ABSTRACT

Title of Thesis: AEROBIC OXIDATION OF *CIS*-2-BUTENE AND 2-BUTYNE IN WATER MEDIATED BY (DPMS)Pt^{II} (DPMS = DI(2-PYRIDYL) METHANE SULFONATE)

Pratheep Khanthapura, Master of Science, 2010

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(dpms)Pt^{II} hydroxo ethylene complex **(2.1)** undergoes ligand substitution--intramolecular hydroxo platination with 2-butyne in water to give Pt^{II} η^1-ketonyl complex **(2.2).** This neutral complex is oxidized by O_2 or H_2O_2 to give Pt^{IV} secondary alkyl complex **(2.4).** Oxidation by O_2 was found to be pH dependent. Also described here is the preparation of Pt^{IV} oxetane **(3.2)** derived from non-cyclic non-strained olefin, *cis*-2-butene. The starting complex here is the (dpms)Pt^{II} chloro *cis*-2-butene **(3.1)** which undergoes chloride abstraction by Ag_2O to give the hydroxo analog before getting oxidized by O_2 to Pt^{IV} oxetane.

AEROBIC OXIDATION OF *CIS*-2-BUTENE AND 2-BUTYNE IN WATER MEDIATED BY (DPMS)Pt^{II} (DPMS = DI(2-PYRIDYL) METHANE SULFONATE)

By

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Chapter 1

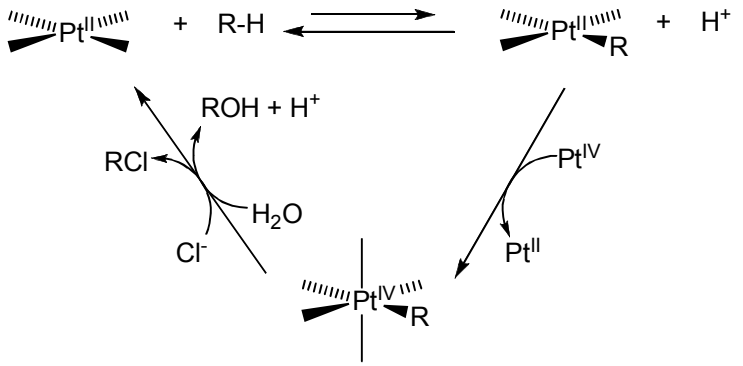
Oxidation of dpmsPt^{II} alkyl complexes with dioxygen

Discovering the most efficient pathways toward conversion of chemical feedstock from mineral oil to more valuable chemicals is an important task for chemists. It is important that these abundant low cost molecules are not just being burnt away but discovered full potential of functionalization through selective oxidation.

It was Shilov's group who reported decades ago that catalytic oxidation of alkanes by a platinum(IV) complex is possible. Combining alkanes, $K_2[PtCl_4]$, and $H_2[PtCl_6]$ in aqueous solution affords oxidized alkane products as shown in equation 1.1.[1]

$$RCH_3 + PtCl_6^{2-} + H_2O\ (Cl^-) \xrightarrow[H_2O,\ 120^oC]{PtCl_4^{2-}} RCH_2OH\ (RCH_2Cl) + PtCl_4^{2-} + 2HCl \qquad (1.1)$$

The proposed mechanism is shown in equation 1.2. According to the mechanism, alkane activation by the Pt^{II} species gives Pt^{II} alkyl complex. Oxidation by $[PtCl_6]^{2-}$ then affords Pt^{IV} alkyl complex. The electrophilicity of the Pt^{IV} alkyl intermediate allows it to be attack by nucleophiles such as H_2O or Cl^- present in the system to give the corresponding alcohols or alkyl chloride and back the Pt^{II} catalyst.[1]



(1.2)

The Shilov's system is attractive but impractical as the oxidant used here is too expensive. An ideal oxidant should not only be highly abundant but be mild enough to only oxidize the alkylplatinum(II) intermediate and leave the other platinum(II) salts untouched.[2]

Dioxygen is the best candidate in this case.[3] From the four-electron reduction of O_2 to two water molecules with a reduction potential of +1.23 V in acidic solution (Fig. 1.1), it can be seen that dioxygen is actually a good oxidant. The inertness of this powerful oxidant toward substrates, however, came from the fact that the ground state configuration of O_2 is a triplet and the slow spin conversion step is required to give the product with a singlet ground state configuration.[4]

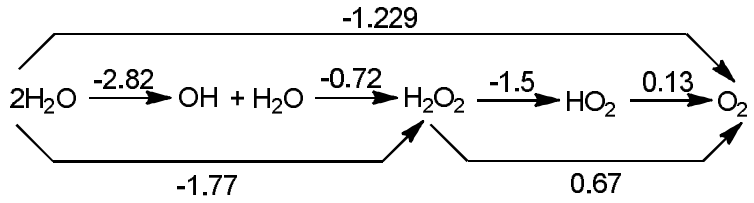


Figure 1.1. Standard Potentials between H_2O and O_2

The general mechanism for the oxidation of a square-planar platinum complex can be describe as an electrophilic attack of the oxidizing agent on the filled d_Z^2 orbital of the Pt^{II} complex (fig. 1.2a).[3] The energy of the platinum complex HOMO can be raised by either having a strong σ-donor group such as an alkyl group attached (fig. 1.2b) or by having an axial ligand with a lone pair of electrons to destabilize the filled d_Z^2 orbital (fig. 1.2c).[3]

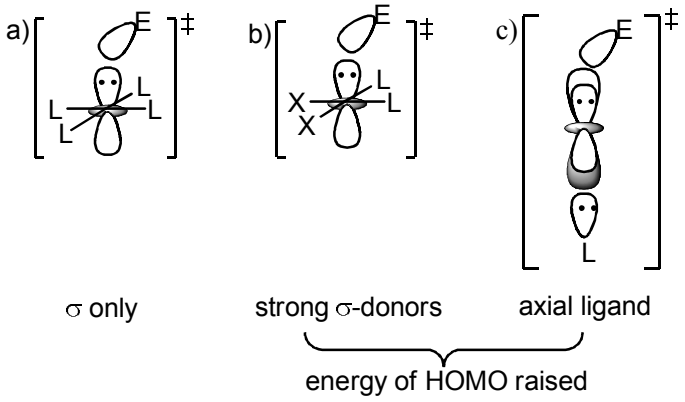
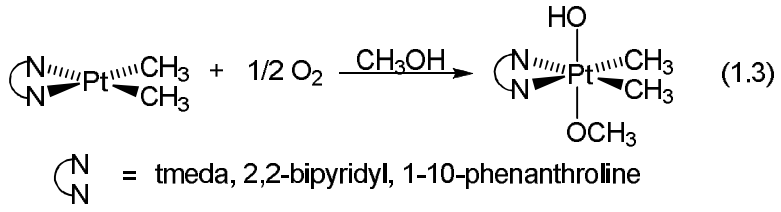
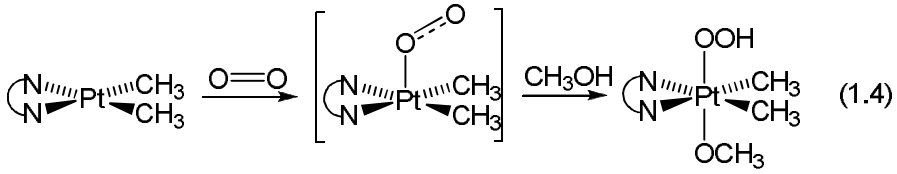


Figure 1.2. Interaction of Pt^{II} complexes with dioxygen

Bercaw and colleagues have demonstrated that dimethylplatinum(II) complexes can be oxidized with O_2 under mild condition to give the platinum(IV) complexes (eq.1.3). The neutral platinum(II) complex here features two strong *σ*-donors methyl groups and two weaker nitrogen-based (tmeda, 2,2-bipyridyl, or 1-10-phenanthroline) *σ*-donors groups.[5]

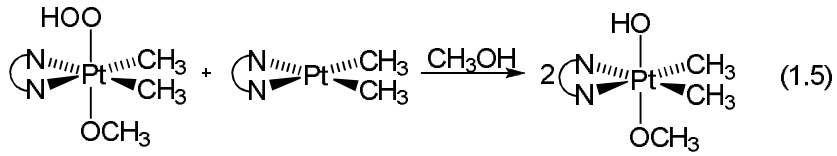


A platinum(IV) complex isolated in this case is the hydroperoxy-methoxy complex (tmeda)Pt(OOH)(OCH_3)(CH_3)$_2$. The proposed mechanism for its formation is shown in equation (1.4).[3] Initial interaction with dioxygen produced the superoxo-Pt^{III} followed by a protonation step. The ratio of the intermediate HOO-Pt(IV)-OCH_3 to the final products depends on the ratio of O_2 and dimethylplatinum(II) complex where higher concentration of O_2 gives higher ratio of the hydroperoxo complex.[3]



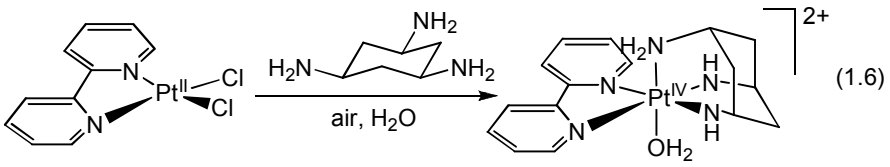
(1.4)

This hydroperoxo complex is itself an oxidant for oxidizing the remaining Pt^{II} complex to give two equivalent of the final product (eq. 1.5).[3]



(1.5)

It is not always necessary to have two strong σ-donors to undergo oxidation with O_2. Sarneski and colleagues have demonstrated that an in situ generated species, [(bipy)Pt(η^2-tach)]$^{2+}$, is oxidized under air to [(bipy)Pt(η^3-tach)(OH_2)]$^{2+}$ (eq. 1.6).[6] In this example the tridentate *fac*-chelating ligand 1,3,5-triaminocyclohexane (tach) is responsible for facilitating oxidation and stabilizing the platinum(IV) that forms.[6]



In achieving oxidative functionalization of mono-hydrocarbyl platinum(II) complexes which are the product of activation of hydrocarbons by platinum(II) species, it is necessary to use such ligand that will not only facilitate oxidation by dioxygen but will also allow further release of the functionalized product by reductive elimination reactions.[7] Recently, a hemilabile *fac*-coordinating ligand, di(2-pyridyl)methanesulfonate (dpms) was developed by Vedernikov (fig. 1.3). This ligand has the ability of changing the coordination mode from dicoordinate (η^2) with square plannar Pt^{II} center to tricoordinate (η^3) with octahedral Pt^{IV} centre.[8]

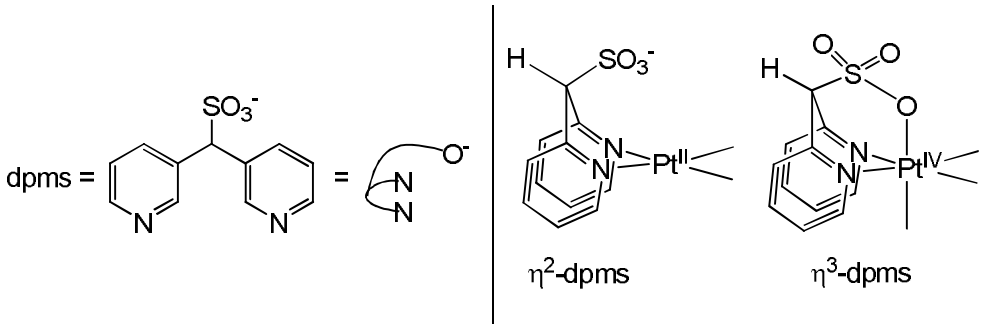
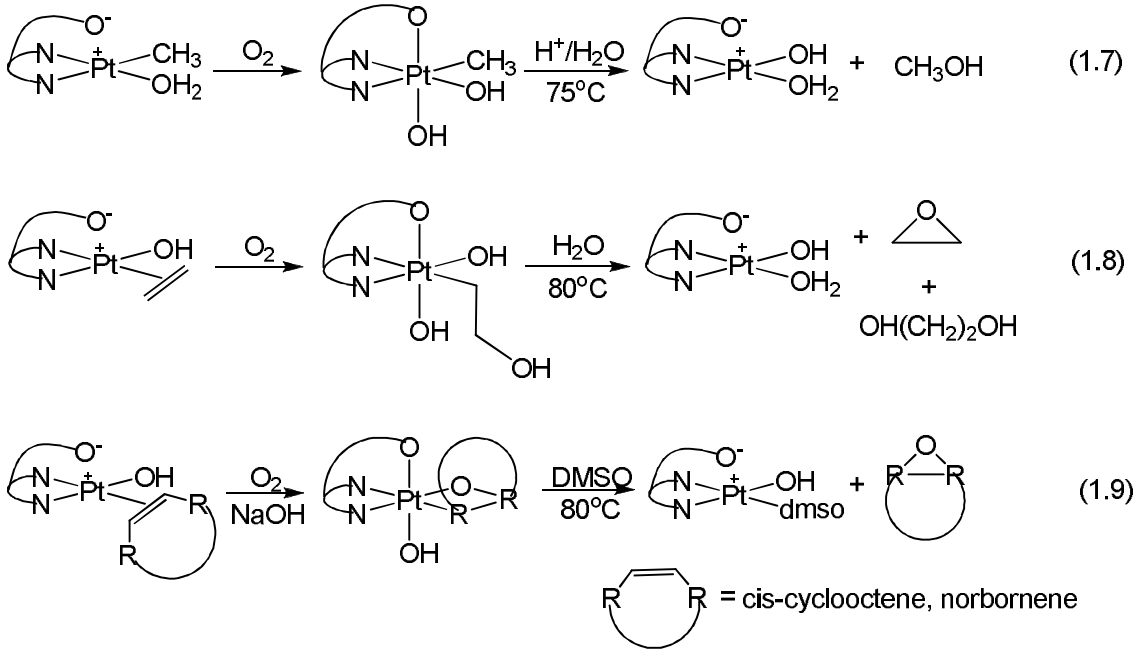


Figure 1.3. dpms ligand and its coordination modes.

Members from our group have demonstrated the versatility of the dpms ligand. Varities of $(dpms)Pt^{II}$ complexes undergo oxidation readily with O_2 at room temperature to give the corresponding Pt^{IV} complexes. For example, monomethyl complex

(dpms)$Pt^{II}Me(H_2O)$ is oxidized under O_2 to give (dpms)$Pt^{IV}Me(OH)_2$ which eliminates methanol upon heating in acidic solutions. (eq.1.7).[9] Pt^{II} ethylene hydroxo complex, (dpms)$Pt^{II}(CH_2CH_2)(OH)$, also undergoes oxidation under mild condition with O_2 to give the hydroxoethyl Pt^{IV} species, (dpms)$Pt^{IV}(CH_2CH_2OH)(OH)_2$ (eq.1.8).[10] Reductive elimination of this specie affords ethylene glycol and ethylene oxide. In the case of (dpms)Pt^{II} with strained cyclic olefins, the oxidation gave the Pt^{IV} oxetane complexes which reductively eliminate the corresponding epoxides (eq.1.9).[11]



No oxidation occurs under the same condition using dipyridylmethane (two pyridyl fragments bridged by a CH_2 group) as the ligand for the monomethyl Pt^{II} complex.[12] This confirms that the sulfonate group does help facilitate aerobic oxidation. On the other hand,

dpms-complexes without any strong donor group like $[(dpms)Pt(OH_2)_2]^{+}BF^{4-}$ do not react with dioxygen.[13]

It was also observed that adding a small amount of base (NaOH) helps promote oxidation with O_2.[10] For example, zwitterionic species such as $(dpms)Pt^{II}(CH_2CH_2)(OH)$ isn't reactive toward oxygen in contrast to the anionic species, $[(dpms)Pt^{II}(CH_2CH_2OH)(OH)]^{-}$, resulting from the attack of OH^{-} at the coordinated ethylene. Not surprising if one considers higher in energy HOMO of the more electron rich complexes making them more reactive. The overall rate of oxidation, however, slows down as the amount of base increases. From these facts, general mechanism of oxidation of the $(dpms)Pt^{II}$ type was proposed (Scheme 1.1).[10]

Scheme 1.1

$$\eta^2\text{-dpms}Pt^{II}(OH)(HX) + OH^- \rightleftharpoons [\eta^2\text{-dpms}Pt^{II}(OH)(X)]^- + H_2O$$

$$[\eta^2\text{-dpms}Pt^{II}(OH)(X)]^- + O_2 \rightleftharpoons [\eta^2\text{-dpms}Pt^{II}(\eta^1\text{-}O_2)(OH)(X)]^-$$

$$[\eta^2\text{-dpms}Pt^{II}(\eta^1\text{-}O_2)(OH)(X)]^- + H^+ \longrightarrow [\eta^3\text{-dpms}Pt^{IV}(O_2H)(OH)(X)]^-$$

$$[\eta^3\text{-dpms}Pt^{IV}(O_2H)(OH)(X)]^- + [\eta^2\text{-dpms}Pt^{II}(OH)(X)]^- + H_2O \longrightarrow 2\ \eta^3\text{-dpms}Pt^{IV}(OH)_2(X) + OH^-$$

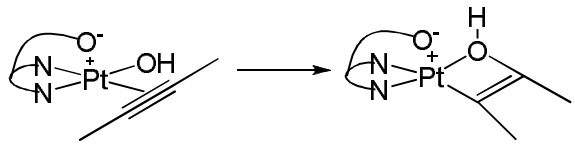
Oxidation is initiated by converting neutral species to more reactive anionic species by base. Followed by reversible attack of the dioxygen at the Pt^{II} center to give the Pt^{III}-superoxo intermediate, similar to what proposed by Bercaw. Next step is the slow proton-coupled electron transfer producing the Pt^{IV}-hydroperoxo complex. As also observed by

Bercaw, one mole Pt^{IV}-hydroperoxo specie can oxidize another Pt^{II} specie to give two mole of the final product.[10]

Here we describe the new chemistry of hydrocarbyl dpms-platinum(II) complexes and their oxidation with dioxygen. Transformation of 2-butyne are described in chapter 2. Oxidation of the resulting complex with oxygen or hydrogen peroxide is also demonstrated. We also describe the preparation of a platinum(IV) oxetane complex derived from an acyclic olefin, *cis*-2-butene, in chapter 3. Also described are preliminary results of reductive elimination of the platinum(IV) oxetane to form *cis*-2,3-dimethyloxirane.

Chapter 2

As mentioned in chapter 1, the formation of platina(II)oxetanes from coordinated cyclic olefin to (dpms)Pt^{II}(OH) complexes has already been established by our group (eq. 1.9). Here we want to know what happens to the alkynes coordinated to (dpms)Pt^{II} center. Will it produce metalla-oxetenes or something else (eq. 2.1)? We use here the symmetrical species, 2-butyne, to study the reactivity of alkynes.



The metal-alkyne bond can generally be described by Dewar-Chatt-Duncanson model (Fig 2.1).[14] A σ-type donation is from alkyne π-electrons to the metal d_σ orbital. Electron rich metal specie also provide significant amount of electron density to the LUMO of an alkyne via π-back donation. An alkyne is different from an alkene in that it can act as 4-electron donor. The available orthogonal π-bond of alkyne can provide another two electrons to an empty d_π orbital of the metal in the π-fashioned donation. In the complex where σ-donation is dominant, an effective positive charge is left on the alkyne making it susceptible for nucleophillic attack.[15, 16]

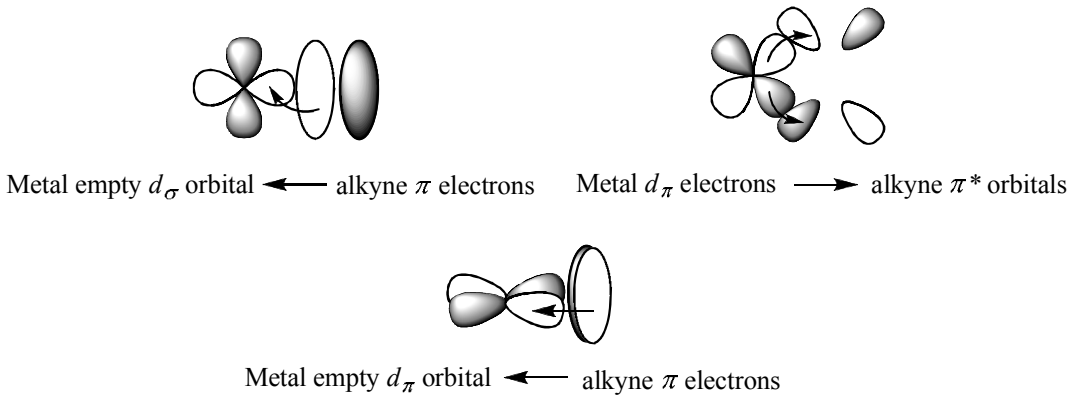
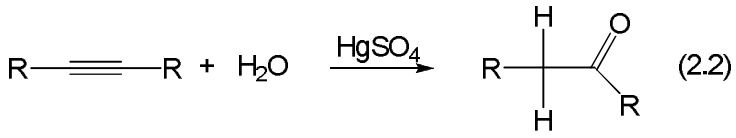


Figure 2.1. The coordination model of alkynes to metal center.

Alkynes coordinated to an electrophilic metal usually undergo hydration in water to give ketones. A classic example is the mercury(II)-catalyzed hydration of alkynes which has been known for decades (eq 2.2).[17]

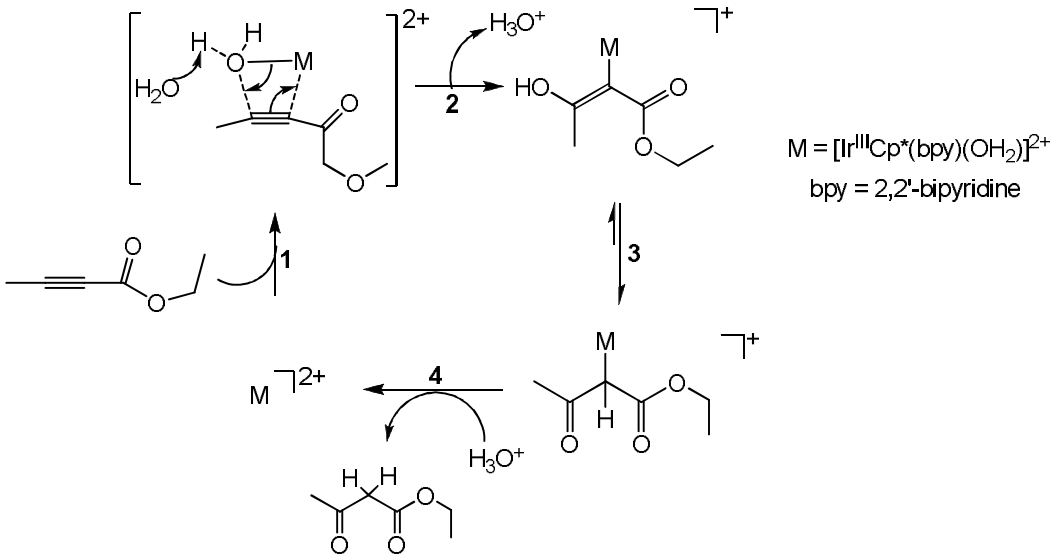


(2.2)

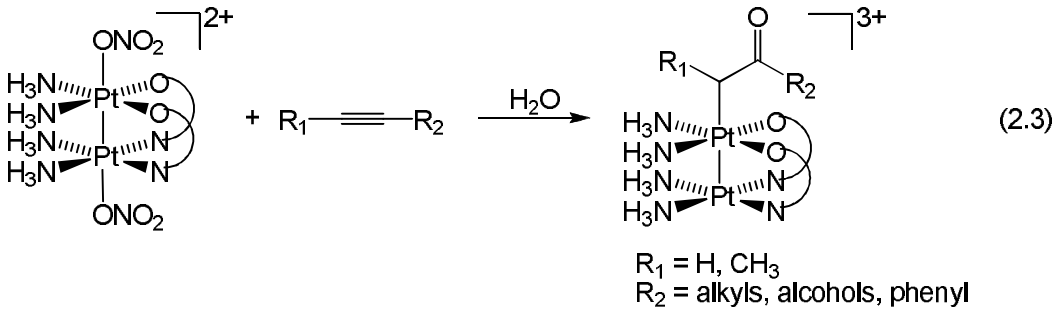
Hydration of alkynes coordinated to a metal center proceeds through enol-keto tautomers at the metal-carbon bond.[18] Both metal-keto and metal-enol form have been isolated. Ogo and collegues have demonstrated that an Ir-aqua complex $[Ir^{III}Cp^*(bpy)(OH^2)]^{2+}$ under acidic condition catalyzes the transformation of tetrolic acid ethyl ester to ethyl acetoacetate (scheme 2.1). By adjusting the conditions they were also able to isolate both the keto and enol intermediate. From the crystal structure of the enol intermediate obtained, Ogo proposed the initial formation of π-complex by the syn addition

of the H_2O ligand to the triple bond (**1**). Subsequent tautomeric transformation affords the keto-intermediate (**3**) which releases the organic product upon protonolysis of M-C bond (**4**).[18]

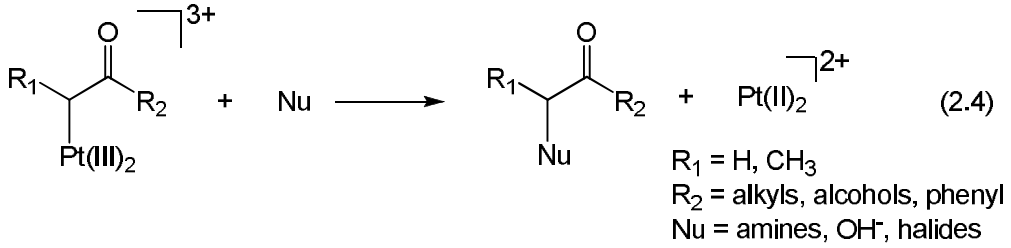
Scheme 2.1



There are only few examples of Pt-mediated functionalization of alkynes. Matsumoto has shown an example of activation of alkynes with a Pt^{III} dinuclear complex (eq. 2.3).[19,20,21] The complex reacts with alkynes in water to give ketonyl-Pt^{III} complexes. The intermediate with a π-coordinated alkyne could not be observed. The authors proposed that coordination of the alkyne triple bond to the N_2O_2-coordinated Pt^{III} occurs initially, followed by the attack of water.[21]



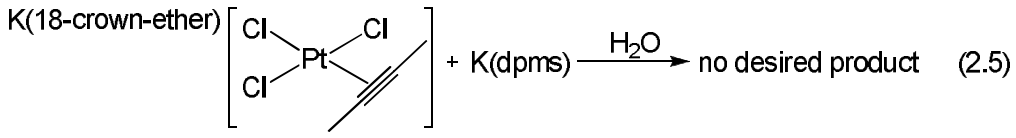
The resulting ketonyl-Pt^{III} complex reacts with various nucleophiles such as amines, halides and hydroxides at the alkyl-Platinum(III) position to give various functionalized ketones (eq. 2.4).[20, 21]



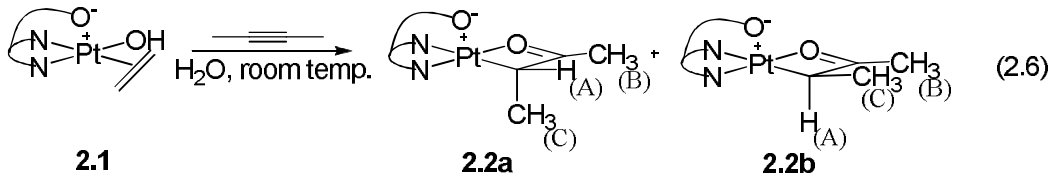
Results and Disscusion

Reactions of dpmsPt^{II} with 2-Butyne

We attempted initially to attach dpms to the 2-butyne Zeise's salt analog [K(18-Crown-6)][$PtCl_3$(2-butyne)], prepared according to a published procedure.[22] However, the butyne complex decomposed in water (cloudy black solution with complex NMR spectra) which is the usual solvent used in our dpms substitution reaction (eq. 2.5).



Olefin substitution by 2-butyne occurs readily with (dpms)Pt^{II} hydroxo ethylene complex **2.1** prepared according to the literature.[10] The reaction takes less than an hour to complete with an excess of 2-butyne in water to give Pt^{II} alkyl η^1-ketonyl complexes **2.2** (eq.2.6). When the reaction was conducted in H_2O, the ^1H NMR spectrum of the reaction mixture with H_2O peak suppression shows a doublet (3H, 0.97 ppm), a singlet (3H, 2.22 ppm), and a quartet (1H, 3.96 ppm, J_{195PtH} = 110 Hz) (fig. 2.2). A duplicated set of similar peaks also appears with smaller ratio (2.5:1), suggesting the presence of two isomeric products. When the reaction was set up in D_2O the doublet at 0.97 ppm appears as a singlet and the quartet at 3.96 ppm no longer showed up. It was presumed that intramolecular hydration occurs where solvent is the source of a proton and the resulting product is the keto form of the tautomerized Pt^{II}enol complex (Scheme 2.2).



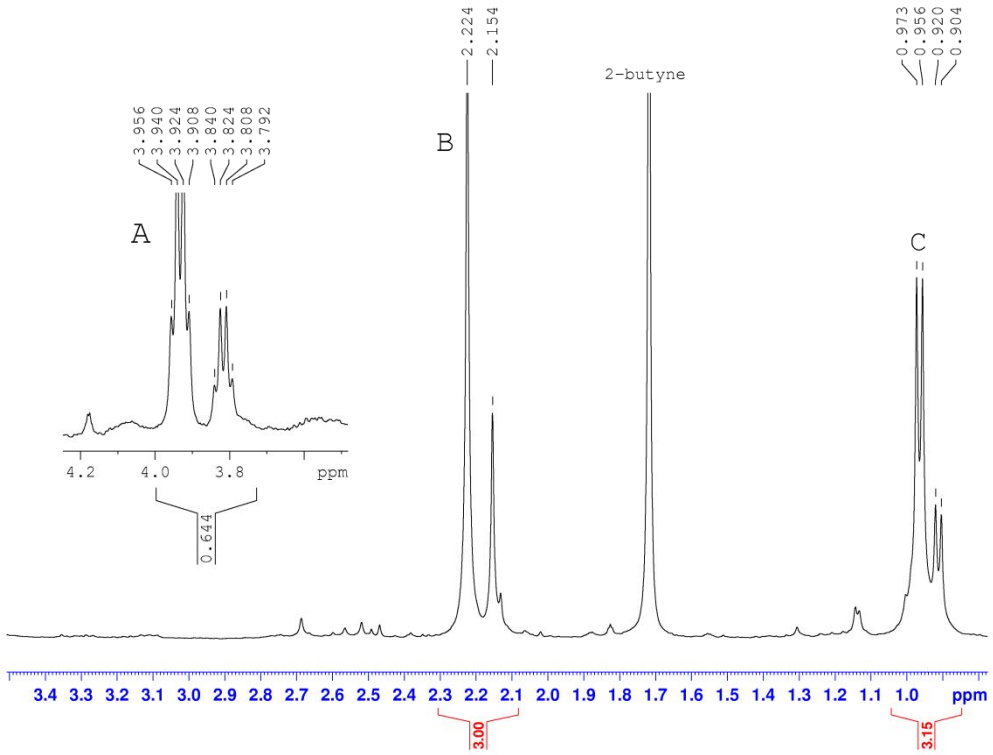


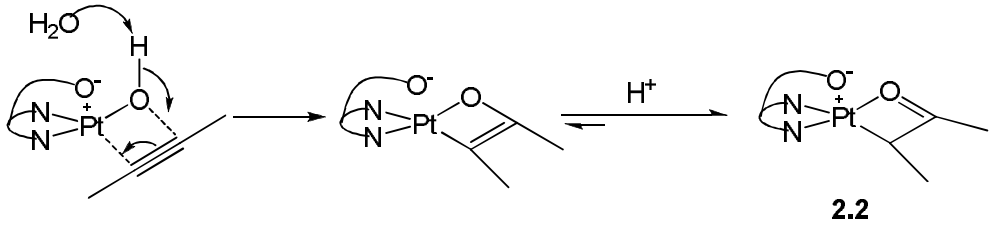
Figure 2.2. ^{1}H NMR spectrum of a reaction mixture containing complex **2.2.** The ligand's hydrogens are not shown.

Complex **2.2** was also characterized by ^{13}C NMR and ESI-MS. ^{13}C NMR showed the carbonyl carbon at 222.6 ppm, the methyl ketone carbon at 29.5 ppm. ESI-MS of the product's solution showed a peak at m/z 516.1 corresponding to **2.2***H^{+}

The formation of **2.2** can be explained this way: 2-butyne substitutes ethylene readily as it's a better ligand.[14] An intramolecular nucleophillic attack at the coordinated triple bond follows as shown in Scheme 2.2. The mechanism is similar to the

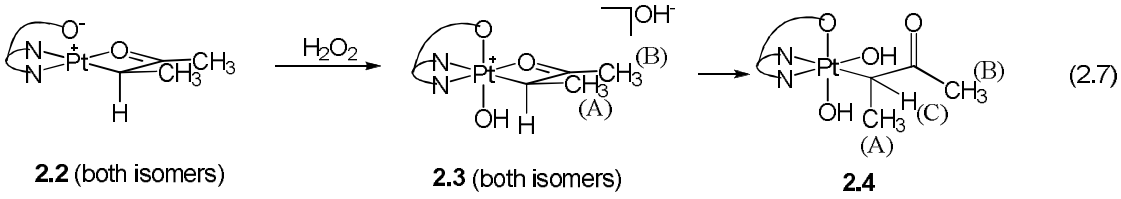
intermolecular hydration of alkyne proposed by the Ogo group using Ir^{III} aqua complex in water (scheme 2.1).[18]

Scheme 2.2



*Oxidation of **2.2** with H_2O_2*

Oxidation of **2.2** with 1 equivalent of hydrogen peroxide occurs readily at room temperature (eq. 2.7). The starting material **2.2** is consumed within an hour which gave rise to two isomeric intermediates assigned as **2.3.** The methyl groups of the intermediates show up as doublets at 0.56 and 0.59 ppm (3H) and two singlets at 2.13 and 2.15 ppm (3H) (fig. 2.3). It is noteworthy that the solution at this point turns basic (by pH paper). These peaks disappear over time while a doublet with distinct platinum satellites rises (-0.12 ppm, 3H, J_{195PtH} = 50.0Hz) along with a singlet (2.29 ppm, 3H) assign as **2.4** (fig. 2.4). The Pt-*CH* resonance appears as a quartet at 5.18 ppm (1H, J_{195PtH} = 114Hz). ^{13}C NMR of **2.4** shows the carbonyl carbon resonance at 215.1 ppm.



2.2 (both isomers) **2.3** (both isomers) **2.4** (2.7)

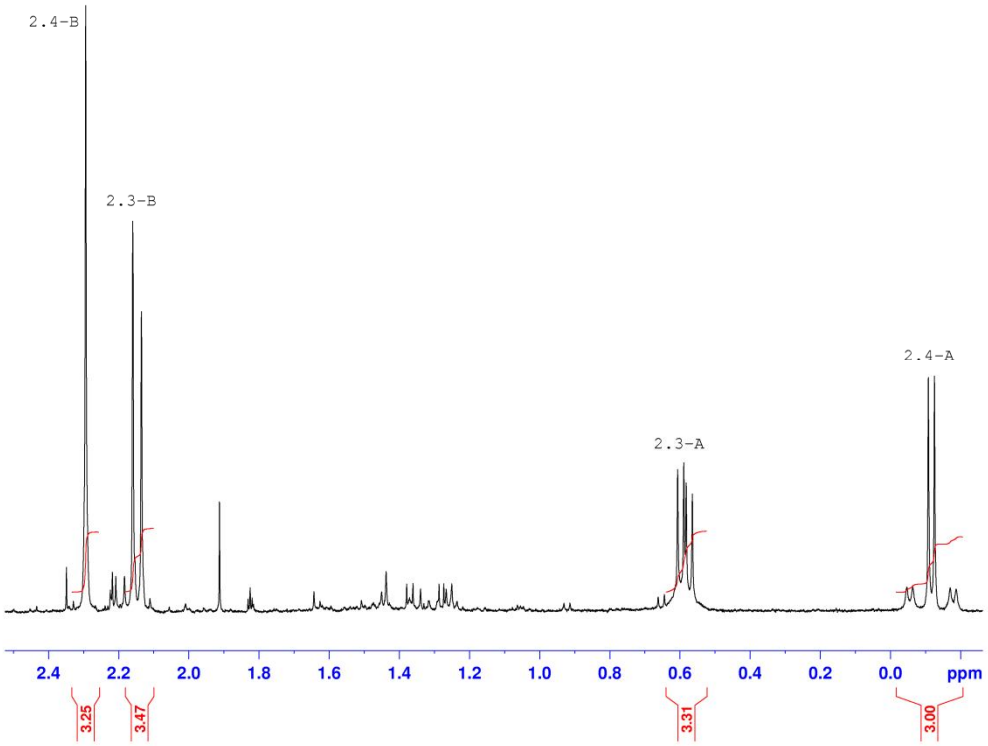


Figure 2.3. ^{1}H NMR spectrum of **2.2** after treatment with H_2O_2 for one hour. Only the methyl group hydrogens are shown and labeled.

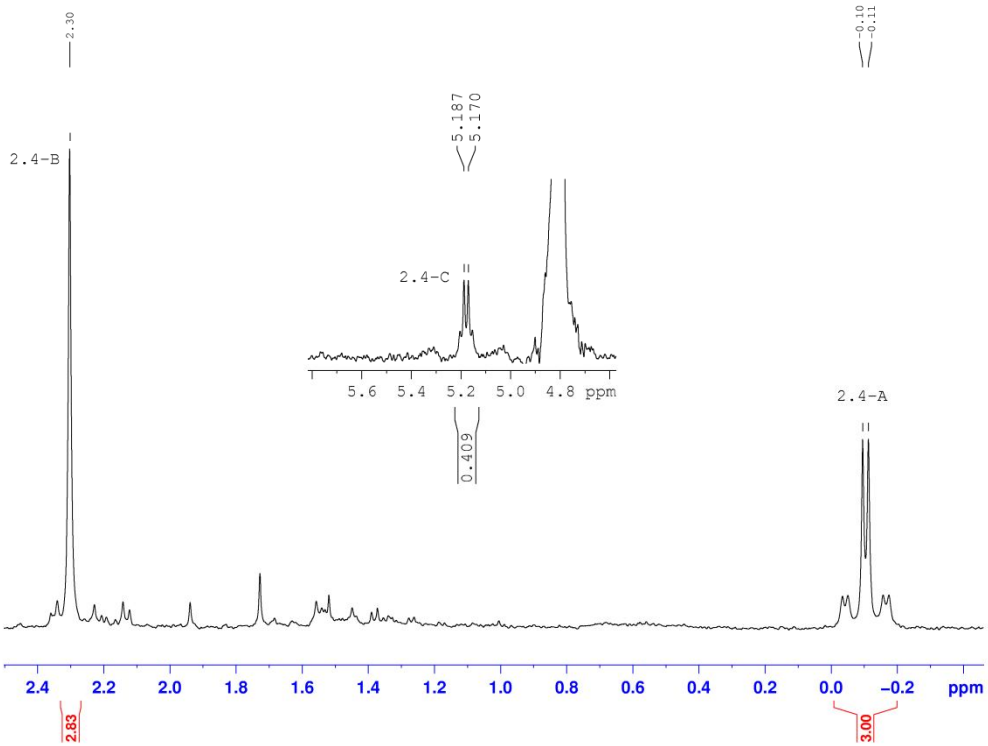


Figure 2.4. ^{1}H NMR spectrum of **2.2** after treatment with H_2O_2 for twenty hours. The dpms ligand hydrogens are not shown.

*Oxidation of **2.2** with O_2*

Oxidation of complex **2.2** with O_2 was found to be pH dependent. Best condition is a slightly acidic solution, with the pH ~ 6-6.5 (table 2.1). Oxidation was complete in three days at 1 atm of O_2. The fact that oxidation is slow compared to oxidation of other (dpms)Pt^{II} monoalkyl hydroxo complexes suggests that complex **2.2** isn't very electron

rich. This is because the alkyl group in the complex **2.2** bears an electron-withdrawing β-oxo group (scheme 1.1).

Table 2.1. Oxidation of **2.2** to **2.4** by Oxygen at different pH

pH	NMR %yield (20 hrs)
4.23	4.3
5.97	**29.1 (82.6)[a]**
6.48	**30.3**
7.01	20.1
7.54	12.5
8.10	5.3
9.58	1.7

a. after three days, %yield

Conclusion

Here we showed that (dpms)Pt^{II} alkyne undergoes a usual for alkynes hydration reaction in water. The η^1-ketonyl complex that forms is able to react with dioxygen to give Pt^{IV} secondary alkyl complex. Reductive elimination has yet to be studied on this complex. Considering the alkyl complex (dpms)$Pt^{IV}Me(OH)_2$ which eliminates methanol upon heating it in acidic solutions (eq. 1.7), complex **2.4** should have similar reactivity and eliminate 3-hydroxy-2-butanone under similar condition. What also should be done next is to study the reactions with different alkynes to establish the reaction substrate scope and its selectivity.

Experimental Procedures

Synthesis of Complex **2.2**

To (dpms)$Pt^{II}(CH_2CH_2)OH$ (217.1 mg) in 10 ml degassed H_2O was added 2-butyne (200 l) and the mixture was stirred for one hour under open air (do not stopper the flask). Initial yellow solution turns brownish with some brownish-black precipitate. Through a micro-glass syringe, 10 l of 1,4-dioxane was then added as an internal standard. Solvent suppression NMR with internal standard shows quantitative yield of two isomers of **2.2**. The solution is then centrifuged for 20 minutes at 10000 rpm. A yellow-brownish solution was then carefully separated from the precipitate using a plastic syringe connected to a small needle. The pH of the resulting solution is around 4.2, measured by a pH meter. The solution was adjusted to final volume of 10 ml before dividing to samples of equal volume (1 ml each). According to ^{1}H NMR, each of this solution contains 0.0047 mmol of complex **2.2.** These solutions were immediately used in subsequent oxidation by H_2O_2 and O_2 at different pH.

^{1}H NMR (50% D_2O v/v), major isomer, δ: 0.97 (d, *J*=6.5 Hz, 3H), 2.22 (s, 3H), 3.96 (q, J_{195PtH} =110Hz, *J*=6.3 Hz, 1H), 6.05 (s 1H), 7.43 (t, *J*=6.5 Hz, 1H), 7.62 (t, *J*=6.5, 1H), 7.81 (d, *J*=7.6 Hz 1H), 7.90 (d, *J*=7.7 Hz 1H), 8.12 (m, 2H), 8.70 (d, *J*=5.9 Hz, 2H). Minor isomer, δ: 0.92 (d, *J*=6.53 Hz, 3H), 2.15 (s, 3H), 3.84 (q, *J*=6.2 Hz, 1H), the pyridyls signals overlap with the major isomer. **^{13}C NMR** (50% D_2O v/v, with dioxane), Major isomer, δ: 15.8, 29.5, 30.2, 76.3, 126.4, 127.1, 129.1, 130.4, 140.4, 140.8, 149.2, 150.5,

153.0, 155.2, 222.6. Minor isomer**,** peaks are too ambiguous to tell**. ESI-MS**: m/z = 516.09 (calculated for H^+ = 516.0557).

*Oxidation of Complex **2.2** by H_2O_2.*

A solution containing 0.0047 mmol of complex **2.2** in 1 ml H_2O from the previous step (Synthesis of Complex **2.2**) was use immediately. The solution was added one equivalent of H_2O_2 (5 l) and stirred for 20 hours. NMR yield calculated using the internal standard is 75.5% based on **2.2**

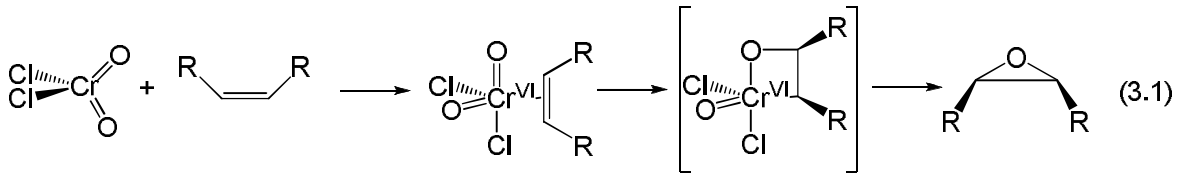
^{1}H NMR (50% D_2O v/v), δ: -0.12 (d, J_{195PtH} =50.0Hz *J*=6.7 Hz, 3H), 2.29 (s, 3H), 5.18 (q, J_{195PtH} =114Hz, *J*=7.0 Hz, 1H), 6.60 (s 1H), 7.92 (m, 2H), 8.11 (d, *J*=7.5,1H), 8.15 (d, *J*=7.8 Hz 1H), 8.39 (m, 2H), 8.70 (d, *J*=5.8 Hz, 1H), 8.85 (d, *J*=5.8 Hz, 1H). **^{13}C NMR** (50% D_2O v/v, with dioxane), δ: 17.0, 32.5, 40.6, 73.8, 128.4, 128.9, 129.8, 130.1, 144.2, 144.4, 148.8, 149.4, 149.7, 150.8, 215.1.

*Oxidation of Complex **2.2** by O_2 at different pH.*

Solutions containing 0.0047 mmol of complex **2.2** in 1 ml H_2O from the previous step (Synthesis of Complex **2.2**) was use immediately. Each of the sample (0.0047 mmol/ml) was adjusted to different pH according to Table 1 with 0.1 N NaOH. The pH was measured using a pH meter. Each reaction vial, equipped with a stir bar was then filled with O_2 and stirred vigorously for 20 hours before an NMR spectrum. The reaction mixture with the optimum pH (5.97) was filled with O_2 again and stirred till completion (70 hrs). The final product gave identical ^{1}H NMR spectrum compared to the product from the oxidation of **2.2** with H_2O_2.

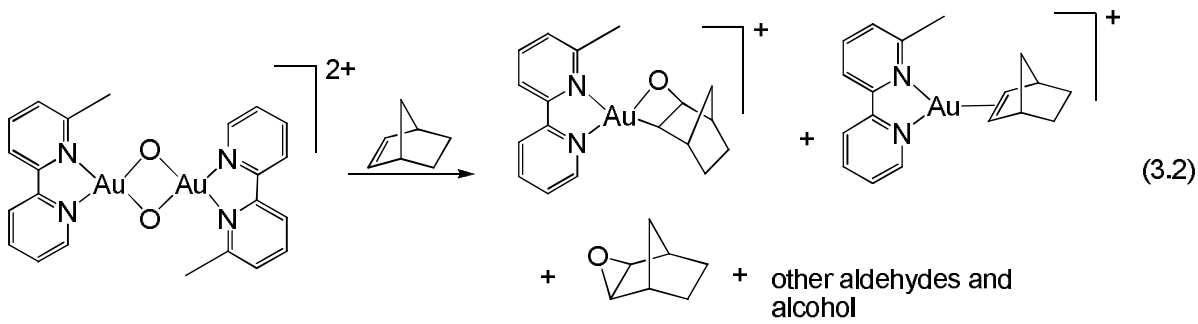
Chapter 3

Metalla-oxetanes are the products that are usually proposed in the oxidation of olefins.[23] For example, Sharpless proposed that epoxides form in a reaction of CrO_2Cl_2 and olefins are via metallaoxetane intermediates (eq. 3.1).[24]



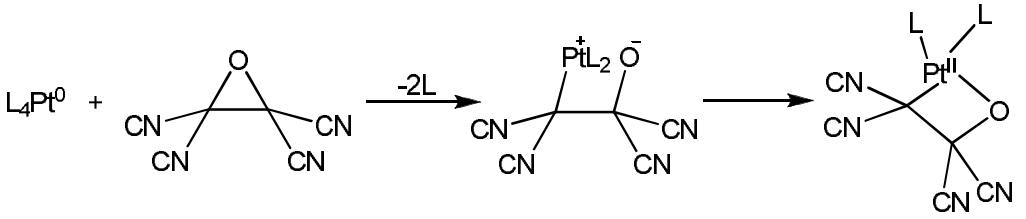
(3.1)

Examples of isolated metallaoxetanes and corresponding reductive elimination to form epoxides are rare. Only recently that a metallaoxetane derived from norbornene has been isolated. Cinellu reported that gold(III) oxo-complexes react with norbornene to give aura(III)oxetane which can form an epoxide and mixture of aldehydes and alcohol as the organic products (eq. 3.2).[25]



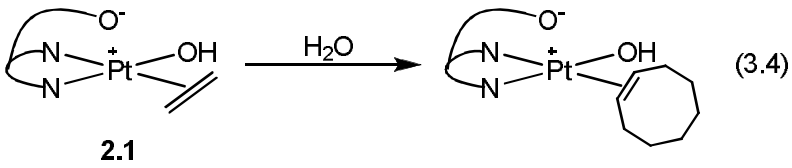
(3.2)

Epoxides with electron withdrawing groups such as tetracyanoethylene oxide oxidatively add to the Pt(0) center to give Pt^{II} oxetanes. The proposed mechanism is an initial attack of Pt(0) center at the electrophillic carbon to produce a non-cyclic intermediate which upon cyclization gives the Pt^{II} oxetane (eq. 3.3).[26]



(3.3)

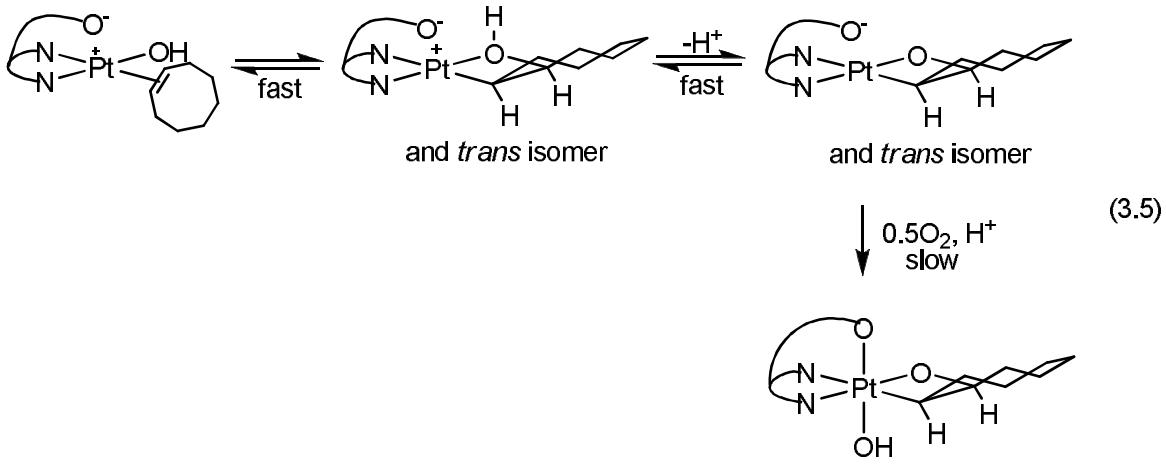
Our group have also recently demonstrated that Pt^{IV} oxetanes of cyclic strained alkenes such as *cis*-cyclooctene and norbornene can be prepared by ligand substitution reaction followed by oxidation with O_2. Olefin substitution occurs readily with the (dpms)Pt^{II} (η^2-CH_2CH_2)OH **2.1** to give the corresponding olefins hydroxo Pt^{II} complexes (eq. 3.4).[11]



2.1

(3.4)

In the presence of a base, intramolecular nucleophillic attack at the sp^2 carbon is driven forward leading to anionic species, capable of reacting with dioxygen. Here again a large amount of base can interfere with the proton transfer step as mentioned in chapter one (eq. 3.5).[10]



(3.5)

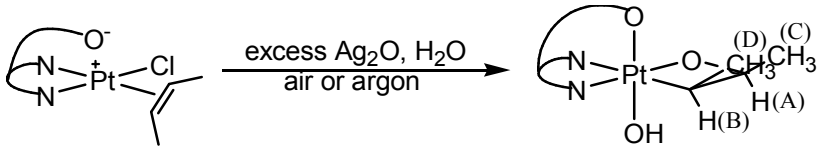
Here we set our goal in preparing a Pt^{IV} oxetane from a non-cyclic olefin. We use the symmetrical cis-2-butene for this study.

Results and Disscission

Ligand substitution between the complex (dpms)Pt^{II} (η^2-CH_2CH_2)OH **2.1** with *cis*-2-butene did not occur. Not so surprising since ethylene is a better ligand than *cis*-2-butene. Julia Khusnutdinova has reported before in her dissertation that the allyl complex (dpms)Pt(η^3-C_3H_5) can be prepared from Pt^{II} chloro propylene complex by substitution of the chloride ligand with the hydroxo group by adding 1 equivalent of NaOH. However, using the same procedure with (dpms)Pt^{II} chloro *cis*-2-butene complex **3.1** cause mainly decomposition due to loss of 2-butene.[27]

To selectively abstract chloride ligand from **3.1** we used Ag_2O. We initially studied the reaction with excess Ag_2O under O_2 or argon (eq.3.6). When complex **3.1** was stirred with 10 equivalent of Ag_2O in H_2O under air or argon for 24 hrs, a new pair of doublets

appears at 0.52 and 1.14 ppm. An ESI-MS spectroscopy shows a peak at m/z 534.16 corresponding to the complex tentatively assigned as **3.2*H**$^{+}$. Since the same oxidized product is obtain under the presence or absence of O_2, our initial assumption is that Ag_2O is responsible for oxidixing the Pt^{II} to Pt^{IV}species.



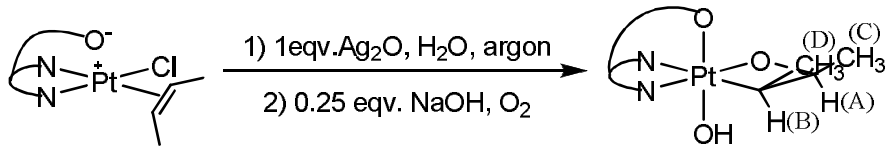
(3.6)

3.1 **3.2**

The complex could be extracted from the dried sample in a purer form by CH_2Cl_2. It was characterized by ^{1}H, ^{13}C NMR, NOE and ESI-MS as Pt^{IV} oxetane **3.2**. Yield is about 25% for this new complex by ^{1}H NMR. Note that loss of 2-butene, although not evident by ^{1}H NMR, could be detected by its odor from the reaction flask during the reaction. Proton NMR of an isolated sample also shows a multiplet of one hydrogen at 3.25 ppm for the *Pt-CH* with J_{195PtH} = 74.7 Hz, and another multiplet of the OCH group hydrogen at 4.91 ppm (fig. 3.1).

When one equivalent of Ag_2O under argon was used we expected the hydroxy analog of **3.1.** The resonances of two methyl group of coordinated 2-butene in **3.1** appears as a doublet at 1.83 ppm. After the reaction ceased, this resonance is about 33% compare to the product which gives rise to two doublets (1.28 ppm, 3H, J_{HH} = 5.9 Hz, 1.90 ppm, 3H, J_{HH} = 5.4 Hz), one for each methyl group. This new product is either the corresponding Pt^{II} hydroxo olefin or the neutral Pt^{II} oxetane complex. No oxidized complex **3.2**, was

detected. Adding 0.25 equivalent of NaOH to the solution (Ag compounds removed) and stirring under oxygen affords **3.2.**



(3.7)

3.1 **3.2**

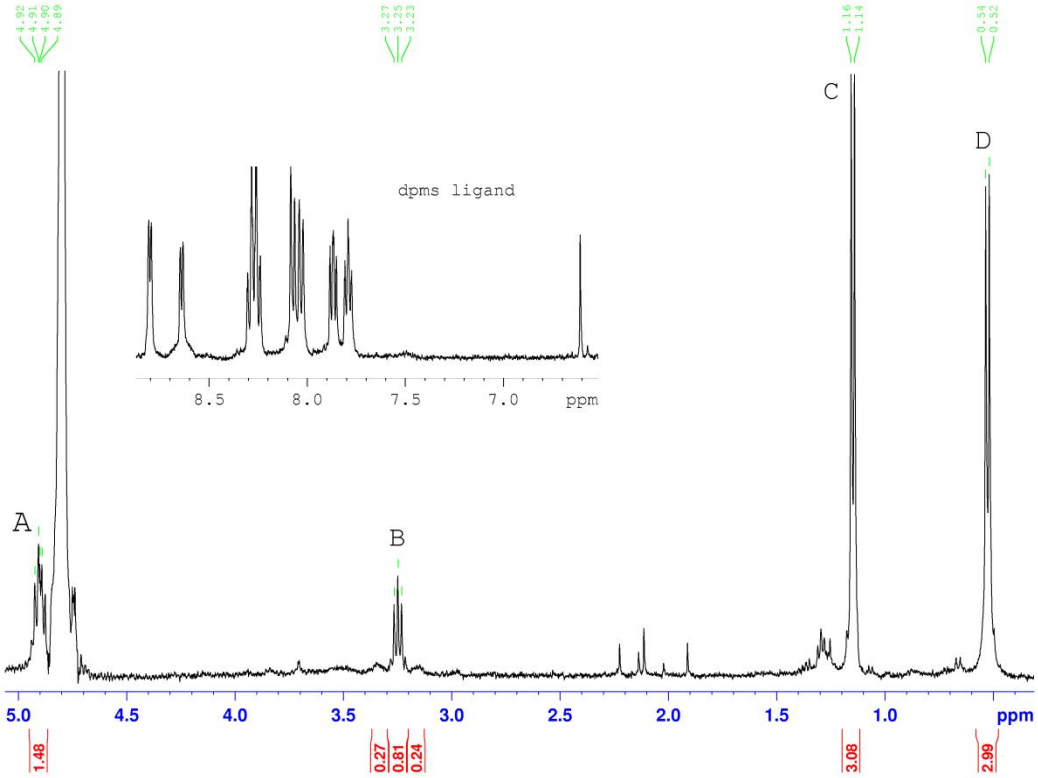


Figure 3.1. ^{1}H NMR spectrum of **3.2**

Preliminary result on reductive elimination of **3.2**

It is known that (dpms)Pt^{IV}oxetanes derived from cyclic olefins eliminate corresponding epoxides upon heating in dmso (eq.1.9). When **3.2** was heated in dmso at ~78°C, ^{1}H NMR shows complete disappearance of peaks that belongs to **3.2** in 2 hours. Instead a new doublet and a doublet of quartets appeared at 1.17 and 2.67 ppm respectively (fig. 3.2). According to the previously reported data for *cis* and *trans*-2,3-dimethyl oxiranes,[28] the product obtained is the *cis*-isomer. The *trans* isomer should give rise to a quartet for the oxirane hydrogens instead of an octet like shape due to virtually no coupling between these oxirane hydrogens.[28] The NMR yield for *cis*-2,3-dimethyl oxiranes is about 42% by interrgration against the solvent.

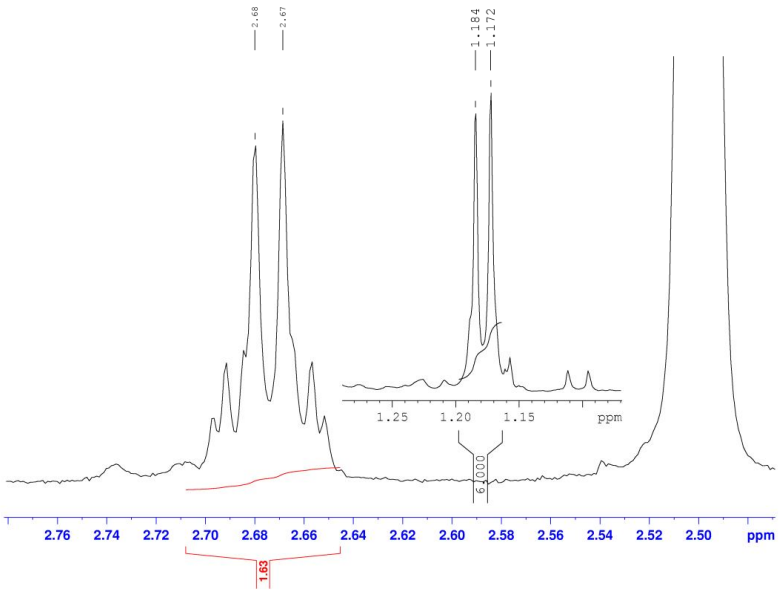


Figure 3.2. Resonances corresponding to *cis*-2,3-dimethyl oxiranes formed after heating **3.2** for 2 hours in dmso-d_6

Conclusion

We have found the pathway towards Pt^{IV} oxetane derived from an a cyclic non-strained olefin by preparing **3.2.** It is yet to be establish which isomer of **3.2** predominates. Ag_2O, when used is excess, oxidizes Pt^{II} to Pt^{IV} complex. Although, ring strain isn't part of the driving force here in forming the Pt^{IV} oxetane, complex **3.2** was stable enough to be isolated.

Experimental Procedures

*Synthesis of **3.2**, with excess Ag_2O*

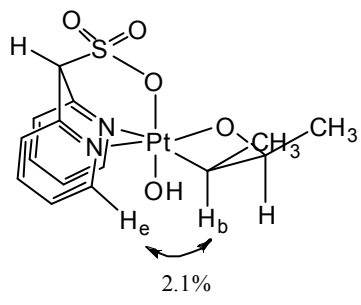
A NMR scale reaction can be set up by mixing **3.1,** 10.2 mg, with 21.6 mg Ag_2O (10 eqv.) and 1 ml D_2O. The mixture was stirred vigorously for 24 hours under air. Through a micro-syringe, 1µl of 1,4-dioxane was then added to the solution as an internal standard. The soluion was then centrifuged and carefully seperated from excess Ag_2O before taking ^1H NMR. Yield by ^1H NMR is about 22% by intergrating any of the methyl group peaks against the internal standard. When stirred under argon for 24 hours, yield by ^1H NMR is about 16%. For large scale set up, moderate purity of **3.2** could be obtained by the following work-up procedure: centrifuge the reaction mixture to separate dark brown solution from excess Ag_2O. Solvent was then evaporated under vacuum to give shiny black solid. CH_2Cl_2 was then used to extract out **3.2** (10ml X 3), giving pale yellow solution after filtering through celite. CH_2Cl_2 was then evaporated to obtain **3.2** as a yellow solid. Isolated yield has not been dertermined.

*Synthesis of **3.2**, with 1 equivalent Ag_2O, and O_2*

452.6 mg of **3.1** was stirred with 0.1027 g Ag_2O and 15 ml H_2O under argon for 24 hours. The mixture was then centrifuged to obtain pale yellow solution. 0.25 eqv. NaOH (212.5 l of 0.1N NaOH solution) was added dropwise while stirring under air. A balloon filled with oxygen was then attached to the flask and continue to stir for another 4 hrs. Solvent was then evaporate under vacuum and CH_2Cl_2 was then used to extract **3.2** (10ml X 3) before filtering through celite to give pale yellow solution. This procedure has not been optimized yet. Isolated yield of **3.2** is 8.4% based on **3.1**.

^{1}H NMR (D_2O, 22°C), δ: 0.52 (d, *J*= 6.54 Hz, 3H), 1.14 (d, *J*= 6.18 Hz, 3H), 3.25 (m, J_{195PtH} = 74.7 Hz, 1H), 4.91 (m, 1H), 6.61 (s 1H), 7.79 (t, *J*= 6.85 Hz, 1H), 7.86 (t, *J*= 7.09 Hz, 1H), 8.02 (dd, *J*= 9.69, 7.92 Hz, 2H), 8.24 (m, 2H), 8.63 (d, *J*= 5.46 Hz 1H), 8.79 (d, *J*= 4.83 Hz 1H). **^{13}C NMR** (D_2O, 22°C, with dioxane), δ: 17.5, 21.3, 25.9, 71.7, 91.6, 128.1, 128.4, 128.7, 129.5, 142.9, 144.0, 148.3, 148.9, 151.2. **ESI-MS**: m/z = 534.16 (calculate for **3.2***H^+= 534.06623).

*Selective 1D-difference NOE experiment (D_2O) for **3.2***



In 1D-difference NOE experiment, NOE was observed between H_b and one of the pyridine ortho hydrogen of the dpms ligand, H_e. Irradiation of a resonance at 3.25 ppm showed positive NOE of a doublet at 8.63 ppm (2.1%). The mixing time was 0.4s and delay time was 4s.

*Reductive Elimination of cis-2,3-dimethyl oxiranes from **3.2***

About 20 mg of **3.2** was added dmso-d_6 (1ml) in a dried glovebox filled with argon atmosphere. The yellow solution was added to a J.Young NMR tube and tightly sealed with a screw cap. The solution was heated at ~78°C for 2 hours. The solution turns brown with formation of pale brown precipitate. The NMR tube was then shaken and, to avoid observing broad spectrums, precipitate was let settled down in the NMR tube for one hour before taking ^{1}H NMR.

Initial **^{1}H NMR** (DMSO, 22°C) δ: 0.45 (d, *J*= 6.39 Hz, 3H), 1.01 (d, *J*= 5.92 Hz, 3H), 1.95 (s, 1H) 2.82 (m, J_{195PtH} = 80.4 Hz, 1H), 4.59 (m, 1H), 6.71 (s 1H), 7.75 (t, 1H), 7.80 (t, 1H) 8.00 (d, 2H), 8.21 (q, 2H), 8.61 (d, *J*= 5.04 Hz 1H), 8.78 (d, *J*= 4.94 Hz 1H).

Final **^{1}H NMR** (DMSO, 22°C) δ: 1.18 (vd, *J*= 4.79 Hz, 6H) 2.67 (m, 2H). The aromatic region was too ambiguous to characterize.

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