Insertion of Dioxygen into a Platinum−Hydride Bond to Form a Novel Dialkylhydroperoxo Pt(IV) Complex

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The selective catalytic oxidation of alkanes using inexpensive and environmentally friendly oxidants is of immense interest to the chemical community and of great potential benefit to the world economy and ecology. Since the earliest reports that the oxidative addition of alkane C−H bonds to transition metal species can occur with high selectivities, substantial research effort has focused on the functionalization of the metal alkyl hydride products.[1] For the development of a commercially viable oxidation process, the use of a clean and cheap oxidant such as air (oxygen) is desirable.[2] Some of the most promising homogeneously catalyzed alkane oxidation reactions reported have been based on platinum.[1c,d,3] Unfortunately, these systems are hampered by the use of expensive and less favorable oxidants. Some Pt(II) complexes, recently including ones with alkyl ligands, have been observed to undergo reaction with dioxygen to form Pt(IV) complexes.[4] Such reactivity of Pt(II) may find utility in platinum-catalyzed alkane oxidation reactions. In this contribution, we report that a *Pt(IV)* dialkyl hydride complex reacts cleanly with dioxygen to produce a dialkyl Pt(IV) hydroperoxide species. Of potential relevance to the development of alkane oxidation systems is that the Pt(IV) dialkyl hydride reactant is analogous to compounds formed by intermolecular oxidative addition of alkane C−H bonds to Pt(II).[5] The novel Pt(IV) product has been crystallographically characterized and displays an η^1-hydroperoxide linkage. Such examples of structurally characterized η^1-hydroperoxides are rare,[6] despite their proposed involvement in a variety of metal-mediated biological oxidations.[7]

Scheme 1

The Pt(IV) complex $Tp^{Me_2}PtMe_2H$ (**1**, Tp^{Me_2} = hydridotris(3,5-dimethylpyrazolyl)borate)[8] formally inserts dioxygen into the Pt−H bond to produce the hydroperoxo Pt(IV) species, Tp^{Me_2}-$PtMe_2(OOH)$ (**2**) (Scheme 1). When a solution of **1** in C_6D_6 was exposed to dioxygen (∼1 atm) at ambient temperature, complex **2** was generated in quantitative spectroscopic yield.[9] The ^1H NMR spectrum of **2** shows singlets with ^{195}Pt satellites at δ 6.01 ($^3J_{Pt−H}$ = 12 Hz) and δ 2.16 ($^2J_{Pt−H}$ = 72 Hz) which are assigned to the hydroperoxo proton and the platinum-bound methyl protons, respectively. The IR spectrum of **2** in CH_2Cl_2 solution (30 mM) exhibits a sharp $\nu_{OO−H}$ absorbance at 3533 cm^{-1}. Absorption bands for the Tp^{Me_2} ligand obscure that expected for $\nu_{O−O}$ (800−900 cm^{-1}).[10] Octahedral geometry with κ^3-coordination of the Tp^{Me_2} at Pt(IV) is supported by the $\nu_{B−H}$ absorbance at 2556 cm^{-1} and a ^{11}B NMR chemical shift of 9.37 ppm.[11] The spectroscopic data are consistent with those for previously reported hydroperoxo transition metal complexes.[6d,12] That the source of the hydroperoxo proton was the hydride ligand of **1** was confirmed by ^1H NMR monitoring of the reaction of $Tp^{Me_2}PtMe_2D$ (**1**-d_1) with dioxygen; $Tp^{Me_2}PtMe_2(OOD)$ (**2**-d_1) was produced with 86% of the label residing in the hydroperoxo proton site.

The molecular structure of **2** has also been determined by single-crystal X-ray diffraction.[13] The ORTEP of **2**·CH_2Cl_2 (inset in Scheme 1)[14] displays a rare example of an η^1-hydroperoxo

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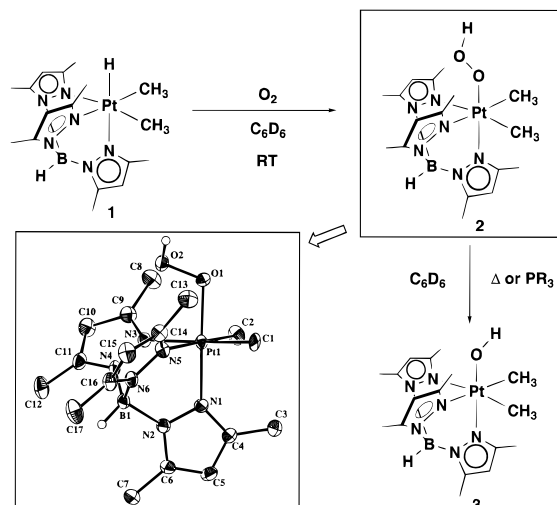
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(9) $Tp^{Me_2}PtMe_2(OOH)$ (**2**): ^1H NMR (C_6D_6) δ 1.99 (s, 3 H, $Tp^{Me_2}CH_3$), 2.06 (bs, 9 H, $Tp^{Me_2}CH_3$), 2.16 (s, $^2J_{Pt−H}$ = 71.8 Hz, 6 H, PtCH$_3$), 2.66 (s, 6 H, $Tp^{Me_2}CH_3$), 5.34 (s, $^4J_{Pt−H}$ = 12.1 Hz, 1 H, Tp^{Me_2}-CH), 5.54 (s, 2 H, Tp^{Me_2}-CH), 6.01 (s, $^3J_{Pt−H}$ = 11.7 Hz, 1 H, PtOOH); $^{11}B\{^1H\}$ NMR (C_6D_6) δ 9.37 (bs, $Tp^{Me_2}B$); IR (CH_2Cl_2, cm^{-1}) 3533 (O−H), 2556 (B−H) Anal. Calcd (Found) for $C_{17}H_{29}BN_6O_2Pt$: C, 36.77 (36.97); H, 5.26 (5.33); N, 15.13 (15.16). **2** is formed by the reaction of **1** with O_2 or more efficiently on a preparative scale by reaction of **1** and H_2O_2. This latter reaction is similar to a reported reaction of a Pt(II)−H with H_2O_2 to generate a Pt(II)−OOH complex.[12b] See Supporting Information for experimental details and further characterization of **2**.

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ligand characterized by X-ray crystallography.[6] The Pt−O−O bond angle is 110.1(3)°. The unit cell contains two molecules of **2** whose −OOH moieties form a six-membered centrosymmetric ring via hydrogen bonding.[15] The intermolecular close contact distance between dissimilar oxygen atoms (O2−O1′) is 2.698(5) Å, and the hydrogen bond distance (H2−O1′) is 1.85 Å. The smaller *trans* influence of the hydroperoxo ligand of **2** compared to that of the hydride ligand of **1** is indicated by the Pt−N bond length for the unique pyrazolyl ring (2.037(4) Å for **2** vs 2.169-(6) Å for **1**).[8] This is also reflected in the ^{195}Pt−H coupling constant of the methine proton of the coordinated pyrazolyl ring *trans* to −OOH ($^4J_{Pt-H} = 12$ Hz) or −H ($^4J_{Pt-H} \approx 6$ Hz).

Insertions of dioxygen into transition metal hydrides to form hydroperoxo complexes have been noted for a small number of organometallic and coordination compounds of Co(III), Rh(III), Ir(III), and Pt(II).[16] Mechanisms of metal deprotonation followed by oxygen binding and protonation,[16d,f] and radical chain pathways involving hydrogen radical abstraction from the metal hydride,[16e,g] have both been suggested. Our results as detailed below are more consistent with the latter.

The reaction of **1** in C_6D_6 with O_2 under ambient conditions of light and temperature for 2 days produced **2** in 98% yield (100% conversion of **1**).[17] A reaction carried out in the dark over the same 2-day period proceeded to only 14% conversion (100% yield of **2**). In a separate experiment, irradiation for 1 h with high-intensity ultraviolet light ($\lambda > 345$ nm) led to 75% conversion of **1** (90% yield of **2**).[18,19] In contrast, as a control experiment, when a degassed solution of **1** (no O_2) was irradiated for 1 h, no reaction was detected. That light promoted the reaction of dioxygen with **1** is strongly suggestive of a radical pathway.

The proposal of a radical mechanism is also supported by experiments in which the reaction of **1** with dioxygen was carried out in the presence of a radical initiator (AIBN = 2,2′-azobis-(2-methylpropionitrile)) and a radical inhibitor (1,4-cyclohexa-diene). In side-by-side experiments, a thermal (50 °C) dark reaction with added initiator (17 mol %) proceeded over a period of 1 h to 31% conversion of **1** (100% yield of **2**) as compared to 4% conversion of **1** (100% yield of **2**) without AIBN. With added inhibitor (40 mol %), the reaction of **1** and O_2 under ambient light and temperature conditions gave 46% conversion with a 94% yield of **2** after 2 days.[17] This is in contrast to the near-quantitative conversion under the same conditions but without added 1,4-cyclohexadiene as described above. These results are consistent with those expected for a reaction occurring by a radical chain

mechanism. A radical mechanism analogous to that established for the autoxidation of alkanes can be proposed.[20] After an initiator abstracts a hydrogen atom from the starting Pt(IV)−H complex, a Pt(III) radical chain carrier would be generated. The Pt(III) radical reacts with O_2 to form a superoxo Pt(IV) species which can abstract a hydrogen atom from the starting Pt(IV)−H, and thus the chain is propagated. Additional mechanistic experiments are in progress.

The hydroperoxo complex **2** is stable at ambient temperature but reacts upon extended thermolysis in solution at 79 °C. Thermolysis of **2** in C_6D_6 led predominantly to formation of the hydroxo species, Tp^{Me_2}PtMe$_2$(OH) (**3**).[21] After 1 week at 79 °C, the reaction had proceeded to 46% conversion with a 93% yield of **3**.[22] The ^1H NMR spectrum of **3** in C_6D_6 shows singlets with ^{195}Pt satellites at δ −1.30 ($^2J_{Pt-H} = 20$ Hz) and δ 2.01 ($^2J_{Pt-H} = 71$ Hz) which are assigned to the hydroxo and platinum-bound methyl protons, respectively. In the IR spectrum of **3** in CH_2Cl_2 solution (30 mM), a sharp band is observed for ν_{O-H} at 3604 cm^{-1}. Similar transformations of metal hydroperoxide complexes to their corresponding hydroxide complexes and O_2 have been reported for cobalt(III) and dicopper(II).[23] This reactivity is also comparable to the decomposition of the organic analogue, *tert*-butyl hydroperoxide, which proceeds via a radical pathway to *tert*-butyl alcohol and O_2.[24]

A more facile conversion of **2** to **3** can be achieved by the reaction of **2** with PMe$_3$ or PPh$_3$, traditional oxygen-atom-acceptor reagents. These reactions, which were carried out in C_6D_6 at ambient temperature, resulted in quantitative spectroscopic yield of **3** and phosphine oxide within 2 days. Complex **3** can also be prepared directly from **1** by reaction with N$_2$O; however, this reaction proceeded with lower conversion.[25]

In summary, a novel O_2 insertion into a Pt(IV)−hydride bond has been observed to form a stable Pt(IV) hydroperoxide compound. This result is especially significant because the reactant is a Pt(IV) alkyl hydride complex directly analogous to those which are produced via oxidative addition of alkane C−H bonds. With the exception of a fluorinated alkyl hydride species,[16g] this is the first report of a transition metal alkyl hydride reacting with oxygen to cleanly generate a hydroperoxide product. This unusual reactivity of a high-valent metal alkyl hydride species with oxygen is promising for the development of commercially viable homogeneous catalytic alkane oxidation. We are continuing our studies of this unique reactivity in this and related systems.

(13) Single crystals of **2** as **2**·CH$_2$Cl$_2$ were grown from a methylene chloride solution layered with pentane at −33 °C. **2**·CH$_2$Cl$_2$ (C$_{17}$H$_{29}$BN$_6$O$_2$Pt·CH$_2$-Cl$_2$): MW = 640.29, pale green-yellow plate, monoclinic, space group = $P2_1/n$, $a = 13.9334(3)$ Å, $b = 10.0051(2)$ Å, $c = 18.0348(3)$ Å, $\beta = 102.4380$ (10)°, $V = 2455.13(8)$ Å^3, $Z = 4$, $R1 = 0.0454$ [$I > 4\sigma(I)$], GOF = 1.064. Selected bond distances (Å) for O1−O2, Pt1−O1, Pt1−C1, Pt1−C2, Pt1−N1, Pt1−N3, Pt1−N5: 1.481(5), 1.980(4), 2.070(5), 2.039(6), 2.037(4), 2.162-(4), 2.170(4), respectively. Selected bond angle (deg) for Pt1−O1−O2, 110.1(3).

(14) Thermal ellipsoids are shown at the 50% probability level. Hydrogens bound to carbon and the CH$_2$Cl$_2$ molecule are not shown.

(15) A diagram of this hydrogen-bonding arrangement is provided in the Supporting Information.

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(17) Yield of **2**, expressed as a percentage, is equal to the molar amount of **2** divided by the molar quantity of **1** consumed. The remaining percentage is comprised of Tp^{Me_2}PtMe$_2$OH (**3**).

(18) Light from an Oriel 200-W Hg/Xe (no. 6291) arc lamp was passed through a 345-nm long-pass quartz filter.

(19) Remaining 10% is comprised of Tp^{Me_2}PtMe$_2$OH (**3**) and an unidentified Pt(IV) species with two methyl ligands and having a 2:1 pattern of pyrazolyl resonances.

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(21) Tp^{Me_2}PtMe$_2$(OH) (**3**): ^1H NMR (C$_6$D$_6$) δ −1.30 (s, $^2J_{Pt-H} = 19.8$ Hz, 1 H, PtOH), 2.01 (s, $^2J_{Pt-H} = 70.8$ Hz, 6 H, PtCH$_3$), 2.02, 2.08 (each, s, 3 H, Tp^{Me_2}CH$_3$), 2.09, 2.61 (each, s, 6 H, Tp^{Me_2}CH$_3$), 5.38 (s, $^4J_{Pt-H} = 12.4$ Hz, 1 H, Tp^{Me_2}CH), 5.51 (s, 2 H, Tp^{Me_2}CH); IR (CH$_2$Cl$_2$, cm^{-1}) 3604 (O−H), 2557 (B−H); high-resolution EI-MS, M$^+$, calcd (found) 539.21438 (539.21413).

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