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Facile Aerobic Oxidation of dpms−Platinum(II) Ethylene Complexes (dpms = di(2-pyridyl)methanesulfonate)

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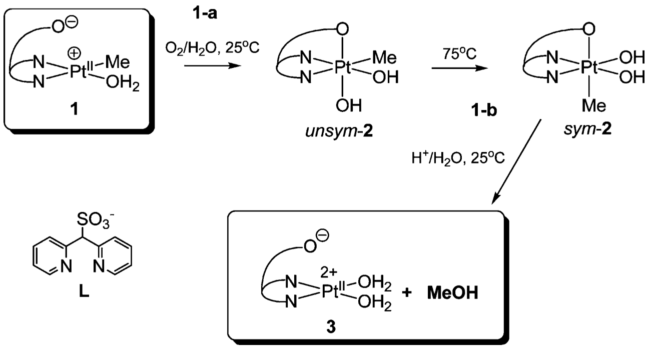
Di(2-pyridyl)methanesulfonato hydroxo platinum(II) ethylene complex **4b**, $LPt^{II}(C_2H_4)OH$, reacts readily with oxygen in aqueous solution to cleanly produce unsymmetrical 2-hydroxyethyl platinum(IV) complex *unsym*-**6b**, $LPt^{IV}(C_2H_4OH)(OH)_2$. The latter eliminates ethylene oxide and ethylene glycol in virtually quantitative yield in neutral aqueous solution at 80 °C and produces the dinuclear μ-hydroxo platinum(II) complex **7** as another reaction product. The oxidation reaction was shown to proceed via an anionic 2-hydroxyethyl hydroxo platinum(II) intermediate, **5b**. The chloro analogues **4a** and **5a** are inert toward dioxygen but can be converted to **6b** under air in the presence of 1 equiv of NaOH. As established by DFT calculations, both the formal charge on the platinum(II) center and the nature of ligands coordinated to it have a crucial effect on the energy of the HOMO of the complexes, which may be related to their ability to undergo an aerobic oxidation.

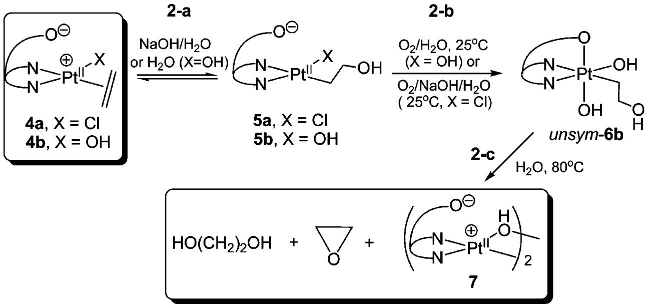
Introduction

The use of atmospheric oxygen for selective oxidation of organic compounds is a challenging but practical goal.[1] In particular, oxygen is an attractive oxidant for the platinum-mediated alkane functionalization involving organoplatinum intermediates.[2−5] Recently we have reported facile oxidation of aqua methylplatinum(II) complex **1** by atmospheric oxygen (Scheme 1-a) and clean elimination of methanol from the resulting dihydroxo methylplatinum(IV) *unsym*-**2** in acidic (Scheme 1-b) and basic aqueous solutions,[6] all enabled by di(2-pyridyl)methanesulfonate ligand (dpms).[7] Importantly, platinum(II) complex **3** resulting from the elimination reaction is inert toward dioxygen. Hence, the presence of a hydrocarbyl attached to the Pt^{II} center is essential for facile oxidation reactions.[6] To the best of our knowledge, such selective direct aerobic functionalization of *mono*methyl platinum(II) complexes involving methyl platinum(IV) intermediates is currently the unique feature of the dpms-based system. The scope of reactions presented in Scheme 1, allowing for the use of dioxygen for functionalization of hydrocarbyl platinum(II) complexes, is currently a focus of our research.

Scheme 1



Scheme 2



In this work we report facile aerobic functionalization of ethylene dpms (L) complexes **4**, which leads cleanly to a mixture of ethylene oxide and ethylene glycol (Scheme 2). Our data suggest that similar to the case of *mono*methyl platinum(II) complex **1** (Scheme 1), aerobic oxidation of **4** occurs via an alkyl platinum(II) intermediate, **5b** (Schemes 2-a, 2-b; X = OH), where the alkyl is 2-hydroxyethyl. Similarly to the chemistry presented in Scheme 1, the oxidation of **5b** leads to an isolable platinum(IV) compound, *unsym*-**6b**, *unsym*-$LPt^{IV}(C_2H_4OH)(OH)_2$ (Scheme 2-b). In neutral aqueous solution *unsym*-**6b** produces ethylene oxide, ethylene glycol, and a dinuclear hydroxo-bridged complex $L_2Pt^{II}_2(\mu\text{-}OH)_2$,[6] **7** (Scheme 2-c). Neither acid nor base additives are required for the C−O reductive elimination from **6b**. No less remarkably, the aerobic oxidation of hydroxo ethylene complex **4b** also proceeds readily in pure water. In contrast, an aerobic oxidation of **4a** is

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impossible in neutral solution but is facile in the presence of 1 equiv of a strong base (Scheme 2-b).

The ability of platinum(II) ethylene complexes **4** to add hydroxide anion and form **5** reversibly (Scheme 2-a) can be readily demonstrated in alkaline solutions and is similar to the reversible nucleophilic addition of alkoxide anions to the ethylene ligand of Zeise's anion, according to a recent report.[8] The question of whether or not the direct aerobic oxidation involves **4b** or **5b** is more complex and will be discussed here. Altogether, the reactions presented in Scheme 2 lead to non-carbonyl/ non-vinylic type products that are typical for the well-established Wacker chemistry.[9−11] Another type of aerobic olefin oxidation includes amidate-bridged polynuclear platinum(III) complexes as catalysts. It leads to ketones and epoxides and includes Pt^{III} alkyl intermediates.[10,11] It may be important to emphasize that, in contrast to those systems, the reactions reported in this work involve the Pt^{IV}/Pt^{II} couple. Chemical transformations presented by Scheme 2, the effect of the ligand X on nucleophilic addition (2-a), aerobic oxidation (2-b), and subsequent C−O elimination (2-c) chemistry, will be discussed below.

Results and Discussion

Synthesis of $LPt^{II}(C_2H_4)X$ Complexes (X = Cl, OH). $LPt^{II}(C_2H_4)Cl$, 4a. Preparation of chloro ethylene LPt^{II} complex **4a** was achieved by reacting equivalent amounts of Zeise's salt and K(L) in aqueous solution at room temperature:

$$K[Pt^{II}Cl_3(\eta^2\text{-}C_2H_4)] + K(L) \rightarrow \underset{\mathbf{4a}}{LPt^{II}(\eta^2\text{-}C_2H_4)Cl} + 2KCl \quad (1)$$

A white precipitate of the poorly water-soluble target compound formed after several minutes with concomitant disappearance of the yellow color of Zeise's salt. The product was isolated in analytically pure form in 80% yield. Complex **4a** was sparingly soluble in water and methanol, stable in aqueous and methanolic solutions at room temperature under an argon and O_2 atmosphere, but decomposed slowly upon heating in water, releasing ethylene. Electrospray ionization mass spectra (ESI-MS) of a dilute aqueous solution of **4a** showed the presence of **4a**·H^+ ion as the only Pt-containing species. Low molecular symmetry of complex **4a** containing a dpms ligand with two nonequivalent pyridine rings was evident from the observation of a pattern of eight multiplets of equal intensity in the aromatic region of the ^1H NMR spectra of **4a**. Platinum-coordinated ethylene exhibited two multiplets with the platinum-195 satellites at 4.9 and 5.1 ppm ($^2J_{PtH}$ = 55 Hz) integrating as 2H each per one dpms ligand. The ethylene resonances were downfield shifted as compared to the 4.6 ppm signal observed for Zeise's salt.[8,12]

Single crystals of $LPt^{II}(CH_2CH_2)Cl$ suitable for X-ray diffraction analysis were prepared by slow crystallization from a reaction mixture. The platinum atom in **4a** is four-coordinate and has a square planar environment, with an angle between the platinum coordination plane and the mean plane of the ethylene ligand of 89.9° (Figure 1). The length of the C−C bond in the coordinated olefin, 1.378 Å, is greater than in free ethylene (1.337 Å) and is almost the same as in Zeise's salt, 1.375 Å.[12] The platinum−sulfonate oxygen distance, Pt1−O11, is slightly shorter than the sum of van der Waals radii of these atoms.

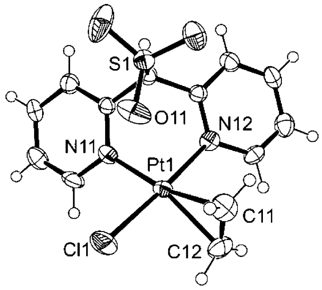

Figure 1. ORTEP drawings of complex **4a**, 50% probability ellipsoids. Selected bond distances, Å: Pt1−O1, 2.890; Pt1−C12, 2.180; Pt1−C11, 2.155; Pt1−N11, 2.062; Pt1−N12, 2.013; Pt1−Cl1, 2.295; C11−C12, 1.378.

$LPt^{II}(C_2H_4)OH$, 4b. Preparation of hydroxo ethylene LPt^{II} complex $LPt^{II}(CH_2CH_2)OH$, **4b**, was performed by reacting the chloro analogue **4a** with 1 equiv of silver(I) oxide under an argon atmosphere in carefully deaerated water at room temperature:

$$\underset{\mathbf{4a}}{2LPt^{II}(\eta^2\text{-}C_2H_4)Cl} + Ag_2O + H_2O \rightarrow \underset{\mathbf{4b}}{2LPt^{II}(\eta^2\text{-}C_2H_4)OH} + 2AgCl \quad (2)$$

According to ^1H NMR spectroscopy, the reaction was complete in 24 h and produced the target hydroxo complex **4b** in a virtually quantitative yield. Pure **4b** was isolated from the pale yellow solution, obtained upon centrifugation of silver compounds, in 76% yield.

Aqueous solutions of analytically pure complex **4b** were slightly alkaline (pH ≈ 8) and contained 3−4% of 2-hydroxoethyl LPt^{II} complex **5b**, according to ^1H NMR spectroscopy. The elevated pH value was due to the weakly basic nature of the $Pt^{II}(OH)$ fragment. A potentiometric titration of a pure sample of **4b** in a standardized 0.0970 M HNO_3 with a standardized 0.1000 M NaOH gave the K_b value of 1.0×10^{-11} (see Supporting Information for more details). On the basis of this result, the pH of a 50 mM solution of **4b** in water should be equal to 7.8, matching our observations. Solutions of **4b** in pure water decomposed very slowly under an argon atmosphere at room temperature. This process could be slowed down significantly at 5−6 °C. When exposed to air, **4b** produced *unsym*-**6b** in virtually quantitative yield, according to ^1H NMR spectroscopy.

The low symmetry of complex **4b**, featuring two nonequivalent pyridine rings, was confirmed by ^1H and ^{13}C NMR. Platinum-coordinated ethylene exhibited two multiplets at 4.7 and 5.0 ppm in ^1H NMR spectrum of aqueous **4b**, slightly more upfield than for the chloro analogue **4a**, each multiplet integrating as 2H per one dpms ligand. Electrospray ionization mass spectra of a dilute aqueous solution of **4b** showed the presence of the **4b**·H^+ ion.

Nucleophilic Addition of OH^- to $LPt^{II}(C_2H_4)X$ Complexes to Produce $Na[LPt^{II}(C_2H_4OH)X]$ (X = Cl, OH). $Na[LPt^{II}(CH_2CH_2OH)Cl]$, 5a. Nucleophilic addition of hydroxide to

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Table 1. DFT-Calculated Energy of the HOMO of Cationic, Neutral, and Anionic Platinum(II) dpms Complexes, eV

$LPt^{II}(C_2H_4)OH_2^+$	$LPt^{II}(C_2H_4)Cl$	$LPt^{II}(C_2H_4)OH$	$[LPt^{II}(C_2H_4OH)Cl]$	$[LPt^{II}(C_2H_4OH)OH]$
−9.08	−5.51	−5.26	−1.95	−1.51

$LPt^{II}(CH_2CH_2)Cl$ was accomplished by reacting solid **4a** with 4 equiv of 0.2 M sodium hydroxide in deaerated D_2O under an argon atmosphere at room temperature. The solid dissolved quickly upon stirring to produce a clear, colorless solution (eq 3):

$$\underset{\mathbf{4a}}{LPt^{II}(\eta^2\text{-}C_2H_4)Cl} + NaOH \rightleftharpoons \underset{\mathbf{5a}}{Na[LPt^{II}(CH_2CH_2OH)Cl]} \quad (3)$$

According to ^1H NMR spectroscopy, the conversion of the starting material **4a** was complete in 10 min. Two dpms-containing species detected by the NMR were 2-hydroxyethyl chloro platinum(II) complex **5a** (96 mol %), which resulted from a nucleophilic attack of OH^- at the ethylene ligand in **4a**, and 2-hydroxyethyl hydroxo complex **5b** (4 mol %), which resulted from the Cl/OH ligand exchange in **5a** (eq 4):

$$\underset{\mathbf{5a}}{Na[LPt^{II}(C_2H_4OH)Cl]} + NaOH \rightarrow \underset{\mathbf{5b}}{Na[LPt^{II}(C_2H_4OH)OH]} + NaCl \quad (4)$$

A ^1H NMR spectrum of the major product **5a** showed the presence of a dpms ligand with two nonequivalent pyridine rings and two sets of signals of diastereotopic hydrogen atoms of the 2-hydroxyethyl ligand. The signals of hydrogens attached to the α-carbon were well resolved, centered at 1.7 and 1.9 ppm, and had broad platinum-195 satellites with $^2J_{PtH} = 41$ and 38 Hz, respectively. In the ^{13}C NMR spectrum of **5a** the α-carbon atom exhibited a singlet with two platinum-195 satellites and $^1J_{PtC} = 728$ Hz.

The presence of **5a** in freshly prepared alkaline aqueous solutions of **4a** (pH = 10) was also confirmed by ESI mass spectrometry.

A slow Cl/OH ligand exchange (eq 4) was further seen in the reaction mixture, causing the **5b**/**5a** ratio to increase over time with a half-life of 16 h under the above conditions. The ligand exchange was complete after 8 days to produce **5b** as the only water-soluble product. Formation of a small amount of dark precipitate was also evident after that time.

Reversibility of the Nucleophilic Attack of Hydroxide Anion at the Ethylene Ligand in $LPt^{II}(CH_2CH_2)Cl$. Reversibility of the nucleophilic addition of hydroxide to **4a** leading to **5a** (eq 3) was confirmed in a separate experiment. A 4.0 mM solution of $Na[LPt^{II}(CH_2CH_2OH)Cl]$ was prepared from **4a** and approximately 1 equiv of NaOH. The solution contained **4a**, **5a**, and **4b** in a 6:87:7 molar ratio as established by ^1H NMR integration. The presence of complex **4a** and some sodium hydroxide in the mixture could result from the reverse reaction given by eq 3. A partial Cl for OH ligand substitution in **4a** then led to **4b** (eq 5):

$$\underset{\mathbf{4a}}{LPt^{II}(\eta^2\text{-}C_2H_4)Cl} + NaOH \rightarrow \underset{\mathbf{4b}}{LPt^{II}(\eta^2\text{-}CH_2CH_2)OH} + NaCl \quad (5)$$

At 1 h after preparation the ratio of $LPt^{II}(CH_2CH_2)Cl$, $LPt^{II}(CH_2CH_2OH)Cl^-$, and $LPt^{II}(CH_2CH_2)OH$ was 6:84:10. Upon mixing of the solution with 1 equiv of aqueous HBF_4, **4a** was produced (eq 6):

$$\underset{\mathbf{5a}}{Na[LPt^{II}(CH_2CH_2OH)Cl]} + HBF_4 \rightarrow \underset{\mathbf{4a}}{LPt^{II}(CH_2CH_2)Cl} + NaBF_4 + H_2O \quad (6)$$

According to ^1H NMR spectroscopy, the mixture contained complexes **4a** and **4b** in an 85:15 ratio, the resulting solution being slightly acidic (pH = 3). The ratio did not change after 1 day. Hence, we could conclude that the nucleophilic addition of hydroxide to **4a** (eq 3) is fully reversible.

$Na[LPt^{II}(CH_2CH_2OH)OH]$, 5b. A chloride-free solution of the hydroxo analogue **5b** could be prepared by reacting ethylene hydroxo complex **4b** with a 1.4-fold excess of an aqueous sodium hydroxide solution under an argon atmosphere (eq 7):

$$\underset{\mathbf{4b}}{LPt^{II}(\eta^2\text{-}C_2H_4)OH} + NaOH \rightleftharpoons \underset{\mathbf{5b}}{Na[LPt^{II}(CH_2CH_2OH)OH]} \quad (7)$$

According to ^1H NMR spectroscopy, the resulting clear yellowish solution contained the target complex as the only dpms-derived species. Thus, the conversion of **4b** to **5b** was virtually quantitative. ^1H and ^{13}C NMR spectra of **5b** exhibited a set of signals characteristic of an unsymmetrical dpms complex. Two sets of diastereotopic hydrogen atoms of the 2-hydroxyethyl ligand with platinum-195 satellites ($^2J_{PtH} = 37$ Hz for both α-CH protons) were seen in the ^1H NMR spectrum of **5b**. The complex decomposed slowly in strongly alkaline solutions (pH > 10) with a half-life of ca. 28 h at room temperature, leading to formation of an unidentified dark precipitate. Complex **5b** was air-sensitive and produced *unsym*-**6b** when oxygen was admitted to its solution.

The identity of **5b** prepared in deaerated H_2O was confirmed by ESI-MS, which showed the presence of the target anionic complex.

Reversibility of the Nucleophilic Attack of Hydroxide Anion at the Ethylene Ligand of $LPt^{II}(CH_2CH_2)OH$. Nucleophilic addition of hydroxide to the ethylene ligand of hydroxo ethylene complex **4b** was demonstrated in the following experiment. A dilute solution of $LPt^{II}(CH_2CH_2)OH$ in deaerated D_2O was combined with approximately 1 equiv of sodium hydroxide under an argon atmosphere. According to ^1H NMR spectroscopy, 10 min after preparation the reaction mixture contained $[LPt^{II}(CH_2CH_2OH)OH]^-$ and $LPt^{II}(CH_2CH_2)OH$ in a 77:23 ratio. This ratio did not change in the course of 10 h, thereby suggesting that a dynamic equilibrium had been reached (eq 7). When this mixture was combined with 1 equiv of HBF_4 in D_2O, $LPt^{II}(CH_2CH_2)OH$ was found to be the only dpms-derived species present in solution (eq 8):

$$\underset{\mathbf{5b}}{Na[LPt^{II}(CH_2CH_2OH)OH]} + HBF_4 \rightarrow \underset{\mathbf{4b}}{LPt^{II}(CH_2CH_2)OH} + NaBF_4 + H_2O \quad (8)$$

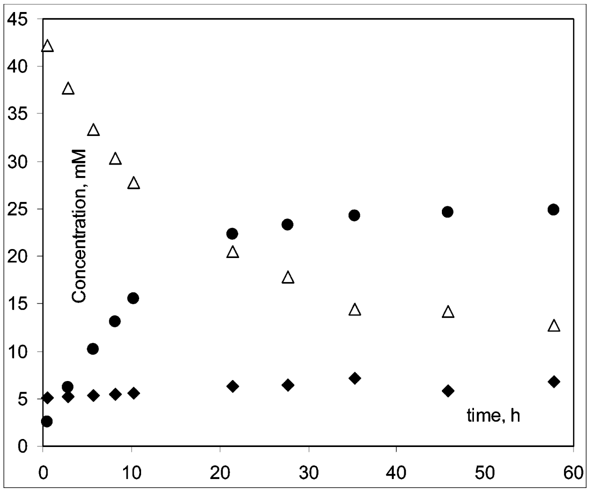

Figure 2. Transformations of a mixture of $LPt^{II}(CH_2CH_2OH)Cl^-$, **5a** (empty triangles), $LPt^{II}(CH_2CH_2)Cl$, **4a** (filled diamonds), and $LPt^{II}(CH_2CH_2)OH$, **4b** (filled circles), prepared from equimolar amounts of **4a** and NaOH in D_2O under an argon atmosphere; $[Pt]_0 = 50$ mM, $[NaOH]_0 = 50$ mM.

On the basis of the established fact of reversibility of addition of OH^- to **4b**, we were able to estimate the equilibrium constant for reaction 7. A potentiometric determination of $[D^+]$[13] combined with ^1H NMR measurements of the [**5b**]/[**4b**] ratio was performed in alkaline D_2O solutions of **4b** at several pD values to give the equilibrium constant K of $(3 \pm 1) \times 10^6$ at 23 °C (see Supporting Information for details).

The 2-hydroxyethyl:ethylene complex ratios observed in the mixtures containing **4** and approximately 1 equiv of sodium hydroxide were slightly different for complexes **4b** and **4a**. More precisely, the 77:23 **5b**/**4b** ratio for the hydroxo ethylene complex **4b** was lower than the 87:6 **5a**/**4a** ratio for the chloro analogue **4a**, suggesting that the chloro ethylene complex **4a** was more electrophilic than the hydroxo complex **4b**.

Relative Electrophilicity of $LPt^{II}(CH_2CH_2)Cl$ and $LPt^{II}(CH_2CH_2)OH$ Complexes. The greater electrophilicity of the chloro complex **4a** as compared to its hydroxo analogue **4b** could be estimated more reliably in an experiment when $LPt^{II}(CH_2CH_2)Cl$ was allowed to react with 1 equiv of aqueous NaOH. Two fast reversible OH^- addition reactions (eqs 3 and 7) and two slow irreversible Cl for OH ligand exchange reactions (eqs 4 and 5) determined the composition of the reaction mixture. Therefore, the **5a**/**5b** ratio measured at any moment of reaction should reflect the relative electrophilicity of the chloro and hydroxo ethylene complexes **4a** and **4b**. The composition of a fresh clear solution prepared from solid $LPt^{II}(CH_2CH_2)Cl$ and NaOH in D_2O was monitored by ^1H NMR spectroscopy. Concentrations of complexes $LPt^{II}(CH_2CH_2)OH$, $LPt^{II}(CH_2CH_2)Cl$, and $LPt^{II}(CH_2CH_2OH)Cl^-$ were calculated from the integral intensity of the coordinated ethylene signals at 4.7 and 5.1 ppm for the first two compounds and from the integral intensity of the signals of the 2-hydroxyethyl ligand at 1.4−2.3 ppm for **5a**, respectively. Complex **5b** was not detected in the course of the whole experiment. The plot of concentrations of complexes **4a**, **4b**, and **5a** versus time is given in Figure 2.

The 2-hydroxyethyl chloro complex **5a** was the major component in the beginning of this experiment along with less than 10% of complexes **4a** and **4b** combined. The concentration of **5a** decreased over time due to reversible elimination of OH^- with concomitant formation of **4a** (eq 3). The reaction was driven by an irreversible Cl/OH ligand exchange in complex **4a** (eq 5), which consumed NaOH released by **5a**. Since no 2-hydroxyethyl platinum(II) complex **5b** was observed by ^1H NMR spectroscopy, the electrophilicity of **4b** was not high enough to compete with **4a** for the nucleophilic hydroxide anion. Trace amounts (<1 mM) of free ethylene (5.43 ppm) due to slow decomposition of complexes **4a** and **5a** were seen in the reaction mixture after 5 h.

Oxidation of $LPt^{II}(CH_2CH_2)OH$ in Aqueous Solution by Molecular Oxygen to Produce *unsym*-$LPt^{IV}(CH_2CH_2OH)(OH)_2$. A yellowish solution of an analytically pure sample of $LPt^{II}(CH_2CH_2)OH$ in water (pH ≈ 8) was stirred under an oxygen atmosphere at room temperature. According to the ^1H NMR, the oxidation was complete in 1 day; no intermediate MePt complexes were detected. A similar reaction under air was approximately 5 times slower. The complex *unsym*-$LPt^{IV}(CH_2CH_2OH)(OH)_2$, *unsym*-**6b**, formed in virtually quantitative yield (Scheme 2-b; eq 9) and could be isolated in high yield in an analytically pure form:

$$\underset{\mathbf{4b}}{2LPt^{II}(\eta^2\text{-}C_2H_4)OH} + 2H_2O + O_2 \rightarrow \underset{unsym\text{-}\mathbf{6b}}{2LPt^{IV}(CH_2CH_2OH)(OH)_2} \quad (9)$$

The observed pseudo-first-order rate constant of the reaction 9 performed under pure O_2 was $(8.2 \pm 0.2) \times 10^{-6}$ s^{-1} at 23 °C in D_2O solution (see Supporting Information for details).

In all cases, the pH of the starting solution was slightly elevated, and it contained a trace amount of the anionic **5b** that could be detected by means of ^1H NMR spectroscopy. Therefore, it was impossible to conclude whether the direct oxidation by oxygen involved the neutral complex **4b** or the anionic complex **5b**.

Attempted Oxidation of $LPt^{II}(CH_2CH_2)OH$ by Oxygen in Acidic Aqueous Solutions. In an attempt to figure out the effect of the formal charge on the platinum(II) atom on the ability of corresponding ethylene complexes to react with O_2, oxidation of **4b** by dioxygen was attempted in an acidic solution. A solution of chloride-free complex **4b** was combined with 1.5 equiv of HBF_4. The resulting cationic complex $LPt^{II}(C_2H_4)OH_2^+$ (eq 10),

$$LPt^{II}(\eta^2\text{-}C_2H_4)OH + HBF_4 \rightarrow [LPt^{II}(CH_2CH_2)(OH_2)]BF_4 \quad (10)$$

exhibited lower field ^1H NMR resonances of the coordinated ethylene ligand, which appeared at 5.0 and 5.3 ppm, as compared to **4b**. The acidic solution was stirred under O_2 at room temperature for several days. Periodically the reaction mixture was transferred with a syringe to an NMR tube and analyzed by ^1H NMR. No oxidation products were detected in the mixture after 4 days. The cationic complex $LPt^{II}(CH_2CH_2)OH_2^+$ slowly released ethylene to give $LPt^{II}(OH_2)_2^+$[6] as the only dpms-containing product seen by ^1H NMR. An estimated half-life of the cationic ethylene complex was ca. 65 h at room temperature.

The results of this experiment suggested that increasing positive charge on the platinum atom prevents platinum(II) from aerobic oxidation. This behavior could be related to the accessibility of the electrons occupying the HOMO of these complexes by the oxidant. Greater positive charge on the metal

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Table 2. Results of Oxidation of 17.6 mM $LPt^{II}(CH_2CH_2)OH$ in Water as a Function of Concentration of Additives of NaOH after 60 min of Reaction at 25 °C and 1 atm O_2

NaOH, equiv ([NaOH], mM)	**5b** before oxidation, %	yield of **6b**, %[a]	**4b** + **5b**, %[a,b]
0 (0)	<4	7 ± 2	93 ± 2
0.06 (1.1)	6	47 ± 2	54 ± 2
0.12 (2.1)	9	72 ± 1	29 ± 2
0.23 (4.0)	19	78 ± 1	21 ± 2
0.35 (6.2)	29	71 ± 1	24 ± 2
0.57 (10.0)	55	56 ± 1	42 ± 1
0.85 (15.0)	82	37 ± 1	58 ± 2
1.4 (25)	100	20 ± 2	80 ± 2

[a] Average of 3 runs. [b] Unreacted $LPt^{II}(CH_2CH_2)(OH)$, **4b**, and $LPt^{II}(CH_2CH_2OH)OH^-$, **5b**, combined.

atom lowered the energy of the HOMO and slowed down or stopped the oxidation completely.

To get a semiquantitative estimate of the effects of ligand X and the formal charge on the platinum atom on the energy of the HOMO in complexes **4** and **5**, we carried out DFT calculations on neutral complexes **4**, anionic complexes **5**, and the cationic complex $LPt(C_2H_4)OH_2^+$ (Table 1).

According to the results obtained, if an oxidation reaction operates by the same mechanism of an electron transfer between the Pt^{II} atom and an oxidant, the reactivity of Pt^{II} complexes toward the oxidant would increase in the series $LPt^{II}(C_2H_4)OH_2^+ < LPt^{II}(C_2H_4)Cl < LPt^{II}(C_2H_4)OH < [LPt^{II}(C_2H_4OH)Cl]^- < [LPt^{II}(C_2H_4OH)OH]^-$.

Oxidation of $LPt^{II}(CH_2CH_2)OH$ by Molecular Oxygen in the Presence of Variable Amounts of NaOH. To find out whether or not complex **6b** resulted from a direct oxidation of the anionic complex **5b** rather than the neutral complex **4b**, we determined an NMR yield of complex **6b** formed in a reaction between mixtures of **4b** + **5b** and dioxygen (1 atm) as a function of concentration of NaOH. The yield was measured after 60 min of stirring a reaction mixture under O_2 (Table 2). As the concentration of NaOH present in a solution increased, the fraction of the anionic Pt(II) complex **5b** grew from 4% to 100% due to the equilibrium shift (eq 7) to the right (Table 2, second column). Yield of **6b** increased more than 10-fold at higher concentrations of NaOH as compared to a NaOH-free solution. The yield passed through a maximum at approximately 0.23 equiv of NaOH (4.0 mM) and then decreased slowly as the amount of NaOH increased to 1.4 equiv (26 mM). The significant acceleration of the reaction at low [NaOH] can be considered as evidence of a direct oxidation of the anionic complex **5b** by O_2. A similar conclusion about higher reactivity of 2-hydroxoethyl trichloroplatinate $Pt^{II}Cl_3(C_2H_4OH)^{2-}$ compared to that of Zeise's anion $Pt^{II}Cl_3(C_2H_4)^-$ in oxidation reactions with $Pt^{IV}Cl_6^{2-}$ was made by Labinger and Bercaw.[14]

A partial inhibition of oxidation reaction 9 at higher concentrations of NaOH could be due to an involvement of a proton transfer at or before the rate-limiting step of the aerobic oxidation of the platinum(II) center. To figure out if the inhibition of the aerobic oxidation (eq 9) by hydroxide anion was specific for complex **5b** or whether it was also possible for other anionic $LPt^{II}(Alk)OH^-$ complexes, we looked at the effect of NaOH additives on the rate of the aerobic oxidation of methyl platinum(II) complex **1** (eq 11):

$$\underset{\mathbf{1}}{2LPt^{II}Me(OH_2)} + O_2 \rightarrow \underset{unsym\text{-}\mathbf{2}}{2LPt^{IV}Me(OH)_2} \qquad (11)$$

In basic solutions complex **1** undergoes a reversible deprotonation to produce anionic $LPt^{II}Me(OH)^-$,[6] **8**, which is an analogue of **5b**. If the anionic complex **8** was more reactive than **1** and the oxidation of the former was inhibited by NaOH, as in the case of **4b**, we should expect the presence of a maximum on the plot of the oxidation product yield versus [NaOH]. The results obtained are given in Table 3. They show undoubtedly the presence of a maximum at 0.10 equiv of NaOH present, [NaOH] = 1.9 mM. An inhibition of the aerobic oxidation is observed at higher concentrations of NaOH.

Two possible mechanistic scenarios of oxidation that account for these facts include the following:

(i) A proton-coupled electron transfer to a Pt(II) coordinated dioxygen ligand (eqs 12 and 13):

$$LPt^{II}(Alk)OH^- + O_2 \rightarrow (\eta^2\text{-}L)Pt^{II}(\eta^1\text{-}O_2)(Alk)OH^- \qquad (12)$$

$$(\eta^2\text{-}L)LPt^{II}(\eta^1\text{-}O_2)(Alk)OH^- + H^+ \rightarrow (\eta^3\text{-}L)LPt^{IV}(O_2H)(Alk)OH \qquad (13)$$

The pendant sulfonate group of the dpms ligand was expected to coordinate to the metal and thus to provide a substantial stabilization to the emerging Pt^{IV} center (eq 13),[6,7] decreasing the redox potential of the $(\eta^2\text{-}L)LPt^{II}/(\eta^3\text{-}L)Pt^{IV}$ couple. A transient peroxo platinum(IV) complex could then react with another Pt(II) species (eq 14):[4]

$$LPt^{IV}(O_2H)(Alk)OH + LPt^{II}(Alk)OH^- + H_2O \rightarrow 2LPt^{IV}(Alk)(OH)_2 + OH^- \qquad (14)$$

(ii) Protonation of the Pt^{II} center leading to a transient Pt^{IV} hydride and subsequent oxidation of the Pt^{IV} hydride (eqs 15 and 16):[15]

$$(\eta^2\text{-}L)LPt^{II}(Alk)OH^- + H^+ \rightarrow (\eta^3\text{-}L)Pt^{IV}H(Alk)OH \qquad (15)$$

$$(\eta^3\text{-}L)Pt^{IV}H(Alk)OH + O_2 \rightarrow (\eta^3\text{-}L)Pt^{IV}(O_2H)(Alk)OH \qquad (16)$$

On the basis of our previous observations,[6] aerobic oxidation of $LPt^{IV}Me_2H$ in neutral aqueous solutions is much slower than that of $LPt^{II}Me(OH_2)$. Hence, we postulate here that the Pt^{IV} hydrides are not viable intermediates of the aerobic oxidation of **6b** (eq 9) and that a proton-coupled electron transfer to the η^1-coordinated dioxygen ligand involving a triplet−singlet spin interconversion might be operative here. Mechanism (i) should be inhibited by electron-withdrawing ligands X in complex **5**, which would decrease the energy of the metal complex HOMO.

DFT Modeling on a Proton-Coupled Electron Transfer from Pt(II) to Coordinated Dioxygen Ligand. The viability of the postulated mechanism of aerobic oxidation of the anionic complex $LPt^{II}Me(OH)^-$ (eqs 12 and 13) can be supported by DFT calculations. To do that, a full geometry optimization and Gibbs energy calculation was carried out for complex **8**, $LPt^{II}Me(OH)^-$, and two proposed reaction intermediates, (η^2-

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[14] Luinstra, G. A.; Wang, L.; Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Organomet. Chem.* **1995**, *504*, 75.

[15] (a) Wick, D. D.; Goldberg, K. I. *J. Am. Chem. Soc.* **1999**, *121*, 11900. (b) Keith, J. M.; Muller, R. P.; Kemp, R. A.; Goldberg, K. I.; Goddard, W. A., III; Oxgaard, J. *Inorg. Chem.* **2006**, *45*, 9631. (c) Denney, M. C.; Smythe, N. A.; Cetto, K. L.; Kemp, R. A.; Goldberg, K. I. *J. Am. Chem. Soc.* **2006**, *128*, 2508.

Table 3. Results of Oxidation of 19.0 mM $LPt^{II}Me(OH_2)$ in Water as a Function of Concentration of Additives of NaOH after 1 h of Reaction at 25 °C and 1 atm O_2

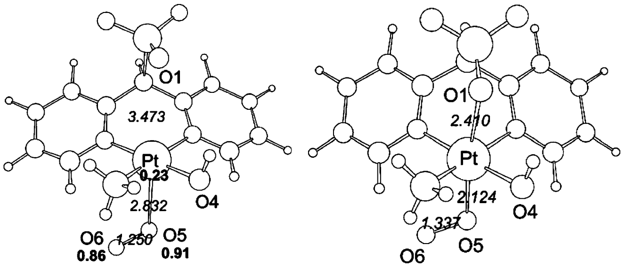
NaOH, equiv ([NaOH], mM)	yield of *unsym*-**2**, %[a]	unreacted **1**, %[a,b]
0 (0)	88 ± 1	6 ± 1
0.10 (1.9)	99 ± 1	0
0.54 (10)	82 ± 1	17 ± 1
1.1 (21)	53 ± 1	45 ± 1
2.2 (42)	22 ± 1	73 ± 1

[a] Average of 3 runs. [b] Another oxidation product, *unsym*-$LPt^{IV}Me_2(OH)$,[7] formed in the amount of 3−5%.

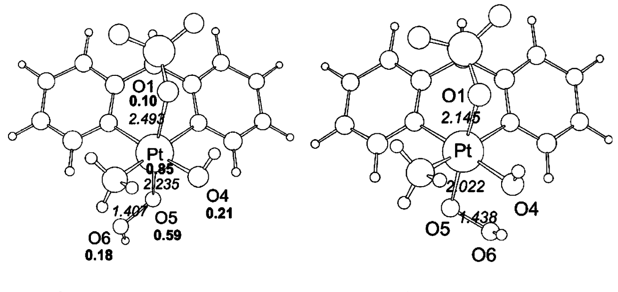
L)$Pt^{II}(\eta^1\text{-}O_2)MeOH^-$, **9**, and ($\eta^3$-L)$LPt^{IV}(O_2H)Me(OH)$, **10**, in both the triplet and the singlet ground-state configurations.

The DFT-calculated Gibbs energy of reaction between **8** and O_2 leading to **^{3}[9]** was found to be 3.5 kcal/mol, suggesting that reaction 12 may be a slightly uphill process only. The optimized structures of **^{3}[9]**, **^{1}[9]**, **^{3}[10]**, and **^{1}[10]** along with spin densities for the triplet species, selected bond lengths, and the relative standard Gibbs energies are given in Figure 3. The spin density on the platinum atom in **^{3}[9]**, 0.23, is not very high, and the Pt−O1 distance is very long, 3.473 Å, meaning that **^{3}[9]** is essentially a Pt^{II} complex. In the singlet species **^{1}[9]** the Pt−O1 distance of 2.410 Å is much shorter and close to one typical for dpms complexes containing a platinum atom in the formal oxidation state +4.[6] Transfer of two electrons from platinum to the antibonding orbital of the coordinated O_2 ligand leads to an expected O5−O6 bond length increase from 1.250 Å in **^{3}[9]** to 1.337 Å in **^{1}[9]**. It is worth noting that the singlet adduct **^{1}[9]** is 19.1 kcal/mol higher in energy that the triplet analogue **^{3}[9]**, thus making a possible spin interconversion too unfavorable. The relative stability of singlet and triplet species changes dramatically when protonation at the atom O6 occurs. The product of protonation of **^{1}[9]**, complex **^{1}[10]**, is 37.1 kcal/mol more stable than **^{3}[10]**, since the protonation site, atom O6, bears greater negative charge, −0.38, in the singlet species **^{1}-[9]** compared to −0.14 on the same atom in **^{3}[9]**. As a result, the energy difference between the singlet and the triplet potential energy surfaces will be rapidly decreasing as we move along the reaction coordinate corresponding to the proton transfer to O6. When the energy difference between two potential energy surfaces becomes sufficiently small, a rapid spin interconversion can occur, leading ultimately to **^{1}[10]**. Therefore, we can expect that higher acidity of the reaction medium will favor a faster electron transfer from the Pt^{II} center to the coordinated oxygen ligand in complexes such as (η^2-L)$LPt^{II}(Alk)OH^-$.

Attempted Oxidation of $LPt^{II}(CH_2CH_2)Cl$ by Molecular Oxygen. According to the data given in Table 1, aerobic oxidation of a neutral chloro complex **4a** should be much slower than that of an anionic hydroxo species **5b** (eq 9) because both the formal positive charge on the metal center in the zwitterionic complex **4a** (see Scheme 2) and the electron-withdrawing chlorine present in it decrease the energy of the complex HOMO. A solution of $LPt^{II}(CH_2CH_2)Cl$ in D_2O was stirred under oxygen for several days at room temperature. A sample of the mixture was periodically transferred with a syringe to an NMR tube and analyzed by ^{1}H NMR. No oxidation products were detected after 4 days; compound **4a** was the only dpms complex present in solution. After 4 days of stirring at room temperature, the reaction mixture was heated under oxygen at 60 °C. According to the ^{1}H NMR, complex **4a** slowly released ethylene with a half-life of 9.5 h. Thus, consistent with the anticipated effect of ligand X on the energy of the HOMO, neutral complex **4a** was less reactive toward dioxygen than **5b**.



a) **^{3}[9]** (0 kcal/mol) b) **^{1}[9]** 19.1 kcal/mol



c) **^{3}[10]** (0 kcal/mol) d) **^{1}[10]** (-37.5 kcal/mol)

Figure 3. DFT-optimized structures of (a) (η^2-L)$Pt^{II}(\eta^1\text{-}O_2)MeOH^-$ in the triplet state, **^{3}[9]**; (b) (η^2-L)$Pt^{II}(\eta^1\text{-}O_2)MeOH^-$ in the singlet state, **^{1}[9]**; (c) (η^3-L)$LPt^{IV}(O_2H)Me(OH)$ in the triplet state, **^{3}[10]**, and (d) (η^3-L)$LPt^{IV}(O_2H)Me(OH)$ in the singlet state, **^{1}[10]**. Selected bond lengths are given in italics, spin densities are in bold, and the relative standard Gibbs energies of species of different multiplicity are given in parentheses.

Oxidation of $LPt^{II}(CH_2CH_2)Cl$ by Molecular Oxygen in the Presence of 1 equiv of NaOH. An aerobic oxidation of $LPt^{II}(CH_2CH_2)Cl$ could be performed in the presence of *1* equiv of NaOH, though at a much slower rate than an aerobic oxidation of its hydroxo analogue **4b**. A fresh solution of $Na[LPt^{II}(CH_2CH_2OH)Cl]$ prepared from **4a** and 1 equiv of NaOH and characterized by the total concentration of platinum of 50 mM was stirred under an atmosphere of oxygen at room temperature for several days. Periodically the reaction mixture was transferred to an NMR tube with a syringe and analyzed by ^{1}H NMR spectroscopy.

The presence of complexes *unsym*-**6b**, **4a**, **4b**, and **5a** in the reaction mixture was confirmed by NMR and ESI-MS. Since the chloro complex **6a** was not observed in the mixture, complex **5a** was inert toward dioxygen. Small amounts of $LPt^{II}(OH)_2^-$ (<5%)[6] resulting from the loss of the ethylene ligand were seen by the end of the reaction.

The plot of concentrations of $LPt^{II}(CH_2CH_2OH)Cl^-$, $LPt^{II}(CH_2CH_2)Cl$, $LPt^{II}(CH_2CH_2)OH$, and *unsym*-$LPt^{IV}(OH)_2(CH_2CH_2OH)$ versus time is given in Figure 4. Complex **5a**, which formed according to eq 3 and persisted as a major species during the first 10−15 min, eventually disappeared with a half-life of 10 h, so that in 3 days *unsym*-**6b** was the only product present in the mixture. In the course of the reaction, complex **4b**, which formed according to eq 5, was detected in concentrations not exceeding 1 mM. The complex eventually disappeared (eq 9) when the oxidation was complete. The concentration of another ethylene complex, **4a**, decreased rapidly in the course of the reaction.

It is interesting to compare the rates of transformations of complex **5a** in two similar experiments, one performed under an argon atmosphere (Figure 2) and another performed under oxygen (Figure 4). In both cases **5a** was prepared from 1 equiv of **4a** and 1 equiv of NaOH and the total initial concentration of Pt was 50 mM.

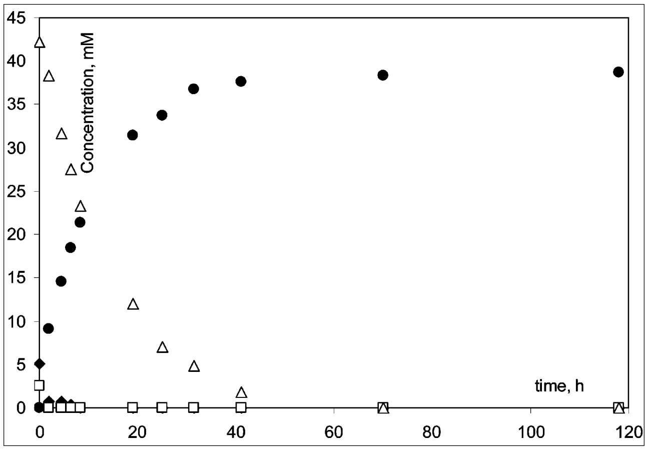
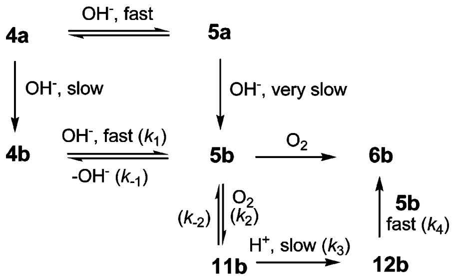


Figure 4. Transformations of $LPt^{II}(CH_2CH_2OH)Cl$ (empty triangles), $LPt^{II}(CH_2CH_2)Cl$ (empty squares), $LPt^{II}(CH_2CH_2)OH$ (filled diamonds), and *unsym*-$LPt^{IV}(OH)_2(CH_2CH_2OH)$ (filled circles) prepared from equimolar amounts of **4a** and NaOH in D_2O under an O_2 atmosphere; $[Pt]_0 = 50$ mM.

Scheme 3



The rate of disappearance of **5a** in the experiment performed under oxygen atmosphere was not significantly different from that in an analogous experiment under argon. The half-life was about 15 h in both cases. Therefore, once again, we can state that **5a** by itself is practically inert toward O_2.

The results of oxidation of **4a** in alkaline solutions are summarized in Scheme 3. Since **4a** forms from **5a** in a fast reversible OH^- elimination reaction (eq 3), involvement of **4a** in a direct aerobic oxidation would lead to faster disappearance of **5a**, which was not observed. Thus, **4a** was inert toward oxygen in basic media, similar to what was observed in its neutral solutions.

Since the aerobic oxidation of **4b** was suggested to occur via anionic complex **5b**, the rate-limiting step of an indirect aerobic oxidation of **5a** might be its irreversible transformation to **4b** via **4a**. A direct transformation of **5a** to **5b** was presumably much slower compared to the **4a** to **4b** transformation due to the anionic nature and decreased electrophilicity of **5a** versus **4a**.

Qualitative Analysis of the Observed pH-Dependence of the Rate of Oxidation of 4b in Alkaline Solutions. On the basis of the observations available we can suggest a qualitative kinetic scheme that accounts for the observed pH-dependence of rate of oxidation of **4b** in alkaline solutions (Table 2). The analysis was based on the following established facts and/or assumptions: (i) formation of **5b** from **4b** and OH^- is reversible (rate constants k_1 and k_{-1}; $K = k_1/k_{-1}$); (ii) oxidation of **5b** proceeds via the triplet η^1-dioxygen adduct **11b**, $[LPt^{II}(\eta^1\text{-}O_2)(C_2H_4OH)OH]^-$ (eq 12), formation of which is reversible (rate constants k_2 and k_{-2}); (iii) a rate-determining protonation of anionic triplet adduct **11b** to form a diamagnetic Pt^{IV} hydroperoxo complex **12b**, $LPt^{IV}(O_2H)(C_2H_4OH)OH$ (eq 13), is irreversible.[4] The protonation is coupled to a spin interconversion in triplet **11b** and oxidation of Pt^{II} to Pt^{IV} (rate constant k_3); (iv) subsequent nucleophilic attack of **5b** at the hydroperoxo ligand of **12b** leading to **6b** is fast (Scheme 3).[4]

Using a steady-state approximation for intermediates **5b**, **11b**, and **12b** and assuming that formation of **11b** from **5b** occurs much slower than addition of OH^- to **4b**, we can get the following rate law (see Supporting Information for details):

$$\frac{dC}{dt} = k_2 \frac{k_3[H^+]}{(k_{-2} + k_3[H^+])} \frac{KK_w}{(KK_w + [H^+])} [O_2]C \qquad (17)$$

Here K_w is the ionization constant for water and C is the combined concentrations of **4b** and **5b**.

Formation of paramagnetic complex **11b** was never documented in our NMR experiments on aerobic oxidation of **5b** even at pH values as high as 13, when the proton-coupled electron transfer (eq 13) might be very slow. If the formation of **11b** was irreversible ($k_{-2} = 0$) and its subsequent transformation of **11b** to **12b** was very slow, noticeable accumulation of paramagnetic **11b** in strongly alkaline reaction mixtures should be reflected in the NMR spectra as line broadening or "disappearance" of a noticeable amount of **4b** + **5b**. Since these changes were not observed, we suggest that reaction 12 was reversible and equilibrium 12 was shifted to the left, $k_2 < k_{-2}$, consistent with results of our DFT calculations for the methyl analogue of **5b**, complex **8**. To account for the observed pH-dependence of the rate of oxidation of **4b** in alkaline solutions, the following formal analysis of eq 17 was performed.

The factor $[H^+]$ in its numerator might cancel out (i) in the case of weak binding of hydroxide by complex **4b** (eq 7), so that $KK_w \ll [H^+]$ (in fact, $KK_w = 3 \times 10^{-9}$, whereas $[D^+] \leq 1 \times 10^{-12}$ for all our experiments performed in alkaline D_2O solutions (Table 2)); (ii) if $k_{-2} \ll k_3[H^+]$, which corresponds to the case of a fast proton-coupled electron transfer in **11b** (eq 13). Therefore, to account for the presence of the maximum, we suggest that transformation of **11b** to **12b** was the rate limiting pH-dependent step, $k_{-2} \geq k_3[H^+]$. Since formation of **5b** from **4b** is also pH-dependent (eq 7), but with a dependence of the opposite character, this results in the appearance of a maximum on the plot of reaction 9 rate versus pH.

Oxidation of $LPt^{II}(CH_2CH_2)Cl$ by H_2O_2 to Produce $LPt^{IV}(OH)(CH_2CH_2OH)Cl$. The use of stronger oxidants such as hydrogen peroxide allowed us to convert complex **4a** to the corresponding 2-hydroxyethyl chloro hydroxo platinum(IV) complex **6a**. The reaction could be carried out at room temperature with 1.5 equiv of H_2O_2 in a dilute aqueous solution (eq 18):

$$LPt^{II}(\eta^2\text{-}C_2H_4)Cl + H_2O_2 \rightarrow \underset{\mathbf{6a}}{LPt^{IV}(OH)(CH_2CH_2OH)Cl} \qquad (18)$$

In 1 day the reaction was complete and the analytically pure product was isolated by filtration as a white solid in 82% yield. The ^1H NMR spectrum of *unsym*-**6a** in water was similar to that of *unsym*-**6b**. The identity of the new compound was also confirmed by ESI-MS in aqueous solution.

Thermal Isomerization and C−O Reductive Elimination from $LPt^{IV}(CH_2CH_2OH)(OH)_2$. As established earlier, the unsymmetrical methyl dihydroxo platinum(IV) complex *unsym*-**2**[6] was many orders of magnitude less reactive in methanol elimination than its symmetrical isomer, *sym*-**2** (Scheme 1). This difference in reactivity was related to the presence of the

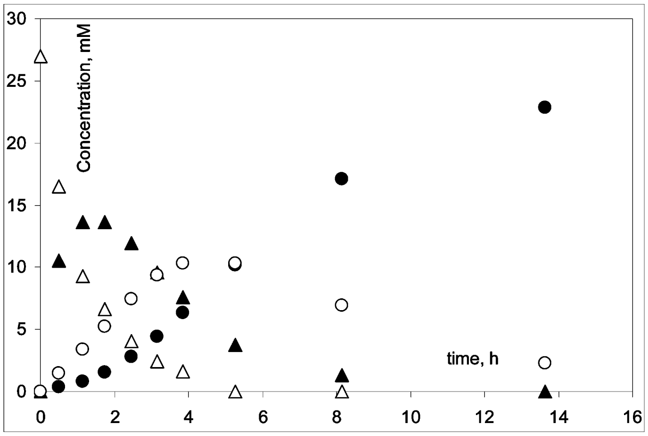


Figure 5. Transformations of *unsym*-$LPt^{IV}(OH)_2(CH_2CH_2OH)$ (empty triangles) to *sym*-$LPt^{IV}(OH)_2(CH_2CH_2OH)$ (filled triangles), ethylene oxide (empty circles), and ethylene glycol (filled circles) in neutral D_2O solution at 80 °C; $[Pt]_0 = 27$ mM.

sulfonate tail, a much better leaving group[16] *trans* to the methyl in *sym*-**2** as compared to *unsym*-**2**, having a pyridine residue *trans* to the methyl. The isomerization of *unsym*-**2** to the reactive *sym*-**2** could be carried out at 80−90 °C in neutral aqueous solutions in high yield. In an attempt to perform similar isomerization of *unsym*-**6b** to *sym*-**6b** a neutral aqueous solution of the former complex was heated at 80 °C. *unsym*-**6b** reacted with a half-life of 1 h to produce, as expected, its symmetrical isomer (eq 19), but the subsequent C−O reductive elimination from *sym*-**6b** leading to ethylene oxide and ethylene glycol occurred at a very fast competitive rate (eq 20; Figure 5):

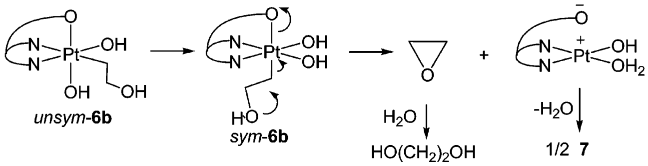
$$\textit{unsym}\text{-}LPt^{IV}(CH_2CH_2OH)(OH)_2 \rightarrow \underset{\textit{sym}\text{-}\mathbf{6b}}{\textit{sym}\text{-}LPt^{IV}(CH_2CH_2OH)(OH)_2} \quad (19)$$

$$2\ \textit{sym}\text{-}LPt^{IV}(C_2H_4OH)(OH)_2 \rightarrow \underset{\mathbf{7}}{L_2Pt^{II}{}_2(\mu\text{-}OH)_2} + C_2H_4O + HOC_2H_4OH + H_2O \quad (20)$$

In 5 h, when all the *unsym*-**6b** reacted, the following water-soluble compounds were found in the reaction mixture: *sym*-**6b** (14% yield on Pt), ethylene glycol (38%), and ethylene oxide (38%). A white, water-insoluble product was identified as the binuclear μ-hydroxo platinum(II) complex **7** described earlier[6] (eq 20; Scheme 2-c). Heating the reaction mixture at 80 °C for an additional 3 h led to a solution containing 11% of *sym*-**6b**, 63% of ethylene glycol, and 26% of ethylene oxide. The changes in the ratio of the two organic products were due to partial hydrolysis of ethylene oxide to produce the glycol. Since ethylene oxide cannot form from ethylene glycol under these conditions, it is evident that ethylene oxide was a primary product of C−O elimination (eq 20). At the same time, it is difficult to say if ethylene glycol was another primary reaction product since it forms readily from ethylene oxide under the reaction conditions. Reductive elimination of ethylene oxide as a result of an intramolecular nucleophilic attack of the HO group of the 2-hydroxyethyl ligand at its α-carbon should be favored entropically over intermolecular reaction between water and *sym*-**6a**, leading to ethylene glycol (Scheme 4).

Complex *sym*-**6b** was characterized in aqueous solution by ^1H NMR spectroscopy. Compared to *unsym*-**6b** it exhibited a distinct set of signals, two sharp triplets of the 2-hydroxyethyl ligand with platinum-195 satellites at 3.16 ppm ($^3J = 5.8$ Hz, $^3J_{195PtH} = 40$ Hz) and 3.51 ppm ($^3J = 5.8$ Hz, $^3J_{195PtH} = 80$ Hz), a signal of the dpms CH-bridge at 6.53 ppm, and a set of four multiplets in the aromatic region typical for a mirror-symmetrical dpms complex.

Scheme 4



The organic products were identified by ^1H NMR and ESI mass spectroscopy in a slightly acidified solution. A peak in the ESI mass spectrum at $(m + H^+)/z = 63.04890$ was assigned to protonated ethylene glycol (calculated for $C_2H_7O_2$, 63.04460), and a peak at $(m + H^+)/z = 45.03391$ was assigned to protonated ethylene oxide (calculated for C_2H_5O, 45.03404). The yields of the organic products were determined by integration of singlets at 3.65 ppm (ethylene glycol) and 2.80 ppm (ethylene oxide).

Interestingly, in contrast to complex *sym*-**2**, no acid catalysis was required for the C−O reductive elimination from *sym*-**6b** (eq 20). The higher reactivity of *sym*-**6b** compared to complex *sym*-**2** may be due to several factors such as higher electrophilicity of the α-carbon atom of the 2-hydroxyethyl group caused by the electron-withdrawing hydroxy group at the β-carbon and the entropic effect mentioned above that helped enhance the effective concentration of the nucleophile near the reactive center and eliminated the entropy penalty associated with bimolecular nucleophilic attack observed for *sym*-**2**.[6] Importantly, analysis of configuration of two dideuterioethylene glycols resulting from 2-hydroxyethylchloroplatinum(IV) intermediates, $Pt^{IV}Cl_5(C_2H_2D_2OH)^{2-}$, derived from *cis*- and *trans*-dideuterioethylenes, proved the viability of the S_N2 mechanism in the C−O elimination reaction.[14]

C−O Reductive Elimination and Attempted C−Cl Reductive Elimination from $LPt^{IV}(OH)(CH_2CH_2OH)Cl$ in Neutral Solution. To compare the relative reactivity of the chloro complex *unsym*-**6a** in C−O and C−Cl reductive elimination, an aqueous solution of *unsym*-**6a** was heated at 80 °C. The reaction was complete in 10 h to give a mixture of ethylene glycol (yield 94%) and ethylene oxide (4%) in almost quantitative yield, according to ^1H NMR. The major Pt-containing product was an unsymmetrical complex (>80%), identified as $LPt^{II}Cl(OH_2)$ by ESI-MS (eq 21):

$$2LPt^{IV}(OH)(C_2H_4OH)Cl \rightarrow 2LPt^{II}Cl(OH_2) + C_2H_4O + HOC_2H_4OH + H_2O \quad (21)$$

No signs of isomerization of **6a** were found in the ^1H NMR spectra of the reaction mixture. Presumably, the isomer with 2-hydroxyethyl *trans* to the sulfonate group was too reactive to be observed at a noticeable concentration in the reaction mixture. No 2-chloroethanol was observed either, suggesting that C−Cl elimination did not occur whereas the C−O elimination did. The result is consistent with the fact that the intramolecular $C(sp^3)$-Cl elimination at a Pt^{IV} center was never reported.[14]

Summary and Conclusions

In summary, aerobic oxidation of ethylene hydroxo platinum(II) complex **4b** supported by the di(2-pyridyl)methanesulfonate

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(16) Smith, M. B.; March, J. *March's Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*, 5th ed.; Wiley: New York, 2001.

ligand is facile in aqueous solution and leads to unsymmetrical 2-hydroxyethyl dihydroxo platinum(IV) complex *unsym*-**6b**. On the basis of the ability of the olefin complex **4b** to add hydroxide anion to produce anionic 2-hydroxyethyl hydroxo platinum(II) species **5b** and the observed effect of an alkali metal hydroxide on the reaction rate, the oxidation of **4b** occurs via intermediate **5b**. The chloro analogues, neutral **4a** and anionic **5a**, both characterized by lower energy of their HOMO, are inert toward oxygen in neutral aqueous solutions. Still, they can be converted to *unsym*-**6b** by O_2 in water in the presence of 1 equiv of NaOH. The C−O reductive elimination from *unsym*-**6b** is clean and fast in neutral aqueous solutions at 80 °C and leads to the formation of ethylene oxide, ethylene glycol, and a platinum(II) complex, presumably via the symmetrical isomer *sym*-**6b**. Thus, one-pot aerobic oxidation of platinum(II)-coordinated ethylene to ethylene oxide and ethylene glycol can be readily and efficiently performed in aqueous media. Attempts at developing a catalytic version of a facile ethylene to ethylene glycol aerobic oxidation in aqueous media are currently underway in our laboratory.

Experimental Section

General Comments. All manipulations were carried out under purified argon using standard Schlenk and glovebox techniques. All reagents for which synthesis is not given are commercially available from Aldrich, Acros, or Pressure Chemical and were used as received without further purification. Methyl aqua di(2-pyridyl)methanesulfonato platinum(II) complex **1** was synthesized according to a published procedure.[6]

^{1}H (400.132 MHz) and ^{13}C NMR (100.625 MHz) spectra were recorded on a Bruker Avance 400 spectrometer. Chemical shifts are reported in ppm and referenced to residual solvent resonance peaks; these peaks were used as an internal standard for NMR integration. Carbon-13 chemical shifts in D_2O solutions are referenced to an external dioxane standard. Elemental analyses were carried out by Chemisar Laboratories Inc., Guelph, Canada. ESI-MS experiments were performed using the high-resolution JEOL AccuTOF-CS instrument.

Computational Details. Theoretical calculations in this work have been performed using the density functional theory (DFT) method,[17] specifically the functional PBE,[18] implemented in the original program package "Priroda".[19,20] In PBE calculations relativistic Stevens−Basch−Krauss (SBK) effective core potentials (ECP)[21] optimized for DFT calculations were used. The basis set was 311-split for main group elements with one additional polarization p-function for hydrogen and an additional two polarization d-functions for elements of higher periods. Full geometry optimization has been performed without constraints on symmetry. For all species under investigation frequency analysis has been carried out. All minima have been checked for the absence of imaginary frequencies.

$LPt^{II}(CH_2CH_2)Cl$, 4a. A solution of K(L) (93.1 mg, 323 μmol) in 1 mL of H_2O was added to the stirred solution of Zeise's salt $KPtCl_3(CH_2CH_2)\cdot H_2O$ (124.8 mg, 323 μmol) in 1 mL of H_2O. A white precipitate formed in several minutes, and the yellow color of Zeise's salt disappeared. The mixture was stirred for 3 h, filtered, 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 ethylene.

^{1}H NMR (D_2O, 22 °C) δ: 4.89 (m, 2H), 5.05 (m, $^2J_{195PtH} = 55$ Hz, 2H) 6.32 (s, 1H), 7.57 (ddd, $J = 7.9$, 5.9, 1.4 Hz, 1H), 7.70 (ddd, $J = 7.7$, 5.9, 1.4 Hz, 1H), 7.92−8.03 (m, 2H), 8.17 (td, $J = 7.7$, 1.4 Hz, 1H), 8.22 (td, $J = 7.9$, 1.4 Hz, 1H), 8.54 (m, 1H), 9.04 (dd, $J = 5.9$, 1.4 Hz, 1H). The coupling constant $^2J_{195PtH}$ for a multiplet at 4.89 ppm was not determined due to overlap with the HDO signal.

X-ray quality crystals of **4a** were obtained by slow crystallization from a mixture prepared by addition of 0.1 M aqueous K(dpms) to an equal volume of 0.1 M aqueous solution of Zeise's salt placed in an NMR tube.

Anal. Found (Calcd for $C_{13}H_{13}ClN_2O_3PtS$): H, 2.38 (2.58); C, 30.49 (30.75); N, 5.41 (5.52). ESI-MS, solution of **4a** in water: $m/z = 508.012$; calculated for **4a**$\cdot H^+$, $C_{13}H_{14}{}^{35}ClN_2O_3{}^{195}PtS$, 508.006.

$LPt^{II}(CH_2CH_2)(OH)$, 4b. Solid $LPt(CH_2CH_2)Cl$ (45.3 mg, 89.2 μmol), Ag_2O (13.7 mg, 59.1 μmol), and 2.6 mL of deaerated H_2O were placed into a 5 mL Schlenk tube, and the mixture was stirred in the dark for 1 day at room temperature under an argon atmosphere. According to ^{1}H NMR, the reaction was complete in 1 day. The yield was quantitative by NMR. The mixture was centrifuged for 30 min at 10 000 rpm, and the solution was carefully separated from the precipitate of AgCl and excess Ag_2O. The resulting pale yellow solution was evaporated to dryness under vacuum to give a yellow, crystalline solid. Yield: 33.3 mg (76%). The air-sensitive complex was perfectly soluble in water and moderately soluble in methanol. It slowly decomposed in aqueous solution at room temperature, but was stable at 7−8 °C for several days under an argon atmosphere. In strongly alkaline solutions (pH > 10) formation of a black precipitate occurred.

^{1}H NMR (D_2O, 22 °C) δ: 4.69 (m, 2H, $^2J_{195PtH} = 54$ Hz), 5.01 (m, $^2J_{195PtH} = 60$ Hz, 2H), 6.30 (s, 1H), 7.55 (ddd, $J = 7.8$, 5.8, 1.1 Hz, 1H), 7.82 (ddd, $J = 7.8$, 5.8, 1.1 Hz, 1H), 7.96 (vd, $J = 7.8$ Hz, 1H), 8.06 (vd, $J = 7.8$ Hz, 1H), 8.15 (vt, $J = 7.8$ Hz, 1H), 8.29 (vt, $J = 7.8$ Hz, 1H), 8.44 (vd, $J = 5.8$ Hz, 1H), 8.75 (vd, $J = 5.8$ Hz, 1H). ^{13}C NMR (D_2O, 22 °C) δ: 74.8, 78.6 (br s, $^1J_{PtC} = 180$ Hz), 126.0, 127.2, 128.9, 130.1, 141.2, 142.6, 148.3, 149.5, 149.6, 150.9. ESI-MS, solution of **4b** in water: $m/z = 490.04173$; calculated for **4b**$\cdot H^+$, $C_{13}H_{15}N_2O_4{}^{195}PtS$, 490.040134. Anal. Found (Calcd for $C_{13}H_{14}O_4N_2PtS$): H, 2.62 (2.88); C, 31.94 (31.90); N, 5.40 (5.72); S, 6.71 (6.55).

$Na[LPt^{II}(CH_2CH_2OH)Cl]$, 5a. A sample of $LPt(CH_2CH_2)Cl$ (27.3 mg, 54 μmol) and 1 mL of 0.2 M NaOH solution in deaerated D_2O were placed into a vial equipped with a magnetic stirring bar. The suspension was stirred under an argon atmosphere to produce a clear, colorless solution in less than 10 min ([Pt] = 0.0538 M, [NaOH] = 0.2 M). The reaction mixture was transferred into an NMR Young tube under an argon atmosphere, and its ^{1}H NMR spectrum was recorded in 10 min after preparation; the ^{13}C NMR spectrum was recorded 1−3 h after preparation. According to NMR, in 10 min after preparation the solution contained 96% of **5a** and 4% of **5b**. The relative amounts of **5a** and **5b** were calculated by integration of multiplets of C(5)-H protons of **5a** and **5b** at 7.41 and 7.51 ppm, respectively. Slow Cl/OH exchange occurred so that in 2.3 h the reaction mixture contained **5a** and **5b** in an 87:13 ratio (half-life 16.4 h). The exchange was complete after 8 days to give complex **5b** as the only species detected by NMR. However, slight decomposition to form platinum black was observed.

^{1}H NMR (D_2O, 22 °C) δ: 1.69 (m, $^2J_{PtH} = 41$ Hz, 1H), 1.98 (m, $^2J_{PtH} = 38$ Hz, 1H), 3.46 (m, 2H), 5.89 (s, 1H), 7.36 (ddd, $J = 7.7$, 5.8, 1.5 Hz, 1H), 7.41 (ddd, $J = 7.7$, 5.5, 1.5 Hz, 1H), 7.66−7.74 (m, 2H), 7.94 (td, $J = 7.7$, 1.5 Hz, 1H), 8.02 (td, $J = 7.8$, 1.5 Hz, 1H), 8.75 (vd, $J = 5.8$ Hz, 1H), 8.86 (vd, $J = 5.5$ Hz, 1H). ^{13}C

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NMR (D_2O, 22 °C) δ: 7.95 ($^1J_{PtC} = 728$ Hz), 65.8, 76.8, 126.2, 127.2, 129.0, 130.4, 139.6, 139.8, 149.4, 151.4, 152.4, 153.6. ESI-MS (negative mode) of **5a**, immediately after preparation (pH ≈ 10): *m/z* 524.1; calculated for $LPt(CH_2CH_2OH)Cl^-$, $C_{13}H_{14}{}^{35}ClSO_4N_2{}^{195}Pt$, 524.0.

Na[LPt^{II}(CH$_2$CH$_2$OH)OH], 5b. Procedure A, from 4b. An 8.8 mg (18 μmol) amount of $LPt(CH_2CH_2)OH$ (**4b**) was dissolved in 1.0 mL of a NaOH solution (25.2 mM) in deaerated D_2O under an argon atmosphere. The resulting yellowish solution was transferred into a NMR Young tube under argon. According to ^1H NMR, compound **5b** was obtained in quantitative yield in less than 10 min. Complex **5b** is air-sensitive and produces **6b** in the presence of oxygen.

Procedure B, from 4a. A sample of $LPt(CH_2CH_2)Cl$ (27.3 mg, 54 μmol) and 1 mL of 0.2 M NaOH solution in deaerated D_2O were placed into a vial equipped with a magnetic stirring bar. The suspension was stirred under argon to produce a clear, yellowish solution in less than 10 min ([Pt] = 0.0538 M, [NaOH] = 0.2 M). The reaction mixture was transferred into an NMR Young tube. The Cl/OH ligand exchange was monitored by ^1H NMR at room temperature (half-life 16.4 h). The ligand exchange was complete in 8 days to give complex **5b** in virtually quantitative yield. Trace amounts of a black precipitate were also observed.

^1H NMR (D_2O, 22 °C) δ: 1.76 (m, $^2J_{PtH} = 37$ Hz, 1H), 1.87 (m, $^2J_{PtH} = 37$ Hz, 1H), 3.42 (m, 1H), 3.55 (m, 1H), 7.28 (ddd, $J = 7.8$, 5.5, 1.3 Hz, 1H), 7.51 (ddd, $J = 7.8$, 5.5, 1.3 Hz, 1H), 7.64 (vd, $J = 7.7$ Hz, 1H), 7.76 (vd, $J = 7.7$ Hz, 1H), 7.98 (td, $J = 7.8$, 1.5 Hz, 1H), 8.02 (td, $J = 7.8$, 1.5 Hz, 1H), 8.71 (vd, $J = 5.5$ Hz, 1H), 8.81 (vd, $J = 5.5$ Hz, 1H) ($CHSO_3$ bridge peak was not seen due to complete H/D exchange in basic solution). ^{13}C NMR (D_2O, 22 °C) δ: 9.1, 64.8, 125.5, 126.3, 128.3, 129.5, 137.9, 139.0, 148.9, 151.8, 153.3 ($CDSO_3$ peak was not seen because of carbon−deuterium coupling and low intensity of resulting lines). ESI-MS (negative mode) of **5b** (pH ≈ 10−11): *m/z* 506.2; calculated for $LPt(CH_2CH_2OH)OH^-$, $C_{13}H_{15}SO_5N_2{}^{195}Pt$, 506.0.

***unsym*-LPt^{IV}(OH)(CH$_2$CH$_2$OH)Cl, *unsym*-6a.** $LPt^{II}(CH_2CH_2)Cl$ (**4a**) (103.1 mg, 203 μmol) and 10 mL of water were placed into a 50 mL round-bottom flask equipped with a stirring bar. To the stirred suspension was added 34.4 mg of 30% H_2O_2 (∼303 μmol). The mixture became cloudy and a white precipitate slowly formed. After 1 day the white solid was filtered off, washed with water (2 × 1 mL), and dried under vacuum. The yield was 90.7 mg (82%).

^1H NMR (D_2O, 22 °C) δ: 3.21−3.84 (m, 4H), 6.73 (s, 1H), 7.84−7.92 (m, 2H), 8.06 (vd, $J = 7.7$ Hz, 1H), 8.08 (vd, $J = 7.8$ Hz, 1H), 8.27 (td, $J = 7.8$, 1.5 Hz, 1H), 8.34 (td, $J = 7.8$, 1.2 Hz, 1H), 8.71 (vd, $J = 6.0$ Hz, 1H), 8.99 (vd, $J = 5.4$ Hz, 1H). Limited solubility of $LPt^{IV}Cl(OH)(CH_2CH_2OH)$ in water (<2 mg/mL) and methanol prevented obtaining a good-quality ^{13}C NMR spectrum. ESI-MS of **6a** in water: *m/z* 542.029; calculated for $LPt^{IV}(OH)(CH_2CH_2OH)Cl{\cdot}H^+$, $C_{13}H_{16}{}^{35}ClO_5N_2{}^{195}PtS$, 542.012. Anal. Found (Calcd for $C_{13}H_{15}ClO_5N_2PtS$): H, 2.49 (2.79); C, 28.41 (28.82); N, 5.07 (5.17); S, 5.68 (5.92); Cl, 6.58 (6.54).

***unsym*-LPt^{IV}(CH$_2$CH$_2$OH)(OH)$_2$, *unsym*-6b. Procedure A, from 4b.** A sample of $LPt(CH_2CH_2)OH$ (106 mg, 216 μmol) was dissolved in 50 mL of distilled water. The solution was placed into a 250 mL round-bottom flask and stirred vigorously under an O_2 atmosphere at room temperature. According to ^1H NMR, the oxidation was complete in 1 day. No signals of potential MePt intermediates could be observed in reaction mixtures by NMR. The reaction mixture was filtered from a white precipitate of $L_2Pt^{II}{}_2(\mu\text{-}OH)_2$ that resulted from partial loss of ethylene. The precipitate was washed with 3 mL of H_2O, and the combined filtrate was evaporated to dryness under vacuum at room temperature to give a pale yellow solid. The yield was 82.2 mg (72%).

If air was used instead of pure O_2 atmosphere, the oxidation was complete in several days. Yield: quantitative by NMR. ^1H NMR (D_2O, 22 °C) δ: 3.00−3.66 (m, 4H), 6.69 (s, 1H), 7.81 (ddd, $J = 7.7$, 5.9, 1.5 Hz, 1H), 7.89 (ddd, $J = 7.9$, 5.5, 1.3 Hz, 1H), 8.06 (dd, $J = 8.0$, 1.3 Hz, 1H), 8.09 (vd, $J = 7.8$ Hz, 1H), 8.24−8.31 (m, 2H), 8.63 (vd, $J = 5.9$, 1H), 8.86 (vd, $J = 5.5$, 1H). ^{13}C NMR (D_2O, 22 °C) δ: 25.2 ($^1J_{PtC} = 543$ Hz), 61.8, 72.1, 127.9, 128.4, 128.6, 129.7, 143.1, 144.1, 148.1, 148.5, 150.7, 151.5. ESI-MS of *unsym*-**6b** in water: *m/z* 524.04528; calculated for **6b**·H$^+$, $C_{13}H_{17}O_6N_2{}^{195}PtS$, 524.04516. Anal. Found (Calcd for for $C_{13}H_{16}O_6N_2PtS$): H, 3.25 (3.08); C, 29.55 (29.83); N, 5.15 (5.35); S, 5.73 (6.13).

Procedure B, from 4a. To a suspension of **4a** (400 mg, 788 μmol) in 10 mL of H_2O was added 1 equiv of NaOH (31.8 mg, 790 μmol). After a few minutes **4a** dissolved completely. The solution was placed into a 250 mL round-bottom flask and stirred vigorously under an O_2 atmosphere. Periodically a 0.3−0.4 mL sample of the reaction mixture was placed into an NMR tube, diluted with 0.3−0.4 mL of D_2O, and analyzed by ^1H NMR. Traces of ethylene were detected in solution in the course of the reaction (singlet at 5.43 ppm) along with small amounts of $LPt^{II}(OH)_2^-$ [6] resulting from the loss of ethylene, characterized by a multiplet at 7.47 ppm (ddd, $J = 7.8$, 5.9, 1.6 Hz). According to the ^1H NMR, the complex *unsym*-**6b** was obtained after 4 days in 80−90% yield and contained admixtures of $LPt(OH)_2^-$ and $LPt^{II}(\mu\text{-}OH)_2$.[6] The reaction mixture was carefully neutralized with dilute H_2SO_4 to pH 7 to precipitate anionic $LPt^{II}(OH)_2^-$ in the form of insoluble $L_2Pt^{II}{}_2(\mu\text{-}OH)_2$, then filtered and washed with small amounts of water. The resulting solution was evaporated and dried under vacuum for 5−6 h (0.3 Torr). The solid was separated from inorganic salts by extraction with anhydrous 2,2,2-trifluoroethanol (3 mL). After evaporation of 2,2,2-trifluoroethanol a yellow solid was obtained, pure by NMR and elemental analysis. Yield: 144.4 mg (35%). Anal. Found (Calcd for $C_{13}H_{16}O_6N_2PtS$): H, 3.20 (3.08); C, 29.54 (29.83); N, 4.96 (5.35); S, 5.85 (6.13).

Attempted Oxidation of LPt^{II}(CH$_2$CH$_2$)Cl by Dioxygen. A solution of $LPt^{II}(CH_2CH_2)Cl$ (**4a**) (2 mg, 4 μmol) in 0.7 mL of D_2O was placed into a vial equipped with a magnetic stirring bar, filled with O_2, and securely capped. Stirring continued for several days at room temperature; the reaction vessel was refilled with O_2 every 12 h. Periodically liquid samples were transferred into an NMR tube with a syringe and analyzed by ^1H NMR. No oxidation products were detected by ^1H NMR after stirring under O_2 for 4 days, and the starting compound **4a** was the only species present in solution. After 4 days of stirring at room temperature, the reaction mixture was placed into an NMR tube, filled with O_2, and heated at 60 °C. According to the ^1H NMR, the starting complex **4a** slowly released ethylene (a singlet at 5.43 ppm) with a half-life of 9.5 h.

Attempted Oxidation of LPt^{II}(CH$_2$CH$_2$)OH (4b) by O$_2$ in an Acidic Aqueous Solution. HBF_4 (50% aqueous; 14.8 mg, 84 μmol) was added to a solution of $LPt^{II}(CH_2CH_2)OH$ (**4b**) (25.8 mg, 53 μmol) in 0.8 mL of D_2O. The ^1H NMR signals of the coordinated ethylene were significantly downfield shifted compared to pure **4b** in water due to the protonation of the hydroxo ligand and formation of $LPt^{II}(CH_2CH_2)OH_2^+$ (**4b**·H$^+$). The solution was placed into a 5 mL vial and stirred under O_2 at rt. The vial was refilled with O_2 every 12 h. Periodically, a sample of the reaction mixture was transferred into an NMR tube with a syringe and analyzed by ^1H NMR. No oxidation products were detected in the reaction mixture after 97 h. The cationic complex $LPt^{II}(CH_2CH_2)OH_2^+$ slowly released ethylene (a singlet at 5.43 ppm) to give $LPt^{II}(OH_2)_2^+$ [6] as the only product detected by ^1H NMR; the half-life of $LPt^{II}(CH_2CH_2)OH_2^+$ in the above solution was 65 h.

^1H NMR (D_2O, 22 °C) of acidified **4b**, δ: 4.99 (m, 2H), 5.25 (m, 2H), 6.39 (s, 1H), 7.56 (ddd, $J = 7.7$, 5.8, 1.5 Hz, 1H), 7.81 (ddd, $J = 7.7$, 5.9, 1.3 Hz, 1H), 7.98 (dd, $J = 7.7$, 1.3 Hz, 1H), 8.09 (vd, $J = 7.7$ Hz, 1H), 8.17 (td, $J = 7.7$, 1.3 Hz, 1H), 8.30 (td, $J = 7.7$, 1.5 Hz, 1H), 8.46 (m, 1H), 8.71 (m, 1H).

Reversibility of the Nucleophilic Attack of OH^- at the Coordinated Ethylene in Complexes 4. $LPt^{II}(CH_2CH_2)OH$. A sample of 0.100 M NaOH in D_2O (102.4 mg, 10.2 μmol) was added to a stirred solution of $LPt^{II}(CH_2CH_2)OH$ (**4b**) (10.2 μmol) in deaerated D_2O (2.31 mL) under an argon atmosphere. According to the ^1H NMR, in 10 min after preparation the reaction mixture contained **5b** and **4b** in a 77:23 molar ratio. The ratio did not change in the course of several hours at rt. The reaction mixture was placed into a vial equipped with a magnetic stirring bar, and 88 mg of 10.2% HBF_4 solution in D_2O (10.3 μmol) was added to the stirred solution under an argon atmosphere. The resulting solution was slightly acidic (pH $\approx$ 3). According to the ^1H NMR, **4b** was the only species present in solution.

$LPt^{II}(CH_2CH_2)Cl$. A sample of $LPt^{II}(CH_2CH_2)Cl$ (**4a**) (5.2 mg, 10.2 μmol) was dissolved in deaerated D_2O (2.6 mL, 2.86 g). According to the ^1H NMR, complex **4a** was the only species present in solution. NaOH solution (0.100 M, 104.0 mg, 10.4 μmol) was added to the stirred mixture under an argon atmosphere. Ten minutes after preparation the mixture contained $LPt^{II}(CH_2CH_2)Cl$, $LPt^{II}(CH_2CH_2OH)Cl^-$, and $LPt^{II}(CH_2CH_2)OH$ in a 6:87:7 ratio. One hour after preparation the ratio was 6:84:10.

The mixture was placed into a vial equipped with a magnetic stirring bar, and 91.0 mg of a 10.2% HBF_4 solution in D_2O was added to the stirred solution. The resulting solution was slightly acidic (pH $\approx$ 3). According to the ^1H NMR, the reaction mixture contained **4a** and **4b** in a 85:15 molar ratio. This ratio remained unchanged after 1 day.

Effect of the NaOH Additives on the Rate of Oxidation of $LPt^{II}(CH_2CH_2)OH$ (4b) by O_2. A stock solution of **4b** was prepared from $LPt^{II}(CH_2CH_2)OH$ (288 μmol) and 18.05 g (16.33 mL) of deaerated D_2O under an argon atmosphere; [**4b**] =17.7 mM. The solution was placed into a 50 mL Schlenk tube and stored under argon for less than 2 days in a refrigerator at 7 °C.

To prepare alkaline solutions of **4a** containing 1−25 mM NaOH, a sample of standardized 0.100 M NaOH (25−595 mg) was slowly evaporated to dryness under vacuum. The residue was dissolved in 2.4 mL of the 17.7 mM stock solution of **4b**. An ^1H NMR spectrum was recorded before oxidation and then in regular intervals.

Each reaction mixture was divided into three parts, 0.8 mL each, which were placed into 10 mL screw-cap vials equipped with a magnetic stirring bar. The vials were filled with O_2 and securely capped. Each sample was vigorously stirred under an O_2 atmosphere at room temperature. After 1 h of stirring under O_2 samples were placed into NMR tubes, and ^1H NMR spectra were recorded immediately. Yields were calculated as an average of three runs. Results are given in Table 2.

When a strongly basified solution of **4b** in D_2O (pD $\approx$ 13) was used in an oxidation experiment and oxidation was significantly slowed down, no noticeable decrease of intensity of signals of **5b** after vigorous stirring under O_2 was observed, suggesting that paramagnetic complex **11b** did not form in an amount exceeding 1%.

Effect of NaOH Additives on the Rate of Oxidation of $LPt^{II}Me(OH_2)$ (1) by O_2. A sample of $LPt^{II}Me(OH_2)$ (99.8 mg, 209 μmol)[6] was dissolved in 12.14 g (10.99 mL) of deaerated D_2O under an argon atmosphere; [**1**] = 19.0 mM. The stock solution was placed into 50 mL Schlenk tube and stored under argon in a refrigerator. For preparation of alkaline reaction mixtures, a sample of standardized 0.1000 M NaOH (200−800 mg) was slowly evaporated to dryness under vacuum and dissolved in 2.1 mL of the 19.0 mM $LPt^{II}Me(OH_2)$ stock solution. ^1H NMR spectra were recorded before reaction with O_2 and then in regular intervals.

Three samples (0.7 mL each) of the reaction mixture were placed into 10 mL screw-cap vials equipped with magnetic stirring bars. The vials were filled with O_2 and securely capped. Each solution was stirred under an O_2 atmosphere at room temperature. After 1 h, samples were placed into NMR tubes, and ^1H NMR spectra were recorded immediately. Yields of *unsym*-$LPt^{IV}Me(OH)_2$[6] and *unsym*-$LPt^{IV}Me_2(OH)$[6] were calculated as an average of three runs by integrating the central line of the PtMe peak at 2.4 and 1.7 ppm, respectively (Table 3).

Transformations of $LPt^{II}(CH_2CH_2)Cl$ (4a) in the Presence of 1 equiv of NaOH under an Argon Atmosphere and in the Presence of O_2. A. Preparation of a Stock Solution Containing 1 equiv of NaOH. A sample of $LPt^{II}(CH_2CH_2)Cl$ (**4a**) (76.4 mg, 150.4 μmol) was placed into a 10 mL vial equipped with a magnetic stirring bar and dissolved in 3.02 mL (3.3221 g) of a 49.8 mM NaOD/D_2O solution upon stirring for 30 min. This solution with [Pt] = 49.8 mM and [NaOD] = 49.8 mM was used for monitoring both the reaction under an argon atmosphere and oxidation with O_2.

B. Cl/OH Exchange under an Argon Atmosphere. A 1.03 mL amount of the stock solution above was placed into a NMR Young tube under argon. A ^1H NMR spectrum was recorded 30 min after preparation of the mixture. This solution was stored under argon at room temperature and periodically analyzed by NMR.

Concentrations of complexes $LPt^{II}(CH_2CH_2)OH$ and $LPt^{II}(CH_2CH_2)Cl$ were calculated from the integral intensity of the H−C(3) proton of the dpms ligand (7.96 ppm, vd) and from the multiplet of coordinated ethylene at 5.05 ppm, respectively. The concentration of $LPt^{II}(CH_2CH_2OH)Cl^-$ was calculated from the integral intensity of the CH_2 signals at 1.4−2.2 ppm using the residual HDO peak as an internal standard. Trace amounts (<1 mM) of free ethylene (5.43 ppm) were detected by ^1H NMR in the reaction mixture in 5 h. The results are given in Figure 2.

C. Reaction under Oxygen. A 1.99 mL amount of the stock solution above was placed into a 30 mL screw-cap vial equipped with magnetic stirring bar. The vial was filled with O_2 and securely capped. The reaction mixture was vigorously stirred at room temperature. Periodically, stirring was halted and a sample of the solution was transferred into an NMR tube and analyzed by ^1H NMR. After recording a spectrum, the solution was returned into the vial, which was refilled with O_2 and stirring was resumed.

A small amount of white precipitate of $L_2Pt^{II}_2(\mu\text{-}OH)_2$ formed by the end of the reaction. The results are given in Figure 4.

C−O Reductive Elimination from *unsym*-6b. An NMR Young tube was charged with a solution of *unsym*-**6b** (11.3 mg, 21.6 μmol) in 0.8 mL of D_2O; [Pt] = 27.0 mM. A ^1H NMR spectrum was recorded before heating. The reaction mixture was heated in a Teflon-sealed NMR Young tube in a heating bath at 80 °C. Periodically the Young tube was removed from the heating bath, cooled to room temperature, carefully shaken to combine liquid condensed on the walls of the tube, and analyzed by NMR. Organic products were identified by ESI-MS and by comparison with ^1H NMR spectra of authentic samples. Ethylene oxide was unstable in neutral, basic, and acidic aqueous solutions and hydrolyzed to give ethylene glycol. Due to a relatively long relaxation time (T_1), the integral intensity of the ethylene oxide peak could be underestimated when the relaxation delay time was too short. For quantitative measurement of ethylene oxide concentration by NMR a delay time of 50 s should be used or correction coefficients must be applied for shorter delay times. The same procedure was used in all experiments.

In the course of the reaction thermal isomerization of *unsym*-**6b** occurred to give the symmetrical isomer *sym*-**6b**, which was unstable under reaction conditions. *unsym*-$LPt^{IV}(CH_2CH_2OH)(OH)_2$ had a half-life of 58 min at 80 °C. The results are given in Figure 5. The reaction was complete after 13.6 h at 80 °C. NMR yields of ethylene glycol and ethylene oxide on **6b** were 85% and 8%, respectively. In the course of the reaction a white precipitate of complex $L_2Pt^{II}_2(\mu\text{-}OH)_2$ formed.

***sym*-$LPt^{IV}(CH_2CH_2OH)(OH)_2$ (*sym*-6b).** ^1H NMR (D_2O, 22 °C) δ: 3.16 (t, J = 5.8 Hz, $^3J_{195PtH}$ = 40 Hz, 2H), 3.51 (t, J = 5.8 Hz,

${}^{2}J_{195\mathrm{PtH}} = 80$ Hz, 2H), 6.53 (s, 1H), 7.87 (ddd, $J = 7.7$, 5.8, 1.3 Hz, 2H), 8.09 (dd, $J = 7.9$, 1.3 Hz, 2H), 8.34 (td, $J = 7.8$, 1.1 Hz, 2H), 8.75 (dd, $J = 5.8$, 1.1 Hz, ${}^{3}J_{195\mathrm{PtH}} = 26.3$ Hz, 2H).

Ethylene Glycol. ^{1}H NMR (D_2O, 22 °C) δ: 3.65 ppm. ESI-MS, solution acidified with HBF_4 and diluted 10-fold with H_2O: $(m + H^+)/z = 63.04890$; calculated for $C_2H_7O_2$, 63.04460.

Ethylene Oxide. ^{1}H NMR (D_2O, 22 °C) δ: 2.80 ppm. ESI-MS in an acidified solution after 10-fold dilution with H_2O: $(m + H^+)/z = 45.03391$; calculated for C_2H_5O, 45.03404.

C−O Reductive Elimination from 6a. A sample of LPt^{IV}(OH)(CH_2CH_2OH)Cl (**6a**) (3.2 mg, 6 μmol) was dissolved in 3.00 mL of D_2O; [Pt] = 2 mM. Then 0.8 mL of the resulting solution was placed into an NMR Young tube and heated at 80 °C. The reaction was complete in 10 h to give a mixture of ethylene glycol and ethylene oxide in quantitative yield according to the ^{1}H NMR and using the HDO peak as an internal standard: ethylene glycol 94%, ethylene oxide 4%. No 2-chloroethanol was detected. According to the ^{1}H NMR and ESI-MS, the major Pt-containing product was the unsymmetrical complex LPt^{II}Cl(OH_2) (NMR yield >80%).

LPt^{II}Cl(OH_2), ^{1}H NMR (D_2O, 22 °C) δ: 7.41 (m, 1H), 7.56 (m, 1H), 7.80 (vd, $J = 7.8$ Hz, 1H), 7.89 (vd, $J = 7.8$ Hz, 1H), 8.06 (vt, $J = 7.8$ Hz, 1H), 8.14 (vt, $J = 7.8$ Hz, 1H), 8.69 (m, 1H), 8.98 (m, 1H). The dpms CH bridge proton was not seen due to H/D exchange. ESI-MS of the acidified reaction mixture prepared under the same conditions in H_2O showed the presence of a peak belonging to LPt^{II}Cl(OH_2)·H^+, m/z 498.001; calculated for LPtCl(OH_2)·H^+, $C_{11}H_{12}O_4{}^{35}ClS^{195}Pt$, 497.985.

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Supporting Information Available: Potentiometric determination of the basicity constant of **4b** in water, equilibrium constant *K* for reaction 7, determination of the rate constant of oxidation of **4b**, computational details, and CIF file for **4a** are available free of charge at http://pubs.acs.org.

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