# Bimetallic Systems. Part 11.<sup>1</sup> Heterobimetallic and Unsymmetrical Diplatinum Complexes from *cis*-[PtR<sub>2</sub>(dppm-*P*)<sub>2</sub>] (dppm Å Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>; R = Me, 1-Naphthyl, or C<sub>6</sub>H<sub>4</sub>Me-*o*): Crystal Structure of $[(C_6H_4Me-o)_2Pt(\mu-dppm)_2Pt-Me_2]^{\dagger}$

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Treatment of cis-[Pt(C<sub>10</sub>H<sub>7</sub>)<sub>2</sub>(dppm-P)<sub>2</sub>] (dppm = Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>, C<sub>10</sub>H<sub>7</sub> = 1-naphthyl) (syn-anti mixture) with  $[Rh_2Cl_2(CO)_4]$  gave  $[(C_{10}H_7)_2Pt(\mu-dppm)_2RhCl(CO)]$  which showed a complex <sup>31</sup>P-{<sup>1</sup>H} n.m.r. spectral behaviour with temperature. The analogue  $[(C_eH_4Me-o)_2Pt(\mu-dppm)_2RhCl(CO)]$ was prepared in solution and behaved similarly. Treatment of cis-[Pt(C<sub>8</sub>H<sub>4</sub>Me-o)<sub>2</sub>(dppm-P)<sub>2</sub>] with [PtMe2(cod)] (cod = cyclo-octa-1,5-diene) gave in solution a slowly equilibrating mixture of the syn- and anti-isomers of cis, cis-[(C<sub>6</sub>H<sub>4</sub>Me-o)<sub>2</sub>Pt(µ-dppm)<sub>2</sub>PtMe<sub>2</sub>], (4a) and (4b), respectively of which the minor (syn) isomer (4a) crystallized out and whose crystal structure has been determined. Treatment of [PtMe2(dppm-PP')] with dppm at -30 °C gave cis-[PtMe2(dppm-P)2] in situ which on treatment with [{Agl(PPh<sub>3</sub>)}, [AuCl(PPh<sub>3</sub>)], or AgPF<sub>6</sub> gave, respectively, [Me<sub>2</sub>Pt( $\mu$ -dppm)<sub>2</sub>AgI], [Me<sub>2</sub>Pt( $\mu$ -dppm)<sub>2</sub>Au]Cl, or [Me<sub>2</sub>Pt( $\mu$ -dppm)<sub>2</sub>Ag]PF<sub>6</sub>, all fully characterized. Solution <sup>31</sup>P-{<sup>1</sup>H} n.m.r. studies showed that treatment of  $[PtMe_2(dppm-P)_2]$  with [MCI(Me)(cod)] gave the donor-acceptor cations  $[Me_2Pt(\mu-dppm)_2MMe]^+$  (M = Pt or Pd) in high yield. Crystals of the title compound are monoclinic, space group  $P2_1/n$ , with a = 12.371(2), b = 21.368(5), c = 21.368(5)21.917(5) Å,  $\beta = 92.84(2)^\circ$ , and Z = 4; the final R factor was 0.063 for 4 506 observed reflections. The structure confirms the cis square-planar co-ordination at both platinum atoms and shows the eight-membered Pt<sub>2</sub>P<sub>4</sub>C<sub>2</sub> ring in a twist saddle conformation with a Pt • • • Pt separation of 4.91 Å. In the crystals used for data collection the o-tolyl groups adopt a syn configuration, which is shown to constitute the minor isomer in chloroform solution.

We have shown previously that some dialkyl- or diarylplatinum(II) complexes with chelating Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub> (dppm) of the type  $[PtR_2(dppm-PP')]$  (1) (R = alkyl or aryl) undergo ring opening with more dppm to give bis-monodentate dppm complexes of the type  $[PtR_2(dppm-P)_2]$  (2).<sup>2,3</sup> The equilibrium constants, K, for the interconversions  $(1) \rightleftharpoons (2)$ were measured for a series of R groups. Although some complexes of type (2) dissociated extremely rapidly in solution, e.g. with  $\mathbf{R} = \mathbf{Me}$  (2a), by working at low temperatures compound (2a) could be isolated and characterized.<sup>3</sup> With R =o-substituted aryl group the equilibrium  $(1) \rightleftharpoons (2)$  was only slowly established (several days at 20 °C) and compounds of type (2) were readily isolated with  $\mathbf{R} = 1$ -naphthyl ( $C_{10}H_7$ ) (2b) or  $C_6H_4Me$ -o (2c); such species existed in solution as syn- and anti-isomers, due to restricted rotation around the platinumaryl bond. We also showed that with the metallacycles  $[Pt(CH_2CH_2CH_2CH_2)(dppm-PP')_x]$  (x = 1 or 2) the equilibrium constant for the interconversion  $(1) \rightleftharpoons (2)$  (where  $R_2 = -CH_2CH_2CH_2CH_2$ ) was by far the largest of any compounds studied ( $K = \sim 430 \text{ dm}^3 \text{ mol}^{-1}$  at 20 °C in CDCl<sub>3</sub>) and, as a consequence, [Pt(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)(dppm-P)<sub>2</sub>] was readily isolated and studied.4

We have previously observed that monodentate dppm complexes of the type *trans*-[PtX<sub>2</sub>(dppm-P)<sub>2</sub>]<sup>n+</sup> [X = C=CR or CN (n = 0); X = C=NR (n = 2)] can be used for the systematic synthesis of heterobimetallic complexes containing a Pt( $\mu$ -



 $dppm)_2M$  moiety, M = Ag, Au, Rh, Ir, Mo, W *etc.*, with *trans*-P co-ordination at platinum.<sup>5</sup> We have also shown that the metallacycle  $[\dot{P}t(CH_2CH_2CH_2CH_2)(dppm-P)_2]$  could be used to synthesize heterobimetallics (with Ag, Au, or Pd) and unsymmetrical homobimetallics (with a PtMe moiety).<sup>4</sup> It was of interest to see if other compounds of type (2) could be used for the systematic synthesis of bimetallic compounds with a cis configuration around platinum, since this would give greater metal-metal separations and different conformational behaviour and chemistry from complexes with a trans conaround platinum. cis,cis-[Me<sub>2</sub>Pt(µ-dppm)<sub>2</sub>figuration PtMe<sub>2</sub>] is known and is thermodynamically unstable with respect to [PtMe<sub>2</sub>(dppm-PP')]. Its method of synthesis is not applicable to the systematic synthesis of other homo- and hetero-bimetallic  $\mu$ -dppm complexes containing a cis-PtR<sub>2</sub> moiety.6

#### **Results and Discussion**

Synthesis of Bimetallic Complexes.—Since the aryl complexes of type cis-[PtR<sub>2</sub>(dppm-P)<sub>2</sub>] ( $R = C_{10}H_7$  or  $C_6H_4$ Me-o) were much more robust than the analogous complex with R = Meand also showed the additional feature of syn- and antiisomerism, we attempted syntheses with them first.

<sup>†</sup> Di-µ-[bis(diphenylphosphino)methane-*PP*']-1,1-dimethyl-2,2-bis(o-tolyl)diplatinum(11,11).

Supplementary data available (No. SUP 56243, 7 pp.): full bond length and angle data, thermal parameters, least-squares planes. See Instructions for Authors, J. Chem. Soc., Dalton Trans., 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Table 1. Microanalytical (%)<sup>a</sup> and conductivity data

Complex	С	н	Halogen	$\Lambda^{b}$
(3) $[(C_{10}H_7)_2Pt(\mu-dppm)_2RhCl(CO)]$	61.2 (61.6)	4.6 (4.2)	2.9 (2.6)	<b>n.</b> c.
(4a) $[(C_6H_4Me-o)_2Pt(\mu-dppm)_2PtMe_2]-2.5CH_2Cl_2^{\circ}$	52.2 (51.95)	4.25 (4.35)		n.d.
(5) $[Me_2Pt(\mu-dppm)_2AgI]$	50.5 (50.8)	4.15 (4.05)	9.95 (10.35)	n.c.
(6a) $[Me_2Pt(\mu-dppm)_2Au]Cl$	50.75 (50.95)	4.25 (4.1)	3.15 (2.9)	20,4 60 e
(6b) $[Me_2Pt(\mu-dppm)_2Ag]PF_6$	50.3 (50.1)	3.9 ( <b>4</b> .0)	9.05 (9.15)	n.d.

<sup>*a*</sup> Calculated values are in parentheses. <sup>*b*</sup> In  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>; n.c. = non-conducting, n.d. = not determined. <sup>*c*</sup> The presence of CH<sub>2</sub>Cl<sub>2</sub> was confirmed by the <sup>1</sup>H n.m.r. spectrum. <sup>*d*</sup> In nitrobenzene at 20 °C. <sup>*e*</sup> In dichloromethane at 20 °C.

Table 2. <sup>31</sup>P N.m.r. data for the bimetallic complexes derived from cis-[PtR<sub>2</sub>(dppm-P)<sub>2</sub>] species

Complex	$\delta(P_A)^a/p.p.m.$	$^{1}J(PtP_{A})/Hz$	$\delta(P_B)/p.p.m.$	<sup>3</sup> J(PtP <sub>B</sub> )/Hz	N <sup>₿</sup> /Hz	Solvent
(5) $[Me_2Pt(\mu-dppm)_2AgI]^c$	+21.9	1 866	-11.6	196	112	$CD_{2}Cl_{2}$ (-60 °C)
(6a) $[Me_2Pt(\mu-dppm)_2Au]Cl$	+ 23.9	1 843	- 32.9	166	92	CDCl <sub>3</sub>
(6b) $[Me_2Pt(\mu-dppm)_2Ag]PF_6^d$	+ 25.2	1 756	-2.7	238	102	CDCl <sub>3</sub>
(3) $[(C_{10}H_7)_2Pt(\mu-dppm)_2RhCl(CO)]$	+ 6.3	ca. 1 840	+ 19.2°	n.r.	n.r.	CDCl <sub>3</sub>
$[(C_6H_4Me-o)_2Pt(\mu-dppm)_2RhCl(CO)]$	+6.5	ca. 1 790	$+20.9^{f}$	n.r.	<b>n</b> .r.	$CD_2Cl_2$
				$^{1}J(PtP_{B})$		
(4a) $syn-[(C_6H_4Me-o)_2Pt(\mu-dppm)_2PtMe_2]$	+ 1.1	1 663	+ 6.4	1 819	24	CD,Cl,
(4b) $anti-[(C_6H_4Me-o)_2Pt(\mu-dppm)_2PtMe_2]$	-0.6	1 669	+ 7.1	1 831	24	$CD_2Cl_2$
	$\delta(\mathbf{P}_{\mathbf{A}})$	<sup>1</sup> J(PtP <sub>A</sub> )	$\delta(\mathbf{P}_{\mathbf{B}})$		$N^{b}$	
(7a) $[Me_2Pt(\mu-dppm)_2PtMe]^+$	+28.8	1 500	+25.8	3 002	90	CDCl <sub>3</sub>
(7b) $[Me_2Pt(\mu-dppm)_2PdMe]^+$	+ 25.7	1 509	+19.3		93	CDCl <sub>3</sub>
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<sup>a</sup> To high frequency of 85% H<sub>3</sub>PO<sub>4</sub> ±0.1 p.p.m. <sup>b</sup>  $N = |{}^{2}J(P_{A}P_{B}) + {}^{4}J(P_{A}P_{B})|$ ; n.r. = not resolved. <sup>c</sup> Spectrum at -60 °C,  ${}^{1}J({}^{107}AgP)$  349,  ${}^{1}J({}^{109}AgP)$  403 Hz. <sup>d</sup> At -60 °C,  ${}^{1}J({}^{107}AgP)$  468,  ${}^{1}J({}^{109}AgP)$  537 Hz. <sup>e</sup>  ${}^{1}J(RhP)$  ca. 130 Hz.  ${}^{f}J(RhP)$  ca. 118 Hz.





Treatment of  $cis-[Pt(C_{10}H_7)_2(dppm-P)_2]$  (2b) (syn-anti mixture) with the equivalent amount of  $[Rh_2Cl_2(CO)_4]$  in dichloromethane readily gave the expected product,  $[(C_{10}H_7)_2-$ Pt(µ-dppm)<sub>2</sub>RhCl(CO)] (3), in good (83%) yield (preparative details are in the Experimental section). The formulation follows from elemental analysis (Table 1), the non-conductivity of its solution in nitrobenzene, the presence of a very strong i.r. absorption band at 1 972 cm<sup>-1</sup> due to v(C=O), and from the <sup>31</sup>P- ${^{1}H}$  n.m.r. spectrum (Table 2) which showed broad resonance for both  $P_A$  (Pt-bonded) and  $P_B$  (Rh-bonded) ( $w_+$  ca. 35 Hz) with associated <sup>195</sup>Pt satellites and <sup>103</sup>Rh coupling. These resonances broadened further at lower temperatures and at -80 °C the spectrum was exceedingly complex: the spectrum did not become sharper on heating to  $+50 \degree C$ . We associate this behaviour with the presence of syn (3a) and anti (3b) isomers and with 'freezing-out' of conformation of the  $Pt(\mu-dppm)_2Rh$ eight-membered ring. It is known that when solutions of  $[Me_2Pt(\mu-dppm)_2PtMe_2]$  are cooled, the P nuclei become inequivalent probably due to the 'freezing-out' of a twist saddle conformation of the eight-membered ring.

When cis-[Pt(C<sub>6</sub>H<sub>4</sub>Me-o)<sub>2</sub>(dppm-P)<sub>2</sub>] (2c) was treated with [Rh<sub>2</sub>Cl<sub>2</sub>(CO)<sub>4</sub>] in CDCl<sub>3</sub> the <sup>31</sup>P-{<sup>1</sup>H} n.m.r. spectrum of the resultant solution suggested the presence of [(C<sub>6</sub>H<sub>4</sub>Me-o)<sub>2</sub>Pt( $\mu$ -O)<sub>2</sub>Pt( $\mu$ 

dppm)<sub>2</sub>RhCl(CO)] (data in Table 2) although the product was not isolated.

We also studied the action of the labile dimethylplatinum complex  $[PtMe_2(cod)]$  (cod = cyclo-octa-1,5-diene) on cis- $[Pt(C_6H_4Me-o)_2(dppm-P)_2]$  (2c) in concentrated dichloromethane solution. After a few days at ca. 20 °C, the required product  $cis, cis-[(C_6H_4Me-o)_2Pt(\mu-dppm)_2PtMe_2]$  separated. It was established by crystallography (see below) that this complex has the two o-tolyl groups in the syn configuration (4a). However, we have established by  ${}^{1}H{-}{{}^{31}P}$  n.m.r. spectroscopy that, when this complex was dissolved in CDCl<sub>3</sub>, it gave resonances corresponding to a single species (the syn isomer) but was gradually partially converted into another species which eventually (after a few hours) became the major species in solution. The  ${}^{31}P-{}^{1}H$  n.m.r. spectrum also showed the presence of two closely related species in solution. The major species is clearly the anti isomer, (4b), the approximate ratio of syn-anti at 20 °C and at equilibrium in CDCl<sub>3</sub> solution is ca. 1:2. The  ${}^{31}P{-}{{}^{1}H}$  n.m.r. data are given in Table 2 and the spectrum is reproduced in Figure 1.

Complexes generated from cis-[PtMe<sub>2</sub>(dppm-P)<sub>2</sub>] (2a).— The interconversion of cis-[PtMe<sub>2</sub>(dppm-PP')] and cis-[Pt-



Figure 1. <sup>31</sup>P-{<sup>1</sup>H} N.m.r. spectrum (40.25 MHz) of  $[(C_6H_4Me-o)_2Pt(\mu-dppm)_2PtMe_2]$  showing the syn ( $\triangle$ ) (4a) and anti ( $\triangle$ ) (4b) isomers. P<sub>A</sub> is bound to the PtMe<sub>2</sub> moiety and P<sub>B</sub> to Pt(C<sub>6</sub>H<sub>4</sub>Me-o)<sub>2</sub>.

<b>Table 3.</b> 'H N.m.r. data for some dimetallic complexes derived from cis-  PtK <sub>2</sub> (dppm-P) <sub>2</sub>   s
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	Complex	$\delta(CH_2)^a/p.p.m.$	<sup>2</sup> J(HH)/Hz	$\delta(CH_3)^{a,b}/p.p.m.$	<sup>2</sup> J(PtH) <sup>b</sup> /Hz	N'/Hz
( <b>6a</b> )	[Me <sub>2</sub> Pt(µ-dppm) <sub>2</sub> Au]Cl	3.88, 4.06	d	+0.79	66.9	n.r.
(6b)	$[Me_2Pt(\mu-dppm)_2Ag]PF_6$	3.54	d	+0.86	63.4	n.r.
( <b>4a</b> )	$syn-[(C_6H_4Me-o)_2Pt(\mu-dppm)_2PtMe_2]^e$	3.5-3.8	d	+0.10	70.3	ca. 14
( <b>4b</b> )	anti-[ $(C_6H_4Me-o)_2Pt(\mu-dppm)_2PtMe_2$ ] <sup>e</sup>	3.19, 3.96	14.1	-0.11	70.4	15.5

<sup>a</sup> In CDCl<sub>3</sub>, to high frequency of SiMe<sub>4</sub>. <sup>b</sup> CH<sub>3</sub> of the methyl ligands. <sup>c</sup>  $N = |{}^{3}J(HP_{cis}) + {}^{3}J(HP_{trans})|$  (Pt methyls); n.r. = not resolved. <sup>d</sup> Broad resonances; <sup>2</sup>J(HH) or <sup>3</sup>J(PtH) not resolved. <sup>e</sup> For the CH<sub>3</sub> of the *o*-tolyl ligands:  $\delta$ (CH<sub>3</sub>) 1.39 p.p.m., <sup>4</sup>J(PtH) 5.9 Hz.

 $Me_2(dppm-P)_2$ ] (2a) goes rapidly even at -60 °C and the conversion to (2a) increases as the temperature is lowered  $[K_{eq} = \sim 39 \text{ (at } 20^{\circ}\text{C}) \text{ and } \sim 940 \text{ dm}^3 \text{ mol}^{-1} (\text{at } -30^{\circ}\text{C})] \text{ and}$ the concentration is increased. Consequently, in attempts to prepare bimetallic complexes from (2a) we used very concentrated solutions and low temperatures, in order to reduce the concentration of free dppm. Treatment of a mixture of (2a) and dppm in a minimum of dichloromethane at -60 °C with  $[{AgI(PPh_3)}_4]$  gave  $[Me_2Pt(\mu-dppm)_2AgI]$  (5) in nearly 90% yield. This complex was characterized by elemental analysis and non-electrical conductivity in nitrobenzene solution (Table 1) and by  ${}^{31}P{}^{1}H$  n.m.r. spectroscopy (Table 2). A gold complex,  $[Me_2Pt(\mu-dppm)_2Au]Cl$  (6a), was prepared similarly, see Experimental section and Tables 1-3 for characterizing data. The ionic nature of this gold complex reflects the greater tendency of gold(I) towards two-co-ordination over silver(I). By treating (2a) (prepared in situ) with AgPF<sub>6</sub> in acetone at -30 °C we prepared the mixed platinum-silver cation, isolated as the PF<sub>6</sub>



salt  $[Me_2Pt(\mu-dppm)_2Ag]PF_6$  (**6b**) in good (~60%) yield, see Experimental section and characterizing data in Tables 1–3.

As mentioned above, we have shown previously that the metallacycle  $[Pt(CH_2CH_2CH_2CH_2)(dppm-P)_2]$  reacts with [MCl(Me)(cod)] (M = Pt or Pd) to give the donor-acceptor complexes  $[(CH_2CH_2CH_2CH_2)Pt(\mu-dppm)_2MMe]^+$ , isolated as the chloride, PF<sub>6</sub>, or BPh<sub>4</sub> salts.<sup>4</sup> We now show that

analogous reactions occur with (2a). Treatment of a concentrated solution of this monodentate-dppm complex with [PtCl(Me)(cod)] at 0 °C readily gave an unsymmetrical diplatinum species, identified as the known cation [Me<sub>2</sub>Pt( $\mu$ -dppm)<sub>2</sub>PtMe]<sup>+</sup> (7a) from the characteristic <sup>31</sup>P n.m.r. parameters (see Table 2 and Experimental section). A similar study with [PdCl(Me)(cod)] showed that only one phosphorus-containing species was produced, which we formulate as (7b).

Crystal Structure of syn- $[(C_6H_4Me-o)_2Pt(\mu-dppm)_2PtMe_2]$ (4a).—An X-ray diffraction study of a crystalline fragment of (4a), obtained by slow diffusion of n-hexane into a dichloromethane solution of the syn-anti mixture, confirmed the cis square-planar co-ordination at both platinum atoms, and furthermore showed the o-tolyl groups to be in a syn configuration (see Figure 2). A <sup>1</sup>H-{<sup>31</sup>P} n.m.r. spectrum of the crystals used in the structure determination dissolved in CDCl<sub>3</sub> established that they comprised the minor isomer exclusively. Thus it may be concluded that at equilibrium in solution the minor isomer of  $[(C_6H_4Me-o)_2Pt(\mu-dppm)_2PtMe_2]$  is the syn isomer and conversely that the major isomer is in the anti configuration.

Relevant bond lengths and angles for the structure of (4a) are



Table 4. Selected molecular geometry parameters for (4a)

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given in Table 4. Any bonding interaction between the metal atoms is clearly precluded by the magnitude of the intramolecular Pt  $\cdots$  Pt separation (4.91 Å) which is the largest internuclear distance thus far reported for a binuclear dppm complex. The dppm-*PP'* bite distances [P(1)  $\cdots$  P(2) 3.22, P(3)  $\cdots$  P(4) 3.33 Å] are correspondingly large and are *ca*. 0.1 Å greater than any so far seen in complexes based on the Pt<sub>2</sub>( $\mu$ dppm)<sub>2</sub> skeleton; the next largest are 3.19 and 3.23 Å in the closely related complex [Me<sub>2</sub>Pt( $\mu$ -dppm)<sub>2</sub>PtMe<sub>2</sub>], where the



Figure 2. Molecular structure of  $[(C_6H_4Me-o)_2Pt(\mu-dppm)_2PtMe_2]$ (4a) showing the principal atomic numbering. Atoms are represented by spheres of arbitrary size

(i) Dona iongino (ii)			
Pt(1)-P(1)	2.279(5)	C(12)-Me(3)	1.49(2)
Pt(1)-P(3)	2.292(5)	C(22)-Me(4)	1.48(2)
Pt(1)-Me(1)	2.11(2)	P(1)-C(1)	1.84(2)
Pt(1)-Me(2)	2.14(2)	P(2)-C(1)	1.90(2)
Pt(2)-P(2)	2.337(5)	P(3) - C(2)	1.85(2)
Pt(2) - P(4)	2.322(4)	P(4) - C(2)	1.91(2)
Pt(2)-C(11)	2.09(1)	P-C <sub>6</sub> H,	1.82(1) - 1.87(1)
Pt(2)-C(21)	2.11(1)	0.5	
(ii) Bond angles (°)			
Me(1)-Pt(1)-Me(2)	81.7(8)	Pt(1)-P(1)-C(1)	121.1(6)
Me(1) - Pt(1) - P(1)	92.5(6)	Pt(2) - P(2) - C(1)	118.6(5)
Me(2) - Pt(1) - P(3)	87.7(5)	Pt(1) - P(3) - C(2)	120.1(5)
P(1) - Pt(1) - P(3)	<b>98.1(2)</b>	Pt(2) - P(4) - C(2)	126.1(5)
Me(1)-Pt(1)-P(3)	169.3(6)	Pt(2)-C(11)-C(12)	121.3(5)
Me(2)-Pt(1)-P(1)	174.0(6)	Pt(2)-C(11)-C(16)	118.7(5)
C(11)-Pt(2)-C(21)	80.9(6)	Pt(2)-C(21)-C(22)	125.2(4)
C(11)-Pt(2)-P(2)	88.3(4)	Pt(2)C(21)C(26)	114.7(4)
C(21)-Pt(2)-P(4)	92.7(4)	Me(3)-C(12)-C(11)	126(1)
P(2)-Pt(2)-P(4)	98.1(2)	Me(3)-C(12)-C(13)	114(1)
C(11)-Pt(2)-P(4)	172.3(5)	Me(4)C(22)C(21)	126(1)
C(21)-Pt(2)-P(2)	169.2(4)	Me(4)-C(22)-C(23)	114(1)
P(1)-C(1)-P(2)	119.2(9)		
P(3)-C(2)-P(4)	124.6(9)		
(iii) Torsion angles (°) <sup>a</sup>			
Pt(1)-P(1)-C(1)-P(2)	28.5	Pt(2)-P(4)-C(2)-P(3)	26.7
P(1)-C(1)-P(2)-Pt(2)	-97.6	P(4)-C(2)-P(3)-Pt(1)	- 79.0
C(1)-P(2)-Pt(2)-P(4)	3.0	C(2)-P(3)-Pt(1)-P(1)	-16.3
P(2)-Pt(2)-P(4)-C(2)	54.9	P(3)-Pt(1)-P(1)-C(1)	67.1

<sup>a</sup> The sign convention is that of W. Klyne and V. Prelog, Experientia, 1960, 16, 521; estimated standard deviations ca. 1.0°.

Pt ••• Pt separation is 4.36 Å.<sup>6</sup> The latter example provides the only previously reported crystal structure of a complex with two *cis* bridging dppm ligands; recently the structure of the related complex [Me<sub>2</sub>Pt( $\mu$ -Me<sub>2</sub>PCH<sub>2</sub>PMe<sub>2</sub>)<sub>2</sub>PtMe<sub>2</sub>], also with *cis* geometry, was reported.<sup>7</sup>

The eight-membered Pt<sub>2</sub>P<sub>4</sub>C<sub>2</sub> ring adopts a twist saddle conformation<sup>8</sup> very similar to that found in the crystal structure of  $[Me_2Pt(\mu-dppm)_2PtMe_2]$ ; the endocyclic torsion angles around the ring are given in Table 4. The bond angles within the ring are all some 8-17° more obtuse than the idealized squareplanar or tetrahedral values (see Table 4), and possibly reflect more steric overcrowding in the presence of two o-tolyl groups than occurs in  $[Me_2Pt(\mu-dppm)_2PtMe_2]$ , where deviations from idealized angles within the ring are in the range 8-12°.6 In the present structure we note that the two Pt-P bond lengths trans to the o-tolyl groups are 0.03-0.06 Å longer than the two Pt-P bonds trans to methyl groups, and that the P-CH<sub>2</sub> bonds on the o-tolyl side of the molecule are ca. 0.06 Å longer than those attached to the PtMe<sub>2</sub> part. Otherwise there are no remarkable bond lengths in the structure (see Table 4). The dihedral angle between the two square planes of co-ordination around the platinum atoms is 109°.

The syn o-tolyl rings are oriented with their methyl groups inclined towards each other [Me(3)  $\cdots$  Me(4) 3.56 Å], pointing in the opposite direction to the methyl groups attached to Pt(1), and with the rings containing Me(3) or Me(4) making angles of 88 or 70°, respectively, with the square plane of co-ordination around Pt(2). The non-bonded intramolecular distances Pt(2)  $\cdots$  Me(3) and Pt(2)  $\cdots$  Me(4) are 3.40 and 3.52 Å, respectively, these being only slightly shorter than the sum of the van der Waals radii for Pt (1.7—1.8 Å)<sup>9</sup> and CH<sub>3</sub> (2.0 Å),<sup>10</sup> with the angles at C(12) and C(22) and at C(11) and C(21) (see Table 4) indicating a certain leaning away of the o-tolyl groups from the metal centre. There are no significant intermolecular contacts.

## Experimental

The general procedures and apparatus were the same as in other recent publications from this laboratory.<sup>11</sup>

Preparation of  $[(C_{10}H_7)_2Pt(\mu-dppm)_2RhCl(CO)]$  (3).—A solution of  $[Rh_2Cl_2(CO)_4]$  (0.016 g, 0.041 mmol) in dichloromethane (1 cm<sup>3</sup>) was added to a solution of cis-[Pt(C<sub>10</sub>-H<sub>7</sub>)<sub>2</sub>(dppm-P)<sub>2</sub>] (2b) (0.100 g, 0.082 mmol) in dichloromethane (5 cm<sup>3</sup>); a yellow-orange solution was formed. The solvent was removed under reduced pressure and the residue triturated with diethyl ether to give the product as yellow microcrystals. Yield: 0.094 g (83%).

Preparation of  $[(C_6H_4Me-o)_2Pt(\mu-dppm)_2PtMe_2]$  (4a).—A mixture of cis-[Pt(C<sub>6</sub>H<sub>4</sub>Me-o)<sub>2</sub>(dppm-P)<sub>2</sub>] (2c) (0.10 g, 0.087 mmol) and [PtMe<sub>2</sub>(cod)] (0.029 g, 0.087 mmol) in dichloromethane (1.0 cm<sup>3</sup>) was put aside for 3 d at room temperature. The white product crystallized out when the walls of the tube were scratched. Yield 0.060 g (45% of the dichloromethane solvate). Addition of diethyl ether to the mother-liquors gave a further crop of crystalline, off-white material (0.035 g). Total yield: 0.095 g (71%).

Preparation of  $[Me_2Pt(\mu-dppm)_2AgI]$  (5).—A mixture of  $[PtMe_2(dppm-PP')]$  (0.10 g, 0.164 mmol) and dppm (0.070 g, 0.182 mmol) in dichloromethane (0.5 cm<sup>3</sup>) was left to stand for 15 min at -30 °C. A solution of  $[{AgI(PPh_3)}_{4}]$  (0.082 g, 0.041 mmol) in dichloromethane (0.5 cm<sup>3</sup>) was added to the cooled reaction mixture which was shaken to ensure mixing and then put aside at -60 °C for 30 min. The solvent was removed under reduced pressure and the oily residue triturated with diethyl

ether and then with methanol. This gave the required product as white microcrystals. Yield: 0.175 g (87%).

 $[Me_2Pt(\mu-dppm)_2Au]Cl$  (6a) was prepared similarly in 74% yield.

Preparation of  $[Me_2Pt(\mu-dppm)_2Ag]PF_6$  (6b).—A mixture of  $[PtMe_2(dppm-PP')]$  (0.10 g, 0.164 mmol) and dppm (0.064 g, 0.164 mmol) in acetone (0.5 cm<sup>3</sup>) was cooled to -30 °C. After 15 min, a solution of AgPF<sub>6</sub> (0.0415 g, 0.164 mmol) in acetone (0.5 cm<sup>3</sup>) was added and the mixture shaken and then set aside at -30 °C for 40 min. The mixture was centrifuged and the yellow solution was decanted from a small amount of dark residue and then evaporated to dryness under reduced pressure; the residue was triturated with diethyl ether to give the off-white solid product. Yield: 0.12 g (59%).

Formation of  $[Me_2Pt(\mu-dppm)_2PtMe]^+$  (7a) from  $[Pt-Me_2(dppm-P)_2]$  (2b) and [PtCl(Me)(cod)].—A mixture of (2a) (20 mg, 0.033 mmol) and dppm (12.6 mg, 0.033 mmol) was equilibrated in CDCl<sub>3</sub> (0.35 cm<sup>3</sup>) at 0 °C for 10 min. [Pt-Cl(Me)(cod)] (11.6 mg, 0.033 mmol) was added and the mixture shaken to give a yellow solution. A <sup>31</sup>P-{<sup>1</sup>H} n.m.r. study of this solution showed the presence of the desired species (see Results and Discussion section).

Formation of  $[Me_2Pt(\mu-dppm)_2PdMe]^+$  (7b).—A mixture of (1a) (20 mg, 0.033 mmol) and dppm (12.6 mg, 0.033 mmol) was equilibrated in CDCl<sub>3</sub> (0.35 cm<sup>3</sup>) at 0 °C for 10 min. [PdCl(Me)(cod)] (8.7 mg, 0.033 mmol) was added and the mixture shaken to give an orange solution. <sup>31</sup>P N.m.r. analysis of this solution showed that only one phosphorus-containing species was present and that this was probably the desired complex (see Results and Discussion section).

Structure Determination.—Crystals of  $[(C_6H_4Me_{-0})_2Pt(\mu-dppm)_2PtMe_2]$  (4a) were grown as colourless, irregularlyshaped fragments (approx. dimensions  $0.2 \times 0.2 \times 0.3$  mm) by slow diffusion of n-hexane into a dichloromethane solution. A <sup>1</sup>H-{<sup>31</sup>P} n.m.r. spectrum of these crystals dissolved in CDCl<sub>3</sub> established that they comprised the *minor* isomer exclusively.

Crystal data.  $C_{66}H_{64}P_4Pt_2$ , M = 1371.3, monoclinic, a = 12.371(2), b = 21.368(5), c = 21.917(5) Å,  $\beta = 92.84(2)^\circ$ , U = 5786(2) Å<sup>3</sup> (by least-squares refinement of diffractometer setting angles for 15 automatically-centred reflections having  $30 < 2\theta < 36^\circ$ ), graphite-monochromated Mo- $K_{\alpha}$  radiation ( $\lambda = 0.71069$  Å), space group  $P2_1/n$  (alt.  $P2_1/c$ , no. 14), Z = 4,  $D_c = 1.57$  g cm<sup>-3</sup>, F(000) = 2704,  $\mu$ (Mo- $K_{\alpha}$ ) = 50.28 cm<sup>-1</sup>.

Data collection and processing. Intensities of 6 454 independent reflections  $(h,k,\pm l, 4 < 2\theta < 45^\circ)$  were measured on a Syntex  $P2_1$  diffractometer in the  $\omega$ -2 $\theta$  scan mode using scan speeds between 2 and 29° min<sup>-1</sup>, with the scans running from 1° below  $K_{\alpha 1}$  to 1° above  $K_{\alpha 2}$ . The 4 506 reflections with  $I > 2.5\sigma$ -(I) were used in the analysis after correction for Lorentz and polarisation factors and for crystal decay (ca. 25%, linear). The data were not corrected for absorption.

Structure analysis and refinement. Solution by Patterson and difference syntheses was followed by full-matrix least-squares refinement with anisotropic thermal parameters for Pt and P atoms using the SHELX program system.<sup>12</sup> All aromatic rings were refined as rigid groups with idealised  $D_{6h}$  geometry, the C atoms having individual isotropic thermal parameters and C-C distances of 1.395 Å. Atoms throughout the structure display somewhat larger thermal parameters than desirable, *e.g.* some aromatic ring C atoms have  $U_{iso}$  in the range 0.10(1)-0.17(1) A<sup>2</sup> (see SUP 56243). This may indicate a small degree of overall disorder in the crystal, or may to some extent be accounted for by inadequate correction for the decay shown by the poor quality crystal fragment during data collection. All bond lengths

Atom	x	У	Z	Atom	x	у	Z
Pt(1)	3 011.4(6)	1 813.2(3)	9 772.0(3)	C(51)	2 115(10)	1 048(5)	7 279(4)
Pt(2)	4 379.2(6)	1 946.1(3)	7 712.1(3)	C(52)	2 511(10)	492(5)	7 043(4)
P(1)	1 532(4)	1 877(2)	9 113(2)	C(53)	2 038(10)	241(5)	6 507(4)
P(2)	2 838(4)	1 392(2)	7 970(2)	C(54)	1 169(10)	546(5)	6 206(4)
P(3)	3 808(4)	2743(2)	9 527(2)	C(55)	772(10)	1 102(5)	6 442(4)
P(4)	3 841(4)	2 933(2)	8 019(2)	C(56)	1 246(10)	1 353(5)	6 979(4)
Me(1)	2 498(17)	956(9)	10 134(9)	C(61)	3 055(11)	716(5)	8 465(5)
Me(2)	4 313(17)	1 677(9)	10 437(9)	C(62)	2 349(11)	206(5)	8 446(5)
Me(3)	4 152(20)	1 359(11)	6 268(10)	C(63)	2 582(11)	-319(5)	8 807(5)
Me(4)	5 125(21)	2 910(13)	6 498(12)	C(64)	3 521(11)	- 335(5)	9 186(5)
C(1)	1 666(14)	1 842(7)	8 283(7)	C(65)	4 227(11)	174(5)	9 205(5)
C(2)	3 383(13)	3 154(7)	8 812(7)	C(66)	3 994(11)	700(5)	8 844(5)
C(11)	4 971(13)	1 120(6)	7 344(8)	C(71)	3 468(11)	3 362(6)	10 067(5)
C(12)	4 769(13)	968(6)	6 730(8)	C(72)	3 060(11)	3 177(6)	10 621(5)
C(13)	5 182(13)	415(6)	6 496(8)	C(73)	2 752(11)	3 627(6)	11 040(5)
C(14)	5 796(13)	13(6)	6 877(8)	C(74)	2 853(11)	4 261(6)	10 905(5)
C(15)	5 998(13)	165(6)	7 491(8)	C(75)	3 262(11)	4 446(6)	10 351(5)
C(16)	5 585(13)	718(6)	7 725(8)	C(76)	3 569(11)	3 996(6)	9 932(5)
C(21)	5 869(10)	2 282(7)	7 420(7)	C(81)	5 284(9)	2 742(7)	9 569(6)
C(22)	5 992(10)	2 701(7)	6 941(7)	C(82)	5 895(9)	3 203(7)	9 877(6)
C(23)	7 021(10)	2 913(7)	6 808(7)	C(83)	7 017(9)	3 143(7)	9 946(6)
C(24)	7 927(10)	2 705(7)	7 154(7)	C(84)	7 529(9)	2 622(7)	9 707(6)
C(25)	7 804(10)	2 286(7)	7 634(7)	C(85)	6 918(9)	2 161(7)	9 399(6)
C(26)	6 775(10)	2 074(7)	7 767(7)	C(86)	5 796(9)	2 221(7)	9 330(6)
C(31)	398(10)	1 333(6)	9 226(7)	C(91)	4 789(10)	3 580(5)	7 934(6)
C(32)	- 54(10)	928(6)	8 784(7)	C(92)	5 800(10)	3 557(5)	8 244(6)
C(33)	-931(10)	551(6)	8 919(7)	C(93)	6 524(10)	4 053(5)	8 196(6)
C(34)	-1 356(10)	579(6)	9 497(7)	C(94)	6 237(10)	4 572(5)	7 838(6)
C(35)	-903(10)	985(6)	9 938(7)	C(95)	5 226(10)	4 595(5)	7 528(6)
C(36)	- 26(10)	1 361(6)	9 803(7)	C(96)	4 502(10)	4 099(5)	7 575(6)
C(41)	781(10)	2 612(4)	9 166(6)	C(101)	2 634(8)	3 180(5)	7 573(5)
C(42)	112(10)	2 834(4)	8 683(6)	C(102)	2 361(8)	2 862(5)	7 031(5)
C(43)	-439(10)	3 399(4)	8 740(6)	C(103)	1 443(8)	3 037(5)	6 676(5)
C(44)	- 321(10)	3 742(4)	9 281(6)	C(104)	799(8)	3 530(5)	6 864(5)
C(45)	349(10)	3 520(4)	9 764(6)	C(105)	1 072(8)	3 848(5)	7 406(5)
C(46)	900(10)	2 955(4)	9 707(6)	C(106)	1 990(8)	3 673(5)	7 760(5)

Table 5. Fractional atomic co-ordinates (x 10<sup>4</sup>) for (4a) with e.s.d.s in parentheses

and angles, however, are normal (see Table 4). No H atoms were included in the final refinement, which converged to R = 0.063and  $R' = \Sigma w^{\frac{1}{2}} \Delta / \Sigma w^{\frac{1}{2}} |F_o| = 0.063$ , employing the weighting scheme  $w = 1/(\sigma^2 F_o + 0.0005 F_o^2)$ . A final difference map showed no unusual features. Complex neutral-atom scattering factors were calculated from the analytical approximation and coefficients given in ref. 13. The final atomic co-ordinates and their standard deviations are given in Table 5.

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