Diplatinum(0) Complexes $[Pt_2(\mu\text{-}R_2PCH_2PR_2)_3(PPh_3)_n]$, n = 0—2: the Molecular Structure of the Complex with R = Me, n = 1

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Two new structural types of binuclear platinum(0) complexes of formulae $[Pt_2(\mu\text{-}R_2PCH_2PR_2)_3(PPh_3)]$, (**2**), and $[Pt_2(\mu\text{-}R_2PCH_2PR_2)_3(PPh_3)_2]$, (**3**), have been characterized by n.m.r. spectroscopy and, for (**2**; R = Me), by *X*-ray crystallography; steric requirements of R determine the preferred structures and complexes (**2**; R = Me or Et) are shown to contain both 3-co-ordinate and 4-co-ordinate platinum(0) centres.

We report two new types of diplatinum(0) complexes, (**2**) and (**3**), in which each platinum atom is 4-co-ordinate, (**3**), or, most remarkably, in which one platinum is 3-co-ordinate and the other 4-co-ordinate, (**2**). Few diplatinum(0) complexes have been characterized previously,[1,2] though many mononuclear complexes of formulae $[PtL_2]$, $[PtL_3]$, and $[PtL_4]$, with L = tertiary phosphine, are known.[3—5] Complex (**1c**) is the only reported diplatinum(0) complex of a diphosphinomethane ligand; it has a manxane-like structure in which each metal centre is 3-co-ordinate.

The complexes (**1**)—(**3**) were prepared in solution in toluene by reaction of $[Pt(PPh_3)_3]$ with the appropriate bidentate ligand. While (**2a**) and (**3a**) could be crystallized from solution as red and yellow crystals respectively in analytically pure form, the other compounds were characterized in solution by variable temperature ^{31}P and ^{195}Pt n.m.r. spectroscopy (Figure 1);† the crystal structure of (**2a**) was determined by *X*-ray diffraction.‡ The molecular structure shown in Figure 2 approximates to C_3 symmetry and the $Pt_2(\mu\text{-dmpm})_3$ moiety displays the manxane skeleton previously found in $[Pt_2(\mu\text{-dppm})_3]$. However, the Pt · · · Pt separation in the latter compound of 3.023(1) Å is appreciably shorter than the corresponding distance of 3.30(1) Å in (**2a**). Interestingly, the trigonal planar co-ordination of Pt(1) in (**2a**) is distorted by the displacement of the metal atom from the plane of its three adjacent phosphorus atoms by 0.22 Å *towards* Pt(2). A distorted tetrahedral co-ordination is found

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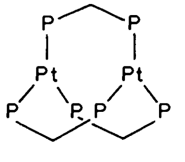
† ^{31}P and ^{195}Pt n.m.r. data in $[^2H_8]$toluene (J in Hz, δ in p.p.m.): (**1a**) at 25 °C, δ 6.8 [s, $^1J(PtP)$ 4372, PPt]; (**1b**) at 25 °C, δ 33.43 [s, $^1J(PtP)$ 4293, $^3J(PtP)$ 41, PPt], −2874 [q, Pt]; (**2a**) at −80 °C, δ −15.9 [m, $^1J(PtP)$ 4460, P^a], −52.9 [m, $^1J(PtP)$ 4040, P^x], +9.1 [q, $^1J(PtP)$ 3240, $^2J(P^xP)$ 32, PtPPh$_3$]; (**2b**) at −85 °C, δ +12.45 [m, $^1J(PtP)$ 4340, $^2J(P^aP^x)$ 24, $^3J(P^aP^{x\prime})$ 19, P^a], −28.59 [m, $^1J(PtP)$ 3967, P^x], +3.06 [q, $^1J(PtP)$ 3412, $^5J(PtP)$ 24, $^2J(P^xP)$ 55, PtPPh$_3$], −2573 [q, Pt^a], −3340 [dq, Pt^x]; (**3b**) at −80 °C, δ +142.1 [s, $^1J(PtP)$ 5069, PtP(deopm)], +0.19 [s, $^1J(PtP)$ 2795, PtPPh$_3$], −3605 [dq, br., Pt].

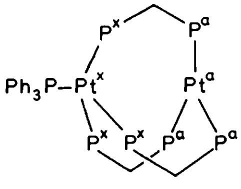
‡ *Crystal data* for (**2a**): $C_{33}H_{57}P_7Pt_2$, M = 1060.8, monoclinic, space group $C2/c$, a = 25.145(4), b = 17.024(5), c = 19.578(4) Å, β = 107.16(2)°, U = 8008 Å^3, Z = 8, D_c = 1.760 g cm^{-3}, μ(Mo-K_α) = 73.5 cm^{-1}, crystal dimensions = 0.45 × 0.25 × 0.25 mm.

The data were measured on an Enraf-Nonius CAD4F diffractometer using a crystal sealed in a Lindemann-glass tube. Full-matrix least-squares refinement of 134 parameters gives R = 0.064 and R_w = 0.091 for 3652 independent reflections [$2 < \theta(\text{Mo-}K_\alpha) < 27°$, $I > 3\sigma(I)$] corrected empirically for absorption. Despite problems posed by pseudosymmetry and crystal decomposition, the non-hydrogen atom skeleton of (**2a**) has been established without ambiguity, although the atomic parameters are not of high accuracy.

The atomic co-ordinates are available 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.



(1)
a; PP = dmpm
b; PP = depm
c; PP = dppm



(2)
a; PP = dmpm
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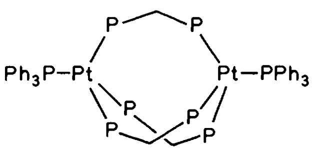

(3)
a; PP = dmpm
b; PP = deopm

dmpm = $Me_2PCH_2PMe_2$, depm = $Et_2PCH_2PEt_2$,
dppm = $Ph_2PCH_2PPh_2$, deopm = $(EtO)_2PCH_2P(OEt)_2$

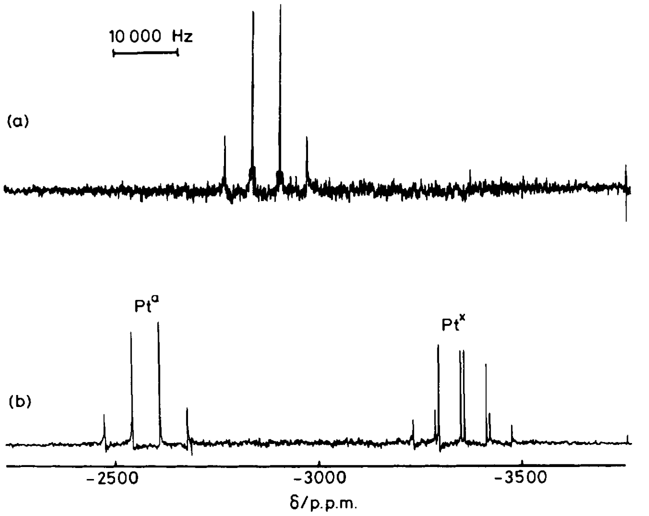

Figure 1. ^{195}Pt N.m.r. spectra (64.274 MHz) of: (a) complex (**1b**) at 25 °C; (b) complex (**2b**) at −80 °C. The same sample was used for both spectra (see text).

about Pt(2), with the Ph_3P–Pt–P angles being on average less obtuse than the remaining P–Pt(2)–P angles.

With the bulkiest ligand $Ph_2PCH_2PPh_2$, dppm, only the known complex (**1c**) was present at 25 °C and at −80 °C.[1] With the ligand $Et_2PCH_2PEt_2$, depm, the complex (**1b**) was the only product detectable at 25 °C, but (**2b**) was the only product at −80 °C and, at intermediate temperatures, signals for both (**1b**) and (**2b**) were observed. Exchange between (**1b**) + PPh_3 and (**2b**) was slow on the n.m.r. time scale, and a sharp signal due to free PPh_3 was observed in the ^{31}P n.m.r. spectrum at all temperatures. The structure of (**2b**) could be deduced from the ^{31}P n.m.r. spectrum† [note the quartet for the Ph_3P resonance due to coupling to 3 P^x atoms and the lower value of ^1J(PtP) for the depm phosphorus atoms at the 4-co-ordinate platinum] but was most clearly demonstrated by the ^{195}Pt n.m.r. spectrum (Figure 1). This gives a quartet for the 3-co-ordinate Pt^a but a doublet of quartets due to ^1J(PtP) couplings for the 4-co-ordinate Pt^x.

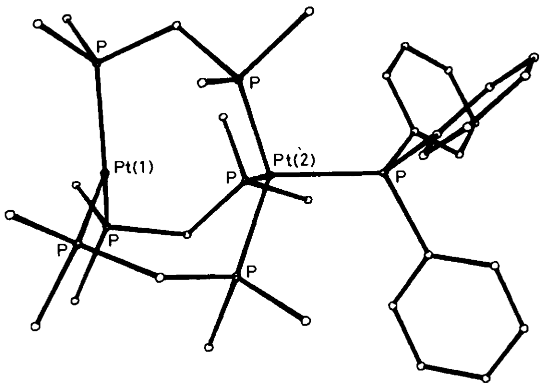

Figure 2. A view of the molecular structure of $[Pt_2(\mu\text{-dmpm})_3(PPh_3)]$, (**2a**). Selected distances (Å) and angles (°) are: Pt(1)–P 2.22(1)—2.24(1), Pt(2)–P 2.26(1)—2.34(1), P–Pt(1)–P 117(1)—123(1), Ph_3P–Pt(2)–P 101(1)—107(1), P(dmpm)–Pt(2)–P(dmpm) 112(1)—117(1).

With the ligand $Me_2PCH_2PMe_2$, dmpm, only the red (**2a**) could be detected by ^{31}P n.m.r. spectroscopy† in solution at 25 °C and −80 °C, though the signals for (**2a**) were broad at 25 °C owing to the onset of an exchange process and though not only (**2a**) but also the yellow (**3a**) could be crystallized from such solutions. The complex (**1a**) was prepared in solution by reaction of dmpm with $[Pt(1,5\text{-cyclo-octadiene})_2]$, but could not be detected from the reactions with $[Pt(PPh_3)_3]$. Finally, the ligand with the smallest cone angle[6] $(EtO)_2PCH_2P(OEt)_2$, deopm, gave the complex (**3b**) at −80 °C in toluene solution. Exchange broadening of signals in both the ^{31}P and ^{195}Pt n.m.r. spectra† was apparent even at −80 °C, but the complex is unambiguously characterized by the doublet of quartets in the ^{195}Pt n.m.r. spectrum due to ^1J(PtP) coupling, by the ^{195}Pt chemical shift and by the magnitude of the coupling $^1J(PtPPh_3)$.

There is a clear correlation of the preferred structure (**1**)—(**3**) with the steric bulk[6] of the ligand $R_2PCH_2PR_2$.

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