

Bimetallic Systems. Part 3.¹ Complexes containing the Ligand Bis(diphenylphosphino)methane bridging from the Platinacycle

PtCH₂CH₂CH₂CH₂ to another Metal

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The metallacycle $[\text{Pt}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)(\text{dppm-PP}')]$ (5) (dppm = $\text{Ph}_2\text{PCH}_2\text{PPh}_2$) is made from $[\text{PtCl}_2(\text{dppm-PP}')]]$ and $\text{Li}(\text{CH}_2)_4\text{Li}$ in diethyl ether. Complex (5) rapidly reacts with dppm to give $[\text{Pt}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)(\text{dppm-P})_2]$ (6) which contains monodentate dppm ligands and is remarkably stable with respect to dissociation. It is shown that (6) is a convenient starting material for making bimetallic species. Thus treatment of (6) with $[\{\text{AgI}(\text{PPh}_3)\}_4]$ gives the neutral complex $[(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)\text{Pt}(\mu\text{-dppm})_2\text{AgI}]$; treatment with $\text{Ag}[\text{PF}_6]$ or $[\text{AuCl}(\text{PPh}_3)]$ gives the salts $[(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)\text{Pt}(\mu\text{-dppm})_2\text{M}]^+\text{X}^-$ ($\text{M} = \text{Ag}$, $\text{X} = \text{PF}_6$; $\text{M} = \text{Au}$, $\text{X} = \text{Cl}$) and treatment with $[\text{MCl}(\text{CH}_3)(\text{cod})]$ ($\text{cod} = \text{cyclo-octa-1,5-diene}$) gives the dative-bonded species $[(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)\text{Pt}(\mu\text{-dppm})_2\text{M}(\text{CH}_3)]\text{Cl}$ ($\text{M} = \text{Pt}$ or Pd). Microanalytical data, solution conductivity data, and ^1H - $\{^{31}\text{P}\}$, ^{31}P - $\{^1\text{H}\}$, and ^{195}Pt - $\{^1\text{H}\}$ n.m.r. data are given and discussed.

We have been interested in making bimetallic complexes from the *cis*-dialkylplatinum(II) species (1a)—(1d).² We have found that, with the exception of the dimethyl species (1a), we could not generate useful amounts of species (1b)—(1d) due to dissociation into chelates (2b)—(2d) and dppm [equation (i); dppm = bis(diphenylphosphino)methane]. The equilibrium constant at 20 °C, K , for equation (i) falls off sharply with increasing bulk of R; $K = 39$, (1a)/(2a); 4, (1b)/(2b); <0.03 , (1c)/(2c) or (1d)/(2d). This effect may be due to unfavourable steric interactions between the monodentate dppm ligands and the R groups in (1a)—(1d) and we therefore reasoned that a metallacycle, which has low steric requirements, may promote formation of a bis(monodentate) species analogous to (1a)—(1d).

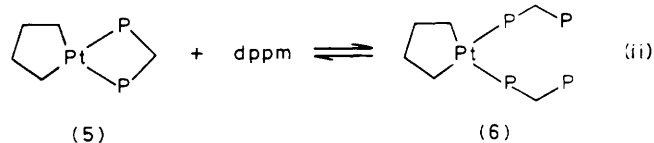
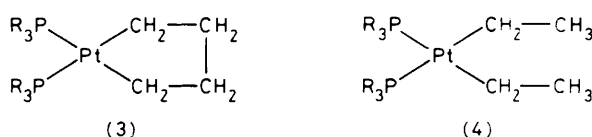
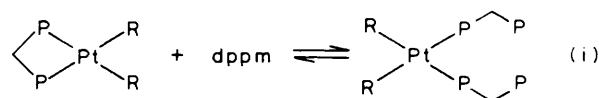
Metallacycles have been well studied³⁻⁵ and are of particular interest because of their possible role in catalysis.^{4,5} Moreover, bis(phosphine)platinacyclopentanes (3) are much more stable than the corresponding diethyl complexes (4) because of (i) the chelate effect and (ii) the β -hydrogens are pointing away from the metal, preventing decomposition *via* β -hydrogen elimination.⁴

For the above reasons we attempted to make metallacycle-dppm complexes.

Results and Discussion

Treatment of $[\text{PtCl}_2(\text{dppm-PP}')]]$ with 1,4-dilithiobutane in diethyl ether gave the platinacycle (5) in good (63—69%) yields. The platinacycle (5) is a white crystalline solid, soluble in benzene, acetone and chlorinated solvents but insoluble in methanol. It has been fully characterised by microanalysis and molecular weight determination (Table 1), i.r. spectroscopy, and by ^1H - $\{^{31}\text{P}\}$ (Table 2), ^{31}P - $\{^1\text{H}\}$ (Table 3), and ^{195}Pt - $\{^1\text{H}\}$ (Table 3) n.m.r. spectroscopy. The ^1H n.m.r. spectrum is consistent with the presence of a platinacyclopentane⁴ and the ^{31}P - $\{^1\text{H}\}$ and ^{195}Pt - $\{^1\text{H}\}$ resonances are similar to other platinum-dppm chelates which we and others⁶⁻⁸ have made.

Addition of one equivalent of dppm to a chloroform solution of (5) at 20 °C rapidly gave an equilibrium mixture of (5), (6), and dppm [equation (ii)]. The equilibrium constant was estimated in CDCl_3 from integration of the ^{31}P - $\{^1\text{H}\}$ n.m.r. spectrum (Figure 1) of the mixture and found to be 430 ± 40



$\text{dm}^3 \text{mol}^{-1}$. Hence K for the metallacycle is *ca.* 100 times K for the corresponding diethyl complex. In practice, this means that the monodentate-dppm species (6) predominates ($>90\%$) in quite dilute solutions (*ca.* 60 mmol dm^{-3}) at ambient temperatures whereas the diethyl analogue (1b) only predominates ($>90\%$) in very concentrated solutions (*ca.* 300 mmol dm^{-3}) at low temperatures (-30 °C). This makes the platinacycle (6) a convenient starting material for the synthesis of bimetallic complexes whereas the diethyl analogue (1b) is not. The bis(dppm) platinacycle (6) is readily isolated in analytically pure condition from its concentrated solutions; it has been fully characterised analytically and spectroscopically (Tables 1—3).

It is interesting to compare the n.m.r. spectroscopic

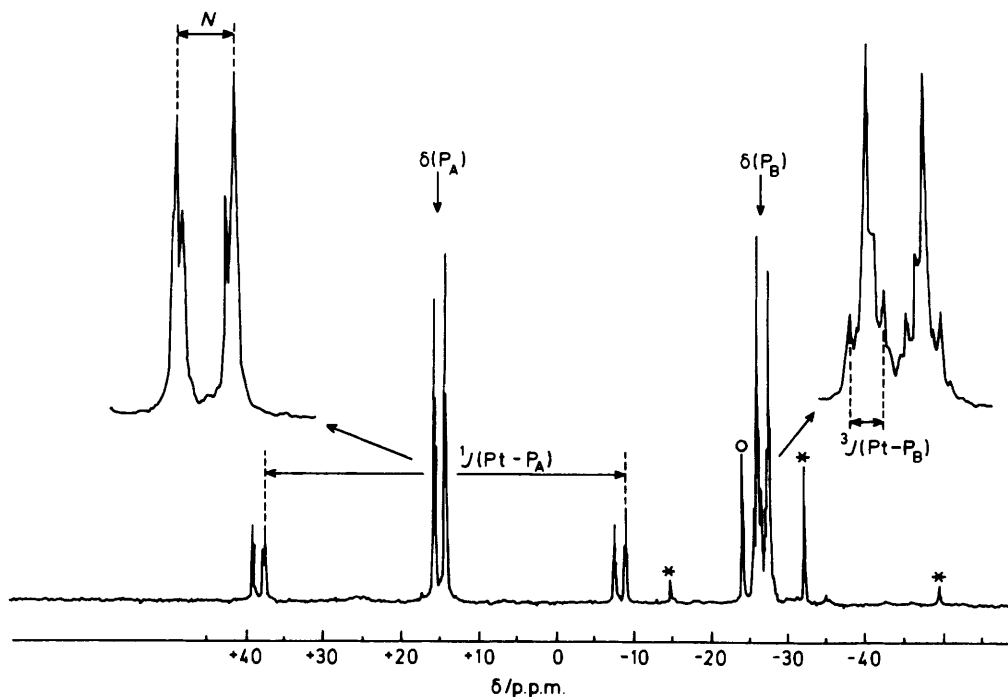


Figure 1. $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum (40.25 MHz), at 20 °C, of what was initially a 59 mmol dm^{-3} solution of $[\text{Pt}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)_2(\text{dppm}-P)_2]$ in CDCl_3 which has undergone some dissociation to dppm (marked O) and the chelate $[\text{Pt}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)(\text{dppm}-PP')$ (marked *) to give an equilibrium mixture

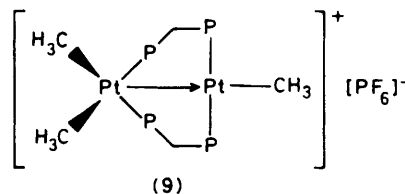
Table 1. Microanalytical (%),^a melting point, and conductivity data

Complex ^d	M.p. ^b /°C	C	H	Other	Λ °/Ω ⁻¹ cm ² mol ⁻¹
(5)	182—183	54.75 (54.8)	4.6 (4.75)	<i>M</i> 622 (636)	
(6)·0.5CH ₂ Cl ₂	138—140	62.1 (62.25)	5.15 (5.0)	Cl 3.05 (3.35)	
(7)·0.5CH ₂ Cl ₂ ^f	150—152	50.6 (50.45)	4.35 (4.1)	I 9.7 (9.8)	2
(8a)	176—180	51.05 (50.95)	3.9 (4.1)	F 9.1 (8.95)	21
(8b)·2CHCl ₃	158—160	44.8 (45.1)	3.65 (3.7)	Cl 15.9 (16.65)	18
(10a)·Et ₂ O·0.4CH ₂ Cl ₂	150—153	51.5 (51.9)	4.7 (4.8)	Cl 4.2 (4.65)	18
(10b)·2MeOH	158—160	60.0 (60.3)	4.8 (4.7)		19

^a Calculated values are in parentheses. ^b Melted with decomposition. ^c 10⁻³ mol dm⁻³ solutions in nitrobenzene at 21 °C. ^d Presence of solvent confirmed by ¹H n.m.r. spectroscopy. ^e Molecular weight in chloroform. ^f Cl analysis: 2.8 (2.75%).

properties of the chelate (5) and the bis(dppm) species (6) as shown in Table 4. The values for the bis(dppm) species (6) are similar to those reported for the unexceptional complex *cis*- $[\text{Pt}(\text{CH}_3)_2(\text{PMePh}_2)_2]$.^{6,7} Relative to the values for the bis(dppm) platinacycle (6), the chelate platinacycle (5) has a high frequency $\delta(\text{PCH}_2\text{P})$ shift, a very low frequency $\delta(\text{P})$ shift and small $^1J(\text{PtP})$ coupling constant, and the value of $\delta(\text{Pt})$ is over 600 p.p.m. to high frequency. We associate all of these properties with the strain in the four-membered chelate ring.

In the Scheme, we show the bimetallic complexes which we have made from the bis(dppm) platinacycle (6). In these reactions (6) can be generated *in situ* from (5) or added as the isolated solid. The reactions were carried out at low temperatures (-30 to -60 °C) in order to minimise dissociation of (6). The platinum-silver complexes (7) and (8a) and platinum-gold complex (8b) were readily made (Scheme) and have been assigned structures on the basis of microanalysis, solution conductivity measurements, and from $^{31}\text{P}\{-^1\text{H}\}$ and $^1\text{H}\{-^31\text{P}\}$



n.m.r. spectroscopy (Tables 1—3). The value of $^1J(^{109}\text{AgP})$ for the salt (8a) is much larger than $^1J(^{109}\text{AgP})$ in the neutral species (7). This difference is due to the different charges and co-ordination numbers for the silver(i) in (7) and (8a).⁹

We found¹⁰ that treatment of the dimethyl species (1a) with $[\text{PtCl}(\text{CH}_3)(\text{cod})]$ (cod = cyclo-octa-1,5-diene) in CDCl_3 gave the known¹¹ dative-bonded complex (9) as essentially the only product. We therefore treated the platinacycle (6) with $[\text{PtCl}(\text{CH}_3)(\text{cod})]$ under similar conditions and obtained a product which we formulate as the dative-bonded species

Table 2. ^1H - $\{^{31}\text{P}\}$ and ^1H n.m.r. data ^a

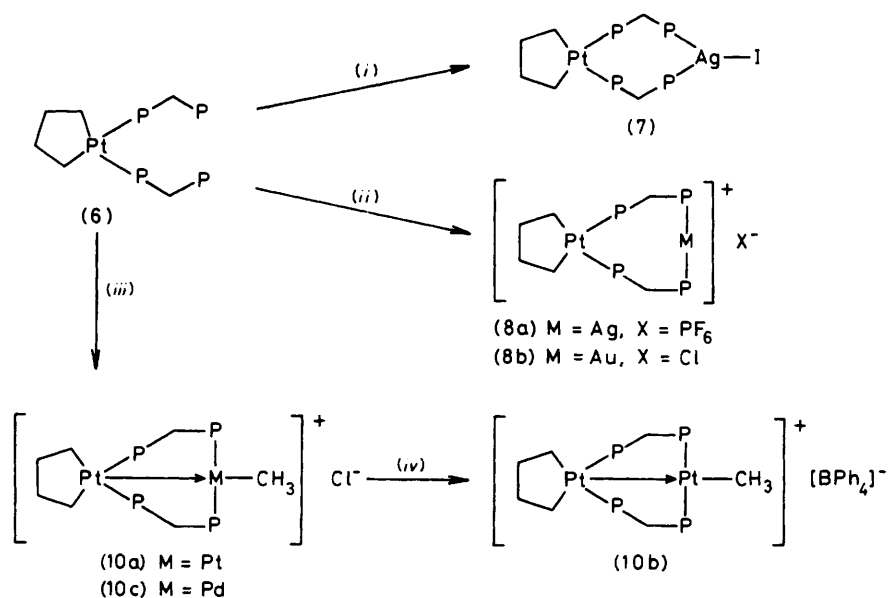
Complex	$\delta(\text{PCH}_2\text{P})$	$^3J(\text{PtPCH}_2)$	$^2J(\text{PCH}_2)$	$^2J(\text{H-C-H})$	$\delta(\text{CH}_2\text{CH}_2)$	$^2J(\text{PtCH}_2)$ or $^3J(\text{PtCH}_2\text{CH}_2)$
(5)	4.37	19.6	9.0		2.52 1.45	76 84
(6)	2.90	13.0	6.4			
(7)	3.19, 2.66	<i>b</i>	<i>b</i>	12.7	<i>c</i>	
(8a) ^d	3.49, 3.39	35.6	<i>b</i>	<i>b</i>	2.18 1.51	56 78
(8b) ^d	4.26, 3.68	41.4	<i>b</i>	14.1	2.24 1.35	63 75
(10a) ^e	3.90, 3.75	<i>b</i>	<i>b</i>	9.0	<i>c</i>	
(10c) ^f	3.92, 3.86	<i>b</i>	<i>b</i>	<i>b</i>	<i>c</i>	

^a Spectra (100 MHz) measured in CDCl_3 at 21 °C unless otherwise stated. Chemical shifts (δ) in p.p.m. (± 0.01) to high frequency of SiMe_4 , and coupling constants (J) are in Hz (± 0.1). ^b Not resolved. ^c Broad resonance in the region δ 1.3–2.5 but with no resolved fine structure. ^d At -40 °C. ^e $\delta(\text{Pt-CH}_3)$ 0.64 p.p.m., $^2J(\text{PtH}) = 79.6$, $J(\text{PtH}) = 12.4$, $J(\text{PH}) = 6.9$ Hz. ^f $\delta(\text{Pd-CH}_3)$ 0.91 p.p.m., $J(\text{PtH}) = 11.5$, $J(\text{PH}) = 5.9$ Hz.

Table 3. ^{31}P - $\{^1\text{H}\}$ and ^{195}Pt - $\{^1\text{H}\}$ n.m.r. data ^a

Complex	$\delta(\text{P}_A)$ ^b	$^1J(\text{PtP}_A)$ ^c	$\delta(\text{P}_B)$ ^b	$^3J(\text{PtP}_B)$ ^c	N ^d	$^1J(\text{AgP}_B)$ ^c	$^1J(\text{PtP}_B)$ ^c	$\delta(\text{Pt})$ ^e
(5)	-29.8	1 295						+480
(6)	+15.7	1 807	-24.6	32	56			-122
(7)	+23.1	1 719	-14.2	161	127	398, 342		
(8a) ^f	+27.7	1 688	-2.2	244	105	532, 461		
(8b)	+25.0	1 765	+32.7	154	86			
(10a)	+31.7	1 401	+24.2	<i>g</i>	87		3 020	
(10c)	+27.9	1 452	+18.7	<i>g</i>	93			

^a In CDCl_3 at 21 °C unless otherwise stated. ^b In p.p.m. (± 0.1) to high frequency of 85% H_3PO_4 . ^c In Hz (± 3). ^d $N = |^1J(\text{P}_A\text{P}_B) + ^3J(\text{P}_A\text{P}_B)|$. ^e In CD_2Cl_2 at +23 °C, to high frequency of $\Xi(^{195}\text{Pt}) = 21.4$ MHz. ^f $\delta(\text{PF}_6)$ -143.7 p.p.m., $J(\text{PF}) = 713$ Hz. ^g Not resolved.



Scheme. Reagents and conditions: (i) $[\text{AgI}(\text{PPh}_3)_4]$ in CH_2Cl_2 ; (ii) For $\text{M} = \text{Ag}$, $\text{X} = \text{PF}_6$, $\text{Ag}[\text{PF}_6]$ in acetone; for $\text{M} = \text{Au}$, $\text{X} = \text{Cl}$, $[\text{AuCl}(\text{PPh}_3)]$; (iii) $[\text{MCl}(\text{CH}_3)(\text{cod})]$, $\text{M} = \text{Pt}$ or Pd ; (iv) $\text{Na}[\text{BPh}_4]$ in methanol

(10a). This follows from microanalysis, a solution conductivity measurement in nitrobenzene, and ^{31}P - $\{^1\text{H}\}$ and particularly ^1H - $\{^{31}\text{P}\}$ n.m.r. spectroscopy. In the ^1H - $\{^{31}\text{P}\}$ n.m.r. spectrum of the diplatinum complex (10a), in addition to resonances due to the CH_2 groups of the metallacycle and dppm ligands, there was a sharp singlet at 0.64 p.p.m. which was assigned to the CH_3 -Pt resonance. This resonance is not only coupled to the near ^{195}Pt but also shows coupling to the remote ^{195}Pt of

12.4 Hz, indicating the presence of a donor-acceptor bond in (10a) similar to that postulated for the trimethyl-diplatinum analogue (9).¹¹ Addition of a methanolic solution of $\text{Na}[\text{BPh}_4]$ solution to a solution of (10a) gave the tetraphenylborate salt (10b) which had almost identical spectral parameters to (10a). In the solid state the diplatinum complexes (10a) and (10b) tenaciously hold on to solvent molecules; for example, the diethyl ether of crystallisation in (10a) was not removed by

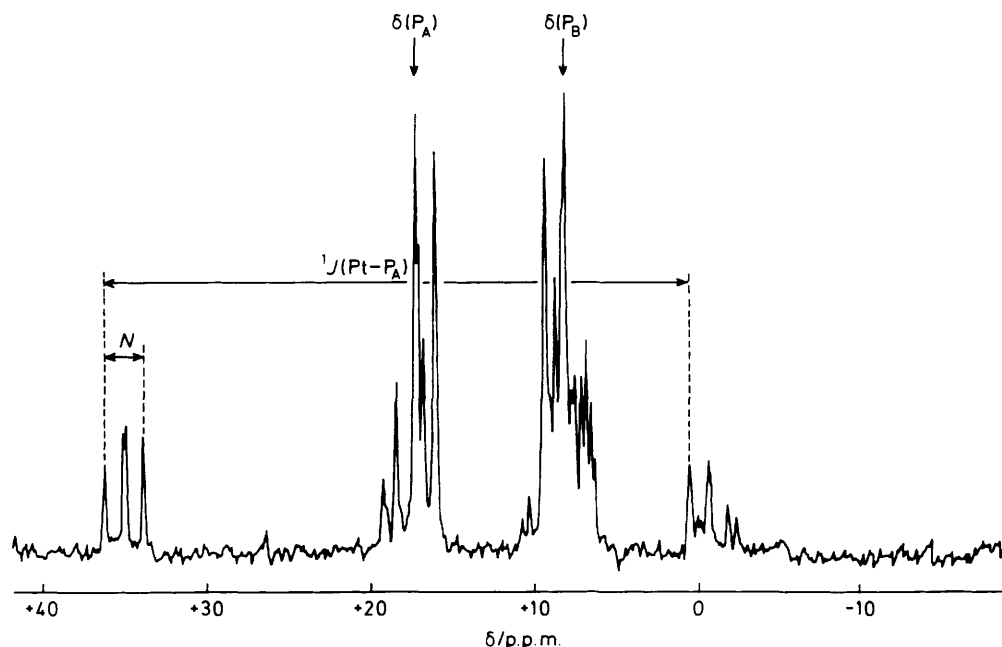


Figure 2. $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum (40.25 MHz) of the product formed from $[\text{Pt}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)(\text{dppm}-P)_2]$ and $[\text{PdCl}(\text{CH}_3)(\text{cod})]$ and assigned structure (10c)

Table 4. Comparison of n.m.r. data ($\delta/\text{p.p.m.}$ and J/Hz) for $[\text{Pt}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)(\text{dppm}-PP')$ (5) and $[\text{Pt}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)(\text{dppm}-P)_2]$ (6)

Complex	$\delta(\text{CH}_2\text{P}_2)$	$\delta(\text{P})$	$^1J(\text{PtP})$	$\delta(\text{Pt})$
(5)	+4.37	-29.8	1 295	+480
(6)	+2.90	+15.7	1 807	-122

drying at 0.005 mmHg for 20 h. As can be seen from the microanalyses in Table 1, solvents of crystallisation are present in all of our bimetallic complexes and we and others^{6,12} have noted the tendency of dppm complexes to occlude solvent molecules. This property unfortunately renders microanalyses of little diagnostic value.

We have also treated (6) with $[\text{PdCl}(\text{CH}_3)(\text{cod})]$ in the hope of making the heteronuclear dative-bonded species (10c). On a small scale, mixing (6) with $[\text{PdCl}(\text{CH}_3)(\text{cod})]$ in CDCl_3 gave essentially one species (by $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectroscopy) to which we assign the structure (10c) on the basis of $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectroscopy (see Figure 2) and the $^1\text{H}\{-^{31}\text{P}\}$ n.m.r. spectrum which showed a methyl resonance at 0.91 p.p.m. flanked by satellites due to coupling to the remote ^{195}Pt [$J(\text{PtH}) = 11.5$ Hz]. One attempt to isolate this species in pure form failed due to substantial decomposition.

The formulation of the species (10a)—(10c) as dative-bonded is reasonable by electron-counting arguments. Without the dative bond the methyl-platinum(II) or -palladium(II) group in (10a)—(10c) would have only fourteen electrons¹¹ whereas with the dative bond they have a more usual sixteen-electron count. It is notable that in the platinum-silver (8a) and platinum-gold (8b) complexes the d^{10} metals are also fourteen-electron centres and dative $\text{Pt}\rightarrow\text{Ag}$ or $\text{Pt}\rightarrow\text{Au}$ bonds may be present. However, linear two-co-ordinate silver(I) or gold(I) are common and stable and hence we have not indicated a dative bond in the structures (8a) and (8b).

We have shown that the metallacycle stabilises the mono-

dentate dppm species (6) with respect to dissociation and hence (6) is a convenient building block for bimetallic complexes since it gives high yields and few by-products.

Experimental

General methods were as previously described.¹³ The starting materials were made by literature methods: $\text{Li}(\text{CH}_2)_4\text{Li}$,⁵ $[\text{PtCl}_2(\text{dppm}-PP')]$,¹⁴ $\{[\text{AgI}(\text{PPh}_3)]_4\}$,¹⁵ $[\text{AuCl}(\text{PPh}_3)]$,¹⁶ $[\text{PtCl}(\text{CH}_3)(\text{cod})]$,¹⁷ $[\text{PdCl}(\text{CH}_3)(\text{cod})]$.¹⁸

Preparation of $[\text{Pt}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)(\text{dppm}-PP')$ (5).—A solution of $\text{Li}(\text{CH}_2)_4\text{Li}$ (7.4 cm³, 0.25 mol dm⁻³ in diethyl ether, 1.85 mmol) was added dropwise (over 5 min) to a stirred, ice-cold suspension of $[\text{PtCl}_2(\text{dppm}-PP')]$ (1.00 g, 1.54 mmol) in benzene (25 cm³) under dinitrogen. The mixture was then stirred at room temperature (21 °C) for 45 min and then warmed (60 °C) on a water bath for 15 min to give a cloudy orange solution. The mixture was then cooled to 0 °C and methanol (10 cm³) added to give a clear yellow-orange solution. The solvent was removed under reduced pressure and the residue triturated with methanol to give the off-white solid product. Yield 0.62 g (63%). The product could be recrystallised from benzene-methanol as white prisms.

Preparation of $[\text{Pt}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)(\text{dppm}-P)_2]$ (6).—A solution of dppm (0.121 g, 0.315 mmol) in dichloromethane (0.5 cm³) was added to a solution of $[\text{Pt}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)(\text{dppm}-PP')]$ (0.200 g, 0.135 mmol) in dichloromethane (0.5 cm³) and the mixture swirled and then set aside for 1 h at 23 °C. The solvent was then removed under reduced pressure without heating and the residue triturated with methanol to give the white solid product. Yield 0.23 g (72%).

Preparation of $[(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)\text{Pt}(\mu\text{-dppm})_2\text{AgI}]$ (7).—A solution of $[\text{Pt}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)(\text{dppm}-P)_2]$ (0.100 g, 0.098

mmol) in chloroform (0.4 cm³) was cooled to -60 °C and then solid [AgI(PPh₃)₄] (0.050 g, 0.025 mmol) was added. The mixture was allowed to warm up (over 10 min) to 23 °C, to give a pale yellow solution and some white solid. The solvent was then removed under reduced pressure to give an oily yellow solid which when triturated with diethyl ether gave the desired off-white product. Yield 0.10 g (81%). Recrystallisation from dichloromethane-hexane gave the dichloromethane solvate.

Preparation of $[(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)\text{Pt}(\mu\text{-dppm})_2\text{Au}]\text{Cl}$ (8b).—This was prepared in an analogous fashion to (7) above from [AuCl(PPh₃)₄] and [Pt(CH₂CH₂CH₂CH₂)(dppm-P)₂] in 67% yield. Recrystallisation from chloroform-hexane gave the chloroform solvate.

Preparation of $[(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)\text{Pt}(\mu\text{-dppm})_2\text{Ag}][\text{PF}_6]$ (8a).—A mixture of [Pt(CH₂CH₂CH₂CH₂)(dppm-PP') (0.050 g, 0.079 mmol) and dppm (0.030 g, 0.078 mmol) in acetone (0.5 cm³) was equilibrated at -40 °C for 30 min. Then Ag[PF₆] (0.020 g, 0.079 mmol) in acetone (0.5 cm³) was added and the mixture shaken and then allowed to warm slowly to room temperature. After 20 min the solvent was removed under reduced pressure *without heating* and the residue triturated with diethyl ether to give an off-white solid. Recrystallisation from dichloromethane-diethyl ether gave the dichloromethane solvate. Yield 0.045 g (45%).

Preparation of $[(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)\text{Pt}(\mu\text{-dppm})_2\text{Pt}(\text{CH}_3)]\text{Cl}$ (10a).—A mixture of [Pt(CH₂CH₂CH₂CH₂)(dppm-PP') (0.050 g, 0.079 mmol) and dppm (0.030 g, 0.079 mmol) in dichloromethane (0.5 cm³) was equilibrated at -40 °C for 20 min. Then [PtCl(CH₃)(cod)] (0.028 g, 0.079 mmol) was added, the mixture shaken and then allowed to warm slowly to room temperature. After 1 h the solvent was removed from the yellow solution under reduced pressure. The residue was triturated with diethyl ether to give the yellow product (0.081 g, 81%).

$[(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)\text{Pt}(\mu\text{-dppm})_2\text{Pt}(\text{CH}_3)][\text{BPh}_4]$ (10b) was made in 95% yield by addition of a methanolic solution of Na[BPh₄] to a methanolic solution of the chloride (10a).

Formation of $[(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)\text{Pt}(\mu\text{-dppm})_2\text{Pd}(\text{CH}_3)]\text{Cl}$ (10c).—A mixture of [Pt(CH₂CH₂CH₂CH₂)(dppm-PP') (20 mg, 0.032 mmol) and dppm (12 mg, 0.032 mmol) in CDCl₃ (0.35 cm³) was cooled to -30 °C and then treated with [PdCl(CH₃)(cod)] (8.4 mg, 0.032 mmol). The mixture was

allowed to warm to room temperature and the solution examined by ³¹P-{¹H} n.m.r. spectroscopy (see Figure 2).

Determination of the Equilibrium Constant, K, for Equation (ii).—Bis(diphenylphosphino)methane (12.5 mg, 0.033 mmol) and [Pt(CH₂CH₂CH₂CH₂)(dppm-PP') (20 mg, 0.032 mmol) were mixed in CDCl₃ (0.5 cm³) and the reaction followed by ³¹P-{¹H} n.m.r. spectroscopy every 10 min for 1 h. Equilibrium was apparently reached within 10 min of mixing and *K* was estimated from integration of the ³¹P n.m.r. signals: *K* = 430 ± 40 dm³ mol⁻¹.

Acknowledgements

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