

Diprotection of Binuclear Platinum(0) Complexes to give Two New Structural Forms of Binuclear Platinum Hydrides, $[\text{Pt}_2\text{H}_2(\mu\text{-R}_2\text{PCH}_2\text{PR}_2)_3]^{2+}$: The Molecular Structure of the Complex with R = Et

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Protonation of $[\text{Pt}_2(\mu\text{-R}_2\text{PCH}_2\text{PR}_2)_3(\text{PPh}_3)_n]$ ($n = 0$, R = Ph or Et; $n = 1$, R = Me; $n = 2$, R = EtO) with $\text{NH}_4[\text{PF}_6]$ gives the diplatinum(II) complex $[\text{Pt}_2\text{H}(\eta^1\text{-dppm})(\mu\text{-dppm})_2]^+$, (**2**), when R = Ph (dppm = $\text{Ph}_2\text{PCH}_2\text{PPh}_2$), but the diplatinum(II) complexes $[\text{Pt}_2\text{H}_2(\mu\text{-R}_2\text{PCH}_2\text{PR}_2)_3]^{2+}$, in structural forms (**3**), R = EtO, or (**4**), R = Me, Et, when the substituents on phosphorus are smaller; the structure of (**4**), R = Et, has been determined crystallographically.

Whereas reaction of $\text{NH}_4[\text{PF}_6]$ with $[\text{Pt}_2(\mu\text{-dppm})_3]$,¹ (**1a**) (dppm = $\text{Ph}_2\text{PCH}_2\text{PPh}_2$) gives only the diplatinum(II) product (**2**)² by monoprotection, the analogous reactions with $[\text{Pt}_2(\mu\text{-R}_2\text{PCH}_2\text{PR}_2)_3(\text{PPh}_3)_n]$ ³ [(**1**), $n = 0$, R = Et; $n = 1$, R = Me; $n = 2$, R = EtO] give the new diplatinum(II) products (**3**) or (**4**) by diprotection, see Scheme 1.

The structures of the new complexes could be deduced from the ¹H and ³¹P n.m.r. spectra.† Thus, while (**3**) and (**4**) gave similar PtH resonances in the ¹H n.m.r. spectrum, which appeared as doublets of triplets with a large coupling to the *trans* phosphorus and smaller couplings to the two *cis* phosphorus atoms on the same platinum centre,⁴ the structural forms were distinguished by the ³¹P n.m.r. spectra which gave two resonances for (**3**) due to P^a and P^x but three resonances for (**4**) due to P^a, P^b, and P^x (see Newman projections, Figure 1). Confirmation of the structure of (**4b**), R = Et, was obtained by an X-ray structure determination of

the $[\text{BPh}_4]^-$ salt,‡ obtained by anion exchange from the PF_6^- salt, which failed to give suitable single crystals.

The structure of (**4b**), shown in Figure 2, contains two planar T-shaped PtP_3 fragments. The angular distortions of these fragments [P–Pt–P(*cis* to P) 98.5(1)–106.7(1)° and P–Pt–P(*trans* to P) 154.1(1), 157.8(1)°] are indicative of distorted square-planar co-ordination geometry around the metal centres, with 'vacant' sites available to the hydrido ligands whose positions were not determined directly by the X-ray analysis. This interpretation is further supported by the mean values of Pt–P(*trans* to H) and Pt–P(*trans* to P) bond lengths [2.338(2) and 2.290(4) Å], which are in accordance

‡ Crystal Data for (**4b**)- $[\text{BPh}_4]_2$: $\text{C}_{75}\text{H}_{108}\text{B}_2\text{P}_6\text{Pt}_2$, $M = 1607.3$, monoclinic, space group $P2_1/c$, $a = 19.373(4)$, $b = 21.727(8)$, $c = 17.701(4)$ Å, $\beta = 100.23(2)^\circ$, $U = 7332$ Å³, $Z = 4$, $D_c = 1.456$ g cm⁻³, Mo- K_α radiation, $\lambda = 0.71069$ Å, $\mu(\text{Mo-}K_\alpha) = 40.2$ cm⁻¹. The crystal was an orange-yellow chunk of dimensions 1.00 × 0.80 × 0.80 mm.

Data were measured on an Enraf-Nonius CAD4 diffractometer. In the structural model refined all phenyl rings were constrained to $6/mmm$ symmetry and C–C = 1.38 Å, and only Pt and P atoms were allowed anisotropic thermal vibrations. Full-matrix least squares refinement of 285 parameters gave $R = 0.039$ and $R_w = 0.047$ for 8404 unique reflections with $I \leq 3\sigma(I)$, which were corrected empirically for absorption effects. All calculations were carried out using the GX program package.

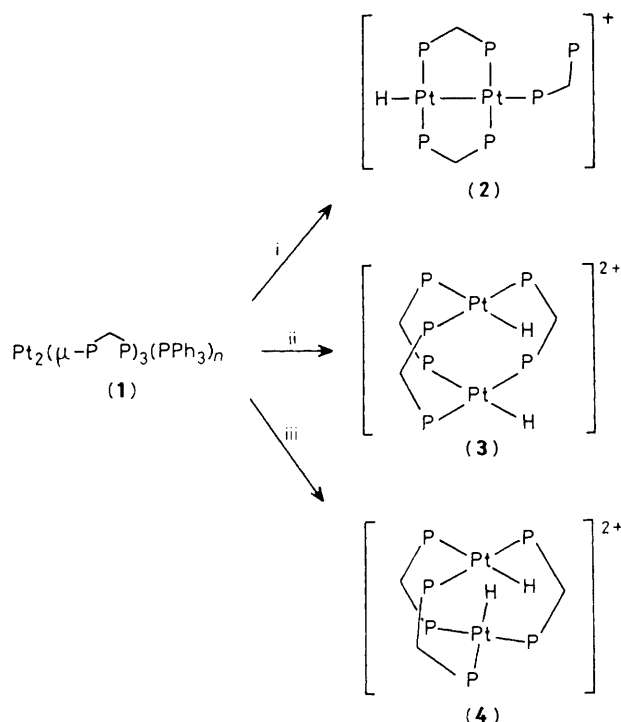
The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this work.

† N.m.r. data (δ , J in Hz) in $[\text{D}_6\text{O}]\text{acetone}$: (**3**), -4.87 [dt, ² $J(\text{P}^x\text{H})$ 217, ² $J(\text{P}^a\text{H})$ 10, ¹ $J(\text{PtH})$ 818, PtH]; 127.5 [m, ¹ $J(\text{PtP}^a)$ 3407, ³ $J(\text{PtP}^a)$ 31, ² $J(\text{P}^a\text{P}^x)$ 31, ² $J(\text{P}^a\text{P}^a)$ 73, P^a], 147.8 p.p.m. [m, ¹ $J(\text{PtP}^x)$ 2724, ³ $J(\text{PtP}^x)$ 17, ² $J(\text{P}^x\text{P}^x)$ 138, P^x].

(**4a**), -6.46 [dt, ² $J(\text{P}^x\text{H})$ 171, ² $J(\text{P}^a\text{P}^b\text{H})$ 19, ¹ $J(\text{PtH})$ 834, PtH]; -11.28 [m, ¹ $J(\text{PtP}^x)$ 2026, ² $J(\text{P}^a\text{P}^x)$ 23, ² $J(\text{P}^b\text{P}^x)$ 24, ² $J(\text{P}^x\text{P}^b)$ 35, ⁴ $J(\text{P}^x\text{P}^x)$ 11, P^x], -18.96 [m, ¹ $J(\text{PtP}^a)$ 2540, ² $J(\text{P}^a\text{P}^b)$ 351, ⁴ $J(\text{P}^a\text{P}^b)$ 5, ² $J(\text{P}^a\text{P}^a)$ 23, P^a], -21.82 p.p.m. [m, ¹ $J(\text{PtP}^b)$ 2486, P^b].

(**4b**), -6.70 [dt, ² $J(\text{P}^x\text{H})$ 166, ² $J(\text{P}^a\text{P}^b\text{H})$ 16, ¹ $J(\text{PtH})$ 765, PtH]; 12.3 [m, ¹ $J(\text{PtP}^x)$ 2104, ² $J(\text{P}^a\text{P}^x)$ 22, ² $J(\text{P}^b\text{P}^x)$ 22, ² $J(\text{P}^x\text{P}^b)$ 36, ⁴ $J(\text{P}^x\text{P}^x)$ 8, P^x], 4.93 [m, ¹ $J(\text{PtP}^a)$ 2559, ² $J(\text{P}^a\text{P}^b)$ 340, ² $J(\text{P}^a\text{P}^b)$ 22, P^a], 2.63 p.p.m. [m, ¹ $J(\text{PtP}^b)$ 2533, P^b].

I.r. (Nujol): (**3**), $\nu(\text{PtH})$ 2074 cm⁻¹; (**4a**), $\nu(\text{PtH})$ 2070 cm⁻¹.



Scheme 1. Reagents: excess of $\text{NH}_4[\text{PF}_6]$; $\text{P} \text{---} \text{P} = \text{R}_2\text{PCH}_2\text{PR}_2$; i, a; R = Ph, $n = 0$; ii, R = EtO, $n = 2$; iii, a; R = Me, $n = 1$ or b; R = Et, $n = 0$.

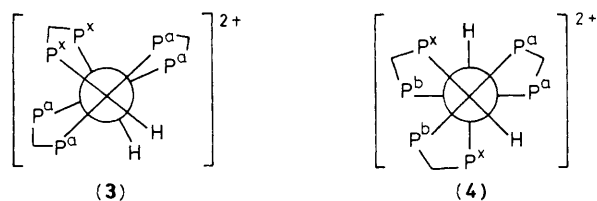


Figure 1

with a higher *trans*-influencing capability of the hydrido ligands.

The PtP_3 fragments are parallel to each other (dihedral angle 1.2°) and locked in a configuration characterized by the torsion angle involving phosphorus atoms in the Pt–P(*trans* to H) bonds at both metal centres [$\text{P}(12)\text{--Pt}(1)\text{--Pt}(2)\text{--P}(23)$ $-124.9(1)^\circ$]. As is evident from the P–Pt–Pt–P torsion angles shown in Figure 2, two $\mu\text{-depm}$ ligands ($\text{depm} = \text{Et}_2\text{PCH}_2\text{PEt}_2$) are twisted around the Pt \rightarrow Pt vector in a direction opposite from the twist of the third ligand (see Newman projection). Thus the structure of (4b) contains a *cis,cis*- $\text{Pt}_2(\mu\text{-depm})_2$ nucleus with an eight-membered dimetallacycle similar to those previously found in *cis,cis*- $[\text{Pt}_2\text{Me}_4(\mu\text{-R}_2\text{PCH}_2\text{PR}_2)_2]$ (R = Ph or Me) complexes.⁵ In (4b) however there are only two monodentate ligands and the third diphosphine, containing P(11) and P(21), forms a *trans*-annular bridge between the metal centres, which are separated by a Pt \cdots Pt distance of 3.059(1) Å.

Complex (3), in which two metal atoms of a *trans,trans*- $\text{Pt}_2(\mu\text{-deopm})_2$ nucleus [$\text{deopm} = (\text{EtO})_2\text{PCH}_2\text{P}(\text{OEt})_2$] are bridged by another *deopm* ligand (Newman projection), could be eclipsed or staggered but fluxional, so that all P^a atoms are equivalent at least on the n.m.r. time scale.

The structural types (3) and (4) can therefore be considered related to '*trans,trans*-face-to-face'⁶ and '*cis,cis*-face-to-face'⁵ molecular frameworks, but are unique in having three bridging $\text{R}_2\text{PCH}_2\text{PR}_2$ ligands.

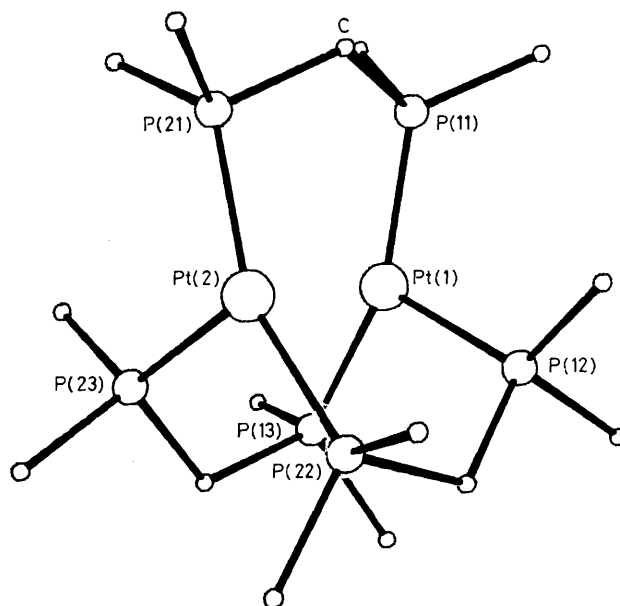


Figure 2. The structure of $[\text{Pt}_2\text{H}_2(\mu\text{-depm})_3]^{2+}$, (4b), with hydrogen and methyl carbon atoms omitted for clarity. Selected torsion angles are: P(12)–Pt(1)–Pt(2)–P(22) $-26.2(1)^\circ$, P(13)–Pt(1)–Pt(2)–P(23) $-26.7(1)^\circ$, and P(11)–Pt(1)–Pt(2)–P(21) $24.2(1)^\circ$.

An earlier crystallographic study has shown that the molecular structure of $[\text{Pt}_2(\text{dppm})_3]$ in which three $\mu\text{-dppm}$ ligands adopt a trigonal rotational orientation around the Pt \rightarrow Pt vector, is subject to severe steric overcrowding.¹ Since formation of structures (3) or (4) would require an even closer mutual approach of the $\mu\text{-dppm}$ ligands, it is likely that diprotonation of $[\text{Pt}_2(\mu\text{-dppm})_3]$ may be precluded by the steric bulk of the phenyl substituents. Regarding diprotonation reactions shown in Scheme 1, it is tempting to speculate that the preferred products, (3) when R = OEt and (4) when R = Me or Et, also reflect steric requirements of R. This however is difficult to substantiate in the absence of sufficient structural data and our efforts to grow crystals of (3) suitable for an X-ray crystallographic study are continuing. The formation of (3) when R = EtO but only (2) when R = Ph can only be rationalized in terms of steric rather than electronic effects of the substituents.

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