Mechanism of O_2 Activation and Methanol Production by (Di(2-pyridyl)methanesulfonate)$Pt^{II}Me(OH_n)^{(2-n)-}$ Complex from Theory with Validation from Experiment

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(S) *Supporting Information*

ABSTRACT: The mechanism of the $(dpms)Pt^{II}Me(OH_n)^{(2-n)-}$ oxidation in water to form $(dpms)Pt^{IV}Me(OH)_2$ and $(dpms)Pt^{IV}Me_2(OH)$ complexes was analyzed using DFT calculations. At pH < 10, $(dpms)Pt^{II}Me(OH_n)^{(2-n)-}$ reacts with O_2 to form a methyl Pt(IV)−OOH species with the methyl group trans to the pyridine nitrogen, which then reacts with $(dpms)Pt^{II}Me(OH_n)^{(2-n)-}$ to form 2 equiv of $(dpms)Pt^{IV}Me(OH)_2$, the major oxidation product. Both the O_2 activation and the O−O bond cleavage are pH dependent. At

higher pH, O−O cleavage is inhibited whereas the Pt-to-Pt methyl transfer is not slowed down, so making the latter reaction predominant at pH > 12. The pH-independent Pt-to-Pt methyl transfer involves the isomeric methyl Pt(IV)−OOH species with the methyl group trans to the sulfonate. This methyl Pt(IV)−OOH complex is more stable and more reactive in the Pt-to-Pt methyl-transfer reaction as compared to its isomer with the methyl group trans to the pyridine nitrogen. A similar structure−reactivity relationship is also observed for the S_N2 functionalization to form methanol by two isomeric $(dpms)Pt^{IV}Me(OH)_2$ complexes, one featuring the methyl ligand trans to the sulfonate group and another with the methyl trans to the pyridine nitrogen. The barrier to functionalize the former isomer with the CH_3 group trans to the sulfonate group is 2−9 kcal/mol lower. The possibility of the involvement of Pt(III) species in the reactions studied was found to correspond to high-barrier reactions and is hence not viable. It is concluded that the dpms ligand facilitates Pt(II) oxidation both enthalpically and entropically.

INTRODUCTION

Selective conversion of methane to methanol at low temperature is crucial for transportation of shale gas produced in remote areas. The Shilov system is the first successful case to activate methane C−H bonds and convert it to methanol and its derivatives. In this system, the kinetics of the oxidation of Pt(II) is important because the oxidation competes with the protonolysis of methyl Pt(II), the reverse reaction of C−H activation.[1] Several oxidants, such as Pt(IV),[2] chlorine,[3] hydroperoxide,[4] Cu(II),[5] and polyoxometalates,[6] have been shown to be effective. One of the most desirable stoichiometric oxidants in this type of chemistry would be dioxygen used directly, without electron-transfer agents. Although N,N-chelating ligand-supported dimethyl Pt(II) complexes can be oxidized by O_2 in methanol solution to form derived dimethyl Pt(IV) hydroxo complexes,[7,8] for monomethyl Pt(II) complexes the aerobic oxidation at room temperature has only been achieved by one of the authors of this paper[9−11] who demonstrated, in particular, that di(2-pyridyl)methanesulfonate (dpms, Figure 1), a facially chelating ligand containing the semilabile sulfonate donor, enables facile dioxygen activation and selective conversion of Pt(II) monomethyl complex $(dpms)Pt^{II}Me(OH_2)$ to its monomethyl Pt(IV) hydroxo counterpart, unsymmetric $(dpms)Pt^{IV}Me(OH)_2$. Moreover,

Figure 1. DPMS ligand and oxidation of its Pt(II) monomethyl complex. Product $(dpms)Pt^{IV}Me(OH)_2$ can further react in water to give methanol.

methanol production from the unsymmetric $(dpms)Pt^{IV}Me(OH)_2$ complex via its mirror-symmetric isomer has also been demonstrated (Figure 1).[9] The reaction sequence in Figure 1

may be considered as a part of an attractive route to aerobic methane C—H functionalization.

To elucidate the mechanism of the transformations in Figure 1 we studied experimentally the kinetics of the oxidation of (dpms)Pt^{II}Me(OH$_2$) in the pH range 4−14, the results of which are to be published separately.[12] This kinetics study showed that at pH > 8 the oxidation rate of the monomethyl Pt(II) complex decreases while the competing Pt-to-Pt methyl transfer reaction leading to the dimethyl Pt(IV) complex (dpms)Pt^{IV}Me$_2$(OH) becomes noticeable. This latter transformation becomes the major reaction at pH ≥ 12. Complex (dpms)Pt^{IV}Me$_2$(OH) is robust and does not undergo any facile C—O or C—C coupling.[9]

The experimental studies[9−12] raise several questions pertinent to the aerobic Pt^{II}—Me bond functionalization: (i) what is the mechanism of O$_2$ activation at the Pt(II) center, (ii) how is the dimethyl Pt(IV) complex (dpms)Pt^{IV}Me$_2$(OH) produced, (iii) are there any Pt(III) intermediates involved, (iv) how does the dpms ligand facilitate oxidation of the monomethyl Pt(II) complex (dpms)Pt^{II}Me(OH$_2$), and (v) how does the symmetric complex (dpms)Pt^{IV}Me(OH)$_2$ produce methanol?

In this paper we report density functional theory (DFT) calculations which allow us to answer these questions and propose a viable reaction mechanism.

■ COMPUTATIONAL DETAILS

Geometry optimization and frequency calculation were carried out at the level of B3LYP[13,14]/LACVP** including solvation by the Poisson−Boltzmann self-consistent polarizable continuum method[15] with dielectric constant = 80.37 and effective radius = 1.4 Å to represent water. Pt was described with the small core (18 explicit electrons) Hay-Wadt[16] angular momentum projected effective core potential.[17,18] Single-point energies were refined using a larger 3-ζ basis set with diffuse and polarization functions (LACV3P**++ augmented with two f functions for Pt, 6-311G**++ on other elements and 6-311G**++ augmented with one d function for S).

Unless otherwise specified all energies in this paper are Gibbs free energies calculated by the following formula

$$G_{298K} = E_{single\ point} + G_{solv} + ZPE + H_{vib} + 6kT - TS_{mod}$$

where $S_{mod} = S_{vib} + 0.54(S_{trans} + S_{rot}) + 0.24$ is Wertz's approximation for the entropy fit to the experimental solvation entropy of small molecules.[19] One explicit water molecule per Pt was added to provide a better description of hydrogen bonding between water and OH$_n$ ligands on Pt. The triplet−singlet (T−S) crossing points were located with Harvey's script.[20] If free hydroxide anion is present, three explicit water molecules were placed to provide a better description of solvation. All calculations were carried out by Jaguar 7.7.[21]

■ RESULTS AND DISCUSSION

The proposed different mechanisms with the predicted Gibbs free energies for each species are shown in Figure 2 for the case of pH = 7 and in Figure 3 for the case of pH = 14. These mechanisms are discussed below in detail.

1. Triplet−Singlet Crossing Point. Starting with monomethyl aqua Pt(II) complex **a** and triplet O$_{2(gas)}$, the reaction proceeds via the triplet−singlet (T−S) crossing point **b** to form the singlet monomethyl Pt(IV)−OOH species **c** with a barrier of 25.4 kcal/mol (pH = 7, Figure 2). The pendant sulfonate group present in **a** is ready to coordinate to the metal, so reducing the free energy cost to transit from 4 coordinate Pt(II) to 6 coorinate Pt(IV) and making the oxidation faster as
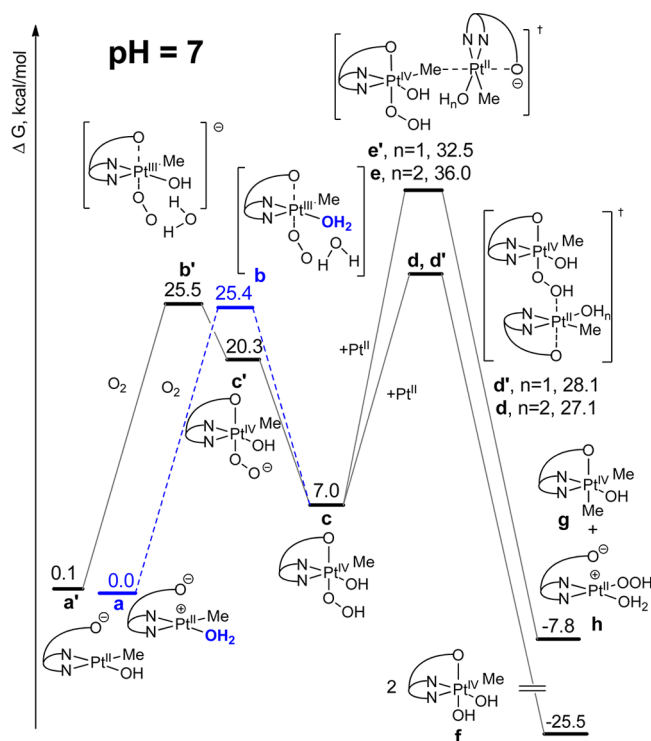

Figure 2. Proposed mechanism of O$_2$ reacting with Pt(II) at pH = 7 in water with the Gibbs free energy along the potential energy surface of the oxidation of Pt(II).

compared to Pt(II) complexes without such a semilabile sulfonate group (vide infra).

The pK_a of the aqua complex **a** was calculated to be 7.1, close to the experimental value 8.15 ± 0.02.[12] As a result, the conjugate base **a′** is an important component present in neutral solutions of **a**. For the reaction of O$_2$ with the conjugate base **a′** to form species **c′**, Pt(IV)−OO$^−$, which is the conjugate base of **c**, the T−S crossing point **b′** has a free energy of 25.5 kcal/mol. Hence, both **a** and **a′** are predicted to react with O$_2$ almost equally fast. The potential energy surfaces for both systems comprised of either **a** or **a′** and triplet O$_2$ are mostly repulsive along the reaction coordinate beyond the T−S crossing point (Pt−O ≈ 2.2 Å) and have a very shallow minimum at Pt−O ≈ 2.6 Å with the corresponding binding enthalpies no lower than −0.1 kcal/mol even with Grimmes' van der Waals correction.[22] This result suggests that no stable Pt(II)−^{3}O$_2$ intermediates are formed along either of the two reaction paths that begin with **a** or **a′**.

Experimentally, the rate of the oxidation of (dpms)Pt^{II}Me-(OH$_n$)$^{(2−n)−}$ with O$_2$ is first order in [Pt(II)] at pH < 8,[12] so implying that the T−S crossing step is the rate-determining step (RDS) in this pH range. The rate decreases about 13-fold when pH is decreased to 4, which suggests that **b′** should be ~2 kcal/mol lower in energy than **b**. This difference is not resolved in our calculations. In principle, hydroxo ligand is more electron donating than H$_2$O, which should facilitate oxidation of the Pt(II) complex **a′**, as shown experimentally. We believe that this difference is because the stabilization of the superoxide ligand O$_2^−$ in **b′** by the hydrogen bond between O$_2^−$ and the explicit water molecule is underestimated in our calculations. The same explicit water molecule is involved in formation of another hydrogen bond to the hydroxo ligand present in **b′**, which diminishes the strength of this molecule as a hydrogen-
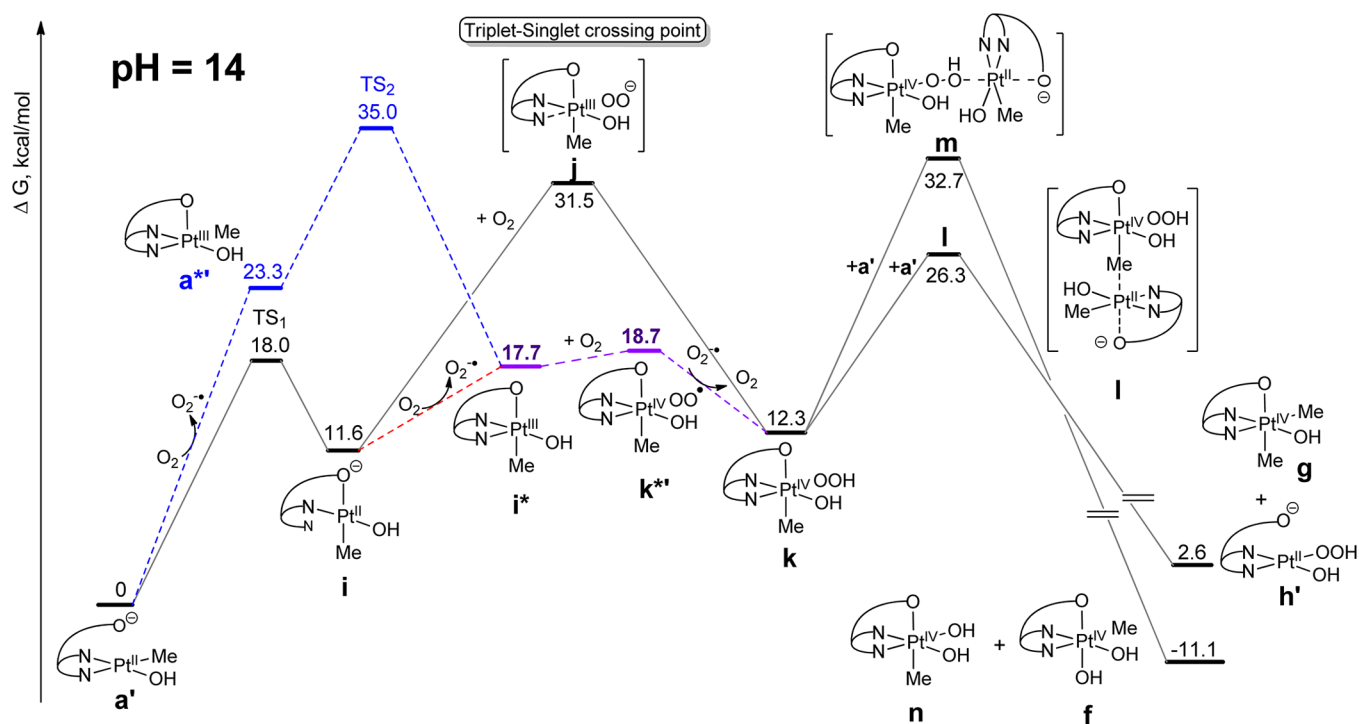
Figure 3. Proposed mechanism of the Pt(IV)-to-Pt(II) methyl transfer at pH = 14 in water with the Gibbs free energy along the potential energy surface.

bond donor. In other words, the explicit water in **b**′ is artificially less acidic than the one in **b**, resulting in weaker stabilization of **b**′ by hydrogen bonding. The use of more than one explicit solvent molecule might improve the theoretical description of O_2^- solvation in water and help solve the problem above.

2. O−O Bond Cleavage. Once hydroperoxo Pt(IV) complex **c** is formed, it can oxidize another Pt(II) species **a** via the O−O bond cleavage with transition state (TS) **d** (pH = 7, Figure 2). The anionic oxygen center resulting from the O−O bond cleavage immediately takes one proton from the aqua ligand to form the observed final product, the unsymmetric (dpms)Pt^IV Me(OH)$_2$ complex **f**. If the aqua ligand on the Pt(II) center is replaced with hydroxide, as in **d**′, the reaction barrier at pH = 7 increases to 28.1 kcal/mol.

At pH higher than 7, oxidation of (dpms)Pt^II Me(OH$_n$)$^{(2-n)-}$ is expected to be slower because formation of **c** takes one extra proton and cleavage of the O−O bond to form two **f** takes the second extra proton from solution. As a result, the free energy of **c** and **d**′ increases by 1.36 kcal/mol per pH unit and twice so, 2.72 kcal/mol per pH unit, for **d** and final products (two **f**). Comparing the energies of **b**, **b**′, **d**, and **d**′, one can predict that the O−O bond cleavage will be the RDS in the oxidation of (dpms)Pt^II Me(OH$_n$)$^{(2-n)-}$ and the overall oxidation reaction rate is expected to be second order in [Pt(II)].

From our kinetics study,[12] the oxidation rate does decrease as the pH grows beyond 8 and changes from first-order to second-order kinetics at pH = 10, so indicating that the transition state corresponding to the RDS changes from **b** to **d**′. Hence, our DFT calculations overestimate the energy of **d**′ compared to **b** by ∼5 kcal/mol. A possible reason for this overestimation is that the single-determinant DFT does not include the resonance between the four lone pairs on the two O atoms with the antibonding orbital of the O−O bond being broken, which provides stabilization of **d**′.

3. Methyl Transfer and Isomerization Paths Not Involving Pt(III) Species. At pH = 7, the direct Pt(IV)-to-Pt(II) methyl transfer from either monomethyl Pt(IV)−OOH species **c** or its conjugate base **c**′ leading to the dimethyl Pt(IV) complex **g** via the transition state **e** or **e**′, respectively, is slower than O−O cleavage (the transition state **d** or **d**′, respectively, Figure 2). As pH increases, the free energies of the transition states **e**, **e**′, **d**, and **d**′ all increase so that both O−O cleavage and Pt(IV)-to-Pt(II) methyl transfer are expected to shut down in strongly alkaline solutions. Therefore, none of the reaction pathways above that including the intermediate **c** or **c**′ can account for production of the dimethyl Pt(IV) complex **g** in strongly alkaline solutions at pH 12−14.

Another possible mechanism of the Pt(IV)-to-Pt(II) methyl group transfer not involving **c** is via its isomer **k** (Figure 3) having the methyl ligand trans to the sulfonate. Isomer **k** is more stable than **c** by 3.1 kcal/mol at pH = 14. Formation of **k** can occur as follows. Complex **a**′ first produces an isomeric complex **i** having the methyl group trans to the sulfonate. This reaction has a free energy barrier of 18.0 kcal/mol. Isomerization is followed by O$_2$ activation via the T−S crossing point **j** to produce **k**. The methyl transfer from **k** to **a**′ occurs via TS **l** and is much faster than from **c** via TS **e**′ (14.0 vs 25.4 kcal/mol free energy barrier if at the same pH), which can be attributed to the sulfonate being a better leaving group than pyridine. The methyl transfer from **k** to **a**′ resulting in formation of the dimethyl Pt(IV) complex **g** produces also hydroperoxo Pt(II) complex **h**′. The latter can rapidly oxidize another (dpms)-Pt^II Me(OH)$^-$ species with a 20.1 kcal/mol barrier at pH = 14. Overall, the RDS for the Pt(IV)-to-Pt(II) methyl transfer mechanism involving intermediate **k** corresponds to the TS **j** (31.5 kcal/mol) whose energy is pH independent. In strongly alkaline solutions the methyl transfer reaction of **k** is faster than O−O bond cleavage via the TS **m**.

In addition to Pt(IV)-to-Pt(II) methyl-transfer mechanisms, several other mechanisms involving Pt(III) intermediates were considered and are presented below.

4. Methyl Transfer and Isomerization Paths via Pt(III). Platinum(III) intermediates have been proposed to be involved in the oxidation of Pt(II) and alkyl transfer between Pt centers. Rivada-Wheelaghan et al. synthesized a stable mononuclear Pt(III)−alkyl compound.[23] Rostovtsev et al. found that in aprotic solvents dimethyl Pt(II) complexes react with O_2 to give EPR active species, suggesting that Pt(III) might be the intermediate in the oxidation.[7,8]

Here we examined five different hypotheses for the methyl-transfer reaction involving several Pt(III) intermediates (Figures 3−5).

1. Pt(II)-to-Pt(IV) Methyl Transfer. In this mechanism a Pt(III) species is an intermediate involved in formation of **k** with the methyl ligand trans to the sulfonate group (Figure 3). The actual methyl-transfer step takes place between the Pt(II) (**a′**) and Pt(IV) (**k**) centers. On the basis of the barrier heights from this theoretical study, we consider this mechanism the most plausible if Pt(III) is ever involved. Staring from **a′** and applying the experimentally found one-electron reduction potential of O_2 (−325 mV vs SHE),[24] it takes 23.4 kcal/mol to form the Pt(III) intermediate **a*′**. Isomerization of **a*′** to form **i*** has a 35.0 kcal/mol barrier. The Pt(III) species **i*** can be further oxidized by oxygen to form the Pt(IV) superoxide complex **k*′**, followed by one-electron transfer from $O_2^{-\bullet}$ or Pt(II) to form **k**.

An alternative mechanism that avoids the high barrier isomerization of the Pt(III) transient **a*′** to **i*** involves isomerization of the Pt(II) complex **a′** to form **i** followed by one-electron oxidation of **i** to give the Pt(III) transient **i***. Because the potential of the $O_2/O_2^{-\bullet}$ couple is pH independent at pH > 4.8,[25] the rate of the methyl transfer would be also pH independent. If the TS for the one-electron oxidation from **i** to **i*** falls into the range of 26−30 kcal/mol, this oxidation mechanism involving Pt(III) transient **i*** may be operational. The generated superoxide **k*′** could react with either Pt(II) directly or water to give O_2 and H_2O_2, which can also oxidize Pt(II).

2. Pt(IV)-to-Pt(III) Methyl Transfer. In the mechanism shown in Figure 4 the methyl radical is transferred from the unsymmetric $(dpms)Pt^{IV}Me(OH)_2$, **f**, to a monomethyl Pt(III) complex **a*′** or **i***. This reaction produces a dihydroxo Pt(III) species **q*** and the $(dpms)Pt^{IV}Me(OH)_2$ complex, **g**. The corresponding transition states, **o** and **p**, have free energies of 41.7 and 39.1 kcal/mol, which is more than 10 kcal/mol higher than the path via TS **l**. Hence, this mechanism is less likely to account for formation of the dimethyl Pt(IV) complex **g**.

3. Pt(II)-to-Pt(III) Methyl Transfer. In this mechanism the methyl free radical is transferred from the monomethyl Pt(II) complex **a′** or **i** to a monomethyl Pt(III) species **a*′** or **i*** to give dimethyl Pt(IV) complex **g** and a Pt(I) intermediate. These four reaction pathways are thermally inaccessible (>40 kcal/mol), and the details are given in the Supporting Information.

4. Pt(III)−C Bond Homolysis. We also considered homolysis of the Pt(III)−C bond as a way to generate free methyl radicals that could be transferred to a methyl Pt species. A similar mechanism has been proposed to account for formation of ethyl chloride in the oxidation of diphosphine Pt(II) complexes by $IrCl_6^{2-}$, a 1e oxidant.[26] We examined this path that begins from the Pt(III) transient **f*** to give a Pt(II) species plus methyl
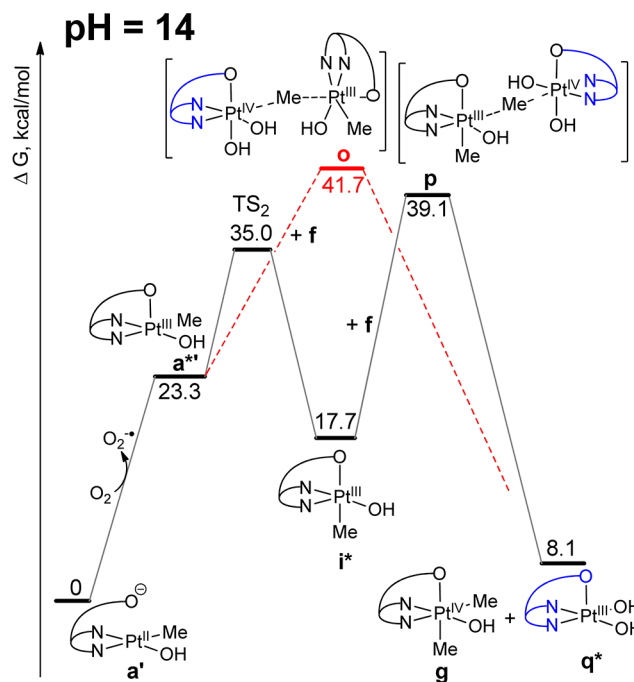
Figure 4. Proposed mechanism of the Pt(IV)-to-Pt(III) methyl transfer at pH = 14 in water with the Gibbs free energy along the potential energy surface.
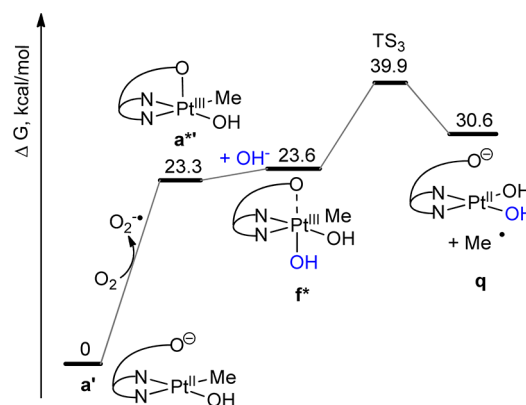
Figure 5. Proposed mechanism of Pt(III)−C bond homolysis at pH = 14 in water with the Gibbs free energy along the potential energy surface.

free radical (Figure 5) and found that this reaction is endergonic with a high activation barrier of 39.9 kcal/mol, which is not accessible at room temperature. This conclusion agrees with our experiment where no methyl free radicals were detected.[12]

5. Pt(III)-to-Pt(III) Methyl Transfer. Starting from two Pt(III) species **a*′** and **f*** with free energy 47.0 kcal/mol above the ground state, the methyl transfer has a 2.3 kcal/mol barrier relative to **a*′**+ **f*** (the TS for this reaction has the same geometry as **u** in Figure 7). The competing reaction (not shown) is the disproportionation of two Pt(III) species, **a*′** and **f***, to form Pt(II) and Pt(IV) complexes **a′** and **f**, which is exergonic by 27.8 kcal/mol. The reorganization energy of this reaction is calculated to be 53 kcal/mol,[27] which gives a free energy barrier of ~3 kcal/mol based on Marcus' theory $\Delta G = (\lambda + \Delta G_0)^2/4\lambda$.[28] This suggests that methyl-coupled electron transfer may be as efficient as the direct electron-transfer

reaction. Given O_2 as the 1e oxidant, the TS of this methyl-transfer reaction is not thermally accessible due to the high energy cost to generate the reactant Pt(III) species $\mathbf{a}^{*\prime}$ and $\mathbf{f}^*$. However, if a stronger 1e oxidant is used, this pathway could become dominant and be comparable with the disproportionation.

To conclude, all considered Pt-to-Pt methyl transfer mechanisms involving Pt(III) transients have high barriers with O_2 as the 1e oxidant. However, if stronger 1e oxidants are used, such as ferrocenium (641 meV vs SHE) as in our recent experiment,[12] the free energy cost to form Pt(III) drops by 22.3 kcal/mol, bringing down the free energy of all channels involving Pt(III) intermediates, especially the channel with two Pt(III) species as reactants. Electron-donating ligands, such as alkyl or phosphine, stabilize the Pt(III) oxidation state, lowering the free energy to form Pt(III) species. For example, if $(tmeda)Pt^{II}(CH_3)_2$ is oxidized by O_2 the calculated free energy cost to form $(tmeda)Pt^{III}(CH_3)_2{}^+$ is 15.1 kcal/mol, which is 8 kcal/mol lower than for one-electron oxidation of $(dpms)Pt^{II}Me(OH)^-$ complex. This result justifies the hypothesis of the involvement of Pt(III) species in the above reaction of $(tmeda)Pt^{II}(CH_3)_2$ and O_2 presented in refs 7 and 8.

In summary, speaking about the possible role of Pt(III) intermediates in the oxidation of the $(dpms)Pt^{II}Me(OH)^-$ complex with O_2 we cannot exclude the possibility of the involvement of Pt(III) species given the expected similar barrier heights for the one- and two-electron pathways in Figures 3−5, but the methyl transfer step is more likely to take place between Pt(II) and Pt(IV) intermediates (e.g., $\mathbf{a}^\prime$ and $\mathbf{k}$).

6. S_N2 Functionalization of the Pt(IV)−CH_3 Bond.
It was shown experimentally[9,10] that methanol can be produced from the monomethyl Pt(IV) complexes $\mathbf{f}$ and $\mathbf{n}$ in acidic or basic aqueous solution. Therefore, we analyzed the reductive elimination and S_N2 functionalization pathways of $\mathbf{f}$ and $\mathbf{n}$ with H_2O, OH^-, and Pt(II) as nucleophiles, as shown in Figures 6 and 7. The symmetric monomethyl Pt(IV) complex $\mathbf{n}$ is more stable than its isomer $\mathbf{f}$ by ∼8 kcal/mol, similar to the relative stability of $\mathbf{c}$ and $\mathbf{k}$ at the same pH. The C−O reductive elimination of methanol for both isomers, $\mathbf{f}$ and $\mathbf{n}$, requires high activation energy, 42.2 and 45.6 kcal/mol, respectively, and is unlikely to happen at room temperature, in agreement with experimental observations.[9,10] For S_N2 functionalization, we calculated that isomer $\mathbf{n}$ is easier to undergo an S_N2 attack by water compared to $\mathbf{f}$ by 4−7 kcal/mol, which can be attributed to the presence of a better leaving group, sulfonate, trans to the methyl group.

For both $\mathbf{f}$ and $\mathbf{n}$, the barriers to form methanol are pH dependent: at pH < 2 the hydroxo ligand on Pt(IV) is protonated, rendering easier reduction to Pt(II) due to the reduced electron density on the metal. In basic solutions S_N2 attack is easier because of the higher nucleophilicity of OH^- vs water. The calculated barriers to form CH_3OH from $\mathbf{n}$ at pH = 0, 7, and 14 are 24.2, 30.0, and 21.6 kcal/mol, demonstrating a trend which is in a qualitative agreement with the experimental observations, showing that $\mathbf{n}$ eliminates methanol more readily in acidic or basic media compared to neutral solutions at 25 °C.

It is also worth noting that the barriers for all reactions of $\mathbf{f}$ to produce CH_3OH are higher as compared to $\mathbf{n}$.

Finally, Pt(II) is a better nucleophile than either OH^- or H_2O, as reflected in the lower reaction barriers of reactions of $\mathbf{f}$ and $\mathbf{n}$ with $\mathbf{a}$ and $\mathbf{a}^\prime$ (Figure 7) vs their reactions with OH or H_2O (Figure 6). This theoretical result accounts for the
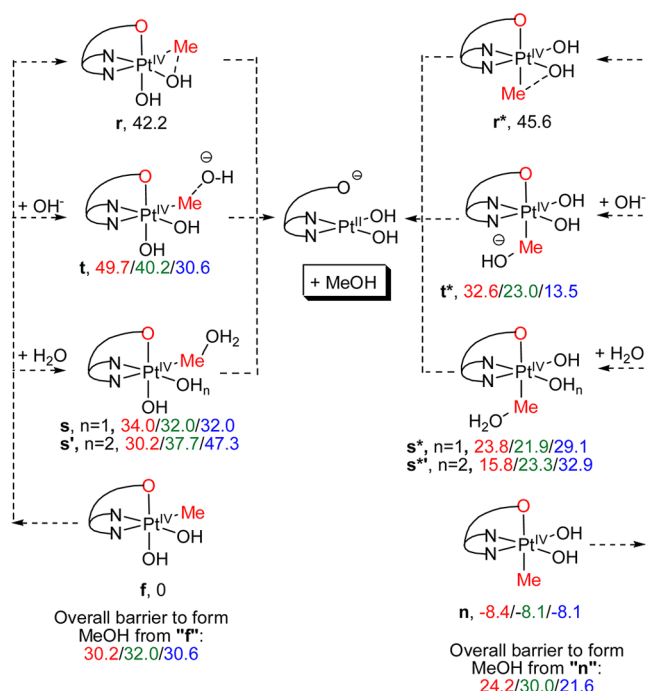

Figure 6. Gibbs free energies for different methanol-forming reactions. Color code for different pH: red = 0, green = 7, blue = 14. Pt(IV) isomer with the methyl trans to the sulfonate ($\mathbf{n}$) undergoes an S_N2 attack much easier than the isomer with the methyl trans to the pyridine nitrogen ($\mathbf{f}$).
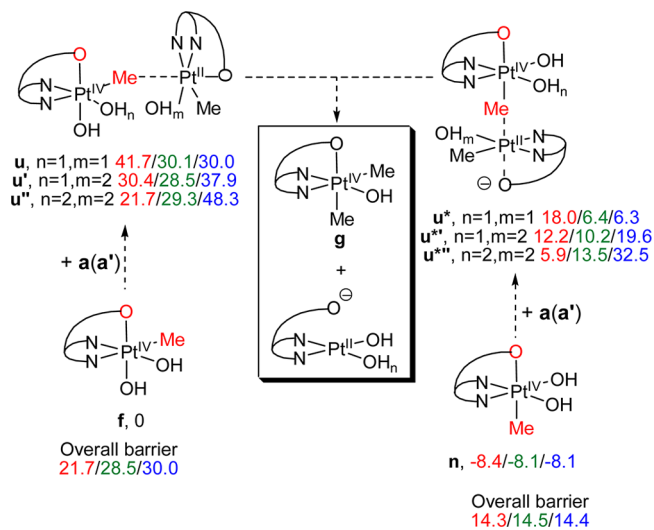
Figure 7. Gibbs free energies for Pt(IV)-to-Pt(II) methyl transfer reactions. Color code for different pH: red = 0, green = 7, blue = 14. Pt(II) complexes $\mathbf{a}$ and $\mathbf{a}^\prime$ are better nucleophiles than water and OH^-, as seen from lower barriers to give dimethyl Pt(IV) from both $\mathbf{f}$ and $\mathbf{n}$.

experimental fact that $\mathbf{n}$ reacts with $\mathbf{a}$ in water at pH 14 to form exclusively the methyl-transfer product, dimethyl Pt(IV) complex $\mathbf{g}$; no methanol is observed in this system.[12] The dimethyl Pt(IV) complex $\mathbf{g}$ is less reactive toward S_N2 attacks than $\mathbf{f}$, as reflected in the higher barriers to form CH_3OH at all pH values (31.7, 36.2, and 32.7 kcal/mol at pH = 0, 7, and 14), in agreement with the experimental observations.[9]

7. Isomerization of Monomethyl Pt(IV) Complex.
Experimentally it was found that $\mathbf{f}$ isomerizes to form $\mathbf{n}$ in neutral aqueous solutions. The lowest energy pathway for this
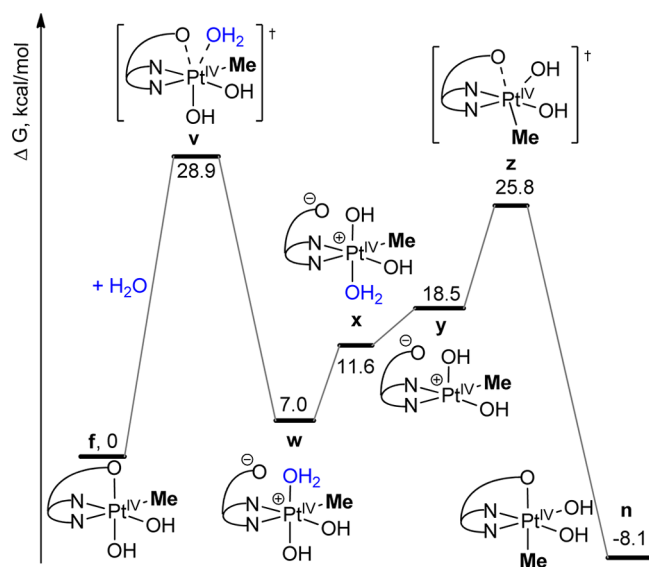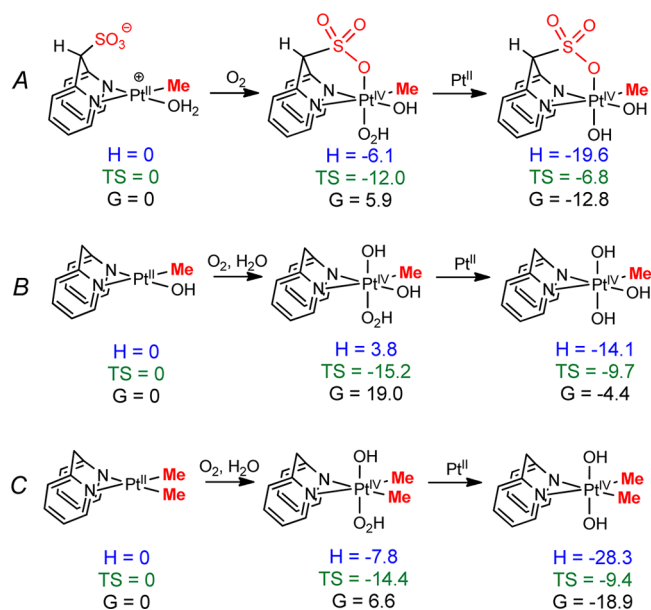
Figure 8. Gibbs free energies for isomerization of Pt(IV) monomethyl complex. Rate-determining step is at **v**.

Figure 9. Enthalpy, entropy, and Gibbs free energies for intermediates with different ligands at 273.15 K, 1 atm, and pH = 7. dpms ligand stabilizes Pt(IV) enthalpically and entropically as compared with the sulfonate-free dpm ligand.

isomerization we found is shown in Figure 8. Dissociation of the axial hydroxo ligand trans to SO_3^- at pH = 7 takes 44.9 kcal/mol, which is not viable; hence, creating the vacant site trans to the weak donor, sulfonate, is difficult. To make a vacant site on the axial position, a stronger donating ligand can be introduced by replacing the sulfonate oxygen with water (**v**) followed by proton transfer, **w → x**. In **x**, the more donating hydroxide and the better leaving group H_2O facilitate water dissociation to give 5-coordinate intermediate **y**. Facile isomerization of **y** (Berry pseudorotation) accompanied by recoordination of SO_3^- (**z**) gives the isomer **n**. The RDS for the overall reaction sequence is at **v** with 28.9 kcal/mol Gibbs free energy barrier, which decomposes to $\Delta H = 26.1$ kcal/mol and $\Delta S = -9.4$ eu. These values agree well with experiment, $\Delta H = 23.8 \pm 0.8$ kcal/mol and $\Delta S = -7.8 \pm 2.2$ eu.[9]

8. Why Does dpms Facilitate Oxidation? Previous studies of aerobic oxidation of Pt(II) complexes were mostly limited to dimethyl complexes.[7,8,29−32] The high reactivity of such compounds toward O_2 can be rationalized as a result of electron donation from methyl ligands which stabilize the emerging Pt(IV) center. To understand the role of the pendant sulfonate group in Pt(II) complexes supported by dpms ligand which enables oxidation with O_2 of electron poorer monomethyl[9,10] and even monophenyl Pt(II) complexes,[11] we calculated the enthalpic and entropic contributions for the oxidation of monomethyl Pt(II) compounds supported by dpms and by its sulfonate-free analog di(2-pyridyl)methane (dpm). The dimethyl Pt(II) complex supported by dpm was also included in this analysis, all shown in Figure 9.

For all the Pt(II) complexes **A**, **B**, and **C** two series of products were considered, hydroperoxo Pt(IV) derivatives, Pt(IV)−OOH, and hydroxo Pt(IV) derivatives, Pt(IV)−OH. Formation of all the Pt(IV)−OOH products is endergonic with the entropic term contributing positively to the reaction Gibbs energy. This is because a gaseous O_2 with its high entropy becomes bound. Instead of catching a free-moving solvent molecule with higher entropy as the other ligand trans to the −OOH, using the tethered sulfonate group with lower entropy to chelate on Pt(IV) lowers the entropic penalty by ~3 kcal/mol, as compared to its dpm analogs **B** and **C** (12.0 vs 15.2 and

14.4 kcal/mol). The sulfonate group in **A** also stabilizes the Pt(IV) center by 9.9 kcal/mol as compared with **B**. Such enthalpic stabilization is comparable with the effect of replacing hydroxo ligand in **B** with a second methyl ligand. Introduction of the second methyl ligand leads to a 11.6 kcal/mol gain in enthalpy as it follows from the comparison of the energies for the Pt(IV)−OH reaction products derived from **C** and **B**. For the Pt(IV)−OH reaction products derived from **A**, we still retain the same ~3 kcal/mol in reduction of the entropic penalty. The enthalpic stabilization by the sulfonate group is not as efficient as by one extra methyl group (19.6 vs 28.3 kcal/mol), but still it is 5.5 kcal/mol more favorable than the case of the sulfonate-free monomethyl complex **B**.

◼ SUMMARY

We applied DFT calculation to elucidate the mechanism of CH_3 functionalization on Pt, including oxidation of the Pt(II) center by O_2, production of dimethyl Pt(IV) complex (dpms)Pt^{IV}Me$_2$(OH) at pH > 10, and methanol formation from Pt(IV)−methyl complexes. At pH < 10, (dpms)Pt^{II}Me$(OH_n)^{(2−n)−}$ reacts with O_2 to form two isomeric methyl Pt(IV)−OOH intermediates, which then oxidize another Pt(II) by cleavage of the O−O bond. The predominant methyl Pt(IV)−OOH intermediate has the methyl ligand trans to the pyridine nitrogen and forms the observed reaction product, the unsymmetric monomethyl Pt(IV)−OH complex (dpms)-Pt^{IV}Me(OH)$_2$. The minor isomeric monomethyl Pt(IV)−OOH species with a methyl group trans to the sulfonate is responsible for the methyl-transfer reaction. At pH ≥ 10, O−O cleavage is inhibited but the Pt-to-Pt methyl transfer is not. As a result, the Pt-to-Pt methyl transfer reaction becomes competitive with O−O bond cleavage and even predominant at pH ≥ 12. A similar relationship between the structure and the reactivity is also observed for monomethyl Pt(IV)−OH complexes in the S_N2 functionalization with water and OH$^-$: the isomer with the methyl ligand trans to the sulfonate is slower to form in aerobic oxidation of Pt(II) precursor, but it is

the most reactive. Interestingly, Pt(III) species do not contribute substantially to the aerobic oxidation and Pt-to-Pt methyl transfer chemistry analyzed here. With O_2 behaving as one-electron oxidant, it is costly to form Pt(III), resulting in high barriers of subsequent reactions involving Pt(III). The isomerization pathway to shift the methyl group from the equatorial to the axial position is found to be via dissociation of the sulfonate group and then water coordination. Finally, the success of the tripod semilabile dpms ligand at enabling facile oxidation of Pt(II) species with O_2 is due to its ability to both lower the reaction enthalpy and diminish the entropy penalty of this reaction. The consequences for the reactivity of Pt(II) complexes toward O_2 resulting from attachment of the sulfonate group to the di(2-pyridyl)methane core are comparable in magnitude with the effect of replacing one hydroxo ligand at the Pt(II) center with one methyl group.

ASSOCIATED CONTENT

Supporting Information

Atomic coordinates and energies of all species. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

REFERENCES

(1) Labinger, J. A.; Bercaw, J. E., The Role of Higher Oxidation State Species in Platinum-Mediated C-H Bond Activation and Functionalization. In *Higher Oxidation State Organopalladium and Platinum Chemistry*; Canty, A. J., Ed.; Springer-Verlag Berlin: Berlin, 2011; Vol. 35, pp 29−59.

(2) Gol'dshleger, N. F.; Tyabin, M. B.; Shilov, A. E.; Shteinman, A. A. *Zh. Fiz. Khim.* **1969**, *43*, 2174.

(3) Horvath, I. T.; Cook, R. A.; Millar, J. M.; Kiss, G. *Organometallics* **1993**, *12*, 8−10.

(4) DeVries, N.; Roe, D. C.; Thorn, D. L. *J. Mol. Catal. A: Chem.* **2002**, *189*, 17−22.

(5) Lin, M. R.; Shen, C. Y.; Garcia-Zayas, E. A.; Sen, A. *J. Am. Chem. Soc.* **2001**, *123*, 1000−1001.

(6) Bar-Nahum, I.; Khenkin, A. M.; Neumann, R. *J. Am. Chem. Soc.* **2004**, *126*, 10236−10237.

(7) Rostovtsev, V. V.; Labinger, J. A.; Bercaw, J. E.; Lasseter, T. L.; Goldberg, K. I. *Organometallics* **1998**, *17*, 4530−4531.

(8) Rostovtsev, V. V.; Henling, L. M.; Labinger, J. A.; Bercaw, J. E. *Inorg. Chem.* **2002**, *41*, 3608−3619.

(9) Vedernikov, A. N.; Binfield, S. A.; Zavalij, P. Y.; Khusnutdinova, J. R. *J. Am. Chem. Soc.* **2006**, *128*, 82−83.

(10) Khusnutdinova, J. R.; Zavalij, P. Y.; Vedernikov, A. N. *Organometallics* **2007**, *26*, 3466−3483.

(11) Khusnutdinova, J. R.; Zavalij, P. Y.; Vedernikov, A. N. *Can. J. Chem.* **2009**, *87*, 110−120.

(12) Sberegaeva, A. V.; Liu, W.-G.; Nielsen, R. J.; Goddard, W. A.; Vedernikov, A. N. *J. Am. Chem. Soc.* submitted for publication.

(13) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.

(14) Lee, C. T.; Yang, W. T.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789.

(15) Tannor, D. J.; Marten, B.; Murphy, R.; Friesner, R. A.; Sitkoff, D.; Nicholls, A.; Ringnalda, M.; Goddard, W. A.; Honig, B. *J. Am. Chem. Soc.* **1994**, *116*, 11875−11882.

(16) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299−310.

(17) Kahn, L. R.; Goddard, W. A. *J. Chem. Phys.* **1972**, *56*, 2685−2701.

(18) Melius, C. F.; Goddard, W. A. *Phys. Rev. A* **1974**, *10*, 1528−1540.

(19) Wertz, D. H. *J. Am. Chem. Soc.* **1980**, *102*, 5316−5322.

(20) Harvey, J. N.; Aschi, M.; Schwarz, H.; Koch, W. *Theor. Chem. Acc.* **1998**, *99*, 95−99.

(21) *Jaguar*; Schrodinger, LLC: New York, 2010.

(22) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, *132*, 154104.

(23) Rivada-Wheelaghan, O.; Ortuno, M. A.; Diez, J.; Garcia-Garrido, S. E.; Maya, C.; Lledos, A.; Conejero, S. *J. Am. Chem. Soc.* **2012**, *134*, 15261−15264.

(24) Wardman, P. *J. Phys. Chem. Ref. Data* **1989**, *18*, 1637−1755.

(25) Bielski, B. H. J.; Cabelli, D. E.; Arudi, R. L.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1985**, *14*, 1041−1100.

(26) Chen, J. Y.; Kochi, J. K. *J. Am. Chem. Soc.* **1977**, *99*, 1450−1457.

(27) The contribution from inner-sphere was calculated as 24.1 kcal/mol. The outer-sphere contribution was estimated to be 29.3 kcal/mol in water with the following parameters: $R_A = R_B = 0.5R_{AB} = 3.5$ Å.

(28) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 966−978.

(29) Vedernikov, A. N. *Chem. Commun.* **2009**, 4781−4790.

(30) Wieghardt, K.; Koppen, M.; Swiridoff, W.; Weiss, J. *J. Chem. Soc., Dalton Trans* **1983**, 1869−1872.

(31) Sarneski, J. E.; McPhail, A. T.; Onan, K. D.; Erickson, L. E.; Reilley, C. N. *J. Am. Chem. Soc.* **1977**, *99*, 7376−7378.

(32) Prokopchuk, E. M.; Jenkins, H. A.; Puddephatt, R. J. *Organometallics* **1999**, *18*, 2861−2866.