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Stoichiometric Aerobic Pt^{II}−Me Bond Cleavage in Aqueous Solutions to Produce Methanol and a Pt^{II}(OH) Complex

Andrei N. Vedernikov,* Seth A. Binfield, Peter Y. Zavalij, and Julia R. Khusnutdinova
Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742

Received November 3, 2005; E-mail: avederni@umd.edu

Catalytic transformation of methane into methanol in protic media mediated by platinum(II) complexes has been attracting much attention since its discovery by Shilov and co-workers.[1−6] Significant progress has been achieved in the understanding of the nature of the key reaction step, methane CH bond cleavage, leading to methyl platinum intermediates (Scheme 1, 1-a, 1-b).[4−7] As a result, a number of new systems was suggested for this purpose.[2] At the same time, the ability of the Shilov system[1] to transform the Pt^{II}-Me intermediates into useful organic derivatives remained mostly unique. A number of studies on aerobic oxidation of *di*methylplatinum(II) complexes into related $Pt^{IV}Me_2(OH)$ and analogous peroxo derivatives[8] and $Pt^{IV}Me_2H$ into $Pt^{IV}Me_2(OOH)$ complexes[9] was carried out, but no information on *stoichiometric* Pt−Me bond cleavage in these systems was reported. In the original Shilov system, the Pt^{II}−Me bond cleavage occurred through a two-step process: (i) oxidation of a *mono*methyl platinum(II) intermediate by H_2PtCl_6 to produce a reactive *mono*methyl platinum(IV) complex, $MePtCl_5^{2-}$ (Scheme 1-c), and (ii) subsequent nucleophilic attack of a water molecule or chloride anion at the methyl carbon atom of the latter to produce a mixture of methanol and methyl chloride (Scheme 1-d).[1] The last reaction was extensively studied.[5,10,11] The challenge remained to carry out the Pt^{II}Me to Pt^{IV}Me transformation in the absence of expensive H_2PtCl_6, ideally, with oxygen as the only oxidant.[5]

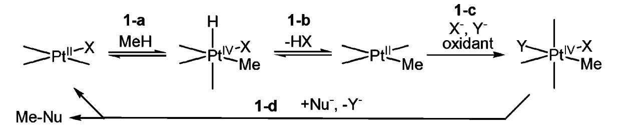
To advance our studies of *aqueous* organoplatinum chemistry, we introduced recently a new family of *fac*-chelating ligands derived from di(2-pyridyl)methanesulfonate, dpms (L, Scheme 2),[12] which combine two moderately good pyridine donors and a tethered *labile* sulfonate group. The latter makes derived Pt^{II}Me complexes such as $K(L)PtMe_2$ (**1**) or $LPtMe(OH_2)$ (**2**) highly hydrophilic, allows tuning of the reactivity of $LPt^{IV}Me_2H$ (**3**) in alkane reductive elimination by changing the solvent polarity, promotes methane activation in dichloromethane,[12] and might serve as a *good leaving group* in reactions such as 1-d.

In this work, we report the first example of clean aerobic cleavage of a Pt^{II}−Me bond in complex **2** to quantitatively produce methanol, the crystallographic characterization of the intermediate *mono*methylplatinum(IV) complex **4**, and some details of the mechanism of its transformation into methanol and hydroxoplatinum(II) complexes **6** and **7**.

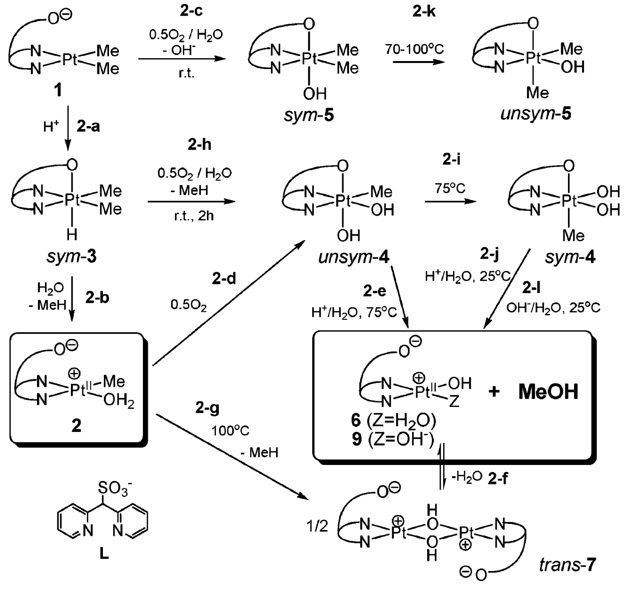
Previously, we have characterized the reactivity of *di*methylplatinum complexes **1** and **3** in water, including protonation of **1** to form dimethylplatinum(IV) hydride **3** (Scheme 2-a), methane reductive elimination of the latter to produce *mono*methylplatinum(II) aqua complex **2** (Scheme 2-b), and an aerobic oxidation of **1** to form the symmetrical $LPt^{IV}Me_2(OH)$ complex (*sym*-**5**) (Scheme 2-c).[12]

In this work, we show that, unlike other known *mono*methyl platinum(II) species,[13] Pt^{II}Me complex **2** can be readily oxidized by oxygen from the air at room temperature to produce a new Pt^{IV}-Me complex **4** in virtually quantitative yield (Scheme 2-d). When heated in acidic solutions at 75 °C for a few hours, **4** quantitatively produced methanol, detected by MS and ^1H NMR spectroscopy, and a hydroxoplatinum(II) complex **6** (Scheme 2-e).[14] Stable at low pH in a protonated form, (**6**$\cdot H^+$), in neutral solutions, **6** slowly eliminated an aqua ligand and formed bis(μ-hydroxo)diplatinum(II) complex **7**, *trans*-$L_2Pt_2(\mu\text{-}OH)_2$ (Scheme 2-f), which was characterized by X-ray diffraction (Figure 1a). Poorly soluble **7** could also be produced by heating **2** in the *absence of air* in neutral aqueous solutions at 95 °C (Scheme 2-g).

Scheme 1



Scheme 2



Pale yellow complex **4** exhibited eight signals in the aromatic region of its ^1H NMR spectra. A single PtMe resonance at 2.45 ppm ($^2J_{PtH}$ = 66.3 Hz) shifted significantly to the downfield region at lower pH, consistent with the reversible protonation of **4**, and integrated as 3H proving that **4** is a *mono*methylplatinum complex. To rule out the possibility that **4** contains a peroxo group which can be found in a number of products of aerobic oxidation of Pt^{II}-Me_2 complexes,[8] we attempted its crystallographic characterization. Very hydrophilic complex **4** failed to produce crystalline material. Fortunately, crystallization was possible from *acidic* solutions of **4**. Single crystals of the hydrogen-bonded adduct of **4** and its OH-protonated form, $(\mathbf{4})_2\cdot H^+BF_4^-\cdot 2C_6H_6$, were isolated from benzene−methanol solutions (Figure 1b), so proving that **4** is a *mono*methyl dihydroxoplatinum(IV) complex. Consistent with these results, an ESI−MS analysis showed (**4**$\cdot H^+$) as the only positively charged Pt-containing species present in acidic aqueous solutions of **4**.

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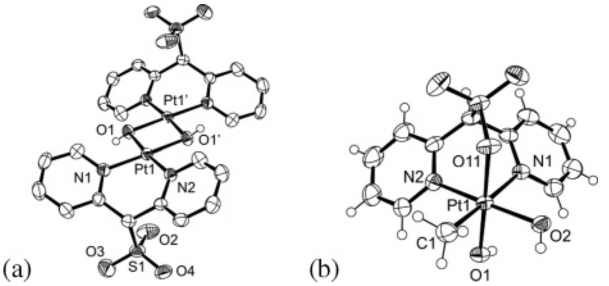

Figure 1. ORTEP drawings (50% probability ellipsoids) of (a) complex **7** (H atoms are omitted for clarity except for the OH fragments); and (b) the neutral organometallic fragment of complex $(\mathbf{4})_2 \cdot H^+$, *unsym*-LPtMe$(OH)_2$.

Interestingly, water-soluble complex **2** turned out to be much more reactive toward oxygen than poorly soluble hydrides **3**. When aqueous solutions of **1** were slightly acidified with HBF_4 to precipitate **3** (Scheme 2-a), and *then* exposed to air, formation of **5** (Scheme 2-c) was suppressed. Instead, methane elimination and formation of **4** in ≥75% isolated yield could be observed (Scheme 2-h). We suggest that unusually facile aerobic oxidation of a Pt^{II}-Me to a Pt^{IV}Me species in our systems is the result of the synergetic effect of Me and *fac*-chelating dpms ligands. Indeed, aqueous solutions of *hydroxo* complex **6** acidified with HBF_4 do not produce Pt^{IV} compounds after heating at 100 °C under air for several days.[15]

One of the key steps of the oxidative Pt−Me bond cleavage described here implies the C−O reductive coupling of complex **4** to form methanol. Much attention has been paid recently to the mechanism of the C−O coupling at the Pt^{IV} center.[3,16] Reaction 2-e could proceed as the S_N2 nucleophilic substitution at the methyl carbon of **4** with a water molecule as a nucleophile. Such mechanism with a proposed reactive five-coordinate Pt^{IV} intermediate was well documented.[3,16] To establish some mechanistic details of reaction 2-e, we performed a kinetic study. We found that the disappearance of *unsym*-**4** and formation of methanol occurred with the pseudo-first-order rate constant $k_{2e} = (2.95 \pm 0.02) \times 10^{-4}$ s^{-1} at 94 °C, $[H^+] = 50$ mM, and showed 3-fold inhibition by HBF_4 when the acid concentration was increased to 530 mM. Correspondingly, *in the absence* of the acid, the rate of disappearance of *unsym*-**4** was the fastest, $k_{2i} = (1.03 \pm 0.02) \times 10^{-3}$ s^{-1} at 94 °C, but only *traces* of methanol were detected after 2 h, when the transformation of **4** was complete. Instead, a new Pt^{IV}Me complex identified as *sym*-**4** formed quantitatively (Scheme 2-i).[17] The estimated reaction 2-i activation parameters, $\Delta H^{\ddagger} = 23.8 \pm 0.8$ kcal/mol and $\Delta S^{\ddagger} = -7.8 \pm 2.2$ eu, are consistent with the slow "dissociation" of the SO_3^- tail of *unsym*-**4** with the subsequent fast isomerization of the resulting five-coordinate intermediate and fast rebuilding of six-coordinate *sym*-**4**. Intrigued with these results, we subjected *sym*-**4** to reaction with water (Scheme 2-j). In a manner similar to that of the unsymmetrical isomer, *sym*-**4** produced methanol *in acidic solutions*, but already at room temperature, much faster than *unsym*-**4** under the same conditions.[18] In contrast to *unsym*-**4**, the reaction was first order in $[H^+]$ with the observed rate constant $k_{2j} = (1.55 \pm 0.03) \times 10^{-3}$ s^{-1} M^{-1} at 66 °C. On the basis of these results, the protonated complex (*sym*-$\mathbf{4} \cdot H^+$) is much more reactive than any of the compounds **4** or (*unsym*-$\mathbf{4} \cdot H^+$), and reaction 2-e proceeds through the rate-limiting isomerization of *unsym*-**4** into *sym*-**4** (Scheme 2-i), protonation of *sym*-**4**, and methanol elimination (Scheme 2-j). We suggest that the inhibiting effect of H^+ on the rate of reaction 2-e originates from the reversible protonation of **4**, which makes it more difficult for the anionic sulfonate group to "depart" from the positively charged metal center. In turn, reversible protonation of *sym*-**4** enhances its electrophilicity, which may be important for the subsequent nucleophilic attack by water. Interestingly, attempts at inducing the C−O reductive coupling of $Pt^{IV}Me_2$ complex *sym*-**5** and its more electrophilic protonated form $LPtMe_2(OH_2)^+$, ($\mathbf{5} \cdot H^+$), to produce methanol at 100 °C in aqueous solutions, neutral or acidic, respectively, resulted in *isomerization* of *sym*-**5** into the more stable *unsym*-**5** (Scheme 2-k). Similar to **4**, the isomerization rate showed 16-fold inhibition by 0.27 M tetrafluoroboric acid at 97 °C,[19] but no detectable amounts of methanol were observed.

Though no kinetic evidence of the S_N2 mechanism of reaction of *sym*-**4** performed in *acidic* media (Scheme 2-j) could be found, such evidence was obtained in *basic* solutions. In basic media, such as in acidic solutions, *unsym*-**4** isomerized to *sym*-**4** at elevated temperatures, and the latter complex produced methanol and anionic $LPt(OH)_2^-$, **9**, already at 25 °C (Scheme 2-l). A reversible deprotonation of *sym*-**4** to form LPtMe(OH)O^-, as shown by ESI−MS,[19] was a competing process. Modeling of the kinetic data suggested that reaction 2-l was first order in $[OH^-]$, consistent with the S_N2 mechanism of the C−O reductive coupling. Similar to acidic solutions, in basic media, the relative reactivity of *unsym*-**4** and *sym*-**4** showed that a good leaving group *trans* to the methyl facilitates methanol formation.

In summary, we have found that dpms ligand allows for selective aerobic oxidation of Pt^{II}−Me bonds and the clean conversion of the Pt-bound methyl ligand to methanol.

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Supporting Information Available: Experimental details, kinetic data, their modeling and proposed interpretation, CIF files for **7** and $(\mathbf{4})_2 \cdot H^+BF_4^- \cdot 2C_6H_6$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) Complex **6**, C_s symmetric according to ^1H and ^{13}C NMR data, was detected in a form of $(\mathbf{6} \cdot H^+)$ by ESI−MS: $m/z = 480.021$, calcd 480.0193.

(15) A stronger oxidant, H_2O_2, converts **6** quickly and quantitatively into a trihydroxoplatinum(IV) species **8**, $LPt(OH)_3$, detected by ESI−MS in the form of $LPt(OH)_3 \cdot H^+$. Observed, $m/z = 496.020$, calcd 496.01421.

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(17) Complex *sym*-**4** was characterized by ^1H and ^{13}C NMR spectroscopy, elemental analysis, and in the form of (*sym*-$\mathbf{4} \cdot H^+$) by ESI−MS.

(18) No *unsym*-**4** was detected in the reaction mixtures by ^1H NMR.

(19) See the Supporting Information.

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