A Fluxional Tetraplatinum Cluster: Solution and Solid State Structure of the Cation $[Pt_4(\mu\text{-}H)(\mu\text{-}CO)_2(\mu\text{-}Ph_2PCH_2PPh_2)_3(Ph_2PCH_2PPh_2)]^+$

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The 58-electron cationic cluster complex $[Pt_4(\mu\text{-}H)(\mu\text{-}CO)_2(\mu\text{-dppm})_3(\text{dppm-}P)]^+$, dppm = $Ph_2PCH_2PPh_2$, has been characterized in solution by n.m.r. spectroscopy and in the solid by *X*-ray analysis of the PF_6^- salt; the cation displays novel fluxionality with rapid rotation of a μ-H below and a $\mu\text{-}Pt(CO)_2(\text{dppm-}P)$ unit above a $Pt_3(\mu\text{-dppm})_3^+$ triangle.

We report the synthesis and solid state structure of a new tetranuclear platinum cluster cation $[Pt_4(\mu\text{-}H)(\mu\text{-}CO)_2(\mu\text{-dppm})_3(\text{dppm-}P)]^+$ (**1**), dppm = $Ph_2PCH_2PPh_2$, and describe its unusual fluxionality, which is apparent from muitinuclear n.m.r. spectroscopy.

Complex (**1**) as the PF_6^- salt was prepared by reaction of $[Pt(O_2CCF_3)_2(\text{dppm})]$ in aqueous methanol with CO (5 atm) at 100 °C for 3 days, followed by anion exchange using $NH_4[PF_6]$. Recrystallization from acetone–pentane gave a deep red, air-stable solid. Its *X*-ray crystal structure analysis† reveals that the cation (**1**) contains a distorted Pt_4 tetrahedron (see Figure 1). Of the six Pt–Pt vectors, five, with lengths in the range 2.613(1)—2.750(1) Å, correspond to metal–metal bonds. The Pt(2)–Pt(4) distance [3.082(1) Å] is substantially longer and appears to preclude direct Pt–Pt bonding. Complex (**1**), like other 58e Pt_4 clusters,[1—5] thus contains a butterfly arrangement of the metal atoms. The hinge torsion angle Pt(2)–Pt(1)–Pt(3)–Pt(4) of 83.7(1)° lies between the values of 70.5° in a regular tetrahedron and those of 89.4 and 96.8° found in different crystalline forms of $[Pt_4(CO)_5(PMe_2Ph)_4]$.[1,2] The edges of the Pt(1)Pt(3)Pt(4) triangle in (**1**) are bridged by three μ-dppm ligands so that the resulting Pt_3P_6 unit is roughly planar. On opposite sides of the plane, the Pt(1)–Pt(3) bond is further bridged by a $Pt(CO)_2(\text{dppm-}P)$ fragment and by a μ-H ligand (the parameters of the μ-H

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† Crystallographic measurements were made with Mo *X*-rays on an Enraf-Nonius CAD4F diffractometer, using a plate-shaped 0.48 × 0.48 × 0.08 mm specimen. *Crystal data:* $C_{102}H_{89}F_6O_2P_9Pt_4$, M = 2519.9, orthorhombic, space group *Pcab* (No. 61), $a = 21.120(6)$, $b = 28.962(4)$, $c = 31.026(4)$ Å, $Z = 8$, $D_c = 1.764$ g cm^{-3}, λ(Mo-K_α) = 0.71069 Å, μ(Mo-K_α) = 61.5 cm^{-1}, $F(000) = 9744$.

The structure is based on 6261 independent, absorption-corrected intensities [$\theta(\text{Mo-}K_\alpha) \leqslant 23°$, $I \geqslant 3\sigma(I)$]. Full-matrix least-squares refinement of 385 parameters (phenyl rings and PF_6^- as rigid groups) gave $R = 0.038$, $R_w = 0.045$. 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.

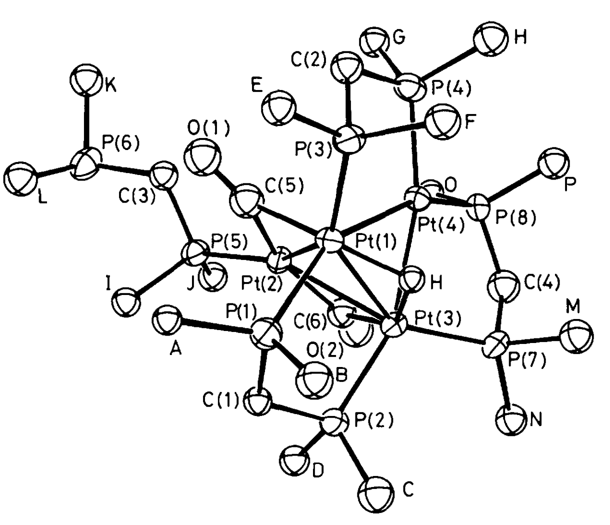
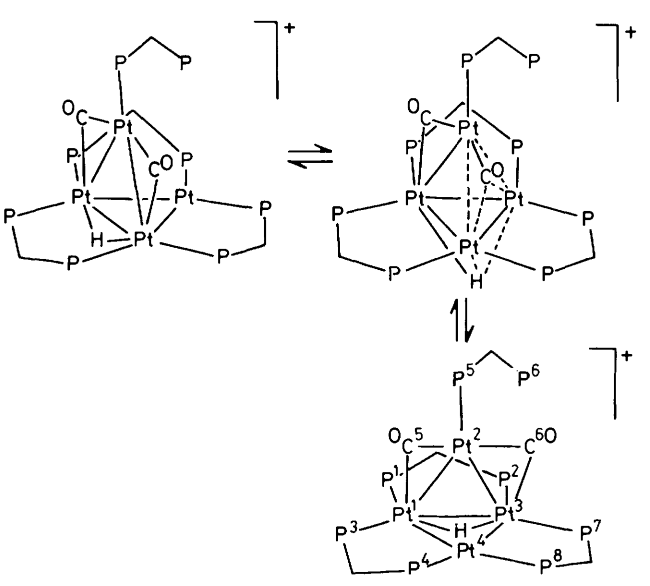


Figure 1. A view of the inner skeleton of the cation (**1**). For clarity, only the *ipso* carbon atoms of the sixteen phenyl rings A—P are shown and hydrogen atoms, apart from the μ-H bridge atom, are omitted. Selected distances are: Pt(1)–Pt(2) 2.750(1), Pt(1)–Pt(3) 2.705(1), Pt(1)–Pt(4) 2.620(1), Pt(2)–Pt(3) 2.720(1), Pt(2) · · · Pt(4) 3.082(1), Pt(3)–Pt(4) 2.613(1), Pt–P 2.250(5)—2.266(5) except for Pt(1)–P(1) 2.360(4) and Pt(3)–P(2) 2.329(5), Pt(1)–C(5) 2.09(2), Pt(2)–C(5) 1.97(2), Pt(2)–C(6) 1.98(2), Pt(3)–C(6) 2.15(2), Pt(1)–H 1.69(12), Pt(3)–H 2.02(13) Å.

ligand have been refined successfully†). In view of the mechanism of fluxionality of (**1**) (see below), it may be significant that both Pt(μ-CO)Pt bridges are unsymmetrical, with the Pt(2)–C bond being the shorter in each (Figure 1), and that the bridging C atoms are displaced by 0.1—0.2 Å from the Pt(1)Pt(2)Pt(3) plane towards Pt(4). We also note the near isomorphism and similar cluster geometries of (**1**) [PF_6] and the neutral species [$Pt_4(CO)_2(\mu\text{-dppm})_3(Ph_2PCH_2P(O)Ph_2)$].[5]

The fluxionality of (**1**) is defined unambiguously from the variable temperature ^1H, ^{13}C (of ^{13}CO enriched samples), ^{31}P, and ^{195}Pt n.m.r. spectra,‡ and is aided particularly by the temperature dependence of the ^{195}Pt (I = ½, abundance 33%) satellite spectra. The symmetry of the ion (**1**) was most readily determined from the ^{31}P n.m.r. spectra. At room temperature, three resonances in a 1 : 1 : 6 intensity ratio were observed due to P^5, P^6, and (P^1—P^4, P^7, P^8) respectively, clearly indicating fluxionality leading to effective 3-fold symmetry of the $Pt_3(\mu\text{-dppm})_3$ unit but no fluxionality of the Pt^2(dppm-*P*) ligand of the type observed previously.[6] At −40 °C, the μ-dppm ^{31}P resonance split into three as expected for the static structure (**1**). Similarly, at room temperature the PtH resonance in the ^1H n.m.r. spectrum appeared as a



Scheme 1

1 : 12 : 52 : 82 : 52 : 12 : 1 septet[6] due to equal coupling to Pt^1, Pt^3, and Pt^4, $^1J(PtH)_{obs.}$ = 508 Hz, whereas at −40 °C a more complex resonance with $^1J(Pt^1H)$ = $^1J(Pt^3H)$ = 670 Hz (1 : 8 : 18 : 8 : 1 quintet) and $^2J(Pt^4H)$ = 168 Hz (1 : 4 : 1 triplet) was observed as expected for the static structure (**1**). The 'average' J(PtH) is expected to be 1/3(2 × 670 + 168) = 503 Hz, in agreement with the observed value, if the hydride is fluxional with respect to the $Pt^1Pt^3Pt^4$ triangle. The ^{13}CO resonance at −40 °C contained quarter intensity satellites due to $^1J(Pt^2C^5)$ = 820 Hz and $^1J(Pt^1C^5)$ = 390 Hz; at room temperature $^1J(Pt^2C^5)$ was essentially unchanged but an 'average' coupling $J(Pt^1C^5)$ = $J(Pt^3C^5)$ = $J(Pt^4C^5)$ = 130 (=390/3) Hz (with associated septet pattern) was observed indicating fluxionality of the carbonyl with respect to the $Pt^1Pt^3Pt^4$ triangle while remaining bonded to Pt^2. Together these and the remaining n.m.r. data‡ clearly define the fluxionality as involving edge to edge migration of the μ-H and $Pt^2(\mu\text{-CO})_2$(dppm-*P*) groups with respect to the $Pt_3(\mu\text{-dppm})_3$ triangle (Scheme 1, complete equivalence requires 6 such 60° steps) so that the time-averaged structure appears to contain a μ_3-H group below, and a rapidly-spinning $\mu_3\text{-}Pt^2(CO)_2$(dppm-*P*) group above, the $Pt_3(\mu\text{-dppm})_3$ unit. This is different from the 'flying butterfly' mechanism proposed for fluxionality of [$Pt_4(\mu\text{-CO})_5L_4$] complexes,[1] and illustrates the value of analysis of the temperature dependence of both coupling constants and multiplicities due to ^{195}Pt coupling in studies of fluxionality of platinum clusters.

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‡ N.m.r. data for (**1**), refs. Me_4Si (^1H), H_3PO_4 (^{31}P), K_2PtCl_4 (^{195}Pt), multiplicities due to ^{195}Pt couplings not reported, J values in Hz, −40 °C, δ(^1H) −7.6 [m, $^1J(Pt^1H)$ = $^1J(Pt^3H)$ = 670, $^2J(Pt^4H)$ 168, Pt*H*]; δ(^{13}C) 246.6 [m, $^1J(Pt^2C)$ 816, $^1J(Pt^1C)$ 390, *CO*]; δ(^{31}P) 18.1 [m, $^2J(P^5P^6)$ 84, $^1J(Pt^2P^5)$ 5400, $^2J(Pt^1P^5)$ = $^2J(Pt^3P^5)$ = 378, $^3J(Pt^4P^5)$ 252, $^3J(P^5P^3)$ = $^3J(P^5P^7)$ = 41, P^5], −31.6 [m, $^3J(Pt^2P^6)$ 80, P^6], −21.8 [m, ^1J(PtP) 2484, $^2J(Pt^4P)$ 105, ^3J(PP) 199, P^1, P^2], −26.0 [m, ^1J(PtP) 3136, ^3J(PP) 199, P^4, P^8], −15.2 [m, ^1J(PtP) 4102, $^2J(Pt^2P)$ 160, $^3J(P^3P^7)$ 144, P^3, P^7]; δ(^{195}Pt) −3384 [m, $^1J(PtP^5)$ 5400, Pt^2], resonances for Pt^1, Pt^3, and Pt^4 not resolved: 20 °C, δ(^1H) −7.4 [m, ^1J(PtH) 508, $^2J(Pt^2H)$ 48, Pt*H*]; δ(^{13}C) 246.0 [m, $^1J(Pt^2C)$ 820, ^1J(PtC) 130]; δ(^{31}P) 18.2 [m, $^1J(Pt^2P)$ 5400, $^2J(P^5P^6)$ 73, $^3J(P^5P)$ 15 (septet), $^2J(PtP^5)$ 336 (septet), *n.b.* 336 = 1/3 (2 × 378 + 252), P^5], −31.4 [m, $^3J(Pt^2P)$ 97, P^6], −21.5 [m, ^1J(PtP) 3200, P^1—P^4, P^7, P^8], δ(^{195}Pt) −3340 [m, ^1J(PtP) 5400, Pt^2].