Journal of Organometallic Chemistry, 304 (1986) 381–390
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

MONONUCLEAR (Pd, Pt) AND BINUCLEAR (Pd,Pd; Pd,Ag; Pt,Ag) COMPLEXES CONTAINING THE BIS(DIPHENYLPHOSPHINO)AMINE LIGAND

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(Received October 29th, 1985)

Summary

By appropriate choice of precursors and solvent, complexes of the type $M(C_6X_5)_2(dppa)_2$ or $M(C_6X_5)_2(dppa)$ (M = Pd, Pt; X = F, Cl; dppa = $Ph_2PNHPPh_2$) can be prepared. Reaction of *trans*-$M(C_6F_5)_2(dppa)_2$ with $AgClO_4$ gives hetero-binuclear complexes of the type $[(C_6F_5)_2M(\mu\text{-dppa})_2Ag]ClO_4$. Addition of dppa to the perchlorato complexes $Pd(OClO_3)(C_6F_5)L_2$ ($L = PR_3$) gives the cationic singly-bridged homo-binuclear species $[\{Pd(C_6F_5)L_2\}_2(\mu\text{-dppa})](ClO_4)_2$. The binuclear Pd^I complex $[\{Pd(C_6F_5)\}_2(\mu\text{-dppa})_2]$ has been obtained from the reaction between $Pd(C_6F_5)_2(dppa)_2$ and $Pd_2(dba)_3 \cdot CHCl_3$ and its insertion reactions have been studied. The dppa ligand acts as monodentate, bidentate-chelate or bidentate-bridging ligand depending on the precursors, the solvent, and the reaction conditions.

Introduction

Tertiary diphosphine ligands are being increasingly used in coordination chemistry [1]. In particular, bis(diphenylphosphino)methane (dppm) has been the subject of much recent work [2] because of its ability to form binuclear bridged complexes with transition metals in low oxidation state. In contrast, other similar systems such as, for instance, the isoelectronic bis(diphenylphosphino)amine (dppa), have received very little attention; although some complexes of various types have been described [3–11], only a very few of them are palladium or platinum derivatives [5,6]. We describe here the synthesis of dppa-containing complexes of Pd^{II}, Pt^{II}, Pd^I and Ag^I in which the ligand plays several roles:

1. Neutral mononuclear M^{II} (M = Pd, Pt) *cis*- or *trans*-complexes containing dppa in terminal monodentate (**A**) or bidentate chelate (**B**) mode.

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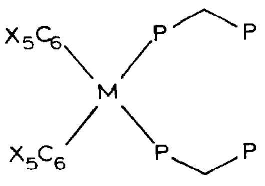
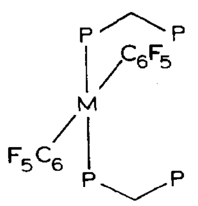


(A)



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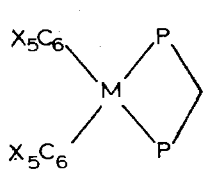
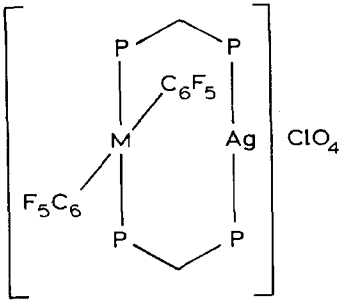


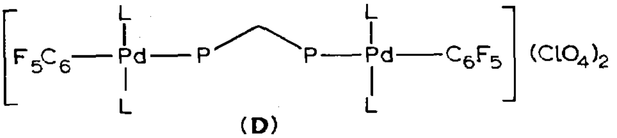
(B)

2. Cationic hetero binuclear M–Ag complexes (M = Pd, Pt) with the metal centres doubly-bridged by two ligand molecules (C).



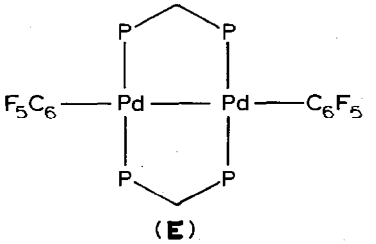
(C)

3. Cationic homo-binuclear Pd^{II} compexes with both metal centres singly-bridged by one ligand molecule (D).



(D)

4. The neutral binuclear Pd^{I} complex (E) and its insertion products.



(E)

A fair amount of work has been carried out with various diphosphine ligands [12] in order to prove the hypothesis that steric effects of the substituents on the P atoms determine the type of complex formed. We show in the discussion below that the precursors, solvents, the reaction conditions used all influence the nature of the products.

Results and discussion

Neutral mononuclear perhalophenyl complexes of Pd^{II} or Pt^{II}

Addition of dppa to benzene solutions of neutral bis (pentahalophenyl)bis(tetrahydrothiophene)M (M = Pd, Pt) results in displacement of the S-ligand, as shown in eqs. 1 and 2:

$$trans\text{-}Pd(C_6F_5)_2(SC_4H_8)_2 + 2\ dppa \xrightarrow{C_6H_6} 2\ SC_4H_8 + \underset{(I)}{trans\text{-}Pd(C_6F_5)_2(dppa)_2} \quad (1)$$

$$cis,trans\text{-}Pt(C_6F_5)_2(SC_4H_8)_2 + 2\ dppa \xrightarrow{C_6H_6}$$

$$2\ SC_4H_8 + \underset{(II)}{trans\text{-}Pt(C_6F_5)_2(dppa)_2} + \underset{(III)}{cis\text{-}Pt(C_6F_5)_2(dppa)_2} + \underset{(VI)}{Pt(C_6F_5)_2(dppa)} \quad (2)$$

As can be seen, the reactions take place with stereoretention. The mixture obtained for M = Pt can be resolved easily since VI is insoluble in benzene, and after filtration, the *cis* and *trans* isomers can be separated because of their different solubilities in diethyl ether (see Experimental). The insolubility of complex VI causes it to separate despite the presence of an excess of dppa.

On the other hand, all the possible complexes $M(C_6X_5)_2(dppa)$ including only a chelated dppa molecule can be readily obtained by a seemingly trivial change in the used precursor.

For example, dichloromethane solutions of *cis*-$M(C_6X_5)_2(OC_4H_8)_2$ react with a stoichiometric (1/1) amount of dppa to give the chelated derivatives, according to eq. 3.

$$cis\text{-}M(C_6X_5)_2(OC_4H_8)_2 + dppa \xrightarrow{CH_2Cl_2} M(C_6X_5)_2(dppa) + 2\ OC_4H_8 \quad (3)$$
$$(M = Pd, X = F\ (IV), Cl\ (V);$$
$$M = Pt, X = F\ (VI), Cl\ (VII))$$

If however, these reactions (eq. 3) are carried out with an excess of dppa (1/2 or higher molar ratio) only for M = Pt, X = F, is the complex $Pt(C_6F_5)_2(dppa)_2$ obtained. In all other cases the same complexes (IV–VII) as before, containing only one molecule of chelated dppa precipitate out, doubtless because of their insolubility, even in the presence of an excess of the ligand.

All these neutral complexes (I–VII) behave as typical non-electrolytes in acetone.

The IR spectra of the two *trans* complexes I and II show a single absorption due to the X-sensitive mode of the C_6F_5 groups [13–16] in the 800–750 cm^{-1} region (see Table 2), as expected from their *trans*-configurations. Complexes III, IV and VI show two absorptions in the same region, in agreement with the presence of two mutually *cis* C_6F_5 groups. Complexes V and VII show absorptions due to the C_6Cl_5 groups [17,18] and two bands near 600 cm^{-1} (Table 2) assigned to ν(M–C) in *cis* derivatives. In these cases the presence of an internal vibration of the phosphine ligand at ~ 810 cm^{-1} precludes the unambiguous assignation of the X-sensitive mode.

As usual in neutral complexes containing dppa, [4,7] the band due to ν(N–H) is shifted toward higher energies relative to that for the free ligand (3230 cm^{-1}). The *trans*-I–II and the chelated complexes show a single band in the 3380–3325 cm^{-1} region, whereas complex III, *cis*-$Pt(C_6F_5)_2(dppa)_2$, exhibits two bands (3336, 3315 cm^{-1}).

The pattern in the 600–400 cm^{-1} region (where internal vibrations of the phosphine ligand appear) is similar for complexes of the same configuration, for instance, for the pair I–II and for complexes IV–VII.

The ^{31}P {^{1}H} NMR spectrum of *trans*-Pt(C_6F_5)$_2$(dppa)$_2$ (II) shows two deceptively simple triplets, one of them with platinum satellites; this pattern corresponds to an AA′BB′ system with a large value of ^{2}J(P–Pt–P) arising from the *trans* geometry of complex II. In *cis*-Pt(C_6F_5)$_2$(dppa)$_2$ the non-coordinated P atoms give rise to a doublet ($^{2}J(P_A-P_B)$ 19 Hz); the coordinated P atoms rise to a single broad peak with platinum satellites, the doublet nature of these signals being unobservable owing to broadening of the signal produced by unresolved P–F couplings.

Complex *trans*-Pd(C_6F_5)$_2$(dppa)$_2$ (I) shows two broad deceptive singlets corresponding to the coordinated P atoms and the non-coordinated P atoms. The complexes M(C_6F_5)$_2$ (dppa) show only one broad singlet, corresponding to the two equivalent P atoms; for M = Pt the spectrum shows the expected Pt satellites (Table 3).

Cationic heteronuclear M^{II}–Ag^{I} complexes (M^{II} = Pd, Pt)

Since in complexes of the type *trans*-M(C_6F_5)$_2$(dppa)$_2$ (M = Pd^{II}, Pt^{II}) the neutral ligand is acting as monodentate, the remaining free P atom in each dppa

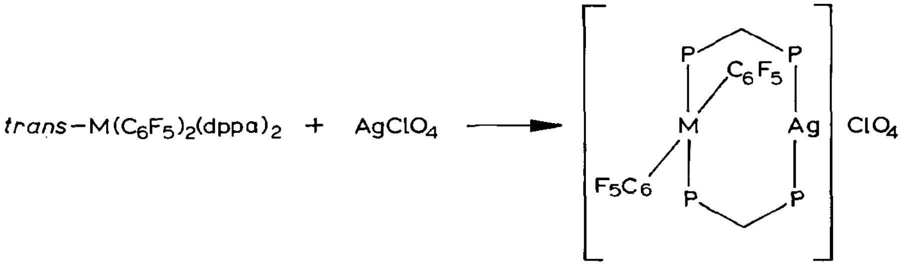
TABLE 1

ANALYSES, CONDUCTIVITIES AND MELTING POINTS OF THE COMPLEXES

Complex	Analyses (Found (calcd.) (%))			Λ	M.p. (°C)
	N	C	H		
(I) *trans*-[Pd(C_6F_5)$_2$(dppa)$_2$]	2.20	59.72	3.53	n.c. [a]	155
	(2.31)	(59.49)	(3.49)		
(II) *trans*-[Pt(C_6F_5)$_2$(dppa)$_2$]	2.41	55.84	3.36	n.c.	210
	(2.15)	(55.40)	(3.25)		
(III) *cis*-[Pt(C_6F_5)$_2$(dppa)$_2$]	2.15	55.46	2.80	n.c.	180
	(2.15)	(55.40)	(3.25)		
(IV) [Pd(C_6F_5)$_2$(dppa)]	1.81	51.40	2.54	n.c.	200
	(1.69)	(52.35)	(2.56)		
(V) [Pd(C_6Cl_5)$_2$(dppa)]	1.33	42.78	2.25	n.c.	257
	(1.41)	(43.65)	(2.54)		
(VI) [Pt(C_6F_5)$_2$(dppa)]	1.90	47.46	2.71	n.c.	255
	(1.53)	(47.27)	(2.31)		
(VII) [Pt(C_6Cl_5)$_2$(dppa)]	1.75	40.19	2.05	n.c.	295
	(1.29)	(40.06)	(1.96)		
(VIII) [(C_6F_5)$_2$Pd(μ-dppa)$_2$Ag]ClO$_4$	2.23	50.64	3.06	60 (140) [b]	100
	(1.97)	(50.80)	(2.99)		
(IX) [(C_6F_5)$_2$Pt(μ-dppa)$_2$Ag]ClO$_4$	1.97	48.38	3.01	63 (262) [b]	196
	(1.85)	(47.81)	(2.80)		
(X) [{Pd(C_6F_5)(PPh$_3$)$_2$}$_2$(μ-dppa)$_2$Ag]ClO$_4$	0.83	58.86	3.78	213	197
	(0.64)	(59.49)	(3.74)		
(XI) [{Pd(C_6F_5)(PPh$_2$Me)$_2$}$_2$(μ-dppa)$_2$Ag]ClO$_4$	0.68	55.63	3.82	207	162
	(0.72)	(54.70)	(3.80)		
(XII) [{Pd(C_6F_5)(PEt$_3$)$_2$}$_2$(μ-dppa)$_2$Ag]ClO$_4$	1.03	45.02	4.95	217	155
	(0.87)	(44.93)	(5.09)		
(XIII) [{Pd(C_6F_5)}$_2$(μ-dppa)$_2$]	2.14	54.84	3.41	n.c.	224
	(2.12)	(54.69)	(3.21)		
(XIV) [{Pd(C_6F_5)}$_2$(μ-dppa)$_2$(μ-p-CH$_3$C$_6$H$_4$N$_2$)]BF$_4$	3.62	52.22	3.25	104	223
	(3.67)	(52.81)	(3.24)		

[a] N.c. denotes non-conducting. [b] $\Lambda_M(B)$ from $\Lambda_c = \Lambda_0 - B\sqrt{c}$.

ligand can potentially coordinate to another electrophilic centre. If the stoichiometric amounts of $AgClO_4$ are added to benzene solutions of complexes I or II the hetero-binuclear cationic $[M(C_6F_5)_2(\mu\text{-dppa})Ag]ClO_4$ complexes are obtained (see eq. 5).



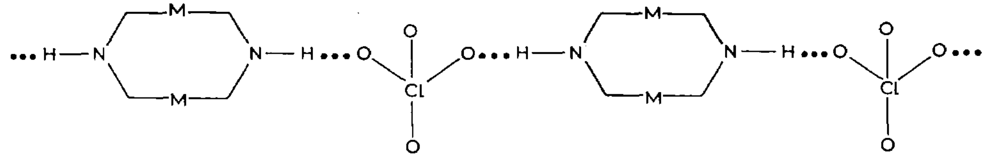
(5)

(M = Pd(VIII), Pt(IX))

The binuclear character of both complexes was established by conductance measurements in nitromethane solutions of various concentrations (3×10^{-3}–4×10^{-4} mol dm^{-3}). The derived B values in the Onsager equation ($\Lambda_c = \Lambda_0 - B\sqrt{c}$) correspond to 1/1 electrolytes (Table 1) [19–21].

Both complexes VIII and IX show IR bands at 1100 vs,br and 620 s cm^{-1} assignable to the ClO_4 anion (T_d) [22]; they also show the characteristic absorptions due to C_6F_5 groups, at 1500 s, 950 s and 780 s cm^{-1}. Bands in the 600–400 cm^{-1} region confirm the presence of the dppa ligand.

In contrast to the neutral complexes I–VII, complexes VIII and IX show no IR absorptions (Nujol mulls) assignable to ν(N–H) in the 3500–3100 cm^{-1} region. In KBr disks a broad band appears at 3050–2950 cm^{-1}, which cannot be unequivocally assigned because of the presence of internal absorptions of dppa in this region. If the band is assigned to ν(N–H), the shift to lower energies in the cationic complexes and the observed broadening of these bands would point to the presence of hydrogen bonds between N–H groups and the perchlorate anion [6]:

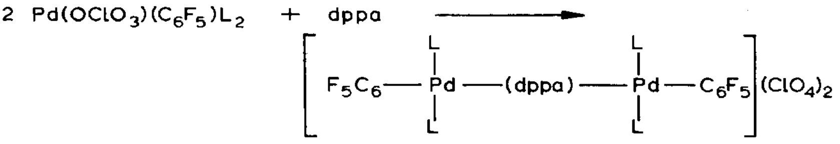


The ^{31}P (^1H decoupled) NMR spectra of $[(C_6F_5)_2M(\mu\text{-dppa})_2Ag]ClO_4$ show a broad signal due to the P atoms coordinated to M (for M = Pt, with Pt satellites) and two complex multiplets corresponding to the P atoms coordinated to Ag; the fine structure arising from the coupling with ^{107}Ag and ^{109}Ag is now well resolved (Table 3).

Finally, the reactions between cis-$Pt(C_6F_5)_2(dppa)_2$ (III) and $AgClO_4$ or $O_3ClOAgPPh_3$ does not lead to a binuclear Pt–Ag derivative. The precipitate which separated was shown to be $Pt(C_6F_5)_2(dppa)$ (VI) by IR spectroscopy.

Cationic homo-binuclear singly-bridged Pd^{II} complexes

The weakly coordinating perchlorato ligand in neutral Pd^{II} complexes of the type $Pd(OClO_3)(C_6F_5)L_2$ (L = tertiary phosphine) can be readily displaced by addition of dppa (2/1) to give cationic singly-bridged binuclear species, according to eq. 6.



$$2\ Pd(OClO_3)(C_6F_5)L_2 + dppa \longrightarrow \left[F_5C_6-\overset{L}{\underset{L}{Pd}}-(dppa)-\overset{L}{\underset{L}{Pd}}-C_6F_5\right](ClO_4)_2 \qquad (6)$$

(L = PPh_3 (X), PPh_2Me (XI), PEt_3 (XII))

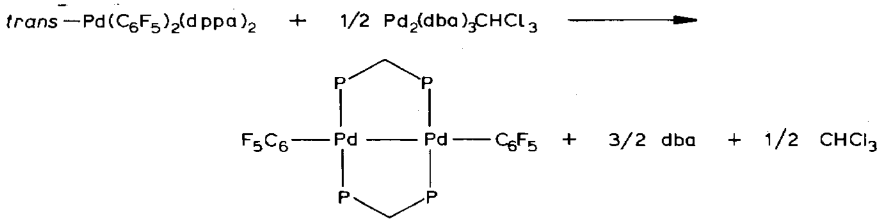
Complexes X–XII behave as (2/1) electrolytes in acetone solutions ($\sim 5 \times 10^{-4}$ M).

The presence of C_6F_5 groups and anionic ClO_4^- in each complex is confirmed by the characteristic IR absorptions (see above). The feature mentioned for the cationic complexes VIII–IX precludes assignment of the ν(N–H) vibration.

Typical absorptions due to dppa and the L (phosphine) ligands, which appear in the 600–400 cm^{-1} region, could not be sorted out (or separately assigned).

The neutral binuclear Pd^I complex $[\{(C_6F_5)Pd\}_2(\mu-dppa)_2]$ and its insertion reactions

Reaction of *trans*-$Pd(C_6F_5)_2(dppa)_2$ (I) with $Pd_2(dba)_3 \cdot CHCl_3$ carried out in oxygen-free dichloromethane gives the yellow binuclear metal–metal-bonded Pd^I complex (XIII), according to eq. 7.



(7)

(XIII)

Complex XIII reacts in deoxygenated acetone at −10°C with $[p\text{-}CH_3C_6H_4N_2]BF_4$ to give the cationic insertion compound XIV, according to eq. 8.

TABLE 2

RELEVANT IR DATA (cm^{-1})

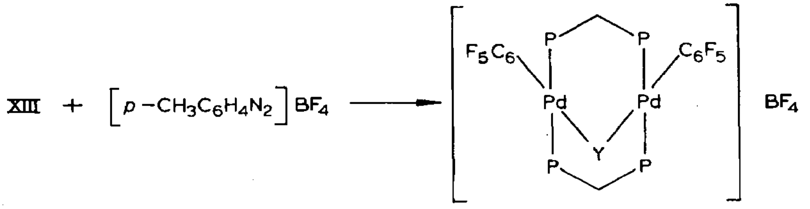
	ν(N–H)	C_6F_5	C_6Cl_5	dppa
I	3335	955,773		529, 504, 473, 442
II	3335	959, 780		531, 506, 480, 446
III	3336, 3215	956, 791, 780		548, 534, 508, 495
IV	3360	951, 779, 768		550, 515, 499
V	3338		615, 607	552, 522, 507
VI	3380	953, 791, 778		562, 518, 501
VII	3350		620, 614	555, 514, 500
VIII		955, 780		527, 484
IX		956, 780		527, 484
X		952, 780		
XI		949, 770		
XII		949		
XIII	3300	938		527, 510, 500, 483
XIV	3150	954		534, 516, 490

TABLE 3

$^{31}P\{^1H\}$ NMR DATA (δ in ppm, J in Hz)

	$\delta(MPPh_2)$	$\delta(MPPh_2CH_2PPh_2)$	J(Pt–P)	N^a	$J(P_A-P_B)$	δ(P–Ag)
I	60.46	30.25				
II	50.14	29.23	2842	32		
III	49.31	30.50	2751		19	
IV	28.73					
VI	17.07		2075			
VIII	59.68					61.15
IX	47.41		2880			56,17
XIII	65.35					

[a] $N = [^2J(P_A-P_B) + ^4J(P_A-P_B)]$.



(8)

(XIV, Y = $[p\text{-}CH_3C_6H_4N_2]^+$)

In acetone solution ($\sim 5 \times 10^{-4}$ M) complex XIII behaves as non-electrolyte whereas complex XIV is a 1/1 electrolyte. The IR band due to the C_6F_5 group, which appears ~ 950 cm^{-1} in Pd^{II} complexes, is shifted to lower energies (938 cm^{-1}) in complex XIII, as expected [23] because of the decrease in the formal oxidation state. Complex XIV presents a broad band at 954 cm^{-1}, shifted to higher energies relative to the precursor, consistent with some increase in the Pd oxidation state [23–25].

The IR absorption due to ν(N–H) appears at 3300 cm^{-1} (XIII), i.e. it is shifted to lower frequencies compared with that for the Pd^{II} precursor but higher than that for free dppa. Complex XIV shows a broad band at 3150 cm^{-1}; such a shift to lower frequencies can again be related to the presence of hydrogen bonds.

The ^{31}P NMR spectrum of complex XIII shows a singlet due to the equivalence of all the four P atoms.

Complex XIII does not undergo insertion of SO_2 or CO.

Experimental

C, H and N analyses were carried out on a Perkin–Elmer 240 microanalyzer. Melting points were determined with a Buchi apparatus and are uncorrected. Conductivities were measured in approx. 5×10^{-4} M acetone solutions with a Philips PW 9501/01 conductimeter. The IR spectra were recorded (in the 4000–200 cm^{-1} range) on a Perkin–Elmer 577 spectrophotometer.

Published methods were used to prepare the compounds: $Ph_2PNHPPh_2$(dppa) [26], $Pd_2(dba)_3 \cdot CHCl_3$ [27], $Pd(C_6F_5)_2(tht_2)$ [28], $Pt(C_6F_5)_2(tht)_2$, $[Pd(\mu\text{-}Cl)(C_6F_5)(tht)]_2$ [29], $Pd(OClO_3)(C_6F_5)L_2$ [29], cis-$M(C_6X_5)_2(THF)_2$ [30].

trans-Pd(C_6F_5)$_2$(dppa)$_2$ (I)

To a solution of *trans*-Pd(C_6F_5)$_2$(tht)$_2$ (0.308 g, 0.5 mmol) in 25 ml of benzene was added dppa (0.385 g, 1 mmol) and stirred for 1 h at room temperature. The resulting solution was filtered and concentrated to 5 ml and Et_2O (ca. 10 ml) was added, to give a white solid. This was filtered off, washed with Et_2O (5 ml), vacuum dried, and identified as *trans*-Pd(C_6F_5)$_2$(dppa)$_2$ (I) (0.494 g, 81% yield).

trans-Pt(C_6F_5)$_2$(dppa)$_2$ (II), cis-Pt(C_6F_5)$_2$(dppa)$_2$ (III), Pt(C_6F_5)$_2$(dppa) (VI)

To a solution of *cis*-, *trans*-Pt(C_6F_5)$_2$(tht)$_2$ (0.352 g, 0.5 mmol) in 30 ml of benzene was added dppa (0.385 g, 1 mmol), and the mixture was stirred for 3 h at room temperature. The resulting white precipitate was filtered off, washed with benzene (10 ml), dried, and identified as Pt(C_6F_5)$_2$(dppa) (0.067 g, 14% yield).

The filtrate was concentrated to $\simeq$ 3 ml and Et_2O (20 ml) was added. The white solid which separated was filtered off, washed with Et_2O (10 ml), dried, and identified as *trans*-Pt(C_6F_5)$_2$(dppa)$_2$ (0.096 g, 15% yield).

Upon evaporation of the filtered solution to a small volume and addition of n-hexane (20 ml) a white solid was formed. This was filtered off, dried, and identified as *cis*-Pt(C_6F_5)$_2$(dppa)$_2$ (0.303 g, 47% yield).

cis-Pt(C_6F_5)$_2$(dppa)$_2$ (III) from cis-(C_6F_5)$_2$Pt(THF)$_2$

To a solution of *cis*-(C_6F_5)$_2$Pt(THF)$_2$ (0.22 mmol) in 5 ml of CH_2Cl_2 was added a solution of dppa (0.190 g, 0.495 mmol) in 5 ml of CH_2Cl_2. The mixture was stirred for 3 h at room temperature then concentrated to $\simeq$ 2 ml. n-Hexane (20 ml) was added, and the white solid which separated was filtered off, dried, and identified as *cis*-Pt(C_6F_5)$_2$(dppa)$_2$ (0.216 g, 74% yield).

M(C_6X_5)$_2$(dppa) (M = Pd, X = F (IV), X = Cl (V); M = Pt, X = F (VI), X = Cl (VII))

To a solution of *cis*-M(C_6X_5)$_2$(THF)$_2$ (M = Pd, X = F for forming IV; M = Pd, X = Cl for V; M = Pt, X = F for VI; M = Pt, X = Cl for VII) (0.25 mmol) in 5 ml of CH_2Cl_2 was added a solution of dppa (0.25 mmol) in 5 ml of CH_2Cl_2. Shortly afterwards a white solid precipitated, and this was filtered off. The filtrate was concentrated to a few ml ($\simeq$ 3 ml) and Et_2O ($\simeq$ 20 ml) was added to obtain more of the white precipitate, which was filtered off. The combined white solids were dried and identified as M(C_6X_5)$_2$(dppa). IV (0.100 g, 55% yield); V (0.160 g, 65% yield), VI (0.155 g, 68% yield); VII (0.183 g, 68% yield).

[(C_6F_5)$_2$M(μ-dppa)$_2$Ag]ClO_4 (M = Pd (VIII), Pt (IX))

To a solution of 0.2 mmol of *trans*-M(C_6F_5)$_2$(dppa)$_2$ (0.242 g, for making VIII; 0.260 for making IX) in benzene (40 ml) was added a solution of $AgClO_4$ (0.041 g, 0.2 mmol). Shortly afterwards a white solid began to precipitate. The mixture was stirred for 4 h at room temperature with exclusion of light, then concentrated to $\simeq$ 20 ml. The white solid was filtered off, dried, and identified as [(C_6F_5)$_2$M(μ-dppa)$_2$Ag]ClO_4. To VIII 0.283 g, 78% yield; to IX 0.301 g, 87% yield.

[{Pd(C_6F_5)L_2}$_2$(μ-dppa)](ClO_4)$_2$ (L = PPh_3 (X), PPh_2Me (XI), PEt_3 (XII))

To a solution of 0.3 mmol of Pd(C_6F_5)($OClO_3$)L_2 (L = PPh_3 to give X, L = PPh_2Me to give XI, L = PEt_3 to give XII) in 25 ml of benzene was added dppa (0.057 g, 0.15 mmol). Shortly afterwards a white solid began to precipitate. The mixture was stirred for 1 h at room temperature then concentrated to ≈ 10 ml. The white solid was filtered off, dried and identified as $[\{Pd(C_6F_5)L_2\}_2(\mu\text{-dppa})](ClO_4)_2$. To L = PPh_3 (X) 0.245 g, 75% yield; to L = $PMePh_2$ (XI) 0.261 g, 85% yield; to L = PEt_3 (XII) 0.232 g, 82% yield.

$[(C_6F_5)Pd(\mu\text{-dppa})_2Pd(C_6F_5)]$ (XIII)

To a solution of *trans*-$Pd(C_6F_5)_2(dppa)_2$ (0.400 g, 0.33 mmol) in 40 ml of (deoxygenated) CH_2Cl_2 under nitrogen was added $Pd_2(dba)_3 \cdot CHCl_3$ (0.169 g, 0.165 mmol). Refluxing for 20 min gave a deep yellow solution, which was concentrated to a few ml. The yellow precipitate was filtered off, stirred with ≈ 10 ml of acetone, again filtered off, and kept at 80°C for 15 h. It was identified as XIII. 0.330 g, 76% yield.

$[(C_6F_5)Pd(\mu\text{-dppa})_2(\mu\text{-}p\text{-}CH_3C_6H_4N_2)Pd(C_6F_5)]BF_4$ (XIV)

To a yellow suspension of 0.197 g (0.15 mmol) of $[(C_6F_5)Pd(\mu\text{-dppa})_2Pd(C_6F_5)]$ in 30 ml of (deoxygenated) acetone under nitrogen at -28°C was added $(p\text{-}CH_3C_6H_4N_2)BF_4$ (0.199 g, 0.15 mmol). The mixture was stirred for 45 min at ≈ -10°C then filtered, and the filtrate was concentrated to a small volume and n-hexane (≈ 20 ml) was added. The orange solid formed was filtered off, dried, recrystallized from acetone/isopropanol-hexane, and identified as $[(C_6F_5)Pd(\mu\text{-dppa})_2(\mu\text{-}pCH_3C_6H_4N_2)Pd(C_6F_5)]BF_4$. 0.176 g, 77% yield, to XIV.

References

1 C.A. McAuliffe and W. Levason, Phosphine, Arsine and Stibine Complexes of the transition Elements, Elsevier, Amsterdam, 1979.
2 R.J. Puddephatt, Chem. Soc. Rev., 12 (1983) 99.
3 S. Payne and A.P. Walker, J. Chem. Soc., C (1966) 498.
4 H. Schmidbaur, F.F. Wagner and A. Wohlleben-Hammer, Chem. Ber., 112 (1979) 496.
5 J. Ellermann and L. Mader, Z. Naturforsch. B 35 (1980) 307.
6 H. Schmidbaur, S. Lanteschlager and B. Milewski-Mahrla, J. Organomet. Chem., 254 (1983) 59.
7 J. Ellermann and W. Wend, J. Organomet. Chem., 258 (1983) 21.
8 A. Blagg, G.R. Cooper, R. Robson and B.L. Shaw, J. Chem. Soc., Chem. Commun., (1984) 933.
9 J. Ellermann, G. Szucsanyi, K. Geibel and E. Wilhelm, J. Organomet. Chem., 263 (1984) 297.
10 G. Liehr, G. Szucsanyi and J. Ellermann, J. Organomet. Chem., 265 (1984) 95.
11 R. Usón, A. Laguna, M. Laguna and B.N. Fraile, J. Chem. Soc., Dalton Trans., in press.
12 K.A. Azam, G. Ferguson, S.S.M. Ling, M. Parvez, R.J. Puddephatt and D. Srokowski, Inorg. Chem., 24 (1985) 2799 and references therein.
13 G.B. Deacon and J.H.S. Green, Spectrochim. Acta, 24A (1968) 125.
14 R. Usón, J. Forniés, J. Gimeno, P. Espinet and R. Navarro, J. Organomet. Chem., 81 (1974) 115.
15 E. Maslowsly, Jr., Vibrational Spectra of Organometallic Compounds Wiley, New York, 1977, p. 437.
16 R. Usón, J. Forniés, P. Espinet, F. Martínez and M. Tomás, J. Chem. Soc., Dalton Trans., (1981) 463.
17 J. Casabó, J.M. Coronas and J. Sales, Inorg. Chim. Acta, 11 (1974) 5.
18 R. Usón, J. Forniés, F. Martínez, M. Tomás and I. Reoyo, Organometallics, 2 (1983) 1390.
19 W.T. Geary, Coord. Chem. Rev., 7 (1971) 81.
20 R.D. Feltham and R.G. Hayter, J. Chem. Soc., (1964) 4587.
21 A. Tiripicchio, M. Tiripicchio-Camellini, R. Usón, L.A. Oro, M.A. Ciriano and F. Viguri, J. Chem. Soc., Dalton Trans., (1984) 125.
22 B.J. Hathaway and A.E. Underhill, J. Chem. Soc., (1961) 3091.
23 R. Usón, J. Forniés and R. Navarro, J. Organomet. Chem., 96 (1975) 307.
24 R. Usón, J. Forniés and R. Navarro, Synth. React. Inorg. Metal-Org. Chem., 7 (3) (1977) 235.

25 R. Usón, J. Forniés, P. Espinet, F. Martínez, C. Fortuño and B. Menjón, J. Organomet. Chem., 256 (1983) 365.
26 H. Nöth and L. Meinel, Z. Anorg. Chem., 349 (1967) 225.
27 T. Ukai, H. Kawazura, Y. Ishii, J.J. Bonnet and J.A. Ibers, J. Organomet. Chem., 65 (1974) 253.
28 R. Usón, J. Forniés, R. Navarro and M.P. García, Inorg. Chim. Acta, 33 (1979) 69.
29 R. Usón, J. Forniés, P. Espinet and R. Navarro, Inorg. Chim. Acta, 82 (1984) 215.
30 R. Usón, J. Forniés, M. Tomás and B. Menjón, Organometallics, 4 (1985) 1912.