Pentafluorophenyl Complexes of Palladium and Platinum containing Chelating, Unidentate, or Bridging $Ph_2PCH_2PPh_2$ Ligands

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The reactions of *cis*-$[M(C_6F_5)_2(thf)_2]$, *trans*-$[M(C_6F_5)_2(tht)_2]$, and $[M_2(\mu\text{-}Cl)_2(C_6F_5)_2(tht)_2]$ (M = Pd or Pt, thf = tetrahydrofuran, tht = tetrahydrothiophene) with dppm ($Ph_2PCH_2PPh_2$) in molar ratios M : dppm = 1 : 1 and 1 : 2 have been studied. Pentafluorophenyl complexes containing dppm acting as endobidentate (chelate), unidentate, or exobidentate (bridging homo- or hetero-metal centres) have been obtained and characterized by i.r. and ^{31}P n.m.r. spectroscopy.

Bis(diphenylphosphino)methane (dppm) is a ligand of current interest, mainly because of its ability to form homo- or heterometallic binuclear bridged complexes with or without metal to metal bonds.[1] In addition to this exobidentate bridging role, dppm can also act as endobidentate (chelate) or as a unidentate ligand.

In previous work we used complexes of the type *trans*-$[MR(R')(dppm)_2]$ ($R = R' = C_6F_5$; $R = C_6F_5$, $R' = Cl$; M = Pd or Pt) as starting materials for the synthesis of complexes of Pd^I or Pt^I[2] and for the preparation of heterobinuclear palladium–gold complexes.[3] Here we give a complete account of our synthetic and structural studies involving MR(R′) moieties and dppm with metal to ligand ratios of 1 : 1 and 2 : 1.

Results and Discussion

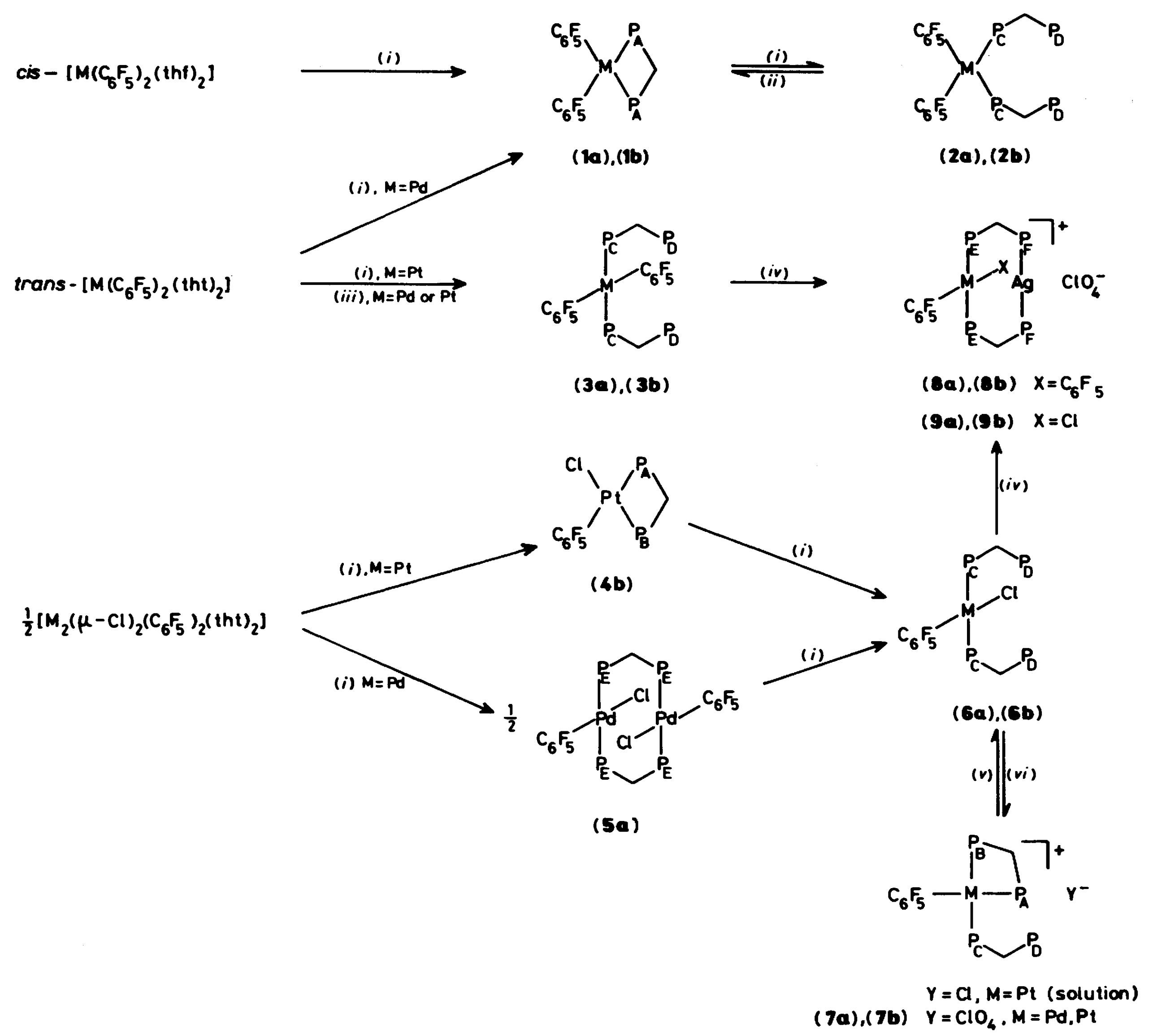
The methods of preparation of the complexes and the interconversions observed are summarized in Scheme 1. Analytical and conductivity data, along with relevant i.r. absorptions, are collected in Table 1, ^{31}P n.m.r. parameters in Table 2.

Synthesis of the Complexes.—Some of us have recently shown that the complexes *cis*-$[M(C_6F_5)_2(thf)_2]$ (M = Pd or Pt) with

Table 1. Analyses,[a] conductivities,[b] and relevant i.r. data (cm^{-1}) for the complexes

Complex	Analysis/%		Λ_M/ Ω^{-1} cm^2 mol^{-1}	600—400 cm^{-1} range	Other bands
	C	H			
(**1a**) $[Pd(C_6F_5)_2(dppm)]$	53.20 (53.75)	2.65 (2.70)	n.c.	530s, 497vs, 471m, 431m	
(**1b**) $[Pt(C_6F_5)_2(dppm)]$	48.10 (48.60)	2.10 (2.40)	n.c.	540s, 503vs, 475m, 435m	
(**2a**) *cis*-$[Pd(C_6F_5)_2(dppm)_2]$	62.00 (61.60)	3.80 (3.70)	n.c.	515s, 495vs, 475m, 455m	
(**2b**) *cis*-$[Pt(C_6F_5)_2(dppm)_2]$	57.10 (57.40)	3.50 (3.40)	n.c.	520s, 496vs, 480m, 462m	
(**3a**) *trans*-$[Pd(C_6F_5)_2(dppm)_2]$	61.50 (61.60)	3.80 (3.70)	n.c.	516s, 502s, 487vs, 458s, 430m, 418m	
(**3b**) *trans*-$[Pt(C_6F_5)_2(dppm)_2]$	57.20 (57.40)	3.40 (3.40)	n.c.	520s, 516s, 487vs, 458s, 430m, 418m	
(**4b**) $[PtCl(C_6F_5)(dppm)]$	47.90 (47.60)	3.15 (2.85)	n.c.	550s, 510vs, 485s, 450m	300s,br[c]
(**5a**) *trans,trans*-$[Pd_2Cl_2(C_6F_5)_2(\mu\text{-}dppm)_2]$	53.30 (53.70)	3.25 (3.20)	n.c.	518vs, 486vs	302s[c]
(**6a**) $[PdCl(C_6F_5)(dppm)_2]$	62.50 (62.40)	4.60 (4.10)	n.c.	495vs, 480s, 460s, 440w, 410m	313s[c]
(**6b**) $[PtCl(C_6F_5)(dppm)_2]$	57.50 (57.65)	3.80 (3.80)	49	500vs, 483s, 465s, 430w, 410m	314s[c]
(**7a**) $[Pd(C_6F_5)(dppm)_2]ClO_4$	58.20 (58.90)	3.55 (3.90)	127	538m, 510(sh), 500s, 488m, 475m	1 100s,br, 620s[d]
(**7b**) $[Pt(C_6F_5)(dppm)_2]ClO_4$	53.80 (54.65)	3.70 (3.60)	101	535m, 515s, 500s, 485(sh), 480s	1 100s,br, 620s[d]
(**8a**) $[(C_6F_5)_2Pd(\mu\text{-}dppm)_2Ag]ClO_4$	52.90 (52.90)	3.30 (3.15)	121	510vs, 490s, 475s, 440w, 411m	1 100s,br, 620s[d]
(**8b**) $[(C_6F_5)_2Pt(\mu\text{-}dppm)_2Ag]ClO_4$	49.05 (49.45)	3.40 (2.95)	130	510vs, 490s, 475s, 440w, 411m	1 100s,br, 620s[d]
(**9a**) $[(C_6F_5)ClPd(\mu\text{-}dppm)_2Ag]ClO_4$	52.20 (52.40)	3.50 (3.45)	125	510vs, 484s, 469s, 420m	300m,[c] 1 100s,br, 620s[d]
(**9b**) $[(C_6F_5)ClPt(\mu\text{-}dppm)_2Ag]ClO_4$	48.60 (48.95)	3.20 (3.20)	119	510vs, 484s, 469s, 420m	295m,[c] 1 100s,br, 620s[d]

[a] Calculated values in parentheses. [b] In 5×10^{-4} mol dm^{-3} acetone solution; n.c. = non-conducting. [c] ν(M–Cl). [d] ClO_4^- (B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 1961, 3091).



Scheme 1. **a**, M = Pd; **b**, M = Pt. (*i*) +dppm; (*ii*) −dppm; (*iii*) +2dppm; (*iv*) $AgClO_4$; (*v*) M = Pt, recrystallization; (*vi*) M = Pt (solution), Pt or Pd ($NaClO_4$)

the labile ligand tetrahydrofuran (thf) are excellent precursors for the synthesis of other *cis*-$[M(C_6F_5)_2L_2]$ complexes.[4] When they are treated with dppm (M:dppm ratio = 1:1) in benzene at room temperature the complexes $[M(C_6F_5)_2(dppm)]$ [M = Pd (**1a**) or Pt (**1b**)] containing the chelate ligand dppm are formed as sparingly soluble white solids. When a M:dppm ratio of 1:2 is used no precipitation is observed and, upon evaporation to dryness and washing with Et_2O, the complexes *cis*-$[M(C_6F_5)_2(dppm\text{-}P)_2]$ [M = Pd (**2a**) or Pt (**2b**)] containing two mutually *cis* unidentate dppm ligands are isolated. Complexes (**2**) (**a** or **b**) can also be obtained from (**1**) (**a** or **b**) and excess of dppm but in order to force the insoluble (**1**) to react the process has to be carried out in refluxing toluene. Under these conditions some palladium(I) complex $[(C_6F_5)Pd(\mu\text{-}dppm)_2Pd(C_6F_5)]$[2a] was formed along with (**2a**), possibly by reduction of (**1a**) or (**2a**) by the excess of phosphine. Both palladium complexes (**1a**) and (**2a**) can be prepared equally well from $[NBu^n{}_4]_2[Pd_2(\mu\text{-}Br)_2(C_6F_5)_4]$[5] and both platinum complexes (**1b**) and (**2b**) from *cis*-$[Pt(C_6F_5)_2(tht)_2]$[5] (tht = tetrahydrothiophene). Complex (**1b**) has been described before[6] but not the related (**2b**).

The reactions of *trans*-$[M(C_6F_5)_2(tht)_2]$ with dppm (M:dppm ratio = 1:1) in refluxing toluene follow different paths for Pd and Pt. When M = Pd an isomerization occurs to give (**1a**), with the two C_6F_5 groups in mutually *cis* positions. Under the same conditions the platinum complex, likely to be more inert towards isomerization, reacts to give *trans*-$[Pt(C_6F_5)_2(dppm\text{-}P)_2]$, (**3b**), and half of the starting material remains unchanged. Complex (**3b**) and its palladium analogue *trans*-$[Pd(C_6F_5)_2(dppm\text{-}P)_2]$, (**3a**), are better obtained from the reaction of *trans*-$[M(C_6F_5)_2(tht)_2]$ and dppm in 1:2 ratio in refluxing benzene. We have not observed formation of either (**1a**) or (**2a**) from complex (**3a**).

The complexes $[M_2(\mu\text{-}Cl)_2(C_6F_5)_2(tht)_2]$[7] were the materials of choice for the preparation of complexes containing the moiety $M(C_6F_5)Cl$. Again the reactions in benzene, using a M:dppm ratio of 1:1, follow different courses for palladium and for platinum. When M = Pt the complex obtained is $[PtCl(C_6F_5)(dppm)]$, (**4b**), a monomeric complex containing one chelating dppm ligand. When M = Pd, however, a white precipitate is obtained which is shown by n.m.r. spectroscopy (see below) to be mainly *trans,trans*-$[(C_6F_5)ClPd(\mu\text{-}dppm)_2\text{-}$

Table 2. $^{31}P\text{-}\{^1H\}$ N.m.r. data (δ/p.p.m., J/Hz)

Complex	P_A	P_B	P_C	P_D	P_E	P_F	$J(P_A-P_B)$	$J(P_A-P_C)$	$J(P_B-P_C)$	$J(P_C-P_D)$	N^a	$J(Pt-P_A)$	$J(Pt-P_B)$	$J(Pt-P_C)$	$J(Pt-P_E)$	$J(^{109,\,107}Ag-P_F)$
(1a)	−32.0															
(1b)	−43.5											1 989				
(2a)			12.1	−27.2												
(2b)			3.8	−27.1										2 382		
(3a)			17.5	−28.9							57					
(3b)			9.2	−29.1							57			2 692		
(4b)	*b*	*b*					60					1 873	3 331			
(5a)					12.1											
(6a)			19.1	−25.4							53					
(6b)	−41.2	−37.7	9.6	−32.6			53	14	370	78		1 875	2 051	2 505		
(7a)	−34.2	−24.9	16.1	−32.3			67		396	90						
(7b)	−41.7	−35.4	9.5	−32.7			52	15	370	78		1 884	2 054	2 532		
(8a)					18.8	10.9										593, 515
(8b)					10.4	7.1					75				2 600	
(9a)					23.0	7.3					78					587, 510
(9b)					19.9	3.9					70				2 658	600, 521

[a] $^2J(P_C-P_D) + {}^4J(P_C-P_{D'})$. [b] Multiplet centred at −51.2 p.p.m.

$PdCl(C_6F_5)]$, (**5a**), contaminated with about 5% of what we believe is $[PdCl(C_6F_5)(dppm)]$, (**4a**). Uncontaminated (**5a**) can be obtained from the same reaction in acetone.

The treatment of complex (**4b**), (**5a**), or $[M_2(\mu\text{-}Cl)_2(C_6F_5)_2(tht)_2]$ with a large excess of dppm leads to the formation of *trans*-$[MCl(C_6F_5)(dppm\text{-}P)_2]$ [M = Pd (**6a**) or (**6b**)], with two unidentate dppm ligands, as white solids. Both complexes (**6a**) and (**6b**) are shown to have this structure in the solid but in solution in $CDCl_3$ the platinum complex (**6b**) isomerizes reversibly to give $[Pt(C_6F_5)(dppm\text{-}PP')(dppm\text{-}P)]Cl$ (see below). The cationic complexes $[M(C_6F_5)(dppm\text{-}PP')(dppm\text{-}P)]ClO_4$ [M = Pd (**7a**) or Pt (**7b**)] can be obtained by treating (**6a**) or (**6b**) with $NaClO_4$ in order to facilitate displacement of the chloro ligand by one P of one of the two dppm-*P* ligands.

Finally, complexes of the types (**3**) and (**6**), having P atoms not involved in bonding can be used as ligands towards other electrophilic centres. Thus, they react with $AgClO_4$ in benzene solution to give heterobimetallic binuclear complexes, (**8**) and (**9**), with dppm bridging different metallic centres.

I.r. and ^{31}P *N.M.R. Spectra*.—The structures of the complexes have been assigned based on their i.r. (Table 1) and ^{31}P n.m.r. (Table 2) spectra.

All the i.r. spectra show characteristic bands of the C_6F_5 group[8] near 1 510, 1 050, 950, and 800 cm^{-1}; the latter are usually of structural interest[5,9] but absorptions of the dppm ligand in this range render them useless in our complexes. In addition to confirming the presence of the counter ion ClO_4^- or the M–Cl bonds, the most valuable information which can be extracted from the i.r. spectra concerns the co-ordination mode of the dppm ligand. In any of the three co-ordination modes this ligand shows a pattern of characteristic absorptions in the range 520—410 cm^{-1} but an extra absorption of medium to strong intensity in the range 550—530 cm^{-1} is observed only when there is a dppm chelating ligand (confirmed by ^{31}P n.m.r. spectroscopy), thus allowing a clear-cut distinction between this and the other two co-ordination modes.

Interestingly, both complexes (**6a**) and (**6b**), which behave differently in solution (see below), show similar i.r. spectra in the solid state, and also closely related *X*-ray powder diffraction diagrams; for this reason they are assigned the same structure in the solid state.

The ^{31}P n.m.r. spectra provide valuable information on the co-ordination mode of the dppm ligand, both from the chemical shift and from the $^1J(Pt\text{-}P)$ values.[6] The parameters collected in Table 2 show that the P atoms of chelating dppm ligands (P_A and P_B) show high negative ^{31}P chemical shifts (−25 to −52 p.p.m.). The complexes containing unidentate dppm ligands show absorptions in two well separated ranges: the co-ordinated P atom (P_C) shows positive ^{31}P chemical shifts (9—20 p.p.m.) and the free P atom (P_D) high negative chemical shifts (−27 to −33 p.p.m.); in addition, the $^1J(Pt\text{-}P)$ values lie in the range 2 500—2 700 Hz [higher than the corresponding values of $^1J(Pt\text{-}P_A)$ or $^1J(Pt\text{-}P_B)$]. Finally, the complexes containing dppm ligands bridging two metal atoms show positive ^{31}P chemical shifts (P_E and P_F) and ^1J (Pt–P) values also in the range 2 600—2 700 Hz; $^1J(Ag\text{-}P)$ in the heterobimetallic complexes is close to 510 (^{107}Ag) and 590 Hz (^{109}Ag).

The complexes $[MCl(C_6F_5)(dppm)_2]$, (**6a**) and (**6b**), deserve some comment. We have already pointed out that the i.r. spectra of both complexes in the solid state are very similar and do not show any absorption in the range 550—530 cm^{-1}, thus excluding the presence of chelating dppm groups. The palladium complex, (**6a**), behaves as a non-conductor in acetone solution and its ^{31}P n.m.r. spectrum in $CDCl_3$ solution is that expected for a structure *trans*-$[PdCl(C_6F_5)(dppm\text{-}P)_2]$. The corresponding platinum derivative, (**6b**), shows complex broadened ^{31}P n.m.r. signals at room temperature which are resolved on cooling; its ^{31}P n.m.r. spectrum at −40 °C (similar to that in the Figure) can be analysed as originating from a molecule with one chelating dppm ligand (P_A and P_B) and one unidentate dppm ligand (P_C and P_D). A similar behaviour is observed for complex (**7b**), $[Pt(C_6F_5)(dppm\text{-}PP')(dppm\text{-}P)]^+$. This and the fact that (**6b**) exhibits a high molar conductivity in acetone solution [(**6a**) is non-conducting] suggests that complex (**6b**) is almost completely ionized in solution, $[Pt(C_6F_5)(dppm\text{-}PP')(dppm\text{-}P)Cl$, and that both (**6b**) and (**7b**) undergo a slow exchange process not involving the counter ion, such as that represented in Scheme 2.

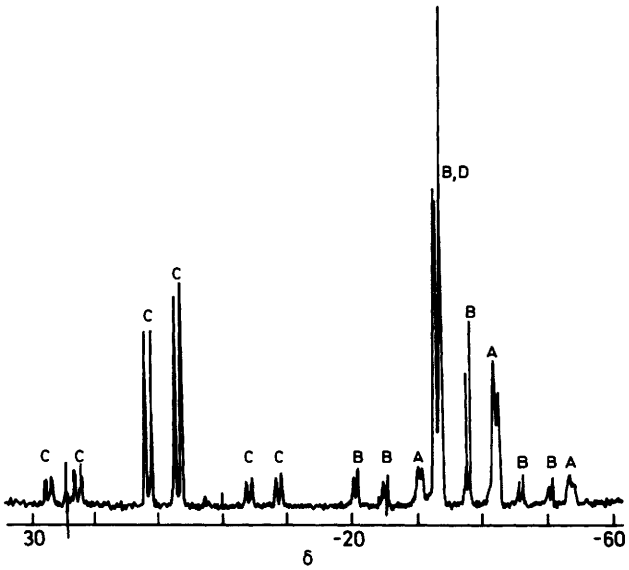
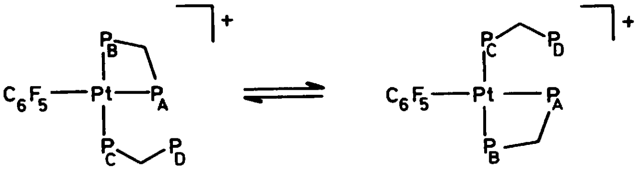


Figure. $^{31}P\text{-}\{H\}$ N.m.r. spectrum of complex (**7b**) at −40 °C in $CDCl_3$ (reference 85% H_3PO_4)



Scheme 2.

The Figure shows the ^{31}P n.m.r. spectrum of complex (**7b**) at −40 °C. The unidentate dppm ligand displays two signals, one at 9.5 p.p.m. (P_C, coupled to P_A, P_D, P_B, and ^{195}Pt) and one at −32.7 p.p.m. (P_D, coupled only to P_C); the chelate ligand displays also two signals, one at −41.7 p.p.m. (P_A, coupled to P_B and ^{195}Pt, and broadened due to unresolved coupling to the ^{19}F atoms in the *trans*-C_6F_5 group) and one at −35.4 p.p.m. (P_B, coupled to P_A, P_C, and ^{195}Pt).

A second point that is worth commenting on is the solution behaviour of complexes (**2a**) and (**2b**). Both complexes are shown by ^{31}P n.m.r. spectroscopy to exhibit the equilibrium depicted in equation (1); the rate of exchange is very slow and

$$cis\text{-}[M(C_6F_5)_2(dppm\text{-}P)_2] \rightleftharpoons [M(C_6F_5)_2(dppm)] + dppm \quad (1)$$

thus the peaks corresponding to all the species in the equilibrium are observed easily even at room temperature. This process had been reported before for complex (**2b**) in CD_2Cl_2.[6]

Experimental

Carbon, H, and N analyses were carried out on a Perkin-Elmer 240 microanalyser. Conductivities were measured with a Philips PW 9509 conductimeter. The i.r. spectra were recorded (in the range 4 000—200 cm^{-1}) on a Perkin-Elmer 599 spectrophotometer, $^{31}P-\{^1H\}$ n.m.r. spectra on a Varian XL-200 instrument (200 MHz for ^1H).

Literature methods were used to prepare the compounds $Ph_2PCH_2PPh_2$ (dppm),[10] $[NBu^n{}_4]_2(Pd_2(\mu-Br)_2(C_6F_5)_4]$,[5] *cis*-$[Pt(C_6F_5)_2(tht)_2]$,[5] *trans*-$[M(C_6F_5)_2(tht)_2]$,[5] $[M_2(\mu-Cl)_2(C_6F_5)_2(tht)_2]$,[7] and *cis*-$[M(C_6F_5)_2(thf)_2]$[4c] (M = Pd or Pt).

$[M(C_6F_5)_2(dppm)]$ [M = Pd (**1a**) *or* Pt (**1b**)] *from cis*-$[M(C_6F_5)_2(thf)_2]$.—To a solution of *cis*-$[Pd(C_6F_5)_2(thf)_2]$ (0.180 g, 0.27 mmol) in benzene (10 cm^3) was added dppm (0.106 g, 0.27 mmol). The mixture was stirred for 1 h at room temperature. Then, the solvent was evaporated to 2 cm^3 and Et_2O (20 cm^3) was added. The precipitate of complex (**1a**) was filtered off and air dried. Yield 72%. Complex (**1b**) was obtained similarly using *cis*-$[Pt(C_6F_5)_2(thf)_2]$ as starting material and a reaction time of 5 h. Yield 70%.

$[Pd(C_6F_5)_2(dppm)]$ (**1a**) *from* $[NBu^n{}_4]_2[Pd_2(\mu-Br)_2(C_6F_5)_4]$.—To a solution of $[NBu^n{}_4]_2[Pd_2(\mu-Br)_2(C_6F_5)_4]$ (0.400 g, 0.26 mmol) in benzene (30 cm^3) was added dppm (0.202 g, 0.52 mmol). The mixture was stirred for 24 h at room temperature. Then, the solvent was evaporated to 5 cm^3 and Pr^iOH (*ca.* 20 cm^3) was added. The white precipitate was filtered off and air dried. Yield 85%.

$[Pt(C_6F_5)_2(dppm)]$ (**1b**) *from cis*-$[Pt(C_6F_5)(tht)_2]$.—To a solution of *cis*-$[Pt(C_6F_5)_2(tht)_2]$ (0.712 g, 1.01 mmol) in benzene (20 cm^3) was added dppm (0.388 g, 1.01 mmol). The mixture was stirred overnight at room temperature. The resulting white precipitate was filtered off, washed with benzene (*ca.* 5 cm^3), and air-dried. Yield 82%.

cis-$[M(C_6F_5)_2(dppm)_2]$ [M = Pd (**2a**) *or* Pt (**2b**)] *from cis*-$[M(C_6F_5)_2(thf)_2]$.—To a solution of *cis*-$[Pd(C_6F_5)_2(thf)_2]$ (0.100 g, 0.17 mmol) in benzene (15 cm^3) was added dppm (0.150 g, 0.39 mmol). The mixture was stirred for 18 h at room temperature. The solution was evaporated to dryness and the resulting solid (**2a**) was washed with Et_2O (*ca.* 20 cm^3) and air-dried. Yield 87%. Complex (**2b**) was obtained by similarly using refluxing toluene as solvent, *cis*-$[Pt(C_6F_5)_2(tht)_2]$ as starting material, and a reaction time of 3 h. Yield 89%.

trans-$[M(C_6F_5)_2(dppm)_2]$ [M = Pd (**3a**) *or* Pt (**3b**)].—To a suspension of *trans*-$[Pd(C_6F_5)_2(tht)_2]$ (1.610 g, 2.61 mmol) in benzene (40 cm^3) was added dppm (2.001 g, 5.22 mmol). The mixture was refluxed for 3 h whereupon a white precipitate was obtained. The solid was filtered off, dried, and heated in the oven at 90 °C for 8 h, to give (**3a**) (yield 93%). Complex (**3b**) was obtained similarly from *trans*-$[Pt(C_6F_5)_2(tht)_2]$. Yield 85%.

$[PtCl(C_6F_5)(dppm)]$ (**4b**).—To a solution of $[Pt_2(\mu-Cl)_2(C_6F_5)_2(tht)_2]$ (0.250 g, 0.26 mmol) in benzene (40 cm^3) was added dppm (0.198 g, 0.52 mmol). The mixture was stirred for 3 h at room temperature. The resulting white precipitate was filtered off and air-dried. Yield 85%.

trans,trans-$[Pd_2Cl_2(C_6F_5)_2(\mu-dppm)_2]$ (**5a**).—To a solution of $[Pd_2(\mu-Cl)_2(C_6F_5)_2(tht)_2]$ (0.206 g, 0.26 mmol) in acetone (40 cm^3) was added dppm (0.19 g, 0.52 mmol). The mixture was stirred for 3 h at room temperature, then evaporated almost to dryness. Addition of Et_2O (*ca.* 20 cm^3) produced a white precipitate, which was filtered off and air-dried. Yield 56%.

$[MCl(C_6F_5)(dppm)_2]$ [M = Pd (**6a**) *or* Pt (**6b**)].—To a solution of $[Pd_2(\mu-Cl)_2(C_6F_5)_2(tht)_2]$ (0.126 g, 0.16 mmol) in benzene (50 cm^3) was added dppm (0.244 g, 0.645 mmol). The mixture was refluxed for 4 h, then filtered and evaporated to dryness. The residue was stirred and washed with Et_2O (*ca.* 20 cm^3), filtered off, air-dried, and heated for 7 h at 90 °C. Yield of complex (**6a**) 83%. Complex (**6b**) was obtained similarly from $[Pt_2(\mu-Cl)_2(C_6F_5)_2(tht)_2]$ in 75% yield.

$[M(C_6F_5)(dppm)_2]ClO_4$ [M = Pd (**7a**) *or* Pt (**7b**)].—To a suspension of $[PdCl(C_6F_5)(dppm)_2]$ (0.730 g, 0.67 mmol) in acetone (40 cm^3) was added $NaClO_4$ (0.179 g, 0.68 mmol) and the mixture was stirred for 3 h at room temperature. The filtered solution was evaporated to dryness and the residue extracted with CH_2Cl_2 (*ca.* 20 cm^3). The filtered CH_2Cl_2 solution was concentrated to *ca.* 2 cm^3. Addition of MeOH (10 cm^3) produced a white precipitate which was filtered off, air-dried, and heated for 14 h at 75 °C to give (**7a**). Yield 80%. Complex (**7b**) was obtained similarly from $[PtCl(C_6F_5)(dppm)_2]$. Yield 82%.

$[X(C_6F_5)M(\mu-dppm)_2Ag]ClO_4$ [X = C_6F_5, M = Pd (**8a**) *or* Pt (**8b**); X = Cl, M = Pd (**9a**) *or* Pt (**9b**)].—To a solution of *trans*-$[Pd(C_6F_5)_2(dppm)_2]$ (0.385 g, 0.319 mmol) in a mixture of benzene (40 cm^3) and CH_3Cl (10 cm^3) was added $AgClO_4$ (0.066 g, 0.319 mmol). The mixture was stirred for 4 h at room temperature. The resulting white precipitate was filtered off, washed with benzene (*ca.* 10 cm^3), air-dried, and heated for 8 h at 90 °C. Yield of (**8a**) 93.3%. Complexes (**8b**), (**9a**), and (**9b**) were obtained similarly from $[Pt(C_6F_5)_2(dppm)_2]$, $[PdCl(C_6F_5)(dppm)_2]$, and $[PtCl(C_6F_5)(dppm)_2]$ respectively. Yields 94 (**8b**), 96 (**9a**), and 94% (**9b**).

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