Hydrogen bonding directs the H_2O_2 oxidation of platinum(II) to a *cis*-dihydroxo platinum(IV) complex[†][‡]

Russell A. Taylor,[a] David J. Law,[b] Glenn J. Sunley,[b] Andrew J. P. White[a] and George J. P. Britovsek*[a]

Received (in Cambridge, UK) 28th February 2008, Accepted 19th March 2008
First published as an Advance Article on the web 11th April 2008
DOI: 10.1039/b803370f

The use of ligands with proximate hydrogen bonding substituents in the oxidation of platinum(II) dimethyl complexes with H_2O_2 leads to the exclusive formation of an unusual *cis*-dihydroxo platinum(IV) complex, which can dehydrate to form a trinuclear metalla-azacrown complex.

The selective oxidation of methane to methanol, catalysed by electrophilic late transition metals such as platinum, has attracted much interest since the first observations by Shilov and Gol'dshleger in the late 1960s and early 1970s.[1,2] The mechanism of the overall reaction (eqn (1)), as proposed by Shilov,[3] consists of three steps: (1) C–H activation at a Pt(II) centre, generating a Pt–Me bond,[4,5] (2) oxidation of the Pt(II) centre to Pt(IV) and (3) functionalisation of the methyl group *via* reductive elimination of methanol and regeneration of the Pt(II) complex.[6] In the original Shilov reaction, the second step was carried out by a stoichiometric Pt(IV) oxidant. Several alternative oxidants have been investigated, but so far with limited success; for example O_2,[7] Cl_2,[8] SO_3[9] and H_2O_2.[10] We have investigated here the reaction between H_2O_2 and Pt(II) dimethyl complexes with the aim of generating *cis*-dihydroxo Pt(IV) dimethyl complexes, which can subsequently generate methanol *via* a C–O reductive elimination process (eqn (2)).

$$CH_4 + H_2O + [PtCl_6]^{2-} \rightarrow CH_3OH + 2H^+ + 2Cl^- + [PtCl_4]^{2-} \qquad (1)$$

$$L_2PtMe_2 + H_2O_2 \rightarrow L_2PtMe_2(OH)_2 \rightarrow L_2PtMe(OH) + MeOH \qquad (2)$$

The oxidative addition reaction of H_2O_2 or related compounds of the type RXXR, where X = O, S or Se, generally results in the formation of *trans*-$L_nPt(XR)_2$ complexes.[11–17] Octahedral *trans*-dihydroxo Pt(IV) complexes are plentiful and rather unreactive due to their low spin d^6 configuration, and the weak *trans* effect of the hydroxo ligand. If the oxidative addition reaction of H_2O_2 could be directed to the more reactive *cis*-dihydroxo Pt(IV) alkyl intermediate, this would offer the possibility of tuning the Pt–C and Pt–O bond strengths by the ancillary ligand, and induce a C–O reductive elimination to the desired methanol product.[18] However, only in a few cases, for example in the reaction of PhOCOOCOPh or PhSSPh with [(phen)$PtMe_2$] (phen = phenanthroline), have minor amounts of the *cis* isomer been observed alongside the major *trans* isomer.[15] The first exclusive formation of a *cis*-dihydroxo Pt(IV) alkyl complex (by O_2 oxidation) was recently reported by Vedernikov and co-workers. By using a facially coordinating tridentate ligand, which forces the two hydroxo ligands *cis* to each other, they indeed observed the formation of methanol.[19]

We have targeted here the synthesis of *cis*-dihydroxo Pt(IV) dimethyl complexes *via* the oxidative addition reaction of H_2O_2 with Pt(II) dimethyl complexes containing ligands with hydrogen bonding amine substituents.[20–23] The role of these hydrogen bonding substituents is to stabilise *cis*-dihydroxo Pt(IV) intermediates and prevent their rearrangement to *trans*-dihydroxo Pt(IV) complexes.

The addition of an excess of H_2O_2 (35 wt% aqueous solution) to the complex [(6,6′-diamino-bipy)Pt(II)Me_2] (bipy = 2,2′-bipyridine) (**1**) in acetone as the solvent at room temperature results in the immediate precipitation of a yellow product. This compound, **2**, is sparingly soluble in acetone but readily dissolves in a D_2O/d^6-acetone mixture. The ^1H NMR spectrum in this solvent mixture shows two signals of equal intensity at 1.68 ppm ($^2J_{H-Pt}$ = 67.5 Hz) and 0.93 ppm ($^2J_{H-Pt}$ = 65.9 Hz), which suggest two distinctly different Pt(IV)–CH_3 groups. When yellow compound **2** is dissolved in d^7-DMF, the ^1H and ^{13}C NMR spectra show six Pt(IV)–CH_3 signals of equal intensity and a complex pattern in the aromatic region (see Fig. S1[†]). X-Ray analysis of crystals, grown by cooling a saturated acetone solution, revealed that complex **2** is a trinuclear Pt(IV) complex with three linked $PtMe_2(OH)(L)$ units joined together by N–Pt bonds to form a 12-membered metalla-azacrown complex (see eqn (3) and Fig. 1).[‡] One of the NH_2 substituents on the bipyridine ligand of one $PtMe_2(OH)(L)$ unit has been deprotonated and binds to the platinum centre of the next, and so on. The possibility of 3-fold symmetry for the trinuclear complex is broken by the chirality of the individual complexes. In the stereoisomer

---

[a] *Department of Chemistry, Imperial College London, Exhibition Road, London, UK SW7 2AY. E-mail: g.britovsek@imperial.ac.uk; Fax: +44 (0)207 5945804; Tel: +44 (0)207 5945863*
[b] *Hull Research and Technology Centre, BP Chemicals Ltd., Saltend, Hull, UK HU12 8DS*

[†] Electronic supplementary information (ESI) available: Synthetic procedures, analytical data, crystallographic information, an ORTEP diagram for **2** and NMR spectra. See DOI: 10.1039/b803370f

[‡] *Crystal data for* **2**: $C_{36}H_{48}N_{12}O_3Pt_3\cdot 2Me_2CO$, M = 1398.29, orthorhombic, *Pbca* (no. 61), a = 8.9391(5), b = 23.5173(17), c = 44.243(5) Å, V = 9300.9(13) Å^3, Z = 8, ρ_{calc} = 1.997 g cm^{-3}, $\mu(Mo_{K\alpha})$ = 9.059 mm^{-1}, T = 173 K, yellow needles, Oxford Diffraction Xcalibur 3 diffractometer; 15 245 independent measured reflections, F^2 refinement, R_1 = 0.153, wR_2 = 0.289, 11 772 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 64°], 588 parameters, R_{int} = 0.1427. CCDC 658926. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b803370f.

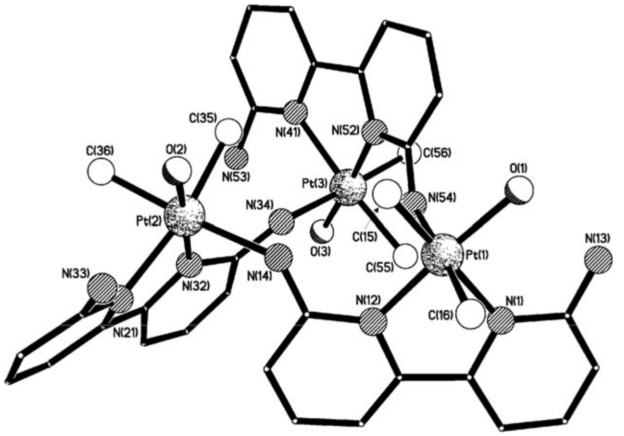
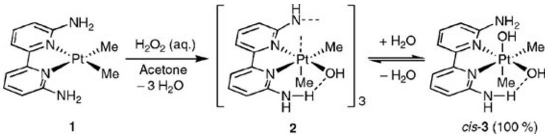


Fig. 1 The molecular structure of the trinuclear complex **2**.

shown in Fig. 1, for both Pt(1) and Pt(2) the ligand orientation results in an *S* configuration, whilst for Pt(3) the ligands are oriented to give an *R* configuration. There does not appear to be any steric reason for this preferred arrangement. In d^7-DMF solution, the trinuclear structure of **2** is maintained, resulting in six distinct Pt–Me signals due to the lack of symmetry.



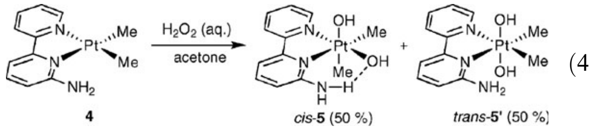
(3)

Trinuclear complex **2** is only sparingly soluble in acetone, but upon addition of H_2O, the equilibrium due to the loss of water, as shown in eqn (3), is reversed. This results in exclusive formation of the *cis*-dihydroxo Pt(IV) dimethyl complex *cis*-**3** (present as a mixture of enantiomers), as shown by the two distinct Pt–Me signals in the ^{1}H and ^{13}C NMR spectra in D_2O/d^6-acetone (see Fig. S5†).

The equatorial hydroxo ligand at each Pt centre occupies a coordination site that places it proximal to the NH_2 substituent of the bipyridine unit bound to the same metal centre, with N···O distances of 2.68(3), 2.77(2) and 2.73(2) Å for O(1)···N(13), O(2)···N(33) and O(3)···N(53), respectively. These distances suggest intramolecular O···H···N hydrogen bonding interactions,[14] but the quality of the data set did not allow the exact location of the H atoms (see ESI† for further details). We have previously established in the solid state structure of [(6-aminobipy)$PtMe_2$] complex **4** (shown in eqn (4)), that the lone pair on the amino nitrogen atom is tied up in the delocalised π-system of the ligand, resulting in a planar sp^2 hybridized nitrogen atom.[23] The interconversion shown in eqn (3) between complex *cis*-**3** and the trinuclear complex **2** indicates that the NH_2 protons are weakly acidic and that the OH ligands on the platinum centre are basic. It is on the basis of these observations that we suggest the HNH···OH hydrogen bonding shown in eqn (3), rather than the OH···NH_2 alternative, which would result in a pyramidalisation of the amino nitrogen atom.

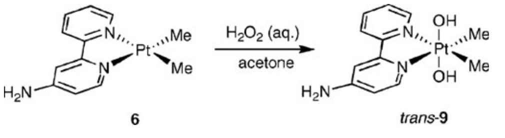
Although the formation of trinuclear compound **2** *via* the loss of H_2O was rather unexpected, it should be mentioned that trinuclear metal complexes of this type are not without precedent. Several of these so-called metalla-azacrown compounds were discovered during the last decade, containing metals such as Ru(II),[24,25] Rh(III),[24,25] Pd(II),[26] Pt(II)[27–29] and one example for Pt(IV).[30] In these trimeric complexes, the ligands are in all cases nucleobases or related model compounds.

In order to gain further support for the hydrogen bonding effect in oxidation reactions with H_2O_2 and its influence on the *cis*/*trans* ratio of the dihydroxo Pt(IV) complex, the reaction of **4** with H_2O_2 in acetone solution was also investigated. This reaction results in the formation of a mixture of exactly 50% of the *cis* dihydroxo Pt(IV) isomer, *cis*-**5** (present as a mixture of enantiomers), and 50% of the *trans* dihydroxo Pt(IV) complex, *trans*-**5′** (eqn (4)). These products could not be separated but are easily identified by their characteristic ^{1}H and ^{13}C NMR data (see Fig. S6–S9†).

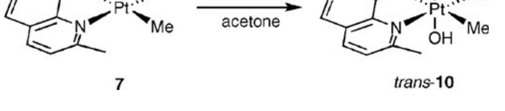


(4)

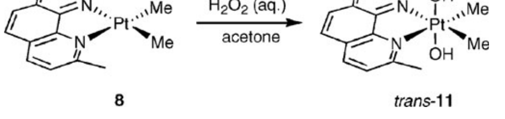
The results presented here provide strong evidence that hydrogen bonding can be used to generate exclusively *cis*-dihydroxo Pt(IV) complexes. In order to rule out any possible electronic or steric effects, we also investigated the reaction of H_2O_2 with the following complexes: [(4-amino-bipy)$PtMe_2$] (**6**), [(6-methyl-bipy)$PtMe_2$] (**7**) and [(2,9-dimethylphen)$PtMe_2$] (**8**). In all cases, a *trans*-dihydroxo Pt(IV) dimethyl complex was the only product observed (eqn (5), eqn (6), eqn (7) and Fig. S10–S13†). Substantial decomposition was observed in the reaction of complex **8**, probably due to severe steric distortions of the dimethylphenanthroline coordination and the consequent instability of the complex.[31]



(5)

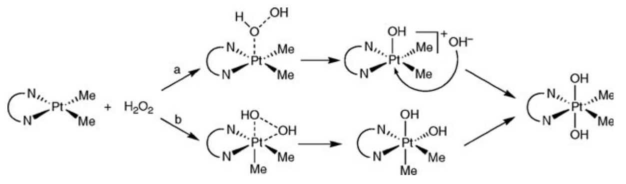


(6)



(7)

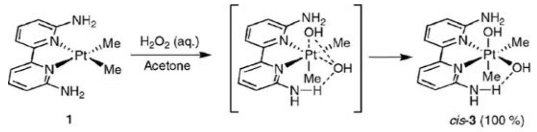
The ability of hydrogen bonding to direct the outcome of the oxidation reaction of Pt(II) complexes with H_2O_2 also has important mechanistic implications. The mechanism of the oxidative addition reaction of H_2O_2 and Pt(II) complexes has been the subject of some debate, and two reaction pathways have been proposed: (a) *via* axial electrophilic attack by the



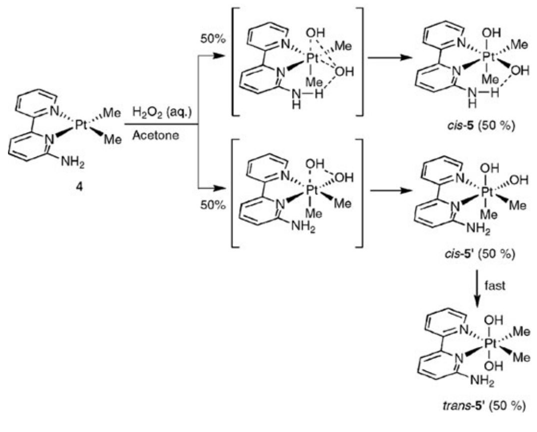
Scheme 1

oxidant at the square planar Pt(II) complex, followed by a heterolytic cleavage of the O–O bond and subsequent attack of the hydroxide anion, or (b) *via* a concerted three-centered transition state and homolytic cleavage of the O–O bond to give a *cis*-dihydroxo complex as the initial kinetic product, which subsequently rapidly isomerises to the thermodynamically more stable *trans*-dihydroxo Pt(IV) complex (Scheme 1).[12,13,17]

In an attempt to explain the observed reaction products in the oxidative addition reactions of H_2O_2 with complexes **1** and **4**, we postulate a *cis*-concerted mechanism (pathway b). In the case of the reaction of complex **1** with H_2O_2, a *cis*-concerted addition of H_2O_2 leads to only one possible intermediate, which upon oxidative addition results in a single *cis*-dihydroxo Pt(IV) complex, *cis*-**3** (eqn (8)). In the case of complex **4**, where only one amine substituent is present, the reaction with H_2O_2 initially generates two isomeric *cis* complexes, *cis*-**5** and *cis*-**5′** (eqns (9a) and (9b)). Complex *cis*-**5′**, which is not observed, rearranges immediately to a *trans*-dihydroxo Pt(IV) complex, *trans*-**5′**, due to the absence of hydrogen bonding in the equatorial plane.



(8)



(9a)

(9b)

In conclusion, we have shown that hydrogen bonding substituents in the proximity of a metal centre can have a dramatic effect on the outcome of a reaction. The reaction of H_2O_2 with a Pt(II) dimethyl complex containing a 6,6′-diamino-bipyridine ligand results in exclusive formation of the *cis*-dihydroxo Pt(IV) dimethyl complex. Instead of methanol formation *via* C–O coupling and reduction of the Pt(IV) centre, deprotonation of the diamino-bipyridine ligand was observed, resulting in the formation of an unusual trinuclear Pt(IV) complex. We are continuing our investigations into the properties of these novel *cis*-dihydroxy Pt(IV) dimethyl complexes, with the aim of developing alkane oxidation catalysts using cheap and environmentally benign oxidants such as H_2O_2.

We are grateful to BP Chemicals Ltd. and the EPSRC for financial support, and to Johnson Matthey for a generous loan of K_2PtCl_4.

Notes and references

1. N. F. Gol'dshleger, V. V. Eskova, A. E. Shilov and A. A. Shteinman, *Russ. J. Phys. Chem. (Transl. of Zh. Fiz. Khim.)*, 1972, **46**, 785.
2. N. F. Gol'dshleger, M. B. Tyabin, A. E. Shilov and A. A. Shteinman, *Russ. J. Phys. Chem. (Transl. of Zh. Fiz. Khim.)*, 1969, **43**, 1222.
3. L. A. Kushch, V. V. Lavrushko, Y. S. Misharin, A. P. Moravsky and A. E. Shilov, *Nouv. J. Chim.*, 1983, **7**, 729.
4. U. Fekl and K. I. Goldberg, *Adv. Inorg. Chem.*, 2003, **54**, 259.
5. M. Lersch and M. Tilset, *Chem. Rev.*, 2005, **105**, 2471.
6. S. S. Stahl, J. A. Labinger and J. E. Bercaw, *Angew. Chem., Int. Ed.*, 1998, **37**, 2180.
7. V. V. Rostovtsev, L. M. Henling, J. A. Labinger and J. E. Bercaw, *Inorg. Chem.*, 2002, **41**, 3608.
8. I. T. Horváth, R. A. Cook, J. M. Millar and G. Kiss, *Organometallics*, 1993, **12**, 8.
9. R. A. Periana, D. J. Taube, S. Gamble, H. Taube, T. Satoh and H. Fuji, *Science*, 1998, **280**, 560.
10. N. DeVries, D. C. Roe and D. L. Thorn, *J. Mol. Catal. A: Chem.*, 2002, **189**, 17.
11. V. De Felice, B. Giovannitti, A. De Renzi, D. Tesauro and A. Panunzi, *J. Organomet. Chem.*, 2000, **593–594**, 445.
12. L. M. Rendina and R. J. Puddephatt, *Chem. Rev.*, 1997, **97**, 1735.
13. K. Thorshaug, I. Fjeldahl, C. Rømming and M. Tilset, *Dalton Trans.*, 2003, 4051.
14. F. Zhang, M. C. Jennings and R. J. Puddephatt, *Chem. Commun.*, 2007, 1496.
15. K.-T. Aye, J. J. Vittal and R. J. Puddephatt, *J. Chem. Soc., Dalton Trans.*, 1993, 1835.
16. A. J. Canty, H. Jin, B. W. Skelton and A. H. White, *Inorg. Chem.*, 1998, **37**, 3975.
17. M. Rashidi, M. Nabavizadeh, R. Hakimelahi and S. Jamali, *J. Chem. Soc., Dalton Trans.*, 2001, 3430.
18. B. S. Williams and K. I. Goldberg, *J. Am. Chem. Soc.*, 2001, **123**, 2576.
19. A. N. Vedernikov, S. A. Binfield, P. Y. Zavalij and J. R. Khusnutdinova, *J. Am. Chem. Soc.*, 2006, **128**, 82.
20. D. Natale and J. C. Mareque-Rivas, *Chem. Commun.*, 2008, 425.
21. C. J. Curtis, A. Miedaner, R. Ciancanelli, W. W. Ellis, B. C. Noll, M. Rakowski DuBois and D. L. DuBois, *Inorg. Chem.*, 2003, **42**, 216.
22. D.-H. Lee, B. P. Patel, E. Clot, O. Eisenstein and R. H. Crabtree, *Chem. Commun.*, 1999, 297.
23. G. J. P. Britovsek, R. A. Taylor, G. J. Sunley, D. J. Law and A. J. P. White, *Organometallics*, 2006, **25**, 2074.
24. S. Korn and W. S. Sheldrick, *Inorg. Chim. Acta*, 1997, **254**, 85.
25. S. Korn and W. S. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1997, 2191.
26. W.-Z. Shen, D. Gupta and B. Lippert, *Inorg. Chem.*, 2005, **44**, 8249.
27. B. Longato, D. Montagner and E. Zangrando, *Inorg. Chem.*, 2006, **45**, 8179.
28. B. Longato, L. Pasquato, A. Mucci, L. Schenetti and E. Zangrando, *Inorg. Chem.*, 2003, **42**, 7861.
29. S.-W. Lai, C.-W. Chan, S.-M. Peng and C.-M. Che, *Angew. Chem., Int. Ed.*, 1999, **38**, 669.
30. X. Zhu, E. Rusanov, R. Kluge, H. Schmidt and D. Steinborn, *Inorg. Chem.*, 2002, **41**, 2667.
31. A. Klein, E. J. L. McInnes and W. Kaim, *J. Chem. Soc., Dalton Trans.*, 2002, 2371.