

Dimerisation of a Diplatinum to a Tetraplatinum Complex during Catalysis of the Water Gas Shift Reaction: the X-Ray Crystal Structure of $[\text{Pt}_4(\mu_2\text{-CO})_2(\mu_2\text{-Ph}_2\text{PCH}_2\text{PPh}_2)_3\{\text{Ph}_2\text{PCH}_2\text{P}(\text{:O})\text{Ph}_2\}]$

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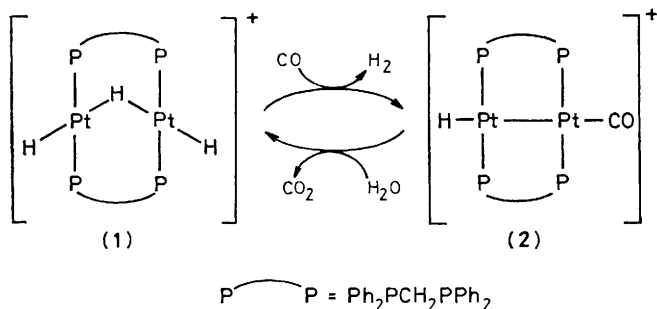
The binuclear complex $[\text{Pt}_2\text{H}_2(\mu\text{-H})(\mu\text{-dppm})_2][\text{PF}_6]$, dppm = $\text{Ph}_2\text{PCH}_2\text{PPh}_2$, is an active catalyst precursor for the water gas shift reaction, especially at low pressures of carbon monoxide; the catalytic solutions are shown to contain cluster complexes such as the tetranuclear $[\text{Pt}_4(\mu\text{-CO})_2(\mu\text{-dppm})_3\{\text{Ph}_2\text{PCH}_2\text{P}(\text{:O})\text{Ph}_2\}]$, whose 'butterfly' structure has been determined by X-ray crystallography.

Known chemistry of the binuclear platinum hydride $[\text{Pt}_2\text{H}_2(\mu_2\text{-H})(\mu_2\text{-dppm})_2]^+$, (**1**) (dppm = $\text{Ph}_2\text{PCH}_2\text{PPh}_2$) and of cationic transition metal carbonyls suggested a catalytic cycle for the water gas shift reaction (Scheme 1).^{1,2} Complex (**1**), as the $[\text{PF}_6]^-$ or $[\text{BPh}_4]^-$ salt, is indeed a catalyst precursor for the water gas shift reaction, but the mechanism is more complex than predicted.

Typical reactions were carried out at 100 °C in a Parr pressure reactor (300 ml) in solvent methanol–water (2:1 v/v).

With $p(\text{CO})$ 110 lb in⁻²,[†] the rate of formation of H_2 or CO_2 was first order with respect to catalyst concentration and the turnover rate was 3.0 ± 0.2 [mol H_2 or CO_2] [mol (**1**)⁻¹ h⁻¹]. However, at lower pressures of CO the turnover rate was

[†] This is the pressure to which the apparatus was charged at room temperature.



Scheme 1

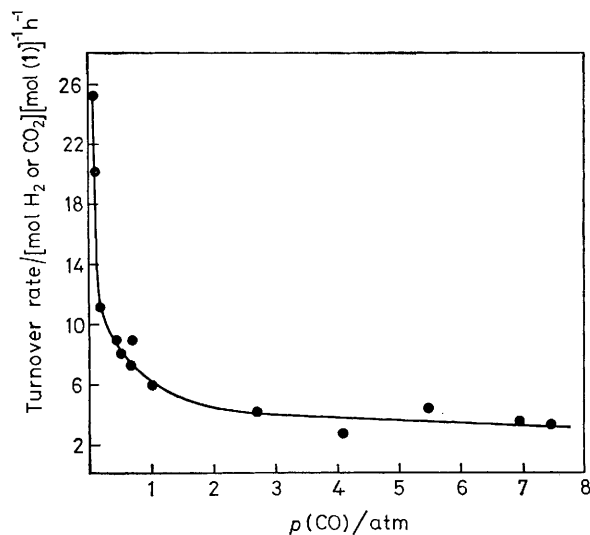


Figure 1. Dependence of turnover rate on the pressure of carbon monoxide, $p(\text{CO})$. In each case the catalyst precursor, (1), as the PF_6^- salt, (0.03 g), was dissolved in the solvent mixture (75 ml), see text.

considerably higher, as shown in Figure 1, and the system is one of the most active yet known under such mild conditions.†

A detailed explanation of the dependence of the rate of catalysis on $p(\text{CO})$ is not yet possible, but it appears to be based on the nature of species present in the catalytic solutions. At low $p(\text{CO})$ evaporation of catalytic solutions gives a complex showing terminal carbonyl bands in the i.r. spectrum [$\nu(\text{CO})$ 2060 and 2030 cm^{-1}] close to values for (2), Scheme 1, [$\nu(\text{CO})$ 2040 cm^{-1}] as well as a complex with $\nu(\text{CO})$ 1750 cm^{-1} . At higher $p(\text{CO})$ this latter crystalline yellow complex, (3), is the major product and is identified as a neutral platinum cluster. The ^{31}P n.m.r. spectrum shows that it is symmetrical, giving only a single ^{31}P resonance, with very complex satellites‡ due to coupling to ^{195}Pt , and the mass spectrum shows fragments containing four platinum atoms. Suitable crystals for X-ray studies have not yet been grown but we find that, when

† For comparison, $[\text{Pt}(\text{PEt}_3)_3]$ gives a corresponding turnover rate of 0.5 h^{-1} at 100 °C and 20 atm CO, $\text{RhCl}_3 \cdot \text{I}^-$ gives a rate of 1 turnover h^{-1} at 100 °C and 1 atm CO in aqueous acetic acid, and $\text{Fe}(\text{CO})_5 \cdot \text{NaOH}$ gives 0.6 turnover h^{-1} at 137 °C and 28 atm CO: T. Yoshida, Y. Ueda, and S. Otsuka, *J. Am. Chem. Soc.*, 1978, **100**, 3941; E. C. Baker, D. E. Hendriksen, and R. Eisenberg, *J. Am. Chem. Soc.*, 1980, **102**, 1020; A. D. King, R. B. King, and D. B. Yang, *J. Am. Chem. Soc.*, 1980, **102**, 1028.

‡ These satellites are more complex than in binuclear $\text{Pt}_2(\mu\text{-dppm})_2$ complexes or in some simpler clusters of platinum: A. Moore, P. S. Pregosin, and L. M. Venanzi, *Inorg. Chim. Acta*, 1981, **48**, 153.

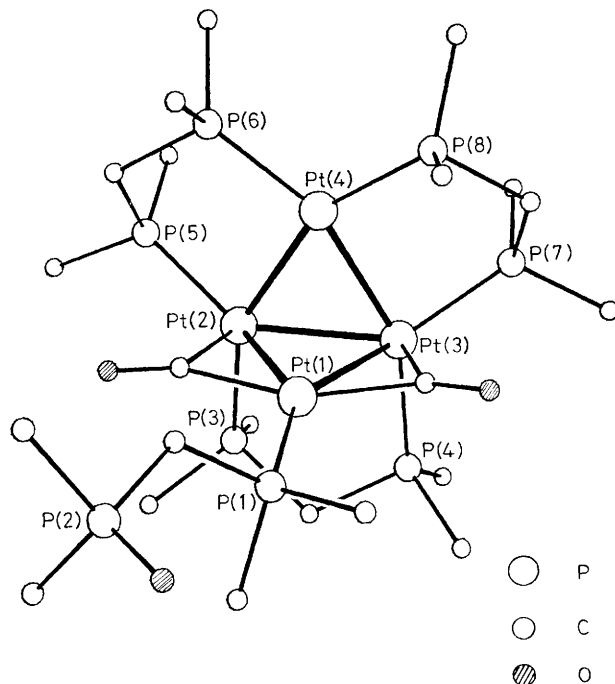
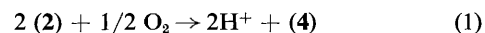


Figure 2. Molecular structure of $[\text{Pt}_4(\mu_2\text{-CO})_2(\mu_2\text{-Ph}_2\text{PCH}_2\text{PPh}_2)_3\{\text{Ph}_2\text{PCH}_2\text{P}(\text{O})\text{Ph}_2\}]$. Hydrogens and five carbon atoms of each phenyl group are omitted for clarity. Selected interatomic distances are: Pt(1)–Pt(2) 2.739(1), Pt(2)–Pt(4) 2.611(2), Pt(4)–Pt(3) 2.617(2), Pt(3)–Pt(2) 2.700(1), Pt(3)–Pt(1) 2.708(2), Pt(1) . . . Pt(4) 3.074(1), Pt–P 2.241(8)–2.337(8), Pt–C 1.99(3)–2.17(3) Å.

the catalysis is carried out in the presence of air, a neutral red cluster is formed which has $\nu(\text{CO})$ 1735 and 1835 cm^{-1} and which crystallizes from the reaction medium. This compound has a complex ^{31}P n.m.r. spectrum, but we have identified it by X-ray diffraction as $[\text{Pt}_4(\mu_2\text{-CO})_2(\mu_2\text{-dppm})_3\{\text{Ph}_2\text{PCH}_2\text{P}(\text{O})\text{Ph}_2\}]$, (4), and its stoichiometry can thus be understood in terms of formation from (2) according to equation (1).



Crystals of (4) are orthorhombic, space group $Pcab$, $M = 2390$, $a = 20.898(3)$, $b = 28.590(4)$, $c = 31.192(5)$ Å, $U = 18\,636$ Å³, $Z = 8$, $D_c = 1.704$ g cm^{-3} . The structure was solved, and refined to $R = 0.069$,¶ on the basis of 8601 diffractometric intensities with $I \geq 3\sigma(I)$, which were collected with Mo- K_α radiation ($\lambda = 0.71069$ Å) and corrected for absorption effects [$\mu(\text{Mo-}K_\alpha) = 59.1$ cm^{-1}].

In the molecular structure of (4) (Figure 2) the metal atoms display a highly distorted tetrahedral arrangement. Five edges of this tetrahedron are spanned by bridging carbonyl and dppm ligands, and the co-ordination sphere of the Pt(1) atom is completed by a phosphorus donor atom of the monodentate $\text{Ph}_2\text{PCH}_2\text{P}(\text{O})\text{Ph}_2$ ligand. The Pt–Pt distances along the bridged edges of the tetrahedron [2.611(2)–2.739(1) Å] are comparable with metal–metal bond lengths [2.669(1)–2.804(1) Å] reported for the platinum(0) clusters $[\text{Pt}_4(\mu_2\text{-CO})_5\text{-}(\text{PPhMe}_2)_4]^3$ and $[\text{Pt}_5(\text{CO})(\mu_2\text{-CO})_5(\text{PPh}_3)_4]^4$. The Pt(1)–Pt(4) separation [3.074(1) Å] is considerably longer, and the di-

¶ The atomic co-ordinates for this structure are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

hedral angle (83.7°) between the Pt(1), Pt(2), Pt(3) and Pt(2), Pt(3), Pt(4) planes is substantially greater, than the value expected for a regular tetrahedron (70.5°). Similar distortions have been observed in the $[\text{Pt}_4(\mu_2\text{-CO})_5(\text{PPhMe}_2)_4]^3$ and $[\text{Pt}_2\text{Co}_2(\text{CO})_5(\mu_2\text{-CO})_3(\text{PPh}_3)_2]^5$ complexes which have been formulated as 'butterfly' clusters and where Pt-Pt separations of 3.543(9) and 2.987(4) Å, respectively, are considered as non-bonding distances. The assumption that the Pt(1) and Pt(4) atoms are not directly bonded to each other leads to a 16-electron configuration for the Pt(1) and Pt(4) atoms, an 18-electron closed shell for Pt(2) and Pt(3) and to a 'butterfly', rather than tetrahedral, formalism for the tetraplatinum cluster in (4).

It is significant that the most common platinum(0) clusters are based on triangular Pt_3 units,^{3,4,6-8} and that the present Pt_4 unit is formed by dimerisation of a Pt_2 complex, albeit with extensive rearrangement of the μ_2 -dppm ligands.

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