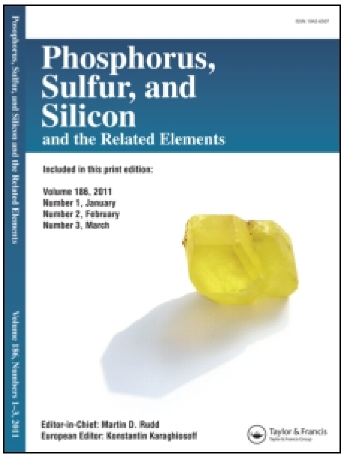

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The Synthesis of Mono- and Bi-Metallic Platinum(II) and/or (IV) Complexes Containing the Ligand Bis(diphenylphosphino) Methylamine

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The Synthesis of Mono- and Bi-Metallic Platinum(II) and/or (IV) Complexes Containing the Ligand Bis(diphenylphosphino) Methylamine

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Complexes of the type [Pt R_2 (dppma-PP′)] (R=Me, Et, Ph, CH_2Ph, C_6H_4 Me-p, C_6H_4OMe-2, CH_2CMe_3, 1-naphthyl, C_6H_4Me-o, dppma=Ph_2PNMe PPh_2) have been prepared from [$PtCl_2$, (dppma-PP′)] and the corresponding alkyl-lithium or Grignard reagents. Equilibrium constants, k, for the conversion of [PtR_2 (dppma-PP′)] into cis-[PtR_2(dppma-P$)_2$] with dppma were studied using ^{31}P NMR spectroscopy at room temperature. Equilibrium is rapidly established for R=C_6H_4-Me-o, at 20°C. Complex of the type cis*-[PtR_2 (dppma-P$)_2$] was isolated R=C_6H_4 Me-o. The complexes [$PtMe_2$(dppma-P$)_2$] and [Pt(o-methoxyphenyl$)_2$(dppma-P$)_2$] were prepared, but unfortunately decomposed once isolated, the only evidence for its formation being from ^{31}P-$\{^1H\}$ NMZR spectroscopy. 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(dppma-PP‘)] with MeI gives [PtR_2Me(I)(dppma-PP′)] with trans addition of MeI. Treatment of [PtR_2(dppma-PP′)] with HCl gives [Pt Cl (R) (dppma-PP′)] for R=$C_6H_2Me_3$-2,4,6, C_6H_4-CH_3-2, C_6H_4-Me-4, Me, 1-naphthyl. The ^1H, ^{31}P NMR parameters for these complexes are discussed. Attempted preparation of complexes of the type [PtR_2 (dppma-P$)_2$M] (R=C_6H_4-Me-2, Me CN-C_6H_4-Me-4); M=Pd, Pt, Au,) are reported.*

Keywords (Diphenylphosphino)methylamine; organometallic; ^{31}P and ^{1}H NMR

INTRODUCTION

In the present article, complexes of dppma (four-membered ring) with nickel(II), palladium(II), or platinum(II), followed by the preparation of dialkyl- and diaryl-platinum(II) complexes have been described. The

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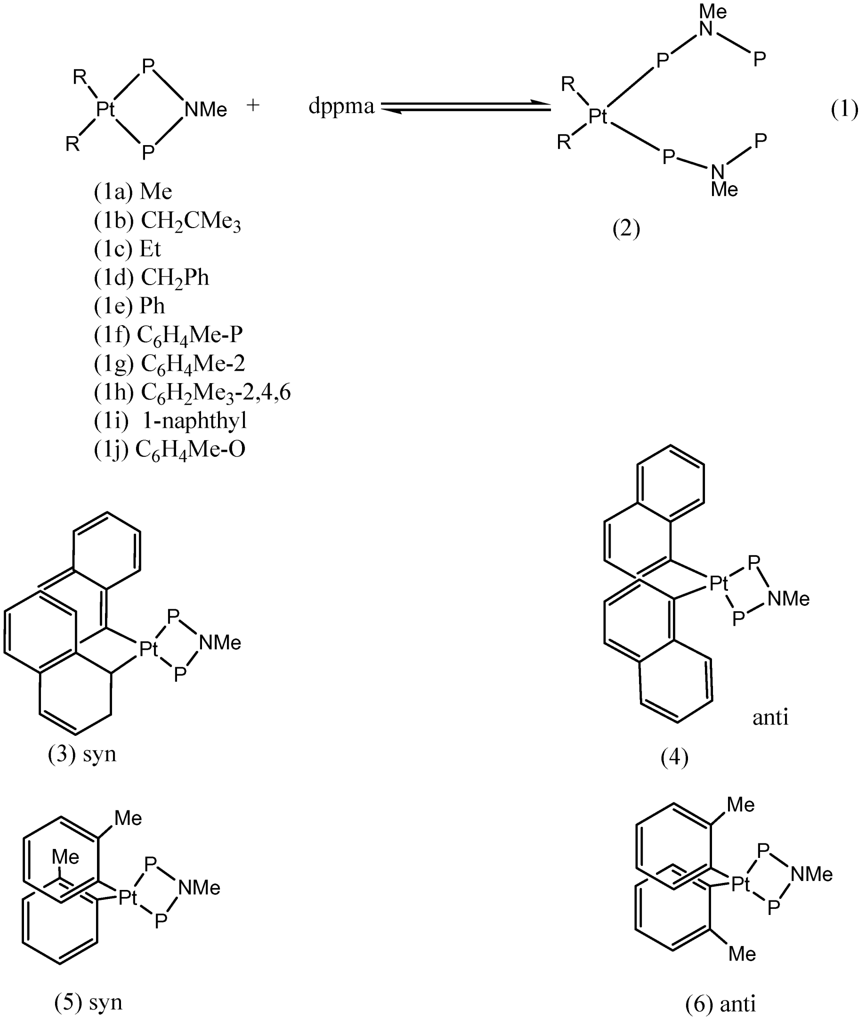
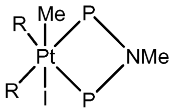
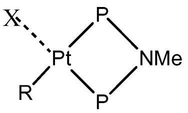
dppma chelate dihalide or pseudohalide of platinum(II) and of palladium (II), which can be used as starting materials for much of the subsequent chemistry, also has been described[1] that a series of platinum complexes of the type [Pt R_2(dppma-PP′)] has been synthesized. Similarly the mononuclear dimethyl platinum complexes(I) analogous to the dimethylplatinum complex of dppm [Me_2 Pt (dppm)][2,3] have been prepared. Also a series of complexes of the type *cis*-[PtR_2(dppma-PP′)][1] have been synthesized and studied regarding the possibility of effecting



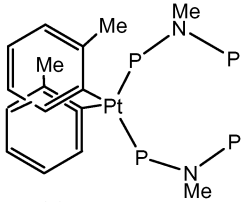
SCHEME 1 Preparation of the complexes of the type [Pt R_2 (dppma-P$)_2$].



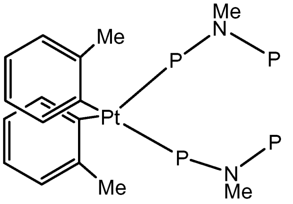
(7a) Me
(7b) CH_2CMe_3
(7c) Et
(7d) CH_2Ph
(7e) Ph
(7f) C_6H_4Me-P



	R	X
(8a)	Me	Cl
(8b)	C_6H_4-Me-O	Cl
(8c)	C_6H_4-Me-P	Cl
(8d)	1-naphthyl	Cl
(8e)	$C_6H_2(Me)_3$	Cl
(8f)	$CH_2C(Me)_3$	Cl
(8g)	C_6H_4OMe	Cl



(9) syn



(10) anti

SCHEME 2 The oxidative addition of MeI to complexes of the type [Pt R_2 (dppma-PP′)] and preparation of complexes of the type [Pt R (Cl) (dppma-PP′)].

a chelate ring-opening reaction to give *cis*-[PtR_2(dppma-P)$_2$] [2] by treatment with dppma (Scheme 1).

RESULTS AND DISCUSSION

The mononuclear dimethyl complex *cis*-[Pt Me_2(dppma-PP′)] (**1a**) is known[4] and is made by the action of methyl magnesium iodide on the dichloride. Similarly the dineopentyl complex (**1b**) was made using neopentyl-lithium; preparative details are in the Experimental section, elemental analytical data in Table I, and characterizing NMR data in Tables II and III. Treatment of *cis*-[Pt Cl_2(dppma-PP′)] with ethyl magnesium bromide gave *cis*-[Pt Et_2(dppma PP′)] (1c) in 45% yield, similar treatment with benzyl magnesium chloride gave the corresponding dibenzyl complex *cis*-[Pt($CH_2Ph)_2$(dppma-PP′)] (**1d**). Also, several diaryl platinium complexes have been prepared of the type *cis*-[Pt(aryl)$_2$(dppma-PP′)] by treating *cis*-[Pt Cl_2 (dppma-PP′)] with the appropriate aryl magnesium bromide (Scheme 2). No difficulty has been experienced in synthesizing complexes, even with bulky aryl groups, and made compounds of the type *cis*-[PtR_2(dppma-PP′)]

TABLE I Microanalytical,[a] Melting Point, and Molecular Weight Data

Complex	M.P.[b](°C)	Analysis % C	H	N	Halogen
(1a)[c]	261–264	50.0(50.0)	4.6(4.6)	2.2(2.2)	1.75(1.85)
(1b)	n.d.	56.9(57)	6.15(5.9)	1.9(1.85)	1.4 (1.55)
(1c)	265–270	52.66(52.8)	4.7(4.7)	2.19(2.2)	
(1d)	> 270	60.45(60.4)	4.9(4.85)	1.9(1.92)	
(1e)	> 273				
(1f)	> 270	60.35(60.3)	4.85(4.8)	1.9(1.8)	
(1g)	249–254	57.25(57.8)	4.5(4.85)	1.7(1.7)	
(1h)[e]	n.d.	60.23(60.5)	3.96(4.1)	1.85(1.9)	
(1i)[d]	n.d.	60.35(60.5)	4.15(4.2)	1.55(1.55)	
(1j)	270–273	60.45(60.3)	4.9(4.8)	1.9(1.8)	
(7a)		43.25(43.85)	4.4(4.2)	1.6(1.8)	
(8a)		47.95(48.45)	4.05(4.05)	2.15(2.2)	5.7(5.5)
[Pt (o-tolyl)$_2$ (dppma-P)$_2$][f]		62.65(63)	4.95(5.01)	2.0(2.2)	
(8b)	—	52.14(52.2)	4.07(4.2)	1.9(1.85)	4.81(4.85)
(8c)	—	48.55(48.85)	3.9(3.8)	1.85(1.65)	4.75(4.75)
(8d)	—	55.52(55.45)	3.95(3.8)	1.85(1.8)	4.69(4.7)
(8e)		53.55(53.3)	4.25(4.2)	1.9(1.99)	5.0(4.95)

[a] Calculated values in parentheses.
[b] With decomposition.
[c] Crystallized with $\frac{1}{6}$molecule of CH_2Cl_2.
[d] Crystallized with $\frac{2}{3}$molecule of CH_2Cl_2.
[e] Crystallized with $\frac{1}{6}$molecule of CH_2Cl_2.
[f] Crystallized with $\frac{2}{3}$molecule of CH_2Cl_2.

(R = Ph (**1e**), C_6H_4Me-p (**1f**), C_6H_4OMe-2 (**1g**), $C_6H_2Me_3$-2,4,c (**1h**), 1-naphthyl (**1i**), and C_6H_4Me-o (**1j**), in yields usually in excess of 64%. It is probable that the low steric requirements of dppma render these syntheses easier than with most other phosphines. The di-1-naphthylplatinum chelate(II) and di-*o*-tolylplatinum showed a sharp singlet ^{31}P-$\{^1H\}$ NMR resonance broadened and then split into two, until at −80°C and two sharp, equally intense singlets, each with platinum satellites, were obtained. The process reversed when the solution was allowed to warm up. This behavior was ascribe to the presence of syn (**3**) and anti (**4**) forms due to restricted rotation about the platinum-naphthyl bond. A similar behavior was observed for the di-o-tolyl complex (**1j**) and ascribed to the presence of syn (**5**) and anti (**6**) 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 shown in Table III. It has been

TABLE II Proton NMR Data[a]

Complex	δ(PNMeP)	^{3}J (PH)	^{4}J (Pt H)	Others	Solvent
(1a)	2.06	8.8	1.4	$\delta(CH_3) = 1.58$, $^{2}J(Pt\ CH_3) = 76$, $^{3}J(PCH_3) = 7.3$, $^{3}J(PCH_3)^{b} = 8.6$	C_6D_6
(1b)	2.17	8.3	1.5	$\delta(CH_3) = 0.76$, $\delta(CH_2) = 1.89$ $^{3}J(PCH_5) = 7.7$	$CDCl_3$
(1c)	2.2	8.5	1.5	$\delta(CH_2CH_3) = 1.8$, $^{2}J(Pt\ C_2H_5) = 76.3$ $^{3}J(PC_2H_3) = 6.2$, $^{3}J(PCH_3)^{b} = 8.2$ $^{3}J(CH_2CH_3) = 7.7$	CD_2Cl_2
(1d)	2.42	8.2	1.4	$\delta(CH_2P) = 3.09$, $^{2}J(Pt\ CH_2) = 99.9$, $J(PH) = 5.1$	
(1e)	2.48	8.5	1.5	—	CD_2Cl_2
(1f)	2.89	—	n.r.	$\delta(CH_3)$p-tolyl = 3.79	CD_2Cl_2
(1g)	2.32	8.8	1.5	$\delta(OCH_3) = 3.6$	CD_2Cl_2
(1h)	2.38	8.8	1.5	$\delta(CH_3) = 2.24, 2.12$	CD_2Cl_2
(1i)	2.46	8.8	1.5	—	CD_2Cl_2
(1j)	2.39	8.8	1.5	$\delta(CH_3)$tolyl = 2.10, $J(PtCH_3) = 3.28$	CD_2Cl_2
[Pt (o-tolyl)$_2$(dppma-P)$_2$ (dppma-P)$_2$]	2.39	8.6	3.05	$\delta(CH_3)$tolyl = 2.15 (major isomer) $J(PtCH_3)$tolyl = 3.05	$CDCl_3$

[a] Spectra measured at 100 MHz, *ca*, 20°C, shifts are in p.p.m relative to $SiMe_4$, error ± 0.01 ppm. Coupling Constants, J, are in Hz ± 0.01 Hz. n.r. = not resolved.

reported previously[2] that the dimethyl platinum (dppm) complex under goes oxidative addition to give Pt (IV) complex. It has been found that the complex [Pt Me_2(dppma)] added methyl iodide similarly, but very slowly (72 h) at room temperature to give *fac*-[Pt Me_3I (dppma)] (**7a**) as indicated by its characteristic $^{31}P\text{-}\{^{1}H\}$ NMR spectrum. It has been found that the other dialkyl complexes [PtR_2(dppma-PP′)] (R = Et) add on methyl iodide to give adduct of type [PtR_2Me(I) (dppma-PP′) (**7b**). 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 NMR spectra, the values of ^{1}J (PtP) are exceptionally low (Table IV). The low value of ^{1}J(PtP) of this complex is associated with strain in the chelate ring, in particular with distortions in the angle P-Pt-P[2] data in Table IV. One would expect the diaryl platinum complexes to be less nucleophilic than the dialkylplatinum complexes because of

TABLE III Phosphorus ^{31}NMR Data[a] for Complexes of Types $[PtR_2(dppma\text{-}PP')](1)$ and *cis*-$[Pt\ R_2(dppma\text{-}P)](2)$

	$[Pt\ R_2(dppma\text{-}PP')]$			$[Pt\ R_2(dppma\text{-}P)_2]$			
R	$\delta(P)$[a]	$^1J(PtP)$	$\delta(P_A)$*	$^1J(PtP_A)$	$\delta(P_B)$	$^3J(PtP_B)$	[N][b]
Me	46.8	1533	29.7	1665	47.8	n.r.	n.r.
CH_2CHe_3	47.2	1365					
Et	47.1	1430	29.2	1540	46.9	52	54
CH_2Ph	48.2	1580					
Ph	43.7	1530	28.6	1610	45.6	54	52
C_6H_4Me-p	43.9	1514	43.8	1616	72.4	56	54
C_6H_4OMe-2	43.1	1682	43.3	1697	73.2	59	54
$C_6H_2Me_3$-2,4,6	42.8	1498					
1-Naphtlyl[e]	45.9[f]	1543	44.5	1683	74.6	n.r.	n.r.
C_6H_4Me-o[g)]	43.9	1514	48.9	1678	72.5	56	54

[a] In CD_2Cl_2 at 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] $[N] = |^2J(P_AP_B) + ^4J(P_AP_B)|$.

[c] Measured at 161 MHz.

[d] At = -60°C, $\delta = 45.2$, $^1J = 1557$ and $\delta = 46.4$, $^1J = 1577$ Hz, see Discussion section.

[e] At -70°C, $\delta = 41.1$, $^1J = 1543$, $\delta = 42.8$, $^1J = 1545$ Hz, see Discussion section.

the greater electronegativity of the aryl group. Steric effects will also be important, and the di-o-tolyl and o-methoxylphenyl complexes did not react with MeI. Although the dimesityl complex (**1h**) did not react with MeI, it reacted with acetyl chloride to give the monomesityl complex (**8a**). The di-2-methoxyphenyl complex (**1g**), the di-1-naphthyl (**1i**), the di-2-tolyl (**1j**), the di-4-toly(**1f**), and the di-neopentyl (**1b**) reacted

TABLE IV Phosphorus ^{31}NMR Data[a] for Some dppma-Platinum Complexes[b] of Configuration (7)

Complex	$\delta(P)$	$^1J(PtP)$	Solvent
(7a)	20.5	986	CD_2Cl_2
(7b)	19.8	887	CD_2Cl_2
(7c)	18.7	728	CD_2Cl_2
(7d)	18.3	874	CD_2Cl_2
(7e)	19.6	898	CD_2Cl_2
(7f)	19.9	980	CD_2Cl_2

[a] Shifts ($\pm$ 0.1 p.p.m) to high frequency of 85% H_3PO_4, ^1J values $\pm$ 3 Hz.

[b] Prepared in situ by adding MeI to a solution of the corresponding complex of type (1) and following the conversions by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy.

similarly to give (**8b–8f**) respectively; details are in the Experimental section, characterizing data are in Table V.

NMR Spectra of the Chelates

There has been much discussion of the effects of chelate ring size on NMR parameters,[2,6–11] and platinum-diphosphine complexes have attracted a lot of attention in this connection.[2,6,8,11] It has been reported that the NMR properties of dppm, dppe ($Ph_2PCH_2CH_2PPh_2$), and dppma do not fit in with the trends established for monodentate phosphines. It is therefore of interest to compare NMR parameters for the complexes described above with parameters reported for dppm in the literature for related compounds. One of the best understood parameters in the platinum-phosphine complex is ^1J(PtP). The values of ^1J(PtP) for the dppma chelates are given in Table III, and they are consistently lower than those of analogous dppe or PMe Ph_2 complexes, 1700–1900 Hz.[1] It has been suggested that the low values of ^1J (PtP) in dppma chelates arise from the very small bond angles at platinum and phosphorus.[8] It seems likely that the ring constraints in dppma chelates result in more p and less s character in the P-Pt bond and consequently a smaller value for ^1J(PtP).

The value of ^1J(PtP) is also sensitive to the nature of the ligand in trans position to the phosphorus; the higher the trans influence of this ligand the lower the coupling constant.[12,13]

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 III, the order of decreasing values of ^1J(PtP) for the dialkyl complexes is Ph CH_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 $C_6H_4Me_3$-o > 1-napthyl > 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 NMR spectra of the platinum (IV) complexes are also singlets with platinum-195 satellites, showing that the configuration is (**7**) and that the methyl iodide has added trans. The values of ^1J(PtP) are the lowest recorded (Table IV). 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).[12]

TABLE V Phosphorus ^{31}P NMR Data[a] for the Complexes of Type [PtR(Cl) (dppma-PP′)] (8)

Complex	$\delta(P_A)$	$^1J(PtP_a)$	$\delta(P_B)$	$^1J(PtP_B)$	$^2J(P_AP_B)$	Solvent
(8a)	54.6	4088	34.5	1328	31.3	$CDCl_3$
(8b)	47.6	4058	31.1	1988	31.1	$CDCl_3$
(8c)[b]	46.1	4009	30.5	1787	31.7	$CDCl_3$
(8d)	46.7	3987	31.3	1389	32.1	$CDCl_3$
(8e)	35.9	3950	21.7	1341	37.2	$CDCl_3$
(8f)[b]	53.2	4387	34.3	1191	30.2	$CDCl_3$
(8g)	47.4	4045	34.3	1978	31.8	$CDCl_3$

[a] Chemical shifts (± 0.1 ppm) to high frequency of 85% H_3PO_4, J values ±3 Hertz in $CDCl_3$; P_A is trans to carbon, P_B is trans to chlorine.

[b] Prepared in situ.

The ^{1}H NMR data for the chelates are given in Table II. The NMe resonance of the dppmas occurs as a triplet of triplets, coupled to phosphorus, and in the $^1H\text{-}\{^{31}P\}$ NMR spectra it occurs as a singlet coupled to platinum-195. The values of $^3J(PH)$ are all *ca* 8.3–8.8 Hz, but the value of $^4J(PtH)$ decreases with an increase in the trans influence of the alkyl or aryl group.

Conversion of the Chelates to cis-Monodentate Ligand-bis-(dppma) Complexes

Since there is ring strain in the four membered ring chelates of type [Pt R_2(dppma-PP′)]. The possibility of opening up the chelate ring to give complexes of type-[Pt R_2(dppma-P)$_2$]-containing monodentate dppma ligand has been studied. $^{31}P\text{-}\{^1H\}$ NMR studies established that such a ring opening did occur and that the ring-opened product was of cis configuration with no resonance attributable to a product with a trans configuration being detected. Therefore the equilibria[1] for a series of complexes were studied, by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy, and measured the equilibrium constants assuming they were of the form K = [PtR$_2$(dppma)$_2$]/[PtR$_2$(dppma)] [(dppma)]. The results are shown in Table VI. The most important results are as follows: (i) the values of *K* drop markedly along the series Me, Et, CH_2 CMe_3; (ii) *K* increases as the temperature decreases; (iii) values of *K* for diaryl complexes, even when bulky, are large. Equilibrium is established rapidly for the dimethyl complexes even at −60°C, while for the phenyl complex it takes about 1 h at −30°C, for the sterically hindered complexes, such as the di-o-methoxy or di-o-tolyl complexes, equilibration takes several

TABLE VI Equilibrium Constants[a] for the Conversion of Chelate-dppma Complexes of Type (1) to bis(unidentate ligand) Complexes of Type (2)

R	K[b]	Comments
Me	39	Equilibrium established rapidly ($<$ 5min) even at -60°C
Et	41	Equilibrium reached in less than 30 min.
CH_2Ph	$<$ 0.03	No complex of type (2) could be detected even in concentrated solution[c]
CH_2CMe_3	$<$ 0.03	No complex of type (2) could be detected even in concentrated solution[c]
C_6H_4-Me-o	58	Take 8d to reach equilibrium
C_6H_4OMe-2	46	Take 7d to reach equilibrium

[a] Measured using ^{31}P-$\{^1H\}$ NMR spectroscopy in CD_2Cl_2 at 21°C, unless stated otherwise. The equilibrium constants were calculated assuming that K = [Pt R_2(dppma-P)$_2$]/[Pt R_2(dppma-PP′)] [dppma].

[b] In dm^3 mol^{-1}, estimated error ca. 10% Equilibria were studied using solutions initially 27 mmol dm^{-3} [PtR_2)dppma-PP′)] unless stated otherwise.

[c] Up to 390 mmol dm^{-3} in $CDCl_3$.

days at 20°C and the bis (dppma) products can be readily isolated; further details are in the Experimental section and characterizing data are in the tables. In the case of the o-tolyl complexes, we also studied the formation of the equilibrium mixture, starting from the pure complex [Pt(o-toly)$_2$(dppma-P)$_2$], and found the ^{31}P-$\{^1H\}$ NMR spectrum of the solution at equilibrium to be virtually identical to the obtained starting form, which is a [Pt(o-tolyl)$_2$(dppma-PP′)]- dppma mixture. The ^{31}P NMR spectrum of the bis(dppma) di-o-tolyl complex at 161 MHz shows the presence of two closely related species each exhibiting an AA′XX′ pattern. These two species are clearly the *syn* and *anti* forms (**9**) and (**10**) caused by restricted rotation around the platinum-o-tolyl 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 iso chronous.[14] The di-1-naphthyl and di (methoxy phenyl) complexes similarly show the presence of rotational (*syn* and *anti*) isomers (Table III).

EXPERIMENTAL

The general experimental techniques and apparatus used were the same as in other papers from the laboratory.[15] The dimethyl complex (**1a**) was made by the literature method[16–23] and the dineopentyl complex (**1b**) by a completely analogous method, *viz*, by treating [$PtCl_2$(dppma-PP′)] with neopentyl lithium.

Preparation of Complex (1c)

A solution of ethyl magnesium bromide was made from magnesium turning (1.2 g, 50 mmol) and bromoethane (5.44 g, 50 mmol) in dry tetrahydrofuran (40 mL). The complex [Pt Cl_2(dppma-PP′)] (3.08 g) was then added, and the mixture was stirred at room temperature for 1 h. Methanol (20 mL) was added. The product was isolated with methanol and formed yellow microcrystals from dichloromethane-ethanol. Yield 64%.

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 mL) under nitrogen. The complex [$PtCl_2$(dppma-PP′) (3.08 g, 4.62 mmol) was then added, and the mixture was stirred at room temperature for 2 h. Methanol (20 mL) was added, and then evaporated to dryness under reduced pressure. The required product was isolated from the residue with dichloromethane and formed yellow microcrystals from dichloromethane ethanol. Yield 85%.

The following 6 compounds were made similarly using the Grignard reagent formed from the appropriate organic bromide (**1e**) and (**1j**), reaction in C_6H_6, yields 56% and 64%; (**1f**), (**1g**), (**1h**), and (**1i**), reaction in thf-C_6H_6, yields 49%, 52%, 60%, and 33%, respectively.

Preparation of [Pt Cl (1-naphthyl)(dppma-PP′) (8d)

A 0.34 moldm^{-3} solution of acetyl chloride was added dropwise to a stirred solution of complex (**1i**) (0.5 g, 0.68 mmol) in dichloromethane (5 mL) and methanol (1 mL). The mixture was stirred under nitrogen for 1.5 h, and then methanol (5 mL) was added and the volume reduced in a stream of dinitrogen. This gave the required product as microcrystals. Yield 70%. The monomesityl (**8e**) and 2-methoxyphenyl (**8g**) complexes were prepared similarly in *ca* 82% yields; see Tables I and V.

Equilibrium Studies on the Interconversion of Complexes of Types (1) and (2)

The mononuclear complexes of type (**1**) (0.41 mmol) were dissolved in CD_2Cl_2 (1.5 mL), and dppma (0.41 mmol) was added. The equilibrium was then studied by $^{31}P\{^1H\}$ NMR spectroscopy at 40.25 MHz. at the appropriate temperature.

Preparation of cis-[Pt(o-tolyl)$_2$(dppma-P)$_2$]

A mixture of [Pt(*o*-tolyl)$_2$(dppma-PP′)] (0.05 g, 0.064 mmol) and dppma (0.026 g, 0.064 mmol) in dichloromethane (0.5 mL) was set aside for 8 days 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 collected by filtration. Yield 0.063 g (88%).

Preparation of cis-[Pt Me$_2$ (dppma-P)$_2$]

A mixture of [Pt Me$_2$(dppma-PP′) (0.039 g, 0.064 mmol) and dppma (0.026 g, 0.064 mmol) in dichloromethane (0.5 mL) 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 (90%).

Preparation of cis-[Pt(o-methoxyphenyl)$_2$(dppma-P)$_2$]

A mixture of *cis*-[Pt (o-methoxyphenyl)(dppma-PP′)] (0.047 g, 0.064 mmol) and dppma (0.026 g, 0.064 mmol) in dichloromethane (0.5 cm^3) was set aside for 7 days at room temperature. The solvent was removed under reduced pressure, without heating, and the residue triturated with diethylether. This gave the required product. Yield (75%).

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