SYNTHESIS AND PHOTOCHEMISTRY OF PT(IV) HYDROXO COMPLEXES

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SYNTHESIS AND PHOTOCHEMISTRY OF PT(IV) HYDROXO COMPLEXES

presented by Lasantha A Wickramasinghe,

a candidate for the degree of doctor of philosophy,

and hereby certify that, in their opinion, it is worthy of acceptance.

________________________________________
Prof. Paul R. Sharp

________________________________________
Prof. Timothy E Glass

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Prof. Justin R. Walensky

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Prof. Sheila Baker
To my dear academic parents

who encouraged me throughout my life
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ABBREVIATIONS

TPP  $meso$-tetraohenylporphyrin
<table>
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<th>Abbreviation</th>
<th>Definition</th>
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<tbody>
<tr>
<td>TME</td>
<td>2,3-dimethyl-2-butene</td>
</tr>
<tr>
<td>DF</td>
<td>2,5-dimethylfuran</td>
</tr>
<tr>
<td>SET</td>
<td>single-electron transfer</td>
</tr>
<tr>
<td>MeTHF</td>
<td>2-methyltetrahydrofuran</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>CH₂Cl₂</td>
<td>Methylene chloride</td>
</tr>
<tr>
<td>tft</td>
<td>trifluoromethylphenyl</td>
</tr>
<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
</tr>
<tr>
<td>TDDFT</td>
<td>Time-Dependent Density Functional Theory</td>
</tr>
<tr>
<td>NTO</td>
<td>Natural Transition Orbitals</td>
</tr>
<tr>
<td>PCM</td>
<td>Polarizable Continuum Model</td>
</tr>
<tr>
<td>hv</td>
<td>Photon</td>
</tr>
<tr>
<td>UV-Vis</td>
<td>Ultraviolet-visible</td>
</tr>
<tr>
<td>DOSY</td>
<td>Diffusion-Ordered Spectroscopy</td>
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LIST OF COMPLEXES
LIST OF COMPUTATIONAL MODEL COMPLEXES
SYNTHESIS AND PHOTOCHEMISTRY OF PT(IV) HYDROXO COMPLEXES

Lasantha A Wickramasinghe

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ABSTRACT

Global energy consumption and the production of clean renewable energy have become greater challenges. Sunlight-induced splitting of water into H₂ and O₂ is one of the leading strategies to achieve clean and renewable energy. Transition metal photochemistry has considerable potential for making this task more viable. Along with water splitting, hydrohalic acid (HX) splitting is being thoroughly investigated. HX splitting is a more facile two electron process whereas water splitting is a relatively difficult four electron oxidation process. Light driven HX splitting and endergonic elimination of X₂ (Br₂ and Cl₂) have received more attention as a potentially more economical and promising solar energy conversion process than water splitting.

Apart from Br₂ or Cl₂ elimination, hydrogen peroxide elimination is of interest and the synthesis of Pt(IV)-dihydroxo complexes was attempted. Concentrated hydrogen peroxide addition to trans-Pt(PEnt₃)₂ClR yielded hydroxo-hydroperoxo complexes trans-Pt(IV)Cl(OH)(OOH)R(PEnt₃)₂ [5 (R = 9-phenanthryl), 4 (R = 4-tft)]. Complex 5 is unstable and reacts with solvent CH₂Cl₂ to give trans,cis-Pt(PEnt₃)₂(Cl)₂(OH)(9-phenanthryl) (3). Protonation of OOH ligand in 4 by HCl gives trans,cis-Pt(PEnt₃)₂(Cl)(OH)(4-tft) (6) and HBr gives analogous trans-Pt(PEnt₃)₂(Br)(Cl)(OH)(4-tft) (7). The characterization of above complexes was done by NMR spectroscopy and X-ray crystallography. Photoelimination of hypohalous acid was studied in detail along with
DFT and TDDFT calculations. Direct detection of HOCl was not successful. Photolysis of 3 or 6 at 313 or 380 nm in the presence of 2,3-dimethyl-2-butene (TME) yields the chlorohydrin (2-chloro-2,3-dimethyl-3-butanol), 3-chloro-2,3-dimethyl-1-butene, and acetone. Expected products from HOCl trapping in TME were tested separately using an authentic sample of HOCl. The results obtain from photolysis of 7 are consistent with cis elimination of HOBr and bromohydrin is detected from the TME reaction. Computational studies of related model complexes suggest a dissociative triplet excited state reaction pathway leading to HOCl elimination.

Photolysis (380 nm) of 4 at -78 ℃ in acetone-d₆ or toluene-d₈ yields HOOOH (16-20%) and trans-Pt(PEt₃)₂Cl(4-tft) (2). The direct detection of HOOOH is done by ¹H NMR spectroscopy. Several other products are observed in acetone-d₆; H₂O₂, (CD₃)₂C(OH)(OOH) and (CD₃)₂C(OOH)₂. Thermal decomposition or room temperature photolysis gives 2, O₂ (not detected) and water. 2,5-dimethylfuran is used as a reagent for chemical detection of ¹O₂. Thermodynamics and kinetics were studied for the thermal decomposition reaction of 4. Computational studies indicate the importance of intramolecular hydrogen-bonding which may control the photolysis and thermolysis pathways.

Photolysis of 6 at 77 K in 2-methyltetrahydrofuran gives platinum(III), hydroxo radical and emission from a triplet excited state. The triplet emission is further confirmed by emission lifetime (phosphorescence) and λ_max comparable to the calculated triplet energy. The photolysis in toluene gives benzyl radical via OH radical mediated hydrogen atom abstraction. Warming the photolyzed solutions of 6 gives phospha-platinacycle trans-Pt(CH₂CH₂PEt₂)(PEt₃)Cl₂(4-tft) (24) by hydrogen atom abstraction from PEt₃, where
abstraction possibly occurs at 77 K. The complex 24 undergoes thermal reductive elimination at room temperature or photolytic reductive elimination even at 77 K.

Reactions of carboxylic acids with the OOH ligand in 4 give Pt(IV)hydroxo-carboxylate complexes $\text{trans-Pt(PEt}_3)_2$(Cl)(OH)(X)(4-tft) [26 (X = acetate), 27 (X = trifluoroacetate) and 28 (X = 2-bromophenylacetate)]. These complexes introduce strong hydrogen bonding between the hydroxo and carboxylate ligands. Photolysis of the carboxylate complexes at room temperature gives phospha-platinacycles analogous to 24 in high yield. DFT calculations showing much shorter hydrogen bonding in the triplet excited state suggest photo-generated hydroxyl radicals are tethered and directed to a hydrogen atom abstraction from the PEt$_3$ group.
CHAPTER 1: INTRODUCTION

1.1 Importance of solar energy.

Photosynthesis is one of the most important chemical processes to sustain and balance life on earth. In this process, plants capture radiant energy (solar energy) to convert carbon dioxide and water from the environment to glucose (food) while giving off oxygen as a byproduct. The vast expanses of forest coverage helps to harness solar energy in order to sustain the life we claim. Solar energy is a renewable and continuous source of energy on earth. Thus, it has caught more attention than other renewable energy sources such as wind and ocean wave power. However, global energy consumption and the production of clean renewable energy have become a great challenge to every single nation. Environmental concerns such as emission of CO$_2$ and other pollutants by fossil fuel combustion also drives us towards finding renewable energy sources. As a result, modern day scientists have put their thoughts on the viable use of solar energy in the field of science.

The use of photovoltaics (solar panels) to generate electricity is one of the modern applications of solar energy. Moreover, conversion of solar energy into more productive form via storing it in chemical bonding has been considered as the key to achieve the goal of renewable energy. Sunlight induced (photocatalytic) splitting of water into molecular hydrogen (H$_2$) and oxygen (O$_2$) has been studied extensively. Recombination of H$_2$ and O$_2$ can be implemented in a fuel cell generating thermal or electrical energy. Water splitting is a difficult and complex four-electron four-proton process. In contrast,
hydrogen halide (HCl and HBr) splitting has been highlighted as a much simpler two-electron two-proton process. The knowledge gained from such adaptable systems can be readily used in the development of this chemistry.

1.2 Relevance of transition metal photochemistry.

In recent years transition metal photochemistry has received a lot of attention toward the development of efficient photocatalysts suitable for water/HX splitting. Synthesis and photochemistry of mono and bi metallic complexes of late transition metals have been rewarded towards the development of photocatalysts.\textsuperscript{9,10} Theoretical studies involving computational modelling have been extensively used along with experimental data to understand the mechanistic and thermodynamic behavior.\textsuperscript{8} Density functional theory (DFT) calculations could be highly acknowledged in transition metal photochemistry for their contribution. DFT calculations have been used extensively to look at the transition states and their properties such as electronics and thermodynamics pertaining to redox reactions.\textsuperscript{11,12}

In the field of transition metal chemistry, reductive elimination has been well explored and understood for many years. When reductive elimination is induced by absorption of a photon this can be termed as photo reductive elimination or more simply photoelimination (eq 1). If elimination is endergonic the photoelimination process accomplishes conversion and storage of solar energy into chemical bonds.

\[
\text{L}_n\text{M(Y)(X)} \xrightarrow{\text{hv}} \text{L}_n\text{M} + \text{Y-X} \quad \text{eq 1}
\]
Photoelimination of a strong oxidant (Y-X) has a higher propensity toward facile re-oxidation or recombination. Such re-oxidation is crucial for engineering such systems to accomplish effective storage of solar energy. Photocatalytic conversion of HX (X= Cl, Br or OH) into H₂ and elimination of X₂ (Cl₂, Br₂ or H₂O₂) is illustrated in Scheme 1.2.1. The HX based photoelimination has a serious drawback due to recombination of X₂ (X= a halogen) with the reduced catalyst as opposed to H₂O₂ photoelimination as H₂O₂ can decompose to O₂ and H₂O. A recent paper by Milstein and co-workers provides insight for splitting of water into H₂ and O₂ in the presence of light⁰¹. With an outstanding enthusiasm Sharp group has discovered ample amount of information regarding the key step in the proposed catalytic cycle. Findings of molecular bromine and chlorine photoelimination were reported after extensive studies.¹¹,¹²,¹⁴ In our studies, we have further focused on the synthesis of novel mononuclear Pt(IV)-hydroxo complexes and photoelimination of hydrogen peroxide (H₂O₂) and hypochlorous acid (Scheme 1.2.1(b)).

The catalytic cycle shown in Scheme 1.2.1(b) is a modification of the HX splitting cycle proposed previously (Scheme 1.2.1 (a))⁹.

**Scheme 1.2.1.** Potential catalytic cycle for HX splitting; (a) general splitting cycle, (b) cycle for hypohalous acid (HOX) and hydrogen peroxide (H₂O₂) elimination.
Few instances of oxidative addition of water to metal complexes are reported. However, such oxidative addition of water to Pt(II) is not being reported up to date. Primarily we were interested in synthesis of Pt(IV)-dihydroxo complexes which can be applied in studies of H$_2$O$_2$ photoelimination. In addition, regeneration of catalyst via clean photoelimination of a single molecule such as H$_2$O$_2$ from a light induced excited metal complex is one of the underlying concerns. Behavior of an excited higher oxidation state metal complex is always hard to predict. For an instance, attempted net Cl$_2$/Br$_2$ photoelimination studies from triphos iridium(III) halide complexes have shown undesirable triphos arm dissociation leading to the formation of various iridium complexes (Scheme 1.2.2$^{14}$).

**Scheme 1.2.2.** Triphos arm dissociation from photolysis of triphos iridium(III) halide

![Scheme 1.2.2](image)

Regeneration of a catalyst under photolysis does not always guarantee molecular photoelimination. Photoreduction of an excited state metal complex may be facilitated by foreign agents like reactive solvents or unsaturated hydrocarbons. Specially in the case of initial dissociation of a radical species which can be captured by unsaturated hydrocarbons making the photoreduction still favorable$^{12}$. Scheme 1.2.3, shown below,
explains the possibility of such photoreduction and the involvement of halogen traps. Photoelimination does not occur in the absence of the traps implies a fast recombination of dissociated Br radical or direct reaction of the trap with the excited metal complex causing photo-reduction. Photochemistry observed with our Pt(IV)hydroxo complexes exhibited diversity in chemical reactivity such as C–H activation and metal–carbon bond formation along with HOX elimination. Photochemistry of Pt(IV)hydroxo-halide complexes yielded net hypohalous acid elimination. Pt(IV)hydroxo complexes (discussed in later) are photoactive even in the absence of unsaturated hydrocarbons. Most surprisingly, photoelimination of dihydrogen trioxide (HOOOH) is observed from a Pt(IV)hydroxo-hydroperoxo complex. Furthermore, observation of C–H activation by hydroxo radical and metal-carbon bond formation creates an opportunity to explore and understand the chemistry of hyroxo radical in various environments. In order to design an ideal photocatalyst for HX/water splitting it is important to understand the salient features belong to this type of photocatalysis.

Scheme 1.2.3. Photoreduction of trans-Pt(IV)(PEt3)2Br3(1-Nap)
1.3 Chemistry of Platinum(IV)-hydroxo complexes.

Pt(IV) hydroxo complexes have been previously prepared mainly by oxidative addition of H$_2$O$_2$. A number of di, tri, and tetra hydroxo Pt(IV) complexes can be found in peroxide mediated synthesis. In general, the oxidative addition to Pt(II) yields trans dihydroxo complexes. A detail mechanism is discussed in Chapter 2. However, an instance of cis oxidative addition was also found in a previous report where, the role of hydrogen bonding to stabilize the cis configuration was highlighted (Scheme 1.3.1). Substituting the two -NH$_2$ groups on the 2,2′-bipyridine with either –CH$_3$ or –H did not yield a cis configuration indicating the role of hydrogen bonding in the cis addition.

**Scheme 1.3.1.** Formation of cis-dihydroxo Pt(IV) with the aid of hydrogen bonding.

The use of O$_2$ as an oxidant in the presence of polar protic solvents such as methanol has been employed in the oxidation of Pt(II) to Pt(IV) hydroxo and hydroperoxo complexes. The oxidative addition of phthaloyl peroxide also caught our attention (Scheme 1.3.2). In our work, we report the synthesis and photochemistry of Pt(IV) hydroxo-carboxylate complexes (discussed in chapter 4) which shows the importance of intramolecular hydrogen bonding in hydroxo radical chemistry. The type of complex shown in Scheme 1.3.2 is analogous to our system though there is no photochemistry reported on them.
Scheme 1.3.2. Pt(IV) hydroxo carboxylate complex from phthaloyl peroxide.

1.4 Chemistry of polyoxides (ROₙR).

Chemistry of polyoxides has not been explored and is not understood enough, though it could be highly potent in oxidation chemistry. A general formula for polyoxides can be given as ROₙR, (n > 2) where R stands for hydrogen, other atoms or alkyl/aryl groups. The simplest form of ROₙR is hydrogen peroxide (H₂O₂). Chemistry related to this simple molecule, H₂O₂ has been developed and utilized for centuries. Dihydrogen trioxide (H₂O₃) is the closest to H₂O₂ in this category. In contrast with H₂O₂, chemistry of H₂O₃ hasn’t been thoroughly investigated until recently. Identification and characterization of H₂O₃ is relatively recent. The existence of H₂O₃ was merely hypothetical for a long time. Studies in the early 1980s suggested H₂O₃ as a possible intermediate formed in low-temperature condensates obtained from electrodissociated hydrogen/oxygen mixture. Antibody catalyze reactions of H₂O and ¹O₂ were also believed to generate H₂O₃ as an intermediate leading to the final product of H₂O₂.
However, development in this area of chemistry will surely rewrite the history of oxidation chemistry and their applications in subsequent fields such as pharmaceutical, atmospheric, environmental and biological chemistry.

H$_2$O$_3$ is less stable in solutions at room temperature, decomposing to water and singlet oxygen. Hence, synthesis and characterization need to be done at a low temperature (ex. -60°C). Characterization using $^1$H and $^{17}$O NMR spectroscopy has been reported in a series of organic solvents at low temperatures (around -65°C).$^{25}$ Observable chemical shift in $^1$H NMR varied significantly with temperature. Laboratory synthesis of HOOOH can be mainly divided into three categories: (1) hydrogenation of ozone (O$_3$), and (2) decomposition of hydrotrioxides (ROOOH, R = SiMe$_3$) (Scheme 1.4.1).$^{25-26}$

**Scheme 1.4.1.** Laboratory synthesis of H$_2$O$_3$.

(1) hydrogenation of ozone

\[
\text{HOOH} + \text{O}_3 \overset{\text{solvent} \ -78 \ ^\circ\text{C}}{\longrightarrow} \text{cis-HOOOH} + \text{O}_2(\Delta_g)/\text{O}_2(\Sigma_g)
\]

(2) decomposition of hydrotrioxide

\[
\text{R}_3\text{EOOOH} + 2\text{H}_2\text{O} \overset{\text{solvent} \ -70 \ ^\circ\text{C}}{\longrightarrow} \text{HOOOH} + \text{R}_3\text{EOH}
\]

E = Si, Ge   R = H, Me
Chemistry we describe later in chapter 2-4 will include various aspects of Pt(IV)hydroxo complexes. They are mainly in four categories; synthesis, characterization, photochemistry and computational modeling. We have been able to synthesize novel trans-Pt(IV)(PEt\textsubscript{3})\textsubscript{2}(R)(OH)(X)(Y) (R=aryl; X=Cl, Br and Y= OOH, CN and acetate) complexes and study their photolchemistry. Photoelimination of HOCl and HOBr from trans-Pt(IV)(PEt\textsubscript{3})\textsubscript{2}(R)(OH)(X)\textsubscript{2} complexes was studied extensively. Detection of hypohalous acid was attempted via chemical reactions such as alkene oxidation leading towards halohydrin formation. Direct detection was not successful due to instability of HOCl/HOBr in the presence of Pt species. First synthesis of Pt(IV)(OH)(OOH) complex and studies of dihydrogen trioxide (H\textsubscript{2}O\textsubscript{3}) photoelimination was accomplished. Direct identification of H\textsubscript{2}O\textsubscript{3} was performed using \textsuperscript{1}H NMR spectroscopy in two different solvent systems at low temperature (-60°C). Photolytic formation of H\textsubscript{2}O\textsubscript{3} was further confirmed via chemical detection of singlet oxygen as one of its decomposition products.

Apart from conventional solution phase photolysis, frozen matrix photolysis were performed and an unusual phosphorescence (confirmed by lifetime measurement) and intramolecular C-H activation motivated us to investigate the behavior of OH radical in various systems. As an advancement of this chemistry, here we report the synthesis of trans-Pt(IV)(PEt\textsubscript{3})\textsubscript{2}(R)(OH)(Cl)(acetate) analogues and intramolecular C-H activation observed in solution phase. This change can be attributed to the control gained via OH radical hydrogen bonding to the acetate ligand.
CHAPTER 2: PHOTOREDUCTION OF PLATINUM(IV) HALO-HYDROXO COMPLEXES

2.1 Introduction

Our group reported efficient molecular bromine photoelimination from the mononuclear Pt(IV) complexes $\text{trans-Pt(PEt}_3\text{)}_2(R)(\text{Br})_3$ ($R = \text{Br, aromatic carbyl ligand}$).<sup>11</sup> These reactions suffer from back reaction of $\text{Br}_2$ with co-product, $\text{trans-Pt(PEt}_3\text{)}_2(R)(\text{Br})$, and hence bromine traps must be added.<sup>11</sup> With the idea of $\text{H}_2\text{O}_2$, instead of $\text{Br}_2$, photoelimination we targeted to prepare the analogous dihydroxo complexes $\text{trans-Pt(PEt}_3\text{)}_2(R)(\text{X})(\text{OH})_2$ ($\text{X} = \text{Cl, Br}$). Simple oxidative addition of hydrogen peroxide to $\text{trans-Pt(PEt}_3\text{)}_2(R)(\text{X})$ type complexes was aimed as a potential route for making dihydroxo complexes. Even though peroxide-assisted oxidation of Pt(II) with different $R$ groups was achieved, the desired dihydroxo complexes were not observed, instead, we isolated monohydroxo complexes. While not the desired complexes, they are also highly photochemically active to net elimination, surprisingly of hypohalous acid ($\text{HOX, X} = \text{Cl, Br}$).<sup>27</sup> Their synthesis and photochemistry is reported herein.

2.2 Complex synthesis and characterization.

Pt(II) complexes $\text{trans-Pt(PEt}_3\text{)}_2\text{Cl}(R)$ [1 ($R = 9\text{-phenanthryl}$), 2 ($R = 4\text{-trifluoromethylphenyl (4-tft)}$)] are resistant to oxidation by hydrogen peroxide and solutions ($\text{CH}_2\text{Cl}_2$, THF, acetone) of the complexes remain unchanged when stirred with excess 30% aqueous hydrogen peroxide. However, slow oxidation does occur with concentrated diethyl ether solutions of hydrogen peroxide (Scheme 2.2.1). The reactions
are accompanied by extensive decomposition of the hydrogen peroxide and can require multiple additions to complete. The final product depends on the R group. With R = 9-phenanthryl, the product is \textit{trans,cis}-Pt(PEt\textsubscript{3})\textsubscript{2}(Cl\textsubscript{2})(9-phenanthryl) (3). The source of the additional chloride is unknown, but as the isolated yield (68%) exceeds 50%, at least a portion of the chloride must originate from the CH\textsubscript{2}Cl\textsubscript{2} solvent. However, both bromo and chloro of \textit{trans}-Pt(PEt\textsubscript{3})\textsubscript{2}(2-trifluoromethylphenyl)(X) were not able to oxidize by H\textsubscript{2}O\textsubscript{2} under above condition. It could be explained due to steric crowding cause by CF\textsubscript{3} group.

\textbf{Scheme 2.2.1} Synthesis of Pt(IV) hydroxo complexes.

The reaction is more rapid with 2 than with 1. However, the product is now the hydroxo-hydroperoxo complex \textit{trans}-Pt(PEt\textsubscript{3})\textsubscript{2}(Cl)(OH)(OOH)(4-tft) (4). Complex 4 is the first Pt(IV)-hydroxo-hydroperoxo to be observed. The NMR properties of 4 are similar to
those of an intermediate (5), observed in the preparation of 3 and assigned as the 9-phenanthryl analog of 4. Complex 4 is readily converted to trans,cis-Pt(PEt$_3$)$_2$(Cl)$_2$(OH)(4-tft) (6), an analog of 3, simply by the addition of aqueous HCl (X = Cl). The same reaction with HBr(aq) yields the mixed bromo-chloro-hydroxo complex trans-Pt(PEt$_3$)$_2$(Br)(Cl)(OH)(4-tft) (7).

Complexes 3, 4, 6, and 7 gave crystals suitable for X-ray analysis. The solid-state structures of 3, 4 and 6 are shown in Figure 2.2.1, Figure 2.2.2 and Figure 2.2.3. Complex 7 is isomorphous and isostructural with 6 and also co-crystallized with ~20% 6 that was present as an impurity in the reaction mixture. Although the presence of a Br atom trans to the 4-trifluoromethylphenyl group is confirmed, the co-crystallization with 6 and disorder make the metrical parameters unreliable and the structure of 7 will not be discussed. Selected metrical parameters for the other complexes are listed in Table 2.2.1 and have been averaged where chemically equivalent parameters are present.

Complexes 3 and 4 crystallized as hydrogen-bonded dimers. In the case of 3, the dimer is asymmetric and only one of the hydroxo-group hydrogen atoms participates in the hydrogen bonding. In contrast, a centrosymmetric dimer is observed for 4 and both the hydroxo and the hydroperoxo groups are involved in hydrogen bonding. However, only the hydroperoxo group participates in the intermolecular hydrogen bonding and forms a 6-membered ring through head-to-tail dimerization of the OOH group. Meanwhile, the hydroxo group is intramolecularly hydrogen bonded to the $\beta$-O of the hydroperoxo group. A similar hydrogen bonding arrangement is found in the dimer structure of Tp*Pt(OOH)(CH$_3$)$_2$ (Tp* = hydrotris(3,5-dimethylpyrazolyl)borate).
Figure 2.2.1. Solid-state structure of the hydrogen-bonded dimer of 3 (30% probability ellipsoids, hydrogen atoms omitted except for the OH-group hydrogen atoms which are represented as arbitrary spheres).

Figure 2.2.2. Solid-state structure of the centrosymmetric hydrogen bonded dimer of 4 (50% probability ellipsoids, hydrogen atoms omitted except for the OH and OOH group hydrogen atoms which are represented as arbitrary spheres).
Figure 2.2.3. Solid-state structure of 6 (one of two independent molecules, 50% probability ellipsoids, hydrogen atoms omitted, except for the OH ligand hydrogen atom which is represented as an arbitrary sphere). Rotational disorder in the CF$_3$ group is not shown.

Table 2.2.1. Selected mean$^a$ metrical parameters for chloro-hydroxo complexes 3 and 6, and hydroperoxo-hydroxo complex 4.

<table>
<thead>
<tr>
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<th>3</th>
<th>6</th>
<th>4</th>
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<tbody>
<tr>
<td>Pt-Cl1</td>
<td>2.356(6)</td>
<td>2.349(1)</td>
<td>2.3541(11)$^b$</td>
</tr>
<tr>
<td>Pt-Cl2</td>
<td>2.444(2)</td>
<td>2.442(9)</td>
<td>--</td>
</tr>
<tr>
<td>Pt-P</td>
<td>2.374(4)</td>
<td>2.371(6)</td>
<td>2.36(1)</td>
</tr>
<tr>
<td>Pt-OH</td>
<td>2.018(2)</td>
<td>2.028(5)</td>
<td>2.032(3)$^b$</td>
</tr>
<tr>
<td>Pt-OOH</td>
<td>--</td>
<td>--</td>
<td>2.104(3)$^b$</td>
</tr>
<tr>
<td>Bond</td>
<td>Pt-C</td>
<td>O-O</td>
<td>Cl1-Pt-Cl2</td>
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<td>------</td>
<td>--------</td>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td></td>
<td>2.088(6)</td>
<td>2.050(1)</td>
<td>88.98(3)</td>
</tr>
<tr>
<td></td>
<td>2.040(4)</td>
<td>1.472(4)</td>
<td>2.050(1)</td>
</tr>
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<td>---------------</td>
</tr>
<tr>
<td>HO-Pt-OOH</td>
<td>--</td>
<td>--</td>
<td>91.54(12)(^b)</td>
</tr>
<tr>
<td>C1-Pt-OOH</td>
<td>--</td>
<td>--</td>
<td>178.14(14)(^b)</td>
</tr>
<tr>
<td>Pt-O1-O2</td>
<td>--</td>
<td>--</td>
<td>110.4(2)(^b)</td>
</tr>
</tbody>
</table>

\(^a\) Mean of chemically equivalent parameters with standard deviation in parenthesis. \(^b\) Single value with estimated error in parenthesis. \(^c\) P atom of PEt\(_3\) ligand near phenanthryl \textit{peri}-hydrogen atom.

Metrical parameters for the complexes are much as expected with essentially identical Pt-P and Pt-Cl distances for all three complexes. The Pt-OH and Pt-C distances in the phenanthryl complex (3) differ slightly from those in the CF\(_3\)-phenyl complexes (4 and 6). The Pt-C distance is longer in 3, possibly due to steric interactions of the \textit{peri}-hydrogen atom of the phenanthryl group with the \textit{cis}-PEt\(_3\) and -Cl ligands, although electronic factors may also be involved. The steric effect of the \textit{peri}-hydrogen atom is evident in the angles around the Pt center, which deviate more from the ideal 90° and 180° angles in 3 than in 6. (For examples of \textit{peri}-hydrogen steric interaction in Pt(IV) organometallic complexes see reference 9.) Larger deviations are also seen in 4 and may be associated with the hydrogen bonding.

Complex 4 is preceded by two crystallographically characterized Pt(IV) η\(^1\)-hydroperoxo complexes: Pt(tmeda)(OOH)(OCH\(_3\))(CH\(_3\))\(_2\)\(^{29}\) and Tp*Pt(OOH)(CH\(_3\))\(_2\) (Tp* = hydrotris (3,5-dimethylpyrazolyl)borate).\(^{28}\) Crystallographic problems with the tmeda structure make the metrical parameters unreliable. Comparison of the O-O bond distance and the Pt-O-OH angle in the Tp* complex to those in 4 shows that they are essentially identical, however, the Pt-OOH distances differ markedly being longer by ~0.1 Å in 4. This is likely due to a difference in the donor \textit{trans} to the OOH ligand. In 4, it is a strong \textit{trans}-
influence aryl ligand, while in the Tp* complex it is a weaker trans-influence pyrazolyl group of the Tp* ligand.

The hydroxo complexes 3 and 6 are new members of a very small group of structurally characterized Pt(IV) hydroxo complexes containing a phosphine ligand. While there are many structurally characterized Pt(IV) hydroxo complexes with a variety of ligands, only fac-Pt(dppbz)Me₃(OH) (dppbz = o-bis(diphenylphosphino)benzene)³¹ and [Pt(PCN)(OH)(H₂O)]BF₄ (PCN = C₆H₃[CH₂P(t-Bu)₂](CH₂)₂N(CH₃)₂)³² contain a phosphine ligand. Unfortunately, the hydroxo and aqua ligands were not differentiated in the PCN complex. In the dppbz complex, the OH group is trans to a strong trans-influence methyl group and the Pt-OH distance, 2.116(7) Å, is consequently longer than the 2.018(2) and 2.028(5) Å distances observed in 3 and 6.

The stereochemistry of the Pt centers in 3, 4, 6 and 7 is established by the X-ray structures and places the phosphine ligands trans to each other and the hydroxo group cis to the R group. While less definitive, the NMR data for the complexes is consistent with the solid-state results. A single phosphine ³¹P NMR resonance with ¹⁰⁵Pt satellites is observed. The Jₚₚₚ values are typical of similar Pt(IV) complexes (1700-1800 Hz) with trans PEt₃ ligands and, as expected, are reduced from the parent Pt(II) complexes 1 and 2.¹¹ Separate signals are observed for the phenyl ring protons in the ¹H NMR spectra of 4, 6, and 7. This signifies a non-rotating phenyl ring on the NMR time scale and an asymmetric environment for the aryl ligand. For 6, this would only be consistent with the OH ligand and a Cl ligand being cis to the phenyl ring, as observed in the solid-state structure.
The complexes also show evidence of hydrogen bonding and exchange in their solution NMR spectra. $^{31}$P NMR chemical shifts for 3 are sensitive to the presence of H$_2$O such that there are slight differences in the shift ($\delta \sim$1) observed for the isolated complexes and those for the reaction mixtures that contain water from H$_2$O$_2$ decomposition. In addition, an OH signal ($\delta$ -0.13) is not observed in the $^1$H NMR spectrum of 3 unless protic impurities are removed by treatment of the NMR sample with base. For 4, 6, and 7, $^1$H NMR spectra in CDCl$_3$ show peaks for the OH ligand at $\delta$ 0.20 (4), -0.48 (6), and -0.6 (7). The OOH ligand of 4 is found at $\delta$ 6.42. The OH and OOH signals are concentration dependent for 4 and 6. (This is presumably also true of 7, but this was not investigated.) With increasing concentration the signals broaden and the OH signals, which have $^{195}$Pt satellites (40 Hz), begin to lose their coupling to the Pt center. In C$_6$D$_6$, the OH signal for 6 lacks satellites, even in dilute solutions, suggesting more rapid exchange than in CDCl$_3$, probably resulting from a greater tendency to form hydrogen-bonded dimers.

The UV-Vis absorption spectra for 3 and 6 are given in Figure 2.2.4. As expected from their pale yellow color the spectra show only a tail-off from the UV into the visible. The spectrum of 3 is much more intense in the UV than that for 6 and is likely dominated by absorptions associated with the phenanthryl moiety. In particular, the vibronically coupled $\pi$-$\pi^*$ transitions are usually located in the 300 nm region and the bands in this region in the spectrum of 3 can be thus assigned. In contrast, the higher energy aryl group $\pi$-system in 6 will shift such bands to higher energy exposing more Pt centered transitions. As we are more interested in the Pt centered transitions we will focus on the spectrum of 6.
Figure 2.2.4. UV-Visible absorption spectra of 3 and 6 in dichloromethane.

Figure 2.2.5. UV-Visible absorption spectrum of 6 in dichloromethane with TDDFT (CAM-B3LYP, pcm) vertical transitions for $6'$ (red vertical lines with the height corresponds to the oscillator strength).
Table 2.2.2. Vertical singlet transitions for 6’ in dichloromethane (CAM-B3LYP, pcm).

<table>
<thead>
<tr>
<th>Transition</th>
<th>Wavelength</th>
<th>Osc. Strength</th>
<th>Contributions (&gt;3%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>365</td>
<td>0.0082</td>
<td>H-3-&gt;LUMO (56%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>HOMO-&gt;LUMO (20%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H-1-&gt;LUMO (17%)</td>
</tr>
<tr>
<td>2</td>
<td>311</td>
<td>0.0054</td>
<td>H-4-&gt;LUMO (40%)</td>
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<td></td>
<td></td>
<td></td>
<td>H-7-&gt;LUMO (15%)</td>
</tr>
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<td></td>
<td></td>
<td>HOMO-&gt;LUMO (12%)</td>
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<td></td>
<td></td>
<td>H-5-&gt;LUMO (8%)</td>
</tr>
<tr>
<td>3</td>
<td>304</td>
<td>0.0313</td>
<td>HOMO-&gt;LUMO (49%)</td>
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<td></td>
<td></td>
<td></td>
<td>H-3-&gt;LUMO (19%)</td>
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<td></td>
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<td></td>
<td>H-4-&gt;LUMO (12%)</td>
</tr>
<tr>
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<td></td>
<td></td>
<td>HOMO-&gt;L+1 (7%)</td>
</tr>
<tr>
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<td></td>
<td></td>
<td>H-6-&gt;LUMO (5%)</td>
</tr>
<tr>
<td>4</td>
<td>292</td>
<td>0.009</td>
<td>H-1-&gt;LUMO (65%)</td>
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<td>H-3-&gt;LUMO (13%)</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>H-1-&gt;L+1 (4%)</td>
</tr>
</tbody>
</table>

To help in the assignment of the low-UV bands in 6, a TDDFT (CAM-B3LYP, pcm) study was undertaken with model complex trans,cis-Pt(PMe$_3$)$_2$(Cl)$_2$(OH)(4-trifluoromethylphenyl) 6’ where the PE$_3$ ligands of 6 are replaced by PMe$_3$ ligands. The calculated vertical singlet transition energies and oscillator strengths (Table 2.2.2) over the region of the experimental spectrum are displayed in Figure 2.2.5 along with the experimental spectrum. A good fit of the calculated transitions for 6’ to the experimental spectrum of 6 is observed, especially in the lower-energy region. The obtained orbital contributions to the transitions are fairly complex (Table 2.2.2) and a natural transition orbital (NTO) analysis$^{33}$ was applied for the five lowest-energy transitions. This yielded one dominant (eigenvalue $\geq$ 0.96) contributing orbital set for each transition. The NTO set for the first (lowest-energy) transition is graphically presented in Figure 2.2.6. In common with the other three sets, the arrival orbital for the first transition is an e$_g$*-type
(pseudo-octahedral symmetry) orbital with strong antibonding interactions between the Pt and the OH and Cl ligands along the HO-Pt-Cl axis. The departure orbital is largely composed of an OH lone-pair and a matching t₂g-type Pt orbital, with minor P, C and Cl components. The departure orbitals for the other three transitions are various combinations of Cl lone-pair, t₂g-type Pt, P, and π-aryl orbitals. The first five triplet excited-state transitions were also calculated and the compositions and energies of the two lowest match closely to those of the corresponding singlets, suggesting facile singlet-triplet intersystem crossing at this level. Also possible is direct excitation into the triplet excited states at lower energies.

![Natural transition orbital (NTO) set for the first singlet excited state of 6’ (isovalue = 0.04). The “arrival” orbital is on the top and the “departure” orbital is on the bottom (H atoms omitted).](image)

**Figure 2.2.6.** Natural transition orbital (NTO) set for the first singlet excited state of 6’ (isovalue = 0.04). The “arrival” orbital is on the top and the “departure” orbital is on the bottom (H atoms omitted).
**Photochemistry.** Complexes 3 and 6 are photosensitive to light in the blue and UV regions. In C₆D₆ (λ = 313 nm), clean conversion of 3 to Pt(II) complex 1 is observed (eq 2) as indicated by ¹H and ³¹P NMR spectroscopy and by the observation two isobestic points when the reaction is monitored by UV-vis absorption spectroscopy. Two Pt products are obtained for 6 in C₆D₆ and for both 3 and 6 in CDCl₃ and CD₂Cl₂. The major products (60-80% yield) are again 1 and 2 but significant amounts (10-35% yield) of the Pt(IV) complexes trans,mer-Pt(PEt₃)₂(Cl)₃R [R = 9-phenanthryl (8), R = 4-trifluoromethylphenyl (9)] are also obtained (eq 3).

\[
\begin{align*}
\text{HO} & \quad \text{Cl} & \quad \text{PEt₃} & \quad \text{Pt} & \quad \text{PEt₃} & \quad \text{Cl} \\
\text{Et₃P} & \quad \text{R} & \quad \text{Cl} & \quad \text{C₆D₆} & \quad \text{hv} & \quad \text{Cl} & \quad \text{PEt₃} & \quad \text{Pt} & \quad \text{PEt₃} & \quad \text{Cl} & \quad \text{HOCl} \\
3 & \quad R = 9\text{-phenanthryl} & \quad 1 & \quad \text{eq 2}
\end{align*}
\]

\[
\begin{align*}
\text{HO} & \quad \text{Cl} & \quad \text{PEt₃} & \quad \text{Pt} & \quad \text{PEt₃} & \quad \text{Cl} \\
\text{Et₃P} & \quad \text{R} & \quad \text{Cl} & \quad \text{hv} & \quad \text{C₆D₆} & \quad \text{Cl} & \quad \text{PEt₃} & \quad \text{Pt} & \quad \text{PEt₃} & \quad \text{Cl} & \quad \text{other products (non-Pt)} \\
3 & \quad \text{in CDCl₃ or CD₂Cl₂} & \quad 1 & \quad 8, \quad R = 9\text{-phenanthryl} & \quad 9, \quad R = 4\text{-trifluoromethylphenyl} & \quad \text{eq 3}
\end{align*}
\]

By stoichiometry, the formation of 1 and 2 implies that 3 and 6 photoeliminate HOCl. To test for the possible presence of HOCl, PPh₃ was added to C₆D₆ solutions of 3 immediately after photoconversion (313 nm) to 1. A 22% yield (based on 3) of OPPh₃ (eq 4) was indicated by ³¹P NMR spectroscopy. No OPPh₃ is observed for the CDCl₃ and
CD$_2$Cl$_2$ photoreaction mixtures. To help identify the oxidant in the photolyzed C$_6$D$_6$ solutions, 2,3-dimethyl-2-butene (TME) was added to a photolyzed solution of 3 in place of PPh$_3$. The expected HOCl oxidation product, chlorohydrin 10, is not observed, nor are other possible oxidation products (see below).

\[
\text{Photolyzed C}_6\text{D}_6 \quad \text{solutions of 3} \quad \xrightarrow{\text{PPh}_3} \quad \text{oPPh}_3 \quad \quad \text{eq 4}
\]

As reaction conditions typically used to generate chlorohydrins from an alkene employ a large excess of HOCl in aqueous acid,\textsuperscript{34} very different from our potential reactions conditions of low HOCl concentration and non-protic solvents, we studied HOCl reactions with TME under conditions similar to ours. Gaseous HOCl was generated by treating solid Ca(OCl)$_2$ with acid (H$_2$SO$_4$ or HCl)\textsuperscript{35} and was vacuum transferred into solution. Alternatively, HOCl solutions were prepared by the reaction of HgO and Cl$_2$ in water-saturated solvents.\textsuperscript{36} HOCl formation was confirmed by UV-Vis absorption spectroscopy after transfer to water (Figure 2.2.7). Approximately 10 mol % ClO$_2$ was also detected in the HOCl from Ca(OCl)$_2$.

TME reactions with HOCl solutions were analyzed by $^1$H NMR spectroscopy and showed that chlorohydrin 10 is formed along with 3-chloro-2,3-dimethyl-1-butene (11) and acetone in about a 1:2:0.2 ratio (Char1). Thus, the oxidant in the photolyzed solutions of 3 and 6 (eq 3) is not HOCl but probably a solvent derived species. Attempts to detect $^1$H NMR signals for this species in photolyzed C$_6$H$_6$ solutions were not successful, although chlorobenzene was detected in 50% yield (relative to 2). Photolysis of HOCl solutions in C$_6$H$_6$ also produced chlorobenzene.
Figure 2.2.7. UV-Visible spectra confirming formation of HOCl from Ca(OCl)$_2$/H$^+$ and HgO/Cl$_2$. Relative amount of ClO$_2$ (12%) determined from extinction coefficients. (Note remarkably well defined vibronic coupling on ClO$_2$ band.)

Chart 1. TME-HOCl reaction products (HOCl from H$_2$SO$_4$ and Ca(OCl)$_2$).

The absence of HOCl in photolyzed solutions of 3 and 6 is consistent with the low stability of HOCl in the presence of Pt complexes and under photolysis.$^{37}$ Fresh benzene solutions of HOCl start out a characteristic yellow color, but become colorless within 15 min and lose their ability to oxidize TME. Dichloromethane and chloroform solutions appear to be more stable (hours), but quickly decolorize under irradiation (313 or 380
nm) and the resulting solutions do not oxidize PPh3. Addition of trans-Pt(PEt3)2Cl(4-trifluoromethylphenyl) (2) to a fresh benzene solution of HOCl results in the immediate formation of trichloro Pt(IV) complex 9 and subsequent TME addition does not give oxidation products indicating that HOCl has been consumed. Thus, HOCl photoelimination from 3 and 6 may occur, but the HOCl would not survive the reaction conditions.

To further investigate the role of 2 in the possible decomposition of photoeliminated HOCl, the photolysis of 6 in the presence of an equimolar amount of 2 was examined. Photolysis proceeds as without added 2 (similar time scale), but the yield (based on 6) of trichloro Pt(IV) complex 9 increases to 48%. From the amount of chlorine in 6, the maximum possible yield of 9 is 50%. If this represents capture of photoeliminated HOCl by 2, the capture efficiency is 96%.

TME was used as a possible HOCl trap. Photolysis of 3 and 6 proceeds as without added trap, but now the amount of 8 and 9 formed in CDCl3 and CD2Cl2 is reduced to just traces. TME oxidation is observed and products from the CD2Cl2 and C6D6 reactions are listed in Table 2.2.3 (3) and Table 2.2.4 (6). In common with HOCl, 11 and acetone are observed for 3, but only small amounts of chlorohydrin (10) are detected and several new products (12-14) are formed. Another product, formed in low yield, has a single 1H NMR signal and could be triacetone triperoxide,38 but this was not confirmed. In contrast to 3, photolysis of 6 with TME in CDCl3 and CD2Cl2 produces chlorohydrin 10 as a major product in addition to 11, 12, 14, and acetone. Chlorohydrin 10 is the only detected TME product for 6 in C6D6, but the yield is only 5%.
Table 2.2.3. TME (0.1 M) product yields\textsuperscript{a} from photolysis of 3 (10 mM).

<table>
<thead>
<tr>
<th>TME Products</th>
<th>CD\textsubscript{2}Cl\textsubscript{2} (% yield)\textsuperscript{a}</th>
<th>C\textsubscript{6}D\textsubscript{6} (% yield)\textsuperscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>380 nm\textsuperscript{b}</td>
<td>313 nm\textsuperscript{b}</td>
</tr>
<tr>
<td>\includegraphics[width=0.1\textwidth]{10.png}</td>
<td>\textless 1</td>
<td>7</td>
</tr>
<tr>
<td>\includegraphics[width=0.1\textwidth]{11.png}</td>
<td>7</td>
<td>8</td>
</tr>
<tr>
<td>\includegraphics[width=0.1\textwidth]{12.png}</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>\includegraphics[width=0.1\textwidth]{13.png}</td>
<td>20</td>
<td>10</td>
</tr>
<tr>
<td>\includegraphics[width=0.1\textwidth]{14.png}</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>Acetone</td>
<td>9</td>
<td>7</td>
</tr>
<tr>
<td>O atom yield\textsuperscript{c}</td>
<td>45</td>
<td>34</td>
</tr>
<tr>
<td>Cl atom yield\textsuperscript{c}</td>
<td>12</td>
<td>20</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Yields are relative to the molar amount of 2 with an estimated error of 1\%. \textsuperscript{b} Short (\textless 6 min) high-intensity irradiations. \textsuperscript{c} O atom yield = 10 yield + 12 yield + 2(13 yield) + acetone yield, Cl atom yield = 10 yield + 11 yield + 14 yield.
Table 2.2.4. TME product yields$^a$ from photolysis of 6 (18 mM, 313 nm).

<table>
<thead>
<tr>
<th>TME Products</th>
<th>[TME] in CDCl₃</th>
<th>[TME] in CD₂Cl₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.13 M</td>
<td>1.8 M</td>
</tr>
<tr>
<td>HO-Cl</td>
<td>18 %</td>
<td>26 %</td>
</tr>
<tr>
<td>Cl-Cl</td>
<td>7 %</td>
<td>9 %</td>
</tr>
<tr>
<td>Cl-OH</td>
<td>3 %</td>
<td>23 %$^b$</td>
</tr>
<tr>
<td>Cl-Cl</td>
<td>8 %</td>
<td>25 %</td>
</tr>
<tr>
<td>Acetone</td>
<td>&lt;1 %</td>
<td>5 %</td>
</tr>
</tbody>
</table>

| O atom yield$^d$ | 22 | 54 | 31 | 39 |
| Cl atom yield$^d$ | 33 | 60 | 25 | 57 |

$^a$ Yields are relative to the molar amount of 2 with an estimated error of 1%. $^b$ TME impurities at this high concentration are significant and may interfere. $^c$ 13 mM 6 (3% epoxide also formed). $^d$ O atom yield = 10 yield + 12 yield + acetone yield, Cl atom yield = 10 yield + 11 yield + 14 yield.

Hydroperoxide 13 is reported to be the major product of the TME reaction with singlet oxygen.$^{39}$ Its formation in the photolysis of 3 (Table 2.2.3) suggests triplet sensitization of O₂ with formation of singlet oxygen.$^{40}$ To investigate this possibility, the photolysis of 3 and TME was conducted in O₂-saturated C₆D₆ solutions. (All other photolyses were conducted in vacuum-degassed solutions backfilled with Ar.) The yield of 13 increased.
greatly such that the total yield of oxygen-containing products exceeds that possible from 3 alone, clearly indicating the involvement of the added O₂ in product formation. Photolysis of an O₂-saturated TME C₆D₆ solution does not produce 13. Thus, if 13 is produced from singlet oxygen in the degassed solutions of 3, the source of the O₂ must be 3, possibly from decomposition of photoeliminated HOCl into O₂ and HCl. Photolysis of 6 with TME in O₂-free and O₂-saturated solutions (Table 2.2.4) does not produce 13, indicating a difference in the photochemistry of 3 and 6.

Complex 7 is also photochemically active. Photolysis of a mixture of 6 (17%) and 7 (83%) gives predominately 2 (69%) with lesser amounts of trans-Pt(PEt₃)₂(Br)(4-trifluoromethylphenyl) 15 (31%), both in the presence and in the absence of TME (eq 5). Seventeen percent of the yield of 2 is from 6 with the remaining 52% coming from 7. Thus, the photolysis of 7 produces 2 and 15 in a 1:0.6 ratio suggesting that the reaction is primarily a net cis-photoelimination of the Br and OH groups. Consistent with HOBr photoelimination, TME products are primarily (21%) bromohydrin 16 (Chart 2) with no detectable chlorohydrin 10.

---

**Chart 2**

- **16**: Br, 21%
- **17**: Br, 4%
- **11**: Cl, 10%
- **14**: Cl, 7.5%
**Computational modeling.** Previously, we found that the M06 functional gave gas-phase thermodynamic estimates for Br$_2$ oxidative-addition to trans-PtL$_2$Br(R) complexes that matched well with toluene solution experimental measurements.$^{11}$ Extending these calculations to the current system using PMe$_3$ model complexes gave the free energies for reductive elimination of HOCl and Cl$_2$ in Scheme 2.2.2 (L = PMe$_3$).

**Scheme 2.2.2.** DFT gas-phase reductive elimination free energies (25°C, 1 atm).

As expected, the reductive-elimination free energies for HOCl and Cl$_2$ from *trans,cis*-Pt(PMe$_3$)$_2$(Cl)$_2$(OH)(9-phenanthryl) (3') and *trans,cis*-Pt(PMe$_3$)$_2$(Cl)$_2$(OH)(4-trifluoromethylphenyl) (6') are positive, indicating thermodynamically unfavorable reactions but favorable reverse oxidative-addition reactions. Chlorine elimination is disfavored over HOCl elimination by ~20 kcal. The Cl-Cl bond enthalpy is ~2 kcal/mol greater than the HO-Cl bond enthalpy, slightly favoring Cl$_2$ elimination.$^{41}$ A Pt-OH bond that is significantly weaker than the Pt-Cl bond must be invoked to explain the favored HOCl elimination. Indeed, the calculated (M06) Pt-OH and Pt-Cl (*trans* to OH) gas-phase bond dissociation enthalpies for 3' and 6' are 63.6 and 55.6, respectively for the Pt-
OH bond and 78.9 and 69.8, respectively for the Pt-Cl bond. Thus, the Pt-Cl bond (trans to OH) in 3' and 6' is stronger than the Pt-OH bond by 14-15 kcal/mol.

The relaxed triplet structures for the Pt(IV) complexes were also explored. Two triplet structures (3'T1 and 3'T2) from 3' and one (6'T2) from 6' were located at 40 to 45 kcal above the singlets (gas phase). Drawings of 3'T1 and 3'T2 are given in Figure 2.2.8. That for 6'T2 is given in the SI (Figure S35). The structures 3'T2 and 6'T2 are similar and only 3'T1 and 3'T2 will be discussed. Triplets 3'T1 and 3'T2 have distorted octahedral geometries and can be viewed as Jahn-Teller structures resulting from single occupancy of an e_g-type orbital. The two structures differ primarily in the extent of OH and Cl dissociation along the HO-Pt-Cl1 axis in the distorted octahedron. Both the Pt-OH and Pt-Cl1 distance increase by ca 0.3 Å on going from 3' to 3'T1. These distances also increase in 3'T2 but the increase is dominated by the Pt-Cl1 distance which increases by nearly 0.4 Å. Accompanying the Pt-Cl1 distance increase is a bending of the PMe_3 ligands in the direction of Cl1 such that the P1-Pt-P2 angle decreases from near linearity in 3' to 159.6° in 6'T2. Changes in the Pt-C and Pt-Cl2 distances are less than 0.1 Å. Both triplets appear to have weak hydrogen bonding between the OH group and Cl2.
Dissociative triplet excited states are a common feature of d⁶-octahedral metal complexes and can result in ligand dissociation reactions, either with heterolytic or homolytic bond cleavage. The loss of an OH and a Cl radical from the triplets was examined by optimizing the Pt(III) doublets Pt(PMe₃)₂(Cl)₂(R) (20', R = 9-phenanthryl; 21', R = 4-trifluoromethylphenyl) and Pt(PMe₃)₂(Cl)(OH)(R) (22', R = 9-phenanthryl; 23', R = 4-trifluoromethylphenyl) derived from OH or Cl removal from 3' and 6'. The resulting structures for R = 4-trifluoromethylphenyl are displayed in Figure 2.2.9. The optimized structures retain the parent configuration and are square pyramidal with a chloro or an hydroxo ligand in the axial position, although facile isomerization is expected for a
square-pyramidal complex. Atomic spin density values reveal spin density on the axial OH (0.3 e-) and Cl (0.5 e-) ligands suggesting substantial radical character for these ligands. (This is consistent with the first excited state NTO set in Figure 2.2.6.) Energetically, the loss of an OH group from either triplet, $3'^{T1}$ or $3'^{T2}$, is nearly energetically neutral, while that from $6'^{T2}$ is slightly (6 kcal) endergonic. Loss of a Cl atom from the triplets is unfavorable being ~18 kcal endergonic for $3'^{T1}$ or $3'^{T2}$ and 22 kcal endergonic for $6'^{T2}$.

**Figure 2.2.9.** Doublet structures 21’ and 23’ (carbon-bonded H atoms omitted for clarity).

Heterolytic bond cleavage with chloride and hydroxide ion dissociation was examined by optimization of the cations $[\text{Pt}(\text{PMe}_3)_2(\text{Cl})(\text{OH})(4\text{-trifluoromethylphenyl})]^+$ (24’) and $[\text{Pt}(\text{PMe}_3)_2(\text{Cl}_2)(4\text{-trifluoromethylphenyl})]^+$ (25’), derived from Cl⁻ and OH⁻ removal from 6’. The gas-phase free energies to dissociate an OH⁻ from 6’ to give 24’ and a Cl⁻ to give 25’ are, of course, very high (>100 kcal) due to charge separation without solvation. Applying a dichloromethane solvent correction (pcm model) lowers the free energies to 90.2 (24’) and 24.2 (25’) kcal. Relative to triplet $6'^{T2}$, the energies are 46.5 and -19.5
kcal. Clearly, hydroxide ion dissociation to $24^+$ is not favorable and unlikely to occur in this system. On the other hand, chloride ion dissociation appears favorable, at least in dichloromethane. However, with benzene as the solvent, an unfavorable energy of 60.4 kcal relative to $6^+$ (15.9 kcal relative to $6^{+\text{TJ}}$) is obtained, indicating that even chloride ion dissociation is probably unfavorable in benzene.

2.3 Discussion.

**Syntheses.** Pt(IV)-hydroxo complexes have been previously prepared by oxidative addition of H$_2$O$_2$ to Pt(II) complexes. However, this has been mostly restricted to Pt(II) complexes with amine or diimine ligands, research driven largely by the anti-tumor activity of Pt amine complexes. These reactions generally occur at, or slightly above, room temperature with 30% aqueous H$_2$O$_2$ to give dihydroxo complexes. The resistance of 1 and 2 to oxidation by 30% H$_2$O$_2$ was therefore unexpected but could be overcome with higher H$_2$O$_2$ concentrations. The Pt(II) oxidative addition mechanism for H$_2$O$_2$ has been proposed to be a 3-centered concerted process similar to C-H oxidative addition or to follow an ionic process similar to that for halogen oxidative addition; (a) oxidant electrophilic attack at an axial position with heterolytic cleavage of the oxidant, and then (b) capture of the 5-coordinate Pt(IV) cation by the oxidant anion or another available anion or ligand (Scheme 2.3.1). The capturing anion or ligand may also participate in the oxidation step by interaction with the Pt center opposite to the attacking oxidant, thereby bypassing the 5-coordinate Pt(IV) cation. In addition, isomerization can occur such that the final product does not contain a *trans* disposition of the added ligands.
Scheme 2.3.1. General mechanism for H₂O₂ oxidative addition.

Applying the ionic mechanism to the current system gives the proposed pathway to 3 and 4 given in Scheme 2.3.2. Here, capture of the 5-coordinate cation (or assistance in the oxidation) is by high-concentration H₂O₂, giving first trans-hydroperoxo-hydroxo 18, which then isomerizes to 4 or 5. Complex 5 is unstable, possibly due to the strong labilizing effect of the trans-9-phenanthryl group, and reaction of the hydroperoxo ligand with CH₂Cl₂ yields chloride ion for formation of 3. A relatively strong basic character for the hydroperoxo group is indicated by its selective protonation over the hydroxo group in the synthesis of 6 and 7 from 4 (Scheme 2.2.1). Since large excess H₂O₂ being used in the synthesis, capture of five-coordinate cation by H₂O₂ in the axial position has received more attention. An alternative mechanism for this has shown in Scheme 2.3.3. Coordination of H₂O₂ gives an ionic Pt(IV) complex, the subsequent reaction of hydroxyl ion with the free/coordinated H₂O₂ can yield hydroperoxo-hydroxo complex.
Scheme 2.3.2. Proposed oxidation of trans-Pt(PEt$_3$)$_2$RCl without H$_2$O$_2$ coordinated intermediate.

\[
\begin{align*}
\text{R-Pt-L} + \text{H}_2\text{O}_2 & \rightarrow \text{R-Pt-O-L} \quad \text{+ OH}^- \quad \text{+ H}_2\text{O}_2 \quad \text{+ OH}^- \\
\text{R-Pt-O-L} & \rightarrow \text{R-Pt-OH-L} \quad \text{+ H}_2\text{O}_2 \\
\text{R-Pt-OH-L} & \rightarrow \text{R-Pt-Cl-L} \quad \text{+ OH}^- \quad \text{+ H}_2\text{O}_2 \\
\text{R-Pt-Cl-L} & \rightarrow \text{R-Pt-Cl-L} \quad \text{+ OH}^- \quad \text{+ H}_2\text{O}_2 \\
\text{R-Pt-Cl-L} & \rightarrow \text{R-Pt-Cl-L} \quad \text{+ OH}^- \quad \text{+ H}_2\text{O}_2 \\
\text{CH}_2\text{Cl}_2 & \rightarrow \text{CH}_2\text{Cl}_2 \\
\text{R = phenanthryl} & \rightarrow \text{R = phenanthryl} \\
\text{3} & \rightarrow \text{3} \\
\text{4 (R = CF$_3$C$_8$H$_4$)} & \rightarrow \text{4 (R = CF$_3$C$_8$H$_4$)} \\
\text{5 (R = phenanthryl)} & \rightarrow \text{5 (R = phenanthryl)}
\end{align*}
\]

Scheme 2.3.3. Proposed oxidation of trans-Pt(PEt$_3$)$_2$RCl via H$_2$O$_2$ coordinated intermediate.

\[
\begin{align*}
\text{R-Pt-L} + \text{H}_2\text{O}_2 & \rightarrow \text{R-Pt-O-L} \quad \text{+ OH}^- \quad \text{+ H}_2\text{O}_2 \\
\text{R-Pt-O-L} & \rightarrow \text{R-Pt-OH-L} \quad \text{+ H}_2\text{O}_2 \\
\text{R-Pt-OH-L} & \rightarrow \text{R-Pt-Cl-L} \quad \text{+ OH}^- \quad \text{+ H}_2\text{O}_2 \\
\text{R-Pt-Cl-L} & \rightarrow \text{R-Pt-Cl-L} \quad \text{+ OH}^- \quad \text{+ H}_2\text{O}_2 \\
\text{R-Pt-Cl-L} & \rightarrow \text{R-Pt-Cl-L} \quad \text{+ OH}^- \quad \text{+ H}_2\text{O}_2 \\
\text{CH}_2\text{Cl}_2 & \rightarrow \text{CH}_2\text{Cl}_2 \\
\text{R = phenanthryl} & \rightarrow \text{R = phenanthryl} \\
\text{3} & \rightarrow \text{3} \\
\text{4 (R = CF$_3$C$_8$H$_4$)} & \rightarrow \text{4 (R = CF$_3$C$_8$H$_4$)} \\
\text{5 (R = phenanthryl)} & \rightarrow \text{5 (R = phenanthryl)}
\end{align*}
\]

**Photochemistry.** Understanding the photoreduction of 3 and 6 is challenging. Stoichiometry indicates HOCl elimination, but without direct detection of HOCl other possibilities exist that could give the final stoichiometry without HOCl ever being formed. (A previous report of HOCl photoelimination from prolonged irradiation of
Pt(IV) complexes assumes HOCl elimination by stoichiometry and bleaching of a dye.\textsuperscript{46} Unfortunately, HOCl is not stable in the presence of Pt(II) complexes 1 and 2, making direct detection difficult. Clearly, a strong oxidant is photochemically produced that oxidizes solvent benzene to chlorobenzene and other unidentified products, which retain some oxidizing power and oxidize added PPh\textsubscript{3}. This behavior parallels that of a benzene solution of HOCl, which decomposes rapidly under photolysis (313 nm), and, just like in the photolysis of 3 and 6, produces chlorobenzene and a solution that oxidizes PPh\textsubscript{3}.

Further support for HOCl formation is provided by the trapping experiments with 2 and TME. Complex 2 reacts with HOCl to produce trichloro complex 9. Any HOCl produced in the photolysis of 6 could react with photogenerated 2 to produce 9. In fact, 9 is observed in a 35\% yield in the absence of added TME. Adding 2 at the beginning of the reaction increases the yield of 9 such that 96\% of the theoretical HOCl would have been consumed in the formation of 9 from 2. With added TME, only traces of 9 form and the expected TME HOCl reaction products, chlorohydrin 10 and chlorinated 11, are observed. However, the yield is rather low, especially for 3, and a number of other products (12-14) are also produced, but these could arise from HOCl decomposition products.

Alternatives to HOCl elimination to consider are ionic and radical processes. Bromide photodissociation is reported for [PtBr\textsubscript{6}]\textsuperscript{2-} in water and MeOH\textsuperscript{42f, 42g, 47} and we have shown that net bromide photodissociation also occurs in CH\textsubscript{2}Cl\textsubscript{2}.\textsuperscript{11} Chloride or hydroxide photodissociation from 3 or 6 would produce a Pt(IV) complex,\textsuperscript{48} perhaps in an excited state and capable of alkene or even benzene oxidation. Alkene chlorination by Pd(IV) chloro complexes has been reported and Pt(IV) complexes are involved in hydrocarbon
oxidation in Shilov-type chemistry.\textsuperscript{49} Arguing against an ionic pathway is the absence of any significant change in reactivity and products on going from CH\textsubscript{2}Cl\textsubscript{2} to benzene (at least for 3) where ion formation should be disfavored. The DFT modeling of chloride and hydroxide photodissociation suggests that chloride dissociation is possible in CH\textsubscript{2}Cl\textsubscript{2}, though probably not in benzene. Hydroxide dissociation is, however, unlikely.

Another ionic pathway to consider is excited-state, single-electron transfer (SET). This has been proposed for photoplatination of aromatic compounds with [PtCl\textsubscript{6}]\textsuperscript{2-}, \textsuperscript{50} and for [PtBr\textsubscript{6}]\textsuperscript{2-} photoreduction in the presence of high bromide ion concentrations\textsuperscript{51} or in methanol solution.\textsuperscript{52} However, it was recently concluded that SET follows Br\textsuperscript{-} photodissociation for [PtBr\textsubscript{6}]\textsuperscript{2-}.\textsuperscript{42g} The photoreduction of 3, 6 and 7 proceeds equally well in the presence of electron-rich TME or simply in toluene, benzene, CH\textsubscript{2}Cl\textsubscript{2}, or CDCl\textsubscript{3} solvent. Oxidation by SET in these various solvents seems unlikely.

A radical reaction pathway would be consistent with the near solvent independence of the photochemistry of 3, 6 and 7 and radical photoelimination from Pt(IV) is known. [PtCl\textsubscript{6}]\textsuperscript{2-} is thought to photoeliminate a chlorine atom\textsuperscript{42g}.\textsuperscript{53} and Pt(IV) methyl complexes photoeliminate a methyl radical.\textsuperscript{54} In addition, the DFT calculations on triplets 3\textsuperscript{T1}, 3\textsuperscript{T2} and 6\textsuperscript{T2} show large spin density on the OH and Cl axial ligands and elongation of the Pt-OH and Pt-Cl bonds, suggesting insipient formation of a geminate Pt(III)/OH radical pair from the triplet excited state. An OH or Cl radical would certainly be reactive enough to drive the photochemistry under a variety of conditions. According to the DFT calculations, OH radical formation is more favorable and the resulting Pt(III) complexes (modeled with 20’ and 21’) have large spin densities on the axial Cl atoms, suggesting possible Cl atom abstraction from Pt by the OH radical (probably within the solvent cage).
with net HOCl elimination. (Teets and Nocera suggested something similar for molecular halogen photoelimination from Au(III) halide complexes.\textsuperscript{10}) To account for the preferred \textit{cis}-elimination indicated by the photochemistry of bromo-hydroxo complex 7, we propose that geometric isomerization of the 5-coordinate Pt(II) complexes (20' and 21') interconverts the axial and equatorial chloro ligands bringing the former \textit{cis}-chloro ligand into the axial position for abstraction by the OH radical. This pathway is summarized in Scheme 2.3. and assumes either direct excitation into the triplet manifold or rapid intersystem crossing following singlet excitation. TDDFT does indicate matching triplet transitions for the first two singlet transitions and small energy gaps, consistent with facile intersystem crossing.

Scheme 2.3.5. Possible photoelimination pathway with DFT gas-phase free energies in kcal/mol for model complexes. (Black for R = 9-phenanthryl, blue for R = 4-CF\textsubscript{3}C\textsubscript{6}H\textsubscript{4}.)
An alternative to HOX elimination that could also follow from OH radical formation is depicted in Scheme 2.3. In this scheme, the OH radical either abstracts a hydrogen atom from solvent or TME or adds to solvent or TME. In either case, a carbon-based radical is then generated which can then abstract a halogen atom from the Pt(III) center. This scheme accounts for solvent oxidation, TME chlorination and formation of the chlorohydrin.

Scheme 2.3.6. Substrate-assisted *cis*-elimination pathway from hydroxo radical/Pt(III) geminate pair.

2.4 Conclusions.

The low kinetic reactivity of the Pt(II) phosphine complexes with H$_2$O$_2$ bodes well for H$_2$O$_2$ photoelimination from Pt(IV) dihydroxo complexes as this is the back reaction and H$_2$O$_2$ disproportionation may not be required to prevent it. When oxidation of the Pt(II) center by H$_2$O$_2$ does occur, the required high H$_2$O$_2$ concentrations result in trapping of the initial oxidation product with H$_2$O$_2$ and hydroperoxo-hydroxo complexes result
instead of the expected dihydroxo complexes. Selective replacement of the hydroperoxo ligand with a halide ligand can occur spontaneously in CH₂Cl₂ or by treatment with HX.

The photochemistry of the hydroxo-halo complexes is net HOX elimination. The photochemical pathway most consistent with the behavior of the system (trapping products and solvent insensitivity) and the DFT modeling is excitation into the lowest energy triplet excited state (either directly or via internal conversion and intersystem crossing) followed by geminate Pt(III)/hydroxo radical pair formation. The hydroxo radical can then either abstract a halide from the Pt(III) center forming HOX that decomposes and reacts with solvent and/or trap or the hydroxo radical can react directly with the alkene trap and/or solvent to produce a carbon-based radical that then abstracts a halogen from the Pt(III) center. Both processes could be operating simultaneously.

2.5 Experimental section.

**General considerations.** Pt(PEt₃)₄⁵⁵ was prepared by a reported procedure. Reagents and solvents were purchased from commercial sources (Aldrich or Acros). Synthetic procedures were performed without exclusion of air with unpurified solvents unless otherwise noted. Platinum complex photolysis samples were prepared under a dinitrogen atmosphere in a Vacuum Atmospheres Corporation drybox or on a Schlenk line. Photolysis solvents were dried, degassed and stored under dinitrogen over 4 Å molecular sieves. NMR spectra were recorded on Bruker AMX-250, -300, or -500 spectrometers at ambient probe temperatures except as noted. NMR shifts are given in δ with positive values downfield of tetramethylsilane, Si(CH₃)₄ (¹H and ¹³C), external H₃PO₄ (³¹P),
external CFCl₃ (¹⁹F), or external K₂PtCl₄ (aq) (¹⁹⁵Pt, δ -1630). ¹³C, ¹⁹F, ¹⁹⁵Pt and ³¹P NMR spectra were recorded in proton-decoupled mode. Microanalyses were completed by ALS Environmental or Atlantic Microlab. UV-Visible absorption spectra were recorded on a Cary 50 or Hewlett-Packard 8452 diode array spectrophotometer in quartz cells. Photolyses were performed in quartz (UV) or borosilicate glass vessels using a Philips PL-S 9W/01, 9 W lamp (313 nm emission), or LED’s (superbrightleds.com) of the indicated wavelength.

**trans-Pt(PEt₃)₂Cl(4-trifluoromethylphenyl)** (2). A solution of 1-chloro(4-trifluoromethy)benzene (23 mg, 0.13 mmol) in THF (~2 mL) was added to a clear orange solution of Pt(PEt₃)₄ (70 mg, 0.10 mmol) in THF (~2 mL). The resulting clear orange solution was stirred for ~20 h at 140 °C in a sealed tube to yield a pale yellow solution. The mixture was cooled to ambient temperature and the volatiles were removed in vacuo. The solid residue was dissolved in ~2 mL CH₂Cl₂ and transferred to a 4 mL vial. The volume was reduced in vacuo to ~0.5 mL followed by the addition of ~1 ml of methanol. The vial was capped and stored in at -20 °C overnight to afford colorless crystals. The mother liquor was pipetted out and the crystals were dried in vacuo to yield 40 mg (63 %) of 2.

³¹P NMR (101 MHz, CDCl₃): 14.5 (s with satellite, Jₚₚ = 2733 Hz).

¹⁹F NMR (235 MHz, CDCl₃): -62.0 (s).
**trans-Pt(PEt\textsubscript{3})\textsubscript{2}(Cl)(9-phenanthryl) (1).** This complex was prepared from 9-chlorophenanthrene by a procedure similar to that for 2.

\(^{31}\text{P} \text{NMR} (101 \text{ MHz, CD}_{2}\text{Cl}_{2}): 14.10 \text{ (s with satellite, } J_{\text{PtP}} = 2735 \text{ Hz).} ^{31}\text{P} \text{NMR} (101 \text{ MHz, C}_6\text{D}_6): 13.97 \text{ (s with satellite, } J_{\text{PtP}} = 2736 \text{ Hz).}

\(^1\text{H} \text{NMR} (250 \text{ MHz, CD}_{2}\text{Cl}_{2}): 8.97-8.93 \text{ (m, 1H), } 8.62-8.57 \text{ (m, 2H), } 7.82 \text{ (s with satellites, } J_{\text{PtH}} = 75 \text{ Hz, 1H), } 7.69-7.65 \text{ (m, 1H), } 7.57-7.46 \text{ (m, 4H), } 1.70-1.40 \text{ (m, 12H, CH}_2\text{), } 1.08-0.96 \text{ (app quintet, } J = 8.2 \text{ Hz, 18H, CH}_3\text{).}

\(^1\text{H} \text{NMR} (250 \text{ MHz, C}_6\text{D}_6): 9.28 \text{ (d, } J_{\text{HH}} = 7.50 \text{ Hz, 1H), } 8.59 \text{ (t, } J_{\text{HH}} = 7.50 \text{ Hz, 2H), } 8.09 \text{ (s with satellites, } J_{\text{PtH}} = 75.0 \text{ Hz, 1H), } 7.75 \text{ (d, } J_{\text{HH}} = 7.50 \text{ Hz, 1H), } 7.58 \text{ (t, } J_{\text{HH}} = 7.50 \text{ Hz, 1H), } 7.49-7.37 \text{ (m, 3H), } 1.62-1.28 \text{ (m, 12H, CH}_2\text{), } 0.89-0.77 \text{ (app quintet, } J = 8.2 \text{ Hz, 18H, CH}_3\text{).}

**Preparation of H\textsubscript{2}O\textsubscript{2} in ether.**\textsuperscript{56} Approximately 7 mL of 30\% H\textsubscript{2}O\textsubscript{2} was placed in a 20 mL vial and then 7 mL of diethylether was added. The vial was capped tightly and the contents stirred vigorously for a minimum of 2 h. (Caution: while we never observed H\textsubscript{2}O\textsubscript{2} decomposition and O\textsubscript{2} evolution, this is a possibility and a mechanism for pressure release should be provided.) The ether layer (upper layer) was then pipetted into another 20 mL vial. The solution was then concentrated in vacuo to 0.5-1 mL. The concentrated solution was not stored but used immediately in the following syntheses.
trans,cis-Pt(PEt$_3$)$_2$Cl$_2$(OH)(9-phenanthryl) (3). trans-Pt(PEt$_3$)$_2$Cl(9-phenanthryl) (1) (10.1 mg, 0.0157 mmol) in 1.5 mL dichloromethane was mixed in a 20 mL vial with 1 mL of a freshly prepared H$_2$O$_2$ solution in diethylether. (The preparation of the H$_2$O$_2$ solution is described above.) The vial was capped with a rubber septum and a needle inserted to release the pressure generated during the reaction. The mixture was stirred and monitored by $^{31}$P NMR spectroscopy. The colorless solution became yellowish orange and conversion of 1 ($\delta$ 14.1) to product 3 along with small amounts of OPEt$_3$ ($\delta$ 50-60) was observed. ($^{31}$P NMR shifts varied with the water content of the reaction mixture.) An intermediate (5) was detected at $\delta$ 6-7 and was gone by the end of the reaction. If the reaction was not complete after 10-12 h additional H$_2$O$_2$ solution was added. Once the reaction was complete, the dichloromethane layer was separated from the aqueous layer (from H$_2$O$_2$ decomposition) and washed with 3 x 5 mL of deionized water and then dried over MgSO$_4$. After filtering, the volatiles were removed in vacuo. The resulting solid was re-dissolved in about 0.5 mL of dichloromethane and 1 mL of hexane was added. A pale orange precipitate (not identified) formed and was removed by filtration. The yellow filtrate was checked by $^{31}$P NMR spectroscopy and showed only product 3. The filtrate was concentrate and then stored at -20 °C to obtain 7.4 mg (68%) of yellow 3. Yellow crystals for the X-ray analysis were grown similarly but in an open vial in the freezer.

Anal. Calc. (found) for PtP$_2$Cl$_2$OC$_{26}$H$_{40}$0.3MeOH0.5H$_2$O: C, 44.26 (44.03); H, 5.86

$^{31}$P NMR (101 MHz, CD$_2$Cl$_2$): 3.22 (s with satellites, $J_{PP} = 1740$ Hz). $^{31}$P NMR (101 MHz, C$_6$D$_6$): 2.29 (s with satellites, $J_{PP} = 1757$ Hz).

$^{195}$Pt NMR (64MHz, CD$_2$Cl$_2$): -1754 (t, $J_{PP} = 1751$ Hz).

$^1$H NMR (250 MHz, CD$_2$Cl$_2$, CDCl$_3$): 9.14 (d, $J_{HH} = 7.50$ Hz, 1H), 8.54 (t, $J_{HH} = 7.50$ Hz, 2H), 8.18 (s with satellites, $J_{PH} = 50.02$ Hz, 1H), 7.78 (d, $J_{HH} = 7.50$ Hz, 1H), 7.64-7.52 (m, 4H), 2.06-1.99 (m, 12H, CH$_2$), 1.02-0.89 (app quintet, $J_{HH} = 8.0$ Hz, 18H, CH$_3$), 0.13 (s, 1H, OH). The OH group signal was observed only after treating the sample with polymer bound diethylamine and could be eliminated by D$_2$O addition.

\[\text{trans-Pt(PET}_3\text{)Cl(OH)(OOH)(4-trifluoromethylphenyl)} \quad (4)\]

$\text{trans-Pt(PET}_3\text{)Cl(OH)(OOH)(4-trifluoromethylphenyl)}$ (2) (13.5 mg, 0.022 mmol) in 1.5 mL of dichloromethane was mixed in a 20 mL vial with a freshly prepared H$_2$O$_2$ solution in diethylether (1 mL). The vial was capped with a rubber septum and a needle inserted to release the pressure generated during the reaction. The mixture was stirred for 3 h at room temperature during which time the solution turned pale yellow and conversion of 2 ($\delta$ 14.4) to $\text{trans-Pt(PET}_3\text{)Cl(OH)(OOH)(4-trifluoromethylphenyl)}$ (4) ($\delta$ 5-4) was observed by $^{31}$P NMR spectroscopy ($^{31}$P NMR shifts varied slightly with the water content of the reaction mixture.). Once the reaction was complete, the dichloromethane layer was separated,
washed with 3 x 5 mL of deionized water and dried with MgSO₄. After filtering, the volatiles were removed \textit{in vacuo}. The resulting solid was re-dissolved in about 0.5 mL of dichloromethane and 1 mL of hexane was added. Evaporation of the solution at -20 °C yielded 13 mg (89 %) of pale yellow crystals that were suitable for X-ray analysis.

\(^{31}\)P NMR (101 MHz, CDCl\(_3\)): 1.09 (s with satellite, \(J_{\text{pp}} = 1770\) Hz).

\(^{19}\)F NMR (235 MHz, CDCl\(_3\)): -62.27 (s).

\(^1\)H NMR (250 MHz, CDCl\(_3\)): 8.05 (d with satellites, \(J_{\text{HH}} = 7.50\) Hz, \(J_{\text{PH}} = 45\) Hz, 1H), 7.88 (d with satellites, \(J_{\text{HH}} = 7.50\) Hz, \(J_{\text{PH}} = 45\) Hz, 1H), 7.29 (m, 2H), 6.42 (s, 1H, OOH), 2.00-1.89 (m, 12H, CH\(_2\)), 1.11-1.00 (app quintet, \(J_{\text{app}} = 7.9\) Hz, 18H, CH\(_3\)), 0.20 (s with satellites, \(J_{\text{PH}} = 40\) Hz, 1H, OH). The OH group signal is concentration dependent in CDCl\(_3\) (and CD\(_2\)Cl\(_2\)). As concentration increases (above ~0.01 mol L\(^{-1}\)) the signal broadens and the \(^{195}\)Pt satellites move in and eventually merge with the main peak. The OOH signal also broadens. D\(_2\)O addition causes complete loss of the OH and OOH signals.

\[\textit{trans,cis-Pt(PEt}_3\text{)\textsubscript{2}(Cl)\textsubscript{2}(OH)(4-trifluoromethylphenyl)}\) (6). Compound 4 was dissolved in 1 mL of dichloromethane and approximately 2 mL of deionized water and 0.05 mL dilute HCl (50 μL of conc HCl in 1-2 mL water) was added and the mixture was stirred for 1 min. \(^{31}\)P NMR spectroscopy showed complete conversion of 4 to 6 (δ 1.09). The
dichloromethane layer was washed with 10 mL of deionized water and dried with MgSO$_4$. After filtration, the volatiles were removed in vacuo. The resulting solid was washed with 1.0 mL of cold hexane and dried in vacuo to give 12.0 mg (88%) of 6. Pale yellow crystals for the X-ray analysis were grown in ether/heptane (1:5) by slow evaporation in the freezer.

$^{31}$P NMR (101 MHz, CDCl$_3$ or CD$_2$Cl$_2$): 1.09 (s with satellites, $J_{PP} = 1708$ Hz). $^{31}$P $^{57}$ NMR (101 MHz, C$_6$D$_6$): 0.16 (s with satellites, $J_{PP} = 1708$ Hz).

$^{19}$F NMR (235 MHz, CDCl$_3$ or CD$_2$Cl$_2$): -62.30.

$^{195}$Pt NMR (64 MHz, CDCl$_3$): -1944 (t, $J_{PP} =1720$ Hz).

$^1$H NMR (250 MHz, CDCl$_3$): 8.16 (d with satellites, $J_{HH} = 7.50$ Hz, $J_{PH} = 42$ Hz, 1H), 7.93 (d with satellites, $J_{HH} = 7.50$ Hz, $J_{PH} = 42$ Hz, 1H), 7.33 (m, 2H), 2.00-1.85 (m, 12H, CH$_2$), 1.13-1.03 (app quintet, $J_{app} = 8.0$ Hz, 18H, CH$_3$), -0.48 (s with satellites, $J_{PH} = 40$ Hz, 1H, OH). The OH group signal is concentration dependent in CDCl$_3$ (and CD$_2$Cl$_2$). As concentration increases (above ~0.01 mol L$^{-1}$) the signal broadens and the $^{195}$Pt satellites move in and eventually merge with the main peak. D$_2$O addition causes complete loss of the OH signal.

$^1$H NMR (250 MHz, C$_6$D$_6$): 8.41 (d with satellites, $J_{HH} = 8.25$ Hz, $J_{PH} = 42$ Hz ,1H), 8.25 (d with satellites, $J_{HH} = 8.25$ Hz, $J_{PH} = 38.5$ Hz ,1H), 7.36 (d, $J_{HH} = 8.25$ Hz,1H), 7.31 (d, $J_{HH} = 8.25$ Hz, 1H), 1.78-1.63 (m, 12H, CH$_2$), 0.81-0.68 (app quintet $J_{app} = 8.0$ Hz, 18H, CH$_3$), -0.4 (br s, 1H, OH).
trans-Pt(PEt$_3$)$_2$(Br)(Cl)(OH)(4-trifluoromethylphenyl) (7). Compound 4 was dissolved in 1 ml of dichloromethane and approximately 2 mL of deionized water and 0.05 mL 50% HBr was added and the mixture stirred for 1 min. $^{31}$P NMR spectroscopy showed complete conversion of 4 to 7 (δ -2.09). The dichloromethane layer was washed with 10 mL of deionized water dried with MgSO$_4$. After filtering, the volatiles were removed *in vacuo*. The resulting solid was washed with 1.0 mL of cold hexane and dried *in vacuo* to give 7. Pale yellow crystals for the X-ray analysis were grown in CH$_2$Cl$_2$/heptane (1:2) by slow evaporation in the refrigerator.

$^{31}$P $^{57}$ NMR (101 MHz, CD$_2$Cl$_2$): -2.09 (s with satellite, J$_{PP}$ = 1703 Hz).

$^1$H NMR (250 MHz, CD$_2$Cl$_2$): 8.15 (d with satellites, J$_{HH}$ = 7.50 Hz, J$_{PH}$ = 44 Hz, 1H), 7.95 (d with satellites, J$_{HH}$ = 9.50 Hz, J$_{PH}$ = 39 Hz, 1H), 7.38-7.34 (m, 2H), 2.00-1.86 (m, 12H, CH$_2$), 1.11-0.98 (app quintet, J$_{app}$ = 7.75 Hz, 18H, CH$_3$), -0.6 (brs, 1H, OH).

**UV-Visible absorption spectra.** *Trans,cis-Pt*(PEt$_3$)$_2$(OH)Cl$_2$(9-phenanthryl) (3) (3.2 mg, 0.0046 mmol) was dissolved in HPLC grade CH$_2$Cl$_2$ and diluted to the mark in a 5.00 mL volumetric flask. This solution (0.92 mM) was used as a stock solution for the analysis. A series of concentrations was prepared by diluting 40, 50, 60, 70 and 80 μL into 5.0 mL volumetric flasks. The solvent blank was obtained and spectra were recorded from 200 to 800 nm for each sample. *Trans-Pt*(PEt$_3$)$_2$(OH)Cl$_2$(4-trifluoromethylphenyl) (6) (20.1 mg,
0.0303 mmol) was dissolved in HPLC grade CH$_2$Cl$_2$ and diluted to the mark in a 10.00 mL volumetric flask. This stock solution (3.03 mM) was used to prepare a series of concentrations was prepared by diluting 20, 30, 40 and 50 μL into 5.0 mL volumetric flasks. All the experimental conditions were kept identical for 3 and 6 except for the concentrations. The absorbance data collected for the above samples were converted to molar extinction coefficient, averaged, and plotted (Figure 2.2.4).

**Preparation of HOCl from Ca(OCl)$_2$.** Solid Ca(OCl)$_2$ (100 mg, 0.70 mmol) was added to a 100 mL Schlenk flask. The stopcock plug was removed from the flask and replaced with a rubber septum. The flask was then connected to a vacuum line. Solvent (H$_2$O, C$_6$D$_6$, or CDCl$_3$; 0.50 mL) was added into a 5 mm NMR tube. The tube was connected to the vacuum line and immersed in LN$_2$. The frozen NMR tube and the Schlenk flask were connected and kept under vacuum for 10 min. After reaching a vacuum of 50 mtorr, the connection to the vacuum line was closed and concentrated H$_2$SO$_4$ or HCl (0.10 mL) was injected through the rubber septum onto the solid Ca(ClO)$_2$. (The Schlenk flask was isolated from the NMR tube prior to the addition of H$_2$SO$_4$ and reconnected 5 min post injection.) The gaseous products were condensed into the NMR tube. The tube was thawed and the solution was transferred into a 1 cm path length quartz cuvette for recording of the UV-Vis absorption spectrum (Fig S2). Solid NaOH (~20 mg, 0.50 mmol) was added to the cuvette with stirring. The spectrum was recorded and showed $\lambda_{max}$ for the ClO$^-$ at 292 nm, as reported in previous studies.$^{58}$

**Synthesis of HOCl from HgO and Cl$_2$.**$^{36}$ Freshly prepared HgO (100 mg, 0.46 mmol) was added to 2 mL of double distilled water (DDW) in an 8 mL vial. Chlorine gas (1 mL, 0.045 mmol), dissolved in 1 mL of DDW, was immediately added and the mixture was
stirred for 30 min. Filtration through diatomaceous earth yielded a clear solution. The solution was transferred to a 1 cm path-length cuvette and the UV-Vis absorption spectrum was recorded (Fig S2).

**Reaction of HOCl with TME.** (A) HOCl was generated from Ca(OCl)₂ as described above but the gaseous products were condensed into a mixture of CDCl₃ (0.50 mL) and TME (2,3-dimethyl-2-butene) (~30 µL) instead of water. The mixture was thawed and ¹H NMR analysis indicated the formation of TME products. (B) A solution of HOCl from HgO and Cl₂ was generated as described above but with water saturated CDCl₃ as the solvent instead of DDW. After thawing the NMR tube, TME was added and the mixture was analyzed by ¹H NMR spectroscopy.

**Photolysis of HOCl.** Three identical samples of HOCl in C₆D₆ were prepared from Ca(OCl)₂ as described above. TME (~30 µL) was added to one and the products determined by ¹H NMR spectroscopy (Chart1). Another sample was photolyzed at 313 nm for 8 min and then TME was added. No TME products were observed except for 11 (TME and Cl₂ yields 11). The third sample was photolyzed at 380 nm for 8 min and then TME was added. No TME oxidation was detected. In other experiments, C₆H₆ samples of HOCl were photolyzed at 313 nm and 380 nm without trap. Chlorobenzene was detected by ¹H NMR in both samples.

**Reaction of HOCl with PPh₃ and 1.** PPh₃ (3.5 mg, 0.015 mmol) was dissolved in 0.8 mL of C₆D₆. A dilute C₆D₆ solution of HOCl, prepared by diluting a 0.05 mL aliquot of a C₆D₆ HOCl solution (prepared from Ca(OCl)₂ as described above) to 0.4 mL, was added in portions until the ³¹P NMR signal for PPh₃ (δ -4.9) disappeared. The only product detected by ³¹P NMR spectroscopy was OPPh₃ (δ 28.0).

**Reaction of HOCl with 1 or 2.** A solution of 1 (0.02 M) in C₆D₆ was mixed with 0.05 mL aliquot of HOCl made in C₆D₆ (prepared from Ca(OCl)₂). The ³¹P NMR signal for 8
was observed. The only product detected by $^{31}$P NMR spectroscopy was 8 and remaining 1. Similar experiment was carried out with 2 and yielded 9.

**Reaction of photolyzed 3 with PPh$_3$.** A sample of 3 (2.0 mg, 0.0029 mmol) was photolyzed at 313 nm in ~0.5 mL C$_6$D$_6$ until all 3 had been consumed. Excess PPh$_3$ (5 mg, 0.019 mmol) was added. A 22 % yield of OPPh$_3$ was observed by $^{31}$P NMR spectroscopy.

**Photolysis of trans,cis-Pt(PEnt)$_2$Cl$_2$(OH)(9-phenanthryl) (3).** Photolysis experiments were performed at 313 and 380 nm in C$_6$D$_6$ and CD$_2$Cl$_2$. A 0.011 M solution of 3 was added to a 5 mm J. Young NMR tube. Photolysis was then carried out with periodic $^{31}$P NMR and $^1$H NMR monitoring. Compound 3 was observed to convert to 1 (colorless) although the solution remained yellow orange and did not become colorless as expected for 1.

**Photolysis of trans,cis-Pt(PEnt)$_2$Cl$_2$(OH)(4-trifluoromethylphenyl) (6).** The photolysis experiments were performed at 313 nm in CDCl$_3$, CD$_2$Cl$_2$ and C$_6$D$_6$. Solutions of 6 (0.018 M) were photolyzed in the presence of variable amounts of TME. Irradiation times were 14-17 min. Spectroscopic analysis (NMR) was carried out within 5 min of the photolysis and the results are given in Table 2.2.4.

**Photolysis of 6 in the presence of 2.** A 5 mm NMR tube was charged with 0.5 mL of a CH$_2$Cl$_2$ solution that was 0.018 M in of 6 and 0.016 M in 2. A capillary tube containing a solution of PPh$_3$ was added to the tube to serve as an integration standard. The sample was then photolyzed at 313 nm. $^{31}$P NMR analysis was carried out at 30 s intervals until all 6 was consumed (13 min total). At the end of the photolysis a 48% conversion of 2
into trichloro complex 9 was indicated. A maximum conversion of 50% is expected from the available chlorine in 6.

Photolysis of trans-Pt(PEt$_3$)$_2$(Br)(Cl)(OH)(4-trifluoromethylphenyl) (7). The photolysis experiments were performed similarly to those for 6 in CD$_2$Cl$_2$ both with and without TME. The bromohydrin 16 was identified by comparison of the NMR properties ($^1$H NMR in CDCl$_3$: δ 1.84, 1.35) with an authentic sample prepared by HBr addition to the epoxide. NMR data for 17 have been reported.$^{59}$

NMR data for trans-Pt(PEt$_3$)$_2$(Br)(4-trifluoromethylphenyl) (15).

$^{31}$P $^{57}$NMR (101 MHz, CD$_2$Cl$_2$): 12.4 (s with satellite, J$_{PtP}$ = 2709 Hz).

$^1$H NMR (250 MHz, CD$_2$Cl$_2$): 7.50 (d with satellites, J$_{HH}$ = 10 Hz, J$_{PtH}$ = 67.50 Hz, 2H), 7.17-7.11 (m, 2H), 1.74-1.59 (m, 12H, CH$_2$), 1.12-0.99 (app quintet, J$_{app}$ = 8.10 Hz, 18H, CH$_3$).

Quantum Yield Determination. Irradiations were performed in the compartment of a Cary 50 UV-Vis spectrometer equipped with a magnet stirrer and temperature control. The sample was contained in a 1 cm quartz cuvette sealed at the top with a quartz microscope slide. The light source was positioned over the sample compartment allowing irradiations through the top of the cuvette.$^{60}$ The photon flux was measured (Fe oxalate actinometry$^{61}$) before and after each sample irradiation and the average of the before and after measurements was used as the photon flux during the sample irradiation. Sample solution concentrations were sufficiently high to assure complete photon absorption (absorbance ≥ 2 at the irradiation wavelength) over the ~3 cm depth of the solution. Reaction progress was monitored by the UV-Vis absorbance of product trans-Pt(PEt$_3$)$_2$Cl$_3$(4-trifluoromethylphenyl) (8) over the region of 310-400 nm where trans-
Pt(PEt$_3$)$_2$Cl(4-trifluoromethylphenyl) (2) does not absorb and trans-Pt(PEt$_3$)$_2$Cl$_2$(OH)(4-trifluoromethylphenyl) (6) absorbance is relatively weak. The yield of 8 from the UV-Vis (0.3 mM) data is 34% and matches the yield determined by $^{31}$P NMR spectroscopy (1 mM). The absorbance increase at three wavelengths (365 nm, 375 nm, 390 nm) during the first 10% of the reaction was used to calculate the quantum yield. The average of three runs gave a final quantum yield for 6 of 51 ± 2% in dichloromethane.

**Computational Details**

Gaussian 09 (revision A.1 or C.1) with the M06 or CAM-B3LYP (TDDFT) functional were used for all calculations. The LANL2DZ basis set was employed for Pt, Cl and P with an added d function ($\alpha = 0.05$) for Pt, d ($\alpha = 0.648$) and p ($\alpha = 0.0467$) functions for Cl, and d ($\alpha = 0.434$) and p ($\alpha = 0.0376$) functions for P. The 6-31G(d) basis set was used for all other atoms. Initial structures were derived from crystal coordinates and were modified with Gaussview. All geometries were optimized with no symmetry constraints in the gas phase. Free energies, enthalpies, and entropies were calculated at 298.15 K and 1 atm. Analytical frequency calculations gave no imaginary frequencies for the complexes except for 3’, which had a small imaginary frequency of -11 cm$^{-1}$ associated with a methyl group rotation. TDDFT calculations included solvent (dichloromethane) with the polarized continuum model (pcm) and employed the gas-phase optimized structures.
CHAPTER 3: DIHYDROGEN TRIOXIDE (HOOOH) PHOTOLEXIMATION
FROM A PLATINUM(IV) HYDROPEROXO-HYDROXO COMPLEX.

3.1 Introduction.

The synthesis of trans-Pt(PEt$_3$)$_2$(Cl)(OH)(OOH)(4-tft) 4 was already discussed in the previous chapter. Here now is reported the thermal and photo chemistry of 4, which includes reductive elimination of HOOOH (H$_2$O$_3$, dihydrogen trioxide or trioxydane), a rare example of O-O bond formation by photo reductive elimination. (Other examples feature hydrogen peroxide elimination). The chemistry discussed later in this chapter includes computational modeling studies on the thermodynamics and mechanisms for these unusual reactions.

3.2 Photochemistry.

Irradiation (380 nm) of trans-Pt(PEt$_3$)$_2$(Cl)(OH)(OOH)(4-tft) 4 (4-tft = 4-trifluoromethylphenyl) at ambient temperature for ~8 min in C$_6$D$_6$ results in Pt-center reduction, yielding the Pt(II) complex trans-Pt(PEt$_3$)$_2$(Cl)(4-tft) 2, water, and presumably O$_2$ (eq 6).
This observation caught our attention as there are at least two possible pathways to water and O\textsubscript{2}. One would be directly through photo-driven OH abstraction of a hydrogen atom from the OOH ligand. (We initially considered this to be the more likely pathway.) The other would be by decomposition of H\textsubscript{2}O\textsubscript{3}, the expected photo reductive- elimination product if the photochemistry of 4 follows that of the analogous hydroxo-halo complexes \textit{trans}-Pt(P\textsubscript{Et\textsubscript{3}}\textsubscript{2})(Cl)(OH)(X)(4-tft) (X = Cl, Br)\textsuperscript{27} and bromo complexes \textit{trans}-Pt(P\textsubscript{Et\textsubscript{3}}\textsubscript{2}(Br)\textsubscript{3}R.\textsuperscript{11} With these possibilities in mind, the photolysis of 4 was reexamined at -78 °C.

An acetone-d\textsubscript{6} sample of 4 in an NMR tube was cooled to -78 °C and irradiated at 380 nm. \textsuperscript{1}H NMR analysis was then carried out at -60 °C and revealed a singlet at δ 13.4 that reached a maximum at 40-60% conversion of 4 into 2 and then declined and disappeared as the irradiation continued. The peak also disappeared when the sample was warmed to RT. The experiment was repeated in toluene-d\textsubscript{8} where H\textsubscript{2}O\textsubscript{3} gives a singlet at δ 9.9.\textsuperscript{26} A singlet at this chemical shift was observed at -60 °C confirming the formation of H\textsubscript{2}O\textsubscript{3} from the photolysis of 4 (eq 7). \textsuperscript{1}H NMR spectral integration indicated an H\textsubscript{2}O\textsubscript{3} yield\textsuperscript{74} of 16 ± 2% in toluene-d\textsubscript{8} and 6 ± 2% in acetone-d\textsubscript{6} at 40-60% conversion of 4. However, it was noticed that the OOH signal of 4 was considerably diminished (by 70%) in acetone-d\textsubscript{6} and that a signal for HOD was present. We interpret this as deuterium exchange of the OH and OOH ligands with residual D\textsubscript{2}O from the acetone-d\textsubscript{6} preparation.\textsuperscript{75,76} Correcting for this exchange increases the H\textsubscript{2}O\textsubscript{3} yield in acetone-d\textsubscript{6} to 20%, similar to that in toluene-d\textsubscript{8}.  

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Also detected in the low temperature acetone-$d_6$ sample were $^1$H NMR peaks in the $\delta$ 9-12 region attributed to H$_2$O$_2$ (9%) and acetone adducts 19 (16%) and 20 (36%) giving a total product yield of 81%. (Yields$^{74}$ include adjustment for H/D-exchange.) Acetone adducts 19 and 20 are known to form in reactions of H$_2$O$_2$ with acetone.$^{77,78,79}$ (Adduct 20 could also form by net addition of OOH and OH from 4 across the acetone double bond. We have observed similar photo reactions of alkenes with halogen analogs of 4.$^{12}$) No high-shift peaks, other than H$_2$O$_3$, are observed in the toluene-$d_8$ samples but the H$_2$O$_2$ $^1$H NMR signal is in the aromatic region and is broad, making it difficult to observe in toluene-$d_8$.

Room temperature photolysis of 4 was also conducted in the presence of singlet-oxygen traps 2,5-dimethylfuran (DF) and 2,3-dimethyl-2-butene (TME). The DF singlet oxygen trapping product, endoperoxide 21$^{80}$ (see above), is not observed in the photolysis of 4 in the presence of DF (C$_6$D$_6$). Instead, its dimer 22 is formed in 25% yield$^{74}$ (Scheme 1). Dimerization of 5 has been reported to be slow at room temperature but rapid above 55-60 °C.$^{75}$ With TME (CD$_2$Cl$_2$) the expected singlet oxygen product, hydroperoxide 13,$^{81}$ is observed in 8% yield$^{74}$ along with tetramethyl-1,2-dioxetane 23$^{82}$ (9%) and acetone.
Further photolysis converts 23 to acetone indicating that acetone is likely a secondary product and the dioxetane is actually produced in 11% yield. Dioxetane 23 is not an expected product from singlet oxygen and its formation appears to be from the direct reaction of H2O3 with TME. This reaction has not been reported but we find that addition of TME to a photogenerated solution of H2O3 at -60 °C does yield 23 (see SI).

**Scheme 3.2.1.** Photolytic trapping reaction.

Complex 4 is also thermally active to elimination. Heating a toluene-d8 solution shows no immediate change until about 80 °C, at which point gas evolution is observed. Like the photolytic reactions, 31P and 1H NMR spectroscopy show the formation of 2 and water indicating that the thermal reaction products are similar to the photolytic reaction (eq 6). We again tested for singlet oxygen by repeating the decomposition in the presence of TME and DF (Scheme 3.2.2). The decomposition rate is unaffected showing that there is no direct reaction between the traps and 4. A 15% yield of dioxetane 23 is produced in the TME reaction. Again, this is not the expected product from singlet oxygen but is one of the same products of the photolytic reaction and a product of the reaction of H2O3 with TME (see above). Photolytic conversion of 23 to acetone was confirmed with this sample. The DF thermal reaction gives a 10% yield of endoperoxide dimer 22, which is
the expected singlet oxygen product above 55-60 °C. A kinetic study of the decomposition (no trap) revealed a first order reaction in 4 with activation parameters $\Delta H^\ddagger = 19(1)$ kcal/mol and $\Delta S^\ddagger = -18(4)$ cal/mol K.

**Scheme 3.2.2.** Thermal trapping reaction.

![Scheme 3.2.2](image)

The chemistry of 4 was modeled using density functional theory (DFT) computations with PMe$_3$ in place of PEt$_3$ (indicated with a prime on the complex numbers). An issue that immediately arises is the hydrogen bonding in 4. While the solid-state structure of 4 is a dimer with intermolecular OOH hydrogen bonding, a DOSY diffusion NMR experiment (SI) in acetone-$d_6$ indicates negligible dimer formation in solution. However, there are still options for intramolecular OH and OOH ligand hydrogen bonding (Figure 3.2.1). In model complex 4a’ the OH ligand is the donor and the OOH ligand the acceptor. This is the intramolecular hydrogen-bonding pattern in the solid-state structure of 4. Complex 4b’ has the reverse pattern. Gas-phase optimization of 4a’ and 4b’ converged to minima with 4b’ at 3.6 kcal/mol higher free energy suggesting that, at least in non-polar, non-hydrogen-bonding solvents, the majority hydrogen-bonding structure for monomeric 4 is of type 4a’, the same intramolecular hydrogen-bonding pattern observed in the solid-state dimer.
Intramolecular hydrogen-bonding models for 4 with calculated relative energies in kcal/mol in parentheses.

Reactive elimination thermodynamic values (gas phase) for 4 were calculated and are given in Table 3.2.1. H2O2 elimination is endergonic by 14.4 kcal/mol. Water and ¹O2 (¹Δg) elimination is exergonic with ΔG = -11.4 kcal/mol. Expectedly, ³O2 (³Σg−) and water elimination is more favorable with a calculated value of -28.2 kcal/mol. The energy difference between ¹O2 and ³O2 elimination corresponds to the O2 singlet-triplet energy gap. Thus, our calculated gap value is 16.8 kcal/mol, somewhat smaller than the experimental value of 22.5 kcal/mol. The fault likely lies with the singlet oxygen as DFT methods are known to have difficulty with open-shell singlets. Thus, the value (~-11.4) for conversion of 4a’ to 2’, H2O, and ¹O2 is likely ~6 kcal/mol too low.

As Pt(IV) complex photochemistry usually involves the lowest-energy triplet excited state, arrived at either through direct excitation or through rapid (fs) internal conversion and intersystem crossing, structures 4a’ and 4b’ were optimized as triplets. No intact structure is found for the triplet from 4b’. Instead, optimization rapidly yields a “plateau” structure with a 5-coordinate Pt η¹-O2 complex and a hydrogen-bonded water molecule. Further optimization gives 2’, ³O2, and H2O, although a stationary point was not achieved.
Table 3.2.1. Energies (DFT) for reductive elimination from 4a’ (gas phase, 25 oC, 1 atm).

<table>
<thead>
<tr>
<th>Products$^a$</th>
<th>$\Delta G$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>($kcal/mol$)$^b$</td>
</tr>
<tr>
<td>$2'$ + H$_2$O$_3$</td>
<td>14.4</td>
</tr>
<tr>
<td>$2'$ + H$_2$O + $^1$O$_2$ ([$^1\Delta_g$])</td>
<td>-11.4$^c$</td>
</tr>
<tr>
<td>$2'$ + H$_2$O + $^3$O$_2$ ([$^3\Sigma_g^-$])</td>
<td>-28.2</td>
</tr>
</tbody>
</table>

$^a$ 2° = trans-Pt(PMe$_3$)$_2$(Cl)(4-tft). b These values will be somewhat more positive in solution due to the entropy difference between solution and the gas phase.$^{85}$ c From the known O$_2$ singlet-triplet energy gap this value is likely ~6 kcal/mol too low (see text).

Figure 3.2.2. Optimized model structures 4a’ and $^3$4a’ (bond distances in Å, blue = Pt, green = Cl, orange = P, red = O, grey = C, white = H, carbon-bonded H-atoms omitted). Calculated relative energies in kcal/mol in parentheses.
In contrast, the triplet from $4a'$ optimizes to a stationary point (37.8 kcal/mol above $4a'$) with minimum structure $3^4a'$ (Figure 3.2.2) containing intact OOH and OH ligands. A comparison of the metrical parameters of $3^4a'$ with $4a'$ shows that the bonds along the Cl-Pt-OH axis have lengthened and that the O-O bond has shortened. The shorter O-O distance in $3^4a'$ is similar to that in the OOH radical$^{86}$ suggesting OOH radical character in $3^4a'$. This is supported by the Mulliken atom spin densities (Figure 3.2.3) which show nearly a full electron spin on the OOH ligand. Substantial spin density is also located on the OH ligand. Thus, $3^4a'$ is a likely model precursor to H$_2$O$_3$ by coupling of the radical-like OH and OOH ligands. (H$_2$O$_3$ formation from OH and OOH radical coupling in photolyzed argon-matrix mixtures of H$_2$O$_2$ and O$_3$ has been proposed.$^{87}$) Triplet $3^4a'$ should also be a good OOH radical donor.

The thermal reductive elimination from 4 was also examined with DFT computations. Three pathways to dioxygen, water, and 2 were considered: 1) concerted H$_2$O$_3$ reductive elimination from $4a'$ or $4b'$ followed by rapid H$_2$O$_3$ decomposition to singlet oxygen and water, 2) intramolecular OOH ligand proton transfer to the OH ligand of $4b'$ to give

![Figure 3.2.3. Mulliken atomic spin densities in $3^4a'$ and 23' (blue = Pt, green = Cl, orange = P, red = O, grey = C, white = H, carbon-bonded H-atoms omitted).](image)
dioxygen and water, and 3) OOH radical dissociation from 4a’ followed by abstraction of the OH ligand to form H₂O₃.

A concerted H₂O₃ reductive-elimination pathway was found but can be eliminated as the transition state is prohibitively high (68.3 kcal/mol) (SI). Relax potential energy scans (unrestricted) to promote proton transfer in 4b’ were conducted to probe the second pathway but failed to directly yield singlet oxygen. Instead, a scan along the O-H-OO coordinate gave η²-O₂-complex 9’ (optimized to a stationary point) and water (Scheme 3.2.3). We have not been able to locate a transition state but the scan suggests a ~25 kcal/mol barrier, consistent with the experimental free energy of activation (24 kcal/mol at 298 K). The negative entropy of activation would also be consistent with the required H-bonding interaction. Separate water and 9’ lie 15.5 kcal/mol above 4b’. (Note that 9’ is isoelectronic with known Ir(III) dioxygen complexes. A transition state (TS9’, SI) for dioxygen loss from 9’ was located at 7.6 kcal/mol above 9’ showing that formation of 9’ and water would be rate-limiting.

Scheme 3.2.3. Hydrogen bonding favorable toward direct elimination of H₂O and O₂.

Thermolysis of the Pt-OOH bond of 4a’ was evaluated by calculating the energy difference between 4a’ and OOH radical plus doublet Pt(PMe₃)₂(Cl)(OH)(4-tft) 23’. (Cl or OH radical loss is higher energy.) Geometry optimization of 23’ yielded three square-
pyramidal isomers with an axial OH ligand \((23')\), an axial Cl ligand \((23a')\) and an axial 4-tft ligand \((23b')\). The lowest-energy isomer is \(23'\) (4.1 kcal/mol to \(23a'\) and 11.7 kcal/mol to \(10c'\)) and with an OOH radical lies only 22.8 kcal/mol above \(4a'\) making Pt-OOH bond homolysis a viable first step in the thermal decomposition (Scheme 3.2.4). Coupled isomerization with Pt-OOH bond breaking could account for the experimental negative activation entropy. Additionally, spin density in \(23'\) is strongly localized on the OH ligand (Scheme 3.2.4) suggesting facile OH abstraction by the OOH radical and formation of \(\text{H}_2\text{O}_3\). Crossing of the singlet thermal pathway and photochemical triplet pathway to \(\text{H}_2\text{O}_3\) may occur at this point.

Finally, it should be noted that thermal access to the triplet is possible although triplet \(^3\text{4a}'\) is calculated to be nearly 40 kcal/mol above singlet \(\text{4a}'\). If the analogous triplet for \(\text{4}\) is situated at a similar energy relative to \(\text{4}\) then thermal access to the triplet would not be consistent with the activation parameters for the thermal elimination.

**Scheme 3.2.4.** Hydrogen bonding favorable toward elimination of \(\text{H}_2\text{O}_3\).
3.3 Conclusion.

In conclusion, hydroperoxo-hydroxo complex 4 has been found to photoreductively eliminate H$_2$O$_3$ in ~ 20% yield at -60 °C. DFT results suggest the photoreaction occurs through a triplet excited state (modeled with $^3$4a’') with high OOH and OH radical character that leads to OH and OOH coupling. The hydrogen peroxide and acetone peroxides 19 and 20, also formed in acetone-d$_6$, may be produced by “leakage” of OOH radicals from the excited state or, in the case of 19 and 20, by direct reaction of acetone with the excited state. DFT results also suggest that the photolysis products may depend on the intramolecular hydrogen-bonding state of 4 with the lowest-energy state yielding the H$_2$O$_3$ products and a slightly higher state giving water and dioxygen. Thermolysis and room temperature photolysis of 4, both give water and dioxygen. In both cases, trapping experiments with TME and DF give results generally inconsistent with trapping of singlet oxygen but consistent with trapping of H$_2$O$_3$. The small yield of singlet oxygen trapping product (13), observed with TME in the room temperature photolysis may result from partial decomposition of H$_2$O$_3$ to singlet oxygen and water prior to reaction with TME. Singlet oxygen emission experiments would provide information on the presence or absence of singlet oxygen in these reactions.$^{83b}$ Given the above results and our previous results$^{12,11}$ with analogous complexes, the trans-Pt(IV)L$_2$(R)X$_3$ system is proving to be a versatile platform for elimination chemistry. Other complexes that should eliminate unusual molecules are currently under investigation.
3.4 Experimental.

**General procedures.** Trans,cis-Pt(PEt)_3(Cl)(OH)(OOH)(4-tft) 4 and trans-Pt(PEt)_3Cl(4-tft) 2 synthesis have reported in Chapter 2. Authentic samples of C(CH_3)_2(OOH)(OH) 19^{89} and C(CH_3)_2(OOH)_2 20^{79} for NMR identification were prepared by literature methods. Reagents and solvents were purchased from commercial sources (Aldrich or Acros). Platinum complex photolysis samples were prepared under a dinitrogen atmosphere in a Vacuum Atmospheres Corporation drybox or on a Schlenk line. Photolysis solvents were purged with an N_2-stream and stored under an N_2 atmosphere in a drybox. NMR spectra were recorded on Bruker AMX-250, -300 and -500 spectrometers at ambient probe temperature or as noted. NMR shifts are given in δ with positive values downfield of TMS (^1H) or external H_3PO_4 (^{31}P). ^{31}P NMR spectra were recorded in proton-decoupled mode. Photolysis were performed at -78 °C in quartz (UV) or borosilicate glass NMR tubes using a home-built tube photoreactor, which consisted of a short section of 4.2 cm PVC pipe lined with 32 LED’s (380 nm, superbrightleds.com, RL5-UV031) connected in series.

**NMR data for trans-Pt(PEt)_3(2(Cl)(OH)(OOH)(4-tft) 4.** ^{31}P NMR (101 MHz, toluene-d_8): 2.9 (s with satellite, ^{31}J_{PP} = 1800 Hz). ^{31}P NMR (101 MHz, acetone-d_6): 3.4 (s with satellite, ^{31}J_{PP} = 1800 Hz). ^1H NMR (300 MHz, toluene-d_8): 8.36-8.28 (m, 2H), 7.38-7.29 (m, 2H), 1.90-1.60 (m, 12H, CH_2), 0.98-0.75 (m, 18H, CH_3), OOH was observed as a broad singlet at 8.5-7.5 region. ^1H NMR (300 MHz, acetone-d_6): 8.7 (s, OOH), 8.30-8.05 (m, 2H), 7.43-7.30 (m, 2H), 2.05-1.85 (m, 12H, CH_2), 1.15-0.95 (m, 18H, CH_3).
NMR data for trans-Pt(PEt$_3$)$_2$(Cl)(4-tft) (2). $^{31}$P NMR (101 MHz, toluene-d$_8$): 14.4 (s with satellite, $J_{PtP} = 2770$ Hz). $^{31}$P NMR (101 MHz, acetone-d$_6$): 15.7 (s with satellite, $J_{PtP} = 2770$ Hz).

**Photolysis of trans-Pt(PEt$_3$)$_2$(Cl)(OH)(OOH)(4-tft) (4).**

**Ambient Temperature.** Complex 4 (8.0 mg, 0.012 mmol, 0.024 M) in 0.5 mL C$_6$D$_6$ was photolyzed at 380 nm for 8 min. $^1$H and $^{31}$P NMR spectroscopy showed the formation of 2 and water.

**With 2,5-dimethylfuran (DF).** Complex 4 (5.7 mg, 0.0087 mmol, 0.017 M) and 2,5-dimethylfuran (0.65 M) in C$_6$D$_6$ (0.50 mL) were photolyzed at 380 nm for 10 min. $^{31}$P NMR spectroscopy showed the formation of 2 and $^1$H NMR spectroscopy showed 2,5-dimethylfuran endoperoxide dimer (25%). $^1$H NMR (250 MHz, C$_6$D$_6$): 5.48 (s, 2H), 1.77 (s, 6H). The dimer was converted to diketone 3-ene-2,5-hexadione by PPh$_3$ addition$^{90}$ and then the solvent was changed to CCl$_4$ for comparison to the literature NMR data.$^{91}$ The $^1$H NMR spectrum matched that reported. $^1$H NMR (250 MHz, CCl$_4$): 6.61 (s, 2H), 2.25 (s, 6H).

**With 2,3-dimethyl-2-butene (TME).** Complex 4 (9.0 mg, 0.014 mmol, 0.027 M) and 2,5-dimethylfuran (0.35 M) in CD$_2$Cl$_2$ (0.50 mL) were photolyzed for 30 min (slow conversion) at 380 nm. Subsequent $^{31}$P NMR spectroscopy showed the formation of 2 and $^1$H NMR spectroscopy showed acetone (4.0 %), tetramethyl-1,2- dioxetane (9.0 %), 3-2,3-dimethyl-3-hydroperoxy-1-butene (8.0%).$^{57}$ The identity of the dioxetane was confirmed by comparison to a sample in CD$_3$CN$^{82}$ and by further photolysis to acetone.
**Low Temperature.** Complex 4 (8.5 mg, 0.013 mmol, 0.026 M) was dissolved in 0.5 mL acetone-d$_6$ or toluene-d$_8$ and then transferred into an NMR tube. The tube was placed into a dry ice/acetone filled Dewar with an unsilvered finger (Figure 1). The cold sample was then photolyzed at 380 nm for ~13-16 min (approximately 50% conversion of 4 into 2). After photolysis the NMR tube was quickly (<30 s) transferred to the precooled (-60 °C) NMR spectrometer probe for recording the NMR spectra (Figs S13-S18). The $^1$H NMR spectrum in acetone-d$_6$ showed peaks for H$_2$O$_3$,$^{25,26}$ H$_2$O$_2$,$^{25}$ C(CD$_3$)$_2$(OOH)$_2$, C(CD$_3$)$_2$)(OOH)(OH) (Figure 3.4.1), and trans-Pt(PEt$_3$)$_2$Cl(4-tft) 2. The spectrum in toluene-d$_8$ showed only H$_2$O$_3$, and 2.

![Figure 3.4.1](image)

**Figure 3.4.1.** The down field region (δ 14-9) of the $^1$H NMR spectrum obtained from photolyzed 4 in acetone-d6 at -78°C (The Pt-OOH signal shifts downfield upon sample cooling to -60 °C) The small signal at δ 9.7 is unidentified. The Pt-OOH peak is from remaining 4.
**H$_2$O$_3$ reaction with TME**

Complex 4 (11.0 mg, 0.017 mmol, 0.0 33M) was dissolved in 0.5 mL toluene-d$_8$ and photolyzed at 380 nm for 15 min at -78 °C. The sample was transferred to the precooled (-65°C) $^1$H NMR probe and H$_2$O$_3$ (14 % yield) was observed. The sample was then transferred to a -78°C bath and TME (~ 20 μL) dissolved in toluene-d$_8$ (0.15 mL) was added. The sample was immediately transferred back into the $^1$H NMR probe at -65°C and the spectrum showed no H$_2$O$_3$. The TME product, tetramethyl-1,2- dioxetane (36 % yield based H$_2$O$_3$ present), was observed at δ 1.11 and converted to acetone (δ 1.57) by photolysis after warming to room temperature.

**DF reaction with $^1$O$_2$ generated by meso-tetraohenylporphyrin (TPP).**

TPP (1.50 mg) was dissolved in 0.70 mL of a DF (~20 μL) solution in C$_6$D$_6$. The mixture was saturated with O$_2$ and then photolysed at 470 nm for 3 min. The $^1$H NMR spectrum (250 MHz, C$_6$D$_6$) showed the endoperoxide 21 at δ 5.81 (s, 2H), 1.42 (s, 6H). Heating the sample at 75°C for 5 min converted 21 to dimer 22: δ 5.48 (s, 2H), 1.77 (s, 6H).

**Thermal decomposition of 4**

**With 2,5-dimethylfuran (DF).** Complex 4 (5.7 mg, 0.0087 mmol, 0.017 M) was dissolved in 0.5 mL of a 0.65 M 2,5-dimethylfuran solution in C$_6$D$_6$. The mixture was heated at 78 °C for 15 min. $^{31}$P and $^1$H NMR spectroscopy showed the formation of 2 and 2,5-dimethylfuran endoperoxide dimmer (14%). $^1$H NMR (250 MHz, C$_6$D$_6$): 5.48 (s, 2H), 1.77 (s, 6H).
With 2,3-dimethyl-2-butene (TME). Complex 4 (5 mg, 0.0076 mmol, 0.015 M) was dissolved in 0.5 mL of a 0.40 M TME solution in C₆D₆. The mixture was heated at ~70 °C for 10 min. ³¹P and ¹H NMR spectroscopy showed formation of 2 and tetramethyl-1,2- dioxetane (15 %). ¹H NMR (250 MHz, C₆D₆): 1.12, s, 12H. The dioxetane was converted to acetone by irradiating the sample at 313 nm for 20 min. The identity of the dioxetane was confirmed by comparison to a sample in CD₃CN.

The rate constants for the thermal decomposition of 4 (6.0 mg, 0.0091 mmol) in 0.50 mL of toluene were determined at four temperatures (65, 70, 75 and 80 °C) by ³¹P NMR spectroscopy at probe temperature. Multiple spectra were collected at constant time intervals. Percentage conversion of 4 at each time interval was determined by integration. The thermally stable complex trans,cis-Pt(IV)(PEt₃)₂Cl₂(OH)(4-trifluoromethylphenyl) was used as an integration internal standard for the reaction at 80 °C and confirmed a 100% conversion of 4 to 2.

![Graph](image.png)

**Figure 3.4.2.** Plot of ln[4] vs time for the first-order decomposition of 4 in toluene at 65 °C.
Figure 3.4.3. Plot of $\ln[4]$ vs time for the first-order decomposition of 4 in toluene at 70 °C.

Figure 3.4.4. Plot of $\ln[4]$ vs time for the first-order decomposition of 4 in toluene at 75 °C.
Figure 3.4.5. Plot of ln[4] vs time for the first-order decomposition of 4 in toluene at 80°C.

Figure 3.4.6. Rate constant/T vs 1/T plot for the thermal decomposition of 4 in toluene at 65, 70, 75 and 80°C.
Application of the Eyring equation yielded the activation parameters given below. Data were analyzed using the LINEST function in the Microsoft EXCEL program.

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Temp (K)</th>
<th>1/T(K)</th>
<th>Rate constant (s(^{-1}))</th>
<th>ln(k/T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>65</td>
<td>338</td>
<td>0.00296</td>
<td>7.00E-004</td>
<td>-13.09</td>
</tr>
<tr>
<td>70</td>
<td>343</td>
<td>0.00292</td>
<td>9.75E-004</td>
<td>-12.77</td>
</tr>
<tr>
<td>75</td>
<td>348</td>
<td>0.00287</td>
<td>1.66E-003</td>
<td>-12.25</td>
</tr>
<tr>
<td>80</td>
<td>353</td>
<td>0.00283</td>
<td>2.30E-003</td>
<td>-11.94</td>
</tr>
</tbody>
</table>

slope = -9.42E+003  
Intercept = 1.48E+001  
R (J/Kmol) = 8.3145  
k_b (J/K) = 1.38E-023  
h = 6.63E-034  

enthalpy (kJ/mol) = 78.32 in kcal/mol 18.72  
entropy (J/Kmol) = -74.50 in cal/Kmol -17.81  
free energy (298K) = 100.5 in kcal/mol 24.03  

Enthalpy std= 5.77 in kcal/mol= 1.34  
Entropy std= 16.7 in cal/Kmol= 3.99
CHAPTER 4: HYDROXO RADICALS, C-H ACTIVATION AND PT-C BOND FORMATION

4.1 Introduction.

Transition metal hydroxo complexes are attracting considerable interest as key species in hydrocarbon oxidation,\textsuperscript{92} C-H activation,\textsuperscript{93} water oxidation,\textsuperscript{94} solar energy conversion and storage,\textsuperscript{8, 73c, 73e, 95} and in other catalytic schemes.\textsuperscript{73d, 96} Room-temperature photolysis of trans,cis-Pt(PEt\textsubscript{3})\textsubscript{2}Cl\textsubscript{2}(OH)(4-tft) leading to HOCl elimination have thoroughly discussed in chapter 2. Here we discuss chemistry derived mainly from the hydroxo radical, unlike reductive elimination of simple molecules. This discussion is laid out mainly as initial observations of this chemistry (section 1) and its advancement (section 2). Firstly, we report an unusual result obtained from 77 K photochemistry of trans,cis-Pt(PEt\textsubscript{3})\textsubscript{2}Cl\textsubscript{2}(OH)(4-tft), which leads to a sequence of hydroxo radical formation, C-H activation, Pt-C bond formation, and C-Cl reductive elimination. Secondly, the advancement of this chemistry with necessary modification to the metal complex, mainly via intramolecular hydrogen bonding. The initial result of C-H activation and Pt-C bond formation was first obtained by photolysis of trans,cis-Pt(PEt\textsubscript{3})\textsubscript{2}Cl\textsubscript{2}(OH)(4-tft) in frozen matrix and it is quite different from room temperature photolysis. The potential importance of intramolecular hydrogen bonding in the photochemistry of Pt(IV) hydroxo complexes was highlighted for trans,cis-Pt(PEt\textsubscript{3})\textsubscript{2}(Cl)(OH)(OOH)(4-tft)\textsuperscript{4} in previous chapter where DFT calculations suggested that the hydrogen-bonding pattern of the hydroxido and the hydroperoxido ligands could affect the outcome of the photochemistry. Changing the OOH in complex \textsuperscript{4} into a carboxylate ligand is expected to have stronger
hydrogen bonding to the OH hydrogen. Remarkably, this simple modification gave results similar to that of the 77 K photolysis, but in solution phase at room temperature as well as -78°C. Even though intramolecular hydrogen bonding is observed for complex 4, irradiation of 4 under similar condition (in CD₂Cl₂) does not yield any of the above results. This remarkable change inspired us to study this chemistry further seeking more information as regards the behavior of the hydroxo radical.

4.2 Section 1: Results and discussion for trans,cis-Pt(PEt₃)₂(Cl)₂(OH)(4-tft) photolysis at 77 K.

Irradiation (380 nm) of trans,cis-Pt(PEt₃)₂(Cl)₂(OH)(4-tft) 6 for several hours in glassy 2-methyltetrahydrofuran (MeTHF) or toluene at 77 K followed by warming to room temperature gives a mixture of a new complex 24 and trans-Pt(PEt₃)₂(Cl)(4-tft) 2 (Scheme 4.2.1). (Yields in Scheme 4.2.1 were determined by ¹H NMR integration against an internal standard.) Complex 2 is the sole Pt-containing product at room temperature and it is produced in minutes instead of hours (discussed in Chapter 2).

**Scheme 4.2.1.** Photolysis of 6 at 77 K in glassy solvents and formation of phospha-platinacycle at 298 K.

New 24 is unstable at room temperature (~ 4 h to decay) and was not isolated but is readily characterized by NMR spectroscopy as the phospha-platinacycle pictured in
Scheme 4.2.1. Most diagnostic for the formation of 24 is the $^{31}$P NMR shift for the P atom in the 4-membered ring. Four-membered ring $^{31}$P NMR signals are strongly upfield shifted from those not in a ring$^{97}$ and this is observed in 24 where the ring-P$_b$ signal is at $\delta$ -65, while that for the unaltered PEt$_3$ ligand (P$_a$) is at $\delta$ -7.7, near that of 6 (The P centers are coupled to each other (doublet, $J_{PP} = 513$ Hz) and to $^{195}$Pt with $J_{PtP} = 1853$ Hz (PEt$_3$) and 1410 Hz (P$_b$) (see Figure 4.2.1). $^1$H-$^1$H COSY and $^1$H-$^{13}$C HMQC NMR spectroscopy and comparisons to data for Pt(II) phospha-platinacycle complexes$^{98}$ allowed identification and assignment of all $^1$H NMR shifts for 24. The ring-system methylene protons appear as diastereotopic pairs. The Pt-bonded methylene group protons, H$_{1a}$ and H$_{1b}$, are found at $\delta$ 2.71 and 1.73, and are bonded to the same carbon, C1, found at $\delta$ -0.2 in the $^{13}$C NMR spectrum. The P-bonded methylene group protons are located at $\delta$ 2.98 and 2.37, and are bonded to C2, found at $\delta$29.7 in the $^{13}$C NMR spectrum. The diastereotopic nature of the methylene protons establishes a cis configuration for the chloro ligands and the stereochemistry for 24 given in Scheme 4.2.1.

After several hours at room temperature in toluene-d$_8$ or MeTHF, or more rapidly in chloroform, platinacycle 24 completely converts to Pt(PEt$_3$)(Et$_2$PCH$_2$CH$_2$Cl)(Cl)(4-trifluoromethylphenyl) 25 by reductive elimination (Scheme 4.2.2). The $^{31}$P NMR spectrum of 25 shows two closely-spaced signals at $\delta$ 13.7 and 13.0 with $^{195}$Pt satellites ($J_{PP} = 2770$ and 2722 Hz, respectively). The shifts and coupling constants are very similar to those of 2,$^{99}$ consistent with the formation of an analogous Pt(II) complex. The $^1$H NMR spectrum shows a distinctive set of multiplets at $\delta$ 3.87 and 2.25 assigned to the chloroethyl group. A crystal grown from the mixture of 2 and 25 was subjected to an X-ray crystal structure analysis, which showed that 2 and 25 co-crystallized in an 11:14
ratio (Figure 4.2.2). Complex 24 is also photo-decomposed (380 nm) to 25 at room temperature or at 77 K. (A Au(III) complex was recently reported to undergo photolytic reductive elimination of aryl chloride.\textsuperscript{100}

complex 2 (s with $J_{PP}$)

Figure 4.2.1. $^{31}$P NMR spectrum observed for 24 and 2 in MeTHF (* represent satellite and signal at $\delta$ 9.40 is an unidentified compound with 5% yield).

Scheme 4.2.2. Reductive elimination of alkyl chloride from phospha-platinacycle.
In addition to its photochemical reactivity, 6 is photoluminescent in MeTHF glass at 77 K. Irradiation at 380 nm gives visible salmon-pink emission ($\lambda_{\text{max}} = 620$ nm). The emission lifetime (38 $\mu$s) and the intensity decrease as the photolysis progresses indicate that emission is from a triplet excited state of a species that is photo-decaying, in other words, the emission is from a triplet of 6. Remarkably, our previously reported DFT calculations (in Chapter 2) of the lowest-energy triplet and singlet of the PMe$_3$ analog of 6 gave a ground-state singlet to lowest-energy triplet gap corresponding to 630 nm.$^{99}$ The calculations also indicate high spin density on a loosely bonded OH ligand in the triplet excited state. Switching solvent from MeTHF to toluene-d$_8$ changes the emission to blue, which, in contrast to the salmon-pink emission, brightens as the photolysis progresses. The blue emission spectrum (Figure 4.2.3) is characteristic of the benzyl radical.$^{101}$
Figure 4.2.3. Benzyl radical emission spectrum from toluene photolyzed sample of 6 at 77 K. Insert shows visible blue emission during photolysis ($\lambda = 380$ nm).

The picture (Scheme 4.2.3) that thus emerges is that photolysis of 6 generates a triplet excited state ($6^T$) that decays to the ground state by emission or progresses to a geminate Pt(III)/OH radical pair (A). The highly reactive OH radical then abstracts H-atoms from solvent or the PEt$_3$ ligand with the ratio depending on the solvent. Greater solvent reaction occurs with the weak C-H bonds of the toluene methyl group and less with the stronger MeTHF bonds (Scheme 4.2.1). Warming the frozen matrix results in carbon/Pt(III) radical pair (B) coupling to form platinacycle 24. Platinacycle 24 formation must occur as the frozen matrix is warmed as it is photosensitive to reductive elimination, even at 77 K. The possibility that coupling of the solvent radical and the Pt(III) radical occurs on warming to give a Pt-solvent complex that then reductively eliminates to give chlorinated solvent can be eliminated since Pt-solvent complexes are not observed by
low-temperature NMR of a photolyzed sample warmed from 77 K to -60 °C; only 2 and 25 are detected.

**Scheme 4.2.3.** Proposed mechanism for the overall observation.

A question that arises is why is the 77 K frozen matrix photochemistry of 6 different from the room temperature solution photochemistry (net HOCl elimination)? A likely explanation is that in the frozen matrix the PEt₃ ligand may be locked into a position
favorable for abstraction and the Cl ligand may be inhibited from attaining a position favorable for abstraction.

4.3 Section 2: Results and discussion for the advancement of the hydroxo radical chemistry discussed in previous section.

The synthesis of new Pt(IV)(OH) complexes with carboxylate ligands (26, 27, and 28) in place of the hydroperoxo ligand were accomplished by simple protonation of the OOH ligand in 4 with acids (Scheme 4.3.1).

Scheme 4.3.1. Protonation of the OOH ligand in 4 with acids.

As shown by the solid-state structures for 26 (Figure 4.3.1) and 27 (Figure 4.3.2), there is strong intramolecular hydrogen bonding between the carboxylate and the hydroxo ligands. The hydroxo ligand $^1$H NMR resonances in 26, 27, and 28 also indicate hydrogen bonding and are downfield shifted compared to the OH signal in non-hydrogen bonded 6. Complex 27 shows a slightly longer hydrogen bond to the carbonyl group than in 26 (O1--O3 = 2.840(6) Å for 27, 2.815(3) Å for 26) consistent with the expected weaker hydrogen bond acceptor properties of the trifluoroacetate ligand.
Figure 4.3.1. Drawing of the solid-state structure of trans-Pt(PET₃)₂(4-tft)(Cl)(OH)(OAc) 26 (50% probability ellipsoids, hydrogen atoms omitted). Rotational disorder in the CF₃ group is not shown. Distances (Å): O₃-O₁ = 2.815(4), O₁-H₁O₁ = 0.75(3), O₃-H₁O₁ = 2.11(3)

Figure 4.3.2. Drawing of the solid-state structure of trans-Pt(PET₃)₂(4-tft)(Cl)(OH)(CF₃CO₂) 27 (50% probability ellipsoids, hydrogen atoms omitted).

Scheme 4.3.2. Photolysis of Pt(IV)(OH)(carboxylate) at -78 or 25 °C.
Remarkably, photolysis (380 nm) of 26-28 at room temperature in CD$_2$Cl$_2$ gives C-H activation products phospha-platinacycles 30-32 in yields as high as 50% (Scheme 4.3.2, Table 4.3.1). At -78 °C the yields of the phospha-platinacycles increase to as high as 90%. The choice of solvent for the photolysis is critical and in toluene the yield of 30 from 26 is 0 at 25 °C and 50% at -78 °C. Since our original studies of 6 were in MeTHF and toluene we repeated the photolysis of 6 in CD$_2$Cl$_2$. As before, at 25 °C phospha-platinacycle 24 is not detected and 2 is the only product. At -78 °C, the yield of 2 drops to 45% and some 24 is formed (15%) but the major secondary product is OPEt$_3$ (24%).

$^{31}$P spectra of phospha-platinacycles 30-32 are similar to that of previously reported 24 (Figure 4.2.1). Signals for the platinum-bonded phospha-platinacycle carbon atoms (C1) are also evident in the $^{13}$C-DEPT NMR (Figure 4.3.3) and HMQC NMR (Figure 4.3.4) spectra and show platinum coupling and two bonded diastereotopic protons. Except complex 30, the other phospha-platinacycles were not attempted to fully characterize. What has changed with the new complexe 30 is the $^1$H NMR signals for the 4-tft ligand ortho-protons. In 24, only one signal is observed whereas in 30 have two signals due to slow 4-tft rotation on the NMR time scale. As this change is most likely due to a change in the ligand cis to the 4-tft ligand we assign the structures of 30-32 as shown in Scheme 4.3.2.
Figure 4.3.3. The $^{13}$C-DEPT NMR spectrum of 30 showing $^{195}$Pt satellites on C1.

Figure 4.3.4. The $^{13}$C-$^1$H HMQC NMR spectrum of 30 showing C1 correlation with H$_{1a}$ and H$_{1b}$. Asterisks mark $^{195}$Pt satellites.
Table 4.3.1. Photolysis products (%)\(^a\) from trans-Pt(PEt\(_3\))\(_2\)(Cl)(X)(OH)(4-tft) in CD\(_2\)Cl\(_2\).

<table>
<thead>
<tr>
<th>X</th>
<th>-78 °C platinacycle</th>
<th>-78 °C Pt(II)(^b)</th>
<th>25 °C platinacycle</th>
<th>25 °C Pt(II)(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OAc (26)</td>
<td>90</td>
<td>10</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>O(_2)CCF(_3) (27)</td>
<td>90</td>
<td>10</td>
<td>15</td>
<td>85</td>
</tr>
<tr>
<td>Br(_2)O(_2)C (28)</td>
<td>81</td>
<td>19</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>CN (29)</td>
<td>30</td>
<td>70</td>
<td>0</td>
<td>95(^e)</td>
</tr>
<tr>
<td>Cl (6)</td>
<td>15(^c)</td>
<td>45(^c)</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>OAc (26)</td>
<td>50(^d)</td>
<td>50(^d)</td>
<td>0</td>
<td>100</td>
</tr>
</tbody>
</table>

\(\text{X} = \text{OAc (26), BrBzO (32)}\)

\(\text{Yields determined by }^{31}\text{P NMR spectral integration.}\)

\(\text{Pt(II)} = \text{trans-Pt(PEt}_3\))\(_2\)(4-tft)X or trans-Pt(PEt\(_3\))\(_2\)(4-tft)Cl.\)

\(\text{OPEt}_3\)_2 (24%) and other unidentified products also observed.

\(\text{Same at 77 K (LN}_2\).\)

\(\text{Remaining unidentified product observed at }\delta 17 \text{ (s) in }^{31}\text{P NMR spectrum.}\)

Scheme 4.3.3. Photo isomerization of phospha-platinacycle.

Monitoring the photolysis of 26 shows the formation of a second phospha-platinacycle 30’. Both 30 and 30’ initially grow in together in a 1:1 ratio but as the photolysis continues 30’ converts to 30 (Scheme 4.3.3). We assign the structure of 30’ to the isomer of 30 where the chloro ligand, instead of the OAc ligand, is cis to the 4-tft ligand (Scheme 4.3.3). Consistent with this assignment the \(^1\text{H NMR spectrum of 30’ shows only}
one ortho-tft proton signal, the same as 24 which also has a chloro ligand cis to the 4-tft ligand. Careful examination of the $^{31}$P NMR spectra of 32 also reveals low concentrations of a second phospha-platinacycle which we assign as the isomer (32') with same structure as 30'. No other isomer was detected from 31.

The above results suggest that intramolecular hydrogen bonding to the hydroxo group is an important factor in the formation of the phospha-platinacycles. However, the cis ligand, subject to abstraction, has also been changed and this may have suppressed the competitive formal reductive elimination to give 2. We investigated this possibility by DFT (gas phase) and by the synthesis and photolysis of two other complexes. The free energy of AcOOH reductive elimination for 26 was calculated and compared to the previously calculated value for HOCl reductive elimination from 6. The values are essentially identical at 32.8 (26) and 32.3 kcal/mol (6) indicating that the net thermodynamics of the elimination are unchanged. The removal of a Cl radical from Pt(III) doublet trans-Pt(PEt$_3$)$_2$(Cl)$_2$(4-tft) and an OAc radical from doublet trans-Pt(PEt$_3$)$_2$(Cl)(OAc)(4-tft) were also compared to evaluate changes in the abstraction step. Acetate radical removal takes only 17.3 kcal/mol while Cl radical loss requires 33.3 kcal/mol. Clearly, replacement of the chloro ligand in 6 with an acetate ligand does not appear likely to inhibit reductive elimination and explain the enhanced yield of phospha-platinacycles for carboxylate complexes 26-28.

To experimentally test the importance of strong cis-ligand bonding, 29 was prepared with a cyan ligand (Scheme 4.3.4). Despite the strongly bonded cyan ligand cis to the OH ligand photolysis of 29 at 25 °C yields only reductive elimination product trans-Pt(PEt$_3$)$_2$(CN)(4-tft) (Scheme 4.3.4) indicating that if cis elimination is supressed a trans
elimination can occur. However, at -78 °C a 30% yield of phospha-platinacycle 33, is obtained. While not as high a phospha-platinacycle yield as the hydrogen-bonded carboxylate systems it is double the yield from 6 suggesting that strong bonding of the ligand adjacent to the OH group can slow reductive elimination and allow greater C-H activation.

**Scheme 4.3.4.** Photolysis of Pt(IV)(OH)(CN) complex in CD$_2$Cl$_2$.

The above results can be interpreted with the three pathways presented in Scheme 4.3.5. All three pathways start from the lowest-energy triplet excited state, which has been previously modelled with DFT for 6 and now for 26 and 27 (see below). The model complexes show elongation of the Pt-OH bond and high spin density on the OH group indicating a weakly interacting Pt(III)-OH geminate radical pair. Path B is phosphine H-atom abstraction by the hydroxyl radical to give water and, after ring closing, the phospha-platinacycle. Competitive with this pathway are the next reductive elimination pathways A and C. In Path A the hydroxyl radical abstracts a ligand from the Pt(III) center while in Path C a solvent H-atom is first abstracted by the hydroxyl radical and then the resulting solvent radical abstracts a ligand from the Pt(III) center. Path C is favoured with toluene and other solvents which contain relative weakly bonded hydrogen atoms and may also be favoured when the hydroxyl radical escapes the first coordination sphere of the Pt center. Path A generally results in abstraction of a *cis* ligand but in the case of 29 where
the CN ligand is not easily given up the OH radical can evidently migrate and abstract the trans Cl ligand. Path B then is favoured by OH radical tethering to the complex preventing escape, migration, and ligand abstraction. Consistent with entropically unfavourable tethering, Path B is more sensitive to temperature than Path A and C and the amount of Path B product (phospha-platinacycle) decreases from -78 to RT. Indeed, the strength of the H-bond tethering is reflected in the yields. At -78 all three carboxylate complexes give comparable yields which drop as the temperature is raised and the other pathways began to operate. However, the strongest H-bonding is expected to be present in 26 and 28 and these give 50% at RT, whereas the weaker H-bonding in 27 limits the yield to 15% at RT as OH escape, migration, and ligand abstraction dominate.

**Scheme 4.3.5.** Plausible reaction pathways for the observed overall results.

The lowest-energy triplet states (\(^{T}26\) for 26 and \(^{T}27\) for 27) were by DFT to examine the H-bonding and the spin density distribution. Both complexes show H-bonding between the carboxylate and OH groups. The OAc complex \(^{T}26\) appears to have a particularly strong interaction with a remarkably short H--O distance of 1.65 Å consistent with strong
tethering of the OH radical and positioning it for efficient abstraction of the PEt$_3$ hydrogen atom. The expected weaker H-bond acceptor property of the CF$_3$OAc ligand is evident in the longer O–H distance of 1.73 Å indicating a weaker tethering and more facile migration of the OH radical away from the PEt$_3$ ligand. Spin density values show the expected high spin density on the OH group indicating high radical character.

**Figure 4.3.5.** Drawings of the DFT triplets trans-Pt(PEt$_3$)$_2$(4-tft)(Cl)(OH)(OAc) $^T_{26}$ (top) and trans-Pt(PEt$_3$)$_2$(4-tft)(Cl)(OH)(O$_2$CCF$_3$) $^T_{27}$ (bottom) (hydrogen atoms omitted except for OH and OAc). Black numbers are distances (Å) and blue numbers in brackets are Mulliken electron spin densities on Cl, Pt, and the OH. Pt = blue, P = orange, Cl = green, F = light blue, O = red, C = grey.

Finally, we sought to incorporate alternative hydroxo hydrogen bonding to enhance path B to the phospha-platinacycle and replaced the 4-tft ligand with a 2-methoxyphenyl group to give 36 (Figure 4.3.6).
Figure 4.3.6. Drawing of the solid-state structure of trans-Pt(PET3)2(2-MeOPh)(Br)(OH)(CN) 36 co-crystallized with ~15% trans-Pt(PET3)2(2-MeOPh)(Br)2(OH) (50% probability ellipsoids, hydrogen atoms omitted). Approximately 15% Br atom occupancy at the CN ligand position not shown.

Photolysis of 36 at -78 °C gives a 40% yield of phospha-platinacycle 37, improved from the 30% yield for analogous 4-tft complex 29. This is not to the 90% level observed for 26 but the hydrogen bonding of the methoxyphenyl ligand with the OH ligand should be relatively weak compared to that in the carboxylic acid complexes and the effect of changing the aryl group on the other pathways is unknown and could be significant.

Scheme 4.3.6. Photolysis of Pt(IV)(OH)(CN)(2-methoxyphenyl) complex at -78°C.
The new platinacycles obtained from the carboxylate and the cyano complexes are unstable to thermal reductive elimination. In the case of the carboxylate complexes 30-32 reductive elimination involving the chloro ligand and the carboxylate ligand occurs forming a mixture of the chloro-substituted PEt₃ ligand complex 39 and the carboxylate-substituted PEt₃ ligand complex 40 (Scheme 4.3.7).

**Scheme 4.3.7.** Thermal reductive elimination of new the phospha-platinacycles

Kinetics for reductive coupling.

Monitoring the elimination reaction of the two isomers of 30 at 29 °C reveals first-order kinetics for both isomers but with slightly different rate constants (Figure 4.3.7). The initial ratio of 30'/30 (0.20) varied during the thermal decomposition and it is 0.30 after ~85% decomposition. This observation indicates the absence of a thermal equilibrium.
between these isomers. Formation of the corresponding Pt(II) complexes 39 and 40 was also examined and the result indicates first-order kinetics for both 39 and 40 (Figure 4.3.8). However, $^1$H NMR integration (against an internal standard) indicated a ~25% loss of Pt by the end of decomposition. This disappearance of Pt makes it difficult to explain the exact mechanism for the thermal reductive elimination.

Based on literature data for such reductive eliminations,\textsuperscript{102,103} here we propose a nonassociative $S_N2$ type mechanism indicating an initial loss of a ligand (trans to alkyl carbon) leading to a unsaturated five-coordinate intermediate. The above five-coordinate Pt intermediate preserves the required configuration for the $S_N2$ type nucleophilic attach on alkyl carbon leading to square planar Pt(II) (Scheme 4.3.8).
Figure 4.3.8. Kinetic plots for first-order formation of each Pt(II) compound at 29°C.

Scheme 4.3.8. Proposed mechanism for the thermal reductive elimination.
Scheme 4.3.9. Proposed kinetics for allyl-carboxylate elimination.

Rate equation derived for overall decomposition of Pt(IV) platinacycle.

\[
\frac{d[\text{Pt(IV)}]}{dt} = \frac{k_1 k_2 [\text{Pt(IV)}]}{k_{-1} + k_2}
\]

eq 8

If \( k_{-1} \ll K_2 \), \( k_{-1} + k_2 \approx k_2 \)

\[
\frac{d[\text{Pt(IV)}]}{dt} = k_1 [\text{Pt(IV)}]
\]

eq 9

The observed product ratio (40:39) of 2.0 from 30 is slightly lower than that of 31 (42:41) which is 2.4. We have attempted to explain this result with more elaborated kinetic equations derived for alkyl-carboxylate reductive elimination (Scheme 4.3.9). If the rate constant for the backward reaction (\( k_{-1} \)) is significantly smaller than \( k_2 \) the overall rate will simplify to eq 9 and it should only be influenced by initial ligand dissociation (\( k_1 \)). If the ligand dissociation is the rate determine step in this reaction, more labile trifluoroacetate would give a slightly higher yield of 42. However this thermal reductive elimination mechanism requires further studies. In order to further study the reaction,
monitoring the kinetics in the presence of acetate can be done. Doing kinetics in a polar protic solvent may change the rate constant of $k_2$ due to stabilization of the anionic ligand. Since the phospha-plainacycles were not isolated the reaction kinetics may have been influenced by impurities and purified samples would be needed.

**Reaction of complex 4 with di and tri protic acids.**

A sulfate-bridged dimer, [trans-Pt(PEt$_3$)$_2$Cl(4-tft)(OH)]$_2$SO$_4$ (43), and a boric acid product that incorporates the OOH ligand, trans-Pt(PEt$_3$)$_2$Cl(4-tft)[κ-O,O-OB(OH)OO] (44), were also prepared by the method shown in Scheme 4.3.1 and characterized by X-ray crystallography (Figure 4.3.9 and Figure 4.3.10) and NMR spectroscopy. Complexes 43 and 44 are photoactive. Photolysis at 380 nm under ambient conditions yield 2, and further characterization of the photolysis products was not attempted.

**Figure 4.3.9.** Drawing of the solid-state structure of [trans-Pt(PEt$_3$)$_2$(4-tft)(Cl)(OH)]$_2$SO$_4$ (50% probability ellipsoids, hydrogen atoms omitted).
Figure 4.3.10. Drawing of the solid-state structure of trans-Pt(PEt$_3$)$_2$Cl(4-tft)[κ-O,O-OB(OH)OO] (44) (50% probability ellipsoids, hydrogen atoms omitted).

4.4 Conclusion.

Irradiation of 6 at 77 K shows salmon pink emission and the life-time measurement indicates generation of a triplet excited state. Formation of a phospha-platinacycle has been confirmed mainly by $^{31}$P NMR and other spectroscopy techniques. Platinum satellites observed in $^1$H-$^1$C HMQC has strengthen the observation of a new metal carbon bond formation. Reductive elimination of the C-Cl is confirmed by x-ray crystallography and NMR spectroscopy. Characteristic emission spectrum observed for photolyzed sample of 6 in toluene at 77 K indicated formation of a benzyl radical. The benzyl radical formation and phospha-platinacycle yields in MeTHF and toluene suggest a competition reaction for OH radical.

Incorporating hydrogen bonding into hydroxo complexes using carboxylate ligands eliminates the difficulty of 77 K photolysis. Spectroscopic data indicate intramolecular
hydrogen abstraction and formation of phospha-platinacycle analogous to the 77 K photolysis, but in solution phase. Reductive elimination of C-Cl and C-carboxylate has also been observed. Strong hydrogen bonding and the ligand field strength in Pt(IV)-carboxylate complex photolysis contrast with the Pt(IV)(OH)(OOH/Cl) system. The overall result of C-H activation and metal-carbon bond formation via hydrogen bonding gives better control of one of competitive reactions shown in Scheme 4.3.5.

4.5 Experimental.

Reagents and solvents were purchased from commercial sources (Aldrich or Acros). MeTHF (anhydrous, Inhibitor-free) and toluene-d$_8$ (Cambridge Isotope Laboratories, Inc.) used as received. MeTHF was stored under a dinitrogen atmosphere in a drybox. NMR spectra were recorded on Bruker AMX-250, -500 and 800 spectrometers at ambient probe temperatures except as noted. NMR shifts use the $\delta$ scale with positive values downfield of TMS ($^1$H and $^{13}$C), external H$_3$PO$_4$ ($^{31}$P), external CFCl$_3$ ($^{19}$F).

Emission spectra and lifetime were obtained on a Cary Eclipse Fluorescence spectrophotometer with samples in borosilicate glass tubes at 77 K. Photolyses were performed at 380 nm in borosilicate glass tubes using a home-built photo-reactor consisting of a short section of 4.2 cm PVC pipe lined with 24 LED’s (superbrightleds.com, RL5-UV031 5mm UV LED) connected in series. Photolysis and emission experiments at 77 K utilized a liquid nitrogen filled Dewar with an unsilvered glass finger.
Apparatus.

Figure 4.5.1. Apparatus (380 nm LED tube photo-reactor and LN₂ Dewar with unsilvered finger) for the photolysis of Pt compounds at 77 K.

\textit{Trans,cis-Pt(PEt}_3\textit{)(Et}_2\textit{PCH}_2\textit{CH}_2\textit{Cl}_2(4-tft)} \ (24). \ \textit{trans,cis-Pt(PEt}_3\textit{)}_2\textit{Cl}_2\textit{(OH)(4-trifluoromethylphenyl)} \ 6 \ (7 \text{ mg, 0.01 mmol}) \ was \ dissolved \ in \ 0.50 \text{ mL of 2-Methyltetrahydrofuran (MeTHF) or toluene-d}_8 \ and \ transfer \ into \ an \ NMR \ tube. \ The \ MeTHF \ sample \ was \ prepared \ in \ air \ and \ was \ degassed \ by \ three \ freeze-pump-thaw \ cycles. \ The \ MeTHF \ sample \ was \ prepared \ under \ N}_2. \ The \ sample \ was \ then \ immersed \ in LN₂ \ and \ irradiated \ at \ 380 \text{ nm for 4 h. After warming to room temperature the NMR spectra were quickly collected and showed complete conversion of 6 into 24 and 2 (yields are given in Scheme 4.2.1). Another sample was warmed only to -60 °C in the NMR spectrometer probe. The }^{31}\text{P NMR spectrum showed 24 and 2 as the only significant products.}

NMR peaks assignments were assisted by $^1\text{H}-^1\text{H COSY and }^1\text{H}-^{13}\text{C HMQC experiments and by comparison to data for Pt(II) phospha-platinacycle complexes.}^{98} \text{ The higher-field}
$^1$H NMR signals for the ring methylene proton pairs (a and b) and the PEt$_2$ methylene groups have been assigned to those proximate to the 4-tft ring where they experience shielding from the ring current.

$^{31}$P{$^1$H} NMR (101 MHz, MeTHF or toluene-d$_8$): -7.7 (d with satellites, $J_{PP} = 1853$ Hz, $J_{PtP} = 513$Hz, PEt$_3$), -65.86 (d with satellites, $J_{PP} = 1410$ Hz, $J_{PtP} = 513$ Hz, PEt$_2$CH$_2$CH$_2$).

$^1$H NMR (800 MHz, toluene-d$_8$): 8.95 (d with satellites, $J_{HH} = 8.0$ Hz, $J_{PH} = 48.8$ Hz, 2H, 4-tft), 7.28 (d, $J_{HH} = 8.0$ Hz, 2H, 4-tft), 2.98 (m with satellites, $J_{PH} \sim 60$ Hz, 1H, H$_{2a}$), 2.71 (m with satellites, $J_{PH} \sim 60$ Hz, 1H, H$_{1a}$), 2.63 (m, 1H, H$_{4a}$ or H$_{4b}$) 2.37 (m with satellites, $J_{PH} \sim 60$ Hz, 1H, H$_{2b}$), 1.77 (overlapping, 1H, H$_{4a}$ or H$_{4b}$), 1.73 (overlapping, 1H & 9H, H$_{1b}$ & P(CH$_2$CH$_3$)$_3$), 1.08-1.03 (m, 6H, P(CH$_2$CH$_3$)$_2$), 0.74-0.68 (m, 9H, P(CH$_2$CH$_3$)$_3$), 0.57 (m, 1H, H$_{3a}$ or H$_{3b}$), 0.25 (m, 1H, H$_{3a}$ or H$_{3b}$). Overlapping peaks were located by a $^1$H-$^1$H COSY spectrum. $^{195}$Pt satellites confirmed in 500 MHz spectra and in $^1$H-$^{13}$C HMQC spectra (see SI for all spectra).

$^{13}$C(DEPH) NMR (201 MHz, toluene-d$_8$, ring carbon signals): -0.2 (d with satellites, $J_{PC} = 26.5$ Hz, $J_{PC} = 450$ Hz, Pt-C1), 29.7 (d, $J_{PC} = 36.4$ Hz, C2).

**Trans-Pt(PEt$_3$)(Et$_2$PCH$_2$CH$_2$Cl)Cl(4-tft) (25).** A photolyzed sample of 6 in MeTHF (or toluene-d$_8$) containing a mixture of 24 and 2 was left over-night at ambient temperature in the dark to convert all 24 into 25. $^{31}$P NMR analysis indicated a 2:25 ratio of 1:2 (MeTHF). The volatiles were then removed in *vacuo* and the solid residue was dissolved in ~1 mL CH$_2$Cl$_2$. Methanol (~1 mL) was added and slow evaporation in a refrigerator at
~5 °C yielded colourless crystals for the X-ray analysis. Complexes 2 and 25 could not be separated by crystallization and the X-ray structural data indicate co-crystallization in an 11:14 ratio.

$^{31}$P{${^1}$H} NMR (101 MHz, CDCl$_3$, toluene-d$_8$, MeTHF): 13.7 (s with satellite, $J_{PP} = 2770$ Hz), 13.0 (s with satellite, $J_{PP} = 2722$ Hz).

$^1$H NMR (250 MHz, CDCl$_3$): 7.47 (d with satellites, $J_{HH} = 7.5$ Hz, $J_{PH} = 65$ Hz, 2H), 7.15 (d, 2H), 3.90 (q of d, $J_{HH} = 7.5$ Hz, $J_{PH} = 2.5$ Hz, 2H, PCH$_2$HCl), 2.28 (m, 2H, PCH$_2$CHCl), 1.75-1.50 (m overlapping with 2, 10H, PCH$_2$CH$_3$), 1.17-1.00 (m overlapping with 2, 15H, PCH$_2$CH$_3$).

$^1$H NMR (500 MHz, toluene-d$_8$): 7.45 (d with satellites, $J_{HH} = 8.0$ Hz, $J_{PH} = 63$ Hz, 2H, 4-tft), 7.20 (d, 2H, 4-tft), 3.79-3.74 (q, $J_{HH} = 8.0$ Hz, 2H, PCH$_2$HCl), 2.02 (q, $J_{HH} = 8.0$ Hz, 2H, CH$_2$), 1.47-1.20 (m overlapping with 2, 10H, P(CH$_2$CH$_3$)), 0.87-0.78 (m overlapping with 2, 9H, P(CH$_2$CH$_3$)$_3$), 0.75-0.67 (m, 6H, P(CH$_2$CH$_3$)$_2$).

**Trans-Pt(PEt$_3$)$_2$Cl(OH)(OAc)(4-tft) (26).** trans-Pt(PEt$_3$)$_2$(Cl)(OH)(OOH)(4-tft) 4 (10 mg, 0.015 mmol) was dissolved in 1.0 mL of dichloromethane and approximately 1 mL of deionized water, 0.05 mL of glacial acetic acid was added and the mixture was stirred for 1 min. $^{31}$P NMR spectroscopy showed complete conversion of 4 to 26. The dichloromethane layer was washed with 4 × 5 mL deionized water and dried with MgSO$_4$. After filtration, volatiles were removed in vacuo. The resulting solid was washed with 1 mL cold hexane and dried in vacuo. Yield: 9.60 mg (92 %). Yellow crystals for the X-ray analysis were grown in hexane/ CH$_2$Cl$_2$ (1:1) by slow evaporation in a freezer.
$^{31}$P{ $^1$H} NMR (101 MHz, CD$_2$Cl$_2$): 4.78 (s with satellite, $J_{PP} = 1760$ Hz), $^1$H NMR (250 MHz, CD$_2$Cl$_2$): 8.10 (d with satellites, $J_{HH} = 8.50$ Hz, $J_{PH} = 42$ Hz, 1H), 8.00 (d with satellites, $J_{HH} = 8.75$ Hz, JPtH = 37 Hz, 1H), 7.30 (d, $J_{HH} = 8.50$, 1H), 7.23 (d, JHH = 8.50, 1H), 4.68 ($J_{PH} = 44$ Hz, 1H, OH), 2.018 (s, 3H, OCOCH$_3$), 1.96–1.76 (m, 12H, CH$_2$), 1.09–0.97 (app quintet, $J = 7.75$ Hz, 18H, CH$_3$).

$^1$H NMR (250 MHz, toluene-d8): 8.34 (d with satellites, $J_{HH} = 8.25$ Hz, $J_{PH} = 39.5$ Hz, 2H), 7.32 (d, $J_{HH} = 7.25$, 1H), 7.215 (d, $J_{HH} = 7.25$, 1H), 5.05 ($J_{PH} = 43$ Hz, 1H, OH), 2.113 (s, 3H, OCOCH$_3$), 1.74–1.60 (m, 12H, CH$_2$), 0.84–0.71 (app quintet, $J = 7.75$ Hz, 18H, CH$_3$).

**trans-Pt(PEt$_3$)$_2$Cl(OH)(OCOCF$_3$)(4-tft)** (27). trans-Pt(PEt$_3$)$_2$(Cl)(OH)(OOH)(4-tft) 4 (15 mg, 0.023 mmol) was dissolved in 1.0 mL of dichloromethane and 0.05 mL of trifluoroacetic acid was added and the mixture was stirred for 1 min. $^{31}$P NMR spectroscopy showed complete conversion of 4 to 27. The dichloromethane layer was washed with 4 × 5 mL deionized water and dried with MgSO$_4$. After filtration, volatiles were removed in vacuo. The resulting solid was washed with 1 mL cold hexane and dried in vacuo. Yield: 15.60 mg (93 %). Yellow crystals for the X-ray analysis were grown in hexane/ CH$_2$Cl$_2$ (1:1) by slow evaporation in a freezer. $^{31}$P{ $^1$H} NMR (101 MHz, CD$_2$Cl$_2$): 6.48 (s with satellite, $J_{PP} = 1725$ Hz), $^1$H NMR (250 MHz, CD$_2$Cl$_2$): 8.12 (d with satellites, $J_{HH} = 8.50$ Hz, $J_{PH} = 30$ Hz, 1H), 8.03 (d with satellites, $J_{HH} = 9.00$ Hz, $J_{PH} = 39$ Hz, 1H), 7.35 (d, $J_{HH} = 8.25$, 1H), 7.27 (d, $J_{HH} = 8.25$, 1H), 3.3–3.0 (broad S, 1H, OH), 2.01–1.74 (m, 12H, CH$_2$), 1.12–0.99 (app quintet, $J = 7.75$ Hz, 18H, CH$_3$).
**Trans-Pt(PEt₃)₂Cl(OH)(2-bromophenylacetato)(4-tft) (28)**. *trans*-Pt(PEt₃)₂(Cl)(OH)(OOH)(4-tft) 4 (20.0 mg, 0.030 mmol) was dissolved in 1.0 mL of dichloromethane and 40 mg (0.188 mmol) 2-bromophenylacetic acid was added and the mixture was stirred for 10 min. ³¹P NMR spectroscopy showed complete conversion of 4 to 28. The dichloromethane layer was stirred with 2 × 5 mL (1.8 M) KOH for 1 min. The dichloromethane layer was washed with 2 × 5 mL deionized water and dried with MgSO₄. After filtration, volatiles were removed in *vacuo*. The resulting solid was washed with 0.50 mL cold pentane and dried in *vacuo*. Yield: 23.0 mg (91%). Yellow crystals for the X-ray analysis were grown in hexane/acetone (1:1) by slow evaporation in a freezer. ³¹P{¹H} NMR (101 MHz, CD₂Cl₂): 4.84 (s with satellite, Jₚₚ = 1754.7 Hz), ¹H NMR (250 MHz, CD₂Cl₂): 8.10 (d with satellites, Jₜₜ = 8.25 Hz, Jₚₘ = 40.0 Hz, 1H), 8.03 (d with satellites, Jₜₜ = 8.75 Hz, Jₚₘ = 38.5 Hz, 1H), 7.57 (d, Jₜₜ = 7.50, 1H), 7.36-7.29 (m, 2H), 7.28-7.20 (m, 2H), 7.20-7.07 (m, 1H), 4.32 (s, Jₚₘ = 43.8 Hz, 1H, OH), 3.81 (s, 2H, CH₂), 2.00–1.73 (m, 12H, CH₂), 1.09–0.96 (app quintet, J = 7.75 Hz, 18H, CH₃).

**Trans-Pt(PEt₃)₂Cl(OH)(CN)(4-tft) (29)**. *trans*-Pt(PEt₃)₂(Cl)(OH)(CN)(4-tft) 29 (10 mg, 0.015 mmol) was dissolved in 1.0 mL of dichloromethane and approximately 1 mL of aqueous KCN (32 mg dissolved in 1.0 mL), 0.05 mL of conc HClO₄ acid was added and the mixture was stirred for 1 min. ³¹P NMR spectroscopy showed complete conversion of 4 to 29. The dichloromethane layer was washed with 4 × 5 mL deionized water and dried with MgSO₄. After filtration, volatiles were removed in *vacuo*. The resulting solid was washed with 1 mL cold hexane and dried in *vacuo*. Yield: 9.5 mg (97 %). ³¹P{¹H} NMR (101 MHz, CD₂Cl₂): -1.75 (s with satellite, Jₚₚ = 1608 Hz), ¹H NMR (250 MHz, CD₂Cl₂): 8.17 (d with satellites, Jₜₜ = 8.25 Hz, Jₚₘ = 28 Hz, 1H), 7.97 (d with satellites,
\( J_{HH} = 8.25 \text{ Hz}, \ J_{PH} = 25 \text{ Hz}, \ 1H \), 7.46-7.38 (m (overlapped dd)), \( J_{HH} = 6.75 \), 2H), 2.10-1.85 (m, 12H, CH\(_2\)), 1.13-1.00 (app quintet, \( J = 7.75 \text{ Hz}, \ 18H, \ \text{CH}_3\)).

**trans-Pt(PEt\(_3\))\(_2\)(Br)(2-methoxyphenyl)** (35). A solution of 1-bromo-2-methoxybenzene (~100 mg, 0.53 mmol) in THF (~2 mL) was added to a clear orange solution of Pt(PEt\(_3\))\(_4\) (200 mg, 0.30 mmol) in THF (~2 mL). The resulting clear orange solution was stirred for ~20 h at 140 °C in a sealed tube to yield a pale yellow solution. The mixture was cooled to ambient temperature and the volatiles were removed in **vacuo**. The solid residue was dissolved in ~2 mL CH\(_2\)Cl\(_2\) and transferred to a 4 mL vial. The volume was reduced in **vacuo** to ~0.5 mL followed by the addition of ~1 ml of methanol. The vial was capped and stored in at -20 °C overnight to afford colorless crystals. The mother liquor was pipetted out and the crystals were dried in **vacuo** to yield 150 mg (80 %) of **trans-Pt(PEt\(_3\))\(_2\)(Br)(2-methoxyphenyl)**. \(^{31}\text{P}\{ ^1\text{H}\} \text{NMR} (101 \text{ MHz}, \text{CD}_2\text{Cl}_2): 12.68 \text{ (s with satellite, } J_{\text{PP}} = 2753 \text{ Hz}), ^1\text{H NMR} (500 \text{ MHz, CD}_2\text{Cl}_2): 7.30 \text{ (d with satellites, } J_{HH} = 7.42 \text{ Hz, } J_{PH} = 78 \text{ Hz, 1H}), 6.92 \text{ (overlapped dd, } J_{HH} = 7.63 \text{ Hz, 1H}), 6.60 \text{ (overlapped dd, } J_{HH} = 7.21 \text{ Hz, 1H}), 6.51 \text{ (d, } J_{HH} = 8.10 \text{, 1H}), 3.70 \text{ (s, 3H, OCH}_3\), 1.70-1.58 \text{ (m, 12H, CH}_2\), 1.10-1.0 \text{ (app quintet, } J_{\text{app}} = 7.83 \text{ Hz, 18H, CH}_3\).

**trans-Pt(PEt\(_3\))\(_2\)Br(OH)(CN)(2-methoxyphenyl)** (36). **trans-Pt(PEt\(_3\))\(_2\)Br(2-methoxyphenyl)** (13.5 mg, 0.020 mmol) in 1.5 mL of dichloromethane was mixed in a 20 mL vial with a freshly prepared H\(_2\)O\(_2\) solution in diethylether (1mL). The vial was loosely capped. The mixture was stirred for 20 min at room temperature during which time the solution turned pale yellow and conversion of **trans-Pt(PEt\(_3\))\(_2\)Br(2-methoxyphenyl)** (\( \delta = 12.5 \)) to presumed **trans-Pt(PEt\(_3\))\(_2\)Br(OH)(OOH)(2-methoxyphenyl)** (\( \delta = 2\)) was observed by \(^{31}\text{P} \text{NMR spectroscopy} \ (^{31}\text{P} \text{NMR shifts varied slightly with the} \)
water content of the reaction mixture). Once the reaction was complete, the
dichloromethane layer was separated, washed with 3 × 5 mL of deionized water to
remove H₂O₂. Approximately 1 mL of aqueous KCN (32 mg dissolved in 1.0 mL), 0.05
mL of conc HClO₄ acid was added and the mixture was stirred for 1 min. ³¹P NMR
spectroscopy showed complete conversion to 36. The dichloromethane layer was washed
with 4 × 5 mL deionized water and dried with MgSO₄. After filtration, volatiles were
removed in vacuo. The resulting solid was washed with 1 mL cold hexane and dried in
vacuo. Yield: 12.0 mg (91 %). Yellow crystals for the X-ray analysis were grown in
hexane/CH₂Cl₂ (1:1) by slow evaporation in a freezer. ³¹P{¹H} NMR (101 MHz, CDCl₃):
-1.29 (s with satellite, J_{PtP} = 1626 Hz), ¹H NMR (250 MHz, CDCl₃): 8.09 (d
with satellites, J_{HH} = 8.00 Hz, J_{PH} = 36 Hz, 1H), 7.13 (t, J_{HH} = 7.25 Hz, 1H), 6.80 (t, J_{HH} = 7.75, 1H), 6.61 (d, J_{HH} = 7.75, 1H), 3.79 (s, 3H, OCH₃), 2.30–2.09 (m, 12H, CH₂),
1.20–1.0 (app quintet, J = 8.00 Hz, 18H, CH₃).

Photolysis of trans-Pt(PEt₃)₂Cl(OH)(OAc)(4-tft) (26). A sample of 26 (10 mg, 0.014
mmol) dissolved in 0.50 mL of CD₂Cl₂ or toluene-d₈ was photolyzed for 120 min or 40
min (toluene-d₈) at -78°C giving complete conversion of 26 into 30 and 2. Other samples
of 26 in CD₂Cl₂ and toluene- d₈ with identical concentrations were photolyzed to
completion (15 min) at 25°C. Yields of 30 and 2 are given in Table 4.3.1.

Data for 30. ³¹P{¹H} NMR (101 MHz, CD₂Cl₂): -2.9 (d with satellites, J_{PtP} = 1800 Hz,
J_{PP} = 529 Hz), -60.7 (d with satellites, J_{PP} = 1566 Hz, J_{PP} = 529 Hz).

¹H NMR (500 MHz, CD₂Cl₂): 7.77 (d with satellites, J_{HH} = 8.0 Hz, J_{PH} = 45 Hz, 1H, 4-
tft), 7.52 (d with satellites, J_{HH} = 8.0 Hz, J_{PH} = 52 Hz, 1H, 4-tft), 7.38 (d, J_{HH} = 8.0 Hz,
1H, 4-tft), 7.31 (d, $J_{HH} = 8.0$ Hz, 1H, 4-tft), 3.11-3.20 (m 1H, H$_{2a}$), 2.85-2.70 (m 2H, H$_{2b}$ and H$_{3a}$), 2.75-2.55 (m with satellites, $J_{PH} \sim 100$ Hz, 1H, H$_{1a}$), 2.40-2.25(m, 1H, H$_{4b}$) 2.15-2.05 (m, 1H, H$_{1b}$), 1.98 (s,3H, OCOCH$_3$), 1.90-1.78 (m, 6H, P$_a$(CH$_2$CH$_3$)$_3$), 1.73-1.66 (m 1H, H$_{3a}$), 1.35-1.28 (m, 1H, H$_{3a}$), 1.20-1.10 (m, 3H, P$_b$(C(4)H$_2$CH$_3$)), 1.00-0.94 (app quintet, $J_{app} = 7.75$ Hz, 9H, P$_a$(CH$_2$CH$_3$)$_3$), 1.81-0.72 (m, 3H, P$_b$(C(3)H$_2$CH$_3$)). Overlapping peaks were located by a $^1$H-$^1$H COSY spectrum.

$^{13}$C(DEPH) NMR (201 MHz, CD$_2$Cl$_2$, ring carbon signals): -8.40 (d with satellites, $J_{PC} = 38.2$ Hz, $J_{PtC} = 478$ Hz, Pt-C1), 29.95 (d, $J_{PC} = 48.2$ Hz, C2).

Partial photolysis of 26 at 2 min intervals at -78°C showed the formation of another phospha-platinacycle (30') assigned as the isomer of 30 shown in Scheme 4.3.3. At the completion of the photolysis almost all 30' had converted to 30.

Data for 30'. $^{31}$P{$^1$H} NMR (101 MHz, CD$_2$Cl$_2$): -6.0 (d with satellites, $J_{PP} = 1848$ Hz, $J_{P_{PP}} = 501$Hz), -64.5 (d with satellites, $J_{PP} = 1392$ Hz, $J_{P_{PP}} = 501$ Hz).

$^1$H NMR (500 MHz, CD$_2$Cl$_2$): 8.67(d with satellites, $J_{HH} = 8.2$ Hz, $J_{PH} = 50$ Hz, 2H, 4-tft o-H), 7.32 (4-tft m-H, observed by COSY to overlap with a peak for 30). Remaining peaks were too weak and/or obscured.

$^{13}$C(DEPH) NMR (201 MHz, CD$_2$Cl$_2$): 139.5 (s, 4-tft o-C), 134.9 (4-tft m-C overlapped with another signal). Peaks assigned by $^1$H-$^{13}$C HMQC. Other peaks could not be assigned without matching $^1$H NMR signal assignments.

**Photolysis of trans-Pt(PEt$_3$)$_2$Cl(OH)(OCOCF$_3$)(4-tft)** (27). A sample of 27 (8 mg, 0.011 mmol) dissolved in 0.50 mL of CD$_2$Cl$_2$ was photolyzed for 40 min at -78°C giving
complete conversion of 27 into 31 and 2. Another sample of 27 with the same concentration was photolyzed to completion (15 min) at 25°C. Yields are given in Table 4.3.1.

Data for 10. $^{31}$P{$^1$H} NMR (101 MHz, CD$_2$Cl$_2$): -0.3 (d with satellites, $J_{PP} = 1813$ Hz, $J_{PP} = 504$ Hz), -59.4(d with satellites, $J_{PP} = 1474$ Hz, $J_{PP} = 504$ Hz).

Photolysis of trans-Pt(PEt$_3$)$_2$Cl(OH) (2-bromophenylacetato)(4-tft) (28). A sample of 28 (9 mg, 0.014 mmol) dissolved in 0.50 mL of CD$_2$Cl$_2$ was photolyzed for 40 min at -78°C giving complete conversion of 28 into 32 and 2. Another sample of 28 with the same concentration was photolyzed to completion (15 min) at 25°C. Yields are given in Table 4.3.1.

Data for 32. $^{31}$P{$^1$H} NMR (101 MHz, CD$_2$Cl$_2$): -2.6 (d with satellites, $J_{PP} = 1803$ Hz, $J_{PP} = 524$ Hz), -59.4(d with satellites, $J_{PP} = 1543$ Hz, $J_{PP} = 524$ Hz).

A small amount of another phospha-platinacycle (32') was observed in the NMR spectra and is assigned as the isomer of 32 shown in Scheme 4.3.2.

Data for 32'. $^{31}$P{$^1$H} NMR (101 MHz, CD$_2$Cl$_2$): -5.9 (d with satellites, $J_{PP} = 1849$ Hz, $J_{PP} = 501$ Hz), -64.2(d with satellites, $J_{PP} = 1501$ Hz, $J_{PP} = 501$ Hz).

Photolysis of trans-Pt(PEt$_3$)$_2$Cl(OH)(CN)(4-tft) (29).

A sample of 5 (9 mg, 0.014 mmol) dissolved in 0.50 mL of CD$_2$Cl$_2$ was photolyzed for 40 min at -78°C giving complete conversion of 29 into of 33 and 34. Another sample of 29 with the same concentration was photolyzed to completion (10 min) at 25°C. Yields are given in Table 4.3.1.
Data for 33. $^{31}$P{$^1$H} (NMR (101 MHz, CD$_2$Cl$_2$): 11.10 (s with satellites, $J_{pp} = 2527$ Hz).

Data for 34. $^{31}$P{$^1$H} NMR (101 MHz, CD$_2$Cl$_2$): -2.6 (d with satellites, $J_{pp} = 1803$ Hz, $J_{pp} = 524$ Hz), -59.4 (d with satellites, $J_{pp} = 1543$ Hz, $J_{pp} = 524$ Hz).

**Photolysis of trans-Pt(PEt$_3$)$_2$Br(OH)(CN)(2-methoxyphenyl) (36).** A sample of 36 (8 mg, 0.012 mmol) dissolved in 0.50 mL of CD$_2$Cl$_2$ was photolyzed for 50 min at -78°C giving complete conversion of 36 into 37 (40%) and trans-Pt(PEt$_3$)$_2$(CN)(2-methoxyphenyl) 38 (60%) was observed.

Data for 37. $^{31}$P{$^1$H} NMR (101 MHz, CD$_2$Cl$_2$): -3.0 (d with satellites, $J_{pp} = 1820$ Hz, $J_{pp} = 471$ Hz), -73.0 (d with satellites, $J_{pp} = 1331$ Hz, $J_{pp} = 471$ Hz).

Data for 38. trans-Pt(PEt$_3$)$_2$(CN)(2-methoxyphenyl).

$^{31}$P{$^1$H} NMR (101 MHz, CD$_2$Cl$_2$): 11.33 (s with satellites, $J_{pp} = 2570$ Hz).

$[\text{trans-Pt(PEt}_3\text{)}_2\text{Cl(4-tft)(OH)}]_2(\mu-\text{SO}_4)$ (43). trans-Pt(PEt$_3$)$_2$(Cl)(OH)(OOH)(4-tft) 4 (10 mg, 0.015 mmol) was dissolved in 1.0 mL of dichloromethane and approximately 1 mL of deionized water, approximately 0.05 mL of conc. H$_2$SO$_4$ acid was added and the mixture was stirred for 1 min. $^{31}$P NMR spectroscopy showed complete conversion to the title product. The dichloromethane layer was washed with 4 $\times$ 5 mL deionized water and dried with MgSO$_4$. After filtration, volatiles were removed in vacuo. The resulting solid was washed with 1 mL cold hexane and dried in vacuo. Yield: 9.90 mg (97.0%). Yellow crystals for the X-ray analysis were grown in hexane/CH$_2$Cl$_2$ (1:1) by slow evaporation in a freezer. $^{31}$P{$^1$H} NMR (101 MHz, CD$_2$Cl$_2$): 8.30 (s with satellite, $J_{pp} = 1735$ Hz).
NMR (250 MHz, CD$_2$Cl$_2$): 8.10 (d with satellites, $J_{HH} = 8.50$ Hz, $J_{PtH} = 44$ Hz, 2H), 7.32-7.23 (m, 2H), 3.16 ($J_{PtH} = 40$ Hz, 1H, OH), 2.20–1.94 (m, 12H, CH$_2$), 1.16–1.04 (app quintet, $J = 7.75$ Hz, 18H, CH$_3$).

*trans*-Pt(PET$_3$)$_2$Cl(4-tft)[κ-O,O-OB(OH)OO] (44). *trans*-Pt(PET$_3$)$_2$(Cl)(OH)(OOH)(4-tft) 4 (10 mg, 0.015 mmol) was dissolved in 1.0 mL of dichloromethane and 40 mg of B(OH)$_3$ (boric acid), dissolved in approximately 1 mL of warm deionized water, was added and the mixture was stirred for 10 min. $^{31}$P NMR spectroscopy showed complete conversion to the title product. The dichloromethane layer was washed with 4 × 5 mL deionized water and dried with MgSO$_4$. After filtration, volatiles were removed in vacuo. The resulting solid was washed with 1 mL cold hexane and dried in vacuo. Yield: 9.9 mg (96.0 %). Yellow crystals for the X-ray analysis were grown in hexane/CH$_2$Cl$_2$ (1:1) by slow evaporation in freezer. $^{31}$P{$^1$H} NMR (101 MHz, CD$_2$Cl$_2$): 5.05 (s with satellite, $J_{PP} = 1707$ Hz), $^1$H NMR (250 MHz, CD$_2$Cl$_2$): 8.04 (d, $J_{HH} = 8.50$ Hz, 1H), 7.94 (d, $J_{HH} = 8.50$, 1H), 7.40-7.25 (m, 2H), 3.35 (s, 1H, OH), 2.10–1.82 (m, 12H, CH$_2$), 1.15–1.01 (app quintet, $J = 7.75$ Hz, 18H, CH$_3$).

**Kinetic experiment**

**Thermal decomposition of a mixture of 30 and 30’**.

A sample of 26 (10 mg, 0.014 mmol) dissolved in 0.50 mL of CD$_2$Cl$_2$ was photolyzed for 50 min at -78°C. At the end of the photolysis complete conversion of 26 into 90 % of 30 and 30’ (two isomers presented) and 10 % of 2 was observed. This sample was kept at 29°C in a water bath and $^1$H NMR spectra (NMR probe at 298 K) were collected at
various time intervals. Kinetic data (integration with respect to an internal standard) for
two isomers presented were plotted separately. Data were analyzed using the LINES
function in the Microsoft EXCEL program. The decomposition is found to be first order.
The decomposed products are \( \text{trans-Pt(PEt}_3\text{(Et}_2\text{PCH}_2\text{CH}_2\text{(acetate))Cl(4-tft)}} \) and \( \text{trans-Pt(PEt}_3\text{(Et}_2\text{PCH}_2\text{CH}_2\text{Cl})(acetate)(4-tft)}} \).

**Table 4.5.1.** Data for kinetic plots shown in Figure 4.3.7 and Figure 4.3.8.

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74. Yield (% = 100*(moles of product/moles of I).


Lasantha A Wickramasinghe is from Sri Lanka which is known as the pearl of Indian ocean. He grew up in Colombo, capital of Sri Lanka. After finishing his high school in Mahanama College he enrolled in chemistry program in Institute of Chemistry Ceylon, where he obtained his BSc degree in chemistry. He later joined the doctoral program in the department of chemistry at the University of Missouri-Columbia. He worked under the guidance of Prof. Paul R Sharp. His graduate research has consisted of synthesis and photochemistry of platinum(IV) hydroxo complexes.