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Oxidative Addition of Alcohols to Dimethylplatinum(II) Complexes

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Oxidative addition reactions of alcohols and of water are rare, although examples are known in both mononuclear [1] and polynuclear [2] complexes. Most examples are found for elements such as tungsten which are oxophilic and, with the late transition elements which have little affinity for oxygen-donors, the reactions typically involve protonation of the metal with the hydroxide or alkoxide ligand remaining as a counterion [1, 2]. Indeed, water and methanol have been used as solvents for reactions of so-called super-nucleophiles with alkyl halides on account of the inertness of the O–H group towards oxidative addition with late transition elements [3]. We now report preliminary studies which show that alcohols react with some dimethylplatinum(II) complexes to give remarkably stable alkoxoplatinum(IV) complexes and that water appears to give very similar reactions.

The complexes [PtMe$_2$($N\widehat{N}$)], where $N\widehat{N}$ = 2,2′-bipyridyl or 1,10-phenanthroline, are among the most reactive complexes known in oxidative addition [4]. They react with methanol or ethanol (used as solvent) over a period of several hours at room temperature to give platinum complexes characterised as containing the ions [PtMe$_2$(OR)($N\widehat{N}$)]$^+$. For example, the product of reaction of methanol with [PtMe$_2$(bipy)] gave a ^{1}H NMR spectrum (Table I) with peaks due to MePt, MeOPt and bipy in the ratio 6:3:8 as expected for a 1:1 adduct, but no Pt–H group was detected in the ^{1}H NMR or IR spectra. The ^{2}H{^{1}H} NMR spectrum of the adduct of MeOD with [PtMe$_2$(phen)] also showed the absence of deuterium in the product. The ^{13}C{^{1}H} NMR spectra confirm the presence of the MePt and MeOPt groups {*e.g.* for [PtMe$_2$(OMe)(bipy)]$^+$ in CD$_2$Cl$_2$, δ(MePt) –2.30 ppm, ^{1}J(PtC) 701 Hz; δ(MeOPt) 57.32 ppm, ^{2}J(PtC) 18 Hz}, and detailed analysis of the ^{1}H and ^{13}C{^{1}H} NMR spectra associated with the bipy and phen ligands clearly show that these ligands have not undergone alcohol addition or (in reactions with MeOD), H, D exchange [5]. It should be noted that the magnitude of the coupling ^{2}J(PtMe) decreases from 86 Hz in [PtMe$_2$($N\widehat{N}$)] to 70–73 Hz in the adducts, exactly as expected for a reaction involving oxidation from Pt(II) → Pt(IV), and the magnitudes of the couplings ^{1}J(PtC) are also as expected [4, 6]. The observation of coupling between ^{195}Pt and the alkoxy ^{1}H or ^{13}C atoms clearly shows that the alkoxy group is directly bound to platinum [7]. A few alkoxoplatinum(II) complexes are known but we know of no other alkoxoplatinum(IV) complexes [7].

During the reaction of methanol with [PtMe$_2$(bipy)] the conductivity of the solution (concentration 6 × 10^{-3} *M*) rose to a limiting value of Λ = 76.5 cm^2 M^{-1} mol^{-1}, in the range expected for a 1:1 electrolyte*. The ionic nature of the complexes is also indicated by the observation that they are soluble in alcohols or in water. Remarkably the adduct of methanol with [PtMe$_2$(bipy)] is soluble and stable in D$_2$O and it is even possible to acidify such solutions with perchloric acid without affecting the NMR spectra, indicating that both MePt and MeOPt groups are stable under these conditions. From the resulting solution a complex analysing as [PtMe$_2$(OMe)(bipy)][ClO$_4$] can be isolated and salts of the platinum-containing complex cations with the large anions [PF$_6$]$^-$ and [BPh$_4$]$^-$ have also been prepared.

The reactions of [PtMe$_2$($N\widehat{N}$)] with alcohols (used as solvent) were monitored using UV-visible spectrophotometry. It is known that the complexes [PtMe$_2$($N\widehat{N}$)] give a prominent MLCT band in the UV-visible spectra, whereas platinum(IV) derivatives give no such band, so that the decay of the MLCT band as oxidative addition proceeds can be used to follow the kinetics of reaction [4, 8]. Observed rate constants for reaction of [PtMe$_2$(bipy)] were 20 × 10^{-3} min^{-1} (MeOH), 9.9 × 10^{-3} min^{-1} (EtOH) and 2.7 × 10^{-3} min^{-1} (^{i}PrOH) and of [PtMe$_2$(phen)] were 23 × 10^{-3} min^{-1} (MeOH) and 11 × 10^{-3} min^{-1} (EtOH) at 21 °C. The rates are greatest for the less bulky, more acidic alcohols.

The above data are most consistent with for formulation of the compounds as [PtMe$_2$(OR)($N\widehat{N}$)]$^+$X$^-$, where X$^-$ is a large anion or, in the parent compounds which are very hygroscopic and hence difficult to characterise by analysis, OH$^-$. The adduct of [PtMe$_2$(phen)] with methanol can be titrated in a 1:1 mole ratio against dilute HCl. We recognise that the formulation with five-coordination is unexpected in that platinum(IV) complexes are almost invariably octahedral. However, we have been unable to detect a sixth ligand about the metal and the NMR data clearly shows that neither the alkoxy nor methyl

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*For example, LiCl gives Λ = 88 cm^2 Ω^{-1} mol^{-1} in MeOH.

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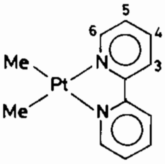
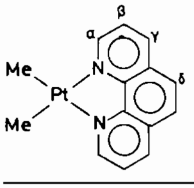
TABLE I. ^{1}H NMR Data.

Complex	PtMe		PtOR^a		N⌒N^b	
	δ/ppm	^{2}J(PtH)/Hz	δ/ppm	J/Hz	δ/ppm	J/Hz
	1.14	86	–	–	9.28(H_6)^c 7.52(H_5) 8.02(H_4) 8.06(H_3)	5.2(J_{56}), 1.5(J_{46}) 7.2(J_{45}), 1.5(J_{35}) 7.7(J_{34})
[PtMe$_2$(OMe)(bipy)]$^+$	1 71	73	2.75	41.0(J_{PtH})	9.04(H_6)^d 7.67(H_5) 8.06(H_4) 8.20(H_3)	5.0(J_{56}) 8.0(J_{45}), 1.3(J_{35}) 7.5(J_{34})
[PtMe$_2$(OEt)(bipy)]$^+$	1.80	72.5	2.90(CH_2) 0.74(CH_3)	14(J_{PtH}) 7(J_{HH})	9.03(H_6)^e 7.67(H_5) 8.05(H_4) 8.20(H_3)	5(J_{56}), 1.5(J_{56}) 8(J_{45}), 1.3(J_{35}) 8(J_{34})
[PtMe$_2$(OH)(bipy)]$^+$	1.84	70	–	–	9.02(H_6)^f 7.90(H_5) 8.34(H_4) 8.72(H_3)	5.5(J_{56}), 1.5(J_{46}) 8.0(J_{45}), 1.3(J_{35}) 8.1(J_{34})
	1.15	86.5	–	–	9.51(H_α)^g 7.82(H_β) 8.63(H_γ) 7.92(H_δ)	5.2($J_{\alpha\beta}$) 8.0($J_{\beta\gamma}$) 1.3($J_{\alpha\gamma}$)
[PtMe$_2$(OMe)(phen)]$^+$	1.80	72.5	2.65	40(J_{PtH})	9.32(H_α) 8.03(H_β) 8.62(H_γ) 8.07(H_δ)	5.0($J_{\alpha\beta}$) 8.0($J_{\beta\gamma}$) 1.8($J_{\alpha\gamma}$)
[PtMe$_2$(OEt)(phen)]$^+$	1.79	73	2.85(CH_2) 0.59(CH_3)	21(J_{PtH}) 7(J_{HH})	9.30(H_α)^i 8.01(H_β) 8.60(H_γ) 8.06(H_δ)	5($J_{\alpha\beta}$) 7($J_{\beta\gamma}$) 2($J_{\alpha\gamma}$)

[a] R = H, Me or Et. [b] N⌒N = bipy or phen. [c] J(PtH) 22 Hz. [d] J(PtH) 14 Hz. [e] J(PtH) 13 Hz. [f] J(PtH) 16 Hz. [g] J(PtH) 21.5 Hz. [h] J(PtH) 14 Hz. [i] J(PtH) 15 Hz.

groups occupy bridging positions. Attempts, so far unsuccessful, to grow crystals suitable for X-ray structure determination are in progress to settle this structural problem. However, this work is significant in showing for the first time that oxidative addition of alcohols to platinum(II) complexes can occur, and that the resulting alkoxoplatinum(IV) complexes are surprisingly robust particularly with respect to hydrolysis. Water appears to give similar adducts with [PtMe$_2$(N⌒N)]; the NMR and UV data (Table I) certainly show that oxidation of Pt(II) → Pt(IV) occurs but the coupling of ^{195}Pt to the presumed hydroxoplatinum proton cannot be observed so that the formulation is more tentative. The reactions are of potential significance for activation of alcohols in catalysis.

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References

1 L. Farrugia and M. L. H. Green, *J Chem. Soc Chem. Comm.*, 416 (1975).
T. Yoshida, T. Matsuda, T. Okano, T. Kitani and S. Otsuka, *J. Am. Chem. Soc.*, *101*, 2027 (1978).
K. W. Chiu, R. A. Jones, G. Wilkinson, A. M. R. Galas, M. B. Hursthouse and K. M. Abdul Malik, *J. Chem. Soc. Dalton Trans.*, 1204 (1981).
T. Yoshida, T. Okano, Y. Ueda and S. Otsuka, *J. Am. Chem. Soc.*, *103*, 3411 (1981).
2 K. A. Azam, A. J. Deeming, R. E. Kimber and P. R. Shukla, *J. Chem. Soc. Dalton Trans.*, 1853 (1976).
M. Akiyama, M. H. Chisholm, F. A. Cotton, M. W. Extine, D. A. Haitko, J. Leonelli and D. Little, *J. Am. Chem. Soc.*, *103*, 779 (1981).
3 G. N. Schrauzer and E. Deutsch, *J. Am. Chem. Soc*, *91*, 3341 (1969).
J. Halpern, R. Cozens and L.-Y. Goh, *Inorg. Chim. Acta*, *12*, L35 (1975).
4 J. K. Jawad and R. J. Puddephatt, *J. Chem. Soc. Dalton Trans.*, 1466 (1977).
5 G. Nord, *Acta Chem. Scand*, *A29*, 270 (1975).
O. Farver, O. Monsted and G. Nord, *J Am. Chem. Soc.*, *101*, 6118 (1979).
O. Wernberg and A. Hazell, *J. Chem. Soc. Dalton Trans.*, 973 (1980).
P. J. Spellane and R. J. Watts, *Inorg. Chem.*, *20*, 3561 (1981).
E. C. Constable and K. R. Seddon, *J. Chem. Soc Chem. Comm.*, 34 (1982).
6 D. E. Clegg, J. R. Hall and G. A. Swile, *J. Organometal Chem.*, *38*, 403 (1972).
J. K. Jawad and R. J. Puddephatt, *J Organomet. Chem.*, *117*, 297 (1976).
7 H. C. Clark and A. B. Goel, *J. Organometal. Chem.*, *178*, C27 (1979).
R. A. Michelin, M. Napoli and R. Ros, *J. Organometal. Chem.*, *175*, 239 (1979).
F. Giordano and A. Vitagliano, *Inorg. Chem.*, *20*, 633 (1981).
A. B. Goel, S. Goel and D. G. Vanderveer, *Inorg Chim. Acta*, *54*, L169 (1981).
8 N. Chaudhury and R. J. Puddephatt, *J. Organometal. Chem.*, *84*, 105 (1975).