ABSTRACT

Title of Thesis: REDUCTIVE ELIMINATION OF (DPMS)PT[IV] COMPLEXES DERIVED FROM ISOMERIC 2-BUTENEs AND 2-BUTYNE (DPMS=DI(2-PYRIDYL)METHANE SULFONATE)

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The (dpms)Pt[II] complexes (dpms = di(2-pyridinyl)methanesulfonate)derived from some cyclic olefins can be readily oxidized to Pt[IV] oxetanes, followed by reductive elimination to produce corresponding epoxides. A catalytic version of this reaction can potentially be achieved if decomposition of active species responsible for olefin substitution is avoided. Several attempts were made to solve this problem, and a more hydrophilic analog of the dipyridinemethanesulfonate ligand was obtained. Furthermore, the reductive elimination step of Pt[IV] oxetanes was studied by using diastereomeric *cis*- and *trans*-2-butene derivatives. We believe that two mechanisms of C-O reductive elimination may be involved in these reactions and that steric repulsion between substituents at the oxetane carbon atoms may play a major role in determining the predominant of the two competing mechanisms. Platinum(IV) η^1-butanone complex was synthesized and characterized, which was found to undergo different types of elimination reaction to give a series of butane derivatives as products.

REDUCTIVE ELIMINATION OF (DPMS)PTIV COMPLEXES DERIVED FROM

ISOMERIC 2-BUTENEs AND 2-BUTYNE (DPMS=DI(2-PYRIDYL)METHANE

SULFONATE

By

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Thesis submitted to the Faculty of the Graduate School of the
University of Maryland, College Park in partial fulfillment
Of the requirements for the degree of
Master of Science
2012

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Acknowledgement

I'm very grateful to my supervisor, Professor Andrei Vedernikov, for his advice and support. His encouragement, guidance and support from the initial to the final level enabled me to develop an understanding of the subject. And thanks to my colleagues, Daoyong Wang, Yang Wen, Shrinwantu Pal, Anna Sberegaeva and Dave Jenkins for the friendship.

Table of Contents

List of Figures

iv

# Chapter I: C-O Reductive Elimination Selectivity of (dpms)Pt^{II}-*cis*-butene/*trans*-butene Complexes

Epoxide derivatives are among the most important reagents in both pharmaceutical and chemical industry.[1] While ethylene oxide and propylene oxide enjoy massive production in the large-scale chemical industry, epoxides with other functional groups are frequently used in pharmaceutical and biochemical synthesis. Industrial production of ethylene oxide requires high temperature and is characterized by the low degree of selectivity.[2] Thus, its consumption of energy and the production of CO_2 as a byproduct may have severe impact on the environment. On the other hand, the production and synthesis of other olefin epoxides usually involves the use of organic hydroperoxides as oxidants.[3] Thus, it is evident that the development of more efficient and environmental friendly procedures for epoxide production with O_2 as the sole oxidant deserves our efforts.

O_2 is a thermodynamically powerful oxidant due to its high reduction potential (**Scheme 1**). However, using O_2 as the oxidant is kinetically unfavorable if the reactants and the products are ground state singlets.[4] One of the solutions is to use transition metals "shuttle" electrons between O_2 and low valent metal species. Such a process can turn O_2 to a more kinetically reactive species (e.g. metal-peroxo complexes).[5a]

Inspired by the "Shilov System" which involves oxidation of low valent Pt^{II} species to Pt^{IV} species, we developed a reaction system that can functionalize Pt^{II} olefin complexes

with O_2 as sole oxidant. The reaction can be performed under mild condition with water as a solvent.[5b, 5c] Although a catalytic version of this reaction has not been developed, the transformation shows some potential in greener approach to epoxides (**Scheme 2**).

Scheme 1. Standard Potentials Between H_2O and O_2
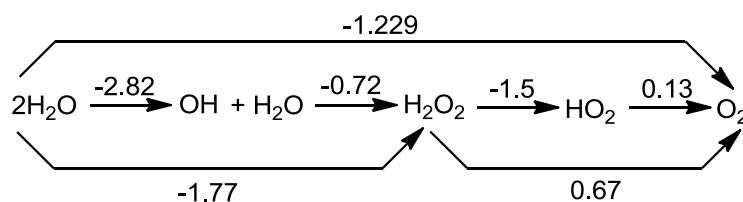
Scheme 2. Previous Research on Cyclic Olefin-derived Pt^{IV} Oxetanes

$$RCH_3 + PtCl_6^{2-} + H_2O\ (Cl^-) \xrightarrow[\text{H}_2\text{O, 120}^\circ\text{C}]{\text{PtCl}_4{}^{2-}} RCH_2OH\ (RCH_2Cl) + PtCl_4^{2-} + 2HCl \qquad \textbf{(1.1)}$$

2
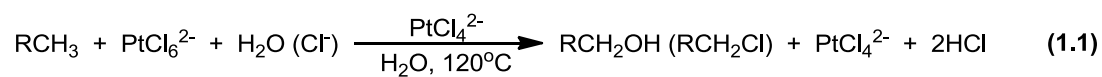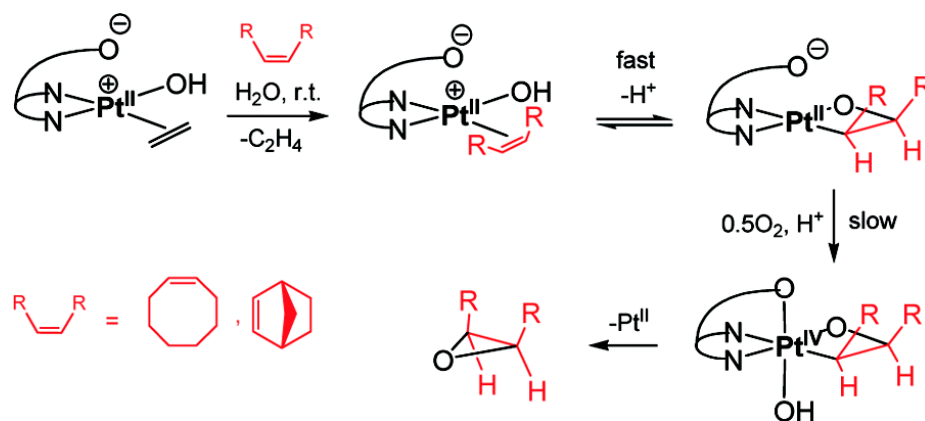
Based on our previous work on mild Pt^{II}-mediated alkene oxidation with O_2, our group has sought to explore the possibility of using O_2 as the terminal oxidant for catalytic functionalization of olefins into epoxides in protic solvents. Platinum(II) hydroxo dimethylsulfoxide complex, $(dpms)Pt^{II}(OH)(DMSO)$ (dpms = di(2-pyridyl)methanesulfonate), in trifluoroethanol solvent was used as a precatalyst for aerobic epoxidation of norbornene (**Scheme 3**). The reaction resulted in slow formation of *exo*-norbornene oxide and a relatively fast decomposition of the precatalyst to form an insoluble dinuclear Pt^{II} complex, $(dpms)_2Pt^{II}_2(\mu\text{-}OH)_2$.[5b] Steps I, II and III were proven experimentally in our group to be relatively fast and selective at 60 ^{o}C. The substitution of an aqua ligand in $(dpms)Pt^{II}(OH)(OH_2)$ by an olefin (step V), is expected to be more facile than the olefin-for-DMSO substitution in $(dpms)Pt^{II}(OH)(DMSO)$ since aqua ligand is a better leaving group than is DMSO. The catalyst decomposition (step IV), is, probably, the step that affects the catalyst stability and impedes the whole reaction. Among steps I-III, step III was found to be most interesting from the point of view of its mechanism. It was termed as "direct C-O elimination". The direct C-O elimination involves retention of configuration of both olefinic carbon atoms and does not involve any external nucleophiles. It was also shown computationally that formation of the new C-O bond and cleavage of the Pt-C bond may occur in a concerted fashion. At the same time, all of the substrates that have been used at this step so far are derivatives of cycloolefins. It would be interesting to explore stereochemical outcome of the C-O reductive elimination of epoxides from Pt^{IV}

oxetanes derived from acyclic olefins where a change of configuration of the olefinic carbon atoms may be possible.

In the industrial production of ethylene epoxide two possible pathways of the epoxide formation in heterogeneous silver-catalyzed ethylene oxidation were possible: concerted addition of surface oxygen atom to a double bond of ethylene (**Scheme 4,** a) and sequential formation of two C-O bonds via an intermediate surface 2-metallaoxetane (**Scheme 4**, b).[6] In fact, 2-metallaoxetanes can serve as key intermediates in a series of reactions that lead to the formation of aldehydes, ketones, esters and epoxides.

Scheme 3. Proposed Catalytic Cycle of (dpms)Pt^{II} Complex-mediated Aerobic Epoxidation of Olefins
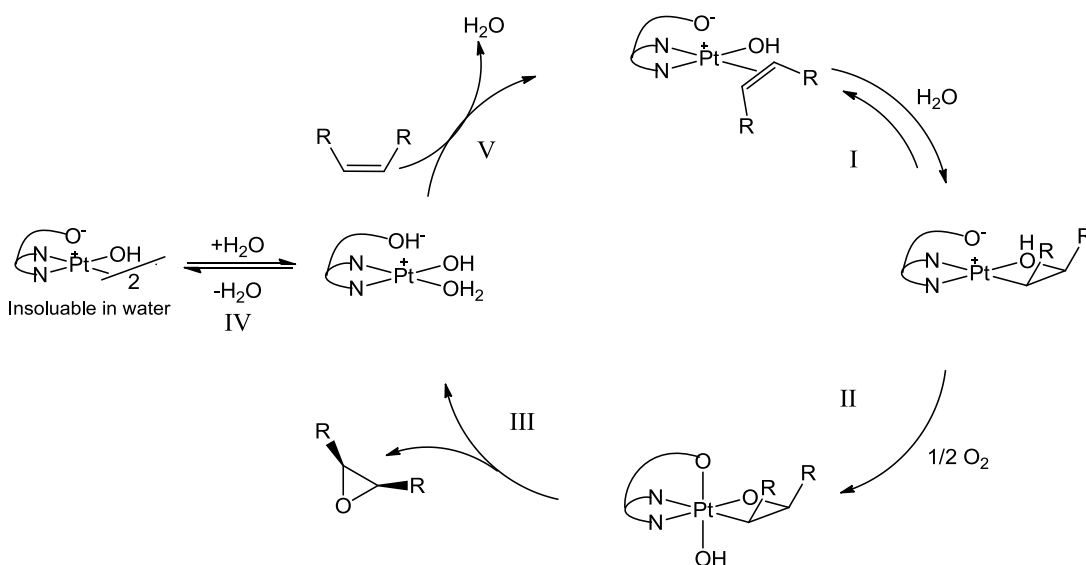
Scheme 4. Possible Intermediate in Ethylene Epoxidation on Ag Catalyst
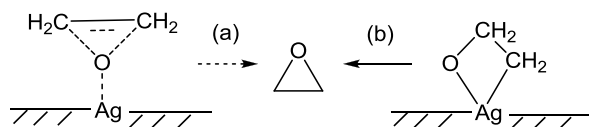
It was originally postulated by Sharpless in 1977 that metallaoxetanes might be involved in homogeneous oxygen-transfer reaction to alkenes.[7] In their initial report, the group found that olefin oxidation with chromyl chloride CrO_2Cl_2 at low temperatures leads to the formation of products of *cis*-addition predominantly: epoxides, *cis*-chlorohydrins and *cis*-dichlorides as primary products. To explain the observed selectivity, the following mechanism was proposed (**Scheme 5**):

Scheme 5. Epoxidation of Olefins with Chromyl Chloride
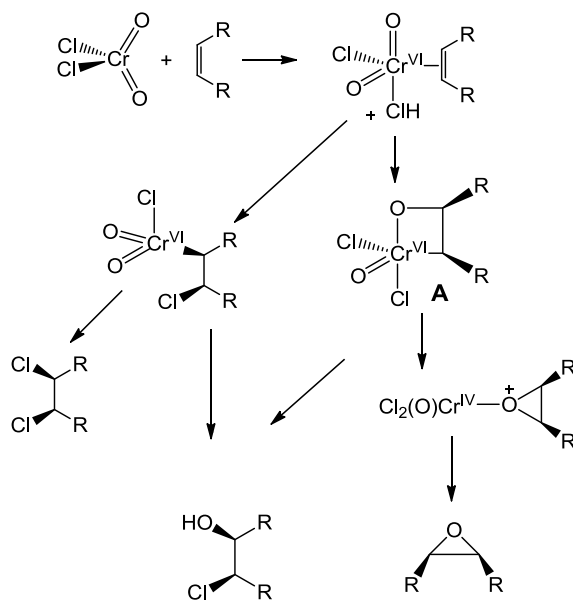
Following the pioneering idea of Sharpless, different experimental and computational results have been published to support the involvement of an oxetane intermediate. Manganaoxetane was suggested as a key intermediate in salen-Mn catalyzed epoxidation reaction.[8] Nonetheless, different mechanistic pathways via [3+2] cylcoaddition process were also considered as even more competitive routes. [9]

The first direct evidence for the formation of epoxide from reductive elimination of metallaoxetane was not published until 2005. Cinellu and co-workers reported reductive elimination of epoxide from an isolated metallaoxetane complex in homogeneous system (**Scheme 6**).[10] However, the reaction was not clean and was accompanied by the formation of aldehydes and other products.

Scheme 6. Gold-mediated Epoxidation of Norbornene.
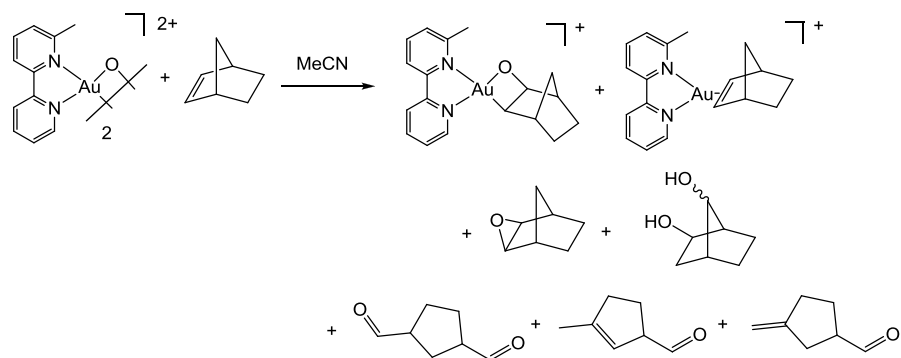
Scheme 7. Possible Mechanisms for Oxidative Addition of Tetracyanoethylene Oxide to Pt^0
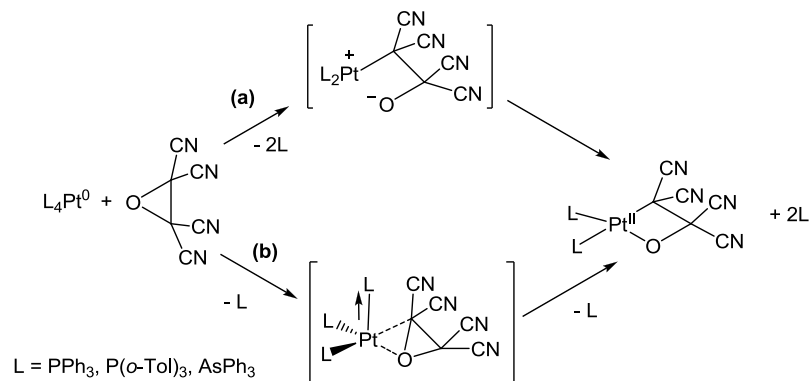
As a matter of fact, the microscopic reverse of reductive elimination, oxidative addition of epoxides, was observed experimentally for low-valent late transition metal complexes, Pt^0,[11] Pt^{II}, [12] and Rh^I.[13] For example, Ibers, Lenarda and Graziani reported the oxidative addition of electron-poor epoxides such as tetracyanoethylene oxide, to Pt(0) complexes L_4Pt (L = PPh_3, $P(o$-Tol$)_3$, $AsPh_3$) in aprotic solvents yielding platina(II)oxetanes.[11] Ibers suggested a step wise mechanism that involves initial nucleophilic attack by L_2Pt^0 at the epoxide ring leading to the cleavage of one of the C-O bonds. The subsequent cyclization produces platinum oxetane (pathway **a**, **Scheme 7**). Alternatively, Jørgensen proposed direct oxidative addition of the C-O bond of epoxide to a L_3Pt^0 center (pathway **b**, **Scheme 7**).

Results and Discussion

We have recently found that a number of Pt^{IV} oxetanes can be readily prepared by oxidation of (dpms)Pt^{II}(OH) complexes derived from cyclic alkenes.[4b] The resulting

7

oxetanes are able to reductively eliminate corresponding cycloolefin oxides stereospecifically to form *cis*-epoxides. Pratheep Khanthapura has then reported in his MS thesis[14] that (dpms)Pt[IV] oxetane **1** derived from *cis*-2-butene eliminates a mixture of *trans*- and *cis*-2-butene oxides upon heating in dmso (**Scheme 8**). In order to get a better understanding of the reactivity of Pt[IV] oxetanes at C-O bond forming step and, in particular, the lack of stereospecificity in the reaction, complex **1** was prepared following the protocol developed by Khanthapura. We have found that the *trans*-:*cis*-epoxide ratio resulting from reductive elimination of **1** determined by integration of the signals corresponding to the α-H of the two isomers is as high as 19 : 1.

This observation suggests that there is an alternative reaction mechanism for C-O elimination from Pt[IV] oxetanes, in addition to concerted direct C-O reductive elimination from Pt[IV] center proposed earlier. Here we propose that the C-O elimination may also operate a non-concerted mechanism (path a, Scheme 8) as it follows from the observed inversion of configuration of one of the oxetane carbon atoms. A reaction sequence involving the oxetane Pt-O bond dissociation (Scheme 8, from **2** to **5**) followed by an S_N2 attack of the resulting alkoxide anion on the carbon atom attached to Pt[IV] center **6** can account for the inversion. Small fraction of *cis*-2,3-dimethyloxirane **7** formed in the reaction as well may be due to the realization of the direct C-O elimination of Pt[IV] oxetanes (path b), the only mechanism observed for Pt[IV] oxetanes derived from cycloolefins.

Scheme 8. Mechanisms of the formation of *cis-* and *trans*-1,2-dimethyloxiranes from complex **1**.
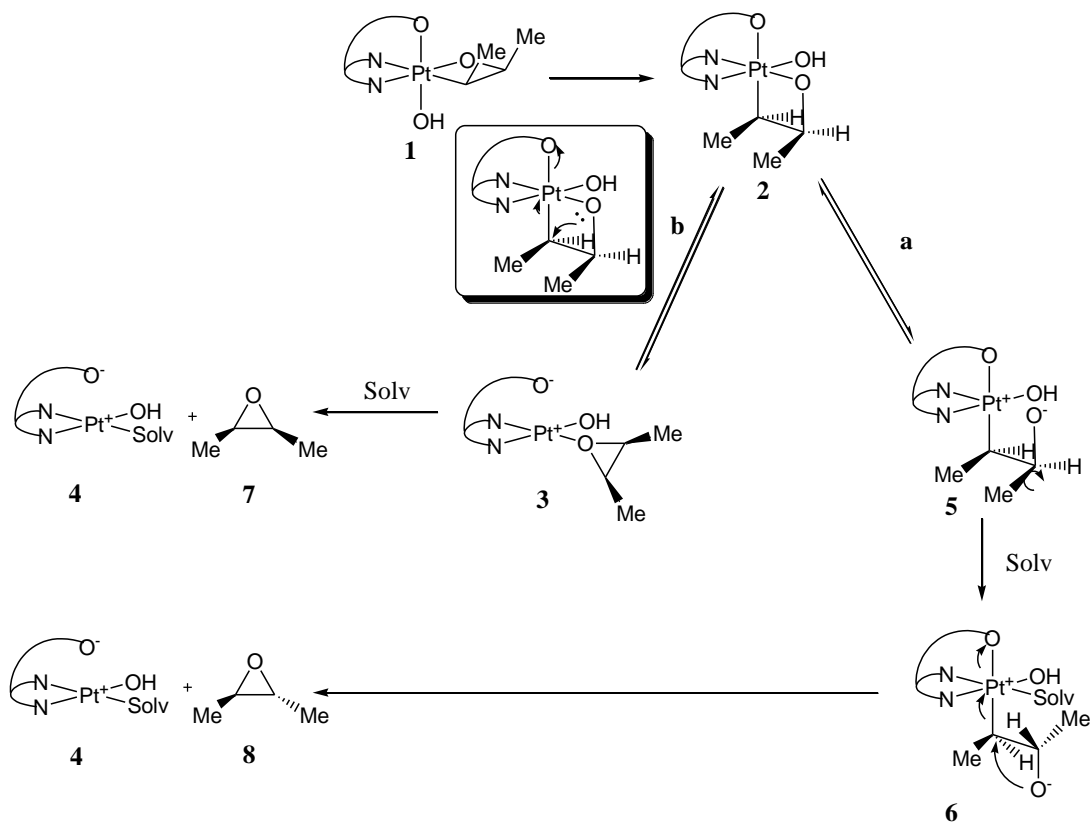
To better understand the reactivity Pt^{IV} oxetanes derived from acyclic alkenes, in this work we also synthesized one of the diastereomeric (dpms)Pt^{IV} –oxetane complexes **10** derived from *trans*-2-butene. We were curious to see if both *cis-* and *trans*-2,3-dimethyloxirane can form in the course of reductive elimination of **10** (Scheme 9). If the *cis*-isomer can form that fact would support additionally the stepwise C-O elimination mechanism **(Scheme 9**, path a). In turn, formation of the *trans*-isomer would support the concerted C-O reductive elimination mechanism (path b).

9

Scheme 9. The formation of *cis-* and *trans*-1,2-dimethyloxiranes from complex **10**.
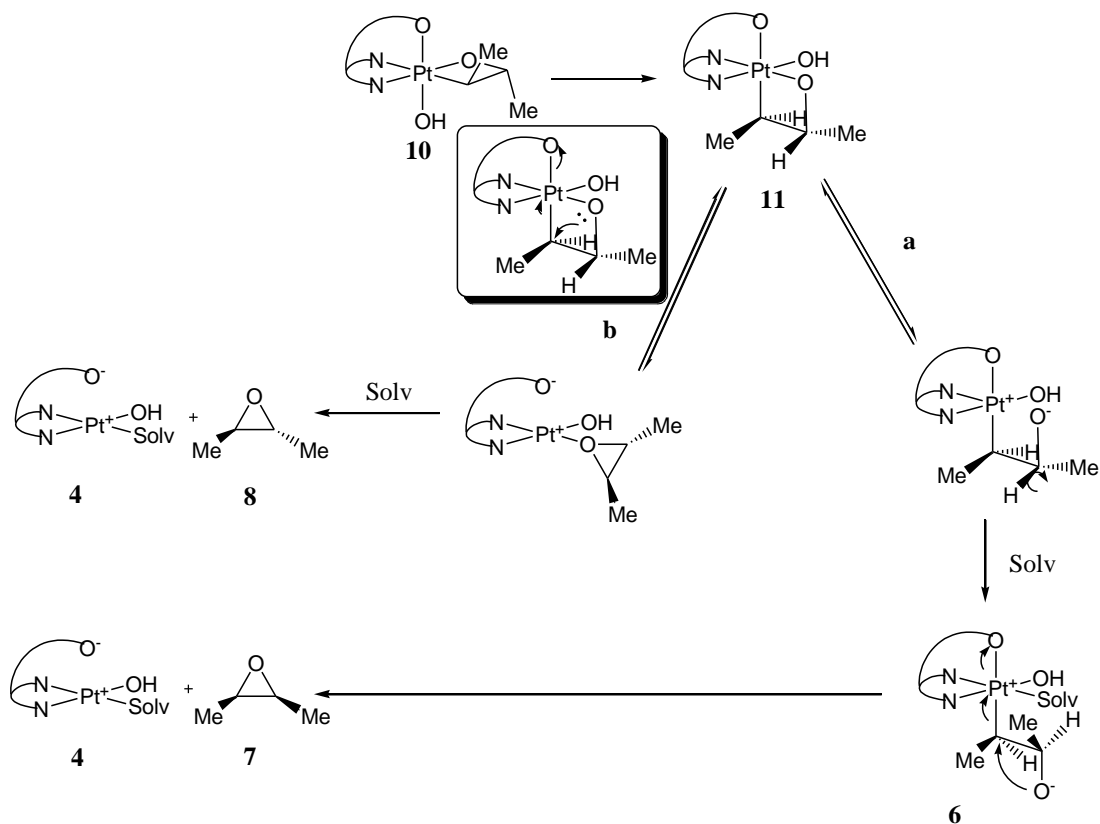
The *trans*-butene derivative **10** could be obtained following a procedure similar to that used for corresponding *cis*-butene derived Pt^{IV} oxetane. When *trans*-2-butene complex **9** was stirred under air for 24 hrs, a pair of doublets appeared at 0.50 and 1.12 ppm. These signals could be assigned to one of two possible diastereomeric Pt^{IV} *trans*-dimethyl-substituted oxetanes formed as the major product. Similar NMR patterns and similar diastereoselectivity were observed in the reaction leading to the corresponding *cis*-butene – derived Pt^{IV} oxetane **1**. To further confirm the formation of this different isomer of the Pt^{IV}

oxetane, mixture of 0.5 equivalents *cis-* and 0.5 equivalents *trans*-butene (dpms)Pt^{II}(Cl) complexes was allowed to react with 6 equivalents of Ag_2O in H_2O. After 12 hours, two sets of overlapping doublets were observed in ^1H NMR, supporting the formation of two different oxetanes (**Fig. 1**).
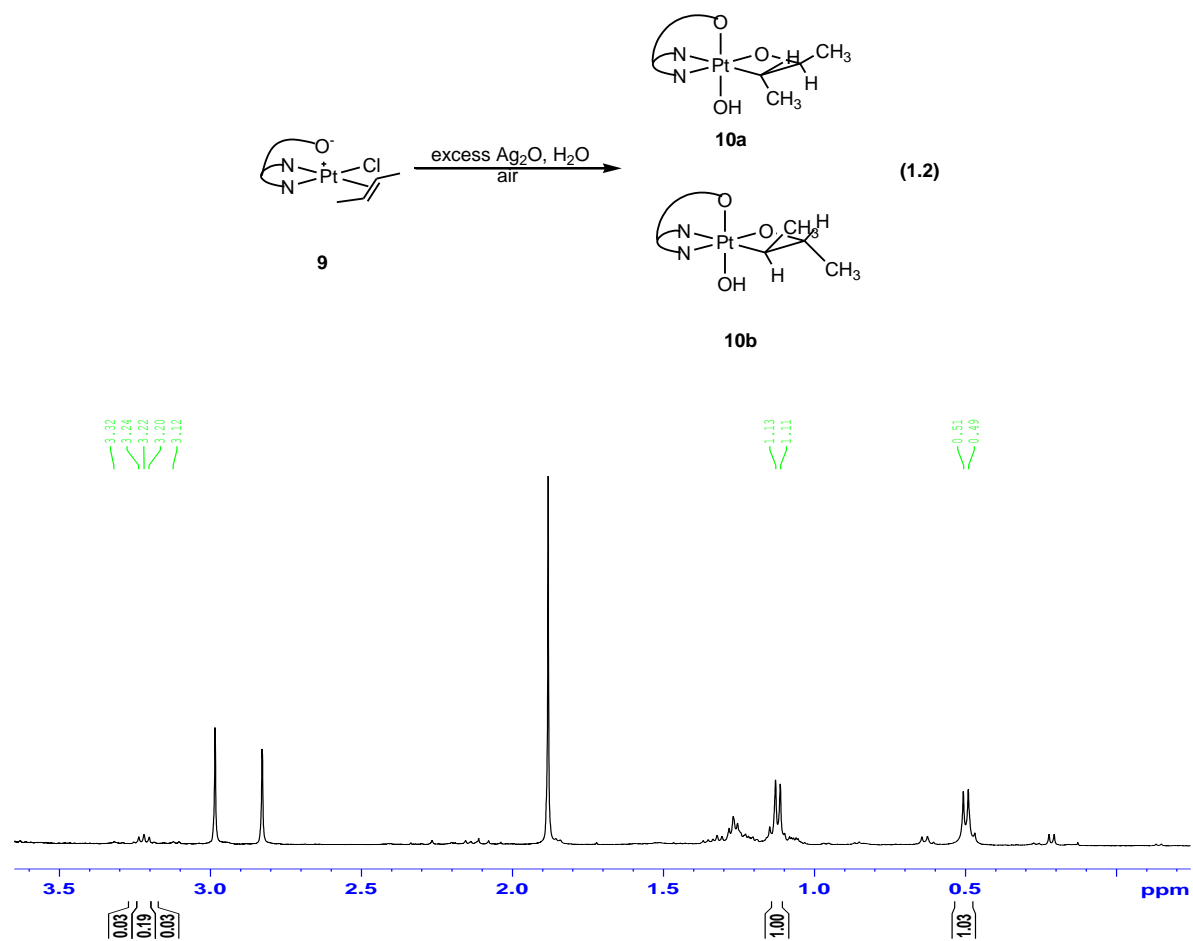
Figure 1. ^1H NMR Spectrum of a mixture of **1** and **10.**

It is worth of noting that the major isomer has been assigned the structure of the diastereomeric compound **10** based on results of our NOE experiments. (**Fig. 2**)
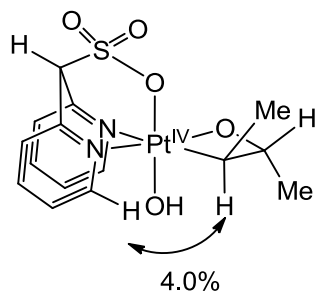
Figure 2. NOE of the PtCH-fragment in complex **10**.

When the oxetane **10** was heated in DMSO at 75-78 °C, ^{1}H NMR shows complete disappearance of peaks that belong to **10** in 5 hours. A new doublet and a doublet of quartets appeared at 1.17 and 2.67 ppm, which correspond to *trans*-2,3-dimethyl oxirane. Hence, the isomeric oxirane **8** expected for the concerted C-O elimination reaction of **10** formed selectively. Trace amount of *cis*-2,3-dimethyloxirane **7** was also detected by NMR. Both complexes derived from two different stereoisomers of 2-butene produced a qualitatively same set of products so confirming the idea of realization of two alternative reaction mechanisms shown in Schemes 8-9.

An analysis of Newman projections below suggests that the observed reaction selectivity might originate from the steric repulsion between two methyl groups of **2**

(**Scheme 10**). In the first scenario, the steric repulsion between two eclipsed methyl group may trigger the cleavage of the oxetane Pt-O bond followed by rotation about the oxetane C-C bond. The resulting staggered conformer with *trans*-arrangement of Pt^{IV} and O^- centers would then undergo an intramolecular S_N attack of the alkoxide oxygen onto the carbon attached to the Pt^{IV} center. In the scenario of the oxetane derived from *trans*-butene, the repulsion was not so strong and the direct reductive elimination would not be impeded.

Scheme 10. Newman Projection Analysis of C-O elimination from Cis- and Trans-butene-derived PtIV Oxetanes 2 and 11.
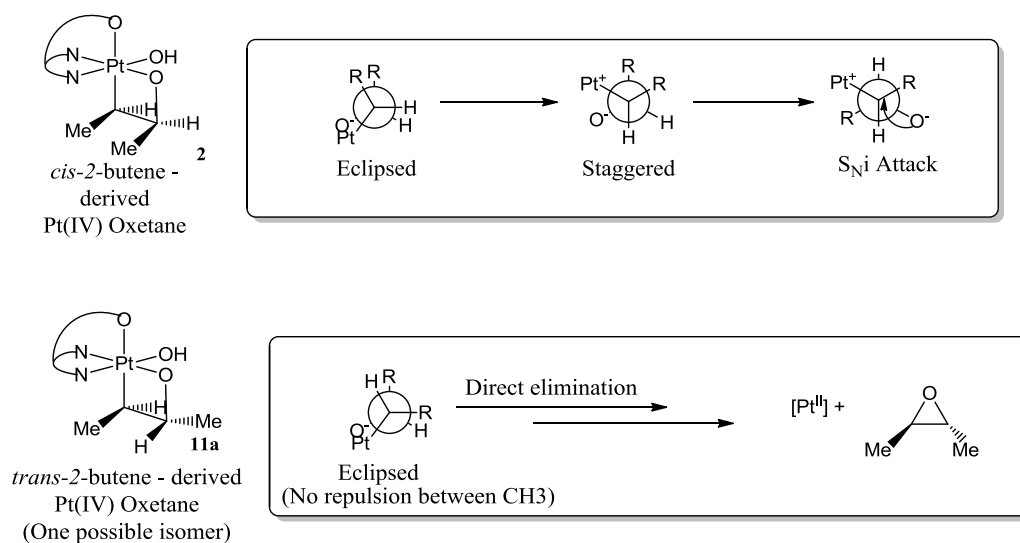
However, Pt-O dissociation of the oxetane **2** would lead to the initial formation of a five-coordinate Pt(IV) "alkoxide" species **5** (Scheme 8). This intermediate could be subsequently stabilized by a coordinating ligand, i.e., DMSO. Importantly, the "alkoxide" could be stabilized by polar solvents especially those that can serve as hydrogen bond

donors with respect to the anionic oxygen center. Such solvents can be expected to lower the barrier of Pt-O bond dissociation and to increase the fraction of product **8**. Vice versa, weakly polar solvents are expected to decrease the fraction of this diastereomeric epoxide. Holding in mind this consideration, we sought to investigate the effect of different solvents on the reactivity of the *cis*-butene − derived oxetane. Following solvents were used: DMSO-d_6, CD$_2$Cl$_2$, THF-d_8.

THF-d^8

CD$_2$Cl$_2$

DMSO-d^6
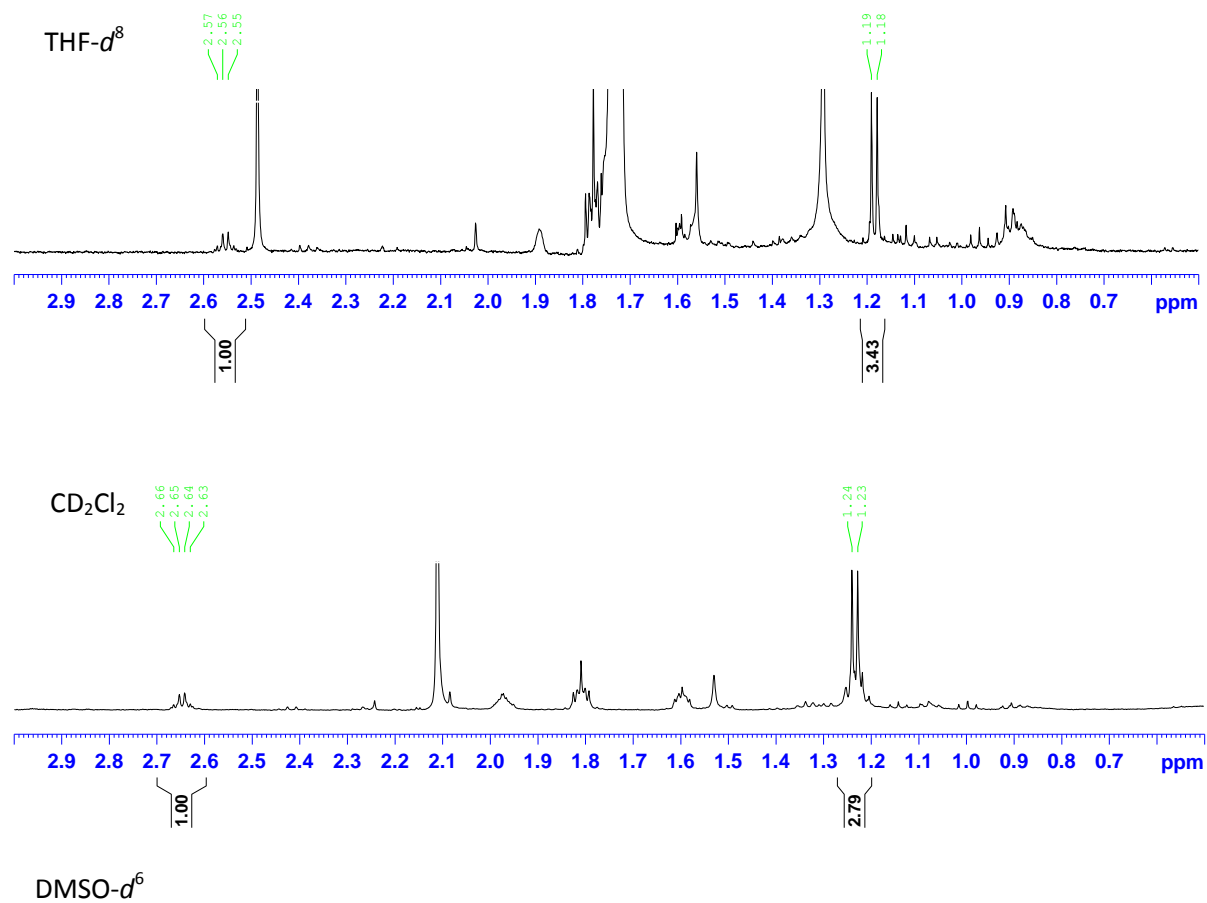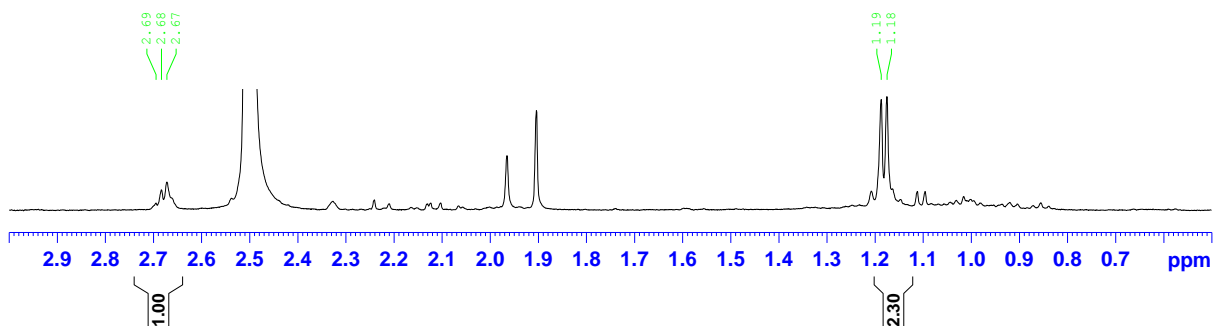
Figure 3. ^{1}H NMR spectra of reaction mixtures containing products of C-O reductive elimination from complex **1** in different solvents. The integrated peaks correspond to the proton signals of oxirane **8.**

It was found that the reaction selectivity was qualitatively the same in any of these solvents (**Figure 3**).

It was noteworthy that even weakly polar solvent such as THF did not reverse the selectivity. However, dichloromethane is capable of serving as a weak hydrogen bond donor with respect to the anionic oxygen atom of the "alkoxide" intermediate. Quantitative analysis of the ratio of the resulting *cis-* to *trans-* oxiranes was not achieved due to only trace amount of *cis*-oxirane detected. However, by comparing the NMR spectra of the reaction mixtures in different media, we can conclude that competitive formation of *cis*-oxirane was not favored noticeably by the either of solvents used in this work.

Altogether, our experimental observations suggest that C-O reductive elimination from *cis*-butene – derived Pt[IV] oxetane **1** can proceed via a mechanism which is different

from direct reductive C-O elimination discussed earlier for cyclic alkene - derived Pt(IV) oxetanes. By comparing the results for *cis*-butene, *trans*-butene and cyclic alkene – derived Pt(IV) oxetanes, we propose two general pathways for oxirane formation: a) direct C-O concerted reductive elimination and b) stepwise C-O reductive elimination involving heterolytic Pt-O bond dissociation and the alkoxide fragment rotation with subsequent intramolecular S_N nucleophilic attack.

Experimental Part

(dpms)Pt^{II}(*trans*-2-butene)Cl, 9. Solution of K(dpms) (93.1 mg, 323 μmol) in 1 mL H_2O was added to a stirred solution of KPtCl$_3$(*trans*-butene)·H_2O (124.8 mg, 323 μmol) in 1 mL H_2O. White precipitate formed in several minutes and yellow color of the (2-butene)chloroplatinate disappeared. The mixture was stirred for 3 h; the precipitate formed was filtered off and dried under vacuum. White powder; yield 136.1 mg (80%). The complex is slightly soluble in water and methanol, stable in aqueous and methanolic solutions at room temperature under an O_2 atmosphere. It decomposes slowly upon heating with the concomitant loss of the olefin.

^{1}H NMR (CF$_3$CH$_2$OD, 22°C), δ: 0.82 (d, *J*= 6.4 Hz, 3H, Me), 1.57 (d, *J*= 4.8 Hz, 3H, Me), 4.59-4.64 (m, *br*, 1H, CH=), 5.40-5.45 (m, 1H, CH=), 5.37 (s 1H, CHSO$_3$), 6.69 (t, *J*= 7.2 Hz, 1H, py), 7.05 (t, *J*= 6.8 Hz, 1H, py), 7.35-7.40 (m, 2H, py), 7.55-7.59 (m, 2H, py), 8.36

(d, J= 6.0 Hz, 1H, py), 8.51 (d, J= 5.2 Hz 1H, py). ^{13}C NMR was not obtained due to the low solubility of **9**

Synthesis of platina(IV)oxetane 10 using excess Ag$_2$O A mixture of 20.4 mg **9** and 50.0 mg Ag$_2$O (6 eqv.) was stirred vigorously for 12 hours. The mixture was then centrifuged to separate AgCl and excess Ag$_2$O before drying by blowing air. The resulting brown solid was then extracted by 10ml×3 DCM. DCM was removed under vacuum at room temperature and the residue was dried at 0.2 Torr at room temperature for 0.5 h to produce a white-yellow solid. Yield about 10%.

^{1}**H NMR** (D$_2$O, 22°C), δ: 0.50 (d, J= 6.4 Hz, 3H, Me), 1.12 (d, J= 6.0 Hz, 3H, Me), 3.22 (m, J_{195PtH} = 40 Hz, 1H, CH=), 4.91 (m, 1H, CH=), 6.59 (s 1H, CHSO$_3$), 7.76 (t, J= 7.2 Hz, 1H, py), 7.84 (t, J= 6.8 Hz, 1H, py), 7.90-8.06 (m, 2H, py), 8.25 (vqt, J= 9.6, 2H, py), 8.62 (d, J= 6.0 Hz 1H, py), 8.78 (d, J= 5.2 Hz 1H, py). ^{13}C NMR was not obtained due to the impurity of the sample.

Reductive Elimination of 10. Complex **10** was added to 1ml of DMSO-d_6 in a glovebox filled with argon. The yellow solution was placed into to a J.Young NMR tube, sealed and heated at ~70°C for 5 hours. The solution turns brown. The NMR tube was then shaken and, to avoid signal broadening, precipitate was let settle down in the NMR tube for one hour before taking ^{1}H NMR.

Oxidation of mixture of *cis*- and *trans*-butene (dpms)Pt^{II}(OH) complexes, A mixture of 5.2 mg *cis*-butene (dpms)Pt^{II}(Cl) complex, 5.2 mg **9** and 25.0 mg Ag_2O (6 eqv.) was stirred vigorously for 12 hours. The solution was then centrifuged and carefully separated from AgCl and excess Ag_2O before drying by blowing air. The resulting brown solid was then extracted by 10ml×3 DCM. DCM was then removed under vacuum at room temperature and the residue was dried at 0.2 Torr at room temperature for 0.5 h to produce a white-yellow solid.

^{1}H NMR (D_2O, 22°C), δ: 0.50 (d, *J*= 6.4 Hz, 3H), 1.12 (d, *J*= 6.0 Hz, 3H), from **9**, δ: 0.52 (d, *J*= 6.54 Hz, 3H), 1.14 (d, *J*= 6.18 Hz, 3H), from **1**.

II. Design and Synthesis of Disulfonate Dipyridyl Ligand

Our group have recently demonstrated that facile aerobic oxidation of (dpms)Pt^{II}(OH)(ethylene) complex can be readily achieved in water to form (dpms)Pt^{IV}(C$_2$H$_4$OH)(OH)$_2$ with subsequent reductive elimination of oxirane from the latter followed by its hydrolysis and formation of ethylene glycol *in situ*. Ethylene substitution in (dpms)Pt^{II}(OH)(ethylene) with some strained cycloolefins, *cis*-cyclooctene and norbornene, occurs readily to give the corresponding olefin hydroxo Pt^{II} complexes (*cis*-cyclooctene) or derived Pt^{II} oxetanes (norbornene). It was also disclosed that formation of the derived Pt^{IV} oxetanes can be facile when oxidation is performed with O$_2$. The subsequent reductive elimination of oxetanes from Pt^{IV} center occurs readily in aqueous phase to form a μ-hydroxo-bridged diplatinum complex (dpms)$_2$Pt^{II}$_2$(μ-OH)$_2$ as another reaction product which precipitated as a yellowish solid. Low solubility of this complex in water renders impossible its utilization in a catalytic olefin epoxidation. Julia Khusnutdinova has reported in her dissertation that the use of (dpms)Pt^{II}(OH)(DMSO) complex in aerobic epoxidation of norbornene led to 20% yield of corresponding epoxide only. [5b]

We propose that utilization of a more hydrophilic ligand bearing an additional neutral or anionic hydrophilic group could diminish the thermodynamic driving force of the reaction leading to the formation of catalytically inactive dinuclear complex and, hopefully, make catalytic epoxidation possible.

Our group has demonstrated that di(2-pyridyl)methanesulfonate (dpms) platinum complexes can mediate the functionalization of different small molecules in aqueous phase.[16] The sulfonate group of the dpms ligand not only supports the facile oxidation with O_2 of hydrocarbyl Pt^{II} complexes to derived Pt^{IV} species, but also increases the solubility of metal complexes in polar solvents such as water. Based on these observations, we anticipated that installation of another sulfonate group on the ligand would lead to a dipyridinemethane**di**sulfonate that would prevent formation of water - insoluble complex $(L)_2Pt^{II}_2(\mu\text{-}OH)_2$ and might enable catalytic aerobic epoxidation of some olefins.

Scheme 11. Four Candidates for More Hydrophilic Ligand Design
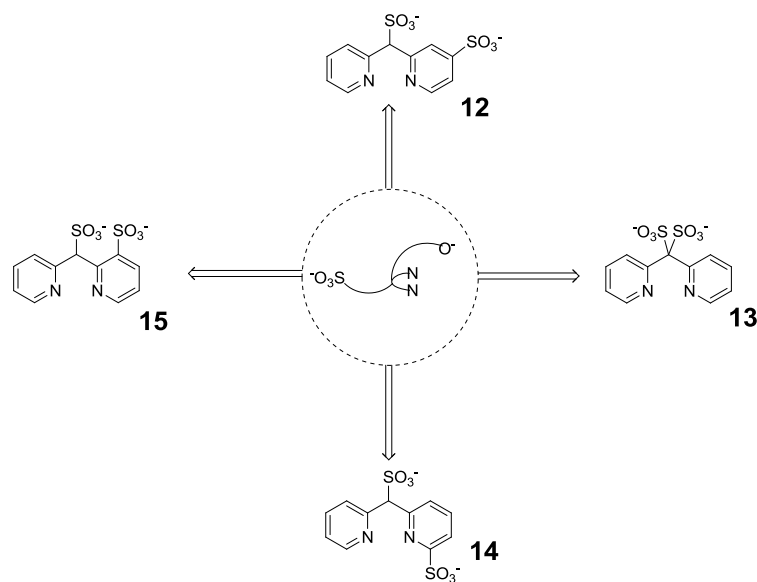
There are four different types of carbon atoms that can be further functionalized in the dpms ligand. Initial analysis has ruled out **14** and **15** types either because the sulfonate

group will impede the coordination of metal to the second pyridine nitrogen (**14)** or the lack of viable route for synthesis (**15**). Thus we set out to seek synthetic route for **12** and **13**.

Scheme 12. Proposed Route for the Synthesis of 1,1-di(2-pyridine)methane-1,1-disulfonate
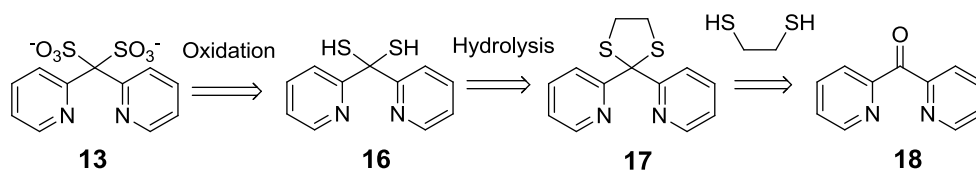
Our attempts to synthesize 2,2-di(2-pyridyl)-1,3-dithiolane **17** failed, due to difficulty to activate the carbonyl group of dipyridyl ketone **18** towards nucleophilic attack by 1,2-ethanedithiol. Different Brönsted and Lewis acids, such as $Et_2O \cdot BF_3$, HOTf and $SnCl_2$[15] were used under various conditions but mixtures of dipyridyl methylene ketone and 1,2-dithiolane remained unchanged.

Scheme 13. Proposed Route for the Synthesis of (2-pyridyl)(4-sulfonato-2-pyridyl) methanesulfonate

21
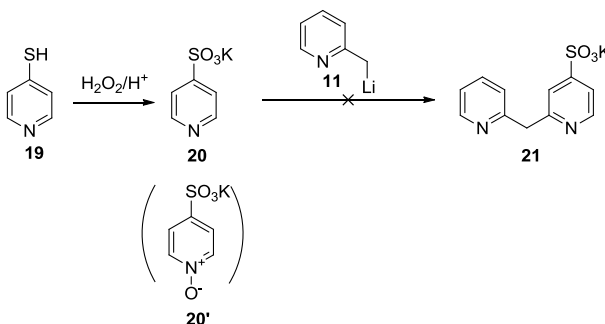
Our attempts to prepare the parent 4-sulfonatodi(2-pyridine)methane **21** involved nucleophilic alkylation of 4-pyridinesulfonate **20** (**Scheme 13**). **20** was obtained by oxidation of 4-mercaptopyridine **19** with acidic hydrogen peroxide solution followed by recrystallization. However, the desired nucleophilic attack of lithiated picoline on the *ortho*-carbon atom of the substrate that would lead to nucleophilic hydride substitution well known in chemistry of pyridines did not occur. No product was detected by GC-MS and ^{1}H NMR spectroscopy.

Scheme 14. Successful Synthesis of disulfonate **27**

Determined by ^{1}H-NMR and MS
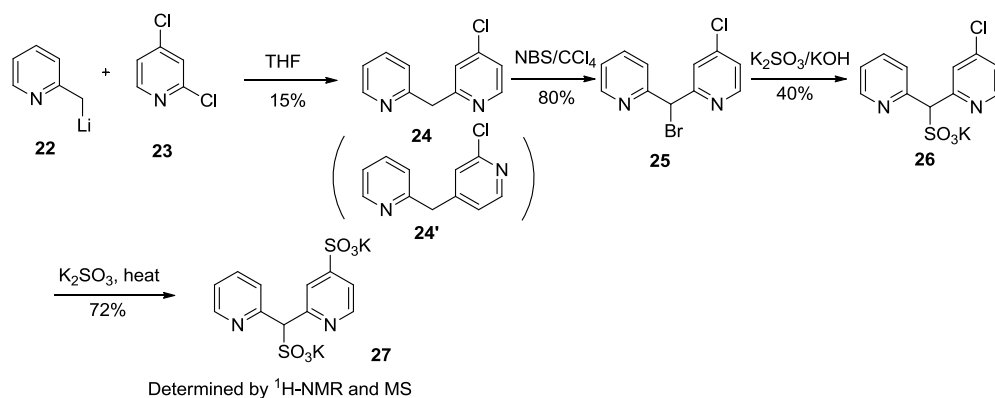
Hence, we proposed another protocol involving an aromatic nucleophilic substitution of chloride as shown in **Scheme 14**.

By changing the starting material to 2,4-dichloro-pyridine **23**, we were able to prepare 4-chlorodi(2-pyridyl)methane **24** and derived methanesulfonate ligand **26**, albeit in

low yield. Sulfonation of the latter with potassium sulfite at 150 ^{o}C afforded the desired disulfonate **27** in 72% yield.

Preliminary results show that mononuclear Pt(II) hydroxo complexes derived from **27** are highly soluble in water. It was observed on ESI-MS the formation of **27**-Pt^{II}Cl ethylene complex by mixing 27 and zeise's salt in aqueous solution. When the solution of **27**-Pt^{II}Cl ethylene complex was oxidized by Ag$_2$O, its oxidized derivative **27**-Pt^{IV}(OH)$_2$CH$_2$CH$_2$OH was also detected by ESI-MS. However, further experiments are needed to explore the reactivity of derived Pt complexes.

Experimental Part

Synthesis of 4-chloro-2-(pyridin-2-ylmethyl)pyridine 24. A flame-dried 200 ml Schlenk flask connected to a vacuum-argon line and equipped with a Teflon valve was filled with purified argon and the Teflon stopcock was replaced with a rubber septum. In the flask 40 ml of THF, 3.72g 2-picoline were introduced with a syringe. The flask was cooled to -78°C and 16mL 2.5 M *n*-butyllithium solution in hexane was added dropwise with stirring. After the addition of *n*-butyllithium was complete, the flask with the dark red solution has been removed from the bath and allowed to warm up to room temperature for 30 minutes. The solution was then cooled down to -78°C again. To the same flask, a solution of 2.96g 2,4-dichloropyridine **23** was added dropwise. The mixture was stirred overnight before it was quenched by 2mL of H$_2$O. The organic and aqueous layers of the resulting red

solution were separated. The aqueous layer was extracted with CH_2Cl_2 (10mL) and the extracts were combined and dried over $MgSO_4$. After filtration, the solvent was removed under reduced pressure and the residual red oil was obtained. 400mg **24** was obtained after column chromatography, yield 10%. Isomer **24'** was also obtained, yield of **25, 5%.**

^{1}H NMR (CCl_3D, 22°C): 4.34 (s, 2H, CH_2py_2), 7.16-7.20 (m, 2H, py), 7.27-7.31 (m, 2H, py), 7.67 (dt, J=1.6, 7.8 Hz, 1H, C4-H, py), 8.46 (vd, J=5.6 Hz, 1H, py), 8.58 (m, 1H, py).

2-(bromo(pyridin-2-yl)methyl)-4-chloropyridine, 25 A 20 mL Schlenk tube equipped with an egg-shaped stirring bar was charged with 0.400 g of N-bromosuccinimide (NBS, 2 mmol) and 4 mL of dry tetrachloromethane. To the stirred suspension 0.390 g of **24** (1.95 mmol) was added. The reaction mixture was refluxed for 2 hours until the initially white precipitate of NBS turned dark brown and floated up (monitored by NMR every 30mins). While warm, the liquid was filtered through a cotton plug. Residue on the walls of the reaction flask was washed with 1 mL of dry tetrachloromethane. The combined solutions were cooled down, washed with 5% sodium carbonate solution (3 x 5 mL) to remove succinimide and dried with anhydrous sodium sulfate. The solvent was removed on a rotavap and the residue was dried under vacuum for 30 min. A reddish oil was obtained as the desired product (crude product). Yield 270mg (60%).

^{1}H NMR ($CDCl_3$, 22°C): 6.20 (s, 1H, $CHBrpy_2$), 7.19-7.24 (m, 2H, py), 7.66-7.72 (m, 2H, py), 7.77 (vd, J=2.0Hz, 1H, py), 8.44 (vd, J=5.2Hz, 1H, py), 8.58 (vd, J=4.8Hz, 1H, py).

Potassium (4-chloropyridin-2-yl)(pyridin-2-yl)methanesulfonate, 26 The crude **25** prepared as described above was immediately used in this step without purification. Potassium sulfite, 150 mg, and 150 mg of 90% potassium hydroxide necessary to suppress hydrolysis of the former were dissolved in 1.5 mL of water. The resulting solution was added to 270mg **25** placed in a 20 mL flask. The reaction mixture was stirred vigorously for 12 h at 50°C. The heavy layer of (dmp)Br slowly disappeared and the solution turned brown. Non-ionic organic products were extracted with dichloromethane (3 x 3 mL). The aqueous phase was neutralized with concentrated HCl, then boiled for 2-3 min. Water was removed on a rotavap and resulting solid was dried under vacuum at 0.3 Torr, 100 ^{o}C for 60 min. The solid was extracted with boiling methanol (3 x 3 mL) and washed with 2 mL of cold methanol to separate **26** from excess of potassium sulfite and potassium chloride. The solvent from combined filtrate was removed. Residue was dried under vacuum at 0.3 Torr, 100°C for 60 min to remove methanol and treated with dry trifluoroethanol (2 mL) to separate **26** from KBr and traces of other inorganic potassium salts. Resulting slurry was left overnight to let KBr precipitate. After filtering and removal of the solvent **26** was dried at 0.3 Torr, 120°C (oil bath) for an hour to remove traces of trifluoroethanol. Yield: 120 mg (40%)

^{1}H NMR (D$_2$O, 22°C): 5.89 (s, 1H, CHSO$_3$py$_2$), 7.55 (dd, J=2.0Hz, 5.6Hz, 1H, py), 7.75 (ddd, J=0.8Hz, 5.6Hz, 8.0Hz 1H, py), 7.91 (vd, J=2.0Hz, 1H, py), 8.08 (d, J=8.0Hz, 1H,

py), 8.27 (td, J=1.6Hz, 8.0Hz, 1H, py), 8.50 (d, J=5.6Hz, 1H, py), 8.67 (dd, J=1.2, 5.2Hz, 1H, py).

Potassium 2-(pyridin-2-yl(sulfonato)methyl)pyridine-4-sulfonate, 27 To a 2 mL Schlenk tube charged with 120 mg of **26** and 150 mg of K_2SO_3, 500 mg of water was added. The mixture was placed into the preheated oil bath for about 2 minutes to allow vapors of boiling water replace air in the tube. The tube was then Teflon-sealed and heated at 150 ^{o}C for 12hours. Water was removed on a rotavap and resulting solid was dried under vacuum at 0.3 Torr, 100C for 60 min. The solid was extracted with boiling methanol (3 x 1 mL) and washed with 1 mL of cold methanol to separate **27** from excess of potassium sulfite and potassium chloride. The solvent from combined filtrate was removed. Residue was dried under vacuum at 0.3 Torr, 100°C for 60 min to remove methanol and treated with dry trifluoroethanol (1 mL) to separate **26** from traces of other inorganic potassium salts. Resulting slurry was left overnight to let KBr precipitate. After filtering and removal of the solvent **27** was dried under at 0.3 Torr, 120°C (oil bath) for an hour to remove traces of trifluoroethanol. Yield: 110 mg (70%)

^{1}H NMR (D_2O, 22°C): 5.80 (s, 1H, CHSO$_3$py$_2$), 7.41-7.46 (m, 1H, py), 7.73 (dd, J=1.2Hz, 5.2Hz, 1H, py), 7.89-7.93 (m, 2H, py), 8.22 (vd, J=0.8Hz, 1H, py), 8.49 (td, J=1.6Hz, 5.2Hz, 1H, py), 8.66 (d, J=5.2Hz, 1H, py).). **^{13}C NMR** (D_2O), δ: 73.01, 119.52, 120.85, 124.16, 125.35, 139.05, 148.25, 150.13, 151.75, 152.99, 155.40. **ESI-MS**: Negative mode, m/z = 328.99 (calculated for [**27**+H$^+$] = 328.88).

# III. Elimination Reaction of (dpms)Pt^{IV}-2-butyne Derivative

The formation of (dpms)Pt^{II} and (dpms)Pt^{IV} 2-butyne derivatives, **28** and **29** respectively, has been studied in our group previously (eq **3.1**). However, the reductive elimination from complex **29** was not previously characterized. Herein, we would like to explore the reactivity of compound **29** under different conditions.

28 and 28' (both isomers)   **29** (both isomers)   **30**   (3.1)

= dpms Ligand
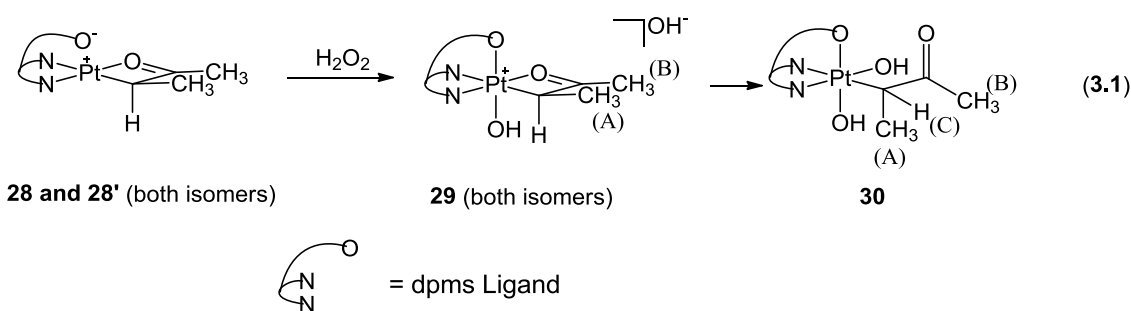
Although the reactivities of different transition metal-alkyl complexes have been well-established,[17] their ketonyl derivatives are still much less studied. The presence of an electron-withdrawing carbonyl group increases the electrophilicity of the vicinal carbon attached to platinum, making the complex a good candidate for the synthesis of β-functionalized ketones (**Scheme 15**). It also has been shown that the alkyne-kenonyl complexes release organic products upon protonolysis of M-C bond.[17] The product resulting from this pathway is virtually the same as from the hydration of alkynes. More interestingly, Zhang's group proposed a mechanism for the gold catalyzed oxidation of

alkynes to vinyl ketones (eq. **3.2**). It was believed by the authors that auryl ketonyl complex was involved in this transformation.[18]

Scheme 15. Different Reactions of a Ketonyl Metal Complex.
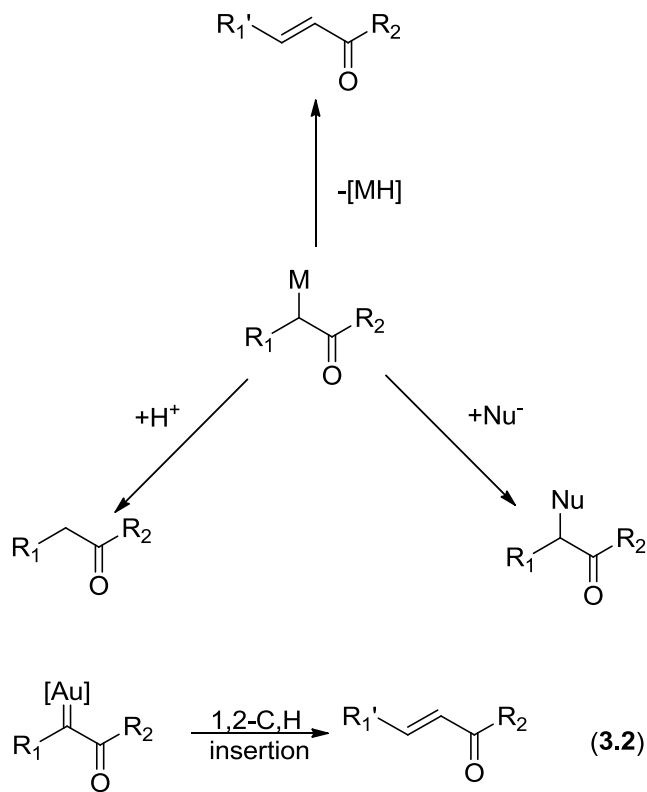

There are only a few reports that studied the reactivity of Pt-ketonyl complexes. Matsumoto prepared a Pt^{III} dinuclear-ketonyl complex via water attack on the π-coordination alkyne (eq. **3.3**). [19]

$$R_1 = H, CH_3$$
$$R_2 = alkyls, alcohols, phenyl$$
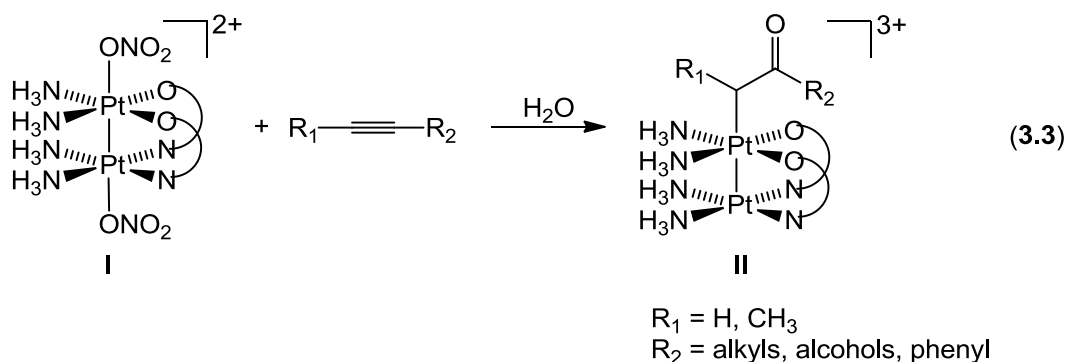
The electron-withdrawing Pt^{III} **I** makes the coordinated alkyne very prone to a nucleophilic attack, thus the intermediate from initial axial π-coordination of the triple $C\equiv C$ bond to the Pt(III) atom was not observed. In the reaction of both internal and terminal alkynes, ketonyl complexes were obtained in satisfactory yield (60%-88%). In the latter case, the water attack always takes place on the internal carbon atom of the terminal triple bond. The authors believe the reactivity of terminal alkynes with Pt(III) was similar to other electrophilic metals such as Hg(II), Pd(II), and Au(III) rather than its Pt(II) counterparts.

The resulting ketonyl-Pt^{III} complexes **II** react with various nucleophiles such as amines, halides and hydroxides at the platinum(III) − bound carbon to give various functionalized ketones (**Scheme 16**).[20] However, when triethylamine was used as a nucleophile, only 3-buten-2-one was identified in a low yield (38%) in the reaction. The presence of the base possibly promoted β-hydride elimination to give the vinyl ketone as a product.

Scheme 16. Effect of Nucleophiles on Elimination Process
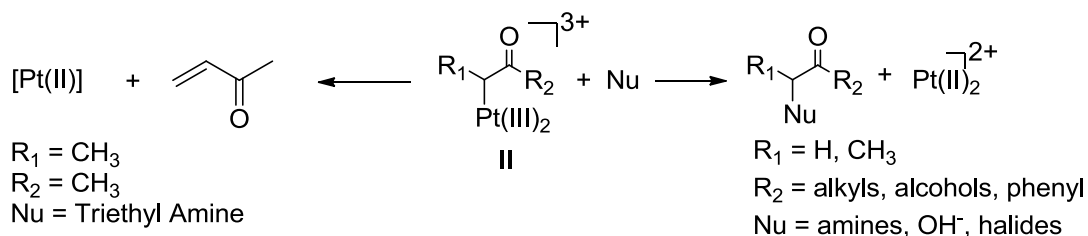
Hann and coworkers found that dicationic Pt^{II} alkyne complexes can be generated by facile displacement of the ethylene ligand in $[Pt(PNP)(C_2H_4)]^{2+}$ (PNP = 2,6-bis(diphenylphosphinomethyl)pyridine) (**Scheme 17**).[21] When terminal alkynes with bulky substituents were used in the reaction, σ-alkynyl complexes were formed as a major product. With less bulky substituents, Pt^{II}-acyl complexes were obtained, which produced ketone and acyl derivatives upon treatment with hydrochloric acid.

Scheme 17. Formation of Pt^{II}-σ-alkynyl complex and Pt^{II}-acyl complex
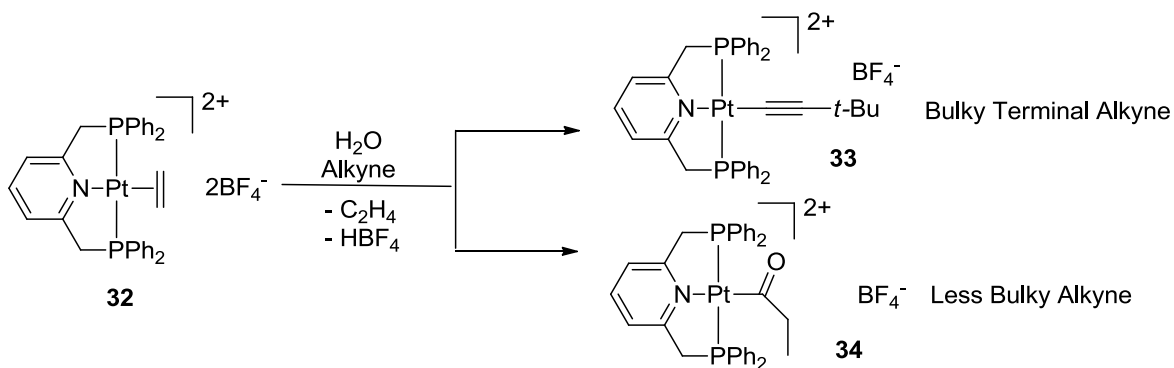
Results and Discussion
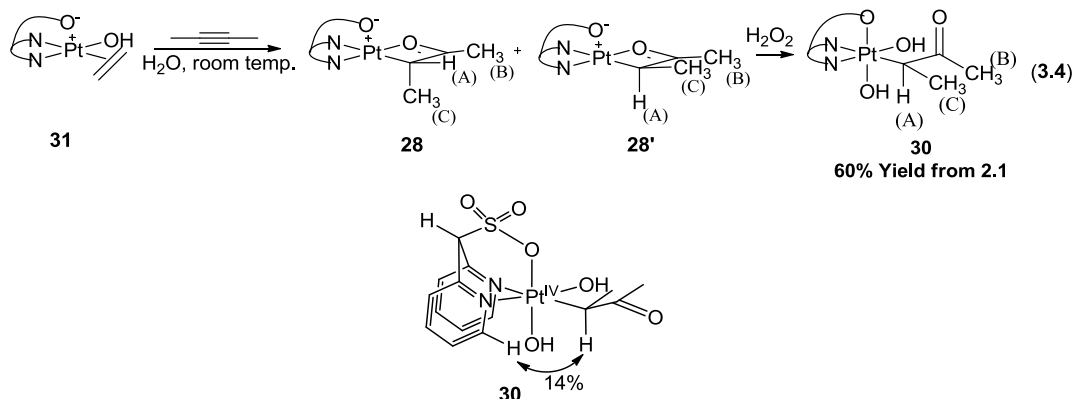
Figure 4. NOE of Two Protons of Complex **30** in Vicinity

Pratheep Khanthapura has reported in his thesis[22] the preparation of (dpms)Pt^{IV} ketonyl complex **30** using a two-step reaction sequence (see above). The yield was found to be 60% based on the Pt^{II} ethylene complex **31** used. It was found that proton (A) on (dpms)Pt^{IV} ketonyl complex **30** shows an NOE interaction with the pyridyl proton in the vicinity. This interaction provides an experimental support for the structure of **30**. The Pt^{IV} ketonyl **30** is unstable at room temperature and slowly decomposes to an unidentified product. However, the complex can be stored in a refrigerator for at least 48 hours without further change. Using the (dpms)Pt^{IV} ketonyl complex **30** prepared according to the scheme given above, we studied its reactivity under different conditions.

31

One might expect a facile reductive elimination from **30** in aqueous solution leading to 3-hydroxybutanone **31** (acetoin). This product may result from a nucleophilic attack of water at the electron-poor Pt^{IV}-bound carbon atom. (**Scheme 18**) However, when **30** was heated at 80 ^{o}C in neutral aqueous solution for 20 hours, the expected product was not detected. Further analysis of NMR spectrum revealed the formation of vinyl methyl ketone **32** in a low yield (30%) due to unidentified side reactions. (**Scheme 18**) It is intriguing that the formal β-hydride elimination is favored over nucleophilic attack at the platinum-bound carbon atom (a mechanism involving the formation of Pt –C carbene followed by 1,2 C-H insertion cannot be excluded).

*Scheme 18.* Elimination of Ketonyl group from Pt Center at 80°C
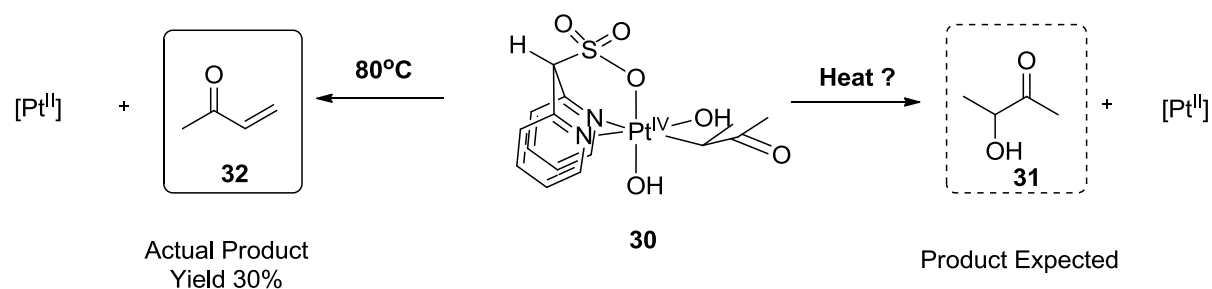
Further attempt to produce 3-hydroxybutanone in the presence of stronger external nucleophiles proved to be a success. Addition of 2 equivalent of KOH to the aqueous solution of the (dpms)Pt^{IV}(ketonyl) complex **30** at room temperature resulted in almost immediate (less than 5 minutes) completion of the expected reductive elimination reaction,

giving quantitative yield of 3-hydroxybutanone. (**Scheme 19**) When the reaction was conducted in D_2O, a fast proton exchange was observed on the carbonyl methyl group. (**Scheme 19**)

Scheme 19. Reductive Elimination of **30** with the Aid of KOH
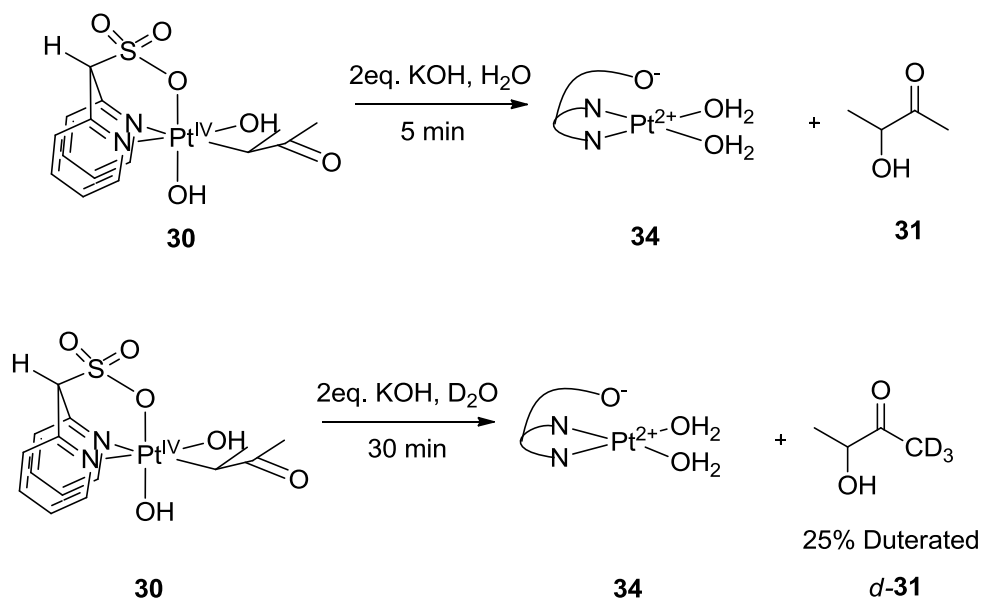
Change of solvent did also affect dramatically the outcome of the reaction. When DMSO was used as a solvent, 3-hydroxybutanone was not observed while 90% of the starting material was consumed in 30 minutes at 80 °C. After comparing the NMR spectrum of the resulting mixture with the ones of suspected products, 2-butanone was found to be the product. This change of reactivity might be attributed to the reducing ability of DMSO, which supposedly converted the $Pt^{IV}(OH)$ fragment to $Pt^{IV}(H)$. Subsequent C-H reductive elimination from Pt^{IV} center gives the same product as the one

33

expected from hydration of 2-butyne. (**Scheme 20**) Surprisingly, the addition of 2 equivalents of KOH to DMSO solution of (dpms)Pt^{IV}(ketonyl) complex did not afford 3-hydroxybutanone.

Scheme 20. Formation of 2-Butanone from **30** in DMSO
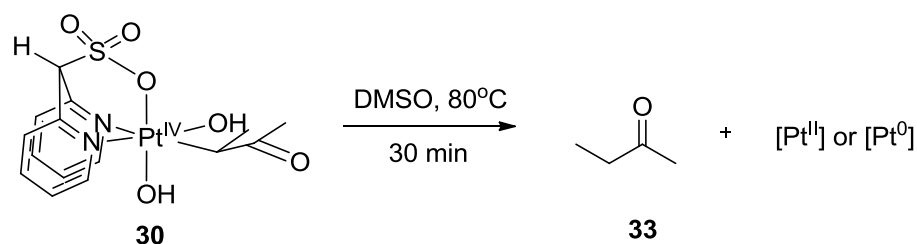
When the reaction was conducted in CH$_3$CN with the addition of 2 equivalent of KOH, 3-hydroxybutanone formed at a much slower rate, so that the conversion rate was 45% after 45 hours at 80 ^{o}C.

Our initial attempts to use different nucleophiles such as methanol and benzyl amine were not as successful. In the case of benzyl amine used in aqueous solution 3-hydroxybutanone was detected in about 20% yield by means of NMR spectroscopy so supporting the idea that benzyl amine acted as a base. These results demonstrate distinct reactivity of (dpms)Pt^{IV} ketonyl complex **30** as compared to its dinuclear Pt^{III} counterparts, where the platinum – bound carbon atom is more susceptible to attacks of external nucleophiles.

Scheme 21. Formation of 2-Butanone **33** in Acidic Condition
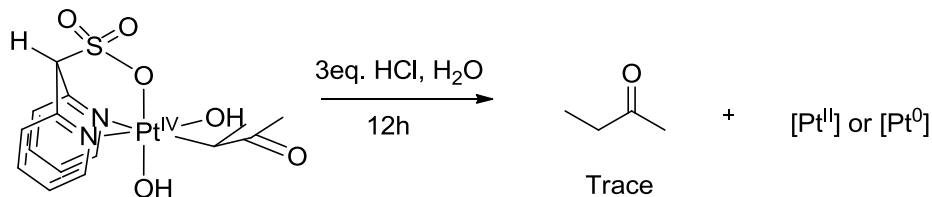
The formation of the formal 2-butyne hydration product, 2-butanone, with DMSO as a solvent prompted us to conduct reaction with an acid as a source of protons for possible Pt-C bond protonolysis. The reaction rate was found to be very slow with 3 equivalent of HCl. (**Scheme 21**)

Catalytic aerobic oxidation of 2-butyne to 3-hydroxybutanone was also attempted with different platinum ketonyl complexes as the possible catalysts. Preliminary results show no catalytic activity of either (dpms)Pt^{II} ketonyl complex or (dpms)Pt^{IV} ketonyl complex. Possible reason for the lack of this activity is the inability of alkyne to get coordinated by the Pt^{II} center.

Conclusion

The (dpms)Pt^{IV}(ketonyl) complex **30** can form different products when reaction conditions are varied: i) 3-hydroxybutanone was obtained quantitatively in aqueous solution with 2 equivalent of KOH; ii) the use of DMSO as the reaction medium led to 2-butanone; iii) in the absence of either base or acid additives to the aqueous solution of

(dpms)Pt^{IV} ketonyl complex **30**, vinyl methyl ketone was observed as the only identifiable organic product.

Experimental Procedures

Synthesis of Complex **28**

To (dpms)Pt^{II}(CH$_2$CH$_2$)OH (217.1 mg) placed into a 100 mL round-bottom flask 10 ml of degassed H$_2$O and 2-butyne (200 µl) were added. The mixture was stirred for one hour without protection from the air. Initial yellow solution turns brownish with some brownish-black precipitate forming. With microsyringe, 10 µl of 1,4-dioxane was then added to the mixture as an internal standard. An aliquot of the mixture was diluted twice with D$_2$O. ^{1}H NMR spectroscopy showed quantitative formation of two isomers of **28**. The solution was then centrifuged for 20 minutes at 10000 rpm. A yellow-brownish solution was 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 the final volume of 10.00 mL before dividing it into ten samples of equal volume (1.00 ml each). According to ^{1}H NMR, each of this solution contained 0.0047 mmol of complex **28.**

^{1}**H NMR** (50% D$_2$O 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 to produce 30

A solution containing 0.0047 mmol of complex **28** in 1 ml H_2O from the previous step (Synthesis of Complex **28**) was used immediately. The solution was combined with one equivalent of H_2O_2 (5 μl) and stirred for 16 hours. NMR yield of **30** calculated using the internal standard is 76% based on **28**.

^{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.

Reaction of 30 in DMSO

Solution of **30** from previous steps was used and the solvent was removed under vacuum. The powdery solid residue was then dissolved in 1mL DMSO-d_6. The solution was

transferred to a Young tube for further reaction. After heating at 80 °C for 2 hours, NMR signal corresponding to **30** disappeared. Formation of 2-butanone and unidentified products was observed. The NMR yield of 2-butanone is 30%.

Reductive Elimination of 30 in the presence of KOH in D₂O

The solution of **30** from the previous steps was used immediately after preparation. 3 μL of 0.2M KOH was added to the solution. The solution color changed from white-grey to yellow upon the addition of KOH. The reaction was complete within 5 minutes at room temperature, based on NMR. The product of reductive elimination was determined to be 3-hydroxybutanone by comparing the NMR spectrum with the spectrum of the purchased 3-hydroxybutanone. Conversion: 100%.

Attempts of Catalysis Reaction Using 30

The solution of **30** from previous steps was used immediately after preparation. 50 mg of 2-butyne was added to the mixture. The mixture was stirred for 20 minutes before the addition of 10 μL of 0.2M KOH and 10 μL of H_2O_2. The solution color changed from white-grey to yellow upon the addition of KOH and H_2O_2. After stirring for 20 hours at room temperature, only the stoichiometric amount of 3-hydroxybutanone corresponding to the original **30** was detected. Prolonged reaction time does not afford more 3-hydroxybutanone.

Reactions of 30 in MeCN solutions

Solution of **30** from previous steps was used and the solvent was removed under vacuum. The powdery solid residue was then dissolved in 1mL MeCN-d_3. The solution was transferred to a Young tube for further reaction. After heating at 80 $^{\circ}$C for 45 hours, NMR signal corresponding to **30** was integrated versus the signal of MeCN-d_3. Formation of 3-hydroxybutanone was observed. The NMR yield of 3-hydroxybutanone is 45%.

*Reaction of **30** in the presence of benzylamine*

The solution of **30** from the previous steps was used immediately after preparation. 30 μL of 0.3M *benzylamine* was added to the solution. The solution color changed from white-grey to orange-yellow upon the addition of amine aqueous solution. Unlike the reaction with KOH solution, the reaction rate was slow at room temperature, based on NMR. The product of reductive elimination was determined to be 3-hydroxybutanone by comparing the NMR spectrum with the spectrum of the purchased 3-hydroxybutanone. Conversion after 24h: 20%.

*Reaction of **30** with methanol*

The solution of **30** from the previous steps was used immediately after preparation. 1 μL of *MeOH* was added to the solution. The solution color remains the same upon the addition of alcohol. No obvious product was observed by ^{1}H-NMR after 24h at room temperature.

Future Direction

Alkyne Chemistry	More dpmsPt^{II} alkyne derivatives are needed to establish the reactivity series
Alkene Chemistry	Develop catalytic epoxidation reaction on more general olefin substrates
	Further clarify the mechanism of reductive elimination
Hydrophilic ligands	Apply above ligands on reactions that involve other small molecule functionalization
	Study the mechanisms of reactions aided by these ligands
	Improve the yield of disulfonate ligand and large scale synthesis
	Develop a series of hydrophilic ligands

References

1. Sharpless, K. B. Searching for New Reactivity (Nobel Lecture). *Angew. Chem., Int. Ed.* **2002**, 41, 2024- 2032. (b) Noyori, R.; Aoki, M.; Sato, K. *Chem. Commun.* **2003,** 1977-1986

2. Kilty P. A., Sachtler W. M. H.. *Catalysis Reviews: Science and Engineering* **10**: 1– 16.

3. Lane, B. S.; Burgess, K. Metal-Catalyzed Epoxidations of Alkenes with Hydrogen Peroxide. *Chem. Rev*. **2003**, 103, 2457.

4. Khusnutdinova, J. R.; *Ligand-Enabled Platinum-Carbon Bond Functionalization Utilizing Dioxygen as the Terminal Oxidant*. Ph.D. Dissertation. University of Maryland College Park, 2009, p.14

5. a). Vedernikov, A. N. *Acc. Chem. Res.* **2012**, ASAP, b). Khusnutdinova, J. R.; Zavalij, P. Y.; Vedernikov, A. N. *Organometallics*, **2007**, *26,* 2402-2413, c). Khusnutdinova, J. R.; Newman, L. L.; Zavalij, P. Y.; Lam, Y. F.; Vedernikov, A. N. *J. Am. Chem. Soc.* **2008**, *130*, 2174-2175

6. Weissermel, K.; Arpe, H.-J., Industrial Organic Chemistry: Important Raw Materials and Intermediates. Wiley-VCH: 2003; 491 pp.

7. Sharpless, K. B.; Teranishi, A. Y.; Backvall, J. E. *J. Am. Chem. Soc.***1977**, 99, 3120.

8. Palucki, M.; Finney, N. S.; Pospisil, P. J.; Gueler, M. L.; Ishida, T.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1998**, 120, 948.

9. Limberg, C.; Köppe, R.; Schnöckel, H. *Angew. Chem., Int. Ed.* **1998**, 37, 496.

10. Cinellu, M. A.; Minghetti, G.; Cocco, F.; Stoccoro, S.; Zucca, A.; Manassero, M. *Angew. Chem., Int. Ed.* **2005**, 44, 6892.

11. Schlodder, R.; Ibers, J. A.; Lenarda, M.; Graziani, M., *J. Am. Chem. Soc.* **1974**, 96, 6893.

12. Lenarda, M.; Ros, R.; Traverso, O.; Pitts, W. D.; Baddley, W. H.; Graziani, M., *Inorg. Chem*. **1977,** 16, 3178.

13. Zlota, A. A.; Frolow, F.; Milstein, D., *J. Am. Chem. Soc.* **1990**, 112, 6411.

14. Khanthapura, P.; *Aerobic Oxidation Of Cis-2-Butene Aad 2-Butyne In Water Mediated Bb (DPMS)Pt^{II}*. M.S. Dissertation. University of Maryland College Park, 2010, p.23

15. a).Vedernikov, A. N.; Fettinger, J. C.; Mohr, F. *J. Am. Chem. Soc.* **2004**, *126*, 11160 b).Vedernikov, A. N.; Binfield, S. A.; Zavalij, P. Y.; Khusnutdinova, J. R. *J. Am. Chem. Soc.* **2006**, *128*, 82

16. a). M. G. Gomes, *Synthesis*, **2005**, 1326, b). Firouzabadi, H.; Iranpoor, N.; Hazarkhani, H. *J. Org. Chem.*, **2001**, 66, 7527.

17. a). Albrecht, M.; *Chem. Rev.,* **2010**, 110, 576, b). Tilset, M.; Lersch, M.; *Chem. Rev.*, **2005**, 105, 2471, c). Dedieu, A.; *Chem. Rev.,* **2000**, 100, 543

18. Lu B.; Li C.; Zhang L, *J. Am. Chem. Soc.* **2010**, *132,* 14070-14072

19. Lin, Y, S.; Misawa, H.; Yamada J.; Matsumoto. K. *J. Am. Chem. Soc.* **2001**, *123,* 569-575

20. Ochiai, M.; Lin, Y, S.; Misawa, H.; Yamada J.; Matsumoto. K. *J. Am. Chem. Soc.* **2004**, *126,* 2536-2545

21. Carlisle S.; Matta A,; Valles H.; Miranda M.; Yoo J.; Hahn C. *Organometallics.* **2011**, 30, 6446-6457

22. Khanthapura, P.; *Aerobic Oxidation Of Cis-2-Butene Aad 2-Butyne In Water Mediated Bb (DPMS)Pt^{II}*. M.S. Dissertation. University of Maryland College Park, 2010, p.15