Synthetic and Nuclear Magnetic Resonance Studies on Dialkyl- and Diarylplatinum Complexes containing Chelating, Monodentate, or Bridging $Ph_2PCH_2PPh_2$ Ligands

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Complexes of the type [PtR_2(dppm-*PP'*)] (R = Me, CH_2CMe_3, Et, CH_2Ph, Ph, C_6H_4Me-*p*, C_6H_4OMe-2, $C_6H_2Me_3$-2,4,6, 1-naphthyl, C_6F_5, or C_6H_4Me-*o*; dppm = $Ph_2PCH_2PPh_2$) have been prepared from [$PtCl_2$(dppm-*PP'*)] and the corresponding alkyl-lithium or Grignard reagents. Equilibrium constants, *K*, for the conversion of [PtR_2(dppm-*PP'*)] into *cis*-[PtR_2(dppm-*P*)$_2$] with dppm were studied using ^{31}P n.m.r. spectroscopy at different temperatures. Equilibrium is rapidly established for R = Me, even at −60 °C, but more slowly for R = Ph, completion taking less than 1 h at −30 °C; for the sterically hindered (*o*-substituted) aryls equilibrium is only established after several days at 20 °C. The values of *K* increase as the temperature is lowered. Complexes of the type *cis*-[PtR_2(dppm-*P*)$_2$] were isolated for R = Me, C_6H_4Me-*o*, or 1-naphthyl. The *o*-tolyl or 1-naphthyl complexes exist as *syn–anti* mixtures in solution, due to restricted rotation around the platinum–aryl bonds. Treatment of several complexes of the type [PtR_2(dppm-*PP'*)] with MeI gives [PtR_2Me(I)(dppm-*PP'*)] with *trans* addition of MeI. Treatment of [PtR_2(dppm-*PP'*)] with HCl gives [PtCl(R)(dppm-*PP'*)] for R = $C_6H_2Me_3$-2,4,6, C_6H_4OMe-2, or 1-naphthyl, whereas [Pt(C_6H_4OMe-2)$_2$(dppm-*PP'*)] with MeI appears to give [PtI(C_6H_4OMe-2)(dppm-*PP'*)]. The ^1H, ^{31}P, and ^{195}Pt n.m.r. parameters for these complexes are discussed. For [PtR_2(dppm-*PP'*)] δ(P) is much more negative (−30 to −40 p.p.m.) than for *cis*-[PtR_2(dppm-*P*)$_2$] (+5 to +20) and the *J* values are much smaller. In contrast, platinum-195 chemical shifts are 600 p.p.m. to high frequency of those for complexes of type *cis*-[PtR_2(dppm-*P*)$_2$], similarly for ^{13}C n.m.r. shifts. The δ(PC*H*$_2$P) values for the chelates are 3.9—4.5 p.p.m., whereas for [PtR_2(dppm-*P*)$_2$] they are 1.8—3.0 p.p.m.

In previous papers we have described platinum complexes of the type *trans*-[PtR_2(dppm-*P*)$_2$] (dppm = $Ph_2PCH_2PPh_2$) and used the free phosphorus atoms to co-ordinate to a second metal to give heterobimetallic compounds.[1–3] Suitable ligands (R) include acetylides and cyanide and also isonitriles (which give dications), all of which have a preference to be *trans* in compounds of the type [$PtR_2(PR_3)_2$]$^{n+}$ (*n* = 0 or 2). It was therefore of interest to try to make complexes of the type *cis*-[PtR_2(dppm-*P*)$_2$] since, if the free phosphorus atoms of such complexes could be co-ordinated to a second metal, the resultant heterobimetallics would be expected to have longer metal–metal separations than those generated from the *trans* compounds and to show different reactivity and fluxional behaviour. We expected that compounds of the type *cis*-[PtR_2(dppm-*P*)$_2$] would be more difficult to synthesize than the corresponding *trans* compounds because of the chelate effect, *i.e.* they might readily dissociate into *cis*-[PtR_2(dppm-*PP'*)] and dppm. In order that compounds of the type *cis*-[PtR_2(dppm-*P*)$_2$] should be stable it is necessary that the groups R should not readily ionize off as R^-, that they should bond strongly to Pt, and that they should prefer to be mutually *cis*; obvious candidates for R are therefore alkyl and aryl groups. We have therefore synthesized a series of complexes of the type *cis*-[PtR_2(dppm-*PP'*)] (**1**) and studied the possibility of effecting a chelate ring-opening reaction to give *cis*-[PtR_2(dppm-*P*)$_2$] (**2**) by treatment with dppm.

Results and Discussion

The mononuclear dimethyl complex *cis*-[$PtMe_2$(dppm-*PP'*)] (**1a**) is known [4,5] and is made by the action of methyl-lithium on the dichloride. We similarly made the dineopentyl complex (**1b**) using neopentyl-lithium: preparative details are in the Experimental section, elemental analytical data in Table 1, and characterizing n.m.r. data in Tables 2—4. Treatment of *cis*-[$PtCl_2$(dppm-*PP'*)] with ethyl-lithium gave a mixture, which we did not separate but treatment of *cis*-[$PtCl_2$(dppm-*PP'*)] with ethylmagnesium bromide gave *cis*-[$PtEt_2$(dppm-*PP'*)] (**1c**) in 35% yield; similar treatment with benzylmagnesium chloride gave the corresponding dibenzyl complex *cis*-[Pt(CH_2Ph)$_2$(dppm-*PP'*)] (**1d**).

Treatment of *cis*-[$PtCl_2$(dppm-*PP'*)] with methylmagnesium iodide gave very little of the dimethyl complex but gave the known[4,5] iodo-bridged complex [Pt_2Me_2(μ-I)(μ-dppm)$_2$]I (**3a**) in 71% yield. The complex was identified by elemental analysis and particularly by comparison of its n.m.r. data (Table 5) with the chloro-bridged analogue (**3b**):[5] it showed a pattern typical of a diplatinum–bis(dppm) complex. This method of preparation of the iodo-bridged complex (**3a**) is an improvement on the previously reported method,[4,5] namely treatment of [PtMe(Cl)(cod)] (cod = cyclo-octa-1,5-diene) with dppm followed by metathesis with sodium iodide. We have also prepared several diarylplatinum complexes of type *cis*-[Pt(aryl)$_2$(dppm-*PP'*)] by treating *cis*-[$PtCl_2$(dppm-*PP'*)] with the appropriate arylmagnesium bromide. We experienced no difficulty in synthesizing complexes even with bulky aryl groups and made compounds of the type *cis*-[PtR_2(dppm-*PP'*)] with R = Ph (**1e**), C_6H_4Me-*p* (**1f**), C_6H_4OMe-2 (**1g**), $C_6H_2Me_3$-2,4,6 (**1h**), 1-naphthyl (**1i**), C_6F_5 (**1j**), or C_6H_4Me-*o* (**1k**) in yields usually in excess of 80%. It is probable that the low steric requirements of dppm render these syntheses easier than with most other phosphines. The di-1-naphthylplatinum chelate (**1i**) showed a sharp singlet ^{31}P-{^1H} n.m.r. resonance at 20 °C but, when its solutions were cooled, the resonance broadened and then split into two, until at −50 °C, two sharp, equally intense singlets, each with platinum satellites, were obtained. The process reversed when the solution was allowed to warm up. We ascribe this behaviour to the presence of *syn* (**4**) and *anti* (**5**) forms due

Table 1. Microanalytical,[a] melting point, and molecular weight data

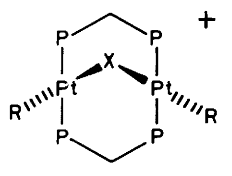
Complex	M.p.[b] (°C)	Analysis (%) C	H	Halogen	M[c]
(1b)	188—189	58.0 (58.25)	6.1 (6.15)		
(1c)	175—177	55.0 (54.65)	5.05 (5.05)		
(1d)	174—175	61.65 (61.5)	4.75 (4.8)		
(1e)	245—247	60.55 (60.55)	4.35 (4.4)		
(1f)	244—246	62.0 (61.5)	5.0 (4.75)		771 (762)
(1g)	212—215	55.95 (55.55)	4.35 (4.65)		
(1h)	279—281	62.8 (63.15)	5.45 (5.45)		
(1i)	235—242	64.15 (64.5)	4.45 (4.80)		847 (837)
(1j)	302—304	48.05 (48.35)	2.6 (2.35)	F 18.95 (19.4)	
(1k)	255—257	61.2 (61.5)	4.75 (4.75)		757 (762)
(9b)	290—294	54.5 (54.05)	4.15 (4.45)		
(9c)	270—280	53.2 (53.15)	4.15 (4.2)	Cl 4.85 (4.9)	
(9d)	195—200	56.2 (56.5)	4.05 (4.2)	Cl 5.2 (4.75)	
[PtMe$_2$(dppm-*P*)$_2$]		68.95 (69.0)	4.9 (4.8)		1 186 (1 218)
[Pt(1-naphthyl)$_2$(dppm-*P*)$_2$]		67.3 (67.1)	4.8 (5.1)		
[Pt(C$_6$H$_4$Me-*o*)$_2$(dppm-*P*)$_2$]		67.3 (67.1)	4.8 (5.1)		

[a] Calculated values in parentheses. [b] With decomposition. [c] Determined in benzene at 37 °C on a Hitachi–Perkin-Elmer apparatus.

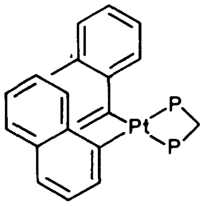
(1)

(2)

	R
(1a)	Me
(1b)	CH_2CMe_3
(1c)	Et
(1d)	CH_2Ph
(1e)	Ph
(1f)	C_6H_4Me-*p*
(1g)	C_6H_4OMe-2
(1h)	$C_6H_2Me_3$-2,4,6
(1i)	1-naphthyl
(1j)	C_6F_5
(1k)	C_6H_4Me-*o*



	R	X
(3a)	Me	I
(3b)	Me	Cl
(3c)	1-naphthyl	Cl



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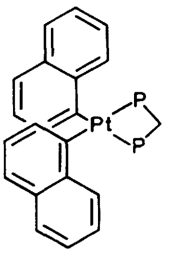

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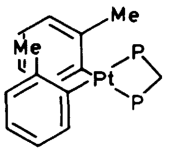

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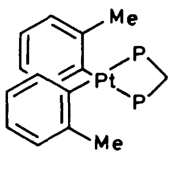

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Table 2. Proton n.m.r. data[a]

Complex	$\delta(\mathrm{PC}H_2\mathrm{P})$	$^3J(PtCH_2)$	$^2J(\mathrm{PH})$	Others
(1a)	4.34	23.0	9.2	δ(Me) 1.0; $^2J(PtCH_3)$ 74.0, $J(\mathrm{PCH_3})$ 7.5[b]
(1b)	4.16	19.8	9.9	$\delta(\mathrm{C}H_2\mathrm{Bu^t})$ 2.01, $^2J(\mathrm{PtC}H_2)$ 78.6, $\delta(\mathrm{Bu^t})$ 0.79, $^4J(\mathrm{PtH})$ 4.4
(1c)	4.11	21.7	8.9	$\delta(\mathrm{C}H_2\mathrm{CH_3})$ 1.67, $^2J(\mathrm{PtCH_2})$ 76.2, $\delta(\mathrm{CH_2C}H_3)$ 1.37, $^3J(\mathrm{PtH})$ 78.6, $^3J(\mathrm{CH_2CH_3})$ 7.7
(1d)	3.9	33.9	9.0	$\delta(\mathrm{CH_2Ph})$ 3.09, $^2J(\mathrm{PtCH_2})$ 99.9, $J(\mathrm{PH})$ 5.1[b]
(1e)	4.35	22.2	9.5	
(1f)	4.39	22.4	9.3	$\delta(\mathrm{CH_3})$ 2.39[c]
(1g)	4.35			$\delta(\mathrm{OCH_3})$ 3.26
(1h)	4.39	23.2	6.1	$\delta(\mathrm{CH_3})$ 2.24, 2.12
(1i)	4.5	23.0	9.3	
(1j)	4.52	39.5	10.2	
(1k)	4.31	22.0	9.3	$\delta(\mathrm{CH_3})$ 2.16
[PtMe$_2$(dppm-*P*)$_2$]	3.04	*ca.* 15		$\delta(\mathrm{CH_3})$ 0.58, $^2J(\mathrm{PtH})$ 58, $^3J(\mathrm{PH})$ 14.7[b]
[Pt(1-naphthyl)$_2$-(dppm-*P*)$_2$][d]	1.97[e,f]	32	n.r.	
	1.80[e,g]	30	n.r.	
[Pt(C$_6$H$_4$Me-*o*)$_2$-(dppm-*P*)$_2$][d]	2.23[e]	n.r.	n.r.	$\delta(\mathrm{CH_3})$ 2.40,[f] 2.49[g]
[PtI(C$_6$H$_4$OMe-2)-(dppm-*P*)$_2$]	2.84	27.6	9.5	$\delta(\mathrm{OCH_3})$ 3.38

[a] Spectra measured at 100 MHz, *ca.* 20 °C, and in $CDCl_3$, unless stated otherwise. Shifts are in p.p.m. relative to $SiMe_4$, error ± 0.01 p.p.m. Coupling constants, *J*, are in Hz ± 0.1 Hz. n.r. = not resolved. [b] $J(\mathrm{PH})_{cis} + J(\mathrm{PH})_{trans}$. [c] $^4J(\mathrm{PH}) = 5.6$ Hz. [d] In CD_2Cl_2. [e] Complex multiplet. [f] Major isomer. [g] Minor isomer.

to restricted rotation about the platinum–naphthyl bond. A similar behaviour was observed for the di-*o*-tolyl complex (**1k**) and ascribed to the presence of *syn* (**6**) and *anti* (**7**) forms at low temperatures: in this case it was necessary to cool the solution to −70 °C before the rotation around the platinum–*o*-tolyl bond was stopped: data are in Table 3.

Table 3. Phosphorus-31 n.m.r. data[a] for complexes of types [PtR_2(dppm-*PP′*)] (**1**) and *cis*-[PtR_2(dppm-*P*)$_2$] (**2**)

	[PtR_2(dppm-*PP′*)]		[PtR_2(dppm-*P*)$_2$]						
R	δ(P)[a]	^1J(PtP)	δ(P_A)[b]	^1J(PtP_A)	δ(P_B)[b]	^3J(PtP_B)	|*N*|[c]	Δ^1J(PtP)[d]	Δδ(co-ord.)[e]
Me	−39.7	1 435	+14.8	1 894	−25.0	37	61	460	54.5
CH_2CMe_3	−37.8	1 212							
Et	−31.5	1 267	+14.5	1 706	−24.1	28	56	440	46.0
CH_2Ph	−33.8	1 570							
Ph	−37.6	1 394	+7.5	1 785	−27.9	52	22	391	45.1
C_6H_4Me-*p*	−37.6	1 392	+7.5	1 783	−28.0	56	24	391	45.1
C_6H_4OMe-2	−41.4	1 565	+5.9	2 029	−27.3	63	22		
$C_6H_2Me_3$-2,4,6	−43.4	1 360							
1-Naphthyl[f]	−41.0[g]	1 421	−7.2[h]	1 825	−29.4	n.r.	28	404	48.2
			−6.3[i]	1 837	−28.9	n.r.	28	416	47.3
C_6F_5	−45.8	2 013	+3.8	2 412	−27.6	68	39	401	49.6
C_6H_4Me-*o*	−42.0[j]	1 375	+6.9[h]	1 769	−27.7	*k*	27	394	48.9
			+6.2[i]	1 774	−27.4	*k*	27		

[a] In $CDCl_3$ at *ca.* 20 °C and 40.25 MHz, unless stated otherwise. Chemical shifts, δ, ±0.1 p.p.m. are to high frequency of 85% phosphoric acid. Coupling constants, *J*, in Hz (±3). P_A is bonded to platinum and P_B is uncomplexed. n.r. = not resolved. [b] In CD_2Cl_2. [c] $|N| = |^2J(P_AP_B) + {}^4J(P_AP_{B'})|$. [d] Δ^1J(PtP) = ^1J(PtP)(bis-dppm complex) − ^1J(PtP)(chelate). [e] ΔδP(co-ord.) = δ(P_A)(bis-dppm complex) − δ(P)(chelate). [f] Measured at 161 MHz. [g] At −50 °C, δ = −43.7, ^1J = 1 460 and −41.8 p.p.m., 1 458 Hz, see Discussion section. [h] Major isomer. [i] Minor isomer. [j] At −70 °C, δ = −45.4, ^1J = 1 421 and −44.0 p.p.m., 1 421 Hz, see Discussion section. [k] ^3J(PtP) was not resolved in the $^{31}P-\{^1H\}$ n.m.r. spectrum but was resolved in the $^{195}Pt-\{^1H\}$ n.m.r. spectrum, see Table 4.

Table 4. Platinum-195[a] and ^{13}C[b] n.m.r. data

Complex	δ(Pt)	^1J(PtP)	^3J(PtP)	δ(CH_2)	^1J(PC)	δ(CH_3)	^1J(PtC)	^2J(PC)
(**1a**)	+599	1 436		45.0 (19.7[c])	26	−27.9	640	106, 6
[$PtMe_2$(dppm-*P*)$_2$]	−80	1 900	30	25.8	n.r.	7.2	602	99, 5
(**1k**)	+626	1 396		45.0	26	26.6[d]		
[Pt(C_6H_4Me-*o*)$_2$(dppm-*P*)$_2$]	+84[e]	1 768	54	*ca.* 25[f]	n.r.	24		
	+67[g]	1 768	54					

[a] In CD_2Cl_2, δ values to high frequency of $\Xi(^{195}Pt)$ 21.4 MHz, error ±0.5 p.p.m., *J* values ±10 Hz. [b] In CD_2Cl_2, δ values to high frequency of tetramethylsilane. [c] ^{13}C Data taken from ref. 9. [d] ^4J(PtC) = 72 Hz. [e] Major isomer. [f] Major and minor isomers not resolved. [g] Minor isomer.

Table 5. Phosphorus-31 n.m.r. data[a] for diplatinum complexes of the type [Pt_2R_2(μ-X)(μ-dppm)$_2$]X

R	X	δ(P)	^1J(PtP)	^3J(PtP)	*N*	Solvent
Me[b]	Cl	+10.6	3 005	34	36	CD_2Cl_2
Me[c]	I	+9.9	2 934	n.r.	n.r.	CD_2Cl_2
Me	I	+10.6	2 942	37	33	$CDCl_3$
Ph[c]	Cl	+8.4	3 037	39	29	$CDCl_3$
1-Naphthyl	Cl	+9.9	3 015	48	20	$CDCl_3$

[a] Chemical shifts, δ, to high frequency of 85% phosphoric acid, error ±0.1 p.p.m., *J* values ±3 Hz. n.r. = Not reported. [b] Data from ref. 5. [c] Data from ref. 6.

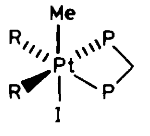
It has been reported previously[4] that the dimethyl complex (**1a**) undergoes oxidative addition to give the platinum(IV) complex [$PtMe_3$I(dppm-*PP′*)] (**8a**); we now find that the other dialkyl complexes [PtR_2(dppm-*PP′*)] readily add on methyl iodide to give adducts of type [PtR_2Me(I)(dppm-*PP′*)] (**8**). These were not isolated but were prepared in solution by adding an excess of methyl iodide to a solution of the complex of type (**1**). In the n.m.r. spectra the values of ^1J(PtP) are exceptionally low (Table 6). The diarylplatinum compounds of type (**1**) add methyl iodide less readily and we found that only the phenyl and *p*-tolyl derivatives gave adducts with methyl iodide, (**8e**) and (**8f**) respectively. One would expect the diarylplatinum complexes to be less nucleophilic than the dialkylplatinum complexes because of the greater electronegativity of the aryl group. Steric effects will also be important and the di-*o*-tolyl and dinaphthyl complexes did not react with MeI. The di-(pentafluorophenyl) complex did not react with methyl iodide, as expected on both electronic and steric grounds. The di-2-methoxyphenyl complex (**1g**) reacted very slowly with MeI in $CDCl_3$ to give what appeared to be the mono(2-methoxyphenyl) complex, *cis*-[PtI(C_6H_4OMe-2)(dppm-*PP′*)] (**9a**) [$^{31}P-\{^1H\}$ n.m.r. evidence]. The complex was not isolated but gave the ^{31}P n.m.r. parameters shown in Table 7. Although the dimesityl complex (**1h**) did not react with MeI it reacted with acetyl chloride to give the monomesityl complex (**9b**). The di-2-methoxyphenyl complex (**1g**) and the di-1-naphthyl complexes reacted similarly to give (**9c**) and (**9d**) respectively: details in the Experimental section, characterizing data in Tables 1 and 7. It is known[6,7] that the chlorophenyl complex *cis*-[PtCl(Ph)(dppm-*PP′*)] exists in equilibrium with the binuclear complex [PhPt(μ-Cl)(μ-dppm)$_2$PtPh]Cl in chloroform solution. We could find no spectroscopic evidence for such an equilibrium involving the mononaphthyl complex (**9d**). However, when the chloronaphthyl complex was boiled in ethanol solution for several hours a yellow solution was formed, which showed the presence of a diplatinum complex. This was not isolated but its $^{31}P-\{^1H\}$ n.m.r. parameters are given in Table 5 and are tentatively interpreted in terms of structure (**3c**).

N.M.R. Spectra of the Chelates.—There has been much discussion of the effects of chelate ring size on n.m.r. parameters[4,8–13] and platinum–diphosphine complexes have attracted a lot of attention in this connection.[4,9,10,13] It has been reported[11] that the n.m.r. properties of dppm and dppe ($Ph_2PCH_2CH_2PPh_2$) chelates do not fit in with the trends established for monodentate phosphines. It is therefore of interest to compare n.m.r. parameters for the complexes described above with parameters reported in the literature for related compounds. One of the best understood parameters in

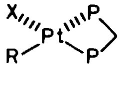
Table 6. Phosphorus-31 n.m.r. data[a] for some dppm–platinum complexes[b] of configuration (**8**)

Complex	δ(P)	^1J(PtP)	Solvent
(**8a**)	−61.2	889	$CDCl_3$
(**8b**)	−56.8	535	CD_2Cl_2
(**8c**)	−46.9	728	CD_2Cl_2
(**8d**)	−50.5	874	CD_2Cl_2
(**8e**)	−57.2	898	$CDCl_3$
(**8f**)	−57.5	903	CD_2Cl_2

[a] Shifts (±0.1 p.p.m.) to high frequency of 85% H_3PO_4, ^1J values ±3 Hz. [b] Prepared *in situ* by adding MeI to a solution of the corresponding complex of type (**1**) and following the conversions by ^{31}P-{^1H} n.m.r. spectroscopy.



(**8a**)	Me
(**8b**)	CH_2CMe_3
(**8c**)	Et
(**8d**)	CH_2Ph
(**8e**)	Ph
(**8f**)	C_6H_4Me-*p*



	R	X
(**9a**)	C_6H_4OMe - 2	I
(**9b**)	$C_6H_2Me_3$-2,4,6	Cl
(**9c**)	C_6H_4OMe-2	Cl
(**9d**)	1-naphthyl	Cl

platinum–phosphine complexes is ^1J(PtP). The values of ^1J(PtP) for the dppm chelates are given in Table 3 and they are consistently lower than those of analogous dppe or $PMePh_2$ complexes, 1 700—1 900 Hz.[6] It has been suggested that the low values of ^1J(PtP) in dppm chelates arise from the very small bond angles at platinum and phosphorus.[10] Crystal structures have shown that the metal–P–C bond angle in dppm chelates is in the range 94—96° [10,14–16] and the P–Pt–P bond angle in [$PtPh_2$(dppm-*PP′*)] is 73°,[10] compared with metal–P–C bond angles of 109° and P–Pt–P bond angles of 90° found in unstrained dppe chelates.[14,15] It seems likely that the ring constraints in dppm chelates result in more *p* and less *s* character in the P–Pt bond and consequently a smaller value for ^1J(PtP). A similar explanation has been given for the small value of the ^{183}W–^{31}P coupling constant in [$W(CO)_4$(dppm)].[12]

The value of ^1J(PtP) is also sensitive to the nature of the ligand in *trans* position to phosphorus: the higher the *trans* influence of this ligand the lower is the coupling constant.[17,18] Strongly bonding ligands with low electronegativity such as Me or Ph have a high *trans* influence and reduce the *s* character in a Pt–P bond in *trans* position and therefore lower the value of ^1J(PtP). As can be seen from Table 3, the order of decreasing values of ^1J(PtP) for the dialkyl complexes is $PhCH_2$ > Me > Et > Me_3CCH_2, which is also the order of decreasing electronegativity. Similarly the order of decreasing ^1J(PtP) for the diaryl complexes is C_6F_5 > 1-naphthyl > Ph, C_6H_4Me-*p* > C_6H_4Me-*o* > $C_6H_2Me_3$-2,4,6, which is also the order of decreasing electronegativity and increasing *trans* influence. The ^{31}P n.m.r. spectra of the platinum(IV) complexes are also singlets with platinum-195 satellites, showing that the configuration is (**8**) and that the methyl iodide has added *trans*. The values of ^1J(PtP) are the lowest recorded (Table 6). A combination of three factors probably causes this: (*i*) the ring strain in the four-membered ring, (*ii*) the high *trans* influence of the alkyl or aryl groups, and (*iii*) the valence state (IV) of the platinum, since the *s* character of the bonds decreases in going from platinum(II) to platinum(IV).[17] The unusually high negative values for the ^{31}P chemical shifts, −30 to −70 p.p.m., are associated with the four-membered ring. It has been established that the platinum-195 shifts in a four-membered ring with phosphorus-,[9] sulphur-,[19] or carbon-[20] donor atoms is several hundred parts per million to high frequency with respect to analogous unstrained complexes. We find that the platinum-195 shifts for our dppm chelates are within the range +500 to +650 p.p.m. (Table 4). Since the shift of the unstrained dialkyl complex [$PtMe_2$($PMePh_2$)$_2$] is −60 p.p.m., it is apparent that our dppm chelates similarly show a large shift to high frequency. We find no obvious trend in δ(Pt) for the small number of compounds that we have studied.

Table 7. Phosphorus-31 n.m.r. data[a] for the complexes of type [PtR(Cl)(dppm-*PP′*)] (**9**)

Complex	δ(P_A)	^1J(PtP_A)	δ(P_B)	^1J(PtP_B)	^2J(P_AP_B)
(**9a**)[b]	−54.5	1 358	−55.6	3 694	46
(**9d**)	−41.1	1 294	−43.3	3 437	41
(**9b**)	−38.7	1 240	−46.0	3 911	43
(**9c**)	−42.2	1 348	−44.6	3 878	46

[a] Chemical shifts δ (±0.1 p.p.m.) to high frequency of 85% H_3PO_4, *J* values ±3 Hz in $CDCl_3$; P_A is *trans* to carbon, P_B is *trans* to chlorine. [b] Iodide, prepared *in situ*, see Discussion section.

The ^1H n.m.r. data for the chelates are given in Table 2. The CH_2 resonance of the dppms occur as a 1:2:1 triplet flanked by satellites due to platinum-195 coupling, and in the ^1H-{^{31}P} n.m.r. spectra it occurs as a singlet with platinum satellites. The values of $^2J(PCH_2)$ are all *ca.* 9—10 Hz, but the value of ^3J(PtH) decreases with an increase in the *trans* influence of the alkyl or aryl group, as does the value of ^1J(PtP) (see above).

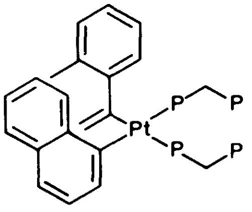
Conversion of the Chelates to cis-*Monodentate Ligand–bis(dppm) Complexes.*—Since there is ring strain in the four-membered ring chelates of type [PtR_2(dppm-*PP′*)] we studied the possibility of opening up the chelate ring to give complexes of type [PtR_2(dppm-*P*)$_2$] containing monodentate dppm ligands. ^{31}P-{^1H} N.m.r. studies established that such a ring opening did occur and that the ring-opened product was of *cis* configuration, no resonances attributable to a product with a *trans* configuration being detected. We therefore studied, by ^{31}P-{^1H} n.m.r. spectroscopy, the equilibria (1) for a series of complexes and measured the equilibrium constants assuming they were of the form K = [PtR_2(dppm)$_2$]/[PtR_2(dppm)][dppm]. The results are shown in Table 8. The most important results are: (*i*) the values of *K* drop markedly along the series Me, Et, CH_2Ph, CH_2CMe_3; (*ii*) *K* increases as the temperature decreases, *e.g.* for the dimethyl complex the value is 61 dm^3 mol^{-1} at +21 °C and 940 dm^3 mol^{-1} at −30 °C in acetone, which is what one would expect from entropy considerations; (*iii*) values of *K* for the diaryl complexes, even when bulky, are large. Equilibrium is established rapidly for the dimethyl complexes even at −60 °C, whilst for the phenyl complex it takes about 1 h at −30 °C; for the sterically hindred complexes, such as the dinaphthyl or di-*o*-tolyl complexes, equilibration takes several days at 20 °C and the bis(dppm) products can be readily isolated; further details are in the Experimental section and characterizing data are in the Tables. In the case of the 1-naphthyl complexes we also studied the formation of the equilibrium mixture, starting from the pure complex [Pt(1-naphthyl)$_2$(dppm-*P*)$_2$], and found the ^{31}P-{^1H} n.m.r. spectrum of the solution at equilibrium to be virtually identical to that obtained starting from a [Pt(1-naphthyl)$_2$(dppm-*PP′*)]–dppm mixture. The ^{31}P n.m.r. spectrum of the bis(dppm) di-1-naphthyl complex at 161 MHz shows the presence of two closely related species each exhibiting an AA′XX′ pattern, as shown in the Figure. These two species are clearly the *syn* and *anti* forms (**10**) and (**11**) caused by restricted rotation around the platinum–naphthyl bonds. Restricted rotation of *o*-substituted aryl groups around aryl–metal bonds was first established in complexes of the type *trans*-[NiBr(*o*-substituted aryl)(PMe$_2$-Ph)$_2$] for which the methyl groups of the phosphines, as a consequence of the restricted rotation, are not isochronous.[21] The di-*o*-tolyl and di(methoxyphenyl) complexes similarly show the presence of rotational (*syn* and *anti*) isomers (Table 3). The ^{195}Pt n.m.r. spectrum of the bis(dppm) di-*o*-tolyl complex also shows two related species (*syn* and *anti* isomers) to be present.

Table 8. Equilibrium constants[a] for the conversion of chelate-dppm complexes of type (**1**) to bis(unidentate ligand) complexes of type (**2**)

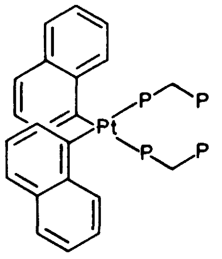
R	K^b	Comments
Me	39	Equilibrium established rapidly (<5 min) even at −60 °C[c]
Et	4	
CH$_2$Ph	<0.03	No complex of type (**2**) could be detected even in concentrated solution[d]
CH$_2$CMe$_3$	<0.03	No complex of type (**2**) could be detected even in concentrated solution[d]
Ph	22	Equilibrium reached in less than 1 h at −30 °C, K = 207 dm^3 mol^{-1}; slow at −50 °C
C$_6$H$_4$Me-*p*	27	
C$_6$H$_4$Me-*o*	58	Takes 5 d to reach equilibrium
1-Naphthyl	78[e]	Takes 7 d to reach equilibrium, K = 25 dm^3 mol^{-1} at +55 °C
C$_6$H$_4$OMe-2	46	Takes 8 d to reach equilibrium

[a] Measured using ^{31}P-{^{1}H} n.m.r. spectroscopy in CD$_2$Cl$_2$ at +21 °C, unless stated otherwise. The equilibrium constants were calculated assuming that K = [PtR$_2$(dppm-*P*)$_2$]/[PtR$_2$(dppm-*PP'*)][dppm]. [b] In dm^3 mol^{-1}, estimated error *ca.* 10%. Equilibria were studied using solutions initially 27 mmol dm^{-3} [PtR$_2$(dppm-*PP'*)] unless stated otherwise. [c] K = 61 (21), 118 (0), 940 (−30 °C) in acetone, 77 in C$_6$D$_6$ (21 °C) and 45 dm^3 mol^{-1} in CDCl$_3$ at 21 °C. [d] Up to 390 mmol dm^{-3}. [e] In CDCl$_3$.

The ^{31}P-{^{1}H} n.m.r. data for the bis(dppm) complexes are given in Table 3. Some generalizations can be made about the n.m.r. parameters of these complexes and the chelates from which they were generated: (*i*) the values of ^1J(PtP) for the complexes are 390—460 Hz higher than for the chelates; (*ii*) the values of δ(P) are 45—55 p.p.m. to higher frequency of the corresponding chelates; (*iii*) the spectra are sharp lines over the temperature range +50 to −60 °C, *i.e.* the compounds are not fluxional nor is there any broadening due to exchange with free dppm. The values of ^1J(PtP) are all consistent with the alkyl or aryl groups being in *trans* position to phosphorus, *i.e.* with a *cis* configuration. We have measured the ^{195}Pt-{^{1}H} n.m.r. spectra of the di-*o*-tolyl- and dimethyl-bis(dppm) complexes. The platinum chemical shifts are 500—600 p.p.m. to low frequency of those for the corresponding chelates. It is now well established that platinum n.m.r. shifts to high frequency are a feature of platinum in four-membered rings.[9] The chemical shifts of the CH$_2$ resonances in the ^{1}H n.m.r. spectra of the chelate complexes are much higher (4.3—4.5 p.p.m.) than those of the monodentate dppm complexes (1.5—2.5 p.p.m.). This may be, in part, due to the electron-withdrawing effect of two adjacent co-ordinated P atoms. We have also measured the chemical shift of the CH$_2$ carbon in [PtMe$_2$(dppm-*PP'*)] (45.0 p.p.m.) (Table 4), a value quite different from that reported (19.7 p.p.m.);[9] we cannot explain this.



(10)



(11)

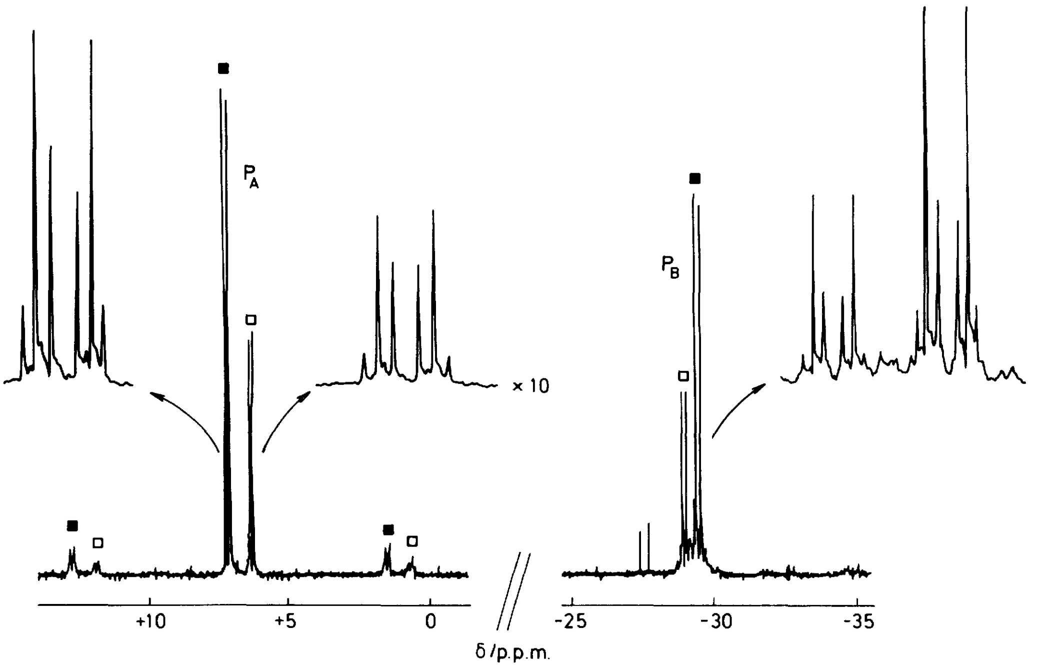


Figure. ^{31}P-{^{1}H} N.m.r. spectrum (161 MHz) of *cis*-[Pt(1-naphthyl)$_2$(dppm-*P*)$_2$] showing the presence of *syn* or *anti* (■ or □) isomers: P$_A$ is bound to the platinum

Experimental

The general experimental techniques and apparatus used were the same as in other recent papers from this laboratory.[22] The dimethyl complex (**1a**) was made by the literature method [5] and the dineopentyl complex (**1b**) by a completely analogous method, *viz.* by treating [$PtCl_2$(dppm-*PP′*)] with neopentyllithium.

Preparation of Complex (**1c**).—A solution of ethylmagnesium bromide was made from magnesium (2.40 g, 100 mmol) and bromoethane (11.0 g, 101 mmol) in dry tetrahydrofuran (40 cm^3). The complex [$PtCl_2$(dppm-*PP′*)] (3.25 g) was then added and the mixture heated under reflux for 1 h, cooled, and methanol (10 cm^3) added. The product was isolated with chloroform and formed yellow microcrystals from dichloromethane–ethanol. Yield 1.1 g (35%).

Preparation of Complex (**1d**).—A solution of benzylmagnesium chloride was made from magnesium (1.2 g, 50 mmol) and benzyl chloride (6.3 g, 50 mmol) in tetrahydrofuran (thf) (40 cm^3) under nitrogen. The complex [$PtCl_2$(dppm-*PP′*)] (3.00 g, 4.62 mmol) and benzene (20 cm^3) were then added and the mixture heated under reflux for 1 h. The mixture was then cooled, methanol (20 cm^3) added, and then evaporated to dryness under reduced pressure. The required product was isolated from the residue with dichloromethane and formed off-white microcrystals from dichloromethane–ethanol. Yield 3.0 g (85%).

The following seven compounds were made similarly using the Grignard reagent formed from the appropriate organic bromide: (**1e**) and (**1j**), reaction in Et_2O–C_6H_6, yields 78 and 56%; (**1f**), (**1g**), (**1h**), (**1i**), and (**1k**), reaction in thf–C_6H_6, yields 63, 80, 94, 60, and 65%.

Preparation of [$Pt_2Me_2(\mu$-I)(μ-dppm$)_2$]I (**3a**).—A solution of methylmagnesium iodide was made from magnesium turnings (0.322 g, 13.8 mmol) and iodomethane (2.00, 14.1 mmol) in Et_2O (20 cm^3). The complex [$PtCl_2$(dppm-*PP′*)] (1.5 g, 2.30 mmol) and benzene (25 cm^3) were added and the mixture heated under reflux for 1.5 h. The mixture was then cooled to *ca.* 0 °C, methanol (10 cm^3) added, the mixture evaporated to dryness, and the required product extracted with dichloromethane. It formed bright yellow microcrystals (1.17 g, 71%) from dichloromethane–methanol.

Preparation of [PtCl(1-naphthyl)(dppm-*PP′*)] (**9d**).—A 0.34 mol dm^{-3} solution of acetyl chloride was added dropwise to a stirred solution of complex (**1i**) (0.50 g, 0.60 mmol) in dichloromethane (5 cm^3) and methanol (1 cm^3). The mixture was stirred under nitrogen for 1.5 h and then methanol (5 cm^3) was added and the volume reduced in a stream of dinitrogen. This gave the required product as microcrystals. Yield 0.43 g (96%), decomp. > 195 °C. The monomesityl (**9b**) and 2-methoxyphenyl (**9c**) complexes were prepared similarly in *ca.* 90% yields, see Tables 1 and 7.

Equilibrium Studies on the Interconversions of Complexes of Types (**1**) *and* (**2**).—The mononuclear complexes of type (**1**) (0.41 mmol) were dissolved in CD_2Cl_2 (1.5 cm^3) and dppm (0.41 mmol) was added. The equilibrium was then studied by ^{31}P-{^1H} n.m.r. spectroscopy at 40.25 MHz at the appropriate temperature.

Preparation of cis- [$PtMe_2$(dppm-*P*$)_2$].—A mixture of [$PtMe_2$(dppm-*PP′*)] (0.16 g, 0.26 mmol) and dppm (0.11 g, 0.29 mmol) in dichloromethane (0.5 cm^3) was put aside at 0 °C for 15 min. The solution was then evaporated to low volume under reduced pressure and diethyl ether or methanol was added to precipitate out the required product. Yield 0.24 g (90%).

Preparation of cis-[Pt(C_6H_4Me-*o*$)_2$(dppm-*P*$)_2$].—A mixture of *cis*-[Pt(C_6H_4Me-*o*$)_2$(dppm-*PP′*)] (0.35 g, 0.46 mmol) and dppm (0.185 g, 0.48 mmol) in dichloromethane (1.5 cm^3) was set aside for 5 d at room temperature. The solvent was removed under reduced pressure, without heating, and the residue triturated with methanol. This gave the required product as a white solid which was filtered off, *etc.* Yield 0.45 g (85%).

Preparation of cis-[Pt(1-naphthyl$)_2$(dppm-*P*$)_2$].—A mixture of [Pt(1-naphthyl$)_2$(dppm-*PP′*)] (0.30 g, 0.36 mmol) and dppm (0.20 g, 0.52 mmol) in chloroform (5 cm^3) was set aside for 5 d at room temperature. The solvent was removed under reduced pressure, without heating, and the residue triturated with diethyl ether. This gave the required product. Yield 0.33 g (75%).

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