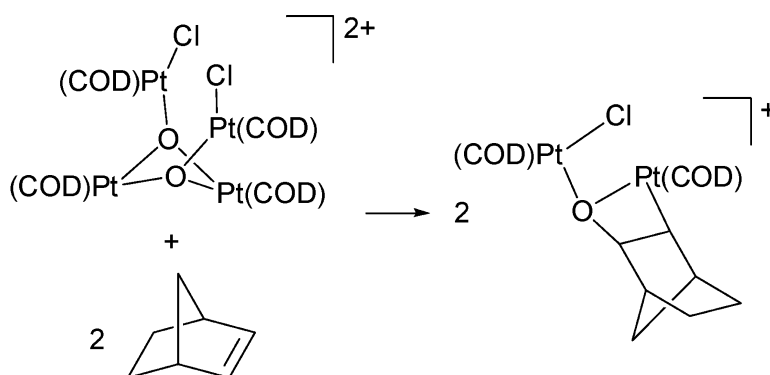


## Alkene Oxidation by a Platinum Oxo Complex and Isolation of a Platinaoxetane

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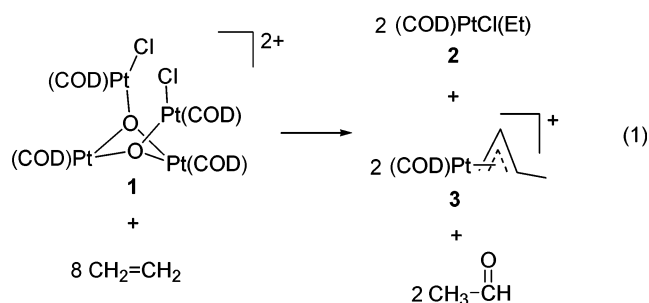
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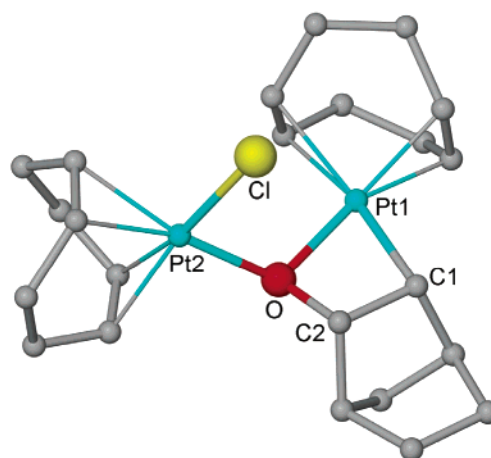
We wish to report the oxidation of ethylene by an isolated platinum oxo complex and the formation of a platinaoxetane from the reaction of this same oxo complex with norbornylene. Oxo complexes and their metal surface analogues, oxygen adatoms, have been implicated in a number of alkene oxidation reactions mediated by second and third series late transition metals.<sup>1–6</sup> These and other reactions are believed to occur through metallaoxetane intermediates.<sup>4,5,7,8</sup> Previous to the work reported here, only one late transition metal oxo complex has been reported to oxidize alkenes<sup>2</sup> and, to the best of our knowledge, a transition metal (early or late) metallaoxetane has not been isolated from the reaction of a transition metal oxo complex with an alkene.<sup>9</sup>

Several years ago, we described the synthesis of oxo complex [(1,5-COD)<sub>4</sub>Pt<sub>4</sub>(μ<sup>3</sup>-O)<sub>2</sub>Cl<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (**1**) from (1,5-COD)PtCl<sub>2</sub> and [(LAu)<sub>3</sub>(μ<sup>3</sup>-O)]BF<sub>4</sub>.<sup>10</sup> Pressurization of a colorless dichloromethane solution of **1** with ethylene results in a slow reaction (hours) ultimately leading to a pale yellow mixture of products. Acetaldehyde is readily identified by NMR spectroscopy as one of the products. The other products are less obvious but through <sup>13</sup>C labeling of the ethylene are identified as the ethyl complex (1,5-COD)Pt(Cl)(CH<sub>2</sub>CH<sub>3</sub>) (**2**)<sup>11</sup> and the allyl complex [(1,5-COD)-Pt<sub>4</sub>(η<sup>3</sup>-CH<sub>2</sub>CHCH(CH<sub>3</sub>))](BF<sub>4</sub>) (**3**)<sup>12</sup> (eq 1). The labeling also indicates that the ethylene is the source of the ethyl group in **2**, the allyl group in **3**, and the acetaldehyde. Yields, based on eq 1, are between 90 and 100% for **2** and **3** and 30–40% for acetaldehyde. Oxygen-17 enrichment of **1** and <sup>17</sup>O NMR spectroscopy reveals that **1** is the source of the acetaldehyde oxygen atom. However, other than acetaldehyde no other oxygen-containing product is detected in the reaction mixture, leaving the fate of the oxygen not used for formation of acetaldehyde unknown.



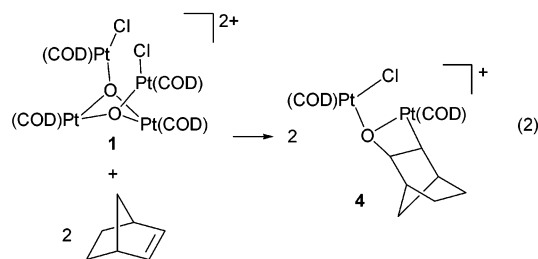
Three apparent intermediates in the reaction are detected by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. The NMR peak positions and <sup>13</sup>C–<sup>1</sup>H coupling experiments suggest that these complexes contain the formylmethyl fragment Pt–CH<sub>2</sub>CH(O).<sup>13</sup> These concentrations never attain a large value and decrease as acetaldehyde is produced. One appears at the same time as the ethyl complex **2** and all three are present before formation of the allyl complex **3** and acetaldehyde.

Oxo complex **1** reacts rapidly (minutes) with norbornylene. <sup>1</sup>H and <sup>13</sup>C NMR spectra of the reaction mixture are complex, but the



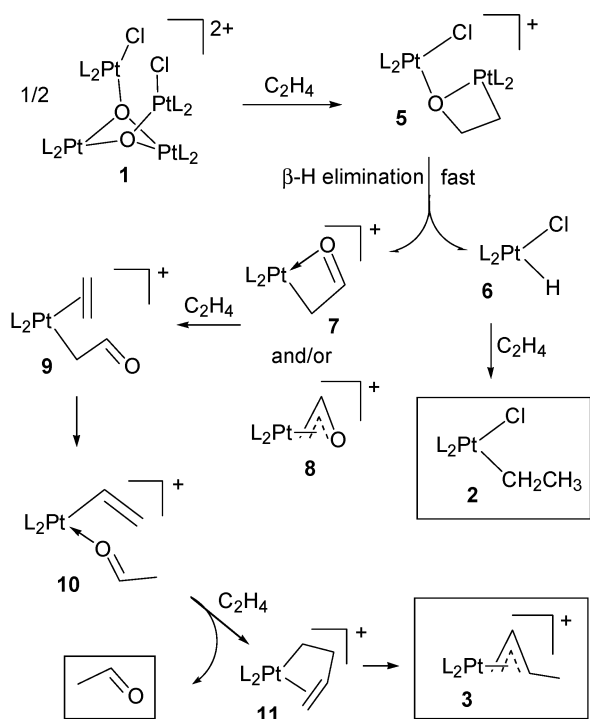
**Figure 1.** Drawing of the cationic portion of platinaoxetane **4**. Selected distances (Å): Pt1–C1, 2.052(5); Pt1–O, 2.053(4); Pt2–O, 2.046(4); C1–C2, 1.543(8); C2–O, 1.474(7). Selected angles (deg): C1–Pt1–O, 69.5(2); Pt1–C1–C2, 92.8(4); C1–C2–O, 101.7(4); C2–O–Pt1, 94.9(3); C2–O–Pt2, 121.4(4); Pt1–O–Pt2, 117.7(2).

<sup>195</sup>Pt NMR spectrum shows only two equal intensity peaks. No volatile products are produced, and fractional precipitation does not alter the spectra, suggesting that a single product is produced. Colorless, well-formed crystals were obtained and subjected to X-ray analysis. The product is revealed to be the platinaoxetane **4** (Figure 1), indicating the reaction stoichiometry given in eq 2. The yield of **4** is nearly quantitative.



A proposed ethylene oxidation pathway, consistent with the isolation of platinaoxetane **4** and the spectroscopic observations of the ethylene reaction, is given in Scheme 1. Formation of platinaoxetane **5**, analogous to **4**, is assumed. β-Hydride elimination from **5** produces hydride complex **6** and formylmethyl complex **7** and/or η<sup>3</sup>-oxaallyl complex **8**.<sup>14</sup> Rapid insertion of ethylene into the Pt–H bond of **6** gives the final ethyl complex **2** concurrent with formylmethyl complex **7** and/or η<sup>3</sup>-oxaallyl **8**. Ethylene reaction with **7** and/or **8** gives formylmethyl complex **9**. Subsequent steps to the allyl complex **3** and acetaldehyde require coupling of two ethylene molecules and the transfer of a hydrogen atom to the formylmethyl ligand. One way this can be accomplished from

Scheme 1



intermediate **9** is by formation of vinyl complex **10** followed by rapid displacement of acetaldehyde and insertion of ethylene to give **11**. The formation of iridium complexes analogous to **11** and **3** from two ethylene ligands via a vinyl complex has been reported.<sup>15</sup> Thus, Scheme 1 accounts for the early appearance of ethyl complex **2**, the observation of formylmethyl intermediates, and the formation of allyl complex **3**. However, the low yield of acetaldehyde and the observation of three formylmethyl species during the reaction indicate that other processes may be occurring.

Scheme 1 does not address the formation of the C–O bond. The rather complex structure of oxo complex **1** allows considerable speculation on this process. Alkene coordination with oxo group displacement is likely. Subsequent C–O bond formation steps could involve: (1) nucleophilic attack of the oxo group on the coordinated and activated alkene or (2) 2 + 2 addition of the alkene to an oxo ligand. Alkene coordination to an Ir center followed by nucleophilic attack of a hydroxo group on a second Ir center has been reported.<sup>13f</sup> DFT calculations are underway to help differentiate these possibilities.

In conclusion, the chemistry exhibited by **1** demonstrates that late transition metal  $\mu$ -oxo complexes can oxidize alkenes through formation of metallaoxetanes. This establishes that oxo complexes and metallaoxetanes are reasonable species to embrace in catalytic alkene oxidation pathways. This also suggests that oxo complexes could be important in alkene oxidation reactions not previously thought to involve oxo complexes (e.g., Wacker chemistry<sup>16</sup>). Future work will be directed at delineating the mode of formation of the

platinooxetane and an examination of its reactivity and full identification of the ethylene reaction intermediates.

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**Supporting Information Available:** Spectroscopic data for **2–4** and the intermediates in the reaction in eq 1 and X-ray crystallographic data for **4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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