Reactions of Platinum Complexes with Dimethylamine-borane

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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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REACTIONS OF PLATINUM COMPLEXES WITH DIMETHYLAMINE-BORANE

(Thesis format: Monograph)

by

Shawn Robinson

Graduate Program in 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
London, Ontario, Canada

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The thesis by

Shawn Michael Robinson

entitled:

Reactions of Platinum Complexes with Dimethylamine-borane

is accepted in partial fulfillment of the requirements for the degree of Master of Science

Date

Chair of the Thesis Examination Board
Abstract

This thesis describes a study of the reactions of platinum complexes with dimethylamine-borane (DMAB) as models for alkane activation. It is concluded that sigma-borane complexes of platinum(II) or platinum(IV) will be difficult to synthesize or even to detect as intermediates in hydride transfer from boranes to platinum.

The complex [PtMe(O$_2$CF$_3$)(bpy)] reacts with DMAB to form an intermediate [PtMeH(bpy)] complex, which undergoes reductive elimination of methane with further degradation to give platinum(0) and free 2,2'-bipyridine. The addition of methyl acrylate to the reaction allowed the trapping of the platinum-hydride, producing [PtCl(CHMeCO$_2$Me)(bpy)] and [Pt(CHMeCO$_2$Me)$_2$(bpy)]. Oxidative addition of methyl iodide produced the complex [PtMe(CHMeCO$_2$Me)Cl(I)(bpy)]. As well, the reaction of [Pt(O$_2$CF$_3$)$_2$(dppe)] with DMAB afforded the [Pt(µ-H)(dppe)$_2$[O$_2$CF$_3$]$_2$ complex. These complexes are characterized by NMR spectroscopy, with additional structural information obtained from the crystal structure of [PtMe(CHMeCO$_2$Me)Cl(I)(bpy)].

Complexes [PtMe$_3$(OTf)(bpy)] and [PtMe$_3$(OTf)(bu$_2$ bpy)] react with DMAB to afford [PtMe$_3$(Me$_2$NH)(bpy)]$^+$, [Pt$_2$Me$_6$(µ-H)(bpy)$_2$]$^+$, [PtMe$_3$(Me$_2$NH)(bu$_2$ bpy)]$^+$, and [Pt$_2$Me$_6$(µ-H)(bu$_2$ bpy)$_2$]$^+$. The addition of dibenzoyl peroxide to [PtMe$_2$(bpy)] yielded [PtMe$_2$(OBn)$_2$(bpy)]. The reaction of [PtMe$_3$(OTf)(dmpe)] with DMAB afforded the [PtMe$_4$(dmpe)] complex. These complexes are characterized by NMR spectroscopy.

Keywords

Dimethylamine-borane, bridging hydride, oxidative addition, reductive elimination, platinum complexes
To my family, friends, and girlfriend
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°
do degrees

α, β, γ, a, b, c
X-ray crystallographic unit cell parameters

µm
micrometres

µµ-L
ligand L, bridging x number of metal atoms (if absent, x = 2)

Å
Angstroms

Ac
acetate, CH₃CO-

amu
atomic mass units

Ar⁢F
3,5-(CF₃)₂C₆H₃

bpy
2,2′-bipyridine

br
broad (NMR)

bu₃bpy
4,4′-tert-butyl-2,2′-bipyridine

c-
cyclo-

C/A
chirality configuration (handedness) for octahedral centres

Cp
cyclopentadienyl

Cy
cyclohexyl

δ
chemical shift (in ppm) relative to the reference signal

ΔG
Gibb’s free energy

ΔS‡
change in entropy at transition state

D
deuterium

d
doublet (NMR)

DCM
dichloromethane

dd
doublet of doublets (NMR)

ddd
doublet of doublets of doublets (NMR)

DMAB
dimethylamine-borane

dmpe
1,2-bis(dimethylphosphino)ethane

DMSO
dimethyl sulfoxide

dⁿ
d orbital, n number of electrons

dppe
1,2-bis(diphenylphosphino)ethane

ESI-MS
electrospray ionization mass spectrometry

ESR
electron paramagnetic resonance spectroscopy

Et
ethyl
Et₂O  
*fac-*  
Hz  
hv  
¹Bu  
IMes  
¹Pr  
Lₙ  
M  
m  
m/z  
Me  
Mes  
MHz  
nH  
ⁿJ(AB)  
nm  
NMR  
ηˣ  
OBz  
Ph  
phen  
ppm  
q  
R  
R/S  
σ*  
S  
s  
Sn2  
spⁿ  
¹'Bu  

diethyl ether
facial
hertz
UV light
iso-butyl
1,3-dimesitylimidazol-2-ylidene
iso-propyl
ligand, n number of ligands
metal
multiplet (NMR)
mass to charge ratio (Mass Spectrometry)
methyl
mesityl
megahertz
peak intensity as n number of protons
coupling constant between nuclei A and B over n bonds
nanometers
nuclear magnetic resonance spectroscopy
hapticity (x number of atoms within bonding distance of metal)
benzoate, -O₂CPh
phenyl
phenanthroline
parts per million
quartet
alkyl group
chirality configuration for tetrahedral centres
antibonding orbital
solvent
singlet (NMR)
bimolecular nucleophilic substitution
hybridized s and p orbitals (n number of p orbitals involved)
tert-butyl
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<td>tert</td>
<td>tertiary</td>
</tr>
<tr>
<td>transphos</td>
<td>bis(diphenylphosphinomethyl)benzo[c]phenanthrene</td>
</tr>
<tr>
<td>triflate, OTf</td>
<td>CF$_3$SO$_3^-$</td>
</tr>
<tr>
<td>UV</td>
<td>ultraviolet</td>
</tr>
<tr>
<td>X</td>
<td>anion (halide unless otherwise specified)</td>
</tr>
<tr>
<td>Z</td>
<td>number of formula units per cell</td>
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CHAPTER 1

GENERAL INTRODUCTION
1.1 HISTORY AND CHEMISTRY OF PLATINUM

Known as one of the more rare elements found on Earth as well as a precious metal, platinum was discovered in the 16th century in the Republic of Columbia. Its name was derived from the Spanish word “platina” meaning “little silver”. European scientists performed the first known scientific investigations on platinum after it was brought to England in 1741. ¹ Today, the main sources of platinum are found in Canadian, South African and Russian mines whereby platinum is extracted as a by-product from copper-nickel ores. These ores also contain small amounts of other platinum group metals such as Ru, Rh, Pd, Os and Ir. Platinum, utilized in a wide variety of areas including the manufacture of dentistry and laboratory equipment to jewellery making, is most commonly used as a catalyst in chemical reactions. ²

After its arrival in Europe during the mid-18th century, the chemistry of platinum has been studied extensively. The area of organometallic chemistry was first introduced by Danish pharmacist W.C. Zeise who prepared the complex and named it Zeise’s salt, K[PtCl₅(C₂H₄)]·H₂O, in 1827.³ Platinum has been an invaluable element in organometallic and coordination chemistry due to the high kinetic stability of its complexes, allowing for easy preparation and separation. Other significant platinum complexes include the first carbonyl complex, [PtCl₂(CO)₂],⁴ one of the first alkyl transition metal complexes, [(PtMe₃)₄],⁵ as well as cis-platin, cis-[PtCl₂(NH₃)₂], which is one of the more vital complexes as it acts as an antitumour chemotherapeutic agent.⁶

The most common oxidation states of platinum are: 0, +2, and +4, with platinum(II) being the most dominant. This two electron separation between the common oxidation states allows for oxidative addition and reductive elimination reactions to occur
easily, as these involve the transfer of two electrons between the ligand and metal.\textsuperscript{6} The geometry of platinum\((0)\) is dominated by four-coordinate tetrahedral and three-coordinate trigonal planar geometries, with rare cases of two-coordinate linear geometry. Platinum\((II)\) forms low spin \textit{d}\textsuperscript{8} complexes that occur mainly as four-coordinate square-planar, while the platinum\((IV)\) complexes obtain a low spin \textit{d}\textsuperscript{6} complex with six-coordinate octahedral geometry. The oxidation states of platinum\((I)\) and platinum\((III)\) are known, although rare, and usually involve metal-metal bonds.\textsuperscript{7(a)} Higher oxidation states of platinum\((V)\) and platinum\((VI)\) are also rare, occurring in a few fluoro complexes, with the negative oxidation states only reported in polynuclear carbonyl anions of the general formula, \([\text{Pt}_3(\text{CO})_5(\mu-\text{CO})_3]^2^-\text{.}\textsuperscript{8}\)

Platinum plays a major role in organometallic chemistry, either as the metal centre of an effective catalyst in numerous reactions or as a model system for nickel and palladium complexes. Often, nickel and palladium complexes react too quickly for any study of reaction intermediates and the study of the reaction mechanism, whereas the platinum analogues have shown to have higher stability and slower reactivity allowing for more detailed studies of these reactions.\textsuperscript{7(b)} Additionally, platinum has an NMR spin active isotope, \(^{195}\text{Pt}\), with a nuclear spin of \(\frac{1}{2}\) and a natural abundance of 33.7\%. Hence, this allows for more NMR studies to be performed, along with \(^{195}\text{Pt-}\text{H couplings in the}\text{ }}^1\text{H NMR spectra to be observed.}\textsuperscript{1}\text{H NMR spectra to be observed.}

Platinum\((II)\) complexes have established the \textit{trans} effect, wherein certain ligands facilitate the departure of a second ligand \textit{trans} to the first, and the replacement or substitution by an external ligand. These same complexes observe the \textit{trans} influence, a change in the ground state thermodynamic properties, which is seen in the coupling
constants in NMR spectroscopy, as well in the lengthening of the M-L bond distances in X-ray crystallography.  

1.2 OXIDATIVE ADDITION

Along with its reverse reaction, reductive elimination, oxidative addition reactions are among the most important elementary transformations in organometallic chemistry, playing a key role in both synthesis and catalysis. Commonly involved in these reactions is the addition of a neutral molecule (A-B) to a single metal centre (M), which results in the formation of two new bonds (M-A and M-B) and an increase by two units in each of coordination number, oxidation state and electron count of the metal complex (Scheme 1.1).  

Due to the nature of the process, the metal complex is required to be both electronically and coordinatively unsaturated, or such a complex must be generated by the dissociation of a two-electron donor ligand prior to the oxidative addition reaction. Moreover, the metal complex must have both nonbonding electron density available for the donation to the incoming ligand ($d^{n} \geq 2$) and a stable oxidation state two units higher. There is a net transfer of electrons from the metal into the $\sigma^{*}$ orbital of the A-B bond and A-B $\sigma$ electrons to the metal.  

Even though the reaction is reversible, the position of the equilibrium, governed by the balance between the A-B bond strength and the sum of the M-A and M-B bond
strengths, is often completely shifted to one side. Furthermore, oxidative addition is particularly favourable for both late transition metals and metal complexes with strongly donor ligands.\(^{7(a), 9}\)

Consequently oxidative addition reactions dominate the various reactions seen with platinum(II) metal complexes containing nitrogen-donor ligands. This is due to the fact that the nitrogen-donor ligands stabilize the platinum(IV) products by way of electronic (strong \(\sigma\)-donor/weak \(\pi\)-acceptor) and steric properties. As well, the “hard” nature of nitrogen enhances the nucleophilicity of the platinum(II) centre causing it to be more reactive towards the \(S_N2\) type oxidative addition pathway, which will be discussed in more detail later.\(^{10}\)

Oxidative additions involving platinum are rather diverse mechanistically and will therefore be discussed separately.

1.2.1 Three-Centre Concerted Addition

One mechanism by which oxidative addition occurs is by way of a concerted mechanism. This pathway is designated for substrates having nonpolar or marginally polar \(\sigma\) bonds (e.g. H-H, C-H, Si-H).\(^{7(a)}\) A necessity for the \emph{cis}-concerted addition of these substrates is coordinative unsaturation at the metal centre.\(^{10}\) Shown below in scheme 1.2, the substrate and metal form a \(\sigma\)-complex as an intermediate. These \(\sigma\)-complexes can sometimes be stable enough for isolation, but there is usually sufficient back donation of electron density from the metal to the \(\sigma^*\) orbital of the incoming ligand to induce bond scission and form the oxidative addition product.\(^{7(a)}\)
One feature of the concerted pathway is the retention of stereochemistry of a chiral carbon in the substrate. Furthermore, these reactions normally observe second order kinetics and show negative entropies of activation, consistent with an ordered $\sigma$ complex transition state. The polarity of the solvent plays little effect on the speed of the reaction. Although much work has been involved, this mechanism has yet to be supported by conclusive experimental evidence.

Intermolecular oxidative addition of aryl halides to platinum(II) complexes are rather rare, although intramolecular addition has been realized using electron-rich complexes and by ligand design. The first example of the latter is the platinum(II) complex $[\text{PtMe}_2\{2-\text{XC}_6\text{H}_4=\text{N(CH}_2\text{)}_2\text{NMMe}_2]\} \ (X = \text{F, Cl, Br})$ that undergoes oxidative addition to yield the platinum(IV) product (Scheme 1.3). This reaction observes first order kinetics and is believed to follow the concerted mechanism pathway with the reactivity following $\text{C-Br>Cl>C-F}$. Along with C-X oxidative addition, there is competitive C-H oxidative addition also observed, which is followed by a reductive elimination of $\text{CH}_4$.\textsuperscript{11}
Scheme 1.3. Concerted oxidative addition with a Pt(II) complex

(X = H, F)  (X = Cl, Br, I)
It is believed that the dimethylamine group dissociates prior to oxidative addition, which is consistent with the proposal stating that it requires ligand dissociation to generate a 5-coordinate platinum(IV) intermediate. This is based on the principle of microscopic reversibility, due to the concerted reductive elimination pathway in which coordinatively saturated platinum(IV) centres require a vacant site created by ligand dissociation.\(^{11}\)

### 1.2.2 Nucleophilic (S\(_{N2}\)) Reaction Pathway

Adopted for polarized A-B substrates is the S\(_{N2}\) type oxidative addition mechanism (Scheme 1.4).\(^9\) Here, the metal acts as a nucleophile, generating a cationic intermediate.\(^{10}\)

![Scheme 1.4. S\(_{N2}\) oxidative addition](image)

The metal complex directly attacks the \(\sigma^*\) orbital of the A-B substrate by in-line attack of the least electronegative atom (A), thus resulting in the displacement of B, which often (not always) recombines with the cationic complex. The relative positions of the A and B groups in the newly formed complex depend on a variety of factors.\(^{7(a)}\)

Diagnostically, this mechanism has been shown to be of S\(_{N2}\) type due to the inversion of configuration at the carbon bearing the leaving group, observation of second-order kinetics, large negative entropies of activation and an increase in the rate of reaction with an increase in the polarity of the solvent. These observations are consistent
with a charged intermediate, as well as a polarized transition state. Likewise, the same reactivity seen for organic S_N2 reactions holds true here, particularly with steric hindrance (CH_3X>RCH_2X>R_2CHX>>R_3CX) and the nucleophilicity of the leaving group (CF_3SO_3>I>Br>Cl>>F). Furthermore, trans stereochemistry of the oxidative addition is indicative of this mechanism, but it is not definitive as rapid isomerisation of the concerted mechanism may be possible.

Unambiguous evidence for the S_N2 type mechanism would be the cationic intermediate and with the use of low temperature ^1H NMR experiments, a few intermediates were observed. The reaction of MeI with the [PtMe_2(bpy)] complex allowed the observation of the cationic [PtMe_3(bpy)]^+ in both CD_3CN and acetone-d_6 (Scheme 1.5). Unambiguous evidence was found using CD_3CN as the solvent where it has the ability to stabilize the platinum(IV) cationic species by coordination. This solvent coordination occurs simultaneously with the oxidation step, contributing to the large -\Delta S^\ddagger. Finally, the rapid displacement of the solvent by the anion occurs due to the large trans effect of the methyl group and the superior Lewis basicity of the anion over the solvent.

Scheme 1.5. S_N2 oxidative addition with a Pt(II) complex
1.2.3 Radical Mechanisms

Although the two electron pathways are more common, oxidative addition can also undergo one electron mechanisms, termed radical reactions. This type of reaction is very sensitive to the nature of the complex and the organic substrate, overall reaction conditions and the presence of any paramagnetic impurities.\(^{(a)}\) Due to these stipulations, radical mechanisms are less easily controlled causing this type of reaction to be less desirable.\(^{9}\) Even with these setbacks, two main radical pathways have been identified: non-chain and chain processes.

1.2.3.1 Non-Chain Pathway

The non-chain reaction pathway has been proposed to occur during the addition of certain alkyl halides to zerovalent complexes (Scheme 1.6).

\[
\text{PtL}_2 + RX \quad \xrightarrow{\text{slow}} \quad \cdot\text{PtXL}_2 + \cdot R \quad \xrightarrow{\text{fast}} \quad \text{RPtXL}_2
\]

**Scheme 1.6.** Non-chain radical oxidative addition

The key factor of this type of mechanism is the one electron oxidation of the metal by the substrate, RX. This then results in two fragments, M\(^{+}\) and RX\(^{-}\), which is followed by the transfer of X\(^{-}\) to the metal, liberating an R\(\cdot\) radical fragment. This solvent-caged radical pair (\(\cdot\text{MX}\) and R\(\cdot\)) has two fates: first, the radical pair can collapse to give the oxidative addition product; or second, escape of the radical pair that can react further with other escaped radicals to form side products. Contrasting the S\(_N\)2 type mechanism, racemisation is seen at chiral carbons rather than inversion.\(^{9}\)
A more electron rich metal and a weaker RX bond (RI>RBr>RCI) accelerates the reaction, reflecting the ability of the substrate to be reduced by the metal.\(^7(a)\),\(^10\) Also contrary to the S\(_N\)2 type reactions, a more stable radical speeds up the reaction (3°>2°>1°>Me) and it is inhibited where X is a good leaving group. Furthermore, the reaction is not affected by the presence of radical inhibitors.\(^9\)

A noteworthy example of a platinum(II) complex with nitrogen-donor ligands that undergoes the non-chain oxidative addition pathway is the photochemical reaction of [PtCl\(_2\)(bpy)] with CHCl\(_3\) to generate [PtCl\(_4\)(bpy)] (Scheme 1.7). Evidence of this pathway being employed is the fact that no radical was detected by ESR spectroscopy or in the presence of spin traps at room temperature exhibiting that a caged radical species with a very short lifetime is the most likely intermediate. As well, the carbene byproduct was trapped via a reaction with CHCl\(_3\) to afford Cl\(_2\)HCCHCl\(_2\), further supporting this mechanism.\(^13\)

\[
\begin{align*}
[\text{Pt}^{III}\text{Cl}_2(\text{bpy})] + \text{CHCl}_3 \xrightarrow{hv} [\text{Pt}^{III}\text{Cl}_3(\text{bpy})] + \cdot\text{CHCl}_2 \\
[\text{Pt}^{III}\text{Cl}_3(\text{bpy})] + \cdot\text{CHCl}_2 \rightarrow [\text{Pt}^{IV}\text{Cl}_3(\text{bpy})]^+ + \text{CHCl}_2^- \\
[\text{Pt}^{IV}\text{Cl}_3(\text{bpy})]^+ + \text{CHCl}_2^- \rightarrow [\text{Pt}^{IV}\text{Cl}_4(\text{bpy})] + \cdot\text{CHCl}
\end{align*}
\]

\textbf{Scheme 1.7.} Non-chain radical oxidative addition with a Pt(II) complex

1.2.3.2 \hspace{0.5cm} \text{Chain Pathway}

This radical pathway usually shows an induction period, a number of atom-abstraction steps and a source of initiator radicals.\(^10\) Facilitated by initiators, such as oxygen, a small amount of an organic radical is produced. The following step, called propagation, shows fast addition of alkyl radicals to the metal to form the metalloradical,
RM•. The rate-determining step, which is next, is the abstraction of a halogen atom from the RX molecule by the metalloradical to regenerate the chain carrier R• and produce the oxidative addition product RMX. Termination, most commonly two organic radicals coupling, limits the number of cycles possible per R•.7(a), 9

\[
\begin{align*}
\text{In} \cdot + X-R & \rightarrow \text{In-}X + R \cdot \quad \text{initiation} \\
R \cdot + M^{(n)} & \rightarrow R-M^{(n+1)} \quad \text{propagation} \\
R-M^{(n+1)} + R-X & \rightarrow R-M^{(n+2)} - X + R \cdot \\
2 R \cdot & \rightarrow \text{side products} \quad \text{termination} \\
R \cdot + M \cdot & \rightarrow \text{side products}
\end{align*}
\]

**Scheme 1.8. Chain pathway**

The evidence for this type of mechanism is the fact that it is sensitive to both radical initiators and inhibitors. Also, the structural effects are consistent with the stability of alkyl radicals generated in the rate-determining step (3°>2°>1°>Me).7(a) Finally, the racemisation at a chiral carbon in the substrate implies this mechanism, as well.

One distinctive example of a platinum(II) complex undergoing this type of reaction pathway is the photoinitiated oxidative addition of iPrI to [PtMe₂(phen)] (Scheme 1.9). Initiation is achieved by generating the triplet-[Pt⁺Me₂(phen')]• which abstracts an iodine from the iPrI, forming the chain carrier iPr•. These organic radicals are then rapidly captured by the platinum(II) complex, with a proposed termination step as the formation of nonradical products by way of reaction of the iPr• radicals with the phen or Me ligands of the complex.14
1.2.4 Ionic Mechanism

The ionic mechanism is typically seen for hydrogen halides, which have a tendency to largely dissociate in solution. The anion and proton are inclined to add to the metal complex in two separate steps, with the order of two possibilities. The first, and most common possibility, is where the complex is basic enough to protonate first, after which the anion will bind to the intermediate to give the final oxidative addition product. Second, and more atypical, is the possibility wherein the halide anion will attack first, followed by protonation of the intermediate, which tends to occur in metal complexes that are electrophilic or cationic. Performing the reaction with an acid that has a noncoordinating anion (e.g. HBF$_4$, HPF$_6$, etc.) allows the isolation of the intermediate as the anion has insufficient nucleophilicity to carry out the second step.
1.3 REDUCTIVE ELIMINATION

Reductive elimination, the reverse of oxidative addition, involves the excision of two cis-ligands from a single metal centre, thus causing a decrease in the oxidation state, electron count and coordination number by two units. Reductive elimination is usually seen as the product forming step in many catalytic or stoichiometric transformations.\(^7(a)\)

A variety of mechanisms were identified for oxidative addition. According to the principle of microscopic reversibility, which states that a reversible reaction proceeds by the same mechanism in both the forward and reverse direction, it makes it obvious to deduce that the same variety of mechanisms would be seen for reductive elimination as well.\(^9\)

There are many factors that affect the rate of reaction of reductive elimination. The effects of electronic and steric properties tend to have the opposite effects on oxidative addition reactions. Initially, thermodynamic effects dominate the control of reductive eliminations. The rate of reaction of first row element complexes is faster than that of second row complexes, and in turn, the second row complexes are quicker than those of third row element complexes. This increase in rate is due to the fact that the second row complexes tend to have weaker metal-ligand bonds. Furthermore, reductive elimination occurs more rapidly for electron-poor complexes than those of electron-rich metal centres as the product formed tends to have more electron density at the metal centre, making it less favourable. Lastly, sterically hindered ancillary ligands tend to increase the reaction rates as the process of reductive elimination relieves the steric congestion when the product is released.\(^9\)
Another factor influencing the rate is the formation of the product. Reductive elimination trends towards being quicker when forming bonds to hydrogen rather than those that form bonds between two heavier atoms. This is seen as the s-orbital of the hydride ligands observes less directionality than an sp"-hybridized orbital, creating greater orbital overlap in the transition state with the hydrogen than with heavier atoms. As well, the coordination number of the metal complex plays a consequential role in the rate of reaction. Odd numbered (3- and 5-coordinate) complexes tend to display faster reaction rates than even numbered (4- and 6-coordinate) complexes due to the changes of the energy of the frontier orbitals. As shown in Figure 1.1, reductive elimination from an even numbered complex leads to a product with a strongly metal-ligand antibonding interaction. On the other hand, reductive elimination from odd numbered complexes leads to an occupation of a molecular orbital that is nonbonding as the dative ligand of the product is located in the nodal plane.\textsuperscript{15}
A *cis* orientation of the outgoing ligands is needed for reductive elimination to occur via the three-centre concerted mechanism. Complexes which have these ligands *trans* to each other must undergo this reaction stepwise or by prior isomerisation to arrive at the *cis*-complex. An illustration of this is shown with the elimination of ethane from two palladium complexes, one with a bidentate ligand forcing *cis* orientation (*cis*-[PdMe₂(dppe)]) and the other having a bidentate ligand forcing *trans* orientation (*trans*-[PdMe₂(transphos)]). The oxidative addition of a C-C bond tends to undergo a three-centre concerted mechanism, so consequently, the reductive elimination must follow the same process. Shown in scheme 1.10, using the same conditions, it was observed that the rate of reaction was found to be greater for the *cis*-complex than that of the *trans*—
complex with the transphos ligand maintaining resistance to isomerisation from trans to cis, preventing the reductive elimination of ethane.\textsuperscript{9}

\textbf{Scheme 1.10. Cis/Trans reductive elimination}

Reductive eliminations from platinum complexes occur differently for the two different geometries, platinum(II) square planar and platinum(IV) octahedral complexes. In the case of platinum(II) complexes, reductive elimination can occur by a variety of mechanisms: associative, dissociative and non-dissociative. Platinum(II) complexes tend to slowly eliminate, which could possibly be due to the difficulty of ligand dissociation. Reductive elimination can be promoted by the oxidative addition of a substrate to give the more susceptible platinum(IV) intermediate. As previously stated, the platinum(IV) complexes readily undergo reductive elimination, but requires the initial loss of a ligand to form the more reactive 5-coordinate intermediate.\textsuperscript{9}

\section{1.4 C-H BOND ACTIVATION}

Alkanes are the least expensive and most abundant hydrocarbon resource, but unfortunately there are very few selective methods available for converting these alkanes into more valuable and transportable products.\textsuperscript{16,17} C-H bond activation is found in an
area of organometallic chemistry that seeks to resolve this problem with the ultimate goal being to formalize a practical method for the functionalization of saturated hydrocarbons. For this method to be practical, it must, at the least, follow these three requirements: i) the C-H bond activation must be a part of a catalytic cycle that produces the useful product; ii) the selectivity of the system must be controllable from both the favourable site of attack in a hydrocarbon possessing different C-H bonds and the C-H bonds in the product must not be much more reactive than those in the starting hydrocarbon; iii) the activity must be sufficiently high, in order to allow for a practical process under moderate conditions.\textsuperscript{18}

During the 1970s, A.E. Shilov observed the first indication of a special organometallic reactivity pattern with preferential activation of primary C-H bonds in an H/D exchange in alkanes using platinum(II) as a catalyst in D\textsubscript{2}O/DOAc. Moving to [PtCl\textsubscript{6}]\textsuperscript{2-} as the oxidant, Shilov observed alkanes, RH, being oxidized to ROH and RCl using the same platinum(II) catalyst with the linear products still preferred:\textsuperscript{19}

\begin{center}
\textbf{Scheme 1.11. Shilov System}
\end{center}

Labinger and Bercaw revisited this system in the 1990s using mechanistic probes initially confirming Shilov’s observations, then going forward to expand on his findings. The current mechanistic view begins with the alkane complex either leading to oxidative
addition of the alkane and loss of a proton or the $\sigma$-alkane complex loses a proton directly (Scheme 1.12). This is followed by the oxidation of the platinum(II) alkyl complex to platinum(IV) alkyl by the platinum(IV) oxidant by an electron transfer. Thereupon, the platinum(IV) becomes a good leaving group, where OH$^-$ and Cl$^-$ can nucleophilically attack the R-Pt(IV) species with the departure of the regenerated platinum(II) catalyst.\textsuperscript{20}

Scheme 1.12. Two pathways for RH addition in Shilov system

Periana and co-workers were able to produce a process that is described as Shilov-like chemistry, but one that proved to be much more efficient. Using Hg(II) salts dissolved in H$_2$SO$_4$ at 180 °C (H$_2$SO$_4$ is both the solvent and reoxidant), they were able to convert the methane to methyl bisulfate, MeOSO$_3$H (a methanol precursor), in an approximate 43% yield (50% methane conversion) (Scheme 1.13). One outstanding advantage to the bisulfate group is the deactivating nature of it, preventing the overoxidation of the methane. The expected cationic intermediate, MeHg$^+$, was observed by NMR spectroscopy, and thus a Shilov-type mechanism was proposed. Ultimately, Periana also developed the same type of reaction, but instead used a platinum(II) complex as the catalyst.\textsuperscript{21}
As mentioned previously, the initial step of C-H bond activation is the formation of the σ-alkane complex. The first step determines both the rate and selectivity of the oxidation, and therefore is essential towards the development of C-H bond activation as a potential solution. Although there has been no actual isolation of a σ-alkane complex, there has been evidence of the formation of these complexes.\(^{7(a)}\)

1.4.1 Direct Observation of σ-complex

Literature has been published in the past decades concerning the observations of a σ-alkane complex with various transition metal complexes.\(^{22}\) One example is the low temperature NMR experiment of \(\text{CpRe(CO)}_3\). Irradiation of the complex at -80 \(^\circ\)C in cyclopentane resulted in the formation of \(\text{CpRe(CO)}(\text{c-pentane})\). In the \(^1\)H NMR spectrum, a resonance found for the \(\text{CH}_2\) bound to the metal is observed at \(\delta\) -2.32 ppm, consistent with either a symmetrical binding of both hydrogens (\(\eta^2\)-H,H) or rapid interchange between two \(\sigma\)-C-H (\(\eta\)-C,H).\(^{23}\)

A second example is the remarkable work by Ball \textit{et al.} in 2007. They were able to obtain NMR data for σ-alkane complexes, of general formula \([\text{Cp’ReL(CO)}(\text{alkane})]\) (L is CO or PF\(_3\); Cp’ is \(\eta^5\)-C\(_5\)H\(_5\), \(\eta^5\)-C\(_5\)Me\(_5\) or \(\eta^5\)-C\(_5\)H\(_4\)\(^i\)Pr; alkane is \(n\)-C\(_5\)H\(_{12}\), \(n\)-C\(_7\)H\(_{16}\), \(c\)-
$\text{C}_5\text{H}_{10}$, $\text{c}-\text{C}_6\text{H}_{12}$ or $\text{i}-\text{C}_4\text{H}_{10}$), were produced using photodissociation experiments in pure alkane solvents.$^{24}$

Scheme 1.14. Photodissociation experiments leading to $\sigma$-alkane complexes.

More recently, Brookhart, Goldberg et. al were able to fully characterize the NMR data of a rhodium(I) $\sigma$-methane complex in solution. The $\sigma$-methane complex was generated directly in the coordination sphere of the rhodium by protonation of the methyl precursor. The spectroscopic characterization of the $\sigma$-methane complex was obtained due to the fact the methyl hydride complex was at higher energy for this system.$^{25}$

Scheme 1.15. $\sigma$-methane complex.

1.4.2 Indirect Observation of $\sigma$-complex

As well as direct evidence, there have been a few indirect observations of $\sigma$-complexes. One broad example is the preparation of a metal alkyl deuteride (eg.
Cp*₂W(CH₃)(D)) that can rearrange to an α-deuteroalkyl hydride complex prior to reductive elimination.⁷(b)

![Scheme 1.16. H/D exchange](image)

Another good example of the indirect observations is the hydrogen/deuterium exchange invoked in rearrangements of longer alkyl deuteride complexes. Seen in scheme 1.17 is the migration of Rh cation along a 10-carbon chain in the rearrangement of a deuterated triazacyclonane complex.²⁶

![Scheme 1.17. Indirect observation of σ-alkane complex.](image)

### 1.5 AMINE-BORANES

Amine-borane compounds, containing a dative bond between boron and nitrogen, known to chemists since the 19th century, have only recently earned more attention and consideration due to their potential as reagents, hydrogen storage materials, polymer precursors and their coordination chemistry. Amine-boranes are classic examples of compounds arising from reactions between Lewis acids and Lewis bases where the group
15 species (N) is considered to provide both electrons for the bond from a lone pair and the group 13 centre (B) is electron deficient and accepts both electrons into a vacant p orbital.27

\[ \text{Scheme 1.18. Bonding in amine-boranes} \]

The analogy found between N-B bonds and C-C bonds is very well known28, and amine-boranes can be considered as an inorganic analogue of alkanes. As well, both boron and nitrogen tend to be tetrahedral, while the B-N bond length is comparable to C-C bonds found in simple alkanes.

Over the past decade, amine-borane chemistry has come to the forefront as a possible solution for major environmental concerns around energy sources: borylation of alkanes or arenes and the dehydrogenative coupling of amine-boranes.29 Due to their high gravimetric hydrogen contents (~20% for ammonia borane) the greatest degree of attention has been directed towards using amine-boranes as portable hydrogen storage materials.30 The presence of protic N-H bonds and hydridic B-H bonds makes the reactivity of primary and secondary amine-boranes complicated. Dihydrogen loss is seen in the presence of transition metal complexes through B-H and N-H bond breaking.29

One challenge that did arise from trying to develop amine-boranes into hydrogen storage materials lies in the regeneration of the spent fuel. The loss of hydrogen in these compounds is usually too exergonic for its regeneration. By altering the substitution on both the nitrogen and boron, the ΔG of dehydrogenation can be made more neutral. A
strong dative N-B σ-bond in the reactant and a weak dative N-B π-bond in the product results in a less exergonic dehydrogenation. Hence, the σ-bond plays an important role in the energetics determining that amine-borane compounds with electron donating groups on nitrogen and electron withdrawing groups on the boron are best suited for less exergonic dehydrogenation, thereby resulting in better reversibility of dehydrogenation.\(^\text{31}\)

A number of examples of catalytic dehydrogenation reactions using amine-boranes have been published recently.\(^\text{32}\) One very recent example was the work done by Manners \textit{et al.}, using skeletal nickel catalysts for the heterogeneous dehydrocoupling of amine-boranes. The nickel catalyst was produced via the base leaching of Al from a commercial 50:50 wt % alloy of Ni and Al at 50 °C, with the product denoted Ni\(_{\text{T50}}\). A toluene solution of dimethylamine-borane with Ni\(_{\text{T50}}\) (5 mol %) produced the product aminoborane in quantitative yields, within 6 hours.\(^\text{33}\)

\[
\begin{align*}
2 \text{Ni/Al} &+ 2 \text{NaOH} + 6 \text{H}_2\text{O} \quad \rightarrow \quad 2 \text{Ni} + 2 \text{Na[Al(OH)\(_d\)]} + 3 \text{H}_2 \\
\text{Me}_2\text{NH} \cdot \text{BH}_3 &+ 5 \text{mol % Ni}_{\text{T50}} \quad \rightarrow \quad 1/2 \left[\text{Me}_2\text{N-BH}_2\right]_2 + \text{H}_2 \\
\text{Toluene, 20 °C}
\end{align*}
\]

\textbf{Scheme 1.19.} Catalytic dehydrocoupling

This is the first example of a heterogeneous, non-hydrolytic first-row amine-borane dehydrogenation catalyst, and is of immediate interest due to its low cost and ready availability.

In conjugation with the dehydrocoupling of amine-boranes is the isolation of the intermediate σ-borane complexes with transition metals. There have been many
publications of the isolation of these complexes\textsuperscript{34}, and one such example is the work published by Sabo-Etienne \textit{et al.} Using ruthenium complexes, they synthesized the first ‘true’ \textit{bis}(σ-B-H) monomeric aminoborane complexes by the dehydrogenation of aminoboranes.\textsuperscript{35}

![Scheme 1.20. σ complexation](image)

These new procedures have recently been tailored for the preparation of new main-group polymeric materials. For example, polyaminoboranes have been synthesized by the catalytic dehydrogenation of primary amine-boranes. As well, 2D boron-nitrogen films have been prepared by the convenient route of the dehydrogenation of ammonia borane.\textsuperscript{30}

### 1.6 DESCRIPTION OF THESIS

The overall scope of this research is the reaction of platinum complexes with dimethylamine-borane in an attempt to isolate the σ-borane complex, as an analogous model study for the isolation of a σ-alkane complex with the same platinum compounds.

Chapter 2 describes the synthesis and reactions of certain platinum(II) complexes with dimethylamine-borane. The platinum-hydride complex produced is studied via \textsuperscript{1}H
NMR spectroscopy, as well as trapped using substituted olefins. These newly synthesized platinum complexes are then studied as well.

Chapter 3 describes the synthesis and reactions of certain platinum(IV) complexes with dimethylamine-borane in hopes of isolating a platinum(IV) σ-borane complex. The products and intermediates of these reactions are studied and characterized within.
1.7 REFERENCES


27. Staubitz, A.; Robertson, A.P.M.; Sloan, M.E.; Manners, I. Chem. Rev. 2010, 110, 4023-4078.


CHAPTER 2

REACTIONS OF PLATINUM(II) COMPLEXES

WITH DIMETHYLAMINE-BORANE
2.1 INTRODUCTION

Over the past decades, C-H bond activation has been at the forefront of organometallic chemistry research. The main goal of such research is the formulation of a practical method of functionalizing saturated hydrocarbons into more valuable and transportable products.\(^1\text{,}^2\text{,}^3\) The first work, performed by Alexander E. Shilov\(^4\) in the 1970s, observed special organometallic reactivity, as alkanes were converted to alcohols and alkyl halides using a platinum(II) catalyst. As Labinger and Bercaw\(^5\) observed in the 1990s, there is still a question about how the C-H bond activation mechanism actually proceeds. This discrepancy is in the coordination of the alkane, the step that determines both the rate and selectivity of the oxidation. Therefore, the determination of the process is essential in the development of C-H bond activation.

\[
\begin{align*}
\left[ \text{L}_2\text{M}^{\text{II}}\text{L} \right]^+ + \text{CH}_4 & \rightleftharpoons \left[ \text{L}_2\text{M}^{\text{III}}\text{H} \right]^+ + \text{S} \\
\text{S} &= \text{solvent}
\end{align*}
\]

Scheme 2.1. \(\sigma\)-C-H complexation.

To date, the \(\sigma\)-alkane complex has been a rather elusive entity. Although there have been direct\(^6\text{,}^7\text{,}^8\text{,}^9\text{,}^{10}\) and indirect\(^11\text{,}^{12}\) observations of the \(\sigma\)-complex, there has yet to be an isolation of one. The most notable observation is the work performed by Brookhart and Goldberg. By direct protonation of the methyl rhodium precursor, they were able to generate and fully characterize the NMR data of the \(\sigma\)-methane complex.\(^10\)

\[
\text{O} \quad \text{O} \quad \text{O} \quad \text{O} \\
\text{P}^\text{Bu}_2 \\
\begin{align*}
\text{N} \quad \text{Rh} \quad \text{CH}_3 & \quad [\text{HB(Ar})^\text{F}]_4(\text{Et}_2\text{O})_2 \quad \text{CDCl}_2\text{F} \\
\text{P}^\text{Bu}_2 \\
\text{C} \quad \text{H} \quad \text{H} \\
\text{H} \\
\text{H}
\end{align*}
\]

Scheme 2.2. \(\sigma\)-methane complex.
Along with C-H bond activation, the search for a renewable energy source is also at the forefront of chemical research. Recently, amine-boranes have gathered much attention, as they have great potential as reagents, polymer precursors and in coordination chemistry.\(^{13}\) Above all, amine-boranes are seen to be a possible solution for the hydrogen storage problem. This is due to their high gravimetric hydrogen contents,\(^ {14} \) as well as the presence of protic (N-H) and hydridic (B-H) bonds.\(^ {15} \)

Recently, there have been numerous publications concerning the catalytic dehydrogenation of amine-boranes.\(^ {16} \) In turn, there have been many reports of the isolation of \(\sigma\)-borane complexes.\(^ {17} \) One example is the work performed by Sabo-Etienne \textit{et al.}, in which they synthesized the first ‘true’ bis(\(\sigma\)-B-H) monomeric aminoborane complex, by way of dehydrogenation of amine-boranes using ruthenium complexes.\(^ {17(e)} \)

![Scheme 2.3. Isolation of a bis(\(\sigma\)-B-H) complex.](image)

A second example of the isolation of a \(\sigma\)-borane complex is the work by Aldridge \textit{et al.}. Of the numerous complexes synthesized, they were able to isolate a \(\sigma\)-borane complex of rhodium with the amine-borane derivative \(\text{tBuH}_2\text{N•BH}_3\).\(^ {17(b)} \)

![Scheme 2.4. Isolation of a \(\sigma\)-borane complex.](image)
The analogy of amine-boranes and alkanes is well known\(^\text{18}\), both being iso-electronic and isosteric, as well as showing comparable bond lengths (B-N/C-C). This thesis will describe the attempt to isolate a \(\sigma\)-borane complex of platinum, which has never been achieved before, as a model study of C-H bond activation and the \(\sigma\)-C-H complex.

Scheme 2.5. Scope of thesis.

### 2.2 RESULTS AND DISCUSSION

#### 2.2.1 Reaction of [PtMe(O\(_2\)CCF\(_3\))(bpy)] with dimethylamine-borane

The dimethyl precursor, [PtMe\(_2\)(bpy)] (2.1), was prepared by the addition of 2,2’-bipyridine to the platinum dimer [Pt\(_2\)Me\(_4\)(\(\mu\)-SMe\(_2\))\(_2\)] (Scheme 2.6). Complex 2.1 was isolated easily as a stable red solid and stored at room temperature. The \(^1\)H NMR spectrum displayed a single methyl platinum resonance at \(\delta = 1.15\) ppm \([J(\text{PtH}) = 86\) Hz].

Scheme 2.6. Synthesis of complex 2.1, [PtMe\(_2\)(bpy)].

To produce the starting material, [PtMe(O\(_2\)CCF\(_3\))(bpy)] (2.2), complex 2.1 was mixed with excess trifluoroacetic acid, HO\(_2\)CCF\(_3\), in ethyl ether for two hours (Scheme 2.7). The solvent was then removed \textit{in vacuo}, leaving complex 2.2 as a bright yellow
solid in 88% yield. The $^1$H NMR spectrum again displays a single methyl platinum peak at $\delta = 1.14$ ppm [$^2J(PtH) = 78$ Hz]. Also, the aromatic region of the spectrum displays 8 different resonances, as expected for an unsymmetrical platinum(II) complex.

Scheme 2.7. Synthesis of complex 2.2, [PtMe(O$_2$CCF$_3$)(bpy)].

The reaction of complex 2.2 with dimethylamine-borane (DMAB) is believed to proceed as shown in scheme 2.8. The $^1$H NMR spectrum of the reaction mixture contains a platinum-hydride singlet resonance at $\delta = -16.5$ ppm [$^1J(PtH) = 1546$ Hz]. A corresponding singlet, believed to be due to the methyl platinum group of the platinum-hydride complex, 2.3, was observed at $\delta = 0.98$ ppm [$^2J(PtH) = 80$ Hz]. Another singlet at $\delta = 0.20$ ppm was observed and can be assigned to methane, CH$_4$. No B-H resonances were observed in the $^1$H NMR spectrum, so the nature of the boron-containing product is unknown.

Scheme 2.8. Complex 2.2 reaction with dimethylamine-borane.

The reaction of scheme 2.8 is believed to proceed initially through a ‘B-H activation’ step in which complex 2.2 abstracts a hydride, resulting in the short-lived Pt-H complex, 2.3. The process can be seen as a ‘B-H activation’, as dimethylamine is still present in the reaction mixture, evident in the $^1$H NMR spectrum. As well, as mentioned
previously, the $^1$H NMR spectrum lacks any B-H resonances, originally occurring for Me$_2$HN-BH$_3$ at $\delta = 1.59$ ppm [$J$(BH) = 96 Hz].

The platinum-hydride complex, 2.3, undergoes a reductive elimination of methane, with further degradation of the resulting complex to platinum(0) and free 2,2'-bipyridine. Found in literature was a similar process in which the complex [PtMeH(bu$_2$bpy)] underwent reductive elimination of methane, followed by the degradation to platinum(0) and free bu$_2$bpy.$^{19}$

Understanding the process of the reaction, with the formation of the platinum-hydride complex in situ, led us to attempt to ‘trap’ the platinum-hydride using substituted olefins.

2.2.2 Reaction of [PtMe(O$_2$CCF$_3$)(bpy)] with DMAB and methyl acrylate

The reaction of complex 2.2 with dimethylamine-borane and methyl acrylate proceeds as displayed in scheme 2.9. The $^1$H NMR spectrum of the reaction mixture allows for the ability to observe the products being produced during the reaction. The first notable aspect of the $^1$H NMR spectrum is the appearance of two quartets in the region $\delta = 4.30-2.30$ ppm and two doublets in the region $\delta = 1.60-1.00$ ppm. These quartets and doublets are diagnostic of the PtCHMe(CO$_2$Me) groups which are formed by insertion of methyl acrylate into the platinum-hydride bond of 2.3, with one quartet pairing with one doublet with the same coupling constant.

Scheme 2.9. Methyl acrylate addition to in situ platinum-hydride complex, 2.3.
The observation of two pairs of these quartet-doublet sets suggested the production of two insertion products. In order to separate, thin-layer chromatography was employed using an eluent of DCM:MeOH in a ratio of 98:2. Two different products eluted and will be discussed separately.

The $^1$H NMR spectrum of the product to elute first displayed no quartet-doublet sets expected for an insertion reaction product. The aromatic region displayed 8 different peaks corresponding to a single, non-symmetric product. A single methyl platinum peak at $\delta = 1.26$ ppm [$^2J$(PtH) = 77 Hz] was observed. This product was identified as the known complex [PtMeCl(bpy)], 2.4, from its $^1$H NMR spectrum, and is believed to form by reaction of [PtMeH(bpy)] with the solvent, chloroform.

The $^1$H NMR spectrum of the second product (Figure 2.1) displayed two pairs of quartet-doublet sets, one with much greater intensity than the other, leading us to believe there are two different insertion reaction products present.

![Figure 2.1](Image)

Figure 2.1. $^1$H NMR spectrum of complex 2.6 (o = 2.5).
A singlet peak at $\delta = 3.64$ ppm was observed and can be assigned to the methyl of the ester group of the newly formed insertion product. Analyzing the $^1$H NMR spectrum, we have been able to identify two of the ligands of the product:

![Figure 2.2. Probable insertion product, complex 2.5/2.6.](image)

The ligand X could not be identified using $^1$H NMR spectroscopy and other techniques were employed. Firstly, a mass spectrum of the mixture was obtained, observing the base peak at m/z = 438.1 amu corresponding to the coordinatively unsaturated [Pt(CHMeCO$_2$Me)(bpy)]$^+$, reinforcing our earlier predictions of the methyl acrylate inserting into the platinum-hydride bond, but with no resolution of the X ligand. The $^{19}$F NMR spectrum displayed a singlet at $\delta = -74.19$ ppm corresponding to a coordinated trifluoroacetate, $\text{O}_2\text{CCF}_3$, ligand. Finally, due to the production of [PtMeCl(bpy)], we proposed the possibility of a chlorine atom binding with platinum, as it is a much better ligand than trifluoroacetate. In order to study our prediction, the complex mixture was stirred with lithium chloride in acetone for a few minutes. The resulting $^1$H NMR spectrum was compared with the previous, showing an increase in the major product and a decrease in the minor product. Therefore, the products can be proposed as:

![Figure 2.3. Insertion products, complexes 2.6 and 2.5.](image)

In both products, chirality can be found at the carbon directly bound to the platinum centre. For tetrahedral chiral centres, R/S configuration is assigned due to the handedness of the centre.
2.2.3 Reaction in Benzene

The use of chlorinated solvents for preparation and separation of the products was believed to be the source of a chlorine atom, which substituted the more labile ligand trifluoroacetate, \(-\text{O}_2\text{CCF}_3\), causing the yields to be low and unwanted side products, such as [PtMeCl(bpy)], to be formed. Therefore, the same reaction mentioned previously was conducted in benzene solution.

A \(^1\text{H}\) NMR spectrum obtained of the reaction mixture showed that the expected reaction did occur, as five sets of quartet-doublet pairs were present in their respective chemical shift regions. As before, the reaction mixture was separated using thin-layer chromatography. Only two bands eluted on the TLC plate, as most of the reaction mixture adsorbed to the silica plate. A \(^1\text{H}\) NMR spectrum was obtained for the first eluted product and shown in figure 2.4.

**Figure 2.4.** \(^1\text{H}\) NMR spectrum of complex 2.7 (Δ, o = isomers).

The aromatic region (δ = 9.6-7.6 ppm) displayed five distinct peaks. Two \(\text{H}^6\) resonances were resolved, but the corresponding \(\text{H}^3\), \(\text{H}^4\) and \(\text{H}^5\) resonances appeared as single multiplets, presumably due to degeneracy of the chemical shifts. Two singlets were
observed at $\delta = 3.53$ and 3.52 ppm, both in the chemical shift region characteristic of methyl protons of an ester functional group, indicating two compounds are present. Also, two quartets, in the expected region of $\delta = 3.50-3.30$ ppm, were observed. Finally, an apparent triplet at $\delta = 1.21$ ppm was found in the expected region of the expected doublets, with the appearance of no doublets. A gCOSY experiment was performed and it was determined that the two quartet resonances were coupled to the triplet. Thus, the resonance at $\delta = 1.21$ ppm was an apparent triplet, made of two coincidentally overlapping doublets. With this evidence from the $^1$H NMR spectrum, we hypothesized that we had produced the symmetrical complex 2.7:

![Figure 2.5. Complex 2.7, [Pt(CHMeCO$_2$Me)$_2$(bpy)]](image)

Again, in our proposed structure, chirality can be found at both carbon centres bound to the platinum centre. Thus, the compound can exist in 4 different isomeric forms: RR, RS, SS, and SR. Of the four isomers, there are two pairs of enantiomers, the racemic (RR/SS) and the meso (SR/RS) isomers. This mixture of isomers, racemic and meso, is what gives rise to the overlapping resonances in the $^1$H NMR spectrum. As observed in the spectrum, there is roughly a 1:1 mixture of the meso and rac isomers, indicating that the stereoselectivity of the second insertion reaction is almost independent of the stereochemistry of the first.

The next step in the characterization of complex 2.6 was the oxidative addition of methyl iodide. These platinum(IV) oxidative addition products could give us more insight into the structures of our products. In addition, platinum(IV) complexes tend to undergo crystal growth more readily.

2.2.4 Oxidative Addition of MeI

The reaction of complex 2.6 with MeI proceeds as shown in scheme 2.10. The $^1$H NMR spectrum of 2.8 displays the expected peaks for the oxidative addition, along with
complementary peaks. The expected methyl platinum peak is observed at $\delta = 2.29$ ppm [$^{2}J(\text{PtH}) = 69$ Hz], with another methyl platinum peak at $\delta = 2.44$ ppm [$^{2}J(\text{PtH}) = 69$ Hz]. This is also the case with the quartets, one at $\delta = 3.52$ ppm and the other at $\delta = 3.33$ ppm, as well as the doublets, one at $\delta = 0.49$ ppm [$^{2}J(\text{PtH}) = 53$ Hz] and the other at $\delta = 0.45$ ppm [$^{2}J(\text{PtH}) = 48$ Hz].

![Scheme 2.10](image)

**Scheme 2.10.** Methyl iodide addition to complex 2.6, [Pt(CHMeCO$_{2}$Me)Cl(bpy)].

The proposed structure of the product 2.8 is consistent with the $^{1}$H NMR spectrum obtained and the complementary peaks are believed to arise from the chirality of the product, causing the presence of two isomers.

![Figure 2.6](image)

**Figure 2.6.** $^{1}$H NMR spectrum of complex 2.8, [PtMe(CHMeCO$_{2}$Me)Cl(I)(bpy)], (Δ, o = isomers).
The aforementioned chirality occurs at two centres in the newly formed platinum(IV) complex. As before, the carbon bound directly to the platinum centre shows chirality and can be designated by the R/S configuration used for tetrahedral centres. The second centre is the platinum atom itself. Now being a six-coordinate octahedral centre, the platinum is subject to the less common, but similar, C/A configuration. Therefore, there are four different isomers possible for this complex: RC, RA, SC, and SA. As shown in figure 2.7, the RC and SA isomers are enantiomers, as well as the RA and SC isomers are enantiomers. The two sets of enantiomers, RC/SA and RA/SC, is what gives rise to the separate resonances observed in the $^1$H NMR spectrum.

![Diagram of isomers](image)

**Figure 2.7. Isomers of complex 2.8.**

Crystals of 2.8 were grown by the slow diffusion of pentane into acetone and the X-ray crystal structure was solved (figure 2.8). The platinum atom displays the expected distorted octahedral geometry, with a methyl group and a chlorine atom $trans$ to the pyridyl group, and the iodine atom $trans$ to the propionic group, showing no significant difference in their Pt-C bond lengths (table 2.1). The single crystals were found to contain the SC/RA isomers. It is also noted that the stereochemistry of the methyl iodide oxidative addition is $cis$, whereas the $trans$ addition is more common. The observed stereochemistry is more stable because it places the bulky CHMe(CO$_2$Me) substituent in the axial position. The reaction probably occurs as shown below.
Scheme 2.11. Probable reaction of MeI addition to complex 2.6.

Table 2.1. Selected bond lengths [Å] and angles [°] for [PtMe(CHMeCO₂Me)ICl(bpy)], 2.8.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length/Angle</th>
<th>Bond</th>
<th>Length/Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(1)-C(15)</td>
<td>2.123(11)</td>
<td>Pt(1)-C(11)</td>
<td>2.132(13)</td>
</tr>
<tr>
<td>Pt(1)-N(1)</td>
<td>2.046(9)</td>
<td>Pt(1)-N(2)</td>
<td>2.160(10)</td>
</tr>
<tr>
<td>Pt(1)-I(1)</td>
<td>2.7284(11)</td>
<td>Pt(1)-Cl(1)</td>
<td>2.295(3)</td>
</tr>
<tr>
<td>C(15)-Pt(1)-C(11)</td>
<td>86.9(5)</td>
<td>C(15)-Pt(1)-N(1)</td>
<td>97.4(4)</td>
</tr>
<tr>
<td>C(15)-Pt(1)-N(2)</td>
<td>175.2(4)</td>
<td>C(11)-Pt(1)-N(1)</td>
<td>93.7(4)</td>
</tr>
<tr>
<td>C(11)-Pt(1)-N(2)</td>
<td>95.3(5)</td>
<td>C(15)-Pt(1)-I(1)</td>
<td>90.2(3)</td>
</tr>
<tr>
<td>C(11)-Pt(1)-I(1)</td>
<td>176.2(4)</td>
<td>C(11)-Pt(1)-Cl(1)</td>
<td>86.0(4)</td>
</tr>
<tr>
<td>C(15)-Pt(1)-Cl(1)</td>
<td>87.9(3)</td>
<td>I(1)-Pt(1)-N(1)</td>
<td>89.2(3)</td>
</tr>
<tr>
<td>I(1)-Pt(1)-N(2)</td>
<td>87.7(3)</td>
<td>Cl(1)-Pt(1)-N(1)</td>
<td>174.7(3)</td>
</tr>
<tr>
<td>Cl(1)-Pt(1)-N(2)</td>
<td>96.4(3)</td>
<td>N(1)-Pt(1)-N(2)</td>
<td>78.3(4)</td>
</tr>
<tr>
<td>Cl(1)-Pt(1)-I(1)</td>
<td>91.32(10)</td>
<td>C(13)-O(1)-C(14)</td>
<td>115.8(11)</td>
</tr>
</tbody>
</table>
Figure 2.8. Crystal Structure of 2.8. (a) Isomer shown: SC.
(b) Crystal lattice packing, isomers: SC and RA.
2.2.5 Reaction of DMAB with a platinum(II) biphosphine complex

The platinum(II) complexes with bidentate nitrogen donor ligands did not seem to produce the desired borane σ-complexes. Another attempt to isolate the σ-complex using DMAB as the substrate was the use of platinum(II) complexes with bidentate phosphorus ligands. It has been shown that phosphorus acts as a stronger acceptor than nitrogen, due to its larger and more diffuse orbitals. This greater accepting nature of the phosphorus ligand will hopefully stabilize the platinum(II) product.

To produce the first precursor, [PtMe₂(dmpe)], 2.9, a solution of 1,2-bis(dimethylphosphino)ethane in diethyl ether was added to the platinum dimer synthesized in situ. Complex 2.9 was isolated easily as a white solid and stored at room temperature. The ¹H NMR spectrum displayed the expected single methyl platinum resonance at δ = 0.32 ppm [²J(PtH) = 69 Hz, ³J(PH) = 9 Hz].

Next, the complex [PtMe(O₂CCF₃)(dmpe)], 2.10, was synthesized by the addition of trifluoroacetic acid to a solution of complex 2.9 in acetone at -78 °C. The solution of the platinum(IV) intermediate, [PtMe₂H(O₂CCF₃)(dmpe)], was then allowed to warm to room temperature resulting in the reductive elimination of methane resulting in the production of complex 2.10 as a white solid. The ¹H NMR spectrum displayed the expected methyl platinum resonance at δ = 0.29 ppm [²J(PtH) = 48 Hz, ³J(PH) = 8 Hz, ³J(PH) = 2 Hz]. Also diagnostic of the production of complex 2.10 is the two separate resonances of the methyl phosphorus groups at δ = 1.70 ppm [³J(PtH) = 52 Hz, ²J(PH) = 12 Hz] and δ = 1.59 ppm [³J(PtH) = 16 Hz, ²J(PH) = 10 Hz].

![Scheme 2.12. Production of complex 2.10, [PtMe(O₂CCF₃)(dmpe)].](image)

The reaction of complex 2.10 and dimethylamine-borane was a complicated one. Once mixed, the two clear solutions formed a green solution. The ¹H NMR spectrum of
the initial mixture showed the resonances of the precursor complex 2.10, as well as a set of new resonances, believed to be methyl platinum resonances, showing coupling to phosphorus and platinum. Once additional DMAB was added to react with the left over starting material, the $^1$H NMR spectrum observed no methyl platinum peaks, and the complexes are believed to degrade.

Indeed, once more than one equivalent of DMAB is added to a solution of complex 2.10, degradation occurs. Adding less than one equivalent was successful in producing the new methyl platinum resonances. These resonances were in a 1:1 intensity ratio and observed at $\delta = 2.72$ ppm [J(PtH) = 34 Hz, J(PH) = 6 Hz, J(PH) = 3 Hz] and $\delta = 0.37$ ppm [J(PtH) = 54 Hz, J(PH) = 7 Hz, J(PH) = 3.5 Hz]. In addition, no platinum-hydride resonance was observed for the reaction mixture. As well, a $^{31}$P NMR spectrum was obtained, but only resonances from complex 2.10 were resolved, as the complex was not concentrated, and thus the resonances were lost in the baseline. Separation and attempts at crystal growth were unsuccessful as the unknown complex degraded in solution.

**Figure 2.9.** $^1$H NMR spectrum of unknown peaks.
After many attempts to optimize the production of the unknown complex, we decided to alter our precursor by altering the bidentate phosphine ligand. Instead of the dmpe ligand, we chose the more bulky dppe ligand, in hopes of stabilizing a platinum(II) product via the greater steric effects of the phenyl groups.

The precursor $[\text{PtMe}_2(\text{dppe})]$, 2.11, was produced when a solution of dppe was added to a solution of platinum dimer, both in benzene, in which the product precipitated out as a white solid. The $^1\text{H}$ NMR spectrum of complex 2.11 contained the expected methyl platinum resonance showing the coupling to both platinum and phosphorus at $\delta = 0.73$ ppm [$^2J(\text{PtH}) = 70$ Hz, $^3J(\text{PH}) = 7$ Hz].

To introduce a labile ligand into complex 2.11, trifluoroacetic acid was used, as described in scheme 2.13. The expected mono-substituted $[\text{PtMe(O}_2\text{CCF}_3)(\text{dppe})]$ was not observed, as the trifluoroacetic acid was added in excess. Instead, the di-substituted $[\text{Pt(O}_2\text{CCF}_3)_2(\text{dppe})]$, 2.12, was observed. The $^1\text{H}$ NMR spectrum of the product contained the expected single multiplet at $\delta = 2.73$ ppm corresponding to the PCH$_2$ groups, with no observable methyl platinum peaks. The $^{31}\text{P}$ NMR spectrum observed a singlet at $\delta = 33.09$ ppm [$^1J(\text{PtP}) = 3840$ Hz]. The presence of only one signal corresponding to PCH$_2$ groups, as well as one observable $^{31}\text{P}$ resonance, is evidence of a symmetrical Pt(II) complex. The platinum-phosphorus coupling constant of 3840 Hz is common for phosphorus atoms trans to an electron withdrawing group, such as a trifluoroacetate group.

Adding one equivalent of dimethylamine-borane to one equivalent of complex 2.12 afforded a translucent brown solution. The $^1\text{H}$ NMR spectrum observed the resonances of the starting material, complex 2.12, as well as new resonances
corresponding to a new compound, in an approximate 1:1 intensity ratio. An additional equivalent of DMAB was added to complete the reaction, and the $^1$H NMR spectrum only contained the signals of the newly synthesized complex.

Firstly, a platinum-hydride signal was observed at $\delta = -2.52$ ppm [quintet, $^1J$(PtH) = 497 Hz, $^2J$(PH) = 41 Hz]. This resonance appears as a quintet due to the coupling to four phosphorus atoms. As well, the platinum satellites display a 1:8:18:8:1 multiplet, unique to a [Pt$_2$(μ-H)] group.

![Figure 2.10. $^1$H NMR platinum-hydride resonance, complex 2.13.](image)

Secondly, one signal was observed as a multiplet for the PCH$_2$ group at $\delta = 2.67$ ppm. As well, the $^{31}$P NMR spectrum only contains one resonance at $\delta = 60.73$ ppm [s, $^1J$(PtP) = 2918 Hz, $^3J$(PtP) = 168 Hz]. The presence of only one signal for the PCH$_2$ groups in the $^1$H NMR spectrum and only one signal in the $^{31}$P NMR spectrum points to a symmetrical [Pt$_2$(μ-H)$_2$] complex. As well, the $^{31}$P NMR spectrum displays two coupling constants to platinum of different magnitude, suggesting a one-bond coupling [$^1J$(PtP) = 2918 Hz] and a three-bond coupling [$^3J$(PtP) = 168 Hz]. Finally, the mass spectrum of the reaction observed a base peak at m/z = 1189.2 amu, corresponding to the platinum-
hydride dimer, complex 2.13. Thus, we can propose that we have synthesized the platinum-hydride dimer, [Pt₂(µ-H)₂(dppe)]²⁺, 2.13.

![Scheme 2.14](image)

**Scheme 2.14.** Production of platinum dimer, [Pt₂(µ-H)₂(dppe)]²⁺, 2.13.

Complex 2.13 has been previously synthesized by Pidcock *et al.* They were able to quantitatively produce [Pt₂(µ-H)₂(dppe)]²⁺ from the treatment of [PtCl₂(dppe)] with LiBEt₃H at -40 °C, producing [PtH₂(dppe)] as an intermediate, as 2.13 is produced upon warming to room temperature. Their ¹H NMR data reported is similar to that obtained in our research, although there are slight differences in the chemical shifts and coupling constants. This is possibly due to the different solvents and temperatures used in either experiment, as well as the different anion found for each complex.

### 2.3 CONCLUSIONS

The platinum(II) complex, [PtMe(O₂CCF₃)(bpy)], 2.2, was not able to arrest the σ-borane complex. Indeed, what did occur was a ‘B-H activation’, leading to the platinum-hydride complex, 2.3, which, in turn, reductively eliminated methane and degraded to platinum(0) and free bipyridine. The platinum-hydride of complex 2.3 was able to be trapped via the addition of a substituted olefin, methyl acrylate, as the methyl platinum group was again lost, by reductive elimination of methane, possibly due to another hydride abstraction. Two new platinum complexes, 2.6 and 2.7, were synthesized, depending on the solvent, in low yields due to separation and unwanted byproducts.

The oxidative addition of MeI to complex 2.6 resulted in the expected platinum(IV) complex, [PtMe(CHMeCO₂Me)Cl(I)(bpy)], 2.8, which is air stable.
As well, the platinum(II) complex, [PtMe(O₂CCF₃)(dmpe)], 2.10, was not capable of arresting the σ-borane complex. The unknown complex produced in the reaction of DMAB and complex 2.10 was not structurally characterized, as the solution degraded quickly. Furthermore, the platinum(II) complex, [Pt(O₂CCF₃)₂(dppe)], 2.12, was unable to arrest the σ-borane complex, as well. The reaction with DMAB yielded the platinum(II) dimer, [Pt(µ-H)(dppe)]₂[O₂CCF₃]₂, 2.13, almost quantitatively. Evidently, no claims for the isolation of a σ-complex using these systems can be made.

2.4 EXPERIMENTAL

General: All reactions were carried out under nitrogen, either using Schlenk techniques or in a dry box, unless otherwise specified. NMR spectra were recorded on Varian Mercury 400 MHz, Varian Inova 400 MHz and 600 MHz. Chemical shifts for ¹H and ¹⁹F are reported in ppm using the residual solvent nuclei as references. Solvents were dried using a Pure Solv™ solvent purification system and distilled under nitrogen before use. All other reagents were used as received with no further purification. The platinum dimer, [Pt₂Me₄(µ-SMe₂)]²² was prepared according to the literature. The proton resonances of the pyridyl groups were assigned according to chart 2.1. TLC was carried out on pre-coated analytical TLC plates of 250 µm thickness and 6 nm pore size silica gel support with short-wave UV light (254 nm) to visualize the spots and bands on the TLC plates. X-ray data were obtained and the solution was determined by Benjamin Cooper in this chapter. A suitable crystal was mounted on a glass fiber and data was collected at low temperature 150(2) K on the Bruker Smart Apex II CCD detector. The unit cell parameters were calculated and refined from the full data set. The crystal data and refinement parameters are listed in table 2.2.

![Chart 2.1. Pyridyl](chart2.1.png)
[PtMe₂(bpy)], 2.1: Complex 2.1 was prepared according to literature, with the ¹H NMR data in full agreement with those reported.²³

[PtMe(O₂CCF₃)(bpy)], 2.2: Complex 2.2 was prepared according to literature, with the ¹H NMR data in full agreement with those reported.²⁴

Degradation Reaction: Dimethylamine-borane complex (2.5 mg, 0.042 mmol) in CDCl₃ (1 mL) was added to a solution of [PtMe(O₂CCF₃)(bpy)], 2.2 (20 mg, 0.042 mmol) in CDCl₃ (2 mL). The yellow solution was allowed to stir for 24 hours. A black precipitate was formed. Due to overlap, the pyridyl resonances were not assigned to specific compounds. NMR (CDCl₃): Platinum-Hydride Intermediate, 2.3: δ (¹H) = 0.98 [s, 3H, ²J(PtH) = 80 Hz, Pt-Me]; -16.50 [s, 1H, ¹J(PtH) = 1546 Hz, Pt-H]. CH₄: δ (¹H) = 0.20 [s, 4H, CH₄].

[PtMeCl(bpy)], 2.4 and [PtCl(CHMeCO₂Me)(bpy)], 2.6: A solution of methylacrylate (4 µL, 0.042 mmol) in CHCl₃ (2 mL) was added to a solution of [PtMe(O₂CCF₃)(bpy)], 2.2, (20 mg, 0.042 mmol) in CHCl₃ (10 mL). With stirring, a solution of DMAB (2 mg, 0.042 mmol) in CHCl₃ (2 mL) was added to the reaction mixture. The reaction was stirred for 24 hours and the solvent was removed in vacuo. The reaction mixture, dissolved in minimal CHCl₃, was spotted on a TLC plate and run in an eluent of MeOH:DCM at a ratio of 2:98. Yield: 2.4 = 3 mg, 18 %. 2.6 = 1.8 mg, 9 %. NMR (CDCl₃): [PtMeCl(bpy)] δ (¹H) = 9.69 [dd, 1H, 3J(H⁶H⁵) = 5 Hz, ⁴J(H⁶H⁴) = 1.75 Hz, ³J(PtH) = ca. 12 Hz, H⁶]; 9.27 [dd, 1H, ³J(H⁶H⁵) = 6 Hz, ⁴J(H⁶H⁴) = 1 Hz, ³J(PtH) = 59 Hz, H⁶]; 8.17 [ddd, 1H, ³J(H⁵H⁴) = 8 Hz, ³J(H⁴H³) = 8 Hz, ⁴J(H⁶H⁴) = 1 Hz, H⁴]; 8.12 [ddd, 1H, ³J(H⁵H⁴) = 8 Hz, ³J(H⁴H³) = 8 Hz, ⁴J(H⁶H⁴) = 1.75 Hz, H⁴]; 8.03 [dd, 1H, ³J(H⁴H³) = 0.5 Hz, H³]; 7.67 [ddd, 1H, ³J(H⁴H³) = 5 Hz, ³J(H⁵H⁴) = 8 Hz, ⁴J(H⁶H⁴) = 0.5 Hz, H⁵]; 7.49 [ddd, 1H, ³J(H⁶H⁵) = 6 Hz, ³J(H⁵H⁴) = 8 Hz, ⁴J(H⁶H⁴) = 0.7 Hz, H⁵³]; 1.26 [s, 3H, ²J(PtH) = 77 Hz, Pt-Me]. [PtCl(CHMeCO₂Me)(bpy)] δ (¹H) = 9.77 [dd, 1H, ³J(H⁶H⁵) = 6 Hz, ⁴J(H⁶H⁴) = 1 Hz, H⁶]; 9.70 [dd, 1H, ³J(H⁶H⁵) = 5 Hz, ⁴J(H⁶H⁴) = 1 Hz, H⁶]; 8.17 [ddd, 1H, ³J(H⁵H⁴) = 8 Hz, ³J(H⁴H³) = 8 Hz, ⁴J(H⁶H⁴) = 1 Hz, H⁴]; 8.10 [ddd, 1H, ³J(H⁵H⁴) = 8 Hz, ³J(H⁴H³) = 7 Hz, ⁴J(H⁶H⁴) = 1 Hz, H⁴]; 8.03 [dd, 1H,
\(3J(H^H H^3) = 8 \text{ Hz}, \ 4J(H^5 H^3) = 1 \text{ Hz}, H^3] \); 8.01 [dd, 1H, \(3J(H^H H^3) = 7 \text{ Hz}, \ 4J(H^3 H^5) = 1 \text{ Hz}, H^3] \); 7.62 [ddd, 1H, \(3J(H^6 H^5) = 6 \text{ Hz}, \ 4J(H^H H^3) = 8 \text{ Hz}, H^3] \); 7.59 [ddd, 1H, \(3J(H^H H^5) = 5 \text{ Hz}, \ 3J(H^5 H^4) = 8 \text{ Hz}, \ 4J(H^5 H^3) = 1 \text{ Hz}, H^5] \); 4.10 [q, 1H, \(3J(H^a H^b) = 8 \text{ Hz}, Pt-C-H]; 3.64 [s, 3H, -CO_2Me]; 1.25 [d, 3H, \(3J(H^a H^b) = 7 \text{ Hz}, Pt-C-Me]. ESI-MS: m/z = 438.1 \text{ amu. Calc. for } [Pt(CHMeCO_2Me)(bpy)]^+ = 438.36 \text{ amu.}"

\[\text{Pt(CHMeCO_2Me)}_2(bpy), 2.7: \] A solution of methyl acrylate (4 \(\mu\text{L}, 0.042 \text{ mmol}) in C_6H_6 (2 mL) was added to a solution of [PtMe(O_2CCF_3)(bpy)], 2.2 (20 mg, 0.042 mmol) in C_6H_6 (10 mL). With stirring, a solution of DMAB (2 mg, 0.042 mmol) in C_6H_6 (2 mL) was added to the reaction mixture. The reaction was stirred for 2 hours and then concentrated in vacuo. The reaction mixture was spotted on a TLC plate and run in an eluent of MeOH:C_6H_6 at a ratio of 10:90. Yield = 3 mg, 14 %. NMR (CD_3OD): Isomer 1: \(\delta (^1H) = 9.53 \text{ [dd, 2H, } 3J(H^H H^5) = 6 \text{ Hz}, \ 4J(H^H H^3) = 1 \text{ Hz, } H^6]; 8.41 \text{ [dd, 2H, } 3J(H^H H^3) = 8 \text{ Hz}, \ 4J(H^H H^3) = 1 \text{ Hz, } H^3] \); 8.26 [ddd, 2H, \(3J(H^H H^3) = 6 \text{ Hz}, \ 3J(H^5 H^4) = 8 \text{ Hz}, \ 4J(H^5 H^3) = 1 \text{ Hz, } H^5] \); 1.21 [d, 6H, \(3J(H^H H^b) = 7 \text{ Hz, Pt-C-Me}]. Isomer 2: \(\delta (^1H) = 9.47 \text{ [dd, 2H, } 3J(H^H H^5) = 6 \text{ Hz}, \ 4J(H^H H^3) = 1 \text{ Hz, } H^6]; 8.41 \text{ [dd, 2H, } 3J(H^H H^3) = 8 \text{ Hz}, \ 4J(H^H H^3) = 1 \text{ Hz, } H^3] \); 8.26 [ddd, 2H, \(3J(H^H H^5) = 6 \text{ Hz}, \ 3J(H^H H^4) = 8 \text{ Hz}, \ 4J(H^H H^3) = 1 \text{ Hz, } H^5] \); 3.52 [s, 6H, -CO_2Me]; 3.43 [q, 2H, \(3J(H^a H^b) = 7 \text{ Hz, Pt-C-Me}].

\[\text{PtCl(I)Me(CHMeCO_2Me)(bpy), 2.8: } \] To a solution of [PtCl(CHMeCO_2Me)(bpy)], 2.6 (5 mg, 0.009 mmol) in acetone (3 mL) was added MeI (1.3 mg, 0.009 mmol) and stirred for 2.5 hours. The solvent was removed in vacuo to leave a yellow solid. Yield = 4 mg, 70 %. NMR (CDCl_3): Isomer 1: \(\delta (^1H) = 9.56 \text{ [dd, 1H, } 3J(H^H H^5) = 5 \text{ Hz}, \ 4J(H^H H^4) = 1 \text{ Hz, } 3J(PtH) = \text{ ca. } 9 \text{ Hz, } H^6]; 8.92 \text{ [dd, 1H, } 3J(H^6 H^5) = 6 \text{ Hz, } 4J(H^6 H^4) = 1 \text{ Hz, } 3J(PtH) = 39 \text{ Hz, } H^6] \); 8.5-7.3 [mult., 6H, \(H^5/H^5'-H^3/H^3'] \); 3.53 [q, 1H, \(3J(H^H H^b) = 7 \text{ Hz, Pt-C-H}]; 3.00 [s, 3H, -CO_2Me]; 2.44 [s, 3H, \(2J(PtH) = 67 \text{ Hz, Pt-Me, trans to iodide}]; 0.50 [d, 3H, \(3J(H^H H^b) = 7 \text{ Hz, } 3J(PtH) = 53 \text{ Hz, Pt-C-Me}]. Isomer 2: \(\delta (^1H) = 9.52 \text{ [dd, 1H, } 3J(H^H H^5) = 5 \text{ Hz, } 4J(H^H H^4) = 1 \text{ Hz, } 3J(PtH) = \text{ ca. } 9 \text{ Hz, } H^6]; 8.82 \text{ [dd, 1H, } 3J(H^6 H^5) = 6 \text{ Hz, } 4J(H^6 H^4) = 1 \text{ Hz, } 3J(PtH) = 39 \text{ Hz, } H^6] \); 8.50-7.30 [mult., 6H, \(H^5/H^5'-H^3/H^3'] \); 3.34 [q, 1H, \(3J(H^H H^b) = 7 \text{ Hz, Pt-C-H}]; 2.88 [s, 3H, -CO_2Me]; 2.29 [s, 3H, \(2J(PtH) = 70 \text{ Hz, Pt-Me, trans to iodide}]; 0.46 [d, 3H, \(3J(H^H H^b) = 7 \text{ Hz, } 3J(PtH) = 47 \text{ Hz, Pt-C-Me}].
[PtMe₂(dmpe)], 2.9: Complex 2.9 was prepared according to literature, with the \(^1\)H NMR data in full agreement to those reported.\(^{25}\)

[PtMe(O\(_2\)CCF\(_3\))(dmpe)], 2.10: Complex 2.10 was prepared according to literature, with the \(^1\)H NMR data in full agreement to those reported.\(^{25}\)

**Reaction of complex 2.10 and DMAB:** A solution of DMAB (3 mg, 0.045 mmol) in acetone-\(d_6\) (0.5 mL) was added to a solution of complex 2.10 (20 mg, 0.045 mmol) in acetone-\(d_6\) (1 mL). The solution turned a deep green colour after 10 minutes of stirring. The green solution would then degrade after ca. 2 days to a brown solution. NMR (acetone-\(d_6\)): Unknown complex: δ (\(^1\)H) = 2.72 [dd, \(J\)(PtH) = 34 Hz, \(J\)(PH) = 6 Hz, \(J\)(PH) = 3 Hz]; 0.37 [dd, \(J\)(PtH) = 54 Hz, \(J\)(PH) = 7 Hz, \(J\)(PH) = 4 Hz].

[PtMe₂(dppe)], 2.11: Complex 2.11 was prepared according to literature, with the \(^1\)H NMR data in full agreement with those reported.\(^{26}\)

[Pt(O\(_2\)CCF\(_3\))\(_2\)(dppe)], 2.12: To a solution of complex 2.11 (80 mg, 0.128 mmol) stirring in acetone (10 mL) was added trifluoroacetic acid (20 \(\mu\)L, 0.256 mmol) at -78 °C. Once the acid was added, the mixture was warmed to room temperature. The solvent was removed in vacuo and the off-white solid was washed with ether (2 x 5 mL). The product, 2.9, was fully dried under vacuum and stored at room temperature. Yield = 85 mg, 83 %. NMR (acetone-\(d_6\)): δ (\(^1\)H) = 7.96 [m, phenyl]; 7.64 [m, phenyl]; 7.57 [m, phenyl]; 2.71 [m, 4H, PCH\(_2\)]. δ (\(^{31}\)P) = 33.09 [s, \(^1\)J(PtP) = 3840 Hz]. δ (\(^{19}\)F) = -69.90 [s, O\(_2\)CCF\(_3\)].

[Pt(\(\mu\)-H)(dppe)]\(_2\)[O\(_2\)CCF\(_3\)]\(_2\), 2.13: To a solution of complex 2.12 (14 mg, 0.017 mmol) in acetone-\(d_6\) (1 mL) was added a solution of DMAB (2 mg, 0.0342 mmol) in acetone-\(d_6\) (0.5 mL) with stirring. The two clear solutions, once mixed, formed a translucent brown mixture. Yield = 19 mg, 94 %. NMR (acetone-\(d_6\)): δ (\(^1\)H) = 7.88 [m, 8H, phenyl]; 7.50 [m, 4H, phenyl]; 7.43 [m, 8H, phenyl]; 2.67 [m, 8H, PCH\(_2\)]; -2.52 [quintet, 2H, \(^1\)J(PtH) = 497 Hz, \(^2\)J(PH) = 41 Hz, Pt-H-Pt]. δ (\(^{31}\)P) = 60.73 [s, \(^1\)J(PtP) = 2918 Hz, \(^3\)J(PtP) = 168 Hz]. ESI-MS: m/z = 1189.22 amu; Calc. for [2.13-H]\(^+\) = 1189.22 amu.
Table 2.2. Crystal data and structure refinement for [PtMe(CHMeCO₂Me)Cl(I)(bpy)], 2.8.

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2.5 REFERENCES


CHAPTER 3

REACTIONS OF PLATINUM(IV) COMPLEXES WITH

DIMETHYLAMINE-BORANE
3.1 INTRODUCTION

As the need for renewable energy sources elevates, the need for the understanding of the production of these sources also rises. Whether it be the manipulation of hydrocarbons or the source of hydrogen storage materials, an understanding of the mechanistic chemistry is essential to an optimized, practical method.

C-H bond activation has been a topic of intense research for many decades, beginning with the work by Shilov.\(^1\) There has been much debate as to how C-H bond activation occurs mechanistically, and more importantly, how the alkane coordinates. As a result, there have been a number of publications\(^2\) concerning the isolation of a \(\sigma\)-alkane complex, to provide information of the interaction of the alkane and the catalyst. The most influential work was produced by Brookhart, Goldberg et.al.\(^2(e)\) In 2009, they published the results of a direct protonation of a methyl rhodium precursor, resulting in the production of a \(\sigma\)-methane complex in solution. They were able to fully characterize the NMR spectra of the \(\sigma\)-methane complex, which was stable in solution.

![Scheme 3.1. \(\sigma\)-methane complex.]

Amine-boranes have received a great amount of attention, as well. This is due to their ability as hydrogen storage materials\(^3\), as well as their analogous nature (isosteric/isoelectronic) to that of simple alkanes.\(^4\) In fact, due to the recent research of catalytic dehydrocoupling of amine-boranes\(^4\), there have been numerous isolations of \(\sigma\)-borane complexes.\(^5\) One example is the work performed by Hall et al., who were able to isolate a \(\sigma\)-borane complex of trimethylamine-borane and a rhodium complex, as an intermediate for catalytic dehydrogenation.\(^5(d)\)
Scheme 3.2. Isolation of a \( \sigma\)-B-H complex of trimethylamine-borane.

A second example of the isolation of a \( \sigma\) - borane complex is the terrific work by Aldridge et al. Of the numerous complexes synthesized, they were able to isolate a \( \sigma\) - borane complex of rhodium with the amine-borane derivative \( \text{tBuH}_2\text{N} \cdot \text{BH}_3 \).\(^{5(b)}\)

Scheme 3.3. Isolation of a \( \sigma\)-borane complex.

As can be noted from these examples, a more bulky (steric) complex seems to arrest these \( \sigma\)-borane and \( \sigma\) - alkane complexes. As mentioned in the previous chapter, there has yet to be an example of a \( \sigma\) - borane or a \( \sigma\) - alkane complex of platinum. In this chapter, the more bulky platinum(IV) complexes will be utilized in an attempt to isolate a \( \sigma\)-borane complex, as a model study of C-H bond activation.

Scheme 3.4. Platinum(IV) \( \sigma\) - borane attempt.
3.2 RESULTS AND DISCUSSION

3.2.1 Reaction of Pt(IV) with DMAB

The platinum(IV) precursor, \textit{fac}-[PtMe_3(OTf)(bpy)] (3.1), was prepared by the addition of methyl triflate to the dimethyl platinum, [PtMe_2(bpy)] (2.1), under an inert atmosphere of nitrogen. Complex 3.1 was isolated as a pure white solid and stored at room temperature. The $^1$H NMR spectrum displayed the two methyl platinum peaks in a 2:1 ratio, with $\delta = 1.29$ ppm [$^2J$(PtH) = 67 Hz] and a broader peak at $\delta = 0.75$ ppm [$^2J$(PtH) = 78 Hz].

\begin{center}
\textbf{Scheme 3.5.} MeOTf addition to complex 2.1.
\end{center}

The reaction of complex 3.1 with dimethylamine-borane is believed to proceed as shown in scheme 3.6. The $^1$H NMR spectrum obtained of the reaction mixture displays a large amount of information pertaining to the products produced throughout this reaction. Two main products were formed and will thus be discussed separately.

\begin{center}
\textbf{Scheme 3.6.} Addition of DMAB to complex 3.1.
\end{center}

The $^1$H NMR spectrum of the first product, complex 3.2, shows the expected four aromatic resonances due to the two equivalent pyridine moieties of the bipyridine ligand.
These data rule out the alternative isomer with the $\mu$-H \textit{trans} to nitrogen, which would display non-equivalent pyridyl groups. The two expected methyl platinum groups were in a 2:1 intensity ratio due to the methyl platinum groups \textit{trans} to (bpy) at $\delta = 0.88$ ppm [$^2J(\text{PtH}) = 70$ Hz] and \textit{trans} to the hydride at $\delta = 0.13$ ppm [$^2J(\text{PtH}) = 65$ Hz], respectively. Both methyl platinum groups showed a small coupling ($<1.5$ Hz) to the bridging hydrido ligand. The greatest evidence for a bridging hydrido ligand is found in the low-frequency Pt-H resonance at $\delta = -11.72$ ppm [$^1J(\text{PtH}) = 447$ Hz]. This resonance appears as an 1:8:18:8:1 multiplet (figure 3.1), due to the coupling to the $^{195}$Pt atoms, thus proving the presence of a [Pt$_2$(\mu-H)] group.

![Figure 3.1. Pt-H-Pt $^1$H NMR resonance of complex 3.2.](image)

The production of complex 3.2 occurs through a proposed two step process. Firstly, as mentioned in the previous chapter, a ‘B-H activation’ step occurs, forming the [PtMe$_3$(bpy)] intermediate. Second, the hydride then acts to replace the labile triflate of the second equivalent of the platinum complex. This is due to the fact the hydride is \textit{trans} to a methyl group, causing the hydride to be more electron rich, which allows for it to displace the triflate ligand easily, forming the dimer [Pt$_2$Me$_6$(\mu-H)(bpy)$_2$][O$_2$CCF$_3$], 3.2.

The $^1$H NMR spectrum of the second product, complex 3.3, displays the expected pair of methyl resonances, with relative peak intensities of 2:1 at $\delta = 1.08$ ppm [$^2J(\text{PtH}) = 67$ Hz, \textit{trans} pyridyl] and 0.35 ppm [$^2J(\text{PtH}) = 69$ Hz, \textit{trans} amine]. As can be seen from
the coupling constants, there is no significant difference in the trans influence of the pyridyl and amine groups, thus the relative peak intensities (integrals) are used to assign the NMR resonances. A second distinctive, and expected, feature of the $^1$H NMR spectrum is the methyl group of the dimethylamine ligand observed at $\delta = 2.06$ ppm [$^3J($PtH$) = 13$ Hz], as well as the expected amine proton as a broad singlet at $\delta = 3.12$ ppm.

As mentioned in the previous chapter, due to the ‘B-H activation’ step, the amine-borane complex seems to dissociate into an amine group, NHMe$_2$, and a borane group, BX$_3$ (X = H, O$_2$CCF$_3$, OTf). With the dimethylamine group in solution, it is able to replace the labile triflate group, forming the complex 3.3.

The mass spectrum of the product mixture displayed the base peak of m/z = 440.1 amu for complex 3.3, as well as a peak at m/z = 793.2 amu which pertains to complex 3.2.

In an attempt to further characterize our product, a reaction was attempted to directly synthesize complex 3.3 (scheme 3.7). Beginning with the platinum(IV) precursor, fac-[PtMe$_3$(OTf)(bpy)] (3.1), a solution of dimethylamine in THF (2.0 M) was added, causing displacement of the labile triflate ligand. As expected the $^1$H NMR spectrum of this product is identical with that formed according to scheme 3.6.

![Scheme 3.7](image)

**Scheme 3.7.** Direct production of complex 3.3.

A paper published by the Puddephatt group in 1996 describes the synthesis of a similar µ-H platinum(IV) complex. Using sodium borohydride with the fac-[PtMe$_3$(OTf)(bpy$_2$)] complex, they were able to synthesize and characterize the Pt$_2$(µ-
H) complex.\(^6\) The resonances observed in the \(^1\)H NMR spectrum of this complex are very near to those of our proposed product, complex 3.2.

Replacing the bpy ligand in our original design, we attempted the same reaction with the bu\(_2\)bpy ligand. We first prepared the dimethyl platinum(II) precursor by the addition of bu\(_2\)bpy to the platinum dimer. The platinum(II) complex was crystallized from the Et\(_2\)O/toluene mixture as a stable, orange solid. The \(^1\)H NMR spectrum displayed the expected methyl platinum resonance at \(\delta = 0.92\) ppm \([\text{\(^2\)}J(\text{PtH}) = 86\) Hz] and the \textit{tert}-butyl resonance at \(\delta = 1.44\) ppm.

Again, to prepare the platinum(IV) precursor, methyl triflate was added to [PtMe\(_2\)(bu\(_2\)bpy)]. \(fac\)-[PtMe\(_3\)(OTf)(bu\(_2\)bpy)], 3.4, was isolated easily as a pale orange solid, that is air-stable. The \(^1\)H NMR spectrum shows the expected \textit{tert}-butyl resonance at \(\delta = 2.80\) ppm, and the methyl platinum resonances in a 2:1 ratio at \(\delta = 1.25\) ppm \([\text{\(^2\)}J(\text{PtH}) = 65\) Hz] and \(\delta = 0.70\) ppm \([\text{\(^2\)}J(\text{PtH}) = 84\) Hz], respectively. As well, the three aromatic resonances were observed, proving a symmetrical platinum(IV) complex, and \textit{trans} addition of the MeOTf.

Treatment of \(fac\)-[PtMe\(_3\)(OTf)(bu\(_2\)bpy)] (3.4) with a stoichiometric amount of DMAB affords the two expected products: dimethylamine complex (3.6) and the \(\mu\)-H complex (3.5) (Scheme 3.8). The \(^1\)H NMR spectrum of the reaction mixture displays all the expected resonances, with an approximate ratio of 2:1 of complex 3.6 to 3.5, based on relative intensities. Firstly, complex 3.6 displays the expected methyl platinum resonances at \(\delta = 1.07\) ppm \([\text{\(^2\)}J(\text{PtH}) = 68\) Hz] and \(\delta = 0.31\) ppm \([\text{\(^2\)}J(\text{PtH}) = 69\) Hz], in a 2:1 ratio, respectively. The \textit{tert}-butyl resonance appears at \(\delta = 1.49\) ppm and the methyl amine resonance appears as a doublet at \(\delta = 2.10\) ppm \([\text{\(^3\)}J(\text{PtH}) = 14\) Hz]. The aromatic region displays three peaks that correspond to complex 3.5, proving an axial dimethyl amine ligand, as in the equatorial position would cause the pyridyl groups to be inequivalent.
The second product, complex 3.5, also displays all expected resonances in the $^1$H NMR spectrum, and agree with literature values. Three aromatic resonances and one tert-butyl resonance appear due to the equivalent pyridyl groups of the bu$_2$bpy ligand, proving a symmetrical complex. Two methyl platinum resonances were observed at $\delta = 0.79$ ppm [$^2J$(PtH) = 70 Hz, $trans$ pyridyl] and $\delta = 0.03$ ppm [$^2J$(PtH) = 65 Hz, $trans$ $\mu$-H], in a 2:1 intensity ratio, respectively. And the final resonance, the Pt-H resonance, is observed at $\delta = -11.80$ ppm [$^1J$(PtH) = 445 Hz]. Again, this resonance appears as a 1:8:18:8:1 multiplet, due to the coupling to the $^{195}$Pt atoms, proving the presence of a Pt$_2$(µ-H) group.

3.2.2 Attempts at the production of a platinum(IV) polymer

The production of the platinum(IV) dimer, complex 3.2, allowed us to envision the possibility of a platinum(IV) polymer. Due to the fact complex 3.2 resulted in a dimer, it was noted that there must be two sites in the platinum(IV) precursor where propagation can occur, resulting in the lengthening in two directions.

Firstly, the platinum(IV) precursor must be synthesized. The first precursor to be attempted was the bis-triflate platinum(IV) complex, [PtMe$_2$(OTf)$_2$(bpy)]. To begin, the dimethyl platinum(II) complex, 2.1, was subjected to one equivalent of iodine, I$_2$. The resulting product, [PtMe$_2$I$_2$(bpy)], 3.7, was recrystallized from dichloromethane as an air stable orange solid. The next step was the installation of the labile triflate groups, which was attempted by the addition of silver triflate with stirring to a solution of complex 3.7.
The $^1$H NMR spectrum of the resulting residue showed a platinum(II) complex (due to coupling constants of bipyridine hydrogens) with no methyl platinum resonances found. What is believed to have occurred is the reductive elimination of ethane. Due to the addition of the labile groups, dissociating easily to the 5-coordinate complex in solution, allowing for reductive elimination of ethane to occur more readily.

As a result of the previous attempt failing, the use of peroxides was envisioned to add both cis and trans to a platinum(II) complex, with the ligands being relatively labile. The peroxide chosen was dibenzoyl peroxide (BnO-OBn), a well known compound.

The production of the precursor, [PtMe$_2$(OBn)$_2$(bpy)], 3.8, was a straightforward one (Scheme 3.9). Dibenzoyl peroxide was added to a solution of complex 2.1 in an open atmosphere. The $^1$H NMR spectrum obtained observed the expected resonances, indicative of the oxidative addition of the peroxide bond across platinum. The spectrum observed both the cis-addition and trans-addition products, deduced by the methyl platinum resonances at $\delta = 1.46$ ppm [$^2J$(PtH) = 67 Hz] for the trans-addition complex, and at $\delta = 2.15$ ppm [$^2J$(PtH) = 67 Hz] and $\delta = 1.93$ ppm [$^2J$(PtH) = 68 Hz], for the cis-addition product. Based on the similarity of the coupling constants in the cis-addition product, the methyl platinum resonances could not be assigned to a specific methyl group.

![Scheme 3.9. Addition of dibenzoyl peroxide to complex 2.1.](image)

Complex 3.8 was treated with DMAB under an inert atmosphere of nitrogen and stirred in acetone. The $^1$H NMR spectrum did not contain any platinum-hydride peaks, although it did contain new methyl platinum resonances. However, the structure of the product could not be determined. The base peak of the mass spectrum was m/z = 502.1 amu, which is consistent with the 5-coordinate [PtMe$_2$(OBn)(bpy)]$^+$, which is believed to
result from the loss of a benzoate ligand. Thus, we were unable to characterize the new complex, and evidently the sought after platinum(IV) polymer would not arise from the reaction of DMAB and complex 3.8.

3.2.3 Reaction of a platinum(IV) phosphine complex with DMAB

Returning to the original scope of this research, we envisioned the possibility of using bidentate phosphine ligands to be more suitable for the isolation of the σ-borane complex. Used in the previous chapter, dmpe was the ligand of choice, allowing for the oxidative addition process of the platinum(II) species to the desired platinum(IV) precursor.

The platinum(IV) precursor [PtMe$_3$(OTf)(dmpe)], 3.9, was produced via the slow addition of methyl triflate to a solution of complex 2.6 in acetone at -78 °C. This precursor was kept at -78 °C, as when the solution warmed to room temperature, reductive elimination of ethane would occur, producing the unwanted byproduct [PtMe(OTf)(dmpe)].

Therefore, the intermediate 3.9 must be used in situ in the following reaction.

To a solution of complex 3.9 prepared in situ at -78 °C, was added a solution of DMAB. The reaction was then monitored via a variable temperature NMR experiment. Once the reaction mixture had reached room temperature, there was one main product observed in the $^1$H NMR spectrum. As shown in scheme 3.10, the main product produced from this reaction was the tetramethyl platinum(IV) complex 3.10. The $^1$H NMR spectrum contained the expected methyl platinum resonances, in a 1:1 intensity ratio, at $\delta = 0.23$ ppm [$^2J(\text{PtH}) = 57$ Hz, $^3J(\text{PH}) = 8$ Hz] and $\delta = -0.45$ ppm [$^2J(\text{PtH}) = 44$ Hz, $^3J(\text{PH}) = 6$ Hz]. Also diagnostic of the production of the tetramethyl species is the occurrence of only one resonance for the PCH$_3$ groups at $\delta = 1.32$ ppm.
To fully characterize the tetramethyl platinum(IV) complex produced in the previous reaction, we proceeded to synthesize it by other, more straightforward means. Firstly, to the precursor [PtMe₂(dmpe)], 2.6, was added a solution of methyl iodide and stirred for two hours. The oxidative addition product [PtMe₃I(dmpe)], 3.11, observed the expected methyl platinum resonances in the ¹H NMR spectrum at δ = 0.93 ppm [²J(PtH) = 57 Hz, ³J(PH) = 7.5 Hz] and δ = 0.81 ppm [²J(PtH) = 70 Hz, ³J(PH) = 7 Hz] in a 2:1 intensity ratio, respectively.

To a solution of the purified complex 3.11 was added one equivalent of methyl lithium. A ¹H NMR spectrum of the resulting mixture displayed the resonances of the [PtMe₃I(dmpe)] (3.11) precursor, as well as the expected resonances of the tetramethyl platinum(IV) complex, in an approximate 6:1 ratio, respectively. The methyl platinum resonances for the tetramethyl platinum(IV) product agrees with the ones previously recorded for the reaction of DMAB with [PtMe₃(OTf)(dmpe)].

3.3 CONCLUSIONS

The platinum(IV) complexes, [PtMe₃(OTf)(bpy)] (3.1) and [PtMe₃(OTf)(bu₂bpy)] (3.4), were unable to arrest the intermediate σ-borane complex, and therefore, it was unable to be isolated. These complexes, however, did react with dimethylamine-borane in an interesting way, forming the [Pt₂(µ-H)]⁺ complexes (3.2 and 3.5), as well as the dimethylamine complexes (3.3 and 3.6).

The next inquiry was the possibility of preparing a platinum(IV) polymer. The precursors, platinum(IV) complexes with two labile ligands, were difficult to prepare, as
reductive elimination of ethane occurred. One platinum(IV) precursor was prepared, complex 3.8, using dibenzoyl peroxide, which, after oxidative addition, installed two relatively labile ligands. Frustratingly, the reaction of complex 3.8 with DMAB did not proceed to the platinum(IV) polymer, and is therefore not a viable route.

Finally, the complex [PtMe₃(O Tf)(dmpe)], 3.9, was viewed as an option to arrest the σ-borane complex, but was unable to, as well. Again, interesting chemistry occurred during the reaction with DMAB, producing the tetramethyl platinum(IV) complex.

Indeed, the σ-borane complex was not isolated using the platinum(IV) complexes mentioned (3.1, 3.4 and 3.9), although some interesting chemistry did occur.

3.4 EXPERIMENTAL

**General:** All reactions were carried out under nitrogen, either using Schlenk techniques or in a dry box, unless otherwise specified. NMR spectra were recorded on Varian Mercury 400 MHz, Varian Inova 400 MHz and 600 MHz. Chemical shifts for 

\[ ^1H \] and \[ ^19F \] are reported in ppm using the residual solvent nuclei as references. Solvents were dried over sodium and benzophenone and distilled under nitrogen before use. All other reagents were used as received with no further purification. The platinum dimer, [Pt₂Me₄(μ-SMe₂)₂]₈ was prepared according to the literature. The proton resonances of the pyridyl groups were assigned according to chart 3.1.

![Chart 3.1. Pyridyl](attachment:chart_3_1.png)

**fac-[PtMe₃(O Tf)(bpy)], 3.1:** Methyl triflate (5.6 μL, 0.05 mmol) was added slowly to a suspension of [PtMe₂(bpy)], 2.1 (19 mg, 0.05 mmol) in benzene (10 mL). The reaction mixture was allowed to stir for 30 minutes. The clear solution was decanted off and the remaining white solid was washed with pentane (3 x 10 mL). The white solid was then
fully dried under vacuum. Yield: 25 mg, 93%. NMR (acetone-d$_6$): $\delta$ (1H) = 9.07 [br, 2H, pyr]; 8.82 [br, 2H, pyr]; 8.45 [br, 2H, pyr]; 8.00 [br, 2H, pyr]; 1.29 [s, 6H, $^2$J(PtH) = 67 Hz, Pt-Me, $trans$ pyr]; 0.75 [s, 3H, $^2$J(PtH) = 78 Hz, Pt-Me, $trans$ OTf].

[Pt$_2$Me$_6$(bpy)$_2$($\mu$-H)][OTf], 3.2, and $fac$-[PtMe$_3$(NHMe$_2$)(bpy)][OTf], 3.3: A solution of DMAB (1 mg, 0.018 mmol) in acetone (1 mL) was added to a solution of [PtMe$_3$(OTf)(bpy)]. 3.1 (10 mg, 0.018 mmol) in acetone (10 mL). The mixture was allowed to stir for 1 hour and the solvent was removed in vacuo. The remaining yellow oil was washed with pentane (3 x 2 mL) and fully dried under vacuum. Yield = 3.2 3 mg, 20%. 3.3 3.1 mg, 43 %. NMR (CD$_2$Cl$_2$): Complex 3.2 $\delta$(1H) = 8.22 [dd, 4H, $^3$J(H$^6$H$^5$) = 6 Hz, $^4$J(H$^6$H$^4$) = 1.2 Hz, $^3$J(PtH) = 13 Hz, H$^6$]; 8.13 [dd, 4H, $^3$J(H$^4$H$^3$) = 7 Hz, $^4$J(H$^4$H$^2$) = 1.6 Hz, H$^2$]; 8.10 [ddd, 4H, $^3$J(H$^4$H$^3$) = 7 Hz, $^3$J(H$^4$H$^3$) = 7 Hz, $^4$J(H$^4$H$^2$) = 1.2 Hz, H$^2$]; 7.46 [ddd, 4H, $^3$J(H$^4$H$^3$) = 6 Hz, $^3$J(H$^5$H$^4$) = 7 Hz, $^4$J(H$^5$H$^4$) = 1.6 Hz, H$^4$]; 0.88 [d, 12H, $^3$J(HH) = ca. 1 Hz, $^2$J(PtH) = 70 Hz, Pt-Me, $trans$ pyr]; 0.13 [d, 6H, $^3$J(HH) = ca. 1 Hz, $^2$J(PtH) = 65 Hz, Pt-Me, $trans$ H]; -11.72 [s, 1H, $^1$J(PtH) = 447 Hz, Pt-H]. Mass Spec. Calc’d = 793.75 amu. Found = 793.2 amu.

Complex 3.3 $\delta$ (1H) = 8.83 [dd, 2H, $^3$J(H$^6$H$^5$) = 6 Hz, $^4$J(H$^6$H$^4$) = 1.6 Hz, $^3$J(PtH) = 13 Hz, H$^6$]; 8.53 [dd, 2H, $^3$J(H$^4$H$^3$) = 8 Hz, $^4$J(H$^4$H$^2$) = 1.2 Hz, H$^2$]; 8.29 [ddd, 2H, $^3$J(H$^4$H$^3$) = 8 Hz, $^3$J(H$^5$H$^4$) = 8 Hz, $^4$J(H$^5$H$^4$) = 1.6 Hz, H$^4$]; 7.82 [ddd, 2H, $^3$J(H$^5$H$^4$) = 6 Hz, $^3$J(H$^5$H$^4$) = 6 Hz, $^4$J(H$^5$H$^4$) = 1.2 Hz, H$^4$]; 3.12 [br, 1H, Me$_2$NH]; 2.06 [d, 6H, $^3$J(HH) = 6 Hz, $^3$J(PtH) = 13 Hz, Me$_2$NH]; 1.08 [s, 6H, $^2$J(PtH) = 67 Hz, Pt-Me, $trans$ pyr]; 0.35 [s, 3H, $^2$J(PtH) = 69 Hz, Pt-Me, $trans$ amine]. Mass Spec. Calc’d = 440.45 amu. Found = 440.1 amu.

$fac$-[PtMe$_3$(OTf)(bu$_2$bpy)], 3.4: Methyl triflate (10 $\mu$L, 0.08 mmol) was added to a suspension of [PtMe$_2$(bu$_2$bpy)], 3.4 (40 mg, 0.08 mmol) in benzene (20 mL). The reaction was allowed to stir for 30 minutes. The clear solution was decanted off and the pale orange solid was washed with pentane (3 x 10 mL). The product was dried fully under vacuum. Yield: 45 mg, 86 %. NMR (acetone-d$_6$): $\delta$ (1H) = 8.95 [br, 2H, H$^6$]; 8.84 [br, 2H, H$^3$]; 7.99 [br, 2H, H$^3$]; 2.80 [s, 18 H, tert-butyl]; 1.25 [s, 6H, $^2$J(PtH) = 67 Hz, Pt-Me, $trans$ pyr]; 0.66 [s, 3H, $^2$J(PtH) = 84 Hz, Pt-Me, $trans$ OTf].
fac-[PtMe₃(NHMe₂)(bu₂bpy)], 3.6, and [Pt₂Me₆(bu₂bpy)₂(μ-H)], 3.5: A solution of DMAB (1 mg, 0.015 mmol) in acetone-d₆ (0.5 mL) was added to a solution of [PtMe₃(OTf)(bu₂bpy)], 3.4 (10 mg, 0.015 mmol) in acetone-d₆ (1 mL). The mixture was allowed to stir for 1 hour and the solvent was removed in vacuo. The remaining yellow oil was washed with pentane and fully dried under vacuum. Yield = 3.6 3 mg, 41 %. 3.5 1.8 mg, 12 %. NMR (acetone-d₆): Complex 3.6 δ (¹H) = 8.93 [d, 2H, ³J(H⁶H⁵) = 5.6 Hz, ³J(PtH) = 12 Hz, H⁶]; 8.90 [d, 2H, ⁴J(H⁵H³) = 1.9 Hz, H³]; 8.01 [dd, 2H, ³J(H⁶H⁵) = 5.6 Hz, ⁴J(H⁵H³) = 1.9 Hz, H³]; 3.81 [br, 1H, Me₂NH]; 2.11 [d, 6H, ³J(HcHd) = 6 Hz, ³J(PtH) = 14 Hz, Me₂NH]; 1.49 [s, 18H, tert-butyl]; 1.07 [s, 6H, ²J(PtH) = 68 Hz, Pt-Me, trans pyr]; 0.31 [s, 3H, ²J(PtH) = 69 Hz, Pt-Me, trans amine]. Complex 3.5 δ (¹H) = 8.48 [d, 4H, ⁴J(H⁵H³) = 1.9 Hz, H³]; 8.30 [d, 4H, ³J(H⁶H⁵) = 6 Hz, ³J(PtH) = 13 Hz, H⁶); 7.73 [dd, 4H, ⁴J(H⁵H³) = 6 Hz, ⁴J(H⁶H⁵) = 1.9 Hz, H³]; 1.49 [s, 36H, tert-butyl]; 0.79 [s, 12H, ²J(PtH) = 70 Hz, Pt-Me, trans pyr]; 0.03 [s, 6H, ²J(PtH) = 65 Hz, Pt-Me, trans H]; -11.80 [s, 1H, ¹J(PtH) = 445 Hz, Pt-H].

[PtMe₂I₂(dmpe)], 3.7: Complex 3.7 was prepared according to literature, with the ¹H NMR data in full agreement with those reported.⁹

[PtMe₂(OBn)₂(bpy)], 3.8: Complex 3.8 was prepared according to literature, with the ¹H NMR data in full agreement with those reported.¹⁰

[PtMe₄(dmpe)], 3.10: To a solution of [PtMe₂(dmpe)], 2.6, (32 mg, 0.09 mmol) in acetone-d₆ (1 mL) was added methyl triflate (10 µL, 0.09 mmol) at -78 °C, with stirring. The reaction mixture was stirred for an additional 30 minutes, in which the intermediate [PtMe₃(OTf)(dmpe)], 3.9, was believed to be produced. To this solution was added DMAB (5 mg, 0.09 mmol) in acetone-d₆ (0.5 mL). Gradual warming of the solution, via a VT NMR experiment, to room temperature for 1.5 hours. Yield = 24 mg, 68 %. NMR (acetone-d₆) : δ (¹H) = 1.88 [m, 4H, PCH₂]; 1.32 [d, 12H, ³J(PtH) = 12 Hz, ²J(PH) = 10 Hz, PCH₃]; 0.23 [t, 6H, ²J(PtH) = 57 Hz, ³J(PH) = 8 Hz, P-Me trans P]; -0.45 [t, 6H, ²J(PtH) = 44 Hz, ³J(PH) = 6 Hz, Pt-Me trans Me].

fac-[PtMe₃(I)(dmpe)], 3.11: Complex 3.11 was prepared according to literature, with the ¹H NMR data in full agreement with those reported.¹¹


3.5 REFERENCES


Appendices

Appendix 1. Chapter 2 $^1$H NMR Spectra

1.1 Dimethylamine-borane
1.2 [PtMe₂(bpy)], 2.1.

1.3 [PtMe(O₂CCF₃)(bpy)], 2.2.
1.4 [PtMeH(bpy)], 2.3.

\[ \text{C}_{10}H_{16}N_2PtO_2CF_3 + \text{Me}_2\text{HN-BH}_3 \rightarrow \text{C}_{10}H_{16}N_2PtHMe \rightarrow \text{Pt(0)} + \text{N}_2 + \text{CH}_4 \]

1.5 [PtCl(CHMeCO_2Me)(bpy)], 2.6.

[Chemical shift diagrams for [PtMeH(bpy)] and [PtCl(CHMeCO_2Me)(bpy)]]
1.6 [Pt(CHMeCO₂Me)₂(bpy)], 2.7.

1.7 [PtMe(CHMeCO₂Me)Cl(I)(bpy)], 2.8.
1.8 $[\text{PtMe}_2(\text{dmpe})]$, 2.9.

1.9 $[\text{PtMe(O}_2\text{CCF}_3)(\text{bpy})]$, 2.10.
1.10 [PtMe₂(dppe)], 2.11.

1.11 [Pt(O₂CCF₃)₂(dppe)], 2.12.
1.12 \([\text{Pt}_2(\mu-\text{H})_2(\text{dppe})_2]^2+\), 2.13.
Appendix 2. Chapter 3 NMR Spectra

2.1 \([\text{PtMe}_3(\text{OTf})(\text{bpy})]\), 3.1.

![NMR Spectrum 1](image1)

2.2 \([\text{Pt}_2\text{Me}_6(\mu-\text{H})(\text{bpy})_2]^+\), 3.2 and \([\text{PtMe}_3(\text{NHMe}_2)(\text{bpy})]^+\), 3.3.

![NMR Spectrum 2](image2)
2.3 [PtMe₂(bu₂bpy)].

2.4 [PtMe₃(OTf)(bu₂bpy)], 3.4.
2.5 \([\text{Pt}_2\text{Me}_6(\mu-\text{H})(\text{bu}_2\text{bpy})_2]^+\), 3.5 and \([\text{PtMe}_3(\text{NHMe}_2)(\text{bu}_2\text{bpy})]^+\), 3.6.

\[
\text{[Diagram of chemical reactions and structures]}
\]

2.6 \([\text{PtMe}_2\text{I}_2(\text{bpy})]\), 3.7.

\[
\text{[Diagram of chemical reactions and structures]}
\]
2.7 [PtMe$_2$(OBn)$_2$(bpy)], 3.8.

2.8 [PtMe$_4$(dmpe)], 3.10.
# Curriculum Vitae

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