Synthesis, Solution and Solid-state Structure (*X*-Ray Analysis), and Some Reactions of the Dimer $[PtMe_2(\mu\text{-}Ph_2PCH_2PPh_2)]_2$

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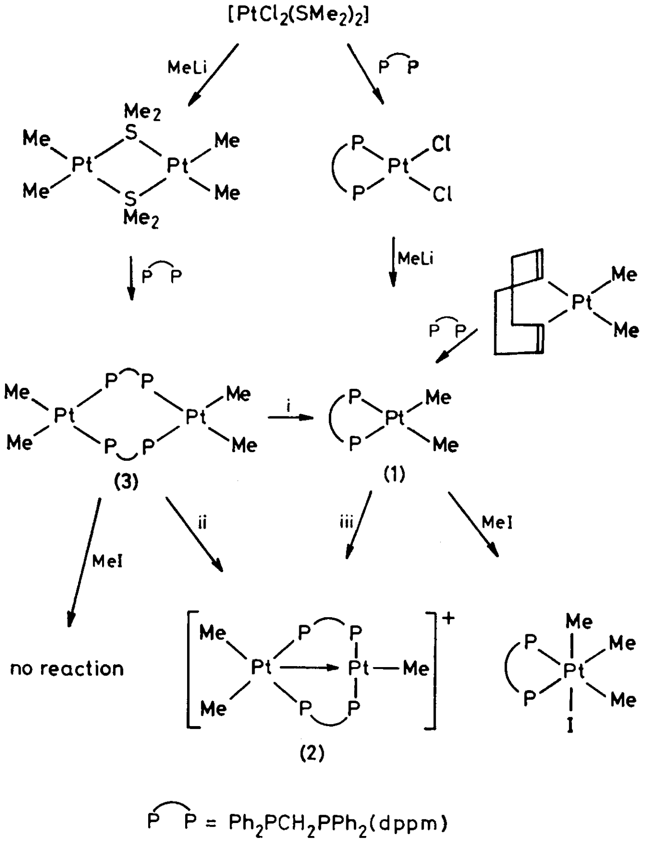
Summary The new dimer $[Pt_2Me_4(\mu\text{-dppm})_2]$ (dppm = $Ph_2PCH_2PPh_2$) has been prepared and its conformation both in the solid state and in solution has been studied; it is thermodynamically less stable than the monomeric form and is much less reactive than the monomer towards oxidative addition.

THE synthesis and reactions of a dimeric form of $[PtMe_2(dppm)]$[1,2] are shown in the Scheme. The complex exhibits novel fluxionality and reactivity, which we suggest may prove to be general in dimers of this type.

The ^1H (100 MHz) and ^{31}P (40·5 MHz) n.m.r. spectra of (**3**) (Scheme) at 35 °C show single resonances for the CH_2P_2 protons, CH_3Pt protons, and ^{31}P atoms of the ligands, but at −50 °C each of these signals is split into two.† However, the ^{195}Pt (85 MHz) resonance is not split at low temperature, and the spectral parameters clearly indicate that the *cis*-stereochemistry with μ-dppm ligands is maintained.[1–3] The results indicate that the structure is unsymmetrical such that the platinum centres are equivalent but the two methyl and phosphorus groups bound to the same platinum atom are non-equivalent, and this conclusion is supported by selective decoupling experiments. Further, there is a higher activation energy for coalescence of the CH_2P_2 proton signals [coalescence temperature, θ_c = 30 °C, $\delta\nu(H^a,H^b)$ 131 Hz] than for the CH_3Pt [θ_c = 0 °C, $\delta\nu(Me^a,Me^b)$ 98 Hz] and ^{31}P [θ_c = *ca.* 10 °C, $\delta\nu(P^aP^b)$ 179 Hz] signals. These data are consistent with the molecule having the twist-saddle conformation,[4–6] in which a twisting motion can give equivalence of the CH_3Pt signals and ^{31}P signals but inversion of the saddle is necessary to give equivalence of the CH_2P_2 protons (Figure 1).



SCHEME. i, 60 °C, benzene solution, Me_2S or dppm catalyst; ii, 1 mol. equiv. of $HClO_4$, Br_2, or I_2; iii, 0·5 mol. equiv. of $HClO_4$.

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† ^1H n.m.r., CD_2Cl_2, −50 °C: $\delta(CH^aH^bP_2)$ 4·25 and 2·95, $^2J(H^aH^b)$ 13·5, $^3J(PtH^a)$ 28 Hz; δ(MePt) 0·63 and −0·35, ^3J(PH) 7·5, ^2J(PtH) 70 Hz; $^{31}P\{^1H\}$ n.m.r., CH_2Cl_2, −50 °C: $\delta(P^a)$ 8·91 p.p.m. from $(MeO)_3PO$, ^1J(PtP) 1790 Hz; $\delta(P^b)$ 4·49 p.p.m., ^1J(PtP) 1830, $^2J(P^aP^b)$ 40, $^3J(P^aP^{b\prime})$ 10 Hz; $^{195}Pt\{^1H\}$ n.m.r., CH_2Cl_2, −50 °C: $\delta(^{195}Pt)$ −880 p.p.m. from *cis*-$[PtCl_2(SMe_2)_2]$, ^1J(PtP) 1800 Hz.

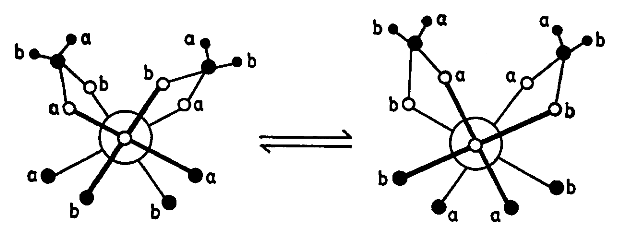

FIGURE 1. The proposed mechanism leading to equivalence of methylplatinum groups (closed circles) and phosphorus atoms (open circles), showing Newman projections along the PtPt axis, non-equivalent atoms being indicated by a, b.

These conclusions regarding the conformation in solution are reinforced by the preliminary results of an *X*-ray single-crystal diffraction study of (**3**). *Crystal data:* $C_{54}H_{56}P_4Pt_2$, $M = 1219{\cdot}1$, monoclinic, space group $P2_1/c$, $a = 13{\cdot}957(7)$, $b = 17{\cdot}218(5)$, $c = 21{\cdot}649(5)$ Å, $\beta = 106{\cdot}45(3)°$, $U = 4990$ Å^3, $D_m = 1{\cdot}65$ g cm^{-3}, $Z = 4$, $D_c = 1{\cdot}623$ g cm^{-3}.

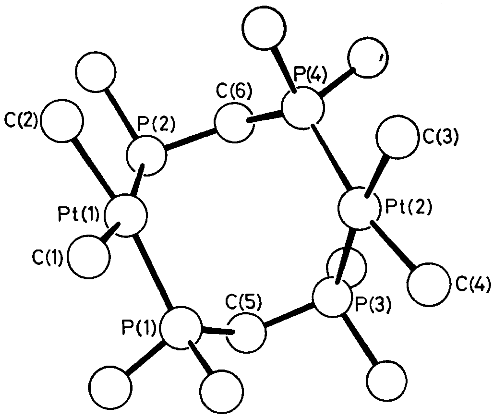

FIGURE 2. A perspective view of the $[Pt_2Me_4(\mu\text{-dppm})_2]$ molecule. For clarity only phenyl carbon atoms directly bonded to phosphorus are shown. Atoms are represented by spheres of arbitrary size.

The structure has been solved and partially refined, using conventional Patterson, Fourier, and least-squares techniques. Currently $R = 0{\cdot}10$ and $R_w = 0{\cdot}12$ for 3855 diffractometric intensity data for which $I \geqslant 3\sigma(I)$.‡ The $[Me_2Pt(\mu\text{-dppm})_2PtMe_2]$ molecules of which the crystal is composed (Figure 2) display *cis*-square-planar co-ordination at both platinum atoms. Any bonding interaction between the metal atoms is clearly precluded by the magnitude of the intramolecular Pt···Pt separation (4·36 Å). The 8-membered $Pt_2P_4C_2$ ring adopts the twist-saddle conformation. In view of the n.m.r. results just discussed it is likely that this conformation persists in solution. Bond angles within the ring [mean P–Pt–P 98(1), Pt–P–C 120—123(1), P–C–P 120(2)°] are all some 8—12° more obtuse than the idealised values of 90 and 109°, possibly reflecting steric overcrowding. This is also apparent in the dppm–P–P bite distances (3·19 and 3·23 Å) which are *ca.* 0·1 Å greater than any so far seen in complexes based on the $Pt_2(\mu\text{-dppm})_2$ skeleton; the next largest is 3·11 Å in the V-frame complex $[ClPt(\mu\text{-}CH_2)(\mu\text{-dppm})_2PtCl]$.[7]

No reaction was observed when benzene solutions of (**1**) or (**3**) were heated at 60 °C but, in the presence of traces of Me_2S or dppm, (**3**) was slowly but quantitatively converted into (**1**) under these conditions. Therefore (**1**) is thermodynamically more stable than (**3**), and (**3**) is clearly formed as a result of kinetic control in the synthesis from the binuclear precursor[8] (Scheme).

Whilst (**1**) reacts rapidly with methyl iodide to undergo oxidative addition, (**3**) is unreactive even in neat methyl iodide. This remarkable difference in reactivity is attributed to the much greater steric hindrance in (**3**) than in (**1**). The more powerful reagents $HClO_4$, Br_2, or I_2 react with (**3**) to cleave a methyl group and give quantitative yields of the cation (**2**).[9,10]

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

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