A High Ratio Hydrido-metal Cluster: Synthesis and *X*-Ray Crystal Structure of $[Pt_5H_8(PBu^t_2Ph)_5]$

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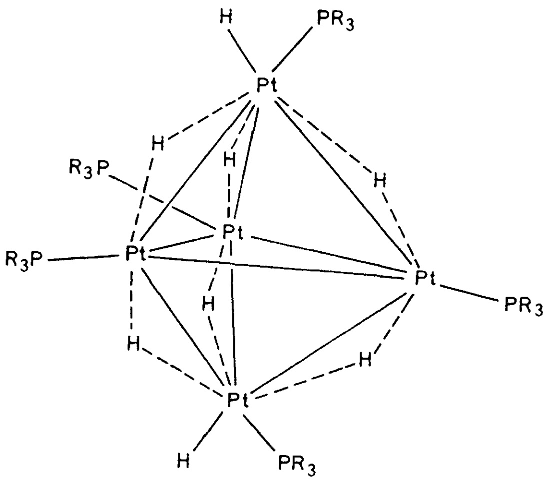
Summary Reaction of $[Pt(C_2H_4)_2(PBu^t_2Ph)]$ with hydrogen affords $[Pt_5H_8(PBu^t_2Ph)_5]$ which has a distorted trigonal bipyramidal solid-state structure and time-averaged D_{3h} symmetry in solution, with two terminal and six bridging hydride ligands.

ALTHOUGH hydrido-transition metal clusters have been known for many years, few are reported in which the ratio hydride: metal exceeds unity.[1] We report here the formation of a cluster of this type by a simple synthetic method which may have much wider application.

We have previously reported the synthesis[2] and some of the chemistry[3] of complexes of the type $[Pt(C_2H_4)_2L]$ ($L = PR_3$ or AsR_3) in which the ethylene ligands are readily displaced, providing a convenient source of the '$Pt(PR_3)$' fragment. Reaction of $[Pt(C_2H_4)_2(PBu^t_2Ph)]$ with H_2 (300 atm) at 15 °C in light petroleum for five days yielded large brown crystals of compound (**1**). Analytical data suggested the stoicheiometry $[\{Pt(PBu^t_2Ph)\}_n]$ and the i.r. spectrum confirmed the presence of both terminal and bridging hydride ligands [$\nu(PtH)$ 2 140 and 1 630 br. cm^{-1}]. Phosphorus-31 (^1H-decoupled) n.m.r. spectroscopy revealed two complicated sets of signals centred at δ 88·2 and 84·4 p.p.m. (relative to external H_3PO_4) which were interpreted in terms of a trigonal bipyramidal cluster of $Pt(PBu^t_2Ph)$ units [$^1J(Pt_{ax}P_{ax})$ 4 850, $^1J(Pt_{eq}P_{eq})$ 4 050, $^2J(Pt_{ax}P_{eq})$ 224, $^2J(Pt_{eq}P_{ax})$ 245, $^2J(Pt_{eq}P_{eq})$ 230, $^3J(P_{ax}P_{eq})$ 7, and $^3J(P_{eq}P_{eq})$ 62 Hz] with the low-field signal ascribed to the axial phosphorus nuclei.



(1) $R_3 = Bu^t_2Ph$

A single-crystal *X*-ray diffraction study was undertaken to determine whether the apparent D_{3h} symmetry of (**1**) was maintained in the solid state and if so, how it was compatible with the presence of both terminal and bridging hydride ligands.

Crystal data: $C_{70}H_{123}P_5Pt_5$, $M = 2095{\cdot}08$, monoclinic, space group $P2_1/n$, $a = 23{\cdot}459(5)$, $b = 14{\cdot}326(3)$, $c = 26{\cdot}313(7)$ Å, $\beta = 115{\cdot}84(2)°$, $U = 7959(3)$ Å^3, $Z = 4$, $D_m = 1{\cdot}8$, $D_c = 1{\cdot}75$ g cm^{-3}, $F(000) = 4\,032$, $\mu(\text{Mo-}K_\alpha) = 89{\cdot}8$ cm^{-1}. Current $R = 0{\cdot}057$ ($R' = 0{\cdot}051$) for 5 867 absorption-corrected intensities [293 K, $2{\cdot}9 < 2\theta < 50°$, $I > 3\sigma(I)$, Syntex P3 diffractometer, Mo-K_α].

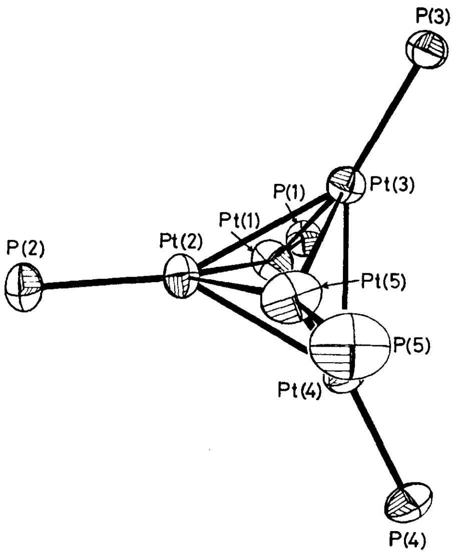


FIGURE. Molecular structure of $[Pt_5H_8(PBu^t_2Ph)_5]$ showing only the metal cluster and ligated phosphorus atoms. Selected distances (Å) and angles are Pt(1)–Pt(2) 2·850(1), Pt(1)–Pt(3) 2·865(1), Pt(1)–Pt(4) 3·134(1), Pt(2)–Pt(3) 2·724(1), Pt(2)–Pt(4) 2·750(1), Pt(2)–Pt(5) 2·869(1), Pt(3)–Pt(4) 2·769(1), Pt(3)–Pt(5) 3·085(1), and Pt(4)–Pt(5) 2·868(1); ∠P(1)–Pt(1)–Pt(5) 18·3 and P(5)–Pt(5)–Pt(1) 15·0°.

The molecule† (Figure) deviates appreciably from D_{3h} symmetry in (a) the long Pt(1)–Pt(4) and Pt(5)–Pt(3) separations relative to the other four axial-equatorial Pt–Pt bonds and (b) the bending of P(1) and P(5) away from the Pt(1)....Pt(5) axis (18·3 and 15·0°, respectively). This latter effect suggests that the terminal hydride ligands are bonded to the axial platinum atoms, particularly as the equatorial phosphorus atoms lie close to the equatorial plane [defined by Pt(2), Pt(3), and Pt(4)] and show little deviation (within 6°) from the line bisecting $\angle Pt_{eq}–Pt_{eq}–Pt_{eq}$.

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† Atomic co-ordinates for this work 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.

Refinement of the structure has so far failed to provide any direct evidence of the hydride ligands. However a ^1H Fourier-transform n.m.r. spectrum (200 MHz) revealed two signals at δ $-5{\cdot}45$ and $-14{\cdot}13$. The signal at δ $-14{\cdot}13$ consisted of a singlet with ^{195}Pt satellites [J(PtH) 750 Hz] in the proportions 1 : 4 : 1, consistent with a terminal hydride ligand. The signal at δ $-5{\cdot}45$ [J(PtH) 470 and J(Pt′H) 630 Hz] was broader and the integrated intensity of the satellites was approximately the same as that of the central signal. Moreover there was evidence of a weak set of 'double' satellites, suggesting that this signal was due to hydride ligands bridging two platinum atoms. An experiment with low pulse width and long repetition time to avoid saturation gave the relative integrated intensities for H_{ortho} : $H_{bridging}$: $H_{terminal}$ of 10 : 6·2 : 1·7, implying the presence in the molecule of six bridging and two terminal hydride ligands. It would therefore be reasonable to place the bridging hydride ligands along each of the six axial-equatorial Pt–Pt bonds. Two terminal hydrides would necessarily reside on the axial platinum atoms as suggested by the crystallographic evidence mentioned above.

The lower solid-state symmetry may be reconciled with the solution n.m.r. data if it is assumed that the axial Pt(H)(PBu^t_2Ph) units rotate with respect to the equatorial Pt_3 triangle. This motion would be accompanied by a time-averaging of the axial-equatorial Pt–Pt separations. It is, however, implicit in the Pt–H coupling pattern that any such motion occurs without simultaneous exchange (on the n.m.r. time scale) of hydride ligands either between two bridging positions or between terminal and bridging positions.

Our studies suggest that complex (**1**) is merely one member of a group of compounds [$(R_3PPt)_xH_y$] which includes trinuclear and tetranuclear clusters. The properties of the phosphine ligand appear crucial in dictating the course of these reactions.

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[1] A. P. Humphries and H. D. Kaesz, *Prog. Inorg. Chem.*, 1979, **25**, 145.
[2] N. C. Harrison, M. Murray, J. L. Spencer, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1978, 1337.
[3] M. Ciriano, M. Green, J. A. K. Howard, J. Proud, J. L. Spencer, F. G. A. Stone, and C. A. Tsipis, *J. Chem. Soc., Dalton Trans.*, 1978, 801.