Diplatinum(0) Complexes [Pt₂(μ -R₂PCH₂PR₂)₃(PPh₃)_n], n = 0—2: the Molecular Structure of the Complex with R = Me, n = 1

Samson S. M. Ling,^a Ian R. Jobe,^a Alistair J. McLennan,^a Ljubica Manojlović-Muir,^{*b} Kenneth W. Muir,^b and Richard J. Puddephatt^{*a}

^a Department of Chemistry, University of Western Ontario, London, Ontario, Canada N6A 5B7

^b Department of Chemistry, University of Glasgow, Glasgow G12 800, Scotland, U.K.

Two new structural types of binuclear platinum(0) complexes of formulae $[Pt_2(\mu-R_2PCH_2PR_2)_3(PPh_3)]$, (2), and $[Pt_2(\mu-R_2PCH_2PR_2)_3(PPh_3)_2]$, (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 [PtL₂], [PtL₃], and [PtL₄], 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 ³¹P and ¹⁹⁵Pt 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 Pt₂(μ -dmpm)₃ moiety displays the manxane skeleton previously found in [Pt₂(μ -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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^{† &}lt;sup>31</sup>P and ¹⁹⁵Pt n.m.r. data in [²H₈]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, Pa], -52.9 [m, ¹J(PtP) 4040, Px], +9.1 [q, ¹J(PtP) 3240, ²J(PxP) 32, PtPPh₃]; (2b) at -85 °C, δ +12.45 [m, ¹J(PtP) 4340, ²J(PaPx) 24, ³J(PaPx') 19, Pa], -28.59 [m, ¹J(PtP) 3967, Px], +3.06 [q, ¹J(PtP) 3412, ⁵J(PtP) 24, ²J(PxP) 55, PtPPh₃], -2573 [q, Pta], -3340 [dq, Pt³]; (3b) at -80 °C, δ +142.1 [s, ¹J(PtP) 5069, PtP(deopm)], +0.19 [s, ¹J(PtP) 2795, PtPPh₃], -3605 [dq, br., Pt].

[‡] Crystal data for (**2a**): C₃₃H₅₇P₇Pt₂, M = 1060.8, monoclinic, space group C2/c, a = 25.145(4), b = 17.024(5), c = 19.578(4) Å, $\beta = 107.16(2)^{\circ}$, U = 8008 Å³, 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 $[2<\theta(Mo-K_{\alpha}) < 27^\circ, I > 3\sigma(I)]$ corrected empirically for absorption. Despite problems posed by pseudosymmetry and crystal decomposition, the nonhydrogen atom skeleton of (2a) has been established without ambiguity, although the atomic parameters are not of high accuracy.



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

b; PP = depm

b; PP = deopm



Figure 1. ¹⁹⁵Pt 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) + PPh₃ and (2b) was slow on the n.m.r. time scale, and a sharp signal due to free PPh₃ was observed in the ³¹P n.m.r. spectrum at all temperatures. The structure of (2b) could be



Figure 2. A view of the molecular structure of $[Pt_2(\mu-dmpm)_3(PPh_3)]$, (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).

deduced from the ³¹P n.m.r. spectrum[†] [note the quartet for the Ph₃P 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 ¹⁹⁵Pt 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.

With the ligand $Me_2PCH_2PMe_2$, dmpm, only the red (2a) could be detected by ³¹P 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 $[Pt(1,5-cyclo-octadiene)_2]$, but could not be detected from the reactions with $[Pt(PPh_3)_3]$. Finally, the ligand with the smallest cone angle6 $(EtO)_2PCH_2P(OEt)_2$, deopm, gave the complex (3b) at -80 °C in toluene solution. Exchange broadening of signals in both the ³¹P and ¹⁹⁵Pt n.m.r. spectra[†] was apparent even at -80 °C, but the complex is unambiguously characterized by the doublet of quartets in the ¹⁹⁵Pt n.m.r. spectrum due to $^{1}J(PtP)$ coupling, by the ^{195}Pt chemical shift and by the magnitude of the coupling ${}^{1}J(PtPPh_{3})$.

There is a clear correlation of the preferred structure (1)—(3) with the steric bulk⁶ of the ligand $R_2PCH_2PR_2$.

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