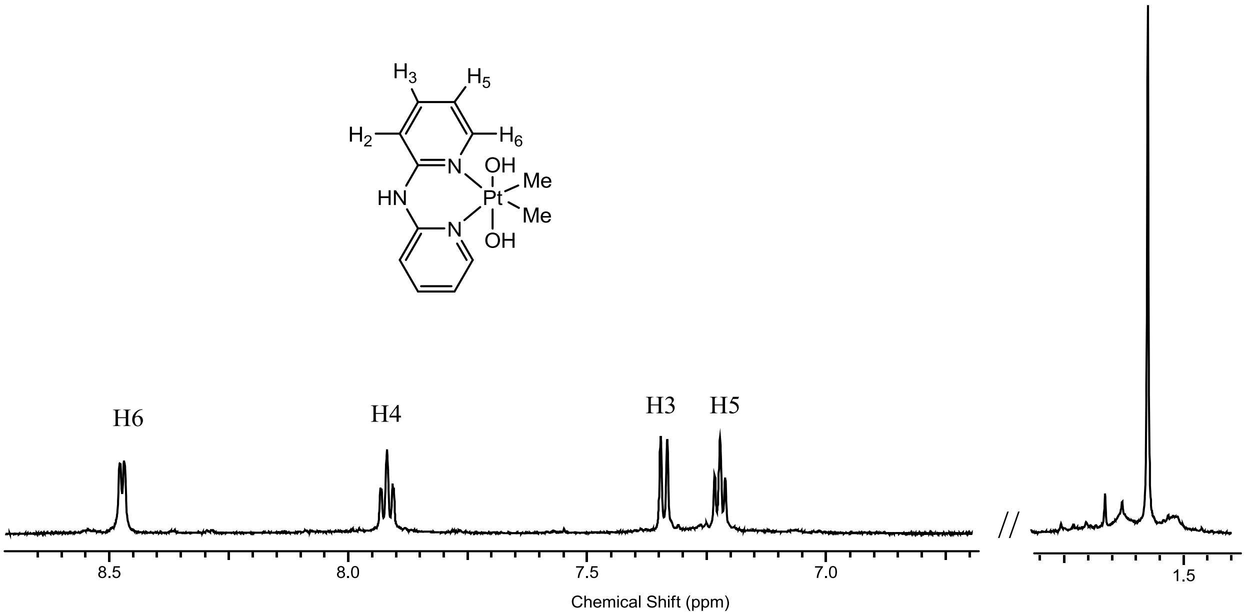
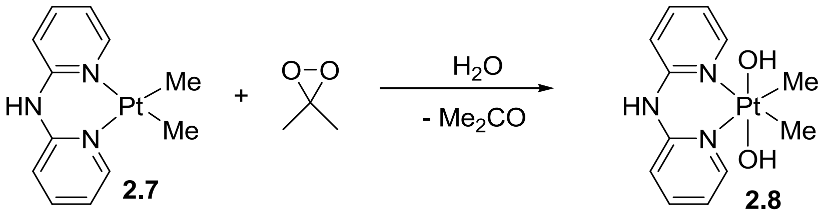


Figure 2.9: ^{1}H NMR spectrum of complex **2.8**, [PtMe$_2$(dpa)(OH)$_2$)]

The ^{1}H NMR spectrum shows the formation of a single platinum complex, with evidence of the formation of a *trans*-oxidative addition product. There is a single methyl platinum resonance located at δ = 1.54 ppm with a coupling of ^2J(Pt-H) = 64 Hz, indicative of the formation of a platinum(IV) species. The aromatic region of this spectrum supports the formation of the product by *trans*-oxidative addition, in that there are only four signals representing the eight bipyridyl protons, demonstrating the symmetry within this molecule. Mass spectrometry data help support the claims of the formation of a complex **2.8**, [PtMe$_2$(dpa)(OH)$_2$], with most prominent peak at 431.1 m/z which represents the formation of complex [**2.8**-H]$^+$. The overall reaction is clean and has been illustrated in scheme 2.12.



Scheme 2.12: Synthesis of complex **2.8**, [$PtMe_2$(dpa)$(OH)_2$]

2.2.4 Reactions of 6-Membered Chelate Rings, [$PtMe_2$(dpk)] and [$PtMe_2$(dpa)] with *m*-CPBA

The oxidation capabilities of *m*-CPBA towards complex **2.5**, [$PtMe_2$(dpk)] were then studied to determine if similar complexes as formed with H_2O_2 would be obtained.[32,33] To a stirring solution of [$PtMe_2$(dpk)] in acetone was added a 1:1 stoichometric amount of *m*-CPBA. The reaction mixture immediately lost its red colour, turning white, with the formation of a precipitate. The product was then purified and characterized by ^1H NMR spectroscopy as shown in figure 2.10.

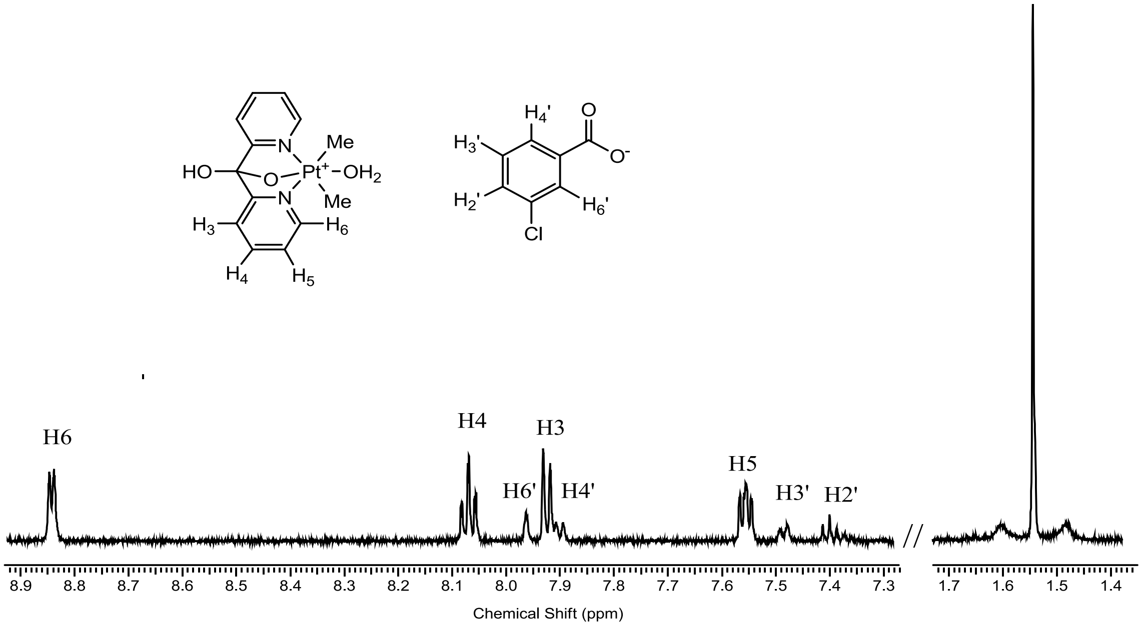
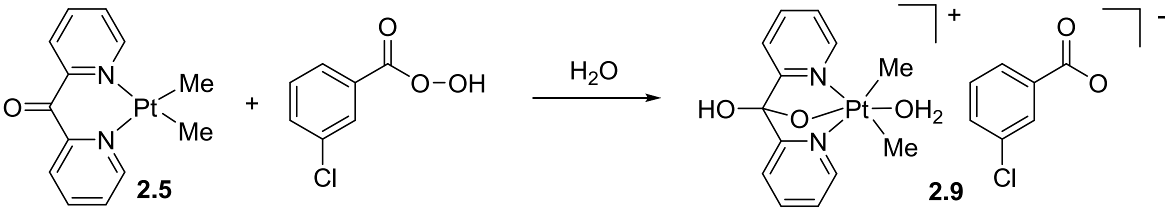


Figure 2.10: ^1H NMR spectrum of complex **2.9**, [$PtMe_2(OH_2)$(dpkOH)]$^+$[*m*-$C_6H_4Cl(COOH)$]$^-$

The ^1H NMR spectrum shows that a *trans*-oxidative addition species has been formed. The single methyl platinum resonance at δ = 1.54 ppm with a coupling of ^2J(Pt-H) = 70 Hz, represents the formation of a platinum(IV) species. Further downfield in this spectrum, it can be seen that there are four resonances representing the eight protons on the bipyridyl rings, thus showing the symmetry of this molecule. Also present within this spectra are signals corresponding to the aromatic ring of the *m*-CPBA, which is similar to that seen in the spectra of complex **2.3**. With this product being purified, this suggests that this is not just residual *m*-CPBA from the reaction mixture, but is coordinated to the platinum(IV) species, most likely as seen in the previous examples, through hydrogen bonding interactions. With this knowledge the proposed reaction equation can be illustrated in scheme 2.13, in the formation of complex **2.9**.



Scheme 2.13: Formation of complex **2.9**, $[PtMe_2(OH_2)(dpkOH)]^+[m\text{-}C_6H_4Cl(COO)]^-$.

Further clarification was necessary and to this end, a single crystal was grown by vapour diffusion of pentane into a 90:10 mixture of chlorobenzene and methanol, in which complex **2.9** was dissolved. The X-ray structure of this product is illustrated in figure 2.11.

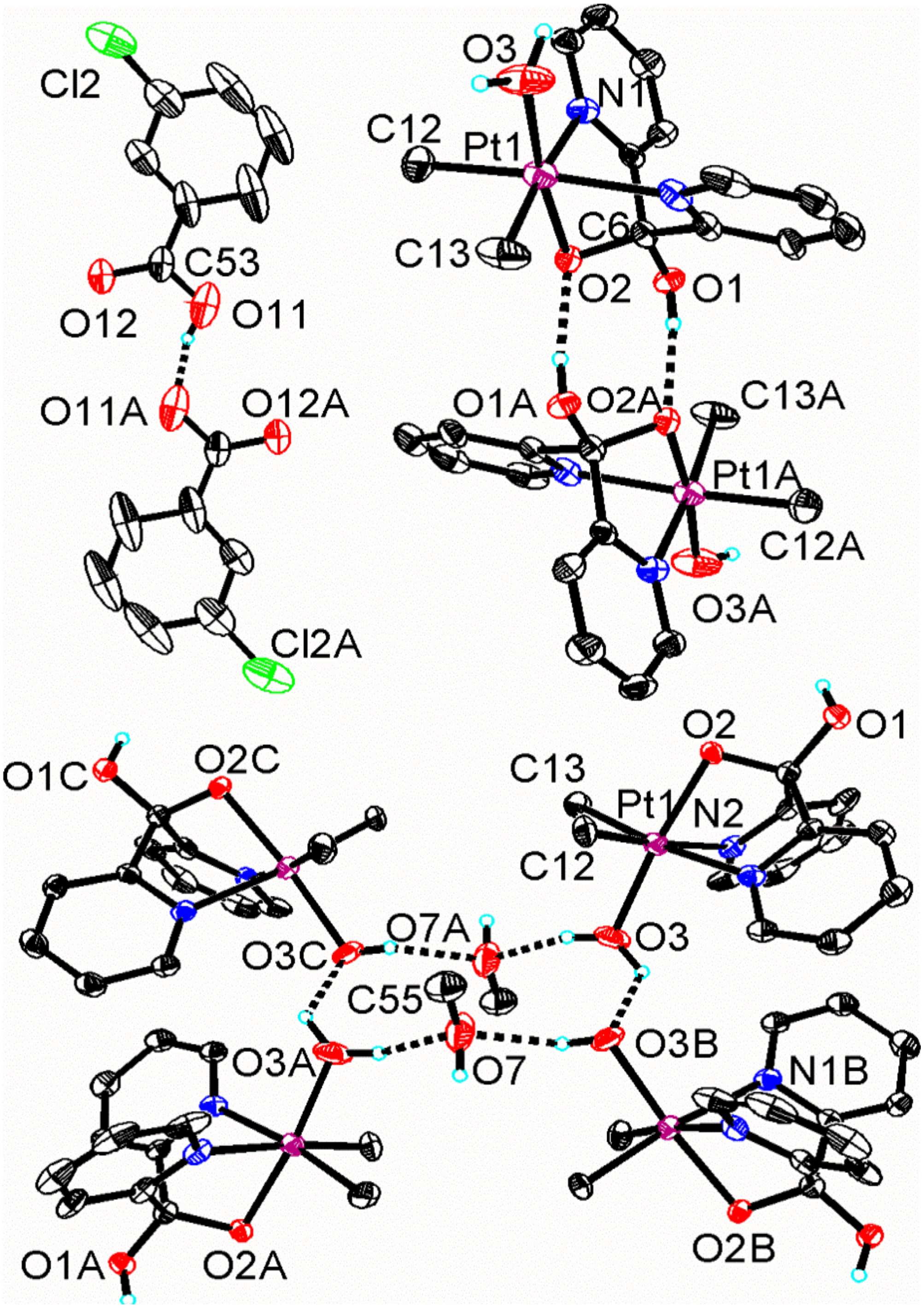


Figure 2.11: Crystal Structure of complex **2.9·2MeOH**. Selected Bond Parameters: Pt(1)-C(12) = 2.019(11); Pt(1)-C(13) = 2.059(9); Pt(1)-O(3) = 2.022(6); Pt(1)-O(2) = 2.023(5); O(3)-O(7A) = 2.616(5); O(1)-O(2A) = 2.668(3); O(11)-O(11A) = 2.373(7) Å.

Table 2.3: Bond lengths [Å] and angles [deg] for complex 2.9·2MeOH

Pt(1)-C(12)	2.019(1)	O(3)-H(10A)	0.9554
Pt(1)-C(13)	2.059(9)	O(3)-H(10B)	0.8226
Pt(1)-O(3)	2.022(6)	O(11)-C(53)	1.28(2)
Pt(1)-O(2)	2.023(5)	O(11)-H(11)	0.8200
Pt(1)-N(2)	2.161(7)	O(12)-C(53)	1.267(1)
Pt(1)-N(1)	2.169(7)	O(3)-O(7A)	2.616(5)
O(1)-C(6)	1.367(1)	O(1)-O(2A)	2.668(3)
O(2)-C(6)	1.420(9)	O(11)-O(11A)	2.373(7)
O(1)-H(1B)	0.8363		
C(12)-Pt(1)-O(3)	90.3(4)	O(11)-C(53)-C(47)	114.6(2)
C(12)-Pt(1)-O(2)	95.8(4)	C(52)-C(47)-C(53)	121.6(2)
O(3)-Pt(1)-O(2)	173.2(3)	C(48)-C(47)-C(52)	120.5(2)
C(12)-Pt(1)-C(13)	89.8(5)	C(47)-C(48)-C(49)	120.1(2)
O(3)-Pt(1)-C(13)	88.1(4)	C(47)-C(48)-H(48)	119.9
O(2)-Pt(1)-C(13)	94.9(3)	C(49)-C(48)-H(48)	119.9
C(12)-Pt(1)-N(2)	174.0(4)	C(50)-C(49)-C(48)	119.1(2)
O(3)-Pt(1)-N(2)	95.7(3)	C(50)-C(49)-Cl(2)	119.8(2)
O(2)-Pt(1)-N(2)	78.2(2)	C(48)-C(49)-Cl(2)	121.1(2)
C(13)-Pt(1)-N(2)	91.1(4)	C(49)-C(50)-C(51)	120.9(2)
C(12)-Pt(1)-N(1)	92.7(4)	C(49)-C(50)-H(50)	119.5
O(3)-Pt(1)-N(1)	98.5(3)	C(51)-C(50)-H(50)	119.5
O(2)-Pt(1)-N(1)	78.2(2)	C(52)-C(51)-C(50)	119.7(2)
C(13)-Pt(1)-N(1)	172.9(4)	C(52)-C(51)-H(51)	120.2
N(2)-Pt(1)-N(1)	85.8(2)	C(50)-C(51)-H(51)	120.2
C(6)-O(2)-Pt(1)	102.7(4)	C(51)-C(52)-C(47)	119.7(2)
O(1)-C(6)-O(2)	111.5(6)	C(51)-C(52)-H(52)	120.1
O(12)-C(53)-O(11)	121.8(2)	C(47)-C(52)-H(52)	120.1
O(12)-C(53)-C(47)	123.6(2)	O(1)-Pt(1)-O(2)	177.99(2)

This structure is very complex and the bonding modes of this structure will be discussed here. Complex **2.9** has crystallized with a molecule of methanol of solvation. It can be seen that there is an interaction between O(3) and O(7A) as well as it's symmetry equivalent with bond distances of 2.62 Å, connecting the methanol molecule to Pt(1) complexes via these hydrogen bonds. There are also hydrogen bonding interactions between O(1) and O(2A) and O(2) and O(1A). These have distances of 2.67 Å, which is in line with what can be considered hydrogen bonding interactions.[31] Finally, although in this case the *meta*-chlorobenzoate is not hydrogen bonded with the platinum complex, it can be seen that there is a hydrogen shared between the two *meta*-chlorobenzoate groups. This means that there is interaction of this hydrogen atom, in which it can shuttle back and forth between these two species, showing both the *meta*-chlorobenzoic acid as well as the *meta*-chlorobenzoate in a dynamic manner. This has been a difficult structure to extract, but based on the results, it proves to show some very interesting bonding interactions, which have overall lead to stabilization of this structure. Taking this one step further, when this structure is expanded, it can be seen to exist as a network of hydrogen bonding interactions between the platinum complexes and solvent methanol, leads to the interesting bonding dynamic illustrated in figure 2.12

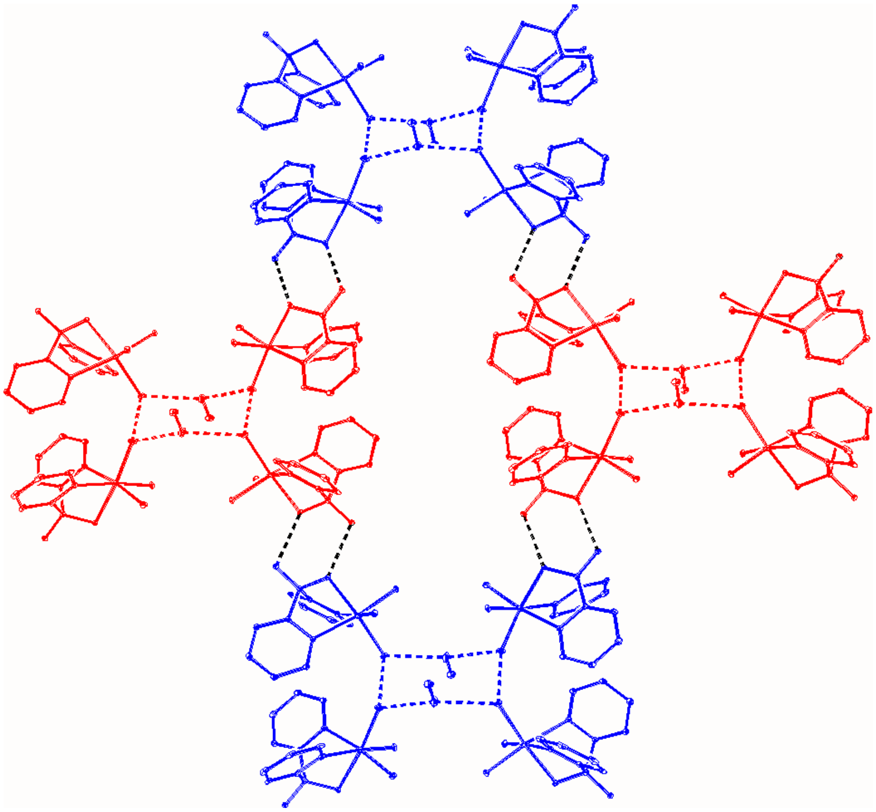


Figure 2.12: Overall bonding structure of complex **2.9**·2MeOH, illustrating a network of hydrogen bonding interactions leading to a sheet structure

Furthering these studies and attempting to find even more interesting hydrogen bonding motifs, a 1:1 stoichiometric amount of *m*-CPBA was added to a stirring solution of complex **2.7**, [PtMe$_2$(dpa)] in acetone, affording a mixture which contained a white precipitate. This precipitate was isolated and purified and the ^{1}H NMR, shown in figure 2.13, illustrates the formation of a platinum(IV) complex.

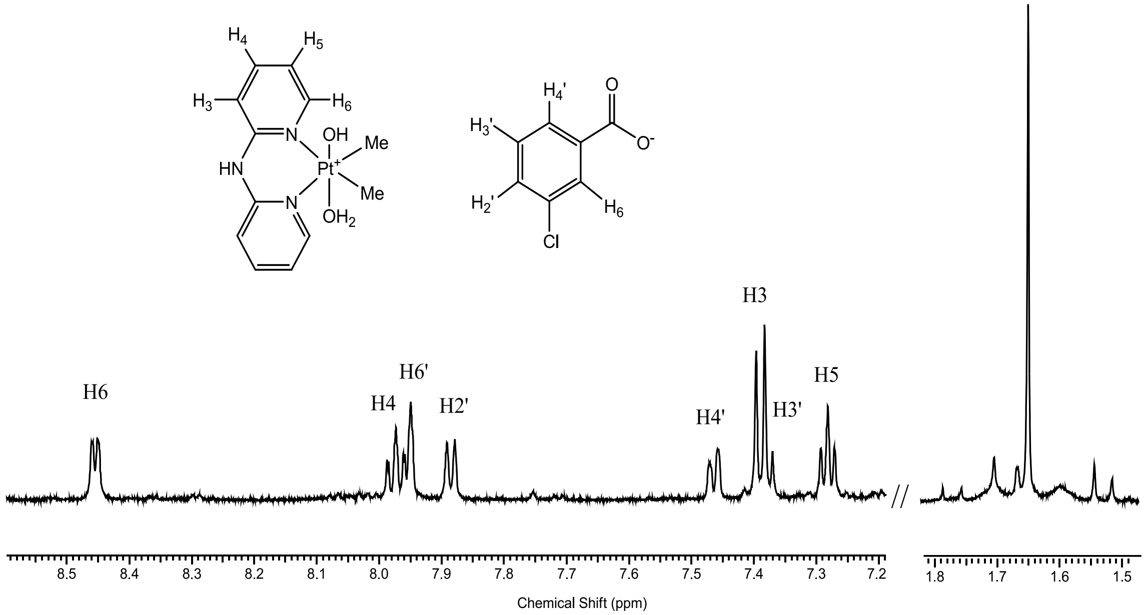
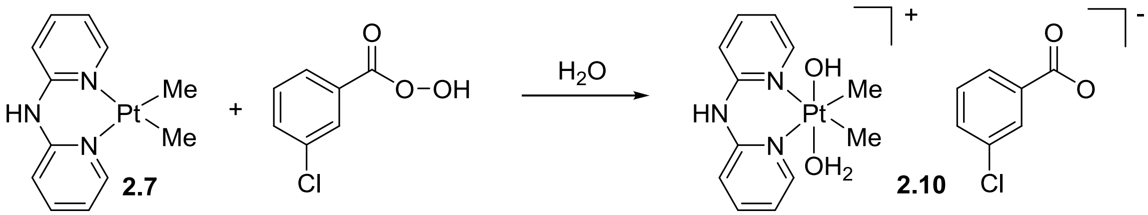


Figure 2.13: ^{1}H NMR spectrum of complex **2.10**, [PtMe$_2$(dpa)(OH)(OH$_2$)]$^+$ [C$_6$H$_4$Cl(COO)]$^-$.

The ^{1}H NMR spectrum shows the formation of a single platinum(IV) species based on the fact that there is one resonance found at $\delta = 1.64$ ppm which has a coupling constant of ^2J(Pt-H) = 64 Hz, with only minor impurities. Upon examination of the downfield region of this spectrum two observations can be made. Through the use of COSY, the proton resonances from the bipyridyl rings can be established and the four signals indicate the presence of symmetry within this molecule and thus makes this a *trans*-oxidative addition product. The second conclusion that can be drawn from this spectrum is that there is the presence of *m*-CPBA within the species formed. As in the previous cases, it is probably the coordination of chlorobenzoate ion to the platinum(IV) complex, which can occur through hydrogen bonding. A suitable crystal for X-ray analysis could not be obtained and thus mass spectrometry and elemental analysis are relied on to verify the formation of complex **2.10,** $[PtMe_2(dpa)(OH)(OH_2)]^+[C_6H_4Cl(COO)]^-$. From the mass spectrometry results, it can be seen that most prominent peak in the spectra is m/z 411.1. This is representative of the formation of $[PtMe_2(dpa)(OH)]^+$, which would lead to suggestion that the group *trans* to the hydroxyl group is a water, which is very labile and would fall off, leaving a five coordinate cationic platinum species represented in the spectrum. The use of elemental analysis has also helped justify the formation of complex **2.10**, in that the elemental values fall into place with the inclusion of a *meta*-chloroperbenzoate species into the overall formula. This fact helps establish that this reaction occurs by the same manner as those platinum(II) complexes previously carried out with *m*-CPBA, and thus this product can classified as complex **2.10**, illustrated in Scheme 2.14.



Scheme 2.14: Synthesis of complex **2.10**, $[PtMe_2(dpa)(OH)(OH_2)]^+[C_6H_4Cl(COO)]^-$.

2.2.5 Reactions of $[PtMe_2(DECBP)]$ with DMDO and *m*-CPBA

The relative inertness of platinum complexes gives advantages in that there can be self-assembly due to secondary bonding interactions, specifically hydrogen bonding. There has been significant interest in self assembly of polymers using simple coordination complexes as building blocks to give functional materials that can self assemble through hydrogen bonding. There has been recent interest in the field of supramolecular chemistry in the use of dimethylplatinum(II) species contianing bidentate nitrogen donor ligands. These interests include the use of amides or esters as functional groups to act as hydrogen bond acceptors.[33,34] Two oxidative addition reactions have been carried out utilizing the platinum(II) complex **2.9**, [$PtMe_2$(DECBP)].[34] The ligand 4,4'-diethoxycarbonbyl-2,2'-bipyridine (DECBP) was prepared by Safa[35], via a modified procedure of Sprintschnik et al.[36] The ester groups on the bipyridyl rings may prove to add some interesting bonding characteristics in the reaction of this complex with peroxides.

Complex **2.11**, [$PtMe_2$(DECBP)], was prepared according to the literature and ^1H NMR data may be found in appendix 2.2.5. To a stirring solution of complex **2.10**, was added DMDO until the initial purple colour of the acetone solution dissipated and the complex **2.12**, [$PtMe_2$(DECBP)$(OH)_2$] was isolated as a white solid. The ^1H NMR spectrum shown in figure 2.14 illustrates the formation of this product, forming the *trans*-dihydroxo oxidative addition product.

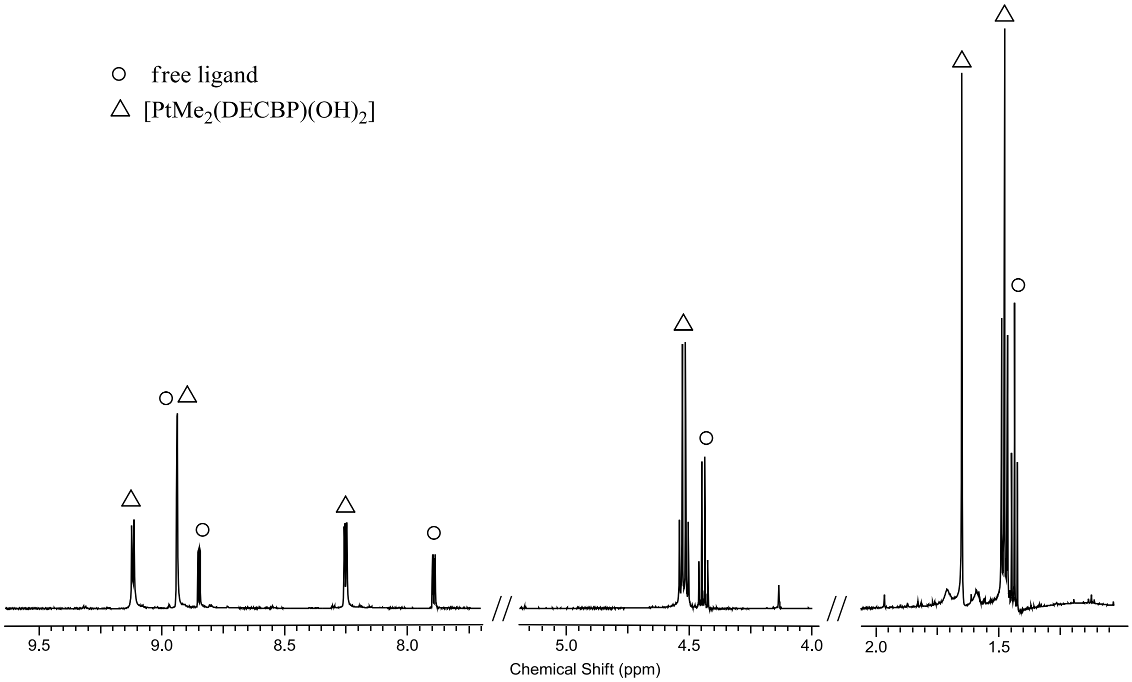
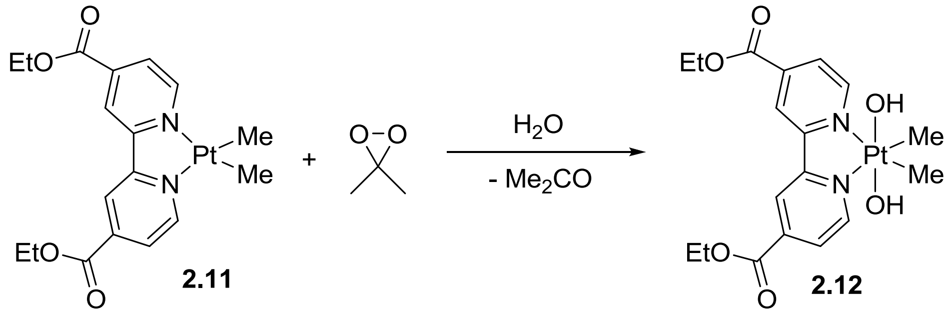


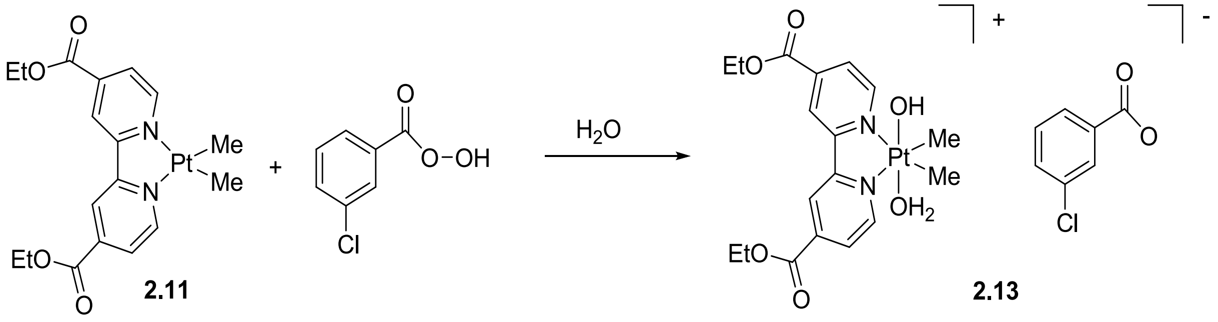
Figure 2.14: ^{1}H NMR spectrum of complex **2.12**, [PtMe$_2$(DECBP)(OH)$_2$] along with free ligand.

In the ^{1}H NMR spectra of complex **2.12**, there is a single methyl platinum methyl platinum resonance at $\delta = 1.65$ ppm with a coupling of ^2J(Pt-H) = 70 Hz. The presence of only one methyl platinum and one set of pyridyl resonances indicate that the complex has a plane of symmetry, as would be expected for the formation of a complex with *trans* geometry, the structure illustrated in scheme 2.15. There are additional proton resonances seen resulting from and assigned to uncoordinated DECBP ligand. These results are identical to those produced by Safa et al. in which a reaction was carried out with [PtMe$_2$(DECBP)] and H_2O_2, and thus no further experimental or characterization was needed for this product.[22]



Scheme 2.15: Synthesis of complex **2.12**, [PtMe$_2$(DECBP)(OH)$_2$]

To complete the study of this platinum(II) complex, oxidation with *m*-CPBA was carried out. [PtMe$_2$(DECBP)] was dissolved in acetone and *m*-CPBA was added to it. Immediately the purple colour of the solution disappeared and there was the formation of a yellow solution. Leaving the mixture to stir, it was found that a gel like material formed. When the gel was dried under high vacuum, the material became a solid powder. The proposed species for this reaction follows that of the previously characterized *m*-CPBA reaction with platinum(II) species, forming complex **2.13**, [PtMe$_2$(OH)(DECBP)(OH$_2$)]$^+$[*m*-C6H4Cl(COO)]$^-$ as outlined in scheme 2.16. This powder was characterized by ^{1}H NMR, which has been illustrated in figure 2.15.



Scheme 2.16: Proposed product for reaction of [PtMe$_2$(DECBP)] with *m*-CPBA forming complex **2.13**.

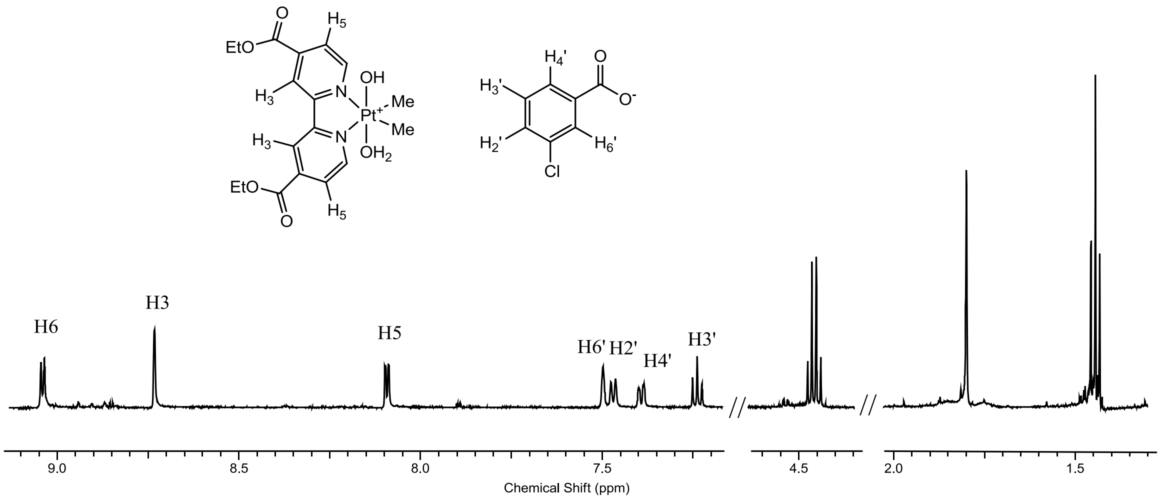


Figure 2.15: ^{1}H NMR spectrum of complex **2.13**, $[PtMe_2(OH)(DECBP)(OH_2)]^+[m\text{-}C_6H_4(COO)]^-$

The ^{1}H NMR shows the formation of a single product, a platinum(IV) species based on the single methyl platinum resonance located at $\delta = 1.78$ ppm with a coupling of $^2J(Pt\text{-}H) = 66$ Hz. The downfield region of this spectrum shows only one set of pyridyl protons, which is consistent with the formation of a product via *trans*-oxidative addition. There is also evidence that some *m*-CPBA is present within this spectrum and must somehow be incorporated into complex **2.13**, as if it were free it would have been washed away during the purification steps. The resonances for these *m*-CPBA protons are also found shifted from that of free *m*-CPBA in CD_2Cl_2, which suggests there is some interaction with the platinum(IV) species. The mass spectrum results indicate the formation of a species containing multiple platinum complexes, in a polymer type arrangement. It can be seen that there is a trimeric species containing three $[PtMe_2(DECBP)(OH)_2]^+$ units with a m/z of 1678.4 g/mol, a dimeric species containing two $[PtMe_2(DECBP)(OH)_2]^+$, with a m/z of 1119.3 g/mol and finally a m/z peak located at 543.1 representative of the species $[PtMe_2(DECBP)(OH)]^+$,which would be the platinum species as a result of a loss of water. With no crystal data it becomes difficult to characterize confidently that complex **2.13** is indeed the structure, thus, SEM (scanning electron microscopy) was utilized to help gather further information regarding this interesting complex.

To demonstrate the gel forming capabilities of this complex, figure 2.16 shows the formation of complex **2.13** in acetone. Electron microscopy was performed on the xerogels (air-dried gels) of the complex in order to study their morphologies. Scanning electron microscopy was utilized for the characterization of complex **2.13**, with the results illustrated if figure 2.17. The results illustrate an interesting perspective on this material in that it appears to form as a microcrystalline solid in the air dried form. In figure 2.17(right), where the resolution has been enhanced, there is evidence of the formation of a network of fibrous structures and this may be attributed to the polymeric nature of this species.

Figure 2.16: Picture display of polymeric nature of complex **2.13**. (Left) solvent acetone. (Right) solvent DCM.

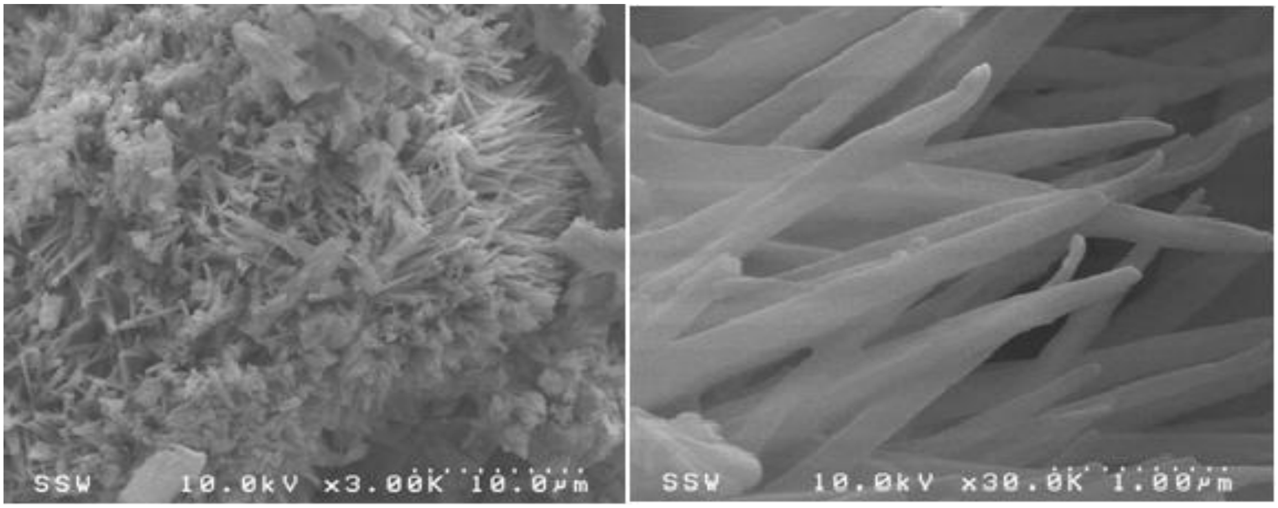


Figure 2.17: SEM images of complex **2.13** as xerogels.

Electron dispersive X-ray spectroscopy (EDX) has been utilized to help determine the chemical composition of complex **2.13**. It can be determined from these results that there is a 1:1 molar ratio of platinum to chlorine, which suggests a 1:1 ratio of $[PtMe_2(OH)(DECBP)(OH_2)]^+$ and $[m\text{-}C_7H_4ClO_2]^-$, and thus helps to justify the proposed structure of this product. It can be suggested that the reason this product forming a gel material as compared to the other platinum(II) complexes used in this chapter, is due to the overall hydrogen bond capabilities exhibited by ester functional groups which have been shown to act as hydrogen bond acceptors.[33,34]

2.3 Conclusion

A variety of platinum(II) complexes prepared from the precursor $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$,[24] have been utilized in reactions with both dimethyldioxirane and *meta*-chloroperbenzoic acid. The goal was to test the reactivity of these platinum(II) species to oxidative addition reactions of these peroxides and peroxy acids. It can be determined that the use of DMDO, lead strictly to the formation of the dihydroxy products as seen with complex **2.2, 2.8** and **2.11**, and a slight variation involving the use of the $[PtMe_2(dpk)]$ where instead of taking up a second hydroxyl, there was attachment of an oxygen from the carbonyl group, forming complex **2.6**. X-ray data has been helpful in clarifying the formation of complex **2.2**, [PtMe$_2$(bpy)(OH)$_2$], where the aid of stabilizing water molecules has lead to crystallization of this difficult to crystallize product.

The *m*-CPBA reactions have illustrated similar results to that of the DMDO. It can be seen that the typical complexes formed when any platinum(II) complexes are reacted with *m*-CPBA are platinum(IV) species in which there are either two hydroxyl groups trans to one another or a hydroxyl and a water molecule, displaying the same arrangement. Characterization of these complexes has been made through the use of ^{1}H NMR, mass spectrometry and more definitively by X-ray analysis. It can be determined that complex **2.4, 2.9, 2.10, 2.13** are complexes containing two separate species, the platinum(IV) species formed and a meta-chlorobenzoate moiety. One of the more interesting cases involved the use of complex **2.11**, [PtMe$_2$(DECBP), in which a gel type species formed, and this to illustrate the hydrogen bonding characteristics capable within these type of platinum system involving hydrogen bond donors and acceptors. Only in once case was there shown to be a prevalence of a *cis*-directed oxidative addition product and this was in complex **2.3**. Further characterization of this complex was difficult, thus relying on the ^{1}H NMR and mass spectroscopy results it has been tentatively classified as the *cis*-addition of a hydroxyl and *meta*-chloroperbenzoic acid species.

These results have helped illustrate the exceptional ability of electron rich platinum(II) complexes containing bidentate nitrogen donors to undergo oxidative addition reactions. The ease in which these peroxides were capable of oxidizing at the platinum center leads to promise towards finding an alternative approach to mediating the oxidative addition step in various types of Shilov chemistry.

2.4 Experimental

All reactions were carried out using standard Schlenk techniques, unless otherwise stated. All NMR spectra were recorded on Varian Mercury 400 or Varian INOVA 400 or 600 MHz spectrometers. ^{1}H NMR chemical shifts are reported in ppm (δ) relative to TMS and referenced to their corresponding solvents. Mass spectrometric analysis was carried out using an electrospray PE-Sciex Mass Spectrometer (ESI-MS) coupled with a TOF detector. The platinum dimer, $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ was prepared according to the literature and utilized in the formation of the Pt(II) complexes.[24]

Dimethyldioxirane. This compound was prepared from a modified procedure of Murray et al.[15] The experimental setup involves the use of a 500mL, three neck round bottom flask with an attached thermometer and reflex condenser. The reflux condenser was attached to a two neck 150mL collection flask being cooled by a dry-ice/acetone and equipped with a vacuum condenser also filled with dry ice/acetone. A mixture of water (102 mL), acetone (72 mL, 0.982 mol), and sodium bicarbonate (24 g, 0.285 mol) was placed in the 500 mL round bottom equipped with a magnetic stir bar and was placed under a gentle stream of nitrogen. The reaction mixture was allowed to stir for 30 minutes while sitting in an ice bath. Upon completion of the 30 minutes, small portions of Potassium peroxymonosulfate (Oxone, 48 g, 0.316 mol) were added over a 30 minute time period. The cooling bath was removed from the reaction mixture and it was allowed to stir for 30 minutes. A slight vacuum as well as moderate heat was then applied to the reaction assembly. The mixture began to reflux and the dimethyldioxirane was obtained in the receiving flask in an acetone solution. The solution was dried with $MgSO_4$, and stored in the freezer for subsequent use. The product was characterized by ^{31}P NMR for dioxirane content using triphenylphosphine and the concentration was found to be ~0.100 M. **^{31}P NMR in acetone-*d*$_6$**: δ = -5.82 (s, PPh_3), 25.50 (s, Ph_3P=O).

Complex 2.1, [PtMe$_2$(bpy)]. The synthetic route was previously reported by Puddephatt et al.[13] To a solution of [Pt_2Me_4(μ-SMe_2)$_2$] (200.0 mg, 0.348 mmol) in 40mL of toluene was added 2,2'-bypyridine (109 mg, 0.697 mmol) in dry diethyl ether (30 mL). An immediate red colour was observed and a precipitate began to crash out. The solution was cooled to 5°C for 16 hours until the precipitate had formed. The solvent was decanted off and the red solid was washed with ether and dried in *vacuo*. The final yield was 81% (234 mg, 0.614 mmol). The ^{1}H NMR spectrum is identical to the literature.[25] **^{1}H NMR in CDCl$_3$.** δ 1.15 (s, 6H, ^2J(PtH) = 85 Hz, Pt-Me), 7.54 (dd, 2H, $^3J(H^5H^6)$ = 6 Hz, $^3J(H^4H^5)$ = 8 Hz, H^5), 8.02 (d, 2H, $^3J(H^3H^4)$ = 8 Hz, H_3), 8.12 (dd, 2H, $^3J(H^3H^4)$ = 8 Hz, $^3J(H^4H^5)$ = 8 Hz, H^4), 9.29 (d, 2H, $^3J(H^5H^6)$= 6 Hz, ^3J(PtH) = 22 Hz, H^6).

Complex 2.2, [PtMe$_2$(OH)$_2$(bpy)]. In a 50mL round bottom flask equipped with a stir bar, a solution of dimethyldioxirane (~0.1M) was added dropwise to a stirring solution [PtMe$_2$(bpy)] (20.0mg, 0.0524mmol) in acetone. Dimethyldioxirane was added until the initial red colour completely dissipated and a clear, colourless solution was obtained. Almost immediately, a white precipitate began to form in the reaction flask. The reaction mixture was allowed to stir for 10 minutes and then the reaction mixture was layered with pentane, leading to the precipitation of a white solid. The solvent was then decanted off and the white solid was washed with pentane and then dried *in vacuo*. The product was produced in an 84% yield (14.4 mg, 0.0347 mmol). **^{1}H NMR in CD$_3$OD**: δ 1.74 (s, 6H, ^2J(PtH) = 70Hz, Me), 7.83 (ddd, $^3\mathrm{J}(H^5H^6)$ = 6 Hz, $^3J(H^5H^4)$ = 8

Hz, $^{4}J(H^{5}H^{3})$ = 1 Hz, H^{5}), 8.27 (ddd, 2H, $^{3}J(H^{4}H^{5})$ = 8 Hz, $^{3}J(H^{3}H^{4})$ = 8 Hz, $^{4}J(H^{4}H^{6}$ = 1 Hz, H^{4}), 8.86 (d, 2H, $^{3}J(H^{3}H^{4})$ = 8 Hz, H^{3}), 9.02 (d, 2H, $^{3}J(H^{6}H^{5})$ = 6Hz, $^{4}J(H^{6}H^{4}$ = 1 Hz, H^{6}).

Complex 2.3, *cis*-[PtMe$_2$(OH)(C$_7$H$_4$O$_2$Cl)(bpy)]. An NMR experiment was conducted for the addition of meta-chloroperbenzoic acid (1.80 mg, 0.0105 mmol) to [PtMe$_2$(bpy)] (4.00 mg, 0.0105 mmol) in acetone-d$_6$. Upon addition, the initial red colour of the solution dissipated and the solution turned to a white mixture, with a white solid precipitating out of solution. **^{1}H NMR in acetone-*d*$_6$**: δ = 1.12 (s, 3H, ^{2}J(PtH) = 75 Hz, PtMe), 1.80 (s, 3H, ^{2}J(PtH) = 69 Hz, PtMe), 7.19 (dd, $^{3}J(H^{2''}H^{3''})$ = 8Hz, $^{3}J(H^{3''}H^{4''})$ = 8Hz, $H^{3''}$), 7.29 (d, $^{3}J(H^{3''}H^{4''})$ = 8Hz, $H^{4''}$), 7.57 (d, $^{3}J(H^{2''}H^{3''})$ = 8Hz, $H^{2''}$), 7.96 (dd, 1H, $^{3}J(H^{5}H^{6})$ = 8Hz, $^{3}J(H^{4}H^{5})$ = 1Hz, H^{5}), 8.00 (dd, 1H, $^{3}J(H^{5'}H^{6'})$ = 8Hz, $^{3}J(H^{4'}H^{5'})$ = 1Hz, $H^{5'}$), 8.39 (dd, 1H, $^{3}J(H^{3}H^{4})$ = 8Hz, $^{3}J(H^{4}H^{5})$ = 1Hz, H^{4}), 8.46 (dd, 1H, $^{3}J(H^{3'}H^{4'})$ = 8Hz, $^{3}J(H^{4'}H^{5'})$ = 1Hz, $H^{4'}$), 8.73 (d, 1H, $^{3}J(H^{3}H^{4})$ = 8Hz, H^{3}), 8.77 (d, 1H, $^{3}J(H^{3'}H^{4'})$ = 8Hz, $H^{3'}$), 9.05 (d, 1H, $^{3}J(H^{5}H^{6})$ = 6Hz, ^{2}J(PtH) = 22Hz, H^{6}), 9.46 (d, 1H, $^{3}J(H^{5'}H^{6'})$ = 6Hz, $H^{6'}$). **ESI-MS (TOF)** [**2.3**-H]$^{+}$**:** Calc. Precise Mass 554.07 g/mol; Determined Precise Mass: 554.1 g/mol. *Anal.* Calc'd. for C$_{19}$H$_{21}$ClN$_2$O$_3$Pt·H$_2$O: C, 39.90; H, 3.70; N, 4.90%. Found: C, 39.69; H, 3.49; N, 4.80%.

Complex 2.4 [PtMe$_2$(OH)(OH$_2$)(bpy)]$^{+}$[C$_6$H$_4$Cl(COO)]$^{-}$. The product was prepared by the addition of *meta*-chloroperbenzoic acid (9.0mg, 0.0526mmol) to [PtMe$_2$(bpy)] (20.0mg, 0.0526mmol) in acetone. The red colour seen initially dissipated and there was formation of a clear solution. The product was layered with pentane to precipitate out a white solid, which was subsequently dried in *vacuo*. The overall yield of the reaction was 81% (23.5 mg, 0.0424 mmol). The product was then characterized by NMR. **^{1}H NMR in CD$_3$OD**. δ = 1.85 (s, 6H, ^{2}J(PtH) =

70Hz, PtMe), 7.86 (dd, 2H, $^3J(H^5H^6)$ = 6 Hz, $^3J(H^5H^4)$ = 8 Hz, H^5), 8.29 (dd, 2H, $^3J(H^4H^3)$ = 8 Hz, $^3J(H^4H^5)$ = 8 Hz, H^4), 8.67 (d, 2H, $^3J(H^3H^4)$ = 8 Hz, H^3), 9.00 (d, 2H, $^3J(H^6H^3)$ = 6 Hz, H^6). *m*-CPBA**:** δ = 7.42 (dd, 1H, $^3J(H^{3'}H^{2'})$ = 8 Hz, $^3J(H^{3'}H^{4'})$ = 8 Hz, $H^{3'}$), 7.47 (d, 1H, $^3J(H^{2'}H^{3'})$ = 8 Hz, $H^{2'}$), 7.90 (d, 1H, $^3J(H^{4'}H^{3'})$ = 8Hz, $H^{4'}$), 7.97 (s, 1H, $H^{6'}$). **ESI-MS (TOF)** [**2.4**-H]$^+$: Calc. Precise Mass: 416.09 g/mol; Determined Precise Mass: 416.1 g/mol. *Anal.* Calc'd. for $C_{19}H_{23}ClN_2O_5Pt$: C, 38.68; H, 3.93; N, 4.75%. Found: C, 38.16; H, 3.20; N, 4.65%.

Complex 2.5, [PtMe$_2$(dpk)]. This product was characterized according to Zhang et al.[19] To a solution of [Pt_2Me_4(μ-SMe_2)$_2$] (250 mg, 0.435 mmol) in acetone (10 mL) was added a solution of di-2-pyridyl ketone (160 mg, 0.848 mmol) in acetone (10 ml). The solution immediately turned orange and the product precipitated as a dark red solid over 30 minutes. The solvent was decanted and the product was washed with pentane (3x2 mL) and ether (3x 2 mL) and then dried *in vacuo*. The yield was 87% (0.310 mg, 0.758 mmol). **^{1}H NMR data in acetone-*d*^{6}**. δ 0.79 (s, 6H, ^2J(PtH) = 86 Hz, Pt-Me), 7.75 (dd, 2H, $^3J(H^5H^6)$ = 5 Hz, $^3J(H^4H^5)$ = 7 Hz, H^5), 8.03 (d, 2H, $^3J(H^3H^4)$ = 7 Hz, H_3), 8.27 (dd, 2H, $^3J(H^3H^4)$ = 7 Hz, $^3J(H^4H^5)$ = 7 Hz, H^4), 8.86 (d, 2H, $^3J(H^5H^6)$= 5 Hz, ^3J(PtH) = 26 Hz, H^6).

Complex 2.6, [Pt(OH)Me$_2$(DPKOH)]. In a 50 mL round bottom flask equipped with a stir bar, a solution of dimethyldioxirane (~0.1M) was added dropwise to a stirring solution of [PtMe$_2$(dpk)] (0.040 g, 0.0761 mmol) in acetone. Dimethyldioxirane was added until the initial red colour completely dissipated and was followed by the formation of a white precipitate. The reaction was allowed to stir for 10 minutes and then the reaction mixture was layered with pentane, to fully precipitate out the white solid. The solvent was then decanted and the white solid was washed with pentane (3x2 mL) and ether (3x2 mL) and then dried *in vacuo*. Yield 80%. ^1H NMR in methanol-d^6: δ 1.51 (s, 6H, $^2J(Pt\text{-}H)$ = 73 Hz, Pt-Me), 7.53 (ddd, 2H, $^2J(H^5\text{-}H^4)$ = 8 Hz, $^2J(H^5\text{-}H^6)$ = 5 Hz, $^2J(H^5\text{-}H^3)$ = 2 Hz, H^5) Hz 7.89 (dd, 2H, $^2J(H^3\text{-}H^4)$ = 8 Hz, $^3J(H^3\text{-}H^5)$ = 2 Hz, 8.04 (ddd, 2H, $^2J(H^4\text{-}H^3)$ = 8 Hz, $^2J(H^4\text{-}H^5)$ = 8 Hz, $^3J(H^4\text{-}H^6)$ = 2 Hz, H^4), 8.82 (dd, 2H, $^2J(H^6\text{-}H^5)$ = 5 Hz, $^3J(H^6\text{-}H^4)$ = 2 Hz, H^6).

Complex 2.7, [PtMe$_2$(dpa)]. This complex was prepared according to the literature. A solution of [$Pt_2Me_4(\mu\text{-}SMe_2)_2$] (139 .0 mg, 0.243 mmol) in acetone (10 mL) and a solution of dipyridylamine (83.1 mg, 0.485 mmol) in acetone (10 mL) was mixed and allowed to stir for 4 hours. The solution turned yellow/orange and the product precipitated as an orange solid over time. The solvent was decanted and the product was washed with pentane (3.x2 mL) and ether (3x2 mL) and then dried *in vacuo*. Yield 93% (179 mg, 0.412 mmol). **^{1}H NMR in acetone-d_6**: δ 0.59 (s, 6H, $^2J(PtH)$ = 86 Hz, Pt-Me), 6.97 (dd, 2H, $^3J(H^5H^6)$ = 6 Hz, $^3J(H^4H^5)$ = 8 Hz, H^5), 7.17 (d, 2H, $^3J(H^3H^4)$ = 8 Hz, H_3), 7.85 (dd, 2H, $^3J(H^3H^4)$ = 8 Hz, $^3J(H^4H^5)$ = 8 Hz, H^4), 8.60 (d, 2H, $^3J(H^5H^6)$= 5 Hz, $^3J(PtH)$ = 26 Hz, H^6), 9.22 (s, broad, NH).

Complex 2.8, [PtMe$_2$(dpa)(OH)$_2$]: [PtMe$_2$(dpa)] (9.8 mg, 0.0247 mmol) was dissolved in acetone and added to it was an extreme excess amount of a DMDO (10 mL). Initially upon addition, there was minimal change in the appearance, with the mixture turning opaque and darker yellow. The solution was concentrated down to a minimal volume under high vacuum and then was layered with pentane. An orange oil was formed upon layering of the solution and this was pumped down to obtain the oil, which was subsequently washed with ether. The product was attempted to be dissolved in acetone and was found to precipitate out in solution as a dark orange solid. This was then layered with pentane and the resulting brown/black precipitate was isolated in the reaction flask. The product was washed with pentane (3x2mL) and ether (3x 2mL) and dried *in vacuo*. **^{1}H NMR in CD$_3$OD**: δ = 1.54 (s, 6H, ^2J(Pt-H) = 64 Hz, Pt-Me), 7.19 (dd, 2H, ^3J(H^5-H^6) = 6 Hz, ^3J(H^5-H^4) = 7 Hz, H^5), 7.31 (d, 2H, ^3J(H^3-H^4) = 9 Hz, H^3), 7.90 (ddd, 2H, ^3J(H^4-H^5) = 7 Hz, ^3J(H^4-H^3) = 9 Hz, ^4J(H^4-H^6) = 1 Hz, H^4), 8.45 (d, 2H, ^3J(H^6-H^5) = 6 Hz, H^6). **ESI-MS (TOF)** [**2.8**-H]$^+$: Calc. Precise Mass: 431.1 g/mol. Determined Precise Mass: 431.1 g/mol.

Complex 2.9, [PtMe$_2$(OH$_2$)Me$_2$(dpkOH)]$^+$[C$_6$H$_4$Cl(COO)]$^-$. [PtMe$_2$(dpk)] (5.40 mg, 0.0131 mmol) was dissolved in acetone and added to the stirring solution was *m*-CPBA (3.3 mg, 0.0131 mmol). The initial red colour of the reaction mixture disappeared and a white solution was formed containing a precipitate. The solution was layered with pentane (3 mL) to precipitate out the remaining product. The product was then washed with pentane (3x2 mL) and ether (3x2 mL) and dried *in vacuo*. Yield 73%. **^{1}H NMR in CD$_3$OD**: δ = 1.54 (s, 6H, ^2J(Pt-H) = 70 Hz, Pt-Me), 7.56 (ddd, 2H, ^3J(H^5-H^6) = 6 Hz, ^3J(H^5-H^4) = 8 Hz, ^4J(H^5-H^3) = 1 Hz, H^5), 7.92 (d, 2H, ^3J(H^3-H^4) = 8 Hz, H^3), 8.07 (ddd, 2H, ^3J(H^4-H^5) = 8 Hz, ^3J(H^4-H^3) = 8 Hz, ^4J(H^4-H^6) = 1 Hz, H^4), 8.45 (dd, 2H, ^3J(H^6-H^5) = 6 Hz, ^4J(H^6-H^4) = 1 Hz, H^6). *m*-CPBA: δ = 7.40 (dd, 1H, ^2J(H$^{3'}$-H$^{2'}$) = 8 Hz, ^2J(H$^{3'}$-H$^{4'}$) = 8 Hz, H$^{3'}$), 7.48 (d, 1H, ^2J(H$^{2'}$-H$^{2'}$) = 8 Hz, H$^{2'}$), 7.90 (d, 1H, ^2J(H$^{4'}$-H$^{3'}$) = 8 Hz, H$^{4'}$), 7.96 (s, 1H, H$^{6'}$). ESI-MS (TOF) [**2.9**-H]$^+$: Calc. Precise Mass: 440.1 g/mol Determine Precise Mass: 440.1 g/mol.

Complex 2.10, [PtMe$_2$(dpa)(OH)(OH$_2$)]$^+$[C$_6$H$_4$Cl(COO)]$^-$. [PtMe$_2$(dpa)] (20.1 mg, 0.0507 mmol) was dissolved in acetone and added to it was a meta-chloroperbenzoic acid (13.0 mg, 0.0527 mmol) dissolved in acetone. The yellow colour of the solution dissipated and a white precipitate was formed. The solution was allowed to stir for ten minutes and then was fully precipitated out with pentane. The solution was decanted and the product was washed with pentane (3x2 mL) and ether (3x2 mL) and then dried *in vacuo*. Yield 65%. **^{1}H NMR in CD_3OD**: δ = 1.65 (s, 6H, ^2J(Pt-H) = 66 Hz, Pt-Me), 7.28 (dd, 2H, $^3J(H^5-H^6)$ = 6 Hz, $^3J(H^5-H^4)$ = 8 Hz, H^5), 7.36-7.39 (d, 2H, H^3), 7.97 (ddd, 2H, $^3J(H^4-H^5)$ = 8 Hz, $^3J(H^4-H^3)$ = 9 Hz, $^4J(H^4-H^6)$ = 2 Hz), 8.45 (d, 2H, $^3J(H^5-H^6)$ = 6 Hz, H^6). *m*-CPBA. 7.35-7.40 (m, 1H, H3'), 7.46 (d, 1H, $^2J(H^{4'}-H^{3'})$ = 8 Hz, $H^{4'}$), 7.88 (d, 1H, $^2J(H^{2'}-H^{3'})$ = 8 Hz, $H^{2'}$), 7.95 (s, 1H, $H^{6'}$) **ESI-MS (TOF)** $[PtMe_2(dpa)OH)]^+$: Calc. Precise Mass: 413.09 m/z; Determined Precise Mass: 413.1 m/z. Anal. Calc'd. for $C_{19}H_{22}ClN_3O_4Pt$ (%): C 39.33; H 3.42; N 7.40%. Found: C 38.88; H 3.78; N 7.16%.

Complex 2.11, $[PtMe_2(DECBP)]$. The preparation of this product followed literature stated by Safa et al.[22] To a solution of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (314.0 mg, 0.180 mmol) in ether (10 mL) was added 4,4'-diethoxycarbonyl-2,2'-bipyridine (108.0 mg, 0.361 mmol). After 5 minutes the solution turned purple and the product precipitated as a purple solid over 1 hour. The solvent was decanted and then the product was washed with pentane (3x5 mL) and then dried *in vacuo*. Yield 91% (172.0 mg, 0.328 mmol). **^{1}H NMR in acetone-d_6:** δ = 1.10 (s, 6H, ^2J(Pt-H) = 86 Hz, Pt-Me), 1.46 (t, 6H, ^3J(H-H) = 7 Hz, CH_3C), 4.48 (q, 4H, ^3J(H-H) = 7 Hz, CH_2C), 8.10 (dd, 2H, $^3J(H^5-H^6)$ = 6 Hz, $^4J(H^5-H^3)$ = 2 Hz, H^5), 8.72 (d, 2H, $^4J(H^3-H^5)$ = 2 Hz, H^3), 9.36 (d, 2H, $^3J(H^6-H^5)$ = 6 Hz, ^3J(Pt-H) = 22 Hz, H^6)

Complex 2.12, $[PtMe_2(DECBP)(OH)_2]$. To a solution of complex $[PtMe_2(DECBP)]$ (20.0 mg, 0.0378 mmol) in acetone, was added an excess volume of DMDO (5 ml). The initial red purple colour of the solution evaporated, turning clear and then over ten minutes a precipitate began to form within the solution. The precipitate was further crashed out with pentane and then the solvent was decanted. The solid white product was washed with pentane (2x3 mL) and ether (2x3 mL) and then dried *in vacuo*. Yield 78%. **^{1}H NMR in CD_2Cl_2**: δ = 1.48 (t, 6H, ^3J(H-H) = 7 Hz, CH_3C), 1.65 (s, 6H, ^2J(Pt-H) = 70 Hz, Pt-Me), 4.52 (q, 4H, ^3J(H-H) = 7 Hz, CH_2C), 8.26 (dd, 2H, ^3J(H^5-H^6) = 5 Hz, ^4J(H^5-H^3) = 1 Hz, H^5), 8.94 (d, 2H, ^4J(H^3-H^5) = 1 Hz, H^3), 9.12 (d, 2H, ^3J(H^6-H^5) = 5 Hz, H^6).

Complex 2.13, $[PtMe_2(OH)(DECBP)(OH_2)]^+[m\text{-}C_6ClH_4(COO)]^-$: To a solution of $[PtMe_2(DECPB)]$ (39.3 mg, 0.0747 mmol) in acetone was added *m*-CPBA (18.4 mg, 0.0747 mmol). Upon addition, the solution began to exhibit a gel like characteristic, eventually forming a solid gel slightly yellow in colour. The product was dried *in vacuo*, with the gel becoming a solid upon removal of the solvent. Yield 83%. **^{1}H NMR in CD_2Cl_2**. δ = 1.44 (t, 6H, ^3J(H-H) = 7 Hz, CH_3C), 1.78 (s, 6H, ^2J(Pt-H) = 66 Hz, Pt-Me), 3.39 (broad), 4.45 (q, 4H, ^3J(H-H) = 7 Hz, CH_2C), 8.09 (dd, 2H, ^3J(H^5-H^6) = 5 Hz, ^4J(H^5-H^3) = 1 Hz, H^5), 8.73 (d, 2H, H^3), 9.04 (d, 2H, ^3J(H^6-H^5) = 5 Hz, H^6). *m*-CPBA: 7.23 (dd, 1H, ^3J(H^5-H^6) = 8 Hz, ^3J(H^5-H^4) = 8 Hz, H^5), 7.37 (d, ^3J(H^6-H^5) = 8 Hz, H^6), 7.45 (d, 1H, ^3J(H^4-H^5) = 8 Hz, H^4), 7.84 (s, 1H, H^2). **ESI-MS (TOF):** Calc. Precise Mass: $[PtMe_2(DECBP)(OH)]^+$: 542.1; $[PtMe_2(DECBP)(OH_2)(OH)]$+ $[PtMe_2(DECBP)(OH)_2]$: 1119.3; 2 x $[PtMe_2(DECBP)(OH_2)(OH)]$+ $[PtMe_2(DECBP)(OH)_2]$: 1678.4 m/z ; Determined Precise Mass: $[PtMe_2(DECBP)(OH)]^+$: 542.1; $[PtMe_2(DECBP)(OH_2)(OH)]^+[PtMe_2(DECBP)(OH)_2]$: 1119.3; 2 x $[PtMe_2(DECBP)(OH_2)(OH)]^+[PtMe_2(DECBP)(OH)_2]$: 1677.4 m/z. **EDX results(%)**: C: 59.8; O: 27.1, Cl: 2.2, Pt; 10.9.

X-ray Structure Determination: X-ray data were obtained and solutions were determined by Matthew McCready in this chapter. Suitable crystals were mounted on a glass fibre and data was collected at low temperature 150(2) K on the Bruker Apex II CCD detector. The unit cell parameters were calculated and refined from the full data set. The crystal data and refinement parameters for all complexes are listed in the following tables.

Table 2.4: Crystallographic data for complex 2.2·7 H_2O

Empirical Formula	$C_{12}H_{18}N_2O_9Pt$	
Formula Weight	529.37	
Wavelength	0.71073 Å	
Crystal System	Monoclinic	
Space Group	$P2_1/n$	
Unit Cell Dimensions	a = 7.271(3) Å	α = 90°
	b = 17.379(8) Å	β = 95.533(8)°
	c = 30.265(13) Å	γ = 90°
Volume	3807(3) $Å^3$	
Z	8	
Density (calculated)	1.847 Mg/m^3	
Absorption Coefficient (μ)	7.415 mm^{-1}	
Crystal Size	0.30 x 0.06 x 0.04 mm^3	
Refinement Method	Full-matrix least-squares on F^2	
Goodness of fit on F^2	1.024	
Final R indicies [I>2σ(I)]	R1= 0.0429, wR2 = 0.0825	
R indicies (all data)	R1 = 0.0647, wR2 = 0.0896	

Table 2.5: Crystallographic data for complex 2.4·CH_2Cl_2

Empirical Formula	$C_{19} H_{21} Cl N_2 O_4 Pt$	
Formula Weight	571.92	
Wavelength	0.71073 Å	
Crystal System	Monoclinic	
Space Group	$P2_1/c$	
Unit Cell Dimensions	a = 12.8754(7) Å	α = 90°
	b = 10.0368(5) Å	β = 93.153(8)°
	c = 15.0169(8) Å	γ = 90°
Volume	1937.66(18) $Å^3$	
Z	4	
Density (calculated)	1.960 Mg/m^3	
Absorption Coefficient (μ)	7.407 mm^{-1}	
Crystal Size	0.07 x 0.07 x 0.02 mm^3	
Refinement Method	Full-matrix least-squares on F^2	
Goodness of fit on F^2	1.063	
Final R indicies [$I>2\sigma(I)$]	R1= 0.0319, wR2 = 0.0729	
R indicies (all data)	R1 = 0.0458, wR2 = 0.0790	

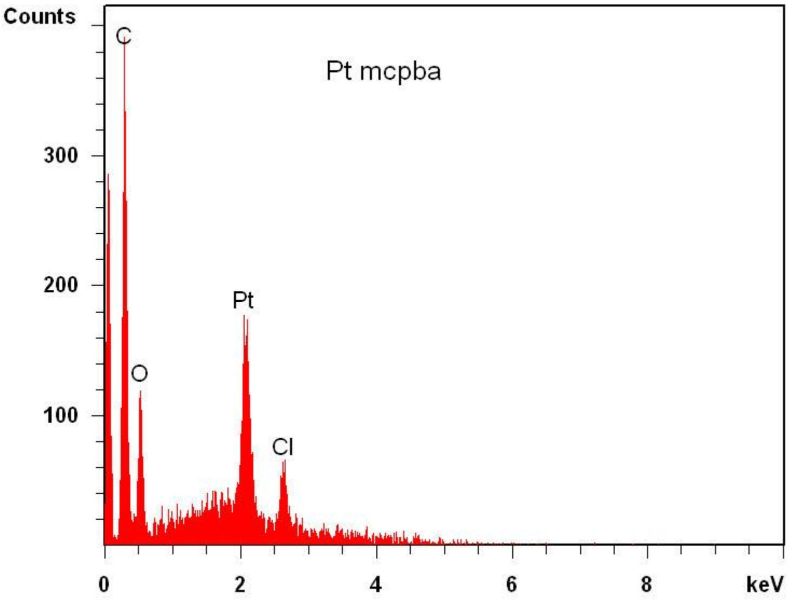
Table 2.6: Crystallographic data for complex 2.9·2MeOH

Empirical Formula	$C_{68} H_{80} Cl_2 N_8 O_{18} Pt_4$	
Formula Weight	2148.66	
Wavelength	0.71073 Å	
Crystal System	Monoclinic	
Space Group	C2/m	
Unit Cell Dimensions	a = 23.271(6) Å	$\alpha = 90°$
	b = 20.83(4) Å	$\beta = 104.39(3)°$
	c = 7.8963(16) Å	$\gamma = 90°$
Volume	3707.7(14) Å^3	
Z	2	
Density (calculated)	1.925 Mg/m^3	
Absorption Coefficient (μ)	7.667 mm^{-1}	
Crystal Size	0.05 x 0.05 x 0.02 mm^3	
Refinement Method	Full-matrix least-squares on F^2	
Goodness of fit on F^2	1.053	
Final R indicies [$I>2\sigma(I)$]	R1= 0.0522, wR2 = 0.1257	
R indicies (all data)	R1 = 0.0755, wR2 = 0.1390	

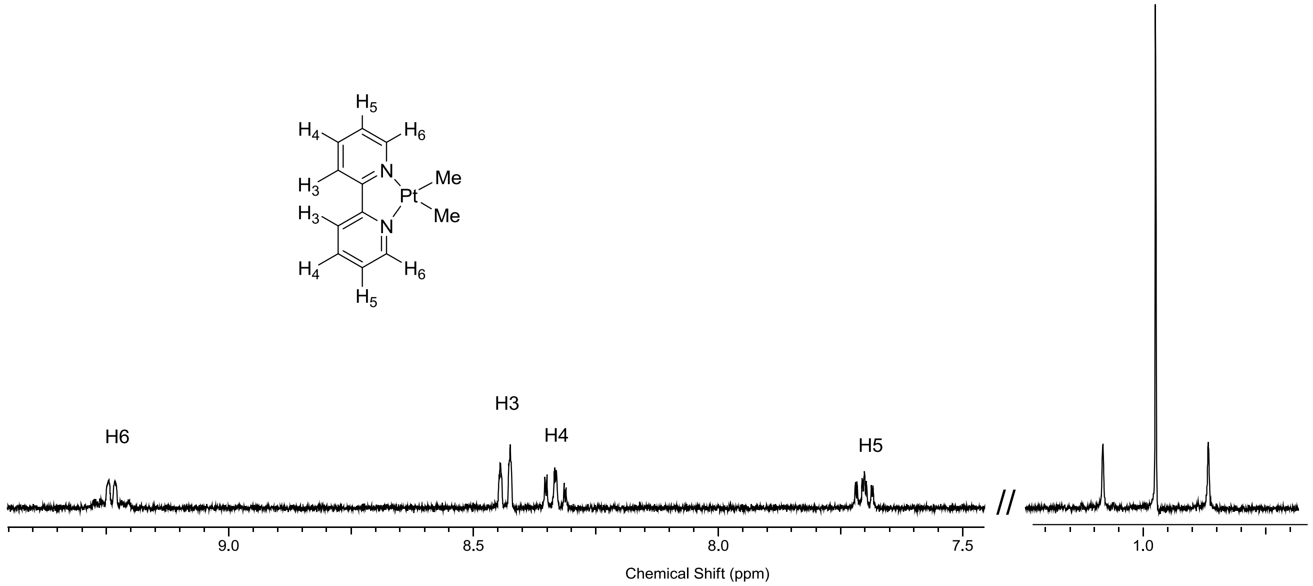
2.5 Appendix

2.5.1 EDX Results

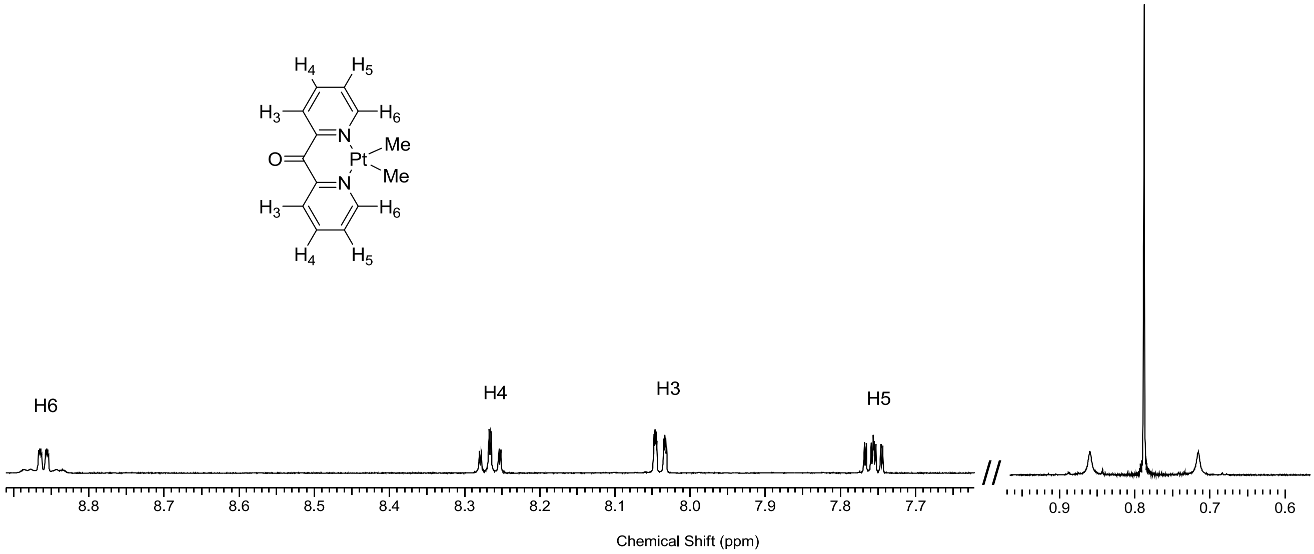
	C (%)	O (%)	Cl (%)	Pt (%)
edx 01	59.2	21.6	3.7	15.5
edx 02	60.4	32.5	0.8	6.4
Minimum	59.2	21.6	0.8	6.4
Maximum	60.4	32.5	3.7	15.5
Std. Dev.	0.8	7.7	2.1	6.5
Average	59.8	27.1	2.2	10.9



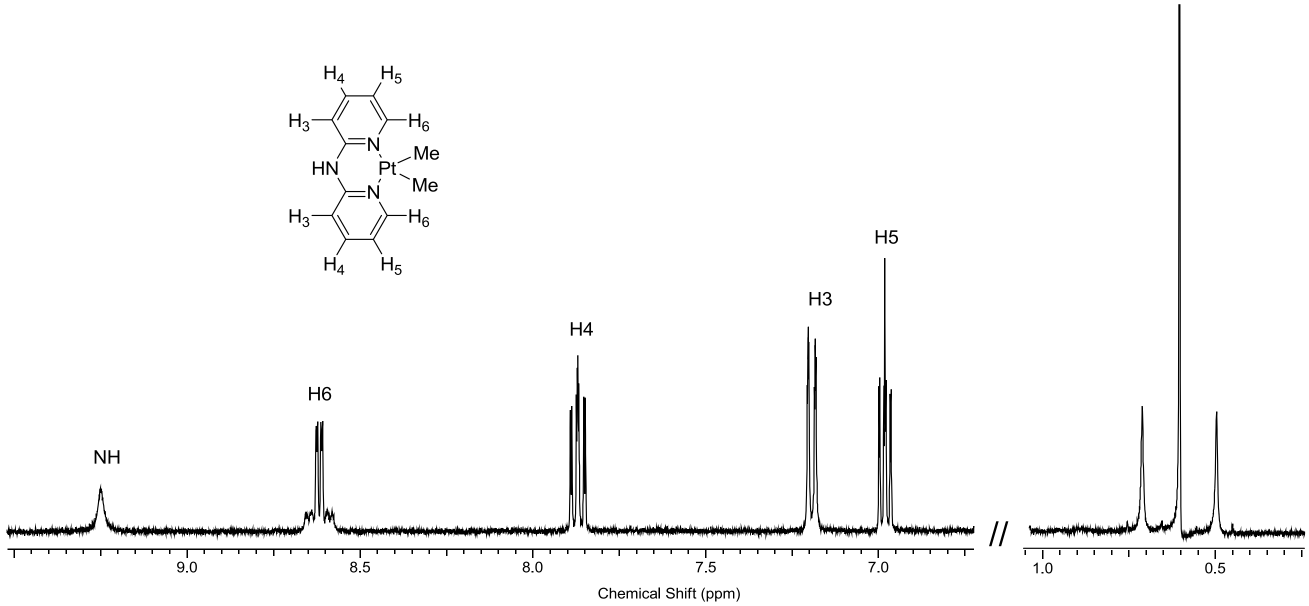
2.5.2 ^{1}H NMR data of complex 2.1, [PtMe$_2$(bpy)]



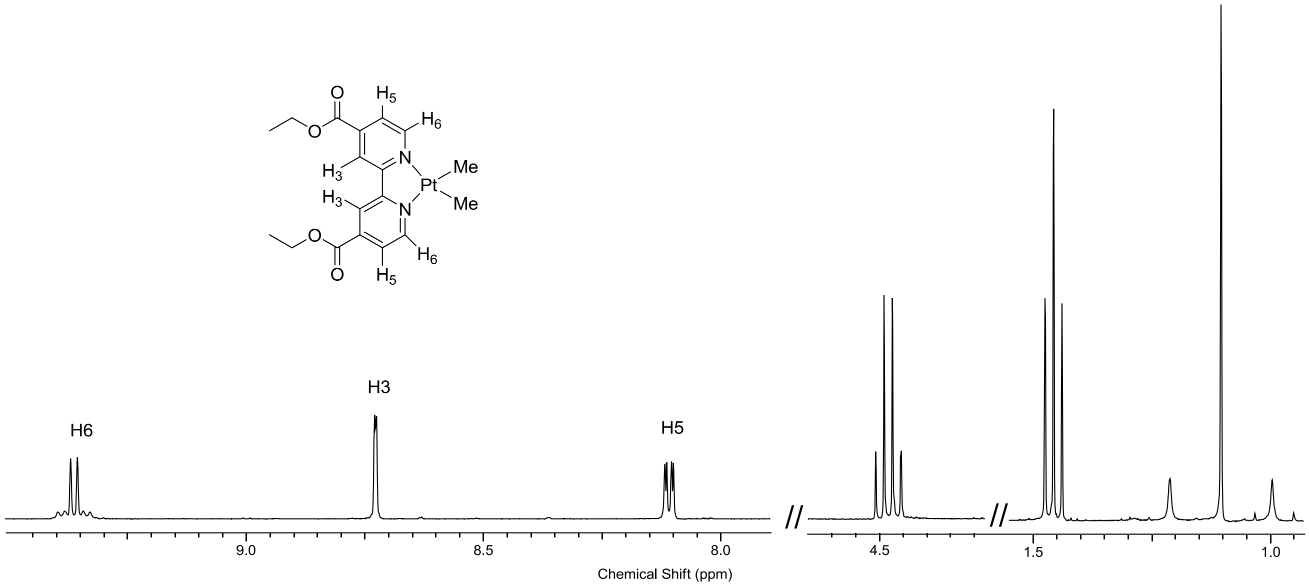
2.5.3 ^{1}H NMR data of complex 2.5, [PtMe$_2$(dpk)]



2.5.4 ^{1}H NMR data of complex 2.7, [PtMe$_2$(dpa)]



2.5.5 ^{1}H NMR data of complex 2.11, [PtMe$_2$(DECBP)]



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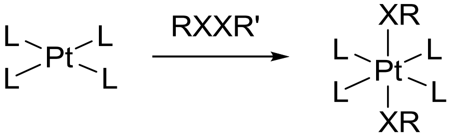
Chapter 3

Reactivity of Platinum(II) Complexes with Phthaloyl Peroxide

3.1 Introduction

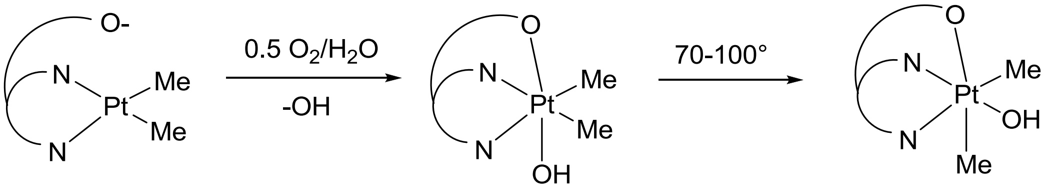
The oxidative addition reactions are among the most significant reactions in the organometallic and bio-inorganic chemistry of the transition metals.[1,2] Oxidative addition of a substrate leads to an increase in the coordination number of the complex due to the formation of two new bonds and an increase in both the oxidation state and electron count at the metal centre.[3,4] The selective oxidation of methane to methanol, catalyzed by electrophilic late transition metals such as platinum, has attracted interest since the first observation by Shilov in the late 1960s.[5] In the original Shilov study, the oxidation step of the cycle was carried out utilizing stoichiometric amounts of platinum(IV), making this system impractical. This has lead to interest by researchers to find alternative oxidants in which to complete this cycle in a more cost effective manner. The success thus far has been limited, with examples of the use of O_2,[6] Cl_2,[7] SO_3,[8] and H_2O_2,[9] as oxidants. The oxidative addition reactions of H_2O_2 and related types of compounds of type RXXR, where X = O, S, or Se, generally to platinum(II) complexes result in the formation of *trans*-[$L_4Pt(XR)_2$] complexes, which can be illustrated in Scheme 3.1.[10]



Scheme 3.1: Typically seen *trans*-oxidative addition of RXXR (R = O, S, Se)

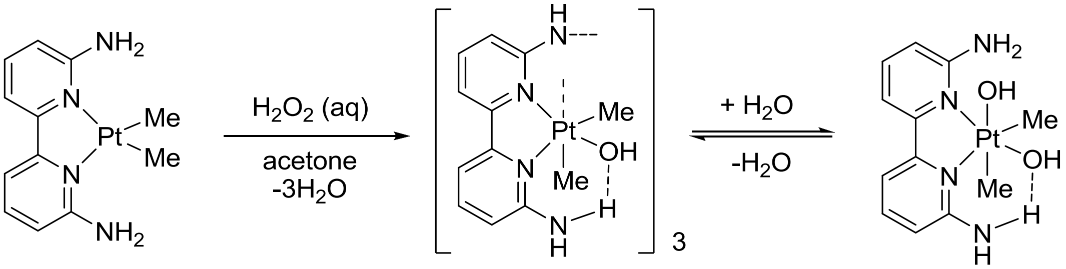
Several *trans*-dihydroxoplatinum(IV) complexes are known and they tend to be rather unreactive due to their low spin d^6 configuration and the weak *trans* effect due to the hydroxo ligands.[10] By directing the reactivity towards forming a *cis*-dihydroxoplatinum(IV) alkyl intermediate, the possibility of tuning the Pt-C and Pt-O bond strengths by ancillary ligand would be plausible and inducing a C-O reductive elimination to the desired methanol product.[11]

The first example of an entirely *cis*-hydroxoplatinum(IV) complex was reported by Vedernikov et al. utilizing a *fac*-tridentate ligand, di(2-pyridyl)methanesulfonate, forcing the hydroxo ligand and oxygen atom *cis* to one another as illustrated in scheme 3.2.[12]



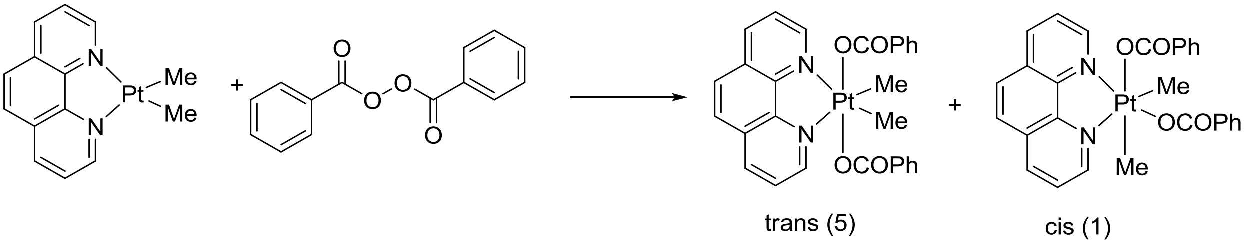
Scheme 3.2: First evidence of a *cis*-hydroxoplatinum(IV) complex

Research has also been conducted involving the formation of *cis*-dihydroxodimethylplatinum(IV) complexes via oxidative additions reaction of H_2O_2 with Pt(II) dimethyl complexes containing hydrogen bonding amine substituents. The role of these hydrogen bonded substituents is in the stabilization of the *cis*-dihydroxo complex, preventing rearrangement to the *trans*-dihydroxo platinum(IV) species. The addition of hydrogen peroxide to [(6,6'-diamino-bpy)Pt(II)Me_2] results in the formation of a trinuclear complex which upon addition of water, can form an exclusively *cis*-dihydroxo platinum(IV) complex, which has been illustrated in scheme 3.3.

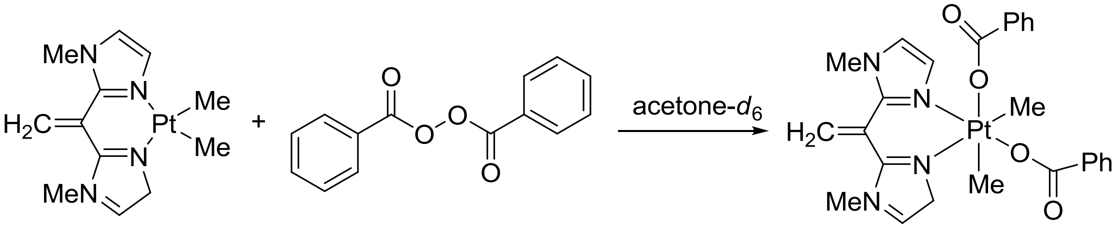


Scheme 3.3: Exclusive *cis*-oxidative addition of H_2O_2 to a platinum(II) complex

There have been numerous studies illustrating the use of dibenzoyl peroxide with platinum(II) complexes, each showing varying degrees of favouring the *cis*-oxidative addition product. Shown here are two examples in the resulting products involved a *cis*-orientation, one showing more prevalence for the formation of this product over the other. The first of these reactions involved the reaction of benzoyl peroxide with [$PtMe_2$(phen)] (phen = 1,10-phenanthroline), in which the products were formed in a 5:1 *trans* to *cis* ratio, which has been illustrated in scheme 3.4.[13] Utilizing a second platinum(II) complex, [$PtMe_2(MIM)_2C{=}CH_2$)] where $(MIM)_2C{=}CH2$ = 1,1-bis(1-methylimidazole-2-yl)ethane, it was found that this complex directed the reaction of benzoyl peroxide towards forming a product of exclusively *cis* nature, which can be seen in scheme 3.5.[14]



Scheme 3.4: *Cis* and *trans*-oxidative addition of benzoyl peroxide at [$PtMe_2$(phen)]

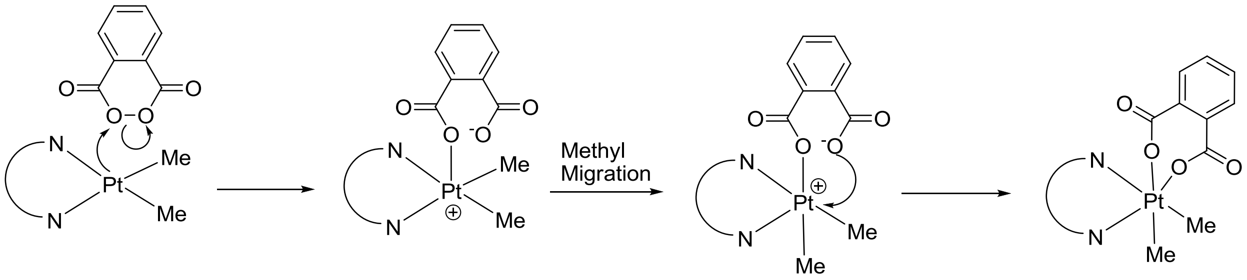


Scheme 3.5: Exclusive *cis*-oxidative addition product utilizing [$PtMe_2(MIM)_2C{=}CH_2$] with benzoyl peroxide.

The concept of directing oxidative addition towards forming a complex of *cis*-geometry becomes important when understanding that the reactivity of these platinum(IV) complexes is greater than their *trans* counterparts.[11] This concept has lead to the idea that the utilization of a cyclic peroxide, phthaloyl peroxide would be helpful to achieving this goal. The coordination of the O-O bond in a *cis*-directed manner due to the steric constraints imposed by the ring is the goal of this study. Phthaloyl peroxide has been widely studied and is a six-membered aromatic diacyl peroxide containing four sp^2-hybridized carbon atoms. It contains a relatively low activation energy (24 kcal/mol) for radical cleavage of the peroxide bond and this can be attributed to the peroxide dihedral angle of 11.4° with the O-O bond distance being stretched to 1.474 Å because of the cyclic nature of this compound.[15,16]

Figure 3.1: Phthaloyl peroxide and peroxide dihedral angle

Utilizing this cyclic peroxide, upon breaking of the O-O bond, instead of resulting in two separate fragments, as with non-cyclic peroxides, the connectedness of the phthaloyl peroxide would lead to a relatively close proximity of the oxygen atoms, even after cleavage has occurred. With the cyclic nature of this peroxide, it would suggest that oxidation at the platinum(II) center by phthaloyl peroxide would most likely lead to the formation of the *cis*-oxidative addition product, which has been illustrated in scheme 3.6.



Scheme 3.6: Proposed *cis*-oxidative addition reaction of the cyclic phthaloyl peroxide with platinum(II) complex.

The goal of this chapter is to explore the reactivity of phthaloyl peroxide with many different platinum(II) complexes. The task is to attempt to understand if the geometry of the oxidative addition reaction may be controlled by applying restraints to the incoming oxidant. As in chapter 2, there have been different platinum(II) complexes utilized in this chapter, with the hopes of probing the full reactivity of this cyclic oxidant. Platinum(II) species containing nitrogen donor ligands are known to be very electron rich complexes and thus are ideal candidates for exemplifying the oxidation potential of this peroxide.[3] Starting with very simple platinum(II) complexes, moving on to more substituted bipyridyl ligands, as well as platinum(II) complexes containing six-membered bidentate nitrogen donor ligands, the reactivity of phthaloyl peroxide has been extensively explored.

3.2 Results and discussion

3.2.1 Reaction of [PtMe$_2$(bpy)] with Phthaloyl Peroxide

In the initial stages of this research, the simplest of the platinum(II) complexes has been used in a reaction with phthaloyl peroxide. Phthaloyl peroxide was prepared by a modified procedure outlined by Russell.[17] Phthaloyl peroxide was mixed in a 1:1 stoichiometric ratio with complex **2.1**, [PtMe$_2$(bpy)] in acetone forming a cloudy white solution. Subsequent layering with pentane induced precipitation of the remaining product, which was then washed and dried *in vacuo*. The ^{1}H NMR spectrum shown in figure 3.2, illustrates the formation of multiple products in the reaction, tentatively characterized as both the *cis* and *trans*-oxidative addition products.

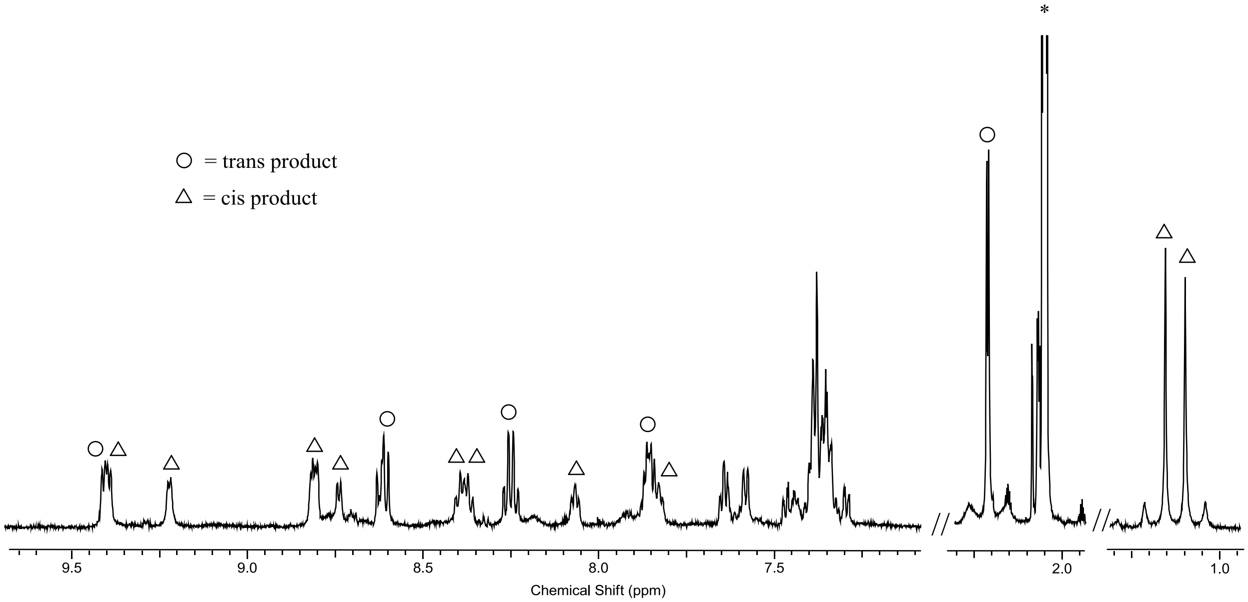
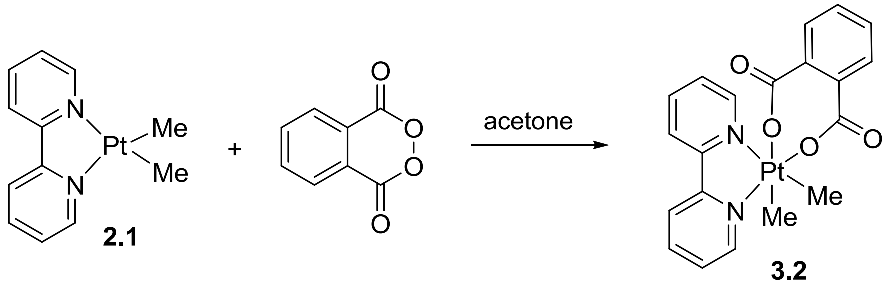


Figure 3.2: ^{1}H NMR spectrum of complex **3.1**: *trans* and complex **3.2**: *cis*-oxidative species from reaction of [PtMe$_2$(bpy)] with phthaloyl peroxide. (Δ = *cis*, o = *trans*, * = solvent)

Complex **3.1**, the *trans*-oxidative addition product has been identified by a single methyl platinum resonance at $\delta = 2.20$ ppm with a coupling of ^2J(PtH) = 66 Hz, but has proven difficult to characterize, so for this reaction, the *cis*-oxidative addition product will be the main focus, and has been named complex **3.2**. This product is easily characterized by ^{1}H and COSY NMR techniques. The characteristic two methyl platinum peaks that result from the lack of symmetry in the molecule, are found at $\delta = 1.10$ and 1.15 with coupling constants of ^2J(Pt-H) = 70 Hz and 69 Hz, respectively. With the resonances showing very close coupling values, it is difficult to distinguish between the two based on which is *trans* to the nitrogen and which to the oxygen. The mass spectrum gives m/z = 546.1, corresponding to [**3.2**-H]$^+$. The expected result of this reaction would be the *cis*-oxidative addition product, directed by the connectivity of the peroxide, as illustrated in Scheme 3.7.



Scheme 3.7: Proposed *cis*-oxidative addition product of the reaction of phthaloyl peroxide with [PtMe$_2$(bpy)]

After numerous attempts, a single crystal was obtained by the slow diffusion of pentane into a mixture of the phthaloyl peroxide and [PtMe$_2$(bpy)] in dichloromethane, stored at 5°C. Single crystal X-ray analysis was utilized in the determination of the platinum(IV) species and the resulting structure of complex **3.2a**, is illustrated in figure 3.3.

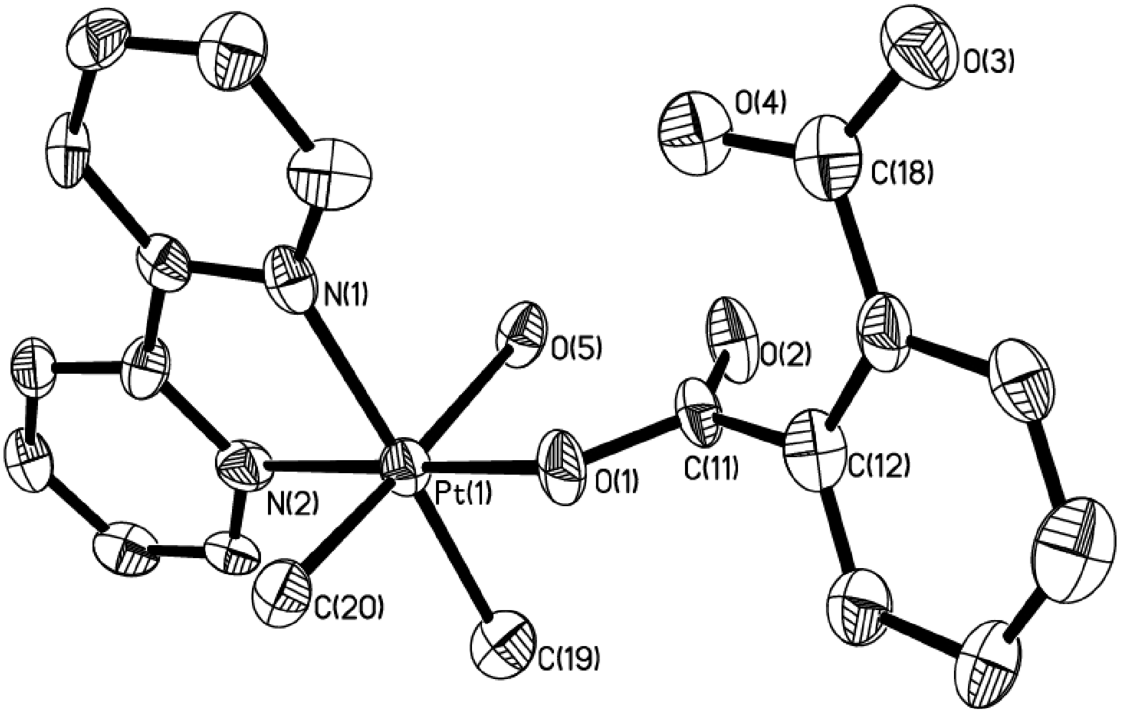
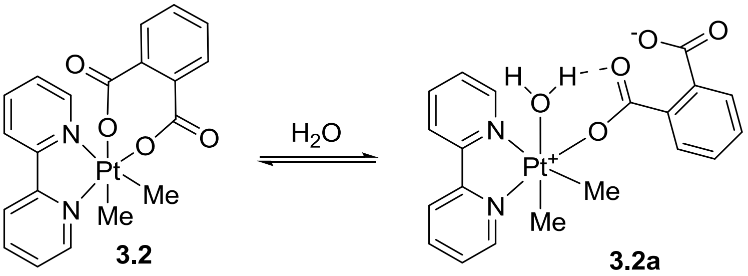


Figure 3.3: Structure of **Complex 3.2a·4.5H$_2$O**. Selected bond parameters; Pt(1)-O(1) = 2.013(9), Pt(1)-O(5) = 2.206(9), Pt(1)-N(1) = 2.100(11), Pt(1)-N(2) = 2.014(11), Pt(1)-C(19) = 2.039(13), Pt(1)-C(20) = 2.059(12) Å

Table 3.1: Bond lengths [Å] and angles [deg] for Complex 3.2a·4.5 H_2O

Pt(1)-O(1)	2.013(9)	Pt(1)-O(5)	2.206(9)
Pt(1)-N(2)	2.014(1)	O(1)-C(11)	1.318(1)
Pt(1)-C(19)	2.039(1)	O(2)-C(11)	1.244(2)
Pt(1)-C(20)	2.059(1)	O(3)-C(18)	1.245(2)
Pt(1)-N(1)	2.100(1)	O(4)-C(18)	1.253(2)
O(1)-Pt(1)-N(2)	172.4(4)	O(1)-Pt(1)-O(5)	96.4(3)
O(1)-Pt(1)-C(19)	86.2(4)	N(2)-Pt(1)-O(5)	89.6(4)
N(2)-Pt(1)-C(19)	98.3(5)	C(19)-Pt(1)-O(5)	92.0(4)
O(1)-Pt(1)-C(20)	83.0(4)	C(20)-Pt(1)-O(5)	176.9(5)
N(2)-Pt(1)-C(20)	90.7(5)	N(1)-Pt(1)-O(5)	89.2(4)
C(19)-Pt(1)-C(20)	91.0(5)	C(11)-O(1)-Pt(1)	125.3(8)
O(1)-Pt(1)-N(1)	96.1(4)	O(2)-C(11)-O(1)	124.1(1)
N(2)-Pt(1)-N(1)	79.3(4)	O(2)-C(11)-C(12)	122.1(1)
C(19)-Pt(1)-N(1)	177.3(5)	O(1)-C(11)-C(12)	113.8(1)
C(20)-Pt(1)-N(1)	87.8(5)	O(3)-C(18)-O(4)	124.9(1)

The structure demonstrates an unexpected result for what was thought to be a simple *cis*-oxidative addition reaction. The expected product involved cleavage of the O-O bond from the peroxide, followed by oxidative addition of both oxygen atoms to the platinum center as illustrated in scheme 3.6. The mechanism expected for this reaction would be a two electron bimolecular S_N2 oxidative addition. It appears however, based on the result of the crystal structure data that instead of coordination of the second oxygen from the phthaloyl peroxide, there has been coordination of a hydroxyl or a water molecule into the vacant site on the platinum center. Based on the mass spectrometry results the resulting crystal is most likely a result of hydrolysis of one of the phthaloyl peroxide oxygen atoms coordinated to the platinum by water in the recrystallization solvent, which has been illustrated in scheme 3.8.



Scheme 3.8: Formation of complex **2a**, via hydrolysis an oxygen atom of phthaloyl peroxide via a water molecule.

The protons on the oxygen atom in this structure were not located, which has lead to some uncertainty in the overall determination of the product. The issue lies with whether a water molecule or a hydroxyl group is bound to the platinum center. Comparison of the bond lengths of the non-coordinated carboxylate between C(18)-O(4) and C(18)-O(3), reveal bond distances that can be considered equivalent. This suggests the presence of carboxylate, compared to that of a carboxylic acid, which would have exhibited differing bond lengths. These results indicate that this product formed does indeed involve the interaction of water with the platinum center. There is also indication of intramolecular hydrogen bonding interactions between the water molecule on the platinum and the oxygen from the phthalate groups, O(5)-O(2), which may lend to overall stabilization of the structure. This structure also displays some very interesting results, with the incorporation of a cluster of water molecules, which have resulted due to the crystallization taking place in a moist solvent environment, which has been illustrated in figure 3.4. There is hydrogen bonds between O(1A)-O(6SC) and O(6SC)-O(4) and symmetry equivalents. These water molecules lead to hydrogen bonding interactions between the oxygen atoms on the platinum center and the oxygen atoms located on the phthaloyl peroxide, lending to the hydrogen bonded network shown in figure 3.4.

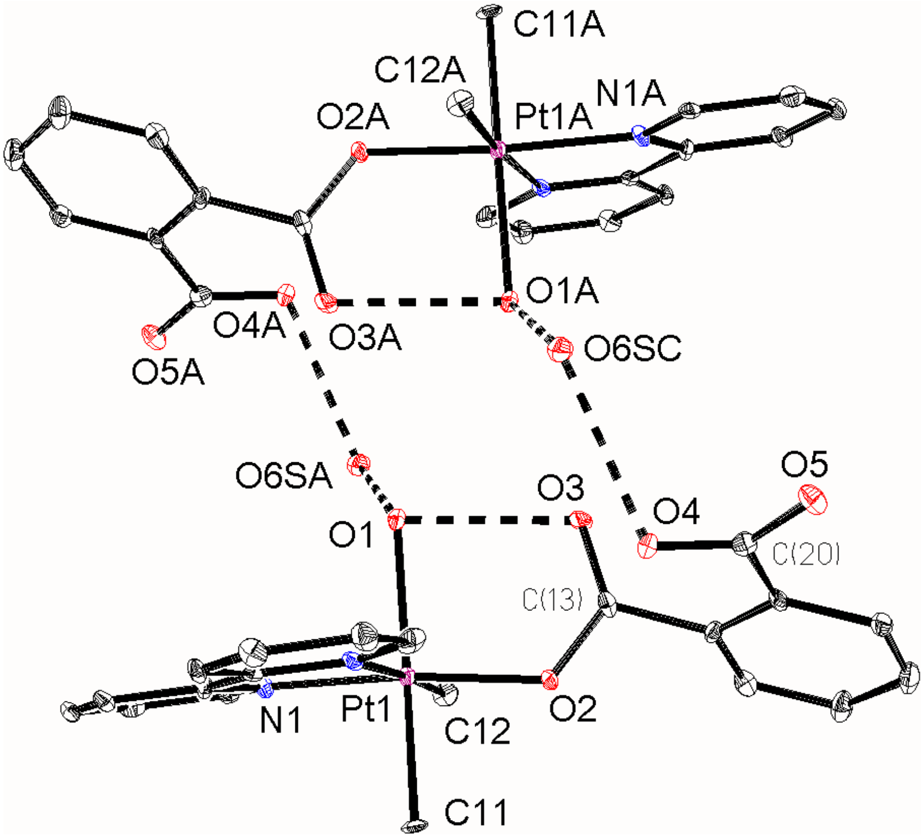


Figure 3.4: Hydrogen bonded network of water molecules with the phthaloyl peroxide on the platinum(IV) complex

Overall, this is a very unique and interesting structure; however the incorporation of the water molecules leaves uncertainty as to the product formed during this reaction. With difficulties in finding solvents for recrystallization due to solubility issues, further study was needed using a more soluble Pt(II) complex.

3.2.2 Reaction of [PtMe$_2$(bu$_2$bpy)] with Phthaloyl Peroxide

The desire to find a platinum(II) complex suitable for forming single crystals has lead to the use of Complex **3.3,** [PtMe$_2$(bu$_2$bpy)], which demonstrates very similar reactivity to that of [PtMe$_2$(bpy)], but is more soluble due to the inclusion of the bulky organic groups.[18] This inherent solubility is being relied on for the production of single crystals to help characterize this cyclic peroxide system. Phthaloyl peroxide was mixed in a 1:1 stoichiometric ratio with [PtMe$_2$(bu$_2$bpy)],[18] and immediately the orange colour of the platinum(II) complex dissipated and a clear and colourless solution was obtained. The solution was layered with pentane and a white precipitate was afforded. The ^{1}H NMR spectrum was obtained in acetone-d_6 and results are similar to those seen for complex **3.1**, with the formation of multiple products, both the *cis* and *trans* oxidative addition products. The *cis*-oxidative addition product was isolated by recrystallization with slow diffusion of pentane into a dichloromethane solution containing complex **3.4,** [PtMe$_2$(bu$_2$bpy)(C$_8$H$_4$O$_4$)] and the ^{1}H NMR spectrum is shown in figure 3.5.

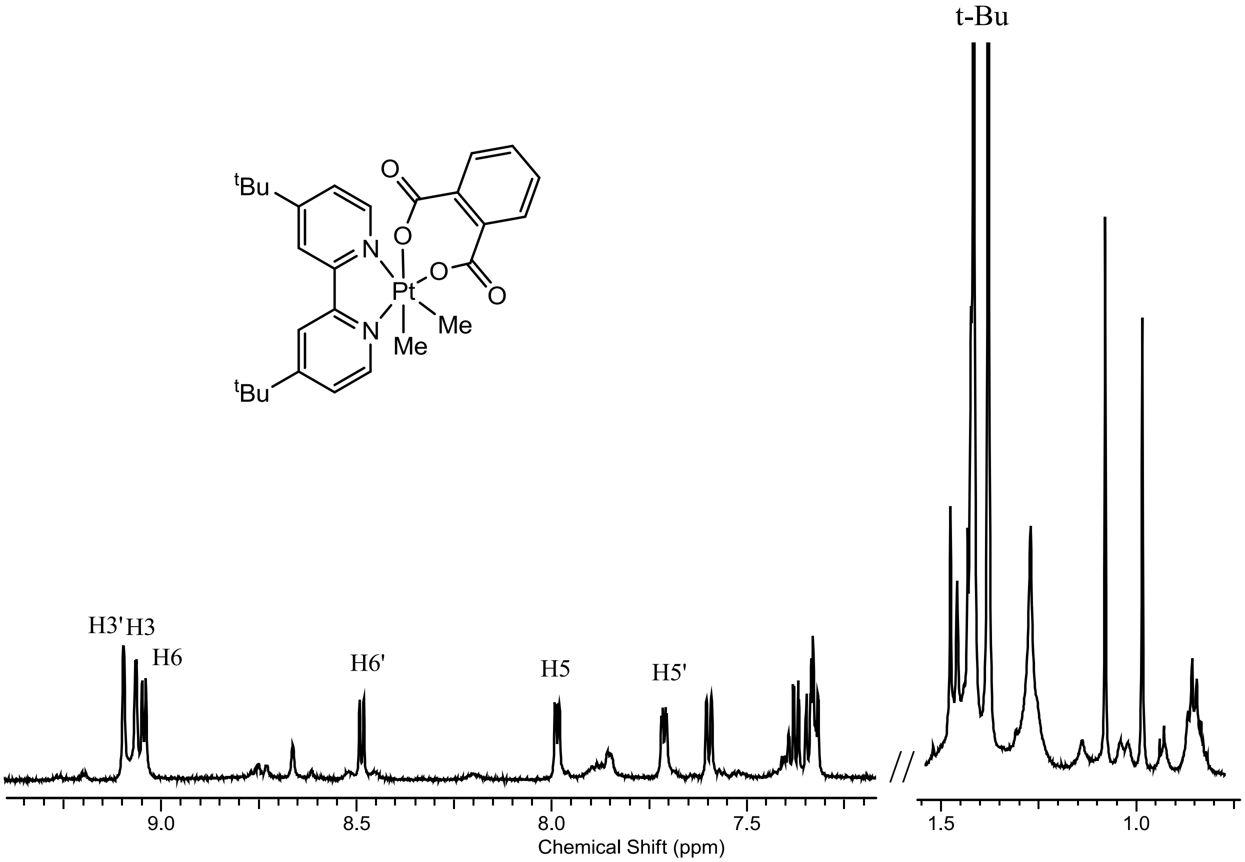
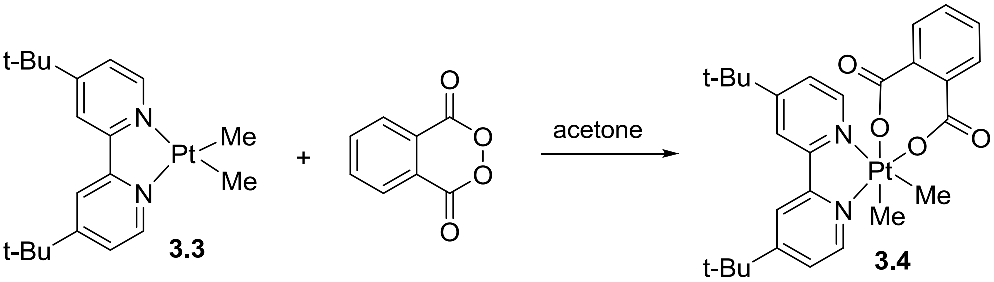


Figure 3.5: ^{1}H NMR spectrum of complex **3.4**, [PtMe$_2$(bu$_2$bpy)(C$_8$H$_4$O$_4$)] via *cis*-oxidative addition.

The *cis*-oxidative addition product is easily characterized by the two methyl platinum singlets at $\delta = 1.01$ and 1.10 with coupling of $^2J(\text{PtH}) = 67$ Hz, and 70 Hz, respectively. The coupling of 67 Hz, is characteristic of the methyl group *trans* to nitrogen, whereas the larger coupling constant of 70 Hz, is typical of the methyl group *trans* to oxygen, based on the *trans*-effect series. Complex **3.4**, was also characterized by mass spectrometry with the main signal present at m/z of 658.2 indicative of the coordination of the phthaloyl peroxide to the platinum center. The reaction for the formation of the *cis*-oxidative addition product, complex **3.3** is shown in scheme 3.9.



Scheme 3.9: Complex **3.4**, *cis*-addition product from the reaction of phthaloyl peroxide with [$PtMe_2(bu_2bpy)$]

Single crystals were grown by a slow diffusion of pentane into a dichloromethane solution of complex **3.4**. The results of the single crystal X-ray analysis, illustrated in figure 3.6, indicate the formation of the proposed species.

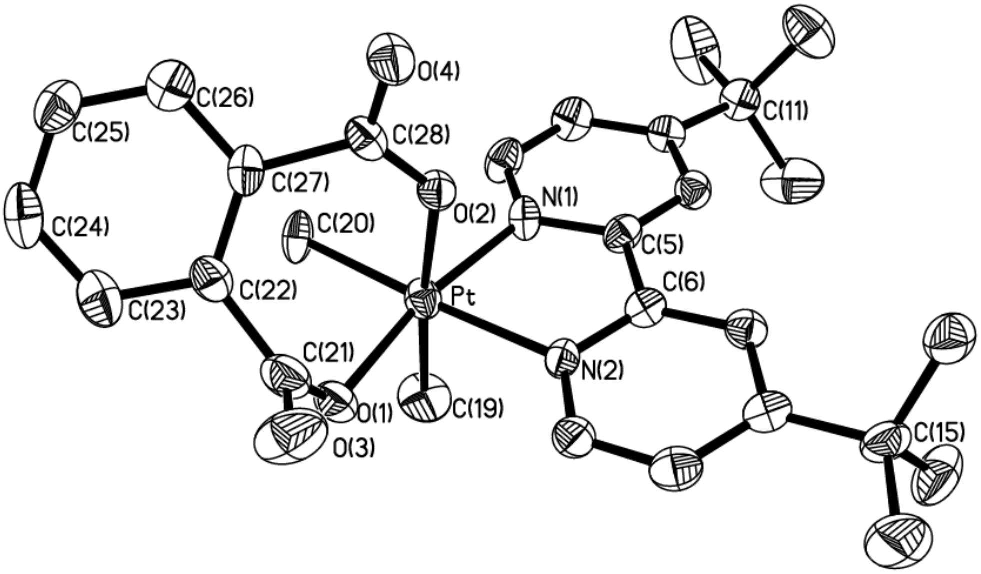
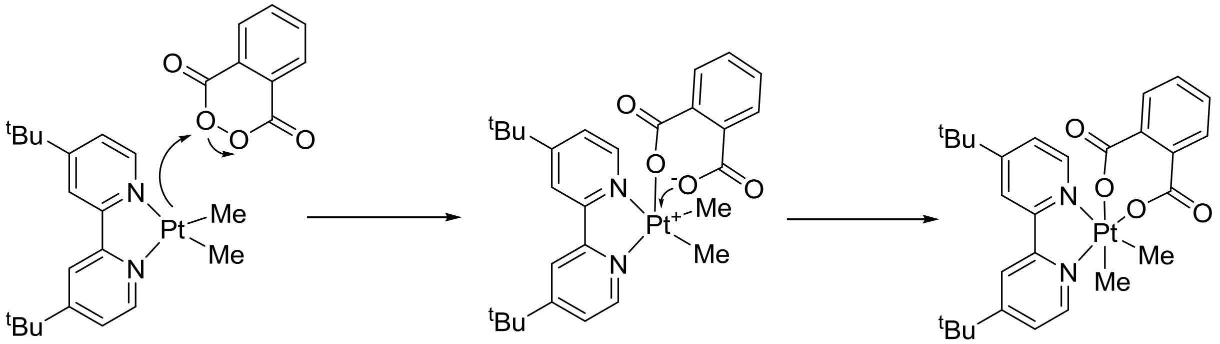


Figure 3.6: Single crystal X-ray structure of Complex **3.4**·CH_2Cl_2**.** Selected bond parameters: Pt-O1 = 2.020(5), Pt-O2 = 2.160(4), O(2)-C(28) = 1.291(8), O(1)-C(21) = 1.296(8), O(4)-C(28) = 1.223(8), O(3)-C(21) = 1.221(9) Å.

Table 3.2: Bond lengths [Å] and angles [deg] for complex 3.4·CH_2Cl_2

Pt-O(1)	2.020(5)	O(1)-C(21)	1.296(8)
Pt-N(1)	2.027(5)	C(28)-O(4)	1.223(8)
Pt-C(20)	2.063(6)	C(28)-C(27)	1.519(9)
Pt-C(19)	2.067(6)	C(22)-C(23)	1.386(1)
Pt-N(2)	2.120(5)	C(22)-C(27)	1.398(1)
Pt-O(2)	2.160(4)	C(22)-C(21)	1.504(1)
O(2)-C(28)	1.291(8)	C(21)-O(3)	1.221(9)
O(1)-Pt-N(1)	169.9(2)	N(2)-Pt-O(2)	81.60(1)
O(1)-Pt-C(20)	91.5(3)	C(28)-O(2)-Pt	133.6(4)
N(1)-Pt-C(20)	98.2(3)	C(21)-O(1)-Pt	121.0(4)
O(1)-Pt-C(19)	88.5(3)	O(4)-C(28)-O(2)	122.6(6)
N(1)-Pt-C(19)	88.8(3)	O(4)-C(28)-C(27)	117.3(6)
C(20)-Pt-C(19)	88.4(3)	O(2)-C(28)-C(27)	120.0(6)
O(1)-Pt-N(2)	91.1(2)	C(23)-C(22)-C(27)	118.1(7)
N(1)-Pt-N(2)	79.3(2)	C(23)-C(22)-C(21)	117.2(6)
C(20)-Pt-N(2)	177.2(2)	C(27)-C(22)-C(21)	124.4(6)
C(19)-Pt-N(2)	92.8(3)	C(22)-C(27)-C(28)	123.0(6)
O(1)-Pt-O(2)	92.26(2	O(3)-C(21)-O(1)	121.0(7)
N(1)-Pt-O(2)	89.44(2)	O(3)-C(21)-C(22)	118.8(7)
C(20)-Pt-O(2)	97.1(2)	O(1)-C(21)-C(22)	120.0(7)
C(19)-Pt-O(2)	174.4(3)		

The crystal structure shows the predicted product of an oxidation of the platinum(II) center by phthaloyl peroxide. Complex **3.4** varies from the previously discussed complex **3.1**, in that there is coordination of both oxygen atoms of the peroxide forming a seven-member chelating ring to the platinum center, instead of insertion of a water molecule. The close proximity of the two oxygen atoms, has led to the *cis*-oxidative addition of the peroxide, instead of the typical *trans*-addition seen for other non-cyclic peroxide systems. The hypothesized mechanism for this reaction is a bimolecular S_N2 oxidative addition in which the platinum attacks the σ* orbital of one of the oxygen, leading to breaking of the peroxy bond and formation of a cationic platinum center and an anionic oxygen atom. There is then coordination of the anionic ligand to the metal center, leading to the formation of the illustrated species. This can be seen outlined in scheme 3.10.

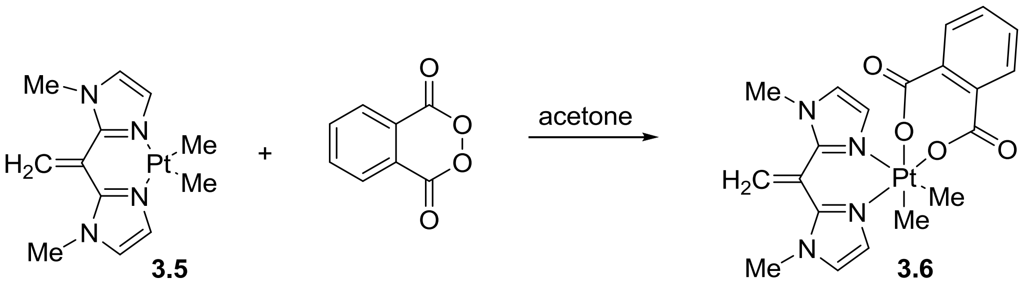


Scheme 3.10: S_N2 reaction mechanism for the *cis*-oxidative addition of phthaloyl peroxide to [$PtMe_2(bu_2bpy)$]

There appears to be multiple C-H···O hydrogen bonds to the single carbonyl atom on the phthaloyl peroxide (O4) from the hydrogen atoms on the bipyridine rings of the neighbouring complex. This interaction may lend to stabilization of the crystal packing of this structure. The O···H distances are determined to be around 2.3 Å, and this finding is not unprecedented for C-H···O interactions as previously reported by Desiraju.[19] The crystal structure has helped prove the formation of this novel product, the *cis*-oxidation addition reaction of phthaloyl peroxide at a Pt(II) center.

3.2.3 Reaction of [$PtMe_2(MIM)_2C{=}CH_2$] with Phthaloyl Peroxide.

Complex **3.5**, [$PtMe_2(MIM)_2C{=}CH_2$] was synthesized by Safa et al,[14] and has shown promise in the formation of purely *cis*-addition of peroxide compounds to the platinum center. In a reaction with dibenzoyl peroxide, there was evidence of a majority *cis*-oxidative addition product with use of this platinum(II) complex, which has been illustrated in the introduction of this chapter in scheme 3.5. This result has lead to interest in utilizing this platinum(II) complex to help exemplify the formation of a platinum(IV) complex in which phthaloyl peroxide coordinates by a strictly *cis*-geometry. The expected formation would be a platinum(IV) complex with the peroxide addition occurring in a *cis*-manner, as illustrated in scheme 3.11.



Scheme 3.11: Expected *cis*-oxidative addition product of phthaloyl peroxide with [$PtMe_2(MIM)_2C{=}CH_2$]

This reaction was completed on an NMR scale involving the addition of phthaloyl peroxide in a 1:1 ratio to [$PtMe_2(MIM)_2C{=}CH_2$] in an acetone-d_6 solution. The resultant solution turned cloudy white with the formation of a precipitate, and was characterized by ^1H NMR spectroscopy. The ^1H NMR spectrum showed complete consumption of the starting platinum(II) complex and lead to the formation of a new product. The ^1H NMR spectrum showed characteristics of what would be expected for the *cis*-oxidative addition of the phthaloyl peroxide forming a platinum(IV) species, as illustrated in figure 3.7.

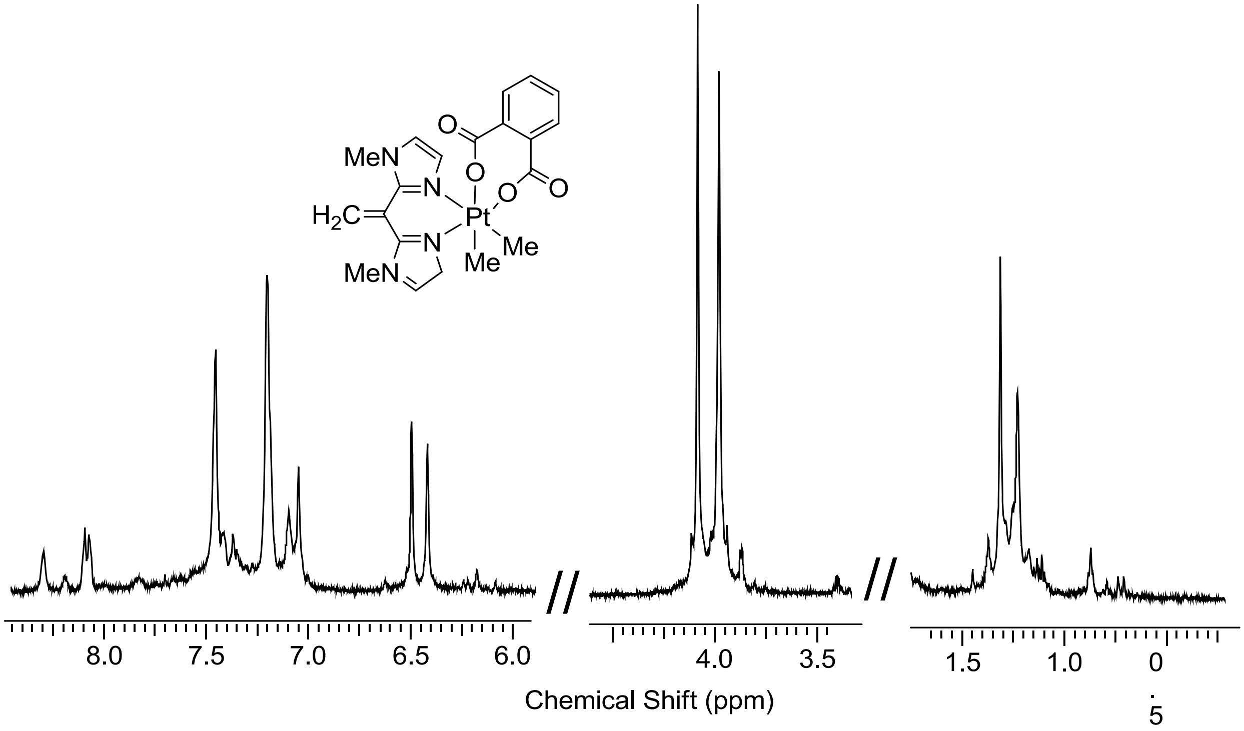


Figure 3.7: ^{1}H NMR spectrum of the complex **3.6**, [$PtMe_2(C_8H_4O_4)(MIM)_2C{=}CH_2$] via the *cis*-oxidative addition of phthaloyl peroxide.

This product produced two methyl platinum signals in the spectrum one at $\delta = 1.23$ and $\delta = 1.31$, with two coupling of ^2J(PtH) = 68 and 71 Hz, respectively. These values demonstrate that a platinum(IV) species was indeed formed, indicating an oxidative addition reaction had occurred. These coupling constants also give evidence for the expected *cis*-oxidative addition reaction. The methylplatinum with the larger coupling of 71 Hz, is assigned to the methyl *trans* to the oxygen, and resonance with the smaller coupling constant of 68 Hz, is assigned to the methyl *trans* to the nitrogen, due to its higher *trans* influence. There is further evidence of the formation of a *cis*-oxidative addition product, and this is shown by the loss of symmetry in the molecule. Originally, [$PtMe_2(MIM)_2C=CH_2$] showed a single peak at δ = 3.92, and this peak integrated to six protons. Upon the addition of the peroxide, this peak was split into two separate singlets each representing 3 protons, with varying chemical shift values of δ = 3.98 and δ = 4.08. Further evidence of the *cis*-oxidative addition product can be found downfield in the spectrum in which the original bridging $CH_{2,}$ found at δ = 6.18, accounting for two protons and existing as a singlet, and now can now be seen as two singlets at δ = 6.42 and δ = 6.50, each accounting for one proton. The aromatic region is difficult to distinguish, but it can be seen that there are 8 distinct signals which correspond to the aromatic protons, and due to the number of signals doubling from the starting material, this structure can be classified as a *cis*-oxidative addition product. The mass spectrum contained a peak at 578.1, corresponding to [**3.6**-H]$^+$, supporting the formation of the proposed structure. Numerous recrystallization attempts have been carried out showing no promise in delivering a single crystal suitable for X-ray analysis.

3.2.4 Reactions of [$PtMe_2$(dpk)] and [$PtMe_2$(dpa)] with Phthaloyl Peroxide

The effect of changing the chelate bite angle of the dipyridyl ligands of dimethylplatinum(II) complexes has been demonstrated to result in varying reactivity. There has been many studied carried utilizing ligands such as di-2-pyridylamine (dpa) and di-2-pyridyl ketone (dpk), which form six membered chelate rings with platinum(II) complexes and tend to show different reactivity than the conventional five membered chelate ring systems.[20] In an attempt to show the reactivity of these larger chelate ring systems, studies utilizing phthaloyl peroxide with both complex **2.5**, [$PtMe_2$(dpk)] and complex **2.7**, [$PtMe_2$(dpa)] have been carried out to try to understand the *trans*-oxidative addition products of this system.

3.2.4a Reactions of [$PtMe_2$(dpk)] with Phthaloyl Peroxide

Complex **2.5**, [$PtMe_2$(dpk)], was synthesized and reacted in 1:1 stoichometric ratio with phthaloyl peroxide. The initial red colour of the solution dissipated and a white precipitate began to form within the reaction mixture. The *trans*-product was found to be insoluble in the acetone solution, whereas the *cis*-product was soluble. In attempts to isolate the *trans*-product, the acetone solution was decanted off the white precipitate and analyzed separately. It was found that this was successful, in that upon purification of both the precipitate and of the acetone solution, that there had been the formation of two different products. The first of these products was characterized as the *cis*-oxidative addition product of phthaloyl peroxide with the [$PtMe_2$(dpk)]. The ^1H NMR spectrum of this complex is shown in figure 3.8.

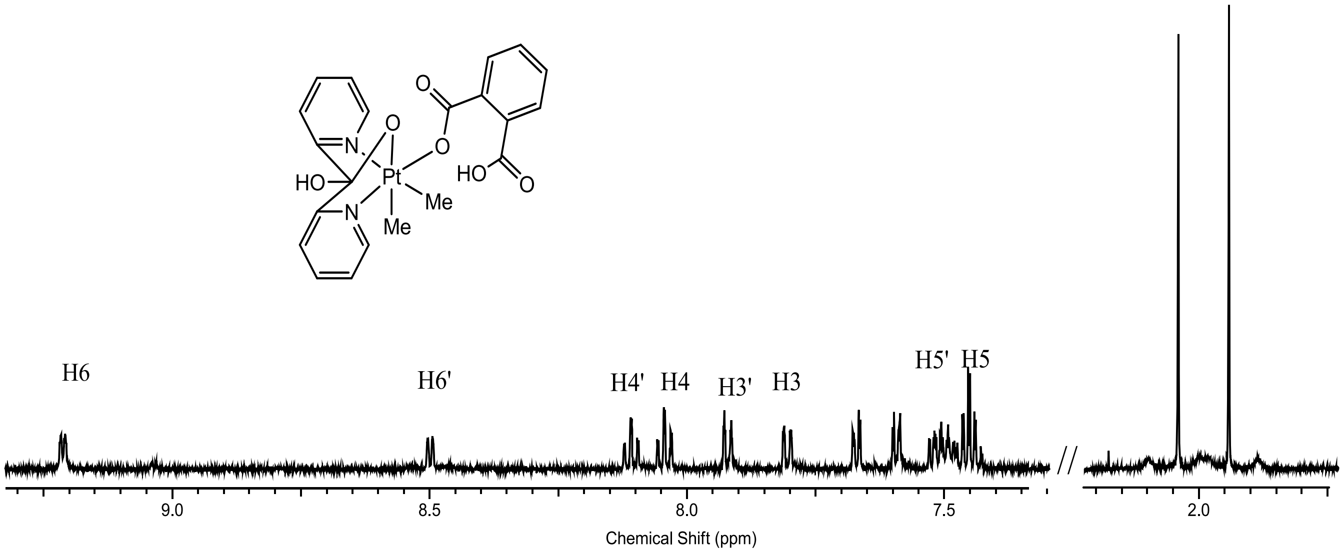
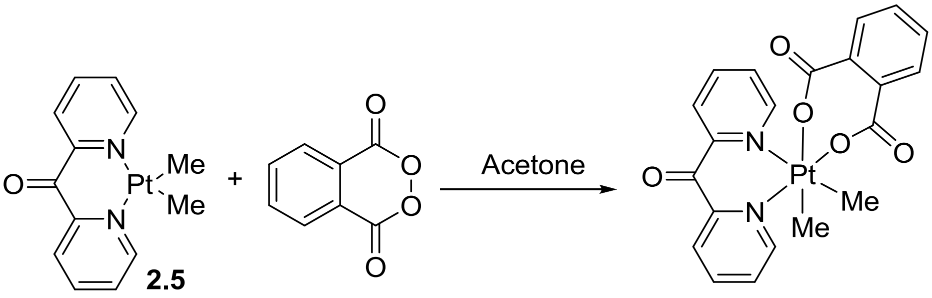


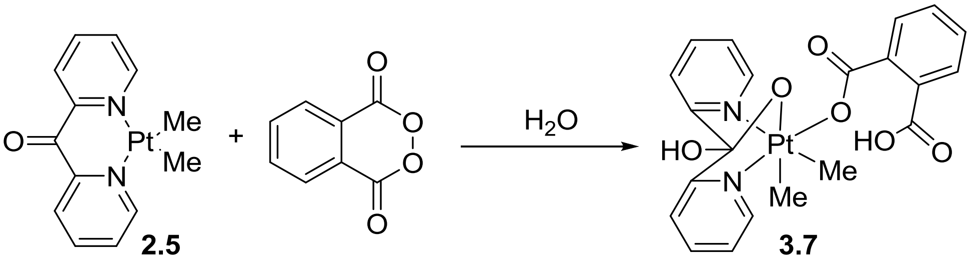
Figure 3.8: ^1H NMR spectrum of complex **3.7**, [$PtMe_2(dpk)(C_8H_4O_2)$]

The ^1H NMR of this product, illustrates the *cis*-oxidative addition nature of the phthaloyl peroxide at the platinum(II) center. It can be seen from this spectrum that there are two methyl platinum proton resonances located at δ = 1.94 ppm and 2.04 ppm each with a coupling of $^2J(PtH)$ = 70 Hz. This illustrates that a platinum(IV) species has indeed been formed and with each of these resonances each representing 3 protons, suggesting a lack of symmetry of the molecule. This lack of symmetry is also evident within the aromatic portion of this spectrum, with varying resonances for the protons on bipyridyl rings. The protons were assigned to each of the rings through the use of COSY, however it was difficult to assign both H^5 and $H^{5'}$, as they seemed to overlap with the phthaloyl peroxide protons, which were also difficult to assign. There are two lines of thinking when it comes to the characterization of this product. It can be seen that a *cis*-oxidative addition species has been formed, however it is difficult to establish which complex actually results from this reaction. The complex could form in which both oxygen atoms from the phthaloyl peroxide species are coordinated which based on previous results would be a likely product, and this is shown in scheme 3.12. There is also the possibility that this species takes on similar characteristics to the previously reported peroxide additions with the [PtMe$_2$(dpk)] in which there is reduction at the carbonyl leads to the insertion of an oxygen forming a hemi-acetal type product.[21]



Scheme 3.12: Proposed reaction of [PtMe$_2$(dpk)] with phthaloyl peroxide forming [PtMe$_2$(dpk)(C$_8$H$_4$O$_2$)].

The inability to form single crystals suitable for X-ray analysis of this complex has led to both mass spectrometry and IR being relied on for characterization of this product. Simple IR experiments have been conducted comparing [PtMe$_2$(dpk)] with that of the newly formed product, specifically viewing the carbonyl region. It can be observed that upon formation of this new complex, that the CO stretch initially observed in the [$PtMe_2$(dpk)] located at 1682 cm^{-1}, has been lost and is not present in the spectrum of complex **3.7**. There are however carbonyl stretches located at lower wavenumbers, around 1650-1600 cm^{-1}, indicative of the phthaloyl peroxide coordinated to the platinum center. With this result and the fact that the elemental analysis results indicate the inclusion of water into the overall formula, we determined that the product formed is complex **3.7,** *cis*-[$PtMe_2$(dpkOH)($C_8H_5O_4$)] shown in scheme 3.13, not the proposed [$PtMe_2$(dpk)($C_8H_4O_2$)] as shown in scheme 3.12.



Scheme 3.13: Formation of *cis*-oxidative addition product via phthaloyl peroxide and [$PtMe_2$(dpk)] forming complex **3.7**.

The use of mass spectrometry has also helped to confirm the formation of the complex **3.7**, however, it has been made difficult due to the solubility issues of this compound. The use of NaI in this mass spectroscopy characterization has lead to a peak of m/z 613.1, which represents [Pt($C_8H_5O_4$)Me_2(dpkOH)Na]$^+$. This result helps to clarify the formation of the proposed species resulting from the *cis*-oxidative addition reaction. With these results in hand, there is support from the findings that have already been made utilizing NMR, IR and elemental analysis.

In work published by Zhang et al. it was found that the use of the [$PtMe_2$(dpk)] in reactions with hydrogen peroxide lead to the formation of a species in which the carbonyl group was involved, forming the complex [Pt(OH)Me_2(dpkOH)].[21] With this in mind the acetone portion of this sample was analyzed after being fully purified. It was found by looking at the ^{1}H NMR spectrum shown in figure 3.9, that this product showed properties indicating that this reaction underwent a *trans*-oxidative addition.

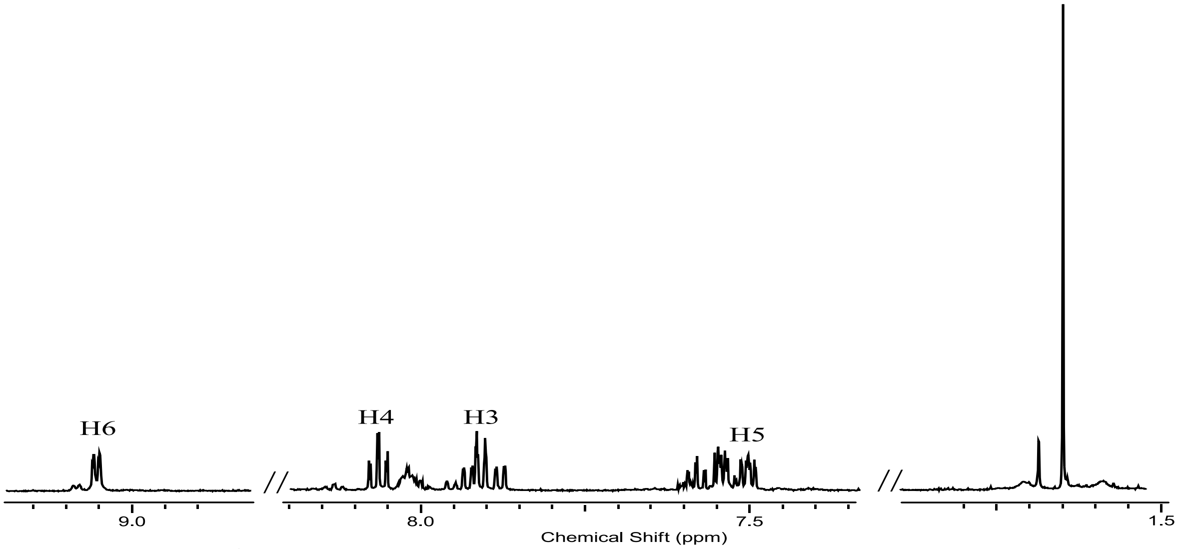


Figure 3.9: ^{1}H NMR spectrum of complex **3.8,** *trans*-[PtMe$_2$(dpkOH)(C$_8$H$_5$O$_4$)]

As shown in the above ^{1}H NMR spectrum, there is a single methyl platinum resonance located at δ = 1.64 ppm with a coupling of ^{2}J(PtH) = 70 Hz. This is indicative that a platinum(IV) species has been formed and as seen in many of the cases of this research, there is reason to believe with these broad satellites that this contains a hydroxyl species within this product. It can also be seen that there are four peaks corresponding to the eight protons of the pyridyl rings, and this leads to the determination that this product is symmetrical about the platinum center. This was formed as the minor product in the reaction and thus gathering substantial amounts for mass spectroscopy and elemental analysis was made difficult. However, through a slow diffusion of pentane into a sample of complex **3.8**, *trans*-[PtMe$_2$(dpkOH)(C$_8$H$_5$O$_4$)] dissolved in dichloromethane, suitable crystals for X-ray analysis were obtained. These crystals proved to be a helpful resource in determining the species formed within this reaction. Based on the crystal structure as shown in figure 3.10, there proved to a similar formation of product as compared to that of Zhang et al. as well as compared to the initial analysis of complex **3.8,** except forming the *trans* isomer.

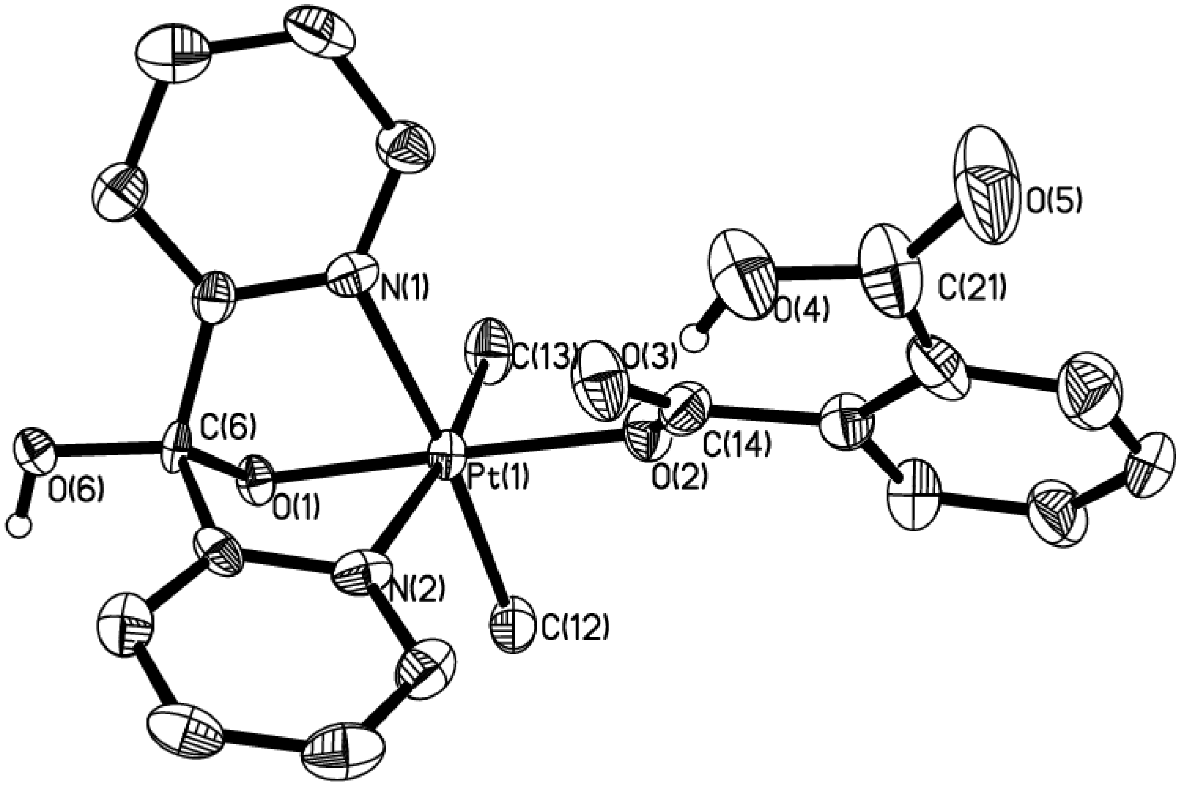
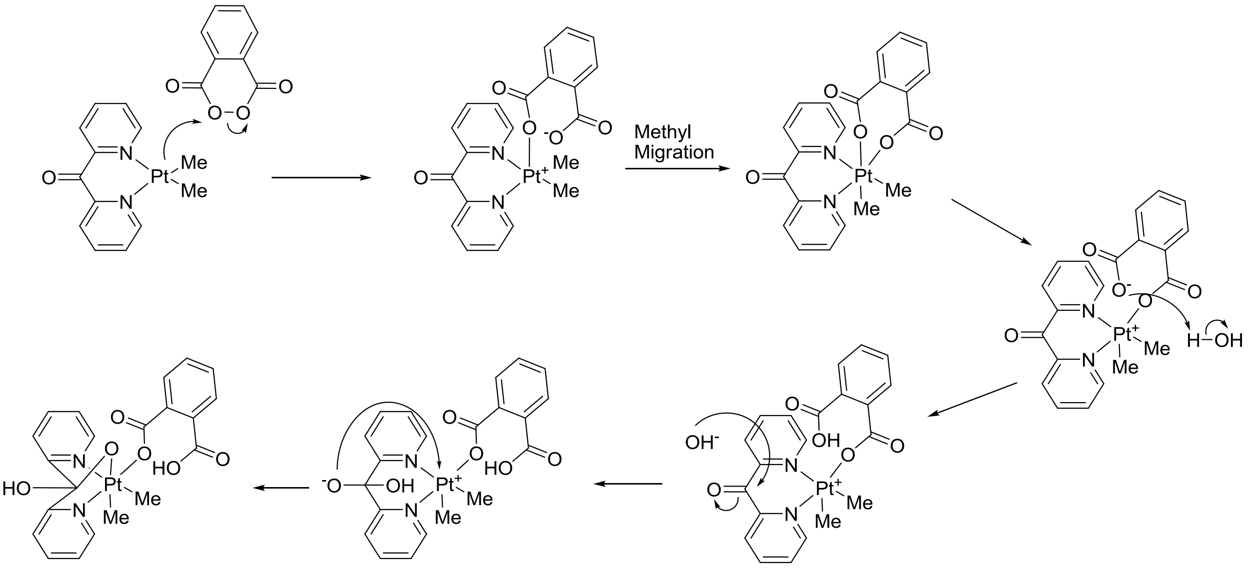


Figure 3.10: Crystal structure of complex **3.8**; Selected Bond Parameters: Pt(1)-N(1) = 2.146(8), Pt(1)-N(2) = 2.153(9), Pt(1)-O(1) = 2.009(6), Pt(1)-O(2) = 2,046(7), Pt(1)-C(12) = 2.062(11), Pt(1)-C(13) = 2.030(11), O(1)-C(6) = 1.438(7), O(2)-C(14) = 1.297(13), O(3)-C(14) = 1.226(13)

Table 3.3: Bond lengths [Å] and angles [deg] for complex 3.8.

Pt(1)-O(1)	2.009(6)	O(1)-C(6)	1.438(11)
Pt(1)-C(13)	2.030(1)	O(2)-C(14)	1.297(13)
Pt(1)-O(2)	2.046(7)	O(3)-C(14)	1.226(13)
Pt(1)-C(12)	2.062(1)	O(4)-C(21)	1.312(14)
Pt(1)-N(1)	2.146(8)	O(5)-C(21)	1.204(15)
Pt(1)-N(2)	2.153(9)		
O(1)-Pt(1)-C(13)	93.3(4)	O(1)-Pt(1)-N(2)	77.8(3)
O(1)-Pt(1)-O(2)	178.8(3)	C(13)-Pt(1)-N(2)	170.9(4)
C(13)-Pt(1)-O(2)	87.7(4)	O(2)-Pt(1)-N(2)	101.3(3)
O(1)-Pt(1)-C(12)	95.0(4)	C(12)-Pt(1)-N(2)	91.8(4)
C(13)-Pt(1)-C(12)	90.9(5)	N(1)-Pt(1)-N(2)	86.6(3)
O(2)-Pt(1)-C(12)	84.3(4)	C(6)-O(1)-Pt(1)	102.1(5)
O(1)-Pt(1)-N(1)	78.6(3)	C(14)-O(2)-Pt(1)	118.6(7)
C(13)-Pt(1)-N(1)	89.8(4)	O(6)-C(6)-O(1)	111.2(8)
O(2)-Pt(1)-N(1)	102.1(3)	O(6)-C(6)-C(5)	108.7(8)
C(12)-Pt(1)-N(1)	173.6(4)	O(5)-C(21)-O(4)	119.7(1)

From the X-ray structure, it can be seen that this product has one of the oxygen atoms from the phthaloyl peroxide species coordinated and one oxygen atom bound to the platinum center. This structure confirms the proposed conformation, and shows that the ligand, dpkOH, acts a *fac*-tridentate ligand in forming the platinum(IV) complex **3.7**. The route in which this species is formed is difficult to fully understand, but it can be suggested that there is an equilibrium between the complex **3.7** and complex **3.8**, the *cis* and *trans* species respectively. Upon inspection, it can be seen that there are two routes of formation. As in the case of most of these peroxide reactions, the peroxide bond is typically broken as one of the oxygen atoms binds to the platinum center leading to the formation of a five-membered, cationic platinum species. Scheme 3.12, shows the result of the other anionic oxygen atom from the phthaloyl peroxide species, coordinating to the cationic platinum center, through a rearrangement of the methyl groups of the metal forming a *cis*-coordianted product. On the other hand, when there is hydrolysis of the carbonyl by either a water or hydroxyl molecule, before the anionic oxygen of the phthaloyl peroxide can coordinate to the platinum center, the result is the formation of complex **3.7** and **3.8**. This overall process for the formation of complex **3.8** has been illustrated in Scheme 3.14 and this route would be the same for complex **3.7**, except for the product would result in the *cis*-isomer.



Scheme 3.14: Proposed pathway for the formation of complex **3.7**, *cis*-[PtMe$_2$(dpkOH)(C$_8$H$_5$O$_8$)]

3.2.4b Reaction of [PtMe$_2$(dpa)] with Phthaloyl Peroxide

A reaction was carried out in which complex **2.7,** [PtMe$_2$(dpa)] was mixed in a 1:1 ratio with phthaloyl peroxide. The initial yellow colour of the solution dissipated and a white precipitate began to form. The white mixture was layered with pentane and the product was isolated and dried *in vacuo*. The ^{1}H NMR spectrum, shown in figure 3.11, illustrates the formation of complex **3.9,** as the major product which has been tentatively characterized as [PtMe$_2$(OH$_2$)(dpa)(C$_8$H$_4$O$_4$)].

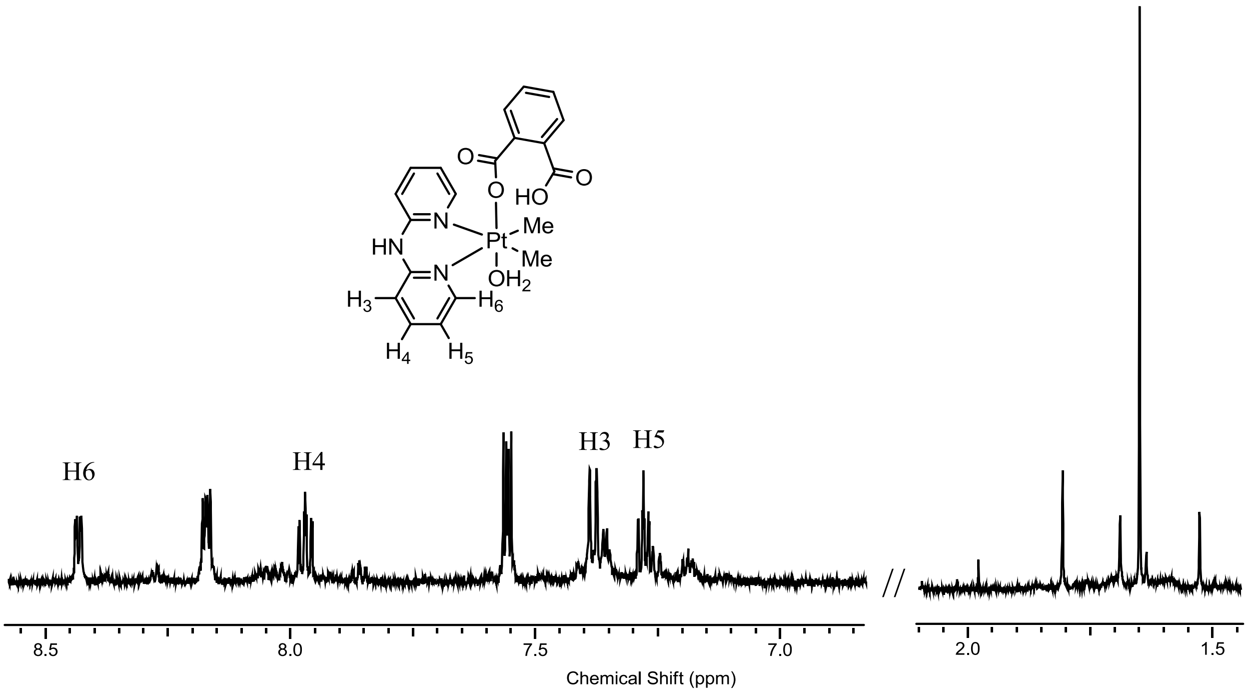


Figure 3.11: ^{1}H NMR spectrum of complex **3.9**, from the reaction of $[PtMe_2(dpa)]$ with phthaloyl peroxide.

The ^{1}H NMR spectrum has helped to distinguish this product as undergoing a *trans*-oxidative addition in which complex **3.9** has been formed. It can be seen in this spectrum that there is a single methyl platinum resonance located at $\delta = 1.61$ ppm with a coupling of ^2J(Pt-H) = 67 Hz. There is symmetry about this complex with the fact that there is a single methyl platinum resonance and only four resonances for the aromatic region of this spectrum representing the eight protons of the pyridyl rings. There is some uncertainty towards assigning the phthaloyl peroxide protons as they are not fully resolved but it can be seen that the two separate resonances integrating to two protons each and thus it can be assigned as the phthaloyl peroxide coordinated to the platinum complex.

There are a variety of possibilities possible for this product and thus mass spectrometry was relied on to help establish the actual structure of complex **3.9**. It can be seen that there is a prominent peak at m/z = 561.1, which represents the species $[PtMe_2(dpa)(C_8H_5O_4)]^+$, resulting in a loss of the water group from the platinum center. Further supporting these claims is a very prominent peak at m/z 411.1, which illustrates the loss of the phthaloyl peroxide from the platinum center, forming $[PtMe_2(OH)(dpa)]^+$. This peak appears to be more prominent compared to that at 561.1 m/z due to the ease in which the phthaloyl group will be lost compared to the hydroxyl. Elemental analysis supports the characterization of complex **3.9,** $[PtMe_2(OH_2)(dpa)(C_8H_4O_4)]$.

3.3 Conclusion

The concept of directing oxidative addition towards forming a complex with *cis*-geometry becomes important when understanding that the reactivity of these platinum(IV) complexes becomes increased compared to their relatively unreactive *trans* counterparts.[11] With this concept in hand, it was important to try to utilize a peroxide complex which could be used to help with the *cis*-coordination at a platinum(II) center. Phthaloyl peroxide was chosen as a strong candidate for this type of chemistry due to it being a cyclic peroxide which even upon breaking of the O-O bond would not lead to complete dissociation of the molecule. Utilizing platinum(II) complexes containing bidentate nitrogen donor ligands with this cyclic peroxide yielded some very interesting results.

The formation of complex **3.2** and complex **3.3** has illustrated the *cis*-coordination of this phthaloyl peroxide complex with both $[PtMe_2(bpy)]$ and $[PtMe_2(bu_2bpy)]$. The use of $[PtMe_2(bu_2bpy)]$ has really helped to exemplify this chemistry in that a crystal structure was obtained of the first ever evidence of *cis*-oxidative addition of phthaloyl peroxide, forming a *cis* platinum(IV) complex. While these complexes did display *cis*-geometry, the *trans* isomer was formed in equilibrium in both cases. However the *cis*-product seems to be the thermodynamically more fovourable. Utilizing [PtMe$_2$(MIM)$_2$C=CH$_2$)] which has previously shown to favour *cis*-geometry with benzoyl peroxide,[14] complex **3.6** was formed in a strictly *cis*-geometry.

Synthesis was then carried out with platinum(II) complexes containing six membered bidentate nitrogen donors, which have shown varying reactivity to the simple five membered chelate rings.[20] The results of the reactions with [PtMe$_2$(dpk)] showed the formation of both the *cis* and *trans*-isomers. The *trans*-isomer was easier to characterize because a crystal was obtained and analyzed as complex **3.8**. The *cis*-isomer was more difficult to establish but though the use of IR and mass spectrometry it was classified as complex **3.7**. The idea of using [PtMe$_2$(dpa)] was that the amine group would leading to hydrogen bonding interactions with the phthaloyl peroxide and this would lead to stabilization of the product and ease in crystallization. This was not the case and it was found that complex **3.9** formed, which was a *trans*-isomer with no evidence of the *cis*-product a curious result based on the peroxide being used.

Aside from the formation of complex **3.6** and **3.9**, there appears to be prevalence for both a *cis* and *trans*-isomer formation even with the utilization of a cyclic peroxide to try to control this geometric obstacle. The prevalence for the formation of *trans*-species with platinum(II) complexes shows itself in the case of these complexes whilst even utilizing a supposed *cis*-directing peroxide, *trans*-platinum(IV) species were formed. The capabilities to form the *cis*-isomers however and especially to obtain crystal data of complex **3.3** show some very exciting accomplishments in directing *cis*-oxidative addition reactions with peroxides.

3.4 Experimental

All reactions were carried out using standard Schlenk techniques, unless otherwise stated. All NMR spectra were recorded on Varian Mercury 400 or Varian INOVA 400 or 600 MHz spectrometers. ^{1}H NMR chemical shifts are reported in ppm (δ) relative to TMS and referenced to their corresponding solvents. Mass spectrometric analysis was carried out using an electrospray PE-Sciex Mass Spectrometer (ESI-MS) coupled with a TOF detector. The platinum dimer, $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ was prepared according to the literature and utilized in the formation of the Pt(II) complexes.[22]

Phthaloyl peroxide. This product was prepared by a variation on that outlined by Russell.[10] A solution of sodium dihydrogen phosphate (15.0 g, 0.125 mol) and disodium hydrogen phosphate (15.0 g, 1.056 mol) in water (400 mL) was cooled to 5°C in an ice-water bath in a 1000 mL round bottom flask. Sodium peroxide (8.0 g, 0.1025 mol) was added to the stirred solution followed by a solution of 1,2-benzenedicarbonyl dichloride (phthaloyl chloride, 15 mL, 0.104 mol) in chloroform (300 mL), also cooled to 5°C. Stirring was continued for 2 hours and then the chloroform layer was separated off and washed twice with water. The chloroform solution was evaporated down with a stream of air, until about 30 mL of solution remained in the flask. The solution was layered with pentane (10 mL) and left in the fridge overnight. A white precipitate formed in the solution and this was filtered with a Buchner funnel and dried thoroughly. The crude phthaloyl peroxide was recrytallized twice from a benzene/pentane mixture, with the product needing slight heat to dissolve in the benzene and an ice bath to crash out product upon addition of pentane. The final product was obtained as a white, light powder in an overall yield of 46% (7.53 g, 0.0459 mmol). **^{1}H NMR in $CDCl_3$:** δ 8.04 (m, 2H, H^3) 8.30 (m, 2H, H^2). **ESI-**

MS(TOF) $[C_8H_4O_4\text{-}H]^+$**:** Calc. Precise Mass = 165.01 m/z; Determined Precise Mass = 165.03 g/mol.

Complex 3.1 and 3.2, 3.2a. The addition of phthaloyl peroxide (7.70 mg, 0.0525 mmol) to a solution of $[PtMe_2(bpy)]$ (20.0 mg, 0.0525 mmol) in acetone was carried out, leading to the formation of a cloudy solution. The product was layered with pentane to precipitate out the remainder of the product. The product was subsequently washed with pentane (3x2 mL) and ether (3x2 mL) and then dried *in vacuo*. ^{1}H NMR was used for characterization of the products.

^{1}H NMR in acetone-d$_6$:

Complex 3.1, *trans*-product: δ = 2.20 (s, 6H, $^2J(PtH)$ = 66 Hz, Me), 7.2 – 7.7 (m, 4H, Ar-H from peroxide), 7.84 (dd, 2H, $^3J(H^5H^6)$ = 6 Hz, $^3J(H^4H^5)$ = 8 Hz, H^5), 8.23 (dd, 2H, $^3J(H^4H^5)$ = 8 Hz, $^3J(H^4H^3)$ = 7 Hz, H^4) 8.60 (d, 2H, $^3J(H^3H^4)$ = 7 Hz, H^3), 9.38 (d, 2H, $^3J(H^6H^5)$ = 6 Hz, H^6).

Complex 3.2, *cis*-product: δ = 1.10 (s, 3H, $^2\mathrm{J}(PtH)$ = 70Hz, PtMe), 1.15 (s, 3H, $^2\mathrm{J}(PtH)$ = 69Hz, PtMe), 7.2-7.7 (m, 4H, Ar-H from peroxide), 7.81 (dd, 1H, $^3J(H^5H^6)$ = 7 Hz, $^3J(H^5H^4)$ = 8 Hz, H^5) 8.05 (dd, 1H, $^3J(H^{5'}H^{6'})$ = 6 Hz, $^3\mathrm{J}(H^{4`}H^{5`})$ = 8 Hz, $H^{5'}$), 8.36 (dd, 1H, $^3J(H^{4'}H^{3'})$ = 8 Hz, $^3\mathrm{J}(H^{4'}H^{5'})$ = 8 Hz, $H^{4'}$), 8.37 (dd, 1H, $^3J(H^3H^4)$ = 8 Hz, $^3J(H^4H^5)$ = 8 Hz, H^4), 8.73 (d, 1H, $^3J(H^3H^4)$ = 8 Hz, H^3), 8.79 (d, 1H, $^3J(H^{3'}H^{4'})$ = 8 Hz, $H^{3'}$), 9.20 (d, 1H, $^3J(H^{6'}H^{5'})$ = 6 Hz, $H^{6'}$), 9.39 (d, 1H, $^3J(H^6H^5)$ = 7 Hz, H^6). **ESI-MS (TOF)** [**3.2**-H]$^+$**:** Calc. Precise Mass: 546.09 g/mol; Determined Precise Mass: 546.1 g/mol. *Anal.* Calc'd. for $(C_{20}H_{18}N_2O_4Pt\cdot H_2O)$ (%): C, 42.63; H, 3.58; N, 4.97%. Found: C, 42.36; H, 3.41; N, 4.51. X-ray structure formed as complex **2a**·4.5 H_2O.

Complex 3.3, $[PtMe_2(bu_2bpy)]$. This complex was prepared following the literature.[18] Solutions of $[PtMe_4(SMe_2)_2]$ (100 mg, 0.174 mmol) and 4,4'-di-tert-butyl-2,2'-bipyridine (0.0934g, 0.348mmol) in toluene were mixed and placed in the fridge for one day to precipitate out the product. The orange solid was separated by decanting of the solvent, washing with pentane and drying *in vacuo*. Yield was 82% (704 mg, 0.142mmol). **^{1}H NMR in acetone-d$_6$**: δ = 0.91 (s, 6H, ^2J(PtH) = 86 Hz, Me), 1.44 (s, 18H, t-Bu), 7.69 (dd, 2H, $^3J(H^5H^6)$ = 6 Hz, $^4J(H^3H^5)$ = 2 Hz, H^5), 8.45 (d, 2H, $^4J(H^3H^5)$ = 2 Hz, H^3), 9.08 (d, 2H, $^3J(H^5H^6)$ = 6 Hz, $^3J(PtH^6)$ = 22 Hz, H^6)

Complex 3.4, [PtMe$_2$(bu$_2$bpy)(C$_8$H$_4$O$_4$)]. Phthaloyl peroxide (6.0 mg, 0.0405 mmol) was added to [PtMe$_2$(bu$_2$bpy)] (20.0 mg, 0.0405 mmol) in 1:1 stoichioometic amounts in acetone. A clear solution was formed upon the mixture of the two compounds. The reaction mixture was then layered with pentane, affording a white precipitate, which was then washed with pentane (3x2 mL) and ether (3x2 mL) and dried in *vacuo*. Isolation of the *cis*-product was achieved through recrystaillization by slow diffusion of pentane into a dichloromethane solution of complex **3.4**. **^{1}H NMR in acetone-*d$_6$*** δ = 1.01 (s, 3H, ^2J(PtH) = 68 Hz, Pt-Me to N), 1.10 (s, 3H, ^2J(PtH) = 70Hz, Pt-Me to O), 1.40 (s, 9H, t-butyl), 1.44 (s, 9H, t-butyl) 7.30-7.70 (m, 4H, peroxide protons), 7.73 (dd, 1H, $^3J(H^{5'}H^{6'})$ = 6 Hz, $^4J(H^{5'}H^{3'})$ = 1Hz, $H^{5'}$), 8.01 (dd, 1H, $^3J(H^5H^6)$ = 6 Hz, $^4J(H^5H^3)$ = 1Hz, H^5), 8.50 (d, 1H, $^3J(H^5H^6$ = 6 Hz, $^3J(PtH^6)$ = 22 Hz, H^6), 9.06 (d, 1H, $^3J(H^{5'}H^{6'})$ = 6 Hz, $H^{6'}$), 9.08 (d, 1H, $^4J(H^3H^5)$ = 1Hz, H^3), 9.12 (d, 1H, $^4J(H^{3'}H^{5'})$ = 1Hz, $H^{3'}$) **ESI-MS(TOF) [3.4-H]$^+$**: Calc. Precise Mass = 658.22 g/mol; Determined Precise Mass = 658.2 g/mol. *Anal.* Calc'd. for $C_{29}H_{36}Cl_2N_2O_4Pt$ (%): C, 48.89; H, 5.04; N, 4.00%. Found: C, 48.82; H, 4.93; N, 3.61.

Complex 3.5, [PtMe$_2$(MIM)$_2$C=CH$_2$]. This complex was prepared according to the literature.[14] [PtMe$_4$(SMe$_2$)$_2$] (200 mg, 0.350 mmol) was added to a stirring solution of [(MIM)$_2$C=CH$_2$] (181 mg, 0.700 mmol) in ether. The complex precipitated out of solution as a light yellow solid and was placed in the fridge overnight. The solid was washed with ether and pentane and then dried *in vacuo*. Yield 79%. **^{1}H NMR in acetone-*d*^{6}**. δ = 0.54 (s, 6H, ^2J(PtH) = 86 Hz, Pt-Me), 3.92 (s, 6H, N-Me), 6.19 (s, 2H, CH_2), 7.20 (d, 2H, $^3J(H^1\text{-}H^2)$ = 2Hz, 3J(Pt-H^1) = 13 Hz, H^1), 7.23 (d, 2H, $^3J(H^2\text{-}H^1)$ = 2 Hz, H^2).

Complex 3.6, [$PtMe_2(C_8H_4O_4)(MIM)_2C{=}CH_2$]. An NMR scale reaction was carried out with the addition of phthaoyl peroxide (3.2 mg, 0.0196 mmol) to a solution of $Pt(MIM)_2C{=}CH_2$ (8.1 mg, 0.0196 mmol) in acetone-d_6. A cloudy, white solution formed in the NMR tube upon addition of the starting materials. The ^{1}H NMR indicates conversion of the initial platinum starting material to an entirely new product. **^{1}H NMR in acetone-*d*$_6$**: δ = 1.23 (s, 3H, ^2J(PtH) = 68 Hz, PtMe to N), 1.31 (s, 3H, ^2J(PtH) = 71 Hz, PtMe to O), 3.98 (s, 3H, MeN), 4.08 (s, 3H, MeN), 6.42 (s, 1H, CH_2), 6.50 (s, 1H, CH_2), 6.90-8.35 (Aromatic protons, 8H). **ESI-MS(TOF)** [**3.6**-H]$^+$**:** Calc. Precise Mass = 579.14 g/mol; Determined Precise Mass = 579.1 g/mol.

Complex 3.7 and 3.8. To a stirring solution of [$PtMe_2$(dpk)] (1.26 mg, 0.0307 mmol) in acetone was added a solution of phthaloyl peroxide (0.50 mg, 0.0307 mmol) in acetone. Initially the red colour of the solution dissipated, turning to a clear solution and over ten minutes of stirring a white precipitate was formed. The acetone solution was separated from the formed precipitate and each sample was characterized independently. The acetone solution was separated and then layered with pentane (3 mL) and a white product precipitated out of solution. Both products were washed with ether (3x2 mL) and pentane (3x2 mL) and then dried *in vacuo*.

Complex 3.7, *cis*-[PtMe$_2$(dpk)(C$_8$H$_4$O$_2$)]. ^{1}H NMR in acetone-*d*^{6}: δ = 1.94 (s, 3H, ^2J(Pt-H) = 70 Hz, Pt-Me), 2.04 (s, 3H, ^2J(Pt-H) = 70 Hz, Pt-Me), 7.47-7.53 (m, 1H, H^5), 7.80 (dd, 1H, ^3J(H^3-H^4) = 8 Hz, H^3), ^4J(H^3-H^5) = 1Hz), H^3), 8.04 (ddd, 1H, ^3J(H^4-H^3) = 8 Hz, ^3J(H^4-H^5) = 8 Hz, ^4J(H^4-H^6) = 1 Hz, H^4), 9.21 (dd, 1H, ^3J(H^6-H^5) = 6 Hz, ^4J(H^6-H^4) = 1 Hz, H^6), 7.47-7.53 (m, 1H, H$^{5'}$), 7.92 (dd, 1H, ^3J(H$^{3'}$-H$^{4'}$) = 8 Hz, ^4J(H$^{3'}$-H$^{5'}$) = 2 Hz, H$^{3'}$), 8.11 (ddd, 1H, ^3J(H$^{4'}$-H$^{3'}$) = 8 Hz, ^3J(H$^{4'}$-H$^{5'}$) = 9 Hz, ^4J(H$^{4'}$-H$^{6'}$) = 1 Hz, H$^{4'}$), 8.50 (dd, 1H, ^3J(H$^{6'}$-H$^{5'}$) = 6 Hz, ^4J(H$^{6'}$-H$^{4'}$) = 1 Hz, H$^{6'}$). **ESI-MS(TOF)** [Pt(C$_8$H$_4$O$_4$)Me$_2$(dpkOH)Na]$^+$: Calc. Precise Mass: 613.1 g/mol. Determined Precise Mass: 613.1g/mol. IR (Nujol mull, cm^{-1}): 1652 υ(CO), 1605 υ(CO). *Anal.* Calc'd. For C$_{12}$H$_{18}$N$_2$O$_5$Pt·H$_2$O (%): C 42.64; H 3.41; N 4.74. Found: C 42.94; H 3.66; N 4.62.

Complex 3.8, ***trans*-[PtMe$_2$(dpkOH)(C$_8$H$_5$O$_4$)].** ^{1}H NMR in methanol-*d*^{4}: δ = 1.64 (s, 6H, ^2J(Pt-H) = 70 Hz, Pt-Me), 7.50 (dd, 2H, ^2J(H^5-H^4) = 8 Hz, ^2J(H^5-H^4) = 5 Hz, H^5), 7.80 (d, 2H, ^3J(H^3-H^4) = 8 Hz, ^4J(H^3-H^5) = 1 Hz), H^3), 8.07 (dd, 2H, ^3J(H^4-H^3) = 8 Hz, ^3J(H^4-H^5) = 8 Hz, H^4), 9.05 (d, 2H, ^3J(H^6-H^5) = 5 Hz, ^4J(H^6-H^4) = 1 Hz, H^6), 7.52-7.92 (m, 4H, pthaloyl peroxide protons).

Complex 3.9, [PtMe$_2$(OH)(dpa)(C$_8$H$_5$O$_4$)]. To a stirring solution of [PtMe$_2$(dpa)] (1.1 mg, 0.027 mmol) in acetone was added phthaloyl peroxide (0.44 mg, 0.027 mmol). The yellow colour of the solution immediately dissipated, forming a white reaction mixture which was allowed to stir for 1 hour. A precipitate formed in the reaction mixture. The remaining acetone solution was decanted and remaining off-white precipitate was subsequently washed with pentane (3x2 mL) and ether (3x2 mL) and then dried *in vacuo*. Yield 73%. **^{1}H NMR in CD$_3$OD**: δ = 1.61 (s, 6H, ^2J(Pt-H) = 67 Hz, Pt-Me), 7.30 (ddd, 2H, ^3J(H^5-H^6) = 6 Hz, ^3J(H^5-H^4) = 8 Hz, ^4J(H^5-H^3) = 1 Hz, H^5), 7.40 (d, 2H, ^3J(H^3-H^4) = 8 Hz, H^3), 7.99 (ddd, 2H, ^3J(H^4-H^5) = 8 Hz, ^3J(H^4-H^3) = 8 Hz, ^4J(H^4-H^6) = 2 Hz, H^4), 8.45 (dd, 2H, ^3J(H^6-H^5) = 6 Hz, ^4J(H^6-H^4) = 2 Hz, H^6), 7.58 (m, 2H, phthaloyl peroxide), 8.19 (m, 2H, phthaloyl peroxide). **ESI-MS(TOF):** Calc. precise mass: $[PtMe_2(OH)(dpa)]^+$ = 413.1; $[PtMe_2(dpa)(C_8H_5O_4)]^+$ = 561.1 g/mol. Determine precise mass: $[PtMe_2(OH)(dpa)]^+$ = 413.1 $[PtMe_2(dpa)(C_8H_5O_4)]^+$ = 561.1 g/mol; . Anal. Calc'd. For $C_{20}H_{21}N_3O_5Pt\cdot 1.5\ H_2O$ (%): C, 39.67; H, 4.00; N, 6.94%. Found: C, 39.71; H, 3.79; N, 6.62.

X-ray Structure Determination: X-ray data were obtained and solutions were determined by Benjamin Cooper and Matthew McCready in this chapter. Suitable crystals were mounted on a glass fibere and data was collected at low temperature 150(2) K on the Nonius Kappa-CCD area detector diffractometer with COLLECT (Nonius B.V.; 1997-2002). The unit cell parameters were calculated and refined from the full data set. The crystal data and refinement parameters for all complexes are listed in the following tables.

Table 3.4: Crystallographic data for complex 3.2a·4.5H_2O

Empirical Formula	$C_{40} H_{36} N_4 O_{19} Pt_2$	
Formula Weight	1266.91	
Wavelength	0.71073 Å	
Crystal System	Triclinic	
Space Group	P-1	
Unit Cell Dimensions	a = 9.0456(12) Å	α = 95.283(3)°
	b = 16.846(2) Å	β = 103.731(3)°
	c = 16.919(2) Å	γ = 103.638(3)°
Volume	2403.5(6) $Å^3$	
Z	2	
Density (calculated)	1.750 Mg/m^3	
Absorption Coefficient (μ)	45.889 mm^{-1}	
Crystal Size	0.07 x 0.03 x 0.02 mm^3	
Refinement Method	Full-matrix least-squares on F^2	
Goodness of fit on F^2	0.882	
Final R indicies [I>2σ(I)]	R1= 0.0595, wR2 = 0.1428	
R indicies (all data)	R1 = 0.0872, wR2 = 0.1652	

Table 3.5: Crystallographic data for complex 3.4·CH_2Cl_2

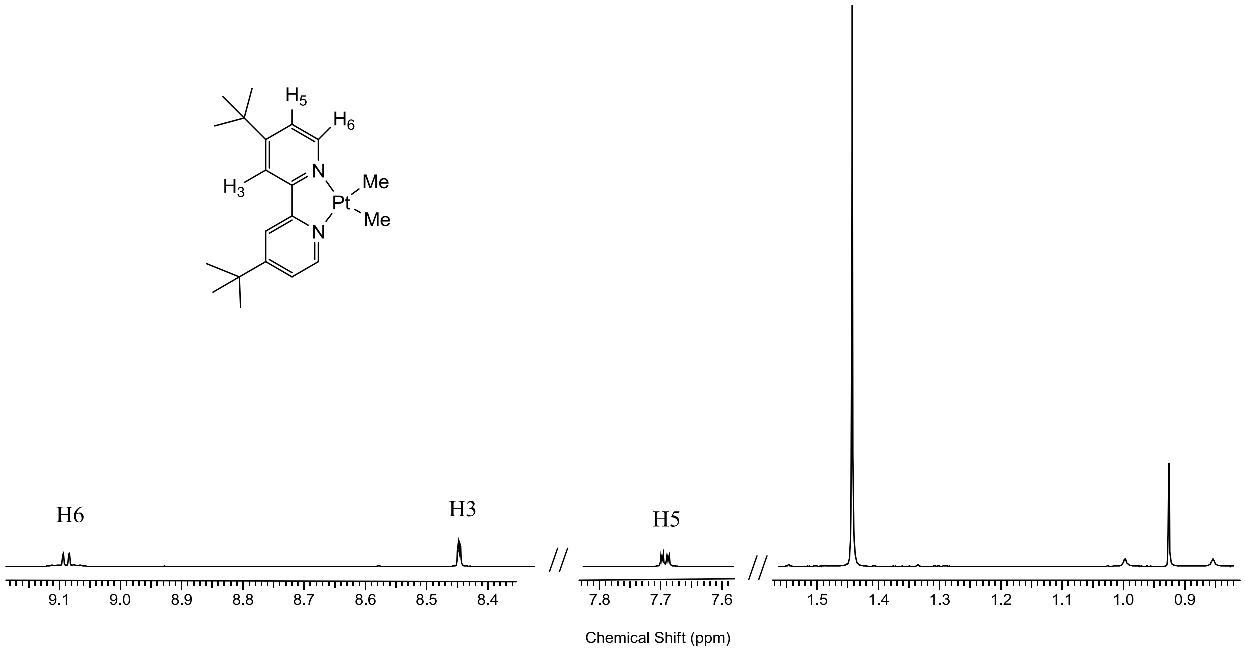
Empirical Formula	$C_{29} H_{36} Cl_2 N_2 O_4 Pt$	
Formula Weight	742.59	
Wavelength	0.71073 Å	
Crystal System	Monoclinic	
Space Group	$P2_1/n$	
Unit Cell Dimensions	a = 15.897(3) Å	α = 90°
	b = 17.898(4) Å	β = 107.08(3)°
	c = 22.069(4) Å	γ = 90°
Volume	6002(2) $Å^3$	
Z	8	
Density (calculated)	1.644 Mg/m^3	
Absorption Coefficient (μ)	4.889 mm^{-1}	
Crystal Size	0.24 x 0.12 x 0.11 mm^3	
Refinement Method	Full-matrix least-squares on F^2	
Goodness of fit on F^2	1.078	
Final R indicies [$I>2\sigma(I)$]	R1= 0.0460, wR2 = 0.1155	
R indicies (all data)	R1 = 0.0726, wR2 = 0.1427	

Table 3.6: Crystallographic data for complex 3.8

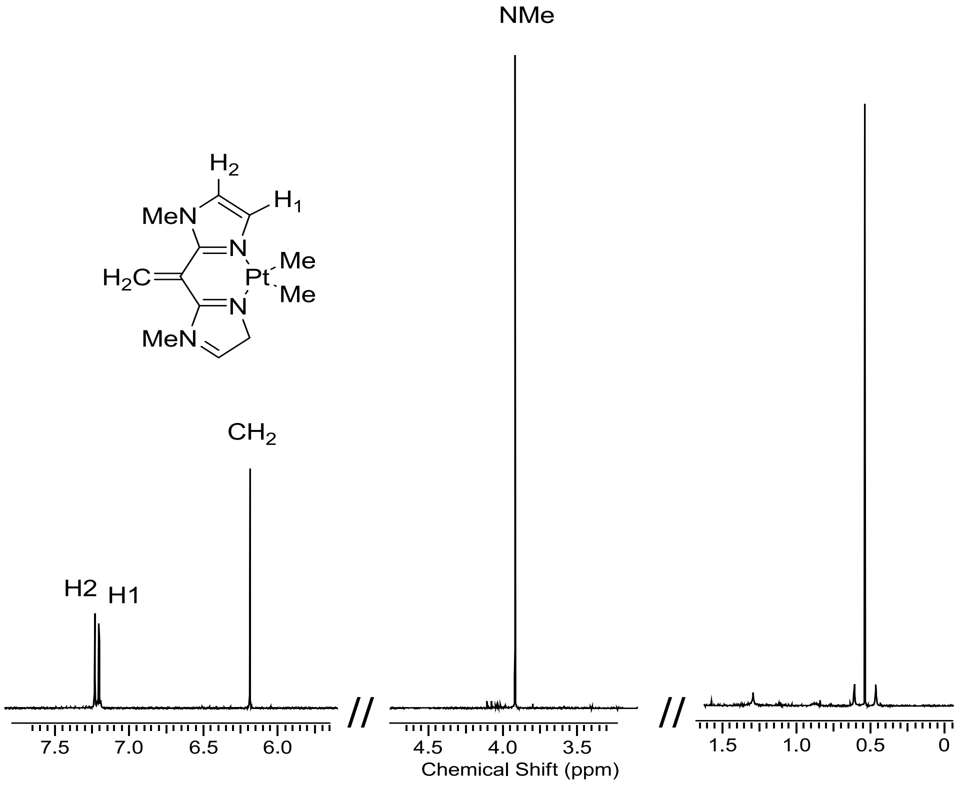
Empirical Formula	$C_{21}H_{20}N_2O_6Pt$	
Formula Weight	591.58	
Wavelength	0.71073 Å	
Crystal System	Monoclinic	
Space Group	C2/c	
Unit Cell Dimensions	a = 34.149(3) Å	$\alpha = 90°$
	b = 7.8620(6) Å	$\beta = 115.614(2)°$
	c = 16.3098(13) Å	$\gamma = 90°$
Volume	3948.6(5) $Å^3$	
Z	8	
Density (calculated)	1.990 Mg/m^3	
Absorption Coefficient (μ)	7.150 mm^{-1}	
Crystal Size	0.55 x 0.08 x 0.06 mm^3	
Refinement Method	Full-matrix least-squares on F^2	
Goodness of fit on F^2	0.936	
Final R indicies [$I>2\sigma(I)$]	R1= 0.0442, wR2 = 0.1207	
R indicies (all data)	R1 = 0.0807, wR2 = 0.1427	

3.5 Appendix

3.4.1 ^{1}H NMR spectrum of complex 3.3, [PtMe$_2$(bu$_2$bpy)]



3.4.2 ^{1}H NMR spectrum of complex 3.4, [PtMe$_2$(MIM)$_2$C=CH$_2$]



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Chapter 4

Mechanism of Oxidative Addition of Iodine to a Dimethylplatinum(II) Complex

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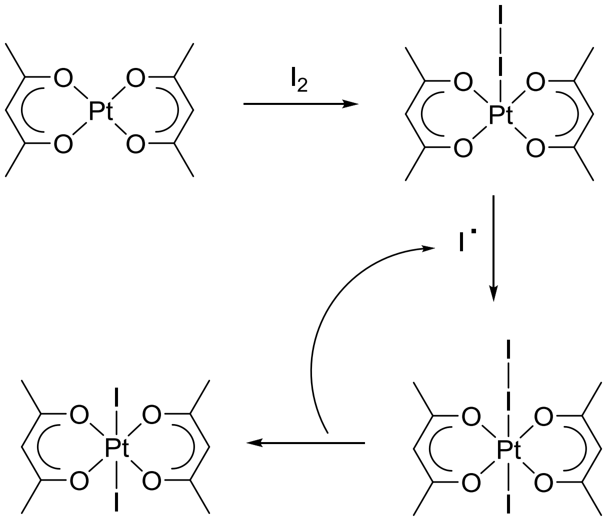
4.1 Introduction

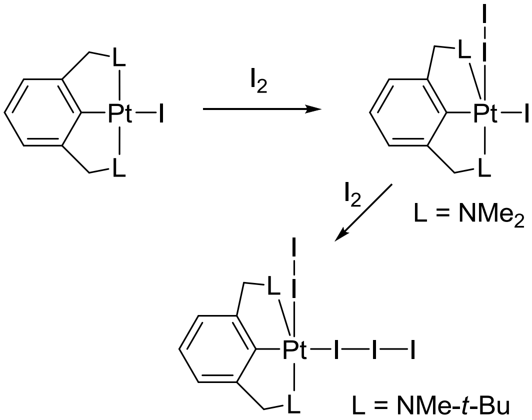
The reactions of oxidative addition and reductive elimination are known to be some of the most significant in the organometallic and bioinorganic chemistry of the transition metals.[1-3] Large number of studies have been carried out with the oxidative addition of halogens to platinum(II) complexes studying their reactivity and mechanistic pathways, as outlined below.[4]

An important aspect in studying this reactivity is by utilizing iodine as it is less reactive than other halogens, allowing for the ability to monitor and model the reaction pathways of these halogens with platinum(II) complexes. An early mechanistic study of the reaction of [Pt(acac)$_2$] with iodine showed that the reaction proceeded by way of an intermediate [Pt(acac)$_2$(I$_2$)], which then rearranged by a free-radical chain mechanism to the product of trans-oxidative addition. This process has been illustrated in Scheme 4.1.[5,6]



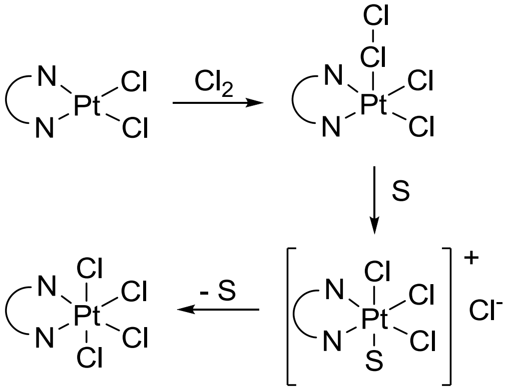
Scheme 4.1: Mechanistic pathway of [Pt(acac)$_2$] with I$_2$

The use of pincer complexes has also been utilized to show the formation of iodine complexes, which have been isolated and structurally characterized, as illustrated in scheme 4.2. These structures illustrate the complicating factor that iodine can also bind to a PtI group to form the corresponding triiodide Pt-I_3. The I-I distances of the I_2 ligand in the complexes formed are 2.822(1) and 2.793(1) Å, which are longer than the I-I distance seen in iodine itself of 2.715(6) Å.[7-9]



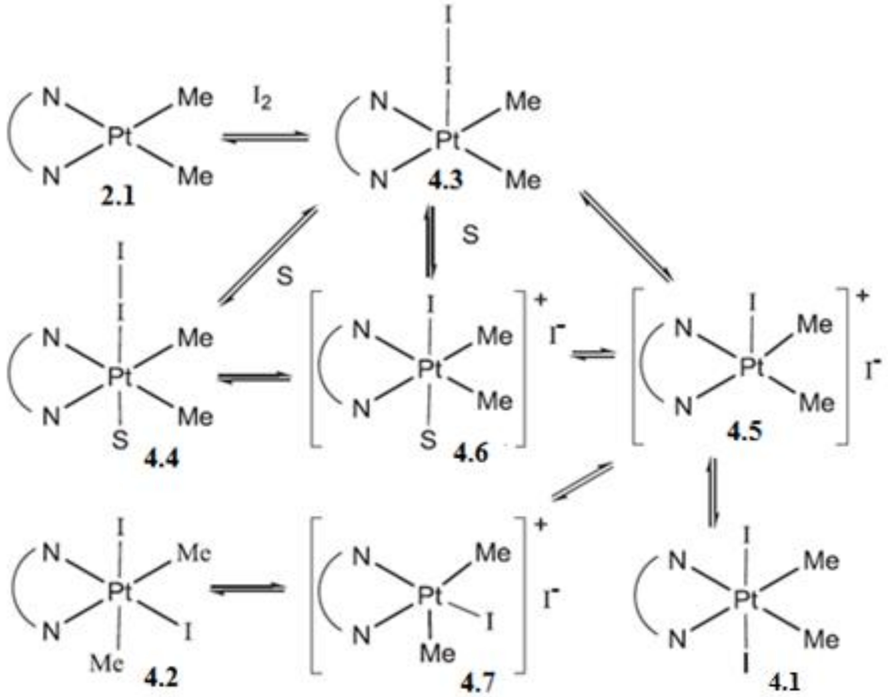
Scheme 4.2: Reaction of a platinum(II) pincer complex with iodine.

It is known that when these reactions are carried out in polar solvents, the dihalogen complex is not usually observed and it is presumed to release a halide ion to give a cationic solvent complex of platinum(IV), which can often be identified as a long-lived reaction intermediate. In some cases, as illustrated in scheme 4.3, the intermediate may be isolated.[4,10-12] It is often unclear as to whether the first step in the conversion is a solvent coordination or chloride dissociation, or if the reaction is concerted.[13] The stepwise, polar mechanism illustrated in scheme 4.3 usually leads to *trans*-oxidative addition[1-8,10-24] but since likely 5-coordinate intermediates are stereochemically non rigid,[25,26] *cis*-oxidative addition can be observed or equilibrium between *trans* and *cis* isomers can be found if thermodynamically favourable. [14, 24-26] There however, appears to be no well-established examples of concerted, non-polar cis oxidative addition of halogens to platinum(II) complexes. [1-4,13]



Scheme 4.3: Polar solvent forming a cationic solvent complex of platinum(IV) (NN = cis-1,4-diaminocyclohexane, S = solvent = H_2O, Me_2NHCO, Me_2SO, acetone).

With further interest in the mechanism of oxidative addition, as well as in the use of oxidative addition reactions in the synthesis of new organometallic complexes, a study of the oxidative addition of iodine to the complex **2.1**, [PtMe$_2$(bpy)], has been carried out.[24,27-32] Past research has lead to a proposed mechanism by way of one of the routes shown in scheme 4.4. In this research, the results of kinetic studies and DFT calculations were augmented with NMR studies, investigating the possible intermediates involved in this reaction.[12,27,28] Low temperature NMR studies are illustrated in this chapter to help show the potential intermediates formed and elucidate the overall mechanism of this reaction. The overall reaction of iodine to [PtMe$_2$(bpy)] seems at first glance to be simple, but the potential involvement of solvent at intermediate stages or of a competing free radical mechanism cause it to be more complicated.



Scheme 4.4: Expected mechanistic routes for oxidative addition of iodine at [PtMe$_2$(bpy)] (NN = 2,2'- bipyridine, S = solvent)

4.2 Results and Discussion

4.2.1 Synthesis and Structure of Complex 4.1 and 4.2

In an attempt to help distinguish the mechanism of oxidative addition of a platinum(II) complex with iodine, low temperature NMR experiments were conducted to find the intermediates being formed. Before the low temperature experiments could be conducted, solvents needed to be selected to determine which would be suitable for forming the desired products. Thus, complex **2.1**, [PtMe$_2$(bpy)] was reacted with iodine to give the product of *trans*-oxidative addition, complex **4.1** as the major product, with a smaller amount of the corresponding *cis*-adduct complex **4.2** as the minor product. Reactions of this nature in toluene gave very little of complex **4.2**, however when using acetone or dichloromethane as solvents, about 5% of complex **4.2** was found and this can be seen in figure 4.1.

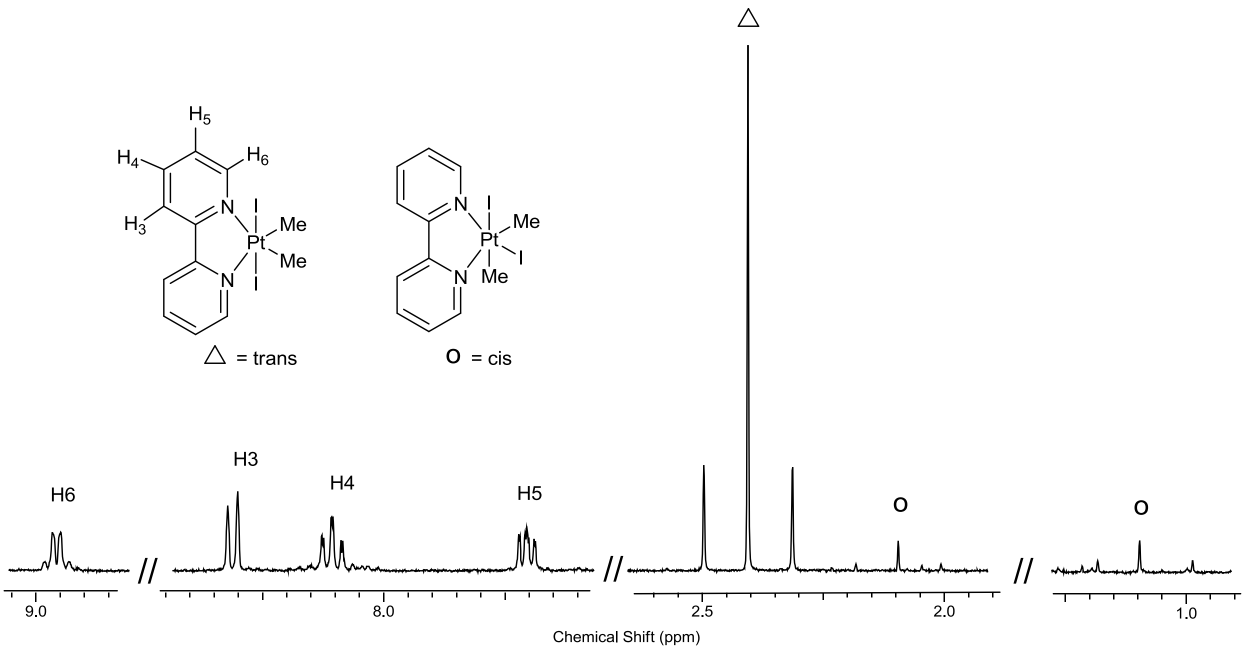


Figure 4.1: ^{1}H NMR spectrum of complexes**,** **4.1** and **4.2** in CD_2Cl_2.

Attempts to grow single crystals of complex **4.1** have given co-crystals of complex **4.1** and **4.2**, in disordered form, in which the proportion of complex **4.2** was always greater. This means that during the crystallization process, which takes several weeks at room temperature, there is isomerisation of complex **4.1**. It is presumed that the equilibration takes place by way of intermediates **4.5** and **4.7**.[25, 26] A structure has been obtained from a crystal containing complex **4.1** and **4.2** in an approximate 41:59 ratio respectively, containing an additional iodine molecule. There is a center of inversion at the midpoint of the I-I bond, which relates the disordered atoms I(4), C(12), and C(13),I(3). The atoms C(11) and C(12) were not disordered. The structure illustrated in figure 4.1, shows one molecule of each complex **4.1** and **4.2** bridged by the iodine molecule.

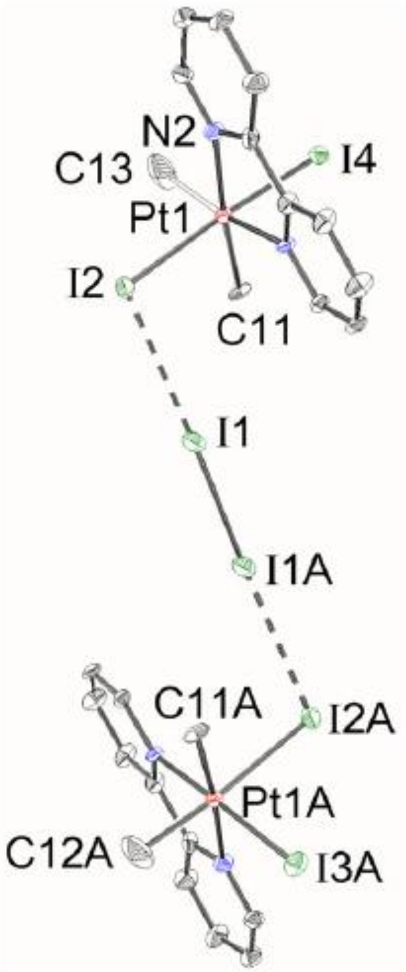


Figure 4.2: Structure of complex **4.2**·0.5I_2, containing disordered 4.1 and 4.2 in ratio 41:59. **Selected Bond Distances:** Pt(1)-N(1) = 2.105(7); Pt(1)-N(2) = 2.193(7); Pt(1)-C(11) = 2.073(8); Pt(1)-C(12) = 1.96(3); Pt(1)-C(13) = 2.18(5); Pt(1)-I(2) = 2.7309(8); Pt(1)-I(3) = 2.543(1); Pt(1)-I(4) = 2.648(2); I(1)-I(1A) = 2.7883(15); I(1)···I(2) = 3.431(2) Å.

Table 4.1: Bond lengths [Å] and angles [deg] for complex 4.2·0.5I$_2$

Pt(1)-C(12)	1.96(3)	Pt(1)-I(3)	2.5434(2)
Pt(1)-C(11)	2.073(8)	Pt(1)-I(4)	2.648(2)
Pt(1)-N(1)	2.105(7)	Pt(1)-I(2)	2.7309(8)
Pt(1)-C(13)	2.18(5)	I(1)-I(1A)	2.7873(2)
Pt(1)-N(2)	2.193(7)	I(1)-I(2)	3.431(2)
C(12)-Pt(1)-C(11)	88.1(1)	N(2)-Pt(1)-I(3)	96.6(2)
C(12)-Pt(1)-N(1)	88.9(1)	C(12)-Pt(1)-I(4)	2.4(10)
C(11)-Pt(1)-N(1)	98.1(3)	C(11)-Pt(1)-I(4)	88.0(3)
C(12)-Pt(1)-C(13)	89.3(2)	N(1)-Pt(1)-I(4)	91.3(2)
C(11)-Pt(1)-C(13)	90.5(2)	C(13)-Pt(1)-I(4)	87.0(15)
N(1)-Pt(1)-C(13)	171.1(2)	N(2)-Pt(1)-I(4)	89.6(2)
C(12)-Pt(1)-N(2)	89.2(1)	I(3)-Pt(1)-I(4)	89.91(7)
C(11)-Pt(1)-N(2)	174.8(4)	C(12)-Pt(1)-I(2)	175.0(1)
N(1)-Pt(1)-N(2)	77.4(3)	C(11)-Pt(1)-I(2)	88.4(3)
C(13)-Pt(1)-N(2)	93.9(2)	N(1)-Pt(1)-I(2)	88.0(2)
C(12)-Pt(1)-I(3)	92.3(9)	C(13)-Pt(1)-I(2)	94.3(2)
C(11)-Pt(1)-I(3)	88.0(3)	N(2)-Pt(1)-I(2)	94.0(2)
N(1)-Pt(1)-I(3)	173.83(2)	I(3)-Pt(1)-I(2)	91.20(5)
C(13)-Pt(1)-I(3)	3.9(16)	I(4)-Pt(1)-I(2)	176.13(4)

4.2.2 Detection of Intermediates by ^{1}H NMR Spectroscopy

Attempts have been made to detect reaction intermediates by monitoring the reactions by ^{1}H NMR spectroscopy. The reactions were however too rapid at room temperature and no intermediates could be detected under these conditions. Initial studies for this reaction were carried out in benzene and have illustrated a complete conversion of complex **2.1** to complex **4.1**. A study of the reaction in toluene-d$_8$ was carried out at -80°C, following by warming to room temperature. It was seen that the reaction was again rapid even at low temperatures and only complex **4.1** was formed without detection of any intermediates, as illustrated in figure 4.2.

With the failed attempts at tracking an intermediate in toluene-d_8, the same reaction was carried out in CD_2Cl_2. Unlike the previous experiment, changing the solvent has given a detectable reaction intermediate as shown by the ^{1}H NMR spectra in figure 4.3. The spectrum in figure 4.3a, at -80°C, shows the presence of three complexes; the starting material [PtMe$_2$(bpy)], the product **4.1** and a new complex which has tentatively been assigned as complex **4.3** (or **4.4**) found in scheme 4.4 (S = CD_2Cl_2). The methylplatinum resonance intermediate appeared at δ = 1.63, with coupling constant ^2J(PtH) = 76 Hz, which can be classified as an intermediate value between 84 Hz and 72 Hz assigned to complex **2.1** and **4.1** respectively. The intermediate was still present in figure 4.3b, at -40°C, but they were absent at in figure 4.3c, at 0°C. The spectrum in figure 4.3c, shows the presence of about 5% of the *cis*-isomer **4.2**.

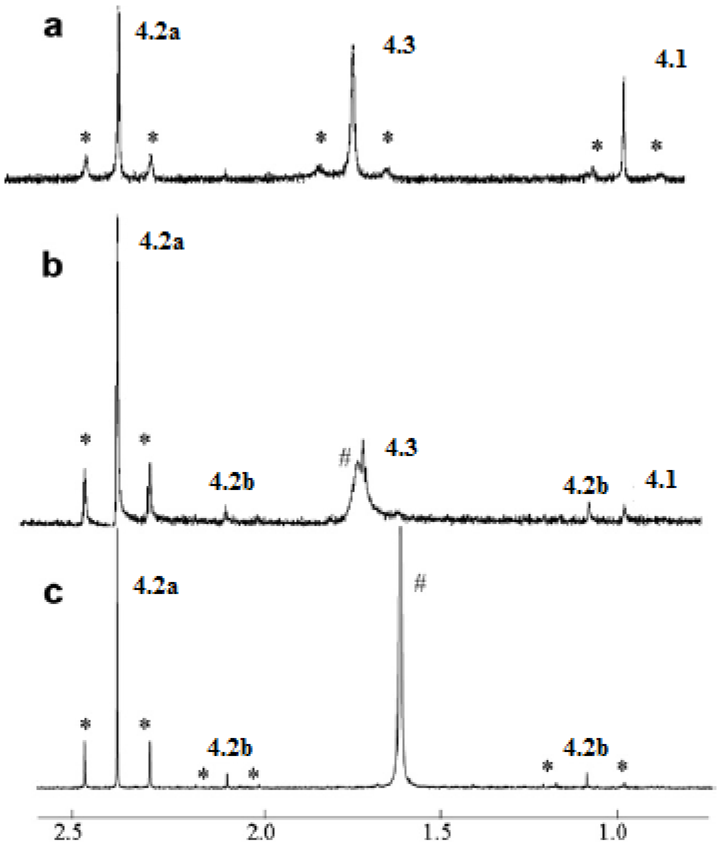


Figure 4.3: ^{1}H NMR spectra in the methylplatinum region during the reaction of [$PtMe_2$(bpy)] with iodine in CD_2Cl_2 solution to give both the *trans*- and *cis*-[PtI_2Me_2(bpy)], **4.1** and **4.2** via intermediate **4.3** or **4.4**.: (a) -80°C, (b) -40°C, (c) 0°C. The peak labelled with # is due to water and ^{195}Pt satellites are marked as *.

With this result, it was important to determine the effect that the solvent had on the overall formation of the intermediate. Thus, similar experiments were carried out using either 50:50 or 70:30 mixtures by volume of CD_2Cl_2/toluene-d_8. No intermediates were detected while using the 50:50 solvent mixture, but intermediates were detected using the 70:30 mixture. It was found, as shown in figure 4.4, that the intermediate was detected at both -80°C and -60°C. The methylplatinum resonance was located at $\delta = 2.18$ with coupling constant $^2J(\text{PtH}) = 76$ Hz. This is most likely to be the same intermediate detected as for the pure CD_2Cl_2 experiment, with the chemical shift variation affected by the toluene co-solvent.

The same experiment was carried out using acetone as solvent and the related spectra are illustrated in figure 4.4 (methylplatinum resonances) and 4.5 (bipyridine resonances). In figure 4.4a, at -80°C, there is evidence of complex **4.1**, trace amounts of $[PtMe_2(bpy)]$ and a third resonance located at $\delta = 1.69$ with a coupling constant $^2J(\text{PtH}) = 76$ Hz, which may be assigned to complex **4.4** (or **4.3**), similar to the spectrum in CD_2Cl_2 (figure 3a). It was then found that as the temperature was decreased to -60°C (figure 4.4b), the intermediate resonance was very broad and shifting and becoming sharper, as seen in figure 4.4c, at -40°C. It has shifted to $\delta = 1.61$ and has the same coupling constant $^2J(\text{PtH}) = 76$ Hz. This peak then began to fully decay as temperatures were increased to 20°C, and the intensity of the resonance representing complex **4.1** increased steadily.

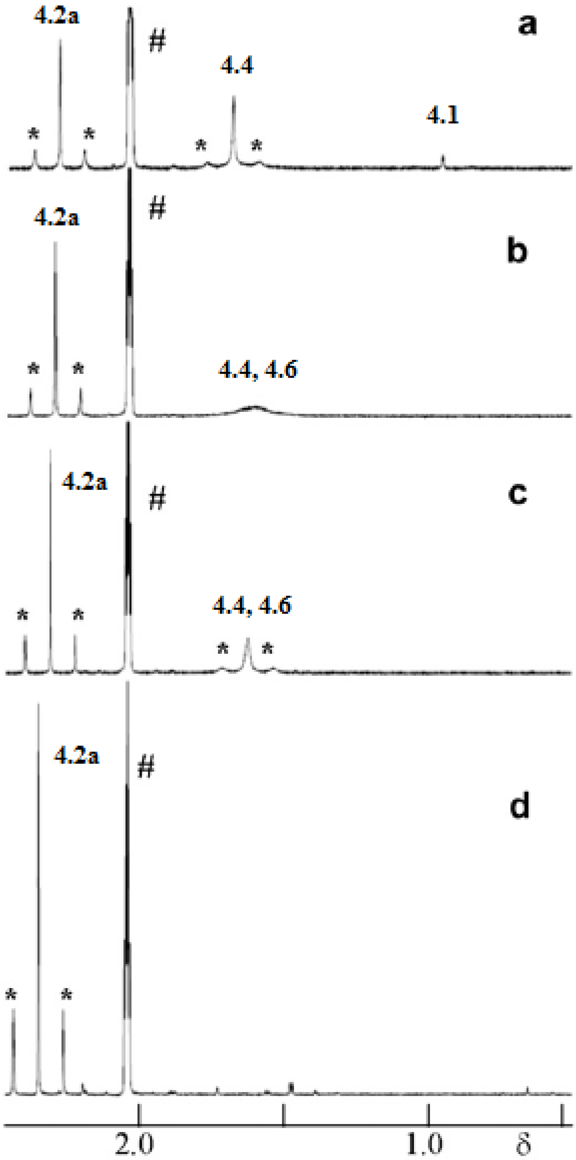


Figure 4.4: ^{1}H NMR spectra in the methylplatinum region during the reaction of [PtMe$_2$(bpy)] with iodine in acetone-d_6 solution to give trans-[PtI$_2$Me$_2$(bpy)], **4.1**, via intermediates **4.4** and **4.6**. (a) -80°C; (b) -60°C; (c) -40°C; (d) 20°C. The peaks are labelled # is due to the solvent CHD$_2$ isotopomer of acetone-d_6 and ^{195}Pt satellites are marked as *.

This results leads to the suggestion that at -80°C, the iodine complex **4.4** is present, but when approaching warmer temperatures it is in rapid equilibrium with the ionic isomer complex **4.6**, [PtIMe$_2$(acetone)(bpy)]I. NMR data of the bipyridine region of this spectrum shown in figure 4.5, helps to verify these results. It was seen that there are separate resonances for complex **4.1** and for the intermediates, with the peaks for the intermediates being shifted further upfield in the spectrum and having much broader appearance.

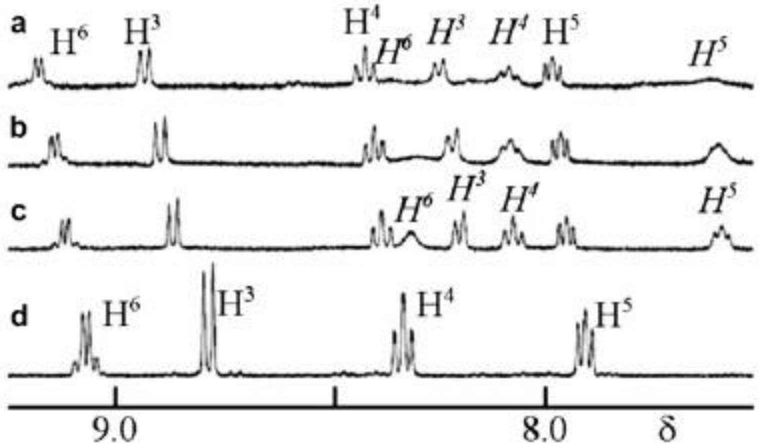


Figure 4.5: ^{1}H NMR spectra in the bipyridine region during the reaction of [$PtMe_2$(bpy)] with iodine in acetone-d_6 solution to give trans-[PtI_2Me_2(bpy)], **4.1**, via intermediates **4.4** and **4.6**. (a) -80°C; (b) -60°C; (c) -40°C; (d) 20°C. The peaks for **4.1** are in normal font, while the peaks representing **4.4** and **4.6** are in italics.

4.3 Conclusion

The study of the mechanism by which oxidative addition of iodine occurs at a platinum(II) complex has been carried out utilizing low temperature ^{1}H NMR spectroscopy. These NMR studies have shown the formation of an intermediate or intermediates during the reaction of [$PtMe_2$(bpy)] with iodine in solvents CD_2Cl_2 and acetone. However, these intermediates were not detected in the reactions carried out in toluene-d_8. The stability of the intermediates follows the series: acetone > CD_2Cl_2 > toluene, suggesting that there is stabilization by solvent coordination. The use of this technique illustrates that the intermediates are symmetric since only one methylplatinum and one bipyridine proton is observed in each case, helping to rule out any of the unsymmetrical proposed intermediates. This leads complex 4.3-4.6 as possible structures, but the full characterization is not possible based on the NMR studies alone. Further kinetic and DFT studies have been carried out, with the results found in the published paper.[33]

4.4 Experimental

The variable temperature ^{1}H NMR spectra were recorded on Varian Inova 400 spectrometer. ^{1}H NMR chemical shifts are reported in ppm (δ) relative to TMS and referenced to their corresponding solvents. The platinum dimer, $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ was prepared according to the literature and utilized in the formation of the Pt(II) complex.[34]

Toluene-*d*$_8$: Complex 2a. Complex **2.1**, $[PtMe_2(bpy)]$, (0.0040 g, 0.0105 mmol) was dissolved in toluene-d_8 and transferred to an NMR tube, cooled to below -80°C in dry ice. To this solution was added a solution of I_2, (0.0027g, 0.0105 mmol) in acetone-d^6, and the tube was placed in the NMR spectrometer (Inova 400) where the probe temperature had been lowered to -80°C. The reaction was monitored by variable temperature ^{1}H NMR spectroscopy, in which the reaction was monitored at 20°C intervals, as the temperature was increased from -80°C to 20°C. ^{1}H NMR of complex **4.1** in toluene-d^8 at 20°C; $\delta = 2.77$ (s, 6H, ^{2}J(Pt-H) = 73 Hz, MePt), 6.45 (broad, 2H, H^5), 6.72- 6.96 (broad, 4H, H^4 and H^3), 8.49 (broad, 2H, H^6).

CD_2Cl_2: Complex 2a, 2b and 4.3/4.4. Complex **2.1**, $[PtMe_2(bpy)]$, (0.0040 g, 0.0105 mmol) was dissolved in CD_2Cl_2 and was transferred to an NMR tube, cooled to below -80°C in dry ice. To this solution was added a solution of I_2, (2.7 mg, 0.0105 mmol) in CD_2Cl_2, and the tube was placed in the NMR spectrometer (Inova 400) in which the temperature of the probe had been precooled to -80°C. The reaction was monitored by variable temperature ^{1}H NMR spectroscopy, in which the reaction temperature was increased at 20°C intervals, as the temperature was increased from -80 to 20°C. Selected ^{1}H NMR in CD_2Cl_2: Complex **4.1** 20°: $\delta = 2.40$ (s, 6H, ^{2}J(Pt-H) = 73Hz, MePt), 7.71 (ddd, 2H, $^{3}J(H_5\text{-}H_4) = 8$ Hz, $^{3}J(H_5\text{-}H_6) = 6$ Hz, $^{4}J(H_5\text{-}H_3) = 1$ Hz,

H^5), 8.10 (ddd, 2H, $^3J(H_4\text{-}H_5)$ = 8 Hz, $^3J(H_4\text{-}H_3)$ = 8 Hz, $^4J(H_4\text{-}H_6)$ = 1 Hz, H^4), 8.31 (d, 2H, $^3J(H_3\text{-}H_4)$ = 8 Hz, H^3), 8.95 (dd, 2H, $^3J(H_6\text{-}H_5)$ = 6 Hz, $^4J(H_6\text{-}H_4)$ = 1 Hz, $^3J(Pt\text{-}H_6)$ = 12 Hz, H^6). Complex **4.3 or 4.4** -80°C: δ = 1.63 (s, 6H, ^2J(Pt-H) = 76 Hz, MePt), 7.20-8.20 (bipy; H^3-H^6). Complex **4.2** at 20°C: δ = 1.09 (s, 3H, ^2J(Pt-H) = 79 Hz, MePt trans N). 2.09 (s, 3H, ^2J(Pt-H) = 70 Hz, MePt trans I).

Toluene-*d*$_8$:CD$_2$Cl$_2$ (1:1). Complex 2a. Complex **2.1**, [PtMe$_2$(bpy)], (4.0 mg, 0.0105 mmol) was dissolved in a 1:1 mixture of toluene-d^8 to CD$_2$Cl$_2$, and then transferred to an NMR tube, cooled to below -80°C in dry ice. To this solution was added a solution of I$_2$, (2.7 mg, 0.0105 mmol) dissolved in a 1:1 mixture of toluene-d^8 to CD$_2$Cl$_2$ and the tube was placed in the NMR spectrometer (Inova 400) where the probe temperature had been lowered to -80°C. The reaction was monitored by variable temperature ^{1}H NMR spectroscopy, in which the reaction was monitored at 20°C intervals, as the temperature was increased from -80°C to 20°C. ^{1}H NMR of complex **4.1** in 1:1 toluene-*d*$_8$/CD$_2$Cl$_2$ mixture at 20°C; δ = 2.43 (s, 6H, ^2J(Pt-H) = 73 Hz, MePt), 6.79 (dd, 2H, $^3J(H_5\text{-}H_4)$ = 8 Hz, $^3J(H_5\text{-}H_6)$ = 6 Hz, H^5), 7.13 (dd, 2H, $^3J(H_4\text{-}H_3)$ = 8 Hz, $^3J(H_4\text{-}H_5)$ = 8 Hz, H^4), 7.19 (d, 2H, $^3J(H_3\text{-}H_4)$ = 8 Hz, H^3), 8.49 (d, 2H, $^3J(H_6\text{-}H_5)$ = 6 Hz).

Toluene-*d*$_8$:CD$_2$Cl$_2$ (3:7). Complex 2a, 4.3/4.4. Complex **2.1**, [PtMe$_2$(bpy)], (4.0 mg, 0.0105 mmol) was dissolved in a 3:7 mixture of toluene-d^8 to CD$_2$Cl$_2$, and then transferred to an NMR tube, cooled to below -80°C in dry ice. To this solution was added a solution of I$_2$, (2.7g, 0.0105 mmol) dissolved in a 3:7 mixture of toluene-*d*$_8$ to CD$_2$Cl$_2$ and the tube was placed in the NMR spectrometer (Inova 400) where the probe temperature had been lowered to -80°C. The reaction was monitored by variable temperature ^{1}H NMR spectroscopy, in which the reaction was monitored at 20°C intervals, as the temperature was increased from -80°C to 20°C. ^{1}H NMR of complex **4.1** in 3:7 toluene-d^8/CD$_2$Cl$_2$ mixture at 0°C; δ = 2.34 (s, 6H, ^2J(Pt-H) = 73 Hz, MePt),7.09 (ddd, 2H, ^3J(H$_5$-H$_4$) = 8 Hz, ^3J(H$_5$-H$_6$) = 6 Hz, ^4J(H$_5$-H$_3$) = 1 Hz, H^5), 7.45 (ddd, 2H, ^3J(H$_4$-H$_3$) = 8 Hz, ^3J(H$_4$-H$_5$) = 8 Hz, ^4J(H$_4$-H$_6$) = 1 Hz, H^4), 7.59 (d, 2H, ^3J(H$_3$-H$_4$) = 8 Hz, H^3), 8.62 (dd, 2H, ^3J(H$_6$-H$_5$) = 6 Hz, ^4J(H$_6$-H$_4$) = 1 Hz, ^3J(Pt-H) = 13 Hz, H^6). ^{1}H NMR of complex **4.3/4.4** in 3:7 toluene-*d*$_8$/CD$_2$Cl$_2$ mixture at -40°C; δ = 1.58 (s, 6H, ^2J(Pt-H) = 76 Hz, MePt), 6.70- 8.1 (bipy H^3-H^6).

Acetone-*d*$_6$: Complex 2a, 4.4/4.6. Complex **2.1**, [PtMe$_2$(bpy)], (4.0 mg, 0.0105 mmol) was dissolved in acetone-*d*$_6$ and transferred to an NMR tube, cooled to below -80°C in dry ice. To this solution was added a solution of I$_2$, (2.7 mg, 0.0105 mmol) in acetone-*d*$_6$, and the tube was placed in the NMR spectrometer (Inova 400) where the probe temperature had been lowered to -80°C. The reaction was monitored by variable temperature ^{1}H NMR spectroscopy, in which the reaction was monitored at 20°C intervals, as the temperature was increased from -80°C to 20°C. ^{1}H NMR of complex **4.1** in acetone-d^6 at 20°C: δ = 2.37 (s, 6H, ^2J(Pt-H) = 73Hz, MePt), 7.91 (dd, 2H, ^3J(H$_5$-H$_4$) = 8 Hz, ^3J(H$_5$-H$_6$) = 6 Hz, H^5), 8.33 (ddd, 2H, ^3J(H$_4$-H$_5$) = 8 Hz, ^3J(H$_4$-H$_3$) = 8 Hz, ^4J(H$_4$-H$_6$) = 1 Hz, H^4), 8.77 (d, 2H, ^3J(H$_3$-H$_4$) = 8 Hz, H^3), 9.05 (d, 2H, ^3J(H$_6$-H$_5$) = 6 Hz, ^4J(H$_6$-H$_4$) = 1 Hz, ^3J(Pt-H$_6$) = 13 Hz, H^6). ^{1}H NMR of complex **4.4/4.6** in acetone-*d*$_6$ at -80°C: δ = 1.67 (s, 6H, ^2J(Pt-H) = 76 Hz, MePt), 7.62 (m, 2H, H^5), 8.07 (dd, 2H, ^3J(H$_4$-H$_3$) = 8 Hz, ^3J(H$_4$-H$_5$) = 8 Hz, H^4), 8.24 (d, 2H, ^3J(H$_3$-H$_4$) = 8 Hz, H^3), 8.56 (d, 2H, ^3J(H$_6$-H$_5$) = 8 Hz, H^6). ^{1}H NMR of complex **6** in acetone-d^6 at -40°C; δ = 1.61 (s, 6H, ^2J(Pt-H) = 76 Hz, MePt), 7.60 (dd, 2H, ^3J(H$_5$-H$_4$) = 8 Hz, ^3J(H$_5$-H$_6$) = 6 Hz, H^5), 8.07 (dd, 2H, ^3J(H$_4$-H$_3$) = 8 Hz, ^3J(H$_4$-H$_5$) = 8 Hz, H^4), 8.24 (d, 2H, ^3J(H$_3$-H$_4$) = 8 Hz, H^3), 8.31 (broad, H^6).

X-ray Structure Determination: X-ray data was obtained and the solutions were determined by Benjamin Cooper and Matthew McCready in this chapter. A suitable crystal was mounted on a glass fibre and data was collected at low temperature 150(2) K on Bruker Smart Apex II CCD detector. The unit cell parameters were calculated and refined from the full data set. Crystal data and refinement parameters for the complex ia listed in the following table.

Table 4.2: Crystallographic data for complex 4.1/4.2·0.5 I_2

Empirical Formula	$C_{12}H_{14}I_3N_2Pt$	
Formula Weight	762.04	
Wavelength	0.71073 Å	
Crystal System	Triclinic	
Space Group	P-1	
Unit Cell Dimensions	a = 6.8372(3) Å	α = 81.616(3)°
	b = 8.9737(3) Å	β = 82.110(3)°
	c = 14.2074(6) Å	γ = 83.090(3)°
Volume	849.72(6) $Å^3$	
Z	2	
Density (calculated)	2.978 Mg/m^3	
Absorption Coefficient (μ)	13.693 mm^{-1}	
Crystal Size	0.078 x 0.038 x 0.037 mm^3	
Refinement Method	Full-matrix least-squares on F^2	
Goodness of fit on F^2	1.042	
Final R indicies [I>2σ(I)]	R1= 0.0446, wR2 = 0.0873	
R indicies (all data)	R1 = 0.0727, wR2 = 0.0976	

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Curriculum Vitae

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Education

MSc. in Inorganic Chemistry **2010-present**
University of Western Ontario, London, ON
Thesis: Reactivity of Dimethylplatinum(II) complexes with peroxides
Expected Completion: September 2012

H.BSc. Specialization in Chemistry **2006-2010**
University of Western Ontario, London, ON
Areas of concentration: Analytical Chemistry, Inorganic Chemistry
Thesis: Fabrication of photovoltaic devices based on copper indium gallium diselenide thin films

Relevant Coursework

Chem9503S: Advanced NMR Spectroscopy I **2011**
University of Western Ontario, London, ON
An overview of the fundamentals of high resolution nuclear magnetic resonance (NMR) spectroscopy. The course has a description of basic pulsed Fourier transform NMR experiment, a general discussion of chemical shifts and coupling constants, emphasis and discusses spin-lattice and spin-spin relaxation, polarization transfer and nuclear Overhauser difference spectroscopy.

Chem9651: Organometallic Chemistry for Bond Activation
University of Western Ontario, London, ON
This course gives the fundamental principles of bond activation by transition metal complexes, with examples of applications in the petrochemical industry or in organic synthesis. Some specific topics will include; ligand substitution reactions, oxidative addition and related reactions, insertion and related reactions, applications in homogeneous catalysis.

Chem9541: Crystallography I **2010**
University of Western Ontario, London, ON
An introduction to single crystal x-ray techniques with focus on structure refinement of a defined crystal structure. Determination and solving of unit cell dimensions, space groups, reciprocal lattices, and data collection.

Chem4471a: Transition Metals and Catalysis **2009**
University of Western Ontario, London, ON
Fundamentals of transition metal catalysis, looking at both heterogeneous and hybrid catalysts, focusing on topics including: electron courting rules, ox. states, catalytic cycles, and industrial homogeneous catalysis.

Teaching Experience

Chem2271a: Structure and Bonding in Inorganic Chemistry **2010**
Chem3371f: Transition Metal Chemistry **2010-2011**
Chem2223b: Organic Chemistry of Biological Molecules **2011**
Chem2281g: Inorganic Chemistry of the Main Group Elements **2012**

Publications

Pellarin, K.R.; McCready, M.S.; Puddephatt, R.J. *Organometallics*. **DOI:** 10.1021/om300616x.

Harati, M.;Jia, J.; Giffard, K.; Pellarin, K.R.; Hewson, C.; Love, D.A.; Laum W.M.; Ding, Z. *Phys. Chem. Chem. Phys.*, **2010**, 12, 15282-15290.

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Presentations

Dye Sensitized Solar Cells: The Bright Future of Photovoltaic **2012**
Chem9658: Seminar Course

Oxidation of Organoplatinum(II) Complexes by Peroxides **2011**
Inorganic Discussion Weekend, Poster Session B

Fabrication of photovoltaic devices based on copper indium gallium diselenide thin films **2010**
38th Southern Ontario Undergraduate Student Chemistry Conference