Reversible Displacement of Dihydrogen by Carbon Monoxide in a Binuclear Platinum Hydride: a New Hydrido(carbonyl)diplatinum(I) Complex

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Received January 2, 1980

Although examples of the displacement of dihydrogen from transition metal complexes by carbon monoxide and of the reverse reaction are not uncommon [1-3], only a few reactions are known of the type described by equation (1) which are readily and quantitatively reversible.

$$L_{n}M \bigvee_{H}^{\prime} + CO \rightleftharpoons L_{n}M - CO + H_{2}$$
(1)

They include displacement of carbon monoxide from the mononuclear complexes $[Ir(CO)_3L_2]^+$ (L = tertiary phosphine or arsine) [4] which is reversible at room temperature and pressure and from the polynuclear complex $[Os_3(CO)_{12}]$. The latter gives $[H_2Os_3(CO)_{10}]$ with H_2 at 120 °C and atmospheric pressure [3] and the reverse also occurs readily at lower temperature [5]. This is the only previously reported example known to us of such a reaction involving a polynuclear complex. We now report the readily reversible reaction of the biplatinum complex $[Pt_2H_2(\mu-H)(\mu-dppm)_2][PF_6]$ (dppm = Ph₂-PCH₂PPh₂) with carbon monoxide:

$$[Pt_{2}H_{2}(\mu-H)(\mu-dppm)_{2}] [PF_{6}] + CO \iff$$

$$(I)$$

$$[Pt_{2}H(CO)(\mu-dppm)_{2}] [PF_{6}] + H_{2} \qquad (2)$$

$$(II)$$

The reactions of equation (2) occur at room temperature and atmospheric pressure. Under these conditions, the displacement of H₂ by excess CO from the previously reported complex (I) [6] (structure shown below) was complete in 48 h (giving 0.997 mol of H₂), while the displacement of CO by excess H₂ from (II) was complete in 72 h (giving 0.95 mol of CO). In each case, quantitative analysis of the gases was carried out by mass spectrometry using helium as internal calibrant, and the product (I) or (II) was isolated in high yield. The new complex (II) was fully characterised by its elemental analysis and its infrared and ¹H and ³¹P nmr spectra. The spectral data prove that complex (II) has the structure shown, with bridging dppm ligands and terminal hydride and carbonyl ligands. An alternative structure, with the roles of these ligands reversed, has been reported recently for the dppe (Ph₂PCH₂CH₂PPh₂) complex (III) formed in a similar way by displacement of H₂ with CO [7]. However, the reversibility of this latter reaction has not been reported. The different structures of (II) and (III) are readily rationalized in terms of dppm having a greater tendency to bridge than has dppe.



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Complex (II) gives a strong band in the infrared at 2040 cm⁻¹ due to the terminal carbonyl group, whereas (III) gives a band at 1740 cm⁻¹ due to the bridging carbonyl [7]. The terminal hydride in (I) is revealed in the ¹H nmr spectrum, as a multiplet due to coupling with ³¹P atoms [δ (PtH) – 6.73 ppm, ²J(PH) 11 Hz, ³J(PH) 6 Hz] with two sets of one quarter intensity satellites due to coupling with the near and far ¹⁹⁵Pt atoms [¹J(PtH) 990 Hz, ²J(PtH) 61 Hz] [6]. The ³¹P nmr spectrum is complex and very similar to that of the analogous complex [Pt2- $Cl(CO)(\mu$ -dppm)₂] [PF₆], whose spectrum has been discussed in detail and whose structure has been confirmed by X-ray crystallography [8]. The spectrum due to the dppm phosphorus atoms was analysed as an AA'BB' spin system, with superimposed spectra due to AA'BB'X and AA'BB'Y spin systems arising from molecules containing one ¹⁹⁵Pt atom [5] [$\delta(P_A)$ 6.81 ppm, ¹J(PtP) 2805, ²J(PtP) 62 Hz; $\delta(P_B)$ 3.60 ppm, ¹J(PtP) 3355, ²J(PtP) 82, ²J(P_AP_B) 46, ³J(P_AP_B) 40 Hz].

Complex (II) is yellow-orange in colour [cf. (III) which is turquoise-green]. It is stable in the solid

state and in dichloromethane solution in the presence of carbon monoxide but solutions rapidly darken in the absence of free CO. Formation of (II) gives a further example of binuclear reductive elimination of H₂ from (I) [9]. As well as undergoing oxidative addition of H₂, (II) adds methanethiol to give the known [Pt₂H₂(μ -SMe)(μ -dppm)₂] [PF₆] [10]. The reactions of equation (2) are of particular interest as models for reactions occurring during heterogeneous catalysis at a platinum surface, where activation of molecular hydrogen is often important.

Acknowledgements

We thank NSERC for financial support (to R.J.P.), NATO for a travel grant (to M.P.B. and R.J.P.), Dr. D. Cole-Hamilton for helpful discussions and Johnson-Matthey Ltd. for the generous loan of platinum.

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