

Preliminary communication

ISOLATION OF THE FIRST MIXED METHOXY- AND CHLORO-BRIDGED BINUCLEAR PLATINUM COMPLEX

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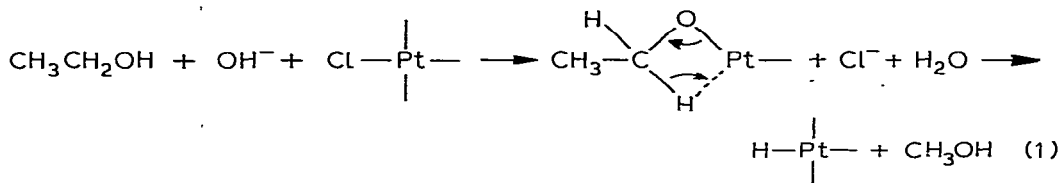
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Summary

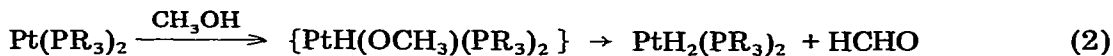
The first methoxyplatinum(II) complex, a stable binuclear complex containing bridging methoxy and chloro groups as well as metalated *t*-butylphosphine, $[\text{Pt}_2(\mu\text{-Cl})(\mu\text{-OCH}_3)(\text{t-Bu}_2\text{PCMe}_2\text{CH}_2)_2]$, has been prepared by treating $[\text{Pt}_2\text{Cl}_2(\text{t-Bu}_2\text{PCMe}_2\text{CH}_2)_2]$ with sodium hydroxide in methanol. A symmetrical structure is proposed on the basis of ^1H and ^{31}P NMR spectroscopic data.

Alkoxyplatinum complexes have been invoked as probable intermediates in the preparation of various hydridoplatinum complexes [1,2]. Chatt and Shaw [1], in preparing the hydrido complex *trans*-PtH(Cl)(PEt₃)₂ by the reduction of *cis*-PtCl₂(PEt₃)₂ with KOH in ethanol, proposed an ethoxyplatinum complex, PtCl(OC₂H₅)(PEt₃)₂, as intermediate, which by hydride-ion transfer would then produce the final hydride (eq. 1). Alcoholic KOH has also been a widely used re-



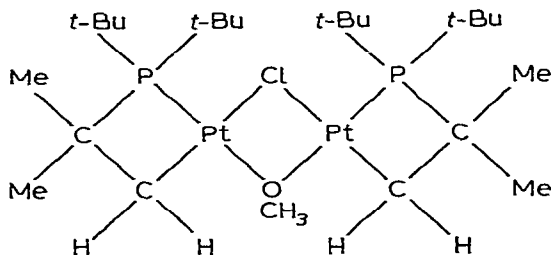
ducing agent in the preparation of hydridocarbonyl complexes [3–5] of metals such as Ru, Rh, Os, Ir etc. Otsuka et al. [2] have also proposed that an unstable methoxy intermediate, PtH(OCH₃)(P-*i*-Pr₃)₂, is formed when Pt(PR₃)₂ (PR₃ = P-*i*-Pr₃, PCy₃, P-*t*-Bu₂Ph) is treated with methanol: decomposition then gives PtH₂(PR₃)₂. This conclusion was based on the observed formation of aldehyde during the reaction (eq. 2), by β -hydrogen elimination [6,7]. Bennett et al. [8] reported the formation of a methoxyplatinum complex from the oxidative addition of methanol to a zerovalent hexenylplatinum complex. Recently some

square planar methoxy-platinum and -palladium complexes have been prepared by the metathesis of $[\text{MR}(\text{Cl})(\text{PPh}_3)_2]$ with NaOMe [9].



Here we wish to report the isolation of a stable methoxy-bridged platinum complex, $[\text{Pt}_2(\mu\text{-Cl})(\mu\text{-OCH}_3)(t\text{-Bu}_2\text{PCMe}_2\text{CH}_2)_2]$ (I), prepared by the reaction of sodium hydroxide with the chloro-bridged complex, $[\text{Pt}_2(\mu\text{-Cl})_2(t\text{-Bu}_2\text{PCMe}_2\text{CH}_2)_2]$ (II) [10], in methanol. This is the first example of a mixed methoxy-, chloro-bridged binuclear platinum complex, although numerous binuclear complexes each containing two identical bridging groups such as halogen [10,11], sulphur [10,12], hydroxy [13], hydrido [12,14,15], pyrazolato [15,16] and others [12] are known. Very recently, the isolation of a binuclear platinum intermediate containing both bridging peroxy and hydroxy groups has been reported [17].

When a suspension of the chloro-bridged binuclear complex II in methanol reacts with two mole equivalents of sodium hydroxide at 50°C , a clear solution is obtained after about 3 h. On cooling to room temperature this gives an air stable white crystalline solid (yield $\approx 85\%$, m.p. 195°C (dec.)). Elemental analyses, and the molecular weight correspond to $[\text{Pt}_2\text{Cl}(\text{OCH}_3)(t\text{-Bu}_2\text{PCMe}_2\text{CH}_2)_2]$ (I). The proton NMR spectrum of this complex consists of resonances due to the protons of the phosphine as three sets of doublets at δ 1.46 ($J(\text{PH})$ 13.2 Hz), 1.43 ($J(\text{PH})$ 13.9 Hz) and 1.35 ppm ($J(\text{PH})$ 6.8 Hz) in the ratio 9/3/0.7, corresponding to the di-*t*-butyl (*t*-Bu₂P), dimethyl (P—CMe₂) and methylene (CH₂—Pt) protons respectively. The signals due to the methylene protons displayed ¹⁹⁵Pt satellites with $J(\text{Pt—H})$ 128 Hz confirming that methylene is bonded to platinum [10]. In addition, the spectrum shows five sets of well-resolved triplets centred at δ 3.49 ppm ($J(\text{PH})$ 2.2 Hz; $J(\text{PtH})$ 32.2 Hz), due to the methoxy protons, in the ratio 0.13/1.0/2.3/1.0/0.13. The overall ratio between the phosphine and the methoxy signals is approximately 17/1 suggesting the presence of one methoxy group for two phosphine molecules, while the symmetrical triplets suggest that the two phosphorus nuclei are symmetrically disposed with regard to the methoxy group. The splitting of triplets into a 1/8/18/8/1 pattern [12,18] by coupling to ¹⁹⁵Pt ($^3J(\text{PtH})$ 32.2 Hz) is consistent with the binuclear structure. Thus, there is strong evidence for the presence of the symmetrical Pt—OCH₃—Pt bridge and the following structure can thus be proposed:



This structure is further supported by the ³¹P NMR spectrum which shows only one peak at δ -22.42 ppm (characteristic of metalated tri-*t*-butylphosphine) [10] with $J(\text{PtP})$ 3306 Hz. Both phosphorus nuclei are thus symmetrically disposed

trans to the bridging methoxy, as suggested by the large $J(\text{P}-\text{H})$ for the methoxy protons.

Complex I represents the first example of the class of bridging alkoxyplatinum complexes and its novelty is increased by the presence of the mixed alkoxy- and chloro-bridges between two platinum. The steric requirement of the metalated tri-*t*-butylphosphine [19] is probably a principal factor in the stability of I. Attempts are underway to prepare other related alkoxy complexes of platinum.

Acknowledgements

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References

- 1 J. Chatt and B.L. Shaw, *J. Chem. Soc.*, (1962) 5073.
- 2 T. Yoshida and S. Otsuka, *J. Amer. Chem. Soc.*, 99 (1977) 2134.
- 3 J. Chatt and B.L. Shaw, *Chem. Ind.*, (1960) 931; (1961) 290.
- 4 L. Vaska, *J. Amer. Chem. Soc.*, 83 (1961) 756; *Chem. Ind.*, (1961) 1402; L. Vaska and J.W. DiLuzio, *J. Amer. Chem. Soc.*, 83 (1961) 1262, 2784.
- 5 K.K. Chow, W. Levason and C.A. McAuliffe, in C.A. McAuliffe (Ed.), *Transition Metal Complexes of P, As and Sb Ligands*, MacMillan Press Ltd., London, 1973 and ref. therein.
- 6 D.H. Gerlach, A.R. Kane, G.W. Parshall, J.P. Jesson and E.L. Muetterties, *J. Amer. Chem. Soc.*, 93 (1971) 3544.
- 7 R.A. Schunn, *Inorg. Chem.*, 15 (1976) 208.
- 8 M.A. Bennett and T. Yoshida, *J. Amer. Chem. Soc.*, 100 (1978) 1750.
- 9 T. Yoshida, T. Okano and S. Otsuka, *J. Chem. Soc. Dalton*, (1976) 993.
- 10 H.C. Clark, A.B. Goel, R.G. Goel, S. Goel and W.O. Ogin, *Inorg. Chim. Acta*, 31 (1978) L441.
- 11 U. Belluco, *Organometallic and Coordination Chemistry of Platinum*, Academic Press Inc., New York, 1974, p. 70-81.
- 12 M.P. Brown, J.R. Fisher, S.J. Franklin and R.J. Puddephatt, *J. Chem. Soc. Chem. Commun.*, (1978) 749 and ref. therein.
- 13 B. Lippert, C.J.L. Lock, B. Rosenberg and M. Zvagulis, *Inorg. Chem.*, 17 (1978) 2971 and ref. therein.
- 14 M. Green, J.A.K. Howard, J. Proud, J.L. Spencer, F.G.A. Stone and C.A. Tsipis, *J. Chem. Soc. Chem. Commun.*, (1976) 671 and ref. therein.
- 15 H.C. Clark and A.B. Goel, to be published.
- 16 F. Bonati and H.C. Clark, *Can. J. Chem.*, 56 (1978) 2513 and ref. therein.
- 17 S. Bhaduri, P.R. Raithby, C.I. Zuccaro, M.B. Hursthouse, L. Casella and R. Ugo, *J. Chem. Soc., Chem. Commun.*, (1978) 991.
- 18 G. Minghetti, G. Banditelli and A.L. Bandini, *J. Organometal. Chem.*, 139 (1977) C80.
- 19 H.C. Clark, A.B. Goel and S. Goel, *J. Organometal. Chem.*, in press.