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Generation and Interconversions of the Di- and Tri-nuclear Platinum Complexes $[Pt_2H_2(dppe)_2]$, $[Pt_2H_3(dppe)_2]^+$, and $[Pt_3H_3(dppe)_3]^+$. Crystal and Molecular Structure of $[Pt_3H_3(dppe)_3]^+[BEt_4]^-$, $(dppe = Ph_2PCH_2CH_2PPh_2)$

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Multinuclear n.m.r. and crystallographic studies on $[Pt_2H_2(dppe)_2]$, $[Pt_2H_3(dppe)_2]^+$, and $[Pt_3H_3(dppe)_3]^+$ are described, the structure of the latter being unambiguously established for the first time.

The study of phosphane-stabilised platinum centres continues to be an area of intense interest.^{1,2} Whilst early studies explored the reactivity of metal centres supported by bulky chelate phosphanes,^{3,4} the potential for the generation of extremely reactive '[PtP₂]' fragments (P = phosphane ligand), in complexes having small PPtP angles,⁵ has led to an upsurge of interest in platinum centres bearing less sterically demanding ligands. This area has been treated theoretically⁶ and has recently been the subject of some elegant experimental work.^{7,8} We report here some investigations concerning the reactivity of mono-, di-, and tri-metallic platinum complexes incorporating the ligand dppe. $[PtH_{2}(dppe)] \qquad [Pt_{2}H_{2}(dppe)_{2}]$ (1)
(2) $Ph_{2}P \qquad H \qquad Pt \qquad Pt \qquad Pt \qquad Ph_{2}P \qquad (3)$

Table 1. ${}^{1}H$ N.m.r. data for $[Pt_{3}H_{3}(dppe)_{3}]^{+}[BEt_{4}]^{-}$ (4).			
Resonance	δ(1H)	T_1/s^a	Rel. int.ª
Pt <i>H</i>	-1.60	0.44(2) ^b	3.1
BCH ₂ CH ₃	-0.08	3.053(4)	8.0
BCH_2CH_3	0.68	4.941(9)	12.0
$P(CH_2)_2P$	2.11	0.22(2)	11.7
PPh(o)	7.54	0.780(3))
PPh(m)	7.04	1.062(3)	60.0
PPh(p)	7.23	1.15(3)	J

^a Measured by inversion recovery in $[{}^{2}H_{8}]$ THF at 297 K after repeated freeze-pump-thaw cycles. Estimated errors in the last digit are shown in parentheses. Integration: Measured using a 90° flip angle (30 µs pulse); recovery time 20 s. Bruker WM spectrometer, 360.1 MHz.^b Central septet resonance.

Treatment of a tetrahydrofuran (THF) suspension of $[PtCl_2(dppe)]$ with LiBEt₃H at -40 °C yields the mononuclear complex $[PtH_2(dppe)]$ (1), which decomposes with elimination of dihydrogen upon warming to room temperature and quantitatively produces (2), formulated as $[Pt_2H_2(dppe)_2]$ on the basis of ¹H, ³¹P, and ¹⁹⁵Pt n.m.r. measurements. The dinuclear nature of the complex is deduced from the characteristic patterns produced in the ³¹P-{¹H} n.m.r. spectrum⁹ and hydride multiplicity confirmed by the ¹⁹⁵Pt-¹H coupled spectrum (Figure 1).[†] A nickel analogue of (2) is known,^{10,11} but there appear to be no reliable literature reports of related platinum compounds[±] as earlier studies involving bulky chelating phosphane ligands have invariably led to relatively stable cis-[PtH₂PP] complexes (PP = $Bu_{2}^{t}P(CH_{2})_{n}PBu_{2}^{t}$, n = 2, 3; or $o-(But_2PCH_2)_2C_6H_4$).^{3,4} Furthermore, the thermal decomposition of the sterically hindered hydride complex $[PtH_2(But_2P(CH_2)_3PBut_2)]$ is reported to yield a dinuclear compound bearing no hydride ligands which results merely from the dimerisation of two '[PtP₂]' fragments.³ Although solvent effects appear to be important in the formation of (2), the principal driving force for the decomposition of (1) is

(4) $\delta({}^{1}\text{H})$ (hydride) -1.60, $\delta({}^{11}\text{B})$ -16.9, $\delta({}^{31}\text{P})$ -82.2, $\delta({}^{195}\text{Pt})$ -3129; ${}^{1}J_{PtH}$ 386, ${}^{1}J_{PtP}$ 2834, ${}^{1}J_{PtPt}$ 259, ${}^{2}J_{PtP}$ 107, ${}^{2}J_{PH}$ 29, ${}^{3}J_{PP}$ 18 Hz.

Chemical shifts in p.p.m., relative to Me_4Si , $BF_3 \cdot OEt_2$, $P(OMe)_3$, or K_2PtCl_4 as appropriate; positive shifts being to high frequency of the reference.

[‡] In an earlier study (H. C. Clark and M. J. Hampden-Smith, J. Am. Chem. Soc., 1986, **108**, 3829) it has been proposed that the thermal decomposition of $[PtH_2\{cy_2P(CH_2)_nPcy_2\}]$ (n = 2, 3; cy = cyclohexyl)leads to the dinuclear complexes $[Pt_2H_2\{cy_2P(CH_2)_nPcy_2\}_2]$. Such a reaction appears entirely feasible. However, the n.m.r. parameters quoted in the earlier paper are not consistent with the results obtained here and closely resemble the data presented by Minghetti and co-workers¹² for the cationic species $[Pt_2H_3(dppe)_2]^+$. Since no details of the determination of hydride multiplicity were reported, we presume that the complex observed previously was $[Pt_2H_3-{cy_2P(CH_2)_nPcy_2}_2]^+OH^-$.



Figure 1. ¹⁹⁵Pt-¹H Coupled n.m.r. spectrum of (2).

presumably the small chelate bite angle and the high *trans*influence of the dppe ligand.⁹ Complex (2) shows an appreciable stability in solution and purified samples remain unchanged after several days in THF at 20 °C. Preliminary studies of reactivity towards Lewis bases reveal that (2) serves as a reactive source of [Pt(dppe)] fragments.

Rapid quenching of (2) with an excess of water or methanol immediately affords the well known cationic platinum species (3),^{12,13} but purging solutions of (2) with a stream of moist dinitrogen slowly yields the trinuclear cluster $[Pt_3H_3(dppe)_3]^+$ (4). Although the latter has been observed previously by Minghetti and co-workers,¹⁴ the hydride multiplicity and the molecular structure were not established in the earlier study.14 We now report a single crystal X-ray diffraction study of the $[Pt_3H_3(dppe)_3]^+$ cation (as its $[BEt_4]^-$ salt) and n.m.r. data⁺ which unambiguously establish the identity of the cluster. The ¹⁹⁵Pt-¹H coupled n.m.r. spectrum shows a 1:3:3:1 quartet of multiplets (${}^{1}J_{PtH}$ 386 Hz) as expected for three hydrides, and further confirmation of the hydride multiplicity was provided by integration of the ¹H n.m.r. spectrum (Table 1).¹⁵ Complex (4) is fluxional in solution at room temperature¹⁴ but broad resonances attributable to the terminal hydride ligands may be detected at $-105 \,^{\circ}\text{C} (\delta - 3.07, {}^{1}J_{\text{PtH}} \, 915 \,\text{Hz}, {}^{2}J_{\text{PH}(trans)} \, 196 \,\text{Hz}).$

The structure adopted by (4) in the solid state is shown in Figure 2.§ The platinum atoms form an isosceles triangle with

⁺ *N.m.r.* data (in THF or $[{}^{2}H_{8}]$ THF): (All at 30 °C except for * recorded at -60 °C): (2) $\delta({}^{1}H)(hydride) +0.30^{*}$, $\delta({}^{3}P) -68.1$, $\delta({}^{195}Pt) -2748$; ${}^{1}J_{PtH} 564$, ${}^{1}J_{PtP} 2201$, ${}^{1}J_{PtPt} 1902$, ${}^{2}J_{PtP} 388$, ${}^{2}J_{PH} 42$, ${}^{3}J_{PP} 44$ Hz.

[§] Crystal data: C₈₆H₉₅BP₆Pt₃, M = 1910.6, monoclinic, space group $P2_1/c$, a = 12.175(3), b = 25.929(5), c = 27.133(4) Å, $\beta = 101.76(1)^\circ$, U = 8385.7 Å³, Z = 4, $D_c = 1.51$ g cm⁻³, monochromated Mo- K_{α} radiation, $\lambda = 0.71069$ Å, $\mu = 52.0$ cm⁻¹. The structure was solved by routine heavy atom methods and refined by full matrix least squares, using 4173 reflections with $I > \sigma(I)$ measured on an Enraf-Nonius CAD4 diffractometer. The final residuals were R = 0.068, R' = 0.080. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



Figure 2. X-Ray crystal structure of cation $[Pt_3H_3(dppe)_3]^+$ (4). Selected intramolecular distances (Å) and angles (°). Pt(1)–Pt(2) 2.683(2), Pt(1)–Pt(3) 2.641(2), Pt(1)–P(1) 2.261(8), Pt(1)–P(2) 2.283(9), Pt(2)–P(3) 2.236(10), Pt(2)–P(4) 2.300(9), Pt(3)–P(5) 2.246(10), Pt(3)–P(6) 2.292(10); Pt(2)–Pt(1)–Pt(3) 99.73(6), Pt(2)–Pt(1)–P(1) 169.2(3), Pt(2)–Pt(1)–P(2) 84.5(2), Pt(3)–Pt(1)–P(2) 173.1(3), P(1)–Pt(1)–P(2) 87.7(3), Pt(1)–Pt(2)–P(3) 160.4(2), Pt(1)–Pt(2)–P(4) 106.2(3), P(3)–Pt(2)–P(4) 86.9(4), Pt(1)–Pt(3)–P(5) 165.5(3), Pt(1)–Pt(3)–P(6) 105.0(3), P(5)–Pt(3)–Pt(6) 86.7(4).



(4) Figure 3. Proposed structure of cation (4), [Pt₃H₃(dppe)₃]⁺.

Pt(2) and Pt(3) separated by *ca.* 4.01 Å which clearly precludes any significant bonding interaction between these centres. Although the hydride ligands could not be located directly from the final difference Fourier map, their positions may be inferred. Vacant sites in the co-ordination spheres of Pt(2) and Pt(3) are indicative of terminal hydrides, whose presence is consistent with long *trans*-PtP bonds [Pt(2)–P(4) 2.300(9), Pt(3)–P(6) 2.292(10) Å]. These lie close to the length of Pt–P *trans* to H [2.312(1) Å] previously observed¹³ during a neutron diffraction study of [Pt₂H₃(dppe)₂]+[BPh₄]⁻. Additionally, the molecular skeleton of (4) has an approximate C_2 axis lying in the plane of the Pt₃ triangle and bisecting the

Pt(2)Pt(3) vector, suggesting that if the symmetry is maintained the remaining hydride would be located close to this axis. The structure of (4) is then best represented as $[Pt_3(\mu^3-H)(\eta^{1-}H)_2(dppe)_3]^+$ (Figure 3), where the bridging hydride links the three metal centres, conferring stability upon the Pt–Pt bonds. Accordingly the Pt(1)–Pt(2) and Pt(1)–Pt(3) separations [2.683(2) and 2.641(2) Å] lie in a range typical of Pt–Pt bonds bridged by one electron donor ligands.^{2,13,16} A μ^3 hydride also stabilises¹⁷ the isoelectronic iridium cluster $[Ir_3H_7(dppp)_3]^{2+}$ [dppp = Ph₂P(CH₂)₃PPh₂].

The possible interconversion of (3) to (4) involves the formal capture of a [Pt(dppe)] fragment by the $[Pt_2H_3(dppe)_2]^+$ cation¹⁸ and it is interesting to speculate that the formation of the thermodynamically favoured cluster (4) may proceed *via* initial protonation of (2) to yield (3) and subsequent abstraction of a [Pt(dppe)] fragment from residual (2). Consistent with this hypothesis is our observation that deprotonation of (3) by DBU¹⁹ (1,8-diazabicyclo[5.4.0]undec-7-ene) leads cleanly and quantitatively to (4) and that $[Pt_2H_2(dppe)_2]$ is detected spectroscopically during the reaction. Further investigations of the cluster building potential of (2) are in progress.

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