Oxidation of Dimethylplatinum(II) Complexes with Dioxygen

Vsevolod V. Rostovtsev, Jay A. Labinger,* and John E. Bercaw*

Arnold and Mabel Beckman Laboratories of Chemical Synthesis, California Institute of Technology, Pasadena, California 91125

Tami L. Lasseter and Karen I. Goldberg*

Department of Chemistry, Box 351700, University of Washington, Seattle, Washington 98195-1700

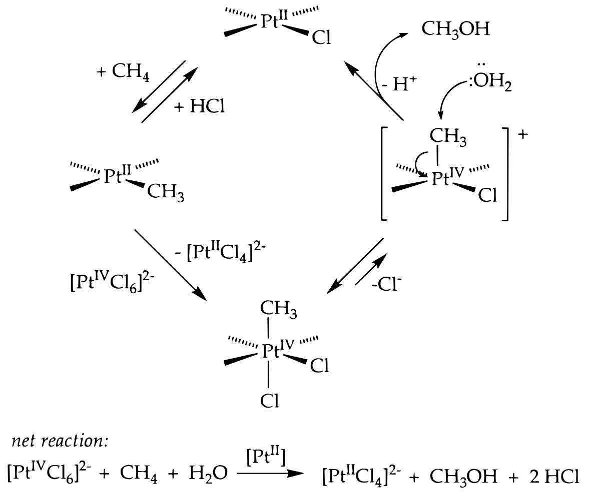
Received June 26, 1998

Summary: Dimethylplatinum(II) complexes (L−L)Pt(CH_3)$_2$ (L−L = bpy, phen, tmeda) are oxidized by dioxygen in methanol to the corresponding alkoxoplatinum(IV) complexes (L−L)Pt(CH_3)$_2$(OH)(OCH_3).

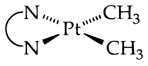
The selective catalytic oxidation of alkanes by aqueous platinum salts, originally reported in 1972,[1] proceeds via the catalytic cycle shown in Scheme 1.[2] The platinum(II) alkyl complex produced by alkane activation is oxidized by $[PtCl_6]^{2-}$ to afford a platinum(IV) alkyl, which undergoes S_N2-type displacement of platinum by water (or chloride), affording alcohol (or alkyl chloride) and regenerating active platinum(II). Clearly, the use of platinum(IV) as a stoichiometric oxidant is impractical. Can an alternate oxidant (preferably O_2) effect this step?[3]

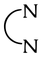
In 1984 Monaghan and Puddephatt reported the oxidation of platinum(II) dialkyls **1** and **2** by alcohols or water to form platinum(IV) alkoxides **4** and **5**, plus dihydrogen.[4] Since that result appears surprising (the last step of the cycle in Scheme 1 amounts to *reduction* of Pt(IV) to Pt(II) by water), and since the original work was carried out without excluding air,[5] we have reinvestigated this chemistry and find that these are in fact oxidations by O_2.

Scheme 1. Oxidation by Aqueous Pt^{IV}

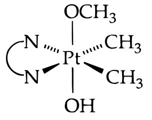


Solutions of dialkylplatinum(II) complexes **1**−**3** in CD_3OD (with or without added water) were maintained under an inert atmosphere for 1−2 days at 20−50 °C. No conversion to the corresponding alkoxoplatinum(IV) complexes **4**−**6** in methanol could be detected by ^1H NMR spectroscopy. The only changes observed were slow incorporation of deuterium into [Pt−CH_3] groups, along with formation of methane isotopomers (CH_3D, CH_2D_2, CHD_3) and new signals attributable to (L-L)-Pt(CH_3)(OCD_3). Presumably methanol protonates dialkylplatinum(II) to give an intermediate dialkylhydridoplatinum(IV) species which undergoes competing H/D exchange and methane elimination.[6]





= bpy (**1**), phen (**2**), tmeda (**3**);



bpy (**4**), phen (**5**), tmeda (**6**).

Admission of O_2 to a methanolic solution of **1** or **2** results in gradual fading of the initially red-orange color to pale yellow and appearance of ^1H NMR signals similar to those previously reported.[4] After all starting material has been converted, evaporation of methanol and addition of CD_2Cl_2 gives a solution containing only **4** or **5**, respectively.[7] Reaction of (tmeda)Pt(CH_3)$_2$ (**3**) with O_2 in dry methanol is more complex but ultimately leads to the analogous product **6**. Shortly after admission of dioxygen the solution becomes yellow-pink (λ_{max} = 480 nm) and then turns yellow-green or blue, depend-

---

[1] Gol'dshleger, N. F.; Es'kova, V. V.; Shilov, A. E.; Shteinman, A. A. *Zh. Fiz. Khim. (Engl. Transl.)* **1972**, *46*, 785.

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

[3] Recently a catalytic cycle based on a related Pt complex for oxidation of methane to methyl bisulfate, with sulfuric acid as the stoichiometric oxidant (but under more stringent conditions), has been reported: Periana, R. A.; Taube, D. J.; Gamble, S.; Taube, H.; Satoh, T.; Fujii, H. *Science* **1998**, *280*, 560.

[4] Monaghan, P. K.; Puddephatt, R. J. *Organometallics* **1984**, *3*, 444.

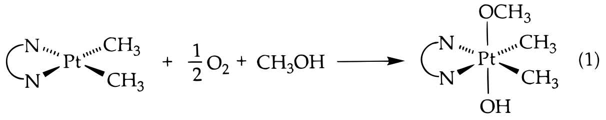
[5] Oxidation of (tris(pyrazolyl)borate)platinum(II) dialkyls by water *in the absence of air* has been reported: Canty, A. J.; Fritsche, S. D.; Jin, H.; Patel, J.; Skelton, B. W.; White, A. H. *Organometallics* **1997**, *16*, 2175.

[6] Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 5961.

[7] In addition to the ^1H NMR signals previously reported,[4] both products exhibit a peak around δ −2.5 assigned to Pt*OH*, integrated approximately as a single proton, indicating that **4** and **5** in CD_2Cl_2 exist predominantly in the neutral forms shown. Conductivity measurements suggest that in methanol the ionic form [(L−L)Pt(CH_3)$_2$-(OH_2)(OCH_3)]$^+$(OH)$^-$ dominates.[4]

S0276-7333(98)00541-X CCC: $15.00

ing on concentration ($\lambda_{max} = 640$ nm), and eventually yields the stable pale yellow product **6** quantitatively.[8] By ^{1}H NMR spectroscopy, after 20 min about 60% of **3** is converted to a 2:1 mixture of Pt(IV) compounds, the major one being **6**. All starting material was consumed after 30 min, while the (as yet unidentified) minor platinum(IV) species converted to **6** over a period of hours. Measurement of unreacted dioxygen by Toepler pump revealed that 0.51 ± 0.01 O_2 is consumed per platinum(II), establishing the stoichiometry of eq 1.



The mechanism of these oxidations is unclear, but several observations suggest the possible involvement of radical intermediates: (i) Oxidation kinetics are not very reproducible and show no obvious simple dependence on reagent concentrations. (ii) Solutions of **3** in aprotic solvents (dichloromethane or trifluorotoluene) exposed to O_2 exhibit color changes similar to those seen in methanol, but these correspond to very low levels of O_2 consumption (yellow stage, 2 ± 2 mol % O_2/Pt; blue stage, 7 ± 6 mol % O_2/Pt). ^{1}H NMR spectra of the blue solutions show broad signals suggesting paramagnetic species. (iii) **2** and **3** are oxidized by peroxides (H_2O_2 or Me_3COOH) in methanol to **5** and **6**, respectively,[9] considerably more rapidly than with dioxygen. These results suggest that oxidation is initiated by generation of small amounts of a catalytic intermediate, possibly a mixed-valence oligoplatinum species analogous to the well-known "platinum blues"[10] which more readily reacts with O_2 to generate an oxidant that can effect eq 1.

The finding that dimethylplatinum(II) complexes can be oxidized to platinum(IV) alkoxides by O_2 (or peroxides), coupled with recent observations of relatively facile C−H activation by Pt(II) under mild conditions,[11] suggests that these reactions constitute a promising approach to the catalytic oxidation of alkanes. Exploration of the scope of this system as well as elucidation of the mechanism of the oxidation by O_2 are subjects of ongoing studies in our laboratories.

Acknowledgment. V.V.R./J.A.L./J.E.B. thank the Army Research Office and the National Science Foundation for providing financial support for this work. K.I.G./T.L.L. acknowledge the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. K.I.G. is an Alfred P. Sloan Research Fellow.

OM980541L

---

(8) A solution of (tmeda)Pt$(CH_3)_2$ (**3**; 341 mg, 1 mmol) in methanol (10 mL) was stirred under air for 20 h. Evaporation, dissolution in CH_2Cl_2, treatment with charcoal, filtration, and addition of petroleum ether gave pale yellow **6** (370 mg, 95%). ^{1}H NMR (200 K, CD_2Cl_2): δ −2.5 (s, 1H, Pt−O*H*), 0.99 (s, 6H, $^2J_{PtH} = 74$ Hz, Pt−C*H*$_3$), 2.39 (s, 4H, −C*H*$_2$−), 2.56 (s, 12H, N−C*H*$_3$), 2.82 (s, 3H, $^3J_{PtH} = 42$ Hz, Pt−OC*H*$_3$). This preparation of **6** did not give satisfactory elemental analyses, but an analytically pure sample was obtained by oxidizing **3** with a slight excess of H_2O_2 and following a similar workup; the NMR was identical. Anal. Calcd for $C_9H_{28}N_2O_3Pt$ (**6**·H_2O): C, 26.56; H, 6.93; N, 6.88. Found: C, 26.37; H, 6.55; N, 6.70. The structure of **6** assigned by NMR was verified by X-ray crystallography (Rostovtsev, V. V.; Henling, L. M.; Labinger, J. A.; Bercaw, J. E. *Acta Crystallogr.* To be submitted for publication).

(9) Oxidation of **2** by H_2O_2 or Me_3COOH in acetone has been shown to give (phen)Pt$(CH_3)_2(OH)_2$, the dihydroxy analogue of **5**: Aye, K.-T.; Vittal, J. J.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1993**, 1835.

(10) Such species exhibit strong visible absorptions, consistent with our observation of intense coloration after little O_2 consumption, and have been shown to function as oxidation catalysts (e.g., in the epoxidation of olefins: Matsumoto, K.; Mizuno, K.; Abe, T.; Kinoshita, J.; Shimura, H. *Chem. Lett.* **1994**, 1325). On the other hand, they all involve bridging ligands, such as amidates, which do not appear in the present systems.

(11) Wick, D. D.; Goldberg, K. I. *J. Am. Chem. Soc.* **1997**, *119*, 10235. Holtcamp, M. W.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1997**, *119*, 848. Holtcamp, M. W.; Henling, L. M.; Day, M. W.; Labinger, J. A.; Bercaw, J. E. *Inorg. Chim. Acta* **1998**, *270*, 467.