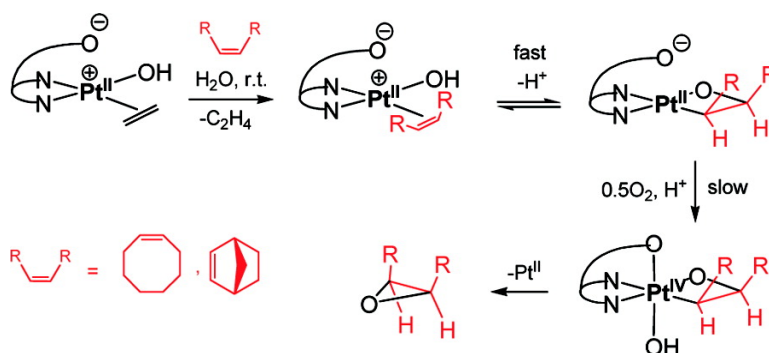


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Direct C(sp³)–O Reductive Elimination of Olefin Oxides from Pt^{IV}-Oxetanes Prepared by Aerobic Oxidation of Pt^{II} Olefin Derivatives (Olefin = *cis*-Cyclooctene, Norbornene)

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The use of platinum metal complexes in higher oxidation states for the selective oxidation of organic compounds resulting in the formation of new C(sp³)–O bonds currently attracts great attention.¹ Understanding reaction mechanisms behind this chemistry therefore constitutes an important goal. A number of model studies of C(sp³)–O reductive elimination from Pt^{IV} alkyls were reported.² In all these cases, the C–O reductive elimination from Pt^{IV} was suggested to occur via an S_N2 nucleophilic substitution at the Pt^{IV}–bound alkyl carbon.^{2a,b} Notably, C(sp³)–O reductive elimination from another d⁶ metal center, Pd^{IV}, was suggested to involve stereochemically distinct S_N2 or direct C–O elimination mechanisms, according to recent reports by Stahl^{1c} and Sanford^{1d} groups, respectively. Mechanistic observations not consistent with an S_N2 mechanism of C(sp³)–I elimination from d⁶ Rh^{III} complexes were recently presented by the Milstein group.³ The question remains whether Pt^{IV} complexes are also able to react via a direct C(sp³)–heteroatom elimination mechanism.

We report here the first, to the best of our knowledge, example of a *direct* C(sp³)–O elimination of olefin oxides from a Pt^{IV} center, a mechanism previously undocumented for this metal. The dpms⁴–Pt^{IV} complexes involved in this chemistry are Pt^{IV} oxetanes derived from *cis*-cyclooctene, **5a** and norbornene, **5b** that were prepared from corresponding Pt^{II} hydroxo olefin complex **2a** or a Pt^{II} oxetane **3b**, via aerobic oxidation of anionic Pt^{II} oxetane intermediates **4a,b** (Scheme 1).

Complex **2a** was synthesized in an analytically pure form, from the ethylene precursor **1**⁵ and cyclooctene in water in 91% isolated yield (eq *a*). An aerobic oxidation of **2a** in H₂O was clean in the presence of 0.25 equiv of NaOH (eq *b–d*). The single product of reaction, **5a**, was isolated in analytically pure form in an 86% yield. An unstable anionic intermediate *cis*-**4a**, a product of an exceedingly rare inner-sphere olefin oxoplatination,⁶ was detected and characterized by ESI-MS and NMR spectroscopy.

Consistent with the results of ¹H, ¹³C NMR, NOE, and ESI-MS characterization, single-crystal X-ray diffraction analysis of **5a** confirmed the presence of a Pt^{IV}-oxetane fragment (Figure 1a). The bond angles within the oxetane ring in **5a** reveal its strained character. Formation of Pt^{II} oxetane precursors **3** from olefin complexes **2** might be additionally enthalpy-driven if a more strained cycloolefin is used. To test this statement and the suggested mechanism of formation of **5** (eq *b–d*), we attempted to prepare the norbornene derivative **2b**. Ligand exchange between **1** and norbornene led to a 6:4 mixture of two isomeric products characterized by elemental analysis and NMR spectroscopy as *cis*- and *trans*-*exo*-Pt^{II}-oxetanes **3b** (82% isolated yield, eq *b*).^{6a} An anionic norbornene-derived Pt^{II} oxetane **4b** could be produced quantitatively (NMR) as a 5.7:1 mixture of *cis* and *trans* isomers upon combination of **3b** with 1.2 equiv of NaOH (eq *c*). The high stability of **4b** in aqueous solutions allowed for its detailed characterization by means of ESI-MS, ¹H, ¹³C NMR spectroscopy. Importantly, **3b** could be

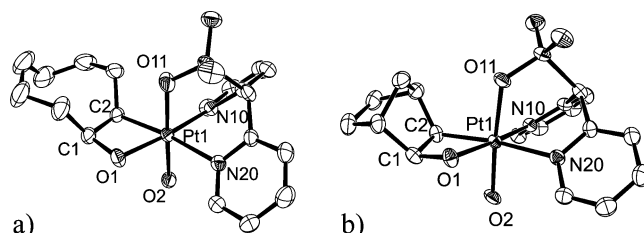
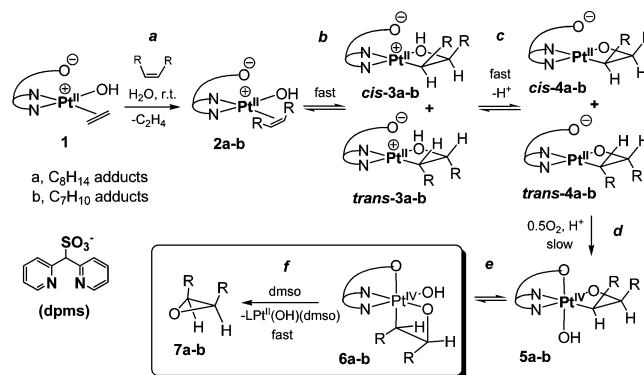


Figure 1. ORTEP plots (50% probability ellipsoids) for complexes **5a** (a) and **5b** (b). Hydrogen atoms are omitted for clarity. Selected bond angles (deg): (a) Pt1–C2–C1, 90.9(2), C2–C1–O1, 101.1(3); (b) Pt1–C2–C1, 91.6(2), C2–C1–O1, 100.6(2).

Scheme 1



cleanly oxidized with O₂ in neutral or alkaline TFE–H₂O solutions to produce a Pt^{IV} oxetane **5b** (eq *d*, Figure 1b) that was isolated in 85% yield.

Both Pt^{IV} oxetanes **5a,b** eliminate epoxides **7a,b** as the only organic products, whose identity was confirmed by NMR spectroscopy and GC–MS, in DMSO solution at 60–80 °C under argon atmosphere and form a Pt^{II} complex (dpms)Pt^{II}(OH)(dmsO), **8** (eq *e*, *f*). A C(sp³)–O elimination of epoxides from transition metal oxetane complexes was suggested as a possible reaction step in certain olefin oxidative transformations.⁷ Still, there is only one report of epoxide elimination from an isolated homogeneous transition metal complex, a Au^{III} norbornene-derived oxetane.^{7d} At the same time, formation of a complex mixture of products besides the epoxide was observed in those experiments.^{7d}

The epoxide elimination from **5a** (*t*_{1/2} = 132 min, Δ*G*[‡] = 25.7 kcal/mol at 60 °C) was quantitative (NMR). The reaction is first order in Pt^{IV} with activation parameters, Δ*H*[‡] = 23.7 ± 0.3 kcal/mol and Δ*S*[‡] = –6.2 ± 0.9 cal/(K·mol). First-order kinetic behavior and clean formation of **7a** were also observed in MeOH (*t*_{1/2} = 388 min, 60 °C), water (*t*_{1/2} = 81 min, 60 °C) and CD₂Cl₂ (*t*_{1/2} = 526 min, 40 °C). In the latter two cases, an insoluble complex identified as (dpms)₂Pt₂(μ-OH)₂⁸ was produced along with **7a**. Interestingly, epoxide elimination occurred even when solid **5a** was heated at 85 °C (*t*_{1/2} = 6 h).

Similar to the cyclooctene derivative **5a**, **5b** eliminated *exo*-norbornene oxide **7b** in DMSO quantitatively (eq *f*). The reaction

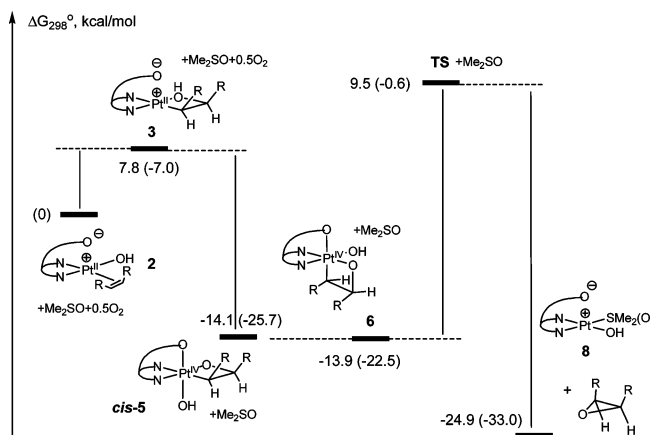
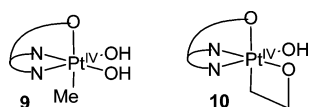


Figure 2. DFT-calculated Gibbs energy reaction profile for aerobic transformation of complexes **2a** and **2b** (numbers in parentheses) to corresponding olefin oxides. Transition states for isomerization of **5a,b** to **6a,b** were not located.

Scheme 2



occurred at a faster rate ($t_{1/2} = 18$ min at 60 °C) than for **5a**, $\Delta H^\ddagger = 22.1 \pm 0.7$ kcal/mol and $\Delta S^\ddagger = -6.9 \pm 2.1$ cal/(K·mol). Still, the similarity of activation parameters observed in both cases suggests that these reactions might have a similar rate-determining step involving isomerization of **5a,b** to **6a,b**.⁸ Complexes **6** possess a better leaving group trans to alkyl, the sulfonate. They are therefore expected to be more prone to C–O elimination.

In support of the C–O elimination mechanism given by eq *e*, *f*, we were able to detect the proposed intermediate **6a** by NMR in CD_2Cl_2 solutions at 40 °C. The highest measured concentration of **6a** did not exceed 13% of the initial concentration of **5a** and was observed at about 50% conversion of **5a**; the intermediate disappeared by the end of reaction.⁹ The structure of **6a** was deduced from the results of ^1H NMR, COSY, and NOE experiments.^{9,10} Our attempts to observe intermediates **6a,b** in reactions of **5a,b** in solvents more polar than CD_2Cl_2 were not successful because of the presumed lower kinetic stability of **6a,b** in these solvents. Modeling of the kinetic data obtained in CD_2Cl_2 is consistent with reversible isomerization of **5a** to **6a** (eq *e*; $\Delta G^\ddagger = 25.1$ kcal/mol) followed by faster epoxide elimination from **6a** (eq *f*; $\Delta G^\ddagger = 24.3$ kcal/mol); complex **5a** being 0.2 kcal/mol more stable than **6a**.

Results of our density functional theory (DFT) calculations (Figure 2) support experimental observations. Transformation of the olefin complex **2a** to the Pt^{II} -oxetane **3a** is thermodynamically uphill, whereas the oxidation of **3a** with O_2 to form **5a** is favored by 14.1 kcal/mol. In turn, the norbornene-derived Pt^{II} oxetane **3b** is significantly more stable than corresponding isomeric hydroxo olefin complex **2b** owing to a noticeable bicycloolefin strain relief achieved in the oxetane form. Reaction path calculations show that C–O elimination from **6a** is a concerted reaction with a Gibbs activation energy of 23.4 kcal/mol. Taking into account the polar character of the transition state that has a significantly elongated Pt–O(S) bond, 2.899 Å, the activation barrier might diminish in polar solvents. In fact, this may explain our failure to detect intermediate **6a** in polar DMSO, water, or MeOH, assuming that the rate of isomerization of **5a** to **6a** is less sensitive to the nature of solvent. The DFT calculated Gibbs activation energy for the C–O elimination of **6b**, 21.9 kcal/mol, is slightly lower than that for cyclooctene analogue **6a**. Consistent with this estimate, no trace of **6b** could be detected by NMR even in the least polar CD_2Cl_2

where the C–O reductive elimination step is expected to be the slowest compared to other solvents used in this work.

Analyzing the origin of the ability of **6a** to react via a direct C–O elimination mechanism, it is worthwhile to compare this complex with nonmetallacyclic analogue $(\text{dpms})\text{Pt}^{\text{IV}}\text{Me}(\text{OH})_2$,⁸ **9** (Scheme 2). Previously complex **9** was shown to react with H_2^{18}O solvent via an $\text{S}_{\text{N}}2$ mechanism to form Me^{18}OH .¹¹ Accordingly, no C–O elimination reaction was observed for complex **9** in DMSO after 2 days at 80 °C. Notably, a very high activation barrier of 37.2 kcal/mol was calculated for direct elimination of MeOH from **9**. Similarly, a high activation barrier of 31.6 kcal/mol was calculated for the parent ethene derived $(\text{dpms})\text{Pt}^{\text{IV}}$ oxetane, $(\text{dpms})\text{Pt}^{\text{IV}}(\text{OH})(\text{OC}_2\text{H}_4)$, **10** suggesting that both the oxetane ring strain and the presence of a Pt–secondary alkyl bond may be responsible for the higher reactivity of **6a,b** compared to **9**.

Altogether, our experimental observations and computational study suggest that the C–O reductive elimination from oxetanes **5a,b** proceeds via a mechanism which is different from $\text{S}_{\text{N}}2$ processes observed for alkyl Pt^{IV} complexes earlier.^{2,5,6,11}

With the mechanistic results in hand, we attempted catalytic oxidation of norbornene with O_2 using **8** as a catalyst. Yet, the preliminary observations using 2,2,2-trifluoroethanol as solvent showed catalyst decomposition and noncatalytic yields of **7b**.⁹

In summary, the isolated and fully characterized **5a,b** are the first reported Pt^{IV} oxetanes that can be prepared by aerobic oxidation of corresponding Pt^{II} olefin precursors and produce olefin oxides via direct $\text{C}(\text{sp}^3)\text{--O}$ reductive elimination from a Pt^{IV} center. Hence, direct $\text{C}(\text{sp}^3)\text{--O}$ reductive elimination may be a more common type of reactivity of d^6 metal complexes than it was previously assumed. Work on catalytic applications of the reactions reported is underway.

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Supporting Information Available: Experimental details, kinetic data, their modeling, and CIF files for **5a** and **5b**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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