Polyhydrido-platinum Clusters: Synthesis and X-Ray Crystal Structures of [Pt₃H₆(PBuᵗ₃)₃], [Pt₄H₂(PBuᵗ₃)₄], and [Pt₄H₈(PPrⁱ₂Ph)₄]

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Summary Hydrogen reacts with [Pt(C₂H₄)₂(PBuᵗ₃)] to give the triangular complex [Pt₃H₆(PBuᵗ₃)₃] (**1**) which is dehydrogenated with C₂H₄ to form the tetrahedral complex [Pt₄H₂(PBuᵗ₃)₄] (**2**), whereas [Pt(C₂H₄)₂(PPrⁱ₂Ph)] reacts with hydrogen yielding directly the four-metal-atom sphenoidal cluster [Pt₄H₈(PPrⁱ₂Ph)₄] (**3**).

THERE is current interest in the application of metal clusters to the problems of homogeneous and heterogeneous catalysis.[1] Whereas many of the reported transition-metal clusters are electronically 'saturated' and relatively inert, a considerable chemistry has developed around some of the formally electron-deficient species such as [Os₃H₂(CO)₁₀].[2] We now report three new phosphine-stabilized clusters of platinum containing the catalytically interesting hydride ligand.

(1)
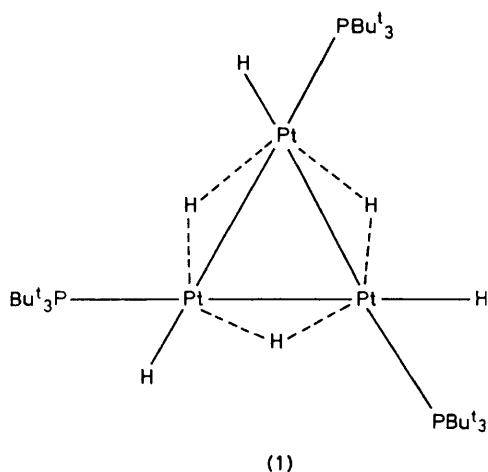
Reaction of [Pt(C₂H₄)₂(PBuᵗ₃)] with H₂ (300 atm, 15 °C, light petroleum, 16 h) gave large yellow crystals of complex (**1**) in good yield. The compound showed ν(PtH) i.r. absorptions at 2 180 and *ca.* 1 500 cm⁻¹, and elemental analysis indicated the formula [(PtPBuᵗ₃)ₓHᵧ]. Preliminary n.m.r. results suggested a triangular cluster (*C*₃ₕ or *C*₃ᵥ, *x* = 3, *y* = 6) and an X-ray diffraction study† (Figure 1) confirmed the triangular metal core. Unfortunately the structure is disordered in that although there
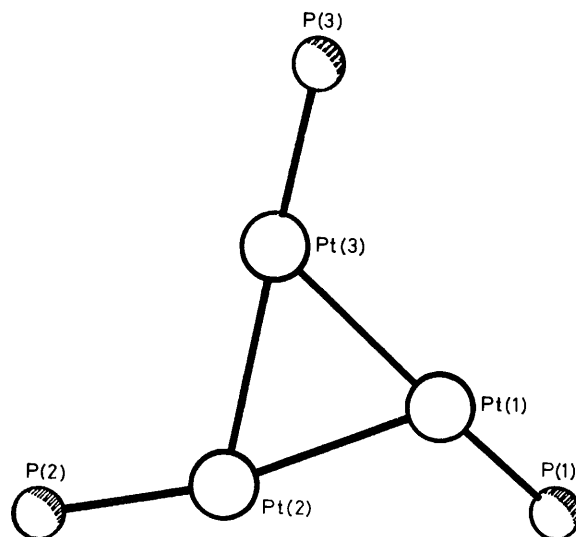

FIGURE 1. Molecular structure of complex (**1**) [Pt₃H₆(PBuᵗ₃)₃] showing only the heavy atoms. Mean distances (Å) and angles (°) are (e.s.d.s in parentheses refer to the mean): Pt–Pt 2·82(3), Pt–P 2·27(8); ∠P–Pt–Pt(*cis*) 115(2), P–Pt–Pt(*trans*) 159(8). Deviations (Å) from the plane of Pt(1), Pt(2), Pt(3): P(1) −1·07, P(2) −0·24, P(3) 0·99.

are only three phosphorus positions, the ligand axis may pivot at phosphorus without greatly affecting the packing of the molecules, thus allowing six platinum positions arranged in two triangles. This 'ball-joint' disordering is presumably a consequence of the almost hemispherical shape of the PBuᵗ₃ ligand. The solid-state structure is of low symmetry resembling the *C*₃ₕ model but with two phosphines on opposite sides of the metal plane.

The low-temperature (−80 °C) ¹H n.m.r. spectrum of complex (**1**) showed two sets of hydride signals of equal intensity at δ −4·00 [d with ¹⁹⁵Pt satellites, H_bridging, ²*J*(PH) 74, ¹*J*(Pt'H) 565, and ¹*J*(Pt''H) 405 Hz] and −7·54 [d with ¹⁹⁵Pt satellites, H_terminal, ²*J*(PH) 25, ¹*J*(PtH) 822, and ²*J*(PtH) 100 Hz]. At the same temperature the ³¹P n.m.r. spectrum indicates a single type of phosphorus nucleus with one short range and two long range couplings to ¹⁹⁵Pt, consistent with *C*₃ molecular symmetry. As the temperature is raised, terminal and bridging hydride

ligands exchange and move around the cluster, although at 90 °C the expected septet of quartets in the ^{1}H spectrum is not fully resolved. We have been unable to compare accurately the intensity of the hydride signal with that of the t-butyl protons. However, consideration of the molecular symmetry and the low-temperature n.m.r. spectra leads to the conclusion that $y = 6$, and the cluster is thus iso-electronic with a number of well established species such as [Pt$_3$(CNBu^t)$_6$] and [Pt$_3$(CO)$_3$(PR$_3$)$_3$].[3]

[Pt$_4$H$_2$(PBu$^t_3$)$_4$]   [Pt$_4$H$_8$(PPr$^i_2$Ph)$_4$]
        (2)   (3)
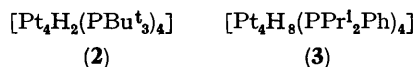
When a toluene solution of complex (1) was treated with ethylene (1 atm, 27 °C, 24 h) ethane was formed and a dark red crystalline compound (2) was isolated from the solution. The ^{31}P n.m.r. spectrum strongly suggested a tetrahedral {PtPBu$^t_3$}$_4$ cluster [28 °C, C$_6$D$_6$, δ 113·0 p.p.m., ^1J(PtP) 4843, ^2J(PtP) 376, and ^3J(PP) 38 Hz] and this was confirmed by a single-crystal X-ray diffraction study‡ (Figure 2a). One triangular face [Pt(1), Pt(2), Pt(3)] lies on a crystallographic mirror plane and the rest of the molecule is disordered about this plane. The molecular parameters are reasonably coherent and the deviations from T_d symmetry which are observed may be artifacts of the crystallographic disorder rather than a specific indication of hydride ligand positions. However, good evidence for the presence of hydrides was obtained from i.r. [v(PtH), 1 800—1 650 cm^{-1}] and ^{1}H n.m.r. data [28 °C, δ −35·4, five lines of the expected septet were observed, J(PtH) 564, J(PH) 0 Hz], the simplicity of the latter spectrum indicating fluxional behaviour. ^{195}Pt n.m.r. spectroscopy (^{1}H decoupled) revealed a second-order spectrum centred at δ 600·1 p.p.m. When the decoupling signal was removed each line of the spectrum split into a binomial triplet [J(PtH) 561 Hz] confirming the presence of two hydride ligands.

The sensitivity of the synthesis to the nature of the phosphine[4] was again demonstrated by the hydrogenolysis of [Pt(C$_2$H$_4$)$_2$(PPr$^i_2$Ph)] (light petroleum, 15 °C, 300 atm, 16 h) which afforded large orange crystals of complex (3) for which ^{31}P n.m.r. data (28 °C) indicated a digonally distorted tetrahedral (sphenoidal) core. A single-crystal X-ray diffraction study§ (Figure 2b) revealed a central Pt$_4$P$_4$ unit with S_4 symmetry and four short and two long Pt–Pt distances. From the i.r. spectrum it was evident that the molecule contained both terminal and bridging hydride ligands [v(PtH) 2 100 and 1 550 br. cm^{-1}]. At ambient temperatures these ligands are rapidly exchanging and were observed in the ^{1}H n.m.r. spectrum as a septet of quintets [δ −4·55, J(PtH) 286 and J(PH) 12·5 Hz]. The integrated intensity of the hydride signal was equivalent to eight hydrogens per molecule. At −80 °C the ^{1}H n.m.r. spectrum was markedly similar to that of (1), though not
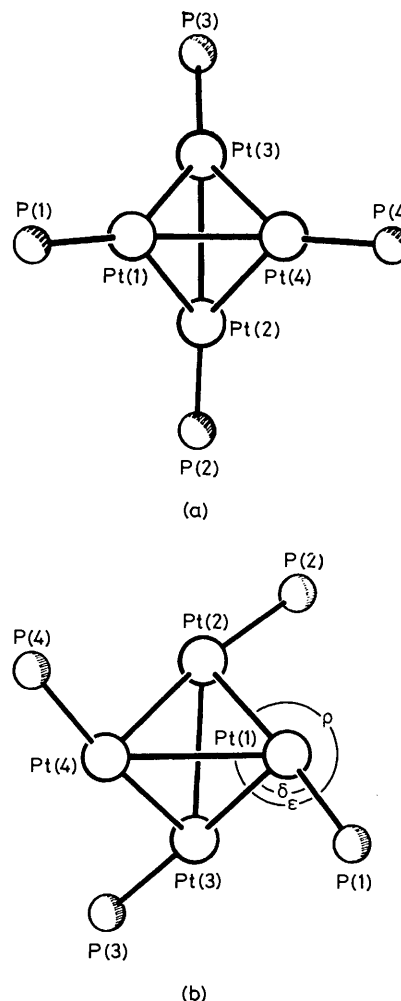

FIGURE 2. (a) Molecular structure of complex (2) [Pt$_4$H$_2$(PBu$^t_3$)$_4$] showing only the heavy atoms. Selected distances (Å) and angles (°) are: Pt(1)–Pt(2) 2·675(3), Pt(1)–Pt(3) 2·676(3), Pt(2)–Pt(3) 2·667(3), Pt(1)–Pt(4) 2·799(3), Pt(2)–Pt(4) 2·810(3), Pt(3)–Pt(4) 2·795(2), mean Pt–P 2·186(12); ∠ P–Pt–Pt range from 137·2(3) to 148·3(4). (b) Molecular structure of complex (3) [Pt$_4$H$_8$-(PPr$^i_2$Ph)$_4$] (molecule 1) showing only the heavy atoms. Selected distances (Å) and angles (°) are: Pt(1)–Pt(2) 2·909(3), Pt(1)–Pt(3) 2·857(2), Pt(2)–Pt(4) 2·848(3), Pt(3)–Pt(4) 2·870(3), Pt(2)–Pt(3) 3·158(3), Pt(1)–Pt(4) 3·010(3), mean Pt–P 2·23(3); the angles P–Pt–Pt fall in three groups, mean δ 104(4), mean ϵ 122(3), and mean ρ 167(3).

as well resolved, suggesting comparable distribution and bonding of the hydride ligands.

Comparison of complexes (2) and (3) reveals a number of striking contrasts such as the colour, the large difference in chemical shift of the hydride signals, and the shorter Pt–Pt

‡ Crystal data: C$_{48}$H$_{110}$P$_4$Pt$_4$ (2), $M = 1$ 591, orthorhombic, space group $Pnam$, $a = 29·730(10)$, $b = 16·612(7)$, $c = 13·279(4)$ Å, $U = 6$ 558(7) Å^3, $Z = 4$, $F(000) = 3$ 080. Current $R = 0·059$ (R' 0·064) for 1 899 intensities [$I > 3\sigma(I)$].

§ Crystal data: C$_{48}$H$_{84}$P$_4$Pt$_4$ (3), $M = 1$ 565, 2 independent molecules per asymmetric unit, orthorhombic, space group $Pna2_1$, $a = 17·047(3)$, $b = 33·292(17)$, $c = 18·741(7)$ Å, $U = 10$ 636(11) Å^3, $Z = 4$, $F(000) = 5$ 952. Current $R = 0·087$ (R' 0·083) for 5 588 intensities [$I > 4\sigma(I)$].

separations in (2), presumably all consequences of the different numbers of cluster-bonding electrons. Neither compound conforms to the concept of a saturated cluster though this is not unexpected as platinum is known[3,5] to deviate frequently from the electron-counting rules which prevail in the centre of the transition series.

The results reported here and previously[4] suggest that by the judicious choice of phosphine ligand it is possible to synthesize platinum clusters of varying size.

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[3] J. W. Lauher, *J. Am. Chem. Soc.*, 1978, **100**, 5305; F. G. A. Stone, *Inorg. Chim. Acta*, 1981, **50**, 33.
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