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LETTER

Phosphine and phosphite complexes of a triplatinum hydride and evidence for slippage of the hydride ligand

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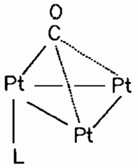
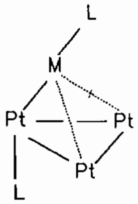
The coordinatively unsaturated cluster complexes $[Pt_3(\mu_3\text{-}H)(\mu\text{-dppm})_3]^+$ (**1**) [1] and $[Pt_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$ (**2**) [2] can easily and reversibly bind one or two additional ligands on the open Pt_3 face and so are useful mimics of chemisorption at a platinum surface. In either the surface or cluster case, the additional ligands can bind as terminal, μ_2- or μ_3-ligands and, in the clusters, the mode of binding of the original ligand may also be affected [3, 4]. For example, phosphine ligands add as terminal ligands to **2**, and in so doing cause a distortion of the μ_3-CO ligand as shown in **4** (dppm ligands omitted for clarity) [3, 4]. Similar distortions caused by neighboring ligands could also occur on surfaces but the current experimental techniques are only just beginning to be able to address problems at this level of sophistication [5, 6]. The distortion in **4** is unusual since it leads to a higher coordination number at Pt^2 (see Fig. 2 for atom labelling) than at Pt^1 and Pt^3, but it is substantiated both by X-ray structure determination in the solid state and by NMR analysis in solution [3, 4]. The structure of **4** has been rationalized in terms of the enhanced π-bonding to the carbonyl ligand from the more electron rich Pt^2 center [3, 4]. This raised the question of whether the hydride cluster **1** would form analogous complexes with phosphine ligands and whether the $Pt_3(\mu_3\text{-}H)$ unit would distort in the same way. Since hydride cannot act as a π-acceptor ligand, the opposite form of distortion might be expected.

Complex **1** does form adducts **3a**–**3d** with phosphite and phosphine ligands. The complex **3a** $[PF_6]\cdot 0.5CH_2Cl_2$ was characterized by X-ray structure analysis. X-ray data for **3a**$\cdot 0.5CH_2Cl_2$: $C_{78.5}H_{77}Cl_1F_6O_3P_8Pt_3$, $M_r = 2058.0$, triclinic, space group $P\bar{1}$, $a = 14.083(3)$, $b = 25.755(3)$, $c = 11.609(2)$ Å, $\alpha = 91.19(1)$, $\beta = 112.39(2)$, $\gamma = 90.36(1)°$, $V = 3892(2)$ Å^3, $Z = 2$, $D_m = 1.791(2)$, $D_c = 1.756$ Mg m^{-3}, $F(000) = 1994$ e, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $\mu = 5.397$ mm^{-1}, $T = 295$ K.



4, L = PR_3



5, L = PR_3

Intensity data were collected on an Enraf-Nonius CAD4F diffractometer by the ω–2θ technique using graphite monochromatized Mo radiation. Full matrix least-squares refinement on F (7581 unique observations with $I > 2.5\sigma(I)$, 326 variables, phenyl rings refined as rigid groups, C–C 1.392 Å, phenyl and methylene H atom contributions included but parameters not refined), converged at $R = 0.045$, $R_w = 0.056$. The cation (Fig. 1) contains a cluster of three platinum atoms, with bridging dppm ligands, and a terminal $P(OMe)_3$ ligand bound to Pt(2) which is perpendicular to the Pt_3 plane (P(7)–Pt(2)—Pt(1) = 91.5(1)°, P(7)–Pt(2)–Pt(3) = 90.8(1)°). The hydride ligand was not located by the structure determination.

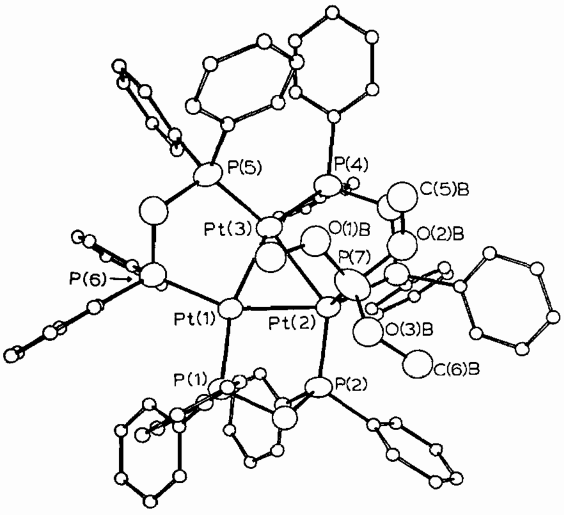


Fig. 1. A view of the structure of cation **3a**. Selected bond distances are Pt(1)–Pt(3) 2.592(1), Pt(1)–Pt(2) 2.635(1), Pt(2)–Pt(3) 2.705(1) Å, Pt–P(dppm) distances range from 2.215(3)–2.339(3) Å, Pt(2)–P(7) 2.268(4) Å.

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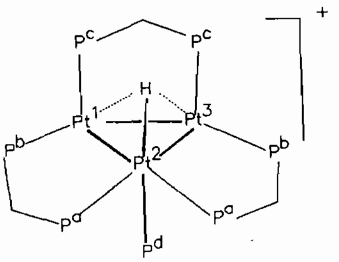
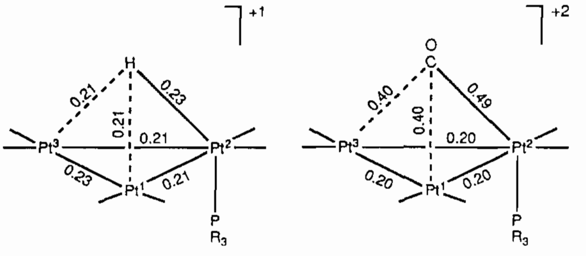


3a, $P^d = P(OMe)_3$
3b, $P^d = P(OEt)_3$
3c, $P^d = P(OPh)_3$
3d, $P^d = PPh_2Me$

The location of the hydride ligand by NMR techniques was complicated by the fluxionality of the complexes. Thus, at room temperature the ^{31}P NMR spectrum of **3a** gave a single resonance for P^a, P^b, P^c and the resonance due to P^d gave equal coupling to the three platinum atoms ($J_{av}(PtP) = 173$ Hz, 1:12:49:84:49:12:1 septet). Similarly, the hydride resonance in the ^1H NMR spectrum gave an average $J(PtH)$ coupling of 592 Hz. This fluxionality, which involves migration of the phosphite ligand between platinum centers [3, 4], could be frozen out at −90 °C and the ^1H, ^{31}P and ^{195}Pt NMR spectra expected for **3a** were then observed. The ^{31}P NMR spectrum contained four resonances due to non-equivalent phosphorus atoms P^a–P^d. The coupling $^1J(Pt^2P^d) = 6230$ Hz was established from both the ^{31}P and ^{195}Pt NMR spectra and coupling of P^d to Pt^1 and Pt^3 was not resolved. The hydride resonance even at −90 °C was very broad, but the 1:8:18:8:1 quintet due to coupling to Pt^1 and Pt^3 ($J(PtH) = 270$ Hz) was resolved, and is characteristic of a $Pt_2(\mu\text{-}H)$ group, and the coupling $^1J(Pt^2H) = 1200$ Hz was also clearly resolved in the ^1H coupled ^{195}Pt NMR spectrum. The 'average' PtH coupling is therefore calculated to be $(1/3 \times 1200) + (2/3 \times 270) = 580$ Hz, which agrees with the observed value from the room temperature NMR spectrum of 592 Hz. The ratio of $^1J(Pt^2H)/^1J(Pt^1H,Pt^3H) = 1200/270$ clearly indicates that the hydride is more strongly bound to Pt^2. We note that the Pt–Pt distances in **3a** (Pt(1)–Pt(3) = 2.592(1) Å, shortest) also suggest a weaker interaction of the hydride with Pt(1) and Pt(3), since hydrogen-bridged metal–metal bonds are longer than unbridged analogs. The distance Pt(2)–Pt(3) = 2.705(1) Å is longer than Pt(1)–Pt(2) = 2.635(1) Å by 50σ and may indicate that the hydride lies closer to Pt(3) than to Pt(1). There is no clear evidence for such a secondary distortion from the low temperature NMR spectra so that, if this distortion is present, a second fluxional process involving migration of the hydride between the Pt(2)–Pt(3) and Pt(2)–Pt(1) bonds must occur rapidly.



3 **4**

Fig. 2. Overlap populations calculated by EHMO for the compounds $[Pt_3(\mu_3\text{-}H)(PH_3)(\mu\text{-}H_2PCH_2PH_2)_3]^+$ and $[Pt_3(\mu_3\text{-}CO)(PH_3)(\mu\text{-}H_2PCH_2PH_2)_3]^{2+}$, which act as models for **3** and **4**. The ratio of overlap populations, $Pt^2L/Pt^1L = 1.2$ (L = CO) and 1.1 (L = H).

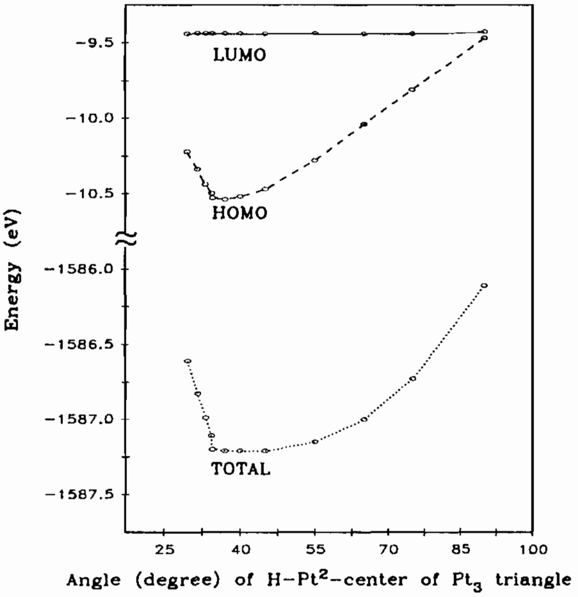


Fig. 3. An energy level diagram for $[Pt_3H(PH_3)(\mu\text{-}H_2PCH_2PH_2)_3]^+$ as a function of the angle θ = H–Pt^2–(center of Pt_3 triangle), showing only the energies of the HOMO and LUMO and the total energy. The shorter PtH distance was maintained at 1.85 Å (the other PtH distance(s) were then determined by the value of θ), and the symmetrical bridging $Pt_3(\mu_3\text{-}H)$ group has $\theta = 34.5°$. The HOMO has the character of a $p_zd_{z^2}$ hybrid orbital on Pt^2 with an sp^3 hybrid orbital on PH_3, and is mostly PtP antibonding. It also takes PtH antibonding character as the H atom moves from the $Pt_3(\mu_3\text{-}H)$ to either the terminal or μ_2-H bonding modes.

The nature of the hydride distortion was unexpected and so extended Hückel molecular orbital (EHMO) calculations were carried out [7]. First, calculations on both $[Pt_3(\mu_3\text{-}CO)(PH_3)(\mu\text{-}H_2PCH_2PH_2)_3]^{2+}$ and $[Pt_3(\mu_3\text{-}H)(PH_3)(\mu\text{-}H_2PCH_2PH_2)_3]^+$ were performed with the face-bridging carbonyl or hydride ligand constrained to the symmetrical μ_3 bonding mode. In each case, the overlap population $Pt^2(\mu_3\text{-}L)$ was greater than Pt^2- or $Pt^3(\mu_3\text{-}L)$ as shown in Fig. 2 (L = CO or H). In addition, a calculation of the energy as a function of the hydride position

(Fig. 3) showed overall a flat energy surface with a minimum in the range $\theta = 35$–$45°$, close to the $Pt_3(\mu_3\text{-}H)$ geometry ($\theta = 34.5°$) but clearly indicating a preference for binding to Pt^2. Thus, in contrast to earlier suggestions [3, 4], the distortion of the μ_3-ligand must be primarily a result of σ-bonding, assisted as a secondary effect by the π-bonding effect in the carbonyl cluster **4**. This is most easily rationalized by considering formation of the adducts from the hypothetical $[Pt_3(PH_3)(\mu\text{-}H_2PCH_2PH_2)_3]$ by addition of the electrophile H^+ or the hypothetical CO^{2+}, whereupon the electrophile binds more strongly to the more electron rich platinum center. Similar distortions are also present in the cluster cations $[Pt_3(\mu_3\text{-}MPPh_3)(\mu\text{-}CO)_3(PPh_3)_4]^+$ (**5**), M = Ag or Au [8, 9], (in plane μ-CO and PPh_3 ligands omitted for clarity), and this is significant since the Ph_3PM^+ cation is isolobal with H^+.

Acknowledgement

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