Synthesis and Reactions of the Heterobimetallic Complex $[ClPd(\mu\text{-}Ph_2PCH_2PPh_2)_2PtCl]$†

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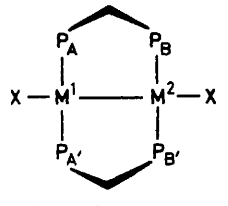
New methods of preparing $[ClPd(\mu\text{-}dppm)_2PdCl]$ (1b) (dppm = $Ph_2PCH_2PPh_2$) are described, such as reduction of $[PdCl_2(dppm\text{-}PP')]$ with zinc dust, formic acid, or hydrazine. Treatment of $[Pd_2Cl_2(\eta^3\text{-allyl})_2]$ with an excess of dppm gives pure (1b) readily, albeit in only 45% yield. $[(\eta^3\text{-}C_3H_5)ClPd(\mu\text{-}dppm)PdCl(\eta^3\text{-}C_3H_5)]$ is also described. The best route to (1b) is to treat $[Pd(PPh_3)_4]$ and dppm with $[PdCl_2(NCPh)_2]$, giving yields of 80—90%. Similar treatment of $[Pt(PPh_3)_4]$ and dppm with $[PtCl_2(NCBu^t)_2]$ gives $[ClPt(\mu\text{-}dppm)_2PtCl]$ (1a), often contaminated, however, with *ca.* 10% of $[PtCl_2(dppm\text{-}PP')]$. Treatment of dppm and $[Pd(PPh_3)_4]$ with $[PtCl_2(NCBu^t)_2]$ gives the previously unknown heterobimetallic complex $[ClPt(\mu\text{-}dppm)_2PdCl]$ (1c) in excellent yield (83—92%) and purity. The corresponding dibromide, di-iodide, and dithiocyanate were prepared from (1c) by metathesis. Complex (1c) readily reacts with some small molecules, SO_2, CO, $MeO_2CC{\equiv}CCO_2Me$ or CS_2, to give 'A-frames' $[ClPt(\mu\text{-}SO_2)(\mu\text{-}dppm)_2PdCl]$, $[ClPt(\mu\text{-}CO)(\mu\text{-}dppm)_2PdCl]$, $[ClPt(\mu\text{-}MeO_2CC{\equiv}CCO_2Me)(\mu\text{-}dppm)_2PdCl]$, and $[ClPt(\mu\text{-}CS_2)(\mu\text{-}dppm)_2PdCl]$ respectively. The addition of SO_2, CO, or CS_2 is reversible and SO_2 promotes or catalyses the displacement of CO. Hydrogen-1, $^{31}P\text{-}\{^1H\}$, and ^{195}Pt n.m.r. data are given and discussed as are some i.r. data.

There is much interest in bimetallic complexes containing $Ph_2PCH_2PPh_2$ (dppm) as bridging ligand. Of particular interest have been the diplatinum (1a)[1–3] and dipalladium (1b)[4–6] complexes which take up some small molecules or atoms reversibly to give 'A-frames' (see below) and have other chemistry, *e.g.* (1a) gives a range of diplatinum hydrides.[3] Complexes (1a) and (1b) are not easy to synthesize. Thus the only route yet reported for the diplatinum complex (1a) is by the cautious addition of hydrochloric acid to the cationic trihydride complex $[Pt_2H_3(\mu\text{-}dppm)_2]^+$, a method which we and others have found unreliable.[7,8] The original method for the synthesis of the dipalladium complex (1b), namely treatment of $[\{PdCl(CO)\}_n]$ with dppm[4,6] is also unreliable. A method of synthesizing (1b) which gives good (>80%), reliable, yields is to treat $[PdCl_2(NCPh)_2]$ with $[Pd_2(dba)_3]$ (dba = dibenzylideneacetone) in dichloromethane in the presence of dppm (mol ratio 2 : 1 : 4 respectively).[6]



(1a) $M^1 = M^2 = Pt, X = Cl$
(1b) $M^1 = M^2 = Pd, X = Cl$
(1c) $M^1 = Pt, M^2 = Pd, X = Cl$
(1d) $M^1 = Pt, M^2 = Pd, X = Br$
(1e) $M^1 = Pt, M^2 = Pd, X = I$
(1f) $M^1 = Pt, M^2 = Pd, X = SCN$
(1g) $M^1 = M^2 = Pd, X = Br$

We thus became interested in trying to devise other syntheses of (1a) and (1b) which would be more reliable or more convenient to use than those previously described. Additionally, we were interested in the possibility of synthesizing a mixed-metal complex, (1c). We first studied the action of various reducing agents (zinc dust, formic acid, hydrazine, or sodium tetrahydroborate) on the readily prepared $[PdCl_2(dppm\text{-}PP')]$. Zinc dust is a convenient reducing agent for the preparation of various Pd^0– or $Pt^0\text{–}PR_3$ complexes in solvents such as tetrahydrofuran (thf) or dimethylformamide (dmf).[9] We found that zinc dust had no effect on $[PdCl_2(dppm\text{-}PP')]$ in boiling thf but in boiling dmf there was a rapid reaction to give a red solution. The brown solid which precipitated on addition of water contained some (1b) ($^{31}P\text{-}\{^1H\}$ n.m.r. evidence) but most of the product was insoluble in common organic solvents. Formic acid, with or without the presence of sodium formate has been used for the reduction of palladium(II) or platinum(II).[10] When $[PdCl_2(dppm\text{-}PP')]$ was boiled in 98% formic acid a red solution formed, which on addition of water precipitated (1b), contaminated with $[PdCl_2(dppm\text{-}PP')]$, and uncharacterized products. Hydrazine hydrate has been extensively used for the preparation of hydrides[10] and zerovalent platinum and palladium complexes, and when an ethanol suspension of $[PdCl_2(dppm\text{-}PP')]$ was warmed with hydrazine hydrate a dark red solution formed and a gas (presumably dinitrogen) was evolved. Addition of concentrated hydrochloric acid to this solution gave a red-brown precipitate. The portion of the product which was soluble in dichloromethane was largely $[Pd_2Cl_2(\mu\text{-}dppm)_2]$ (1b) contaminated with a small amount of $[PdCl_2(dppm\text{-}PP')]$. Overall yields were *ca.* 40% but the contaminant was difficult to remove. The reduction of $[PdCl_2(dppm\text{-}PP')]$ by $NaBH_4$ under conditions similar to those used to prepare $[Pt_2H_3(\mu\text{-}dppm)_2]^+$ gave only palladium metal.

It is known that treatment of η^3-allylpalladium chloride with an excess of triphenylphosphine (⩾5 mol equivalents) in hot ethanol rapidly gives a quantitative yield of $[Pd(PPh_3)_4]$.[11] We hoped that dppm would effect a similar reduction but that the palladium(I) complex (1b) would be formed. We found that η^3-allylpalladium chloride reacted rapidly with dppm (2 mol per Pd) in hot ethanol and that up to 45% yield of pure (1b) crystallized out of the reaction mixture. However, the mother-liquors contained a large number of other species, as evidenced by $^{31}P\text{-}\{^1H\}$ n.m.r. spectroscopy. Thus as a preparative method it is convenient in that pure (1b) is produced rapidly but the yield is unsatisfactory. Several other products have been identified as a result of treating η^3-allylpalladium

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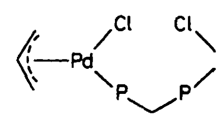
† Bis[μ-bis(diphenylphosphino)methane]-dichloropalladium-platinum(*Pd–Pt*).

chloride with dppm, *e.g.* [$PdCl(\eta^3-C_3H_5)(dppm-P)$], [$Pd(\eta^3-C_3H_5)(dppm-P)_2]^+$ and [$Pd(\eta^3-C_3H_5)(dppm-PP')]^+$.[12] The products depend on the molar proportions, the solvent, and the counter ion. We now find that treatment of η^3-allylpalladium chloride with 0.5 mol equivalent of dppm in acetonitrile gives [$(\eta^3-C_3H_5)ClPd(\mu$-dppm$)PdCl(\eta^3-C_3H_5)$]. This formulation follows from elemental analysis and molecular weight data (see Experimental section), a singlet $^{31}P-\{^1H\}$ n.m.r. resonance for which the chemical shift, $\delta(P)$, at the relatively high value of +14.1 p.p.m. shows that the ^{31}P nuclei are not in a four-membered ring. The ^1H n.m.r. spectrum shows a sharp quintet resonance at δ 5.73 p.p.m. [$^3J(HH) = 10.0$ Hz] and a broad singlet at δ 3.7 p.p.m. Both of these signals are associated with the η^3-allyl moiety. The absence of coupling to phosphorus suggests that an intermolecular exchange process is occurring. The CH_2 resonance of the dppm is a sharp triplet at δ 3.86 p.p.m. [$^2J(PH) = 12.1$ Hz]. We assign the dppm-bridged structure (2) to this complex.



(2)

We then turned our attention to the possibility of using another type of redox reaction for the synthesis of (1a) and (1b), *i.e.* by treating a metal(II) species with a metal(0) species. We thus treated the readily available [$Pd(PPh_3)_4$] with dppm and [$PdCl_2(NCPh)_2$] in benzene and found that this gave the desired palladium(I) complex (1b) in yields of 80—90% and in high purity. The analogous reaction with platinum, namely treatment of [$Pt(PPh_3)_4$] with dppm and [$PtCl_2(NCBu^t)_2$] in benzene gave the diplatinum(I) complex (1a) in up to 70% yield, but sometimes the product contained [$PtCl_2$(dppm-*PP'*)], which was difficult to remove. It has been shown that the chloride ligands of the diplatinum(I) complex (1a) are readily substituted by amines, carbon monoxide, or tertiary phosphines including triphenylphosphine.[13-15] However, in benzene as solvent we found no evidence of substitution by triphenylphosphine of the product (1a).

Thus this redox method is very good for the preparation of the dipalladium complex (1b) but less good for the diplatinum complex (1a). However, we were encouraged to attempt to use it to make the previously unknown, mixed, platinum-palladium complex (1c). We therefore treated the red solution formed from [$Pd(PPh_3)_4$] and dppm in benzene with the labile platinum(II) complex [$PtCl_2(NCBu^t)_2$] and obtained excellent (83—92%) yields of the hoped for platinum-palladium complex (1c). A preliminary account of this work has been published.[16] The product was obtained either as a benzene solvate, [$ClPt(\mu$-dppm$)_2PdCl]\cdot C_6H_6$, or from dichloromethane-hexane, as a dichloromethane solvate. Microanalytical and molecular weight data are in Table 1. This mixed complex (1c) is remarkably stable towards disproportionation to the homonuclear species (1a) and (1b); thus its solutions in CH_2Cl_2 or $CHCl_3$ are stable for weeks at ambient temperatures but darken in the presence of alcohols or on prolonged boiling. The main decomposition products, detected by $^{31}P-\{^1H\}$ n.m.r. spectroscopy, are [$PdCl_2$(dppm-*PP'*)] and [$PtCl_2$(dppm-*PP'*)]. The i.r. absorption spectrum of (1c) shows only one absorption in the region 200—400 cm^{-1}. This is at 249 cm^{-1} and is assigned to $\nu(M-Cl)$, M = Pd or Pt. Interestingly, the metal-chlorine stretching frequencies for both (1a) [1] and (1b) [6] are the same (249 cm^{-1}). These low values indicate the high *trans* influence of the metal-metal bonds.

The chloride ligands in (1c) are readily displaced by bromide, iodide, or thiocyanate when (1c) is treated with the appropriate alkali-metal salt in either acetone or acetonitrile (see Experimental section and Tables 1 and 2 for further details and characterizing data). With the dithiocyanato-complex (1f) a broad band at 2 090 cm^{-1} indicates that the SCN ligand is *S*-bound,[17] as in its *S*-bonded dipalladium analogue.[6]

Since substitution at square-planar palladium(II) is usually of the order of 10^6 times faster than substitution at an analogous platinum(II) complex we hoped to be able to effect metathesis of chloride at the palladium centre without causing much substitution at the platinum centre. However, treatment of a dichloromethane solution of (1c) with 0.5 mol equivalent of sodium iodide in acetone rapidly gave a mixture of three orange $Pd-Pt(\mu$-dppm$)_2$ complexes together with the starting dichloride (1c) (as shown by $^{31}P-\{^1H\}$ n.m.r. spectroscopy). Thus it would seem that complete chloride/iodide scrambling occurs rapidly. Recently, the lability of the chlorides in the dipalladium(I) complex (1b) has been demonstrated by exchange studies with the dibromide (1g): on mixing equimolar proportions of (1b) and (1g), complete halogen scrambling occurs within less than 5 min at room temperature.[18]

The $^{31}P-\{^1H\}$ n.m.r. spectra of the complexes [$XPt(\mu$-dppm$)_2PdX$] are very characteristic. They are all examples of AA'BB' spin systems with satellites due to platinum-195 coupling. The spectra can be analysed in terms of the parameters *K*, *L*, *M*, and *N*, given by $K = J(AA') + J(BB')$, $L = J(AB) - J(AB')$, $M = J(AA') - J(BB')$, and $N = J(AB) + J(AB')$.[19] The $^{31}P-\{^1H\}$ n.m.r. spectrum of [$ClPt(\mu$-dppm$)_2PdCl$] (1c) is shown in Figure 1 and the parameters *N*, *L*, and *M* can be reliably calculated (see Table 2 for data). The spectra for (1d), (1e), and (1f) were less well resolved. Values of $^1J(PtP_A)$ can also be measured directly from the spectra. However, for (1c) the value of $^2J(PtP_B)$ cannot be unequivocally derived from the $^{31}P-\{^1H\}$ n.m.r. spectrum since the satellites are obscured. However the value of $^2J(PtP_B)$ is readily measured from the $^{195}Pt-\{^1H\}$ n.m.r. spectrum (Figure 2).

A comparison of the ^{31}P chemical shifts and values of $^1J(PtP_A)$ for compounds (1c), (1d), and (1f) with those published for the diplatinum [7] and dipalladium [18] analogues shows that for all three sets of compounds $\delta(P)$ moves to lower frequency in going from Cl to Br to I, and for the two sets of platinum-containing complexes, $^1J(PtP_A)$ decreases in the order Cl > Br > I.

The CH_2 resonances of the bridging dppm molecules in the ^1H and $^1H-\{^{31}P\}$ n.m.r. spectra are also good diagnostic signals. For our compounds (1c)—(1f) the $^1H-\{^{31}P\}$ spectra are sharp, 1 : 4 : 1 triplets with $^3J(Pt-CH)$ *ca.* 70 Hz. In the ^1H spectra the resonances are deceptively simple quintets with average separation of *ca.* 4 Hz, together with satellites due to coupling to platinum-195. The value of $\delta(CH_2)$ for the Pd-Pt complex (1c) lies between the values for the Pt_2 and Pd_2 complexes (1a) and (1b) respectively.

We find that $CDCl_3$ solutions of the mixed Pd-Pt complex (1c) do not change even after one week at 20 °C, *i.e.* there is no tendency for disproportionation into the homonuclear complexes (1a) and (1b). Moreover, we found no evidence from $^{31}P-\{^1H\}$ n.m.r. studies for the formation of any of the mixed species (1c) from equimolar mixtures of the diplatinum and dipalladium complexes (1a) and (1b) even after three weeks at 20 °C in $CDCl_3$ solution. When the mixture of (1a) and (1b) was boiled for 12 h, again no mixed-metal species was detected, although small amounts of [$PtCl_2$(dppm-*PP'*)] and [$PdCl_2$(dppm-*PP'*)] were formed. We therefore conclude that the formation of the mixed-metal species (1c) in high yield (see above) is as a result of kinetic rather than thermodynamic factors.

Table 1. Microanalytical, molecular weight, and melting point data of mixed platinum–palladium complexes containing bridging dppm

Complex	M.p. (°C) [a]	Analysis (%) [b] C	H	Other	*M* [b]
(1c) $[ClPt(\mu\text{-dppm})_2PdCl]\cdot C_6H_6$	262—264	54.9 (55.1)	4.0 (4.1)	Cl, 6.35 (5.8)	1 136 (1 141)
(1d) $[BrPt(\mu\text{-dppm})_2PdBr]$	240—242	49.0 (48.8)	3.8 (3.6)	Br, 12.75 (13.0)	[c]
(1e) $[IPt(\mu\text{-dppm})_2PdI]$	260—262	45.3 (45.3)	3.65 (3.35)	I, 19.35 (19.2)	[c]
(1f) $[(NCS)Pt(\mu\text{-dppm})_2Pd(SCN)]$	235—239	52.4 (52.6)	3.85 (3.7)	N, 2.35 (2.35)	[c]
$[ClPt(\mu\text{-}SO_2)(\mu\text{-dppm})_2PdCl]\cdot 0.5CH_2Cl_2$	>170 [d]	48.35 (48.6)	3.65 (3.65)	Cl, 8.55 (8.5)	1 251 (1 205)
$[ClPt(\mu\text{-}CO)(\mu\text{-dppm})_2PdCl]\cdot CHCl_3$	>205 [d]	48.65 (48.5)	3.55 (3.5)	Cl, 13.15 (13.75)	[c]
$[ClPt(\mu\text{-}MeO_2CC{\equiv}CCO_2Me)(\mu\text{-dppm})_2PdCl]$	>250 [d]	52.1 (52.4)	3.95 (3.9)	Cl, 5.8 (5.55)	1 311 (1 283)

[a] Uncorrected; all complexes decomposed on melting. [b] Calculated values are in parentheses. [c] Not sufficiently soluble. [d] Decomposed without melting.

Table 2. $^{31}P\text{-}\{^1H\}$ N.m.r. data for the complexes $[XPt(\mu\text{-dppm})_2PdX]$ [a]

X	$\delta(P_A)$/p.p.m.	$^1J(PtP_A)$/Hz	$\delta(P_B)$/p.p.m.	$^2J(PtP_B)$/ Hz	*N*/Hz	*L*/Hz	*M*/Hz	$J(P_AP_B)$/ Hz [b]	$J(P_AP_{B'})$/ Hz [b]
Cl	+4.5	2 922	−4.0	78 [c]	86	33	7	59	26
Br	+2.8	2 891	−5.7	(73)	85	(31)	(8)	58	27
I	−2.0	2 861	−10.4	(39)	78	(28)	(7)	53	25
SCN	+4.0	2 835	−1.8	(78)	82	(21)		52	31

[a] All spectra measured in $CDCl_3$; chemical shifts (δ) (in p.p.m. ±0.1 p.p.m.) relative to 85% H_3PO_4 (positive shift is to high frequency); coupling constants (*J*) in Hz (±3 Hz). Values in parentheses are estimated from poorly resolved spectra. The notation P_A and P_B is defined in structure (1). [b] The values of $J(P_AP_B)$ and $J(P_AP_{B'})$ are the most likely values calculated from *N* and *L* (*N*, *L*, and *M* are defined in the text). [c] The value of $^2J(PtP_B)$ from the $^{195}Pt\text{-}\{^1H\}$ n.m.r. spectrum is 67 (±10) Hz.

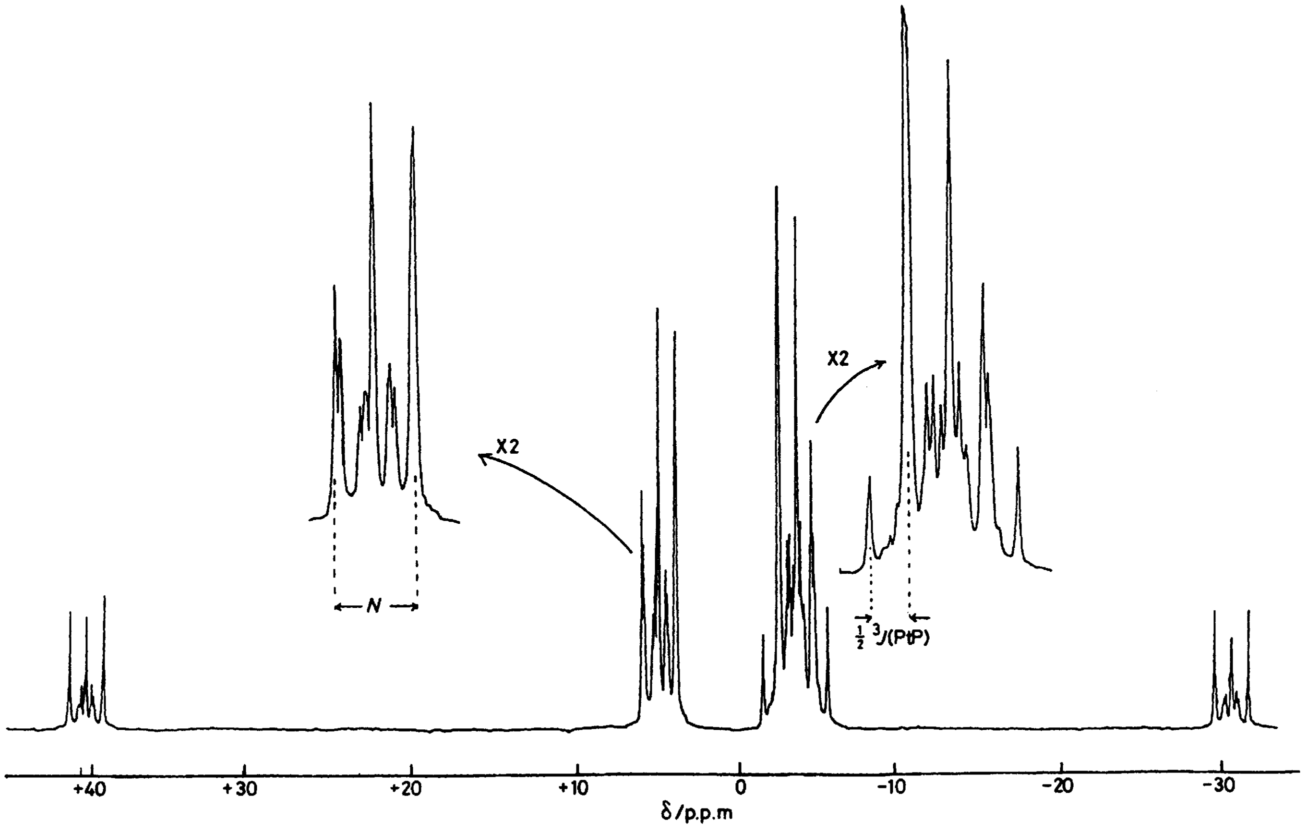


Figure 1. $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum (*ca.* 40.25 MHz) of $[ClPt(\mu\text{-dppm})_2PdCl]$ (1c) in $CDCl_3$ at *ca.* 21 °C

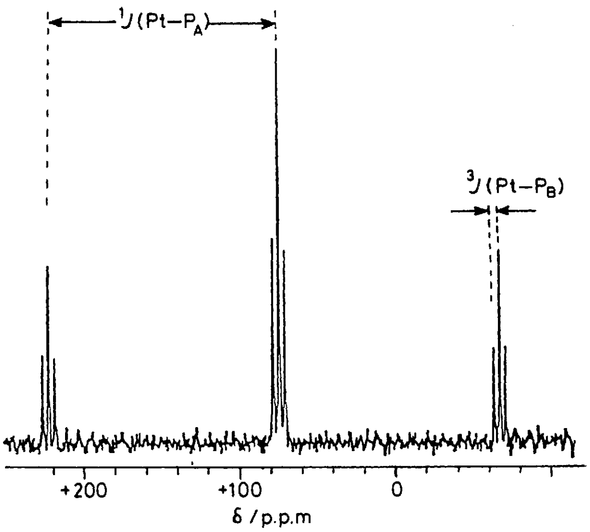
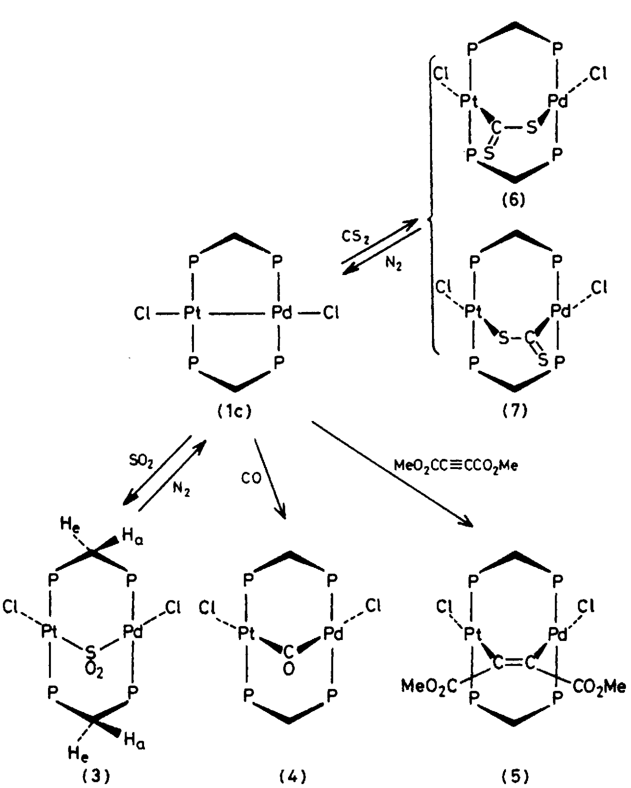


Figure 2. ^{195}Pt-{^{1}H} n.m.r. spectrum (*ca.* 19.2 MHz) of [ClPt(μ-dppm)$_2$PdCl] (1c) in CD_2Cl_2 at *ca.* 21 °C; δ(Pt) = 76 p.p.m. to high frequency of Ξ(^{195}Pt) = 21.4 MHz



Scheme. Some reactions of [ClPt(μ-dppm)$_2$PdCl] (1c) giving 'A-frames'

Formation of 'A-frames' from the Mixed Platinum-Palladium Complex (1c).—We found that some small molecules insert into the Pt–Pd bond of (1c) in a similar fashion to insertions into the homonuclear species (1a) and (1b). As discussed below and summarized in the Scheme, the range of small molecules (or atoms or ions) which will insert into (1c) is more limited than with (1a) or (1b), being confined to SO_2, CO, CS_2, and $MeO_2CC{\equiv}CCO_2Me$.

Insertion of SO_2. When sulphur dioxide was bubbled through an orange dichloromethane or chloroform solution of (1c) the solution rapidly turned red and on addition of methanol a deep red crystalline solid was produced. On the basis of elemental analysis and molecular weight determination (Table 1) the complex was formulated as [ClPt(μ-SO_2)(μ-dppm)$_2$PdCl] (3). The i.r. spectrum (Nujol) shows bands at 1 031 and 1 157 cm^{-1}, which are assigned to ν(S–O), and a strong band at 274 cm^{-1}, assigned to ν(M–Cl); these bands correlate with those of the corresponding bridging SO_2 complexes of the dipalladium [20] and diplatinum [21] analogues.

The ^{31}P-{^{1}H} n.m.r. spectrum of the SO_2 adduct (3) shows a similar pattern to that of [ClPt(μ-dppm)$_2$PdCl] since the spin system is the same (AA′BB′). The most significant and informative differences are in the chemical shifts δ(P_A) and δ(P_B) and in the ^{195}Pt–^{31}P coupling constants, as can be clearly seen in Figure 3. The shifts to higher frequency of both δ(P_A) and δ(P_B) (Table 3) are similar to those observed for the diplatinum [21] and dipalladium [20] analogues. An increase of 575 Hz in the value of ^1J(PtP$_A$) relative to the starting complex (1c) is of a similar magnitude to the increase observed for [Pt_2Cl_2(μ-SO_2)(μ-dppm)$_2$].[21] It has been shown [20] that the Pd–Pd distance in [Pd_2Cl_2(μ-SO_2)(μ-dppm)$_2$] is about 0.5 Å longer than in [Pd_2Cl_2(μ-dppm)$_2$] and it was therefore concluded that the metal–metal bond had been cleaved by the insertion of SO_2. It is assumed that the diplatinum and the mixed complexes behave similarly and therefore it might be expected that the long-range ^{195}Pt–^{31}P coupling constant J(PtP$_B$) would decrease in these complexes. However, it has been postulated [22] that J(PtP$_B$) in the metal–metal bonded species is made up of two components which are opposite in sign and will tend to negate one another (see below). Studies

$$J(\mathrm{PtP_B}) = {}^2J(\mathrm{P_B{-}Pt{-}Pt}) + {}^3J(\mathrm{P_B{-}C{-}P_A{-}Pt})$$

on a series of diplatinum compounds with the Pt_2(μ-dppm)$_2$ skeleton show that ^2J is negative and ^3J is positive. Hence, when the metal–metal bond is cleaved by insertion of, *e.g.* SO_2, the ^2J term disappears and there is an increase in the numerical value of J(PtP$_B$). The value of the long-range ^{195}Pt–^{31}P coupling constant in diplatinum complexes has been correlated with the metal–metal bond strength.[22]

The pertinent ^{1}H n.m.r. data are given in Table 4. The two protons in the CH_2 of the bridging dppm ligands are non-equivalent in 'A-frames'.[4,21] It can be seen from structure (3) that the methylene hydrogens H_a and H_e are not equivalent whereas in the metal–metal bonded species (1c) the methylene hydrogens are equivalent on the n.m.r. time-scale because of rapid 'ring flipping'. It is interesting that most of the homonuclear 'A-frames' for which the crystal structure has been determined adopt a 'boat' configuration [23] in the solid state as depicted in (3). One of the protons in the methylene groups of the mixed-metal 'A-frames' such as (3) resonates at lower δ, by 0.5—1.5 p.p.m., than the other and is quite strongly coupled to platinum (Table 4). The proton resonating at higher δ is only weakly coupled to platinum (<10 Hz). We assign the strongly coupled proton as H_e, with a torsion angle (Pt–P–C–H) of *ca.* 180° [see (3)] and the weakly coupled proton as H_a, with a torsion angle (Pt–P–C–H) of *ca.* 60°. This assumes a Karplus type behaviour for these three-bond couplings, which we have discussed previously.[24] A similar Karplus type dependence of ^3J(*Pt*–N–C–*H*) on the torsion angle, in platinum amine complexes, is well established.[25,26]

The SO_2 is readily displaced from the mixed-metal adduct

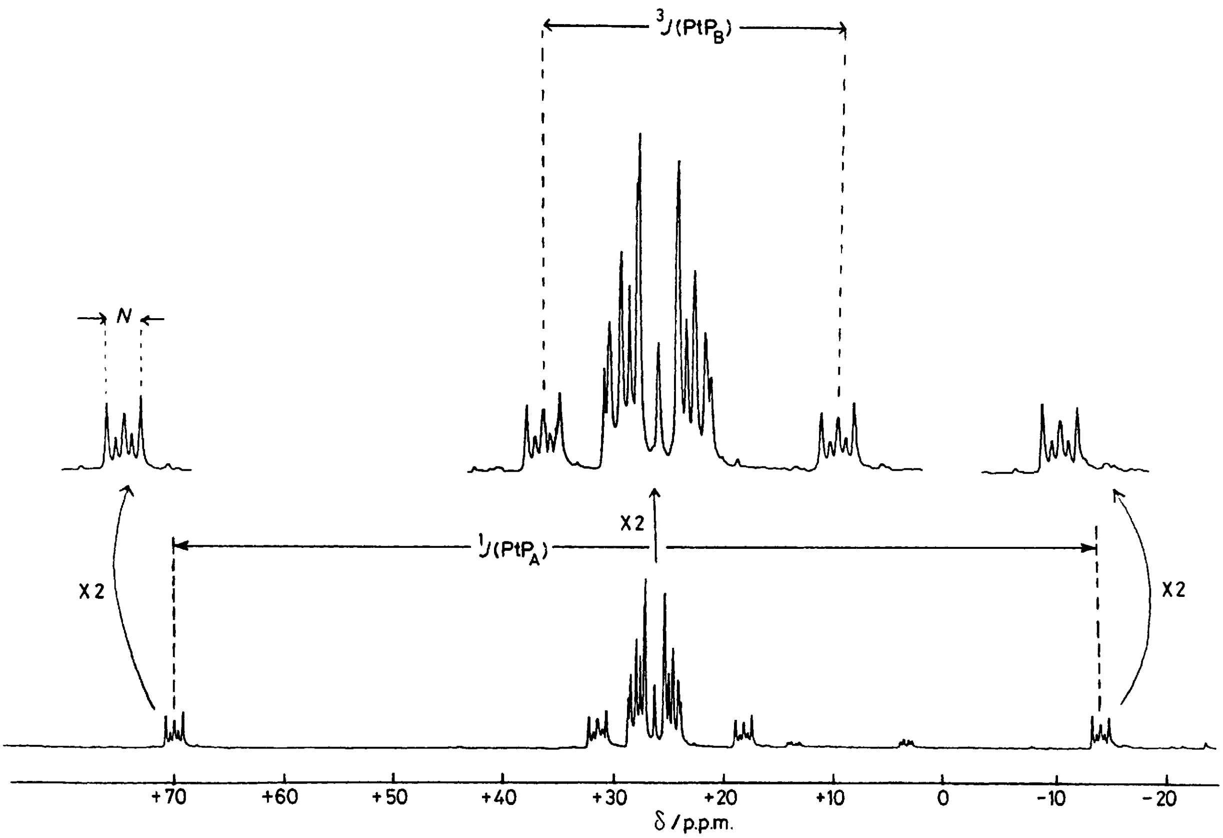


Figure 3. $^{31}P-\{^1H\}$ n.m.r. spectrum (*ca.* 40.25 MHz) of $[ClPt(\mu-SO_2)(\mu-dppm)_2PdCl]$ (3) in $CDCl_3$ at *ca.* 21 °C

Table 3. $^{31}P-\{^1H\}$ n.m.r. data for mixed platinum–palladium 'A-frames' [a]

Complex	$\delta(P_A)$/p.p.m.	$^1J(PtP_A)$/Hz	$\delta(P_B)$/p.p.m.	$^3J(PtP_B)$/Hz	N/Hz [b]
(1c) $[ClPt(\mu-dppm)_2PdCl]$	+4.5	2 922	−4.0	78	86
(3) $[ClPt(\mu-SO_2)(\mu-dppm)_2PdCl]$	+27.2	3 496	+23.8	562	64
(5) $[ClPt(\mu-MeO_2CC{\equiv}CCO_2Me)(\mu-dppm)_2-PdCl]$	+3.0	3 125	−0.5	185	24
(6)/(7) $[ClPt(\mu-CS_2)(\mu-dppm)_2PdCl]$	+6.6	3 494	+10.0	198	44

[a] Spectra measured in $CDCl_3$; chemical shifts (δ) in p.p.m. relative to 85% H_3PO_4; positive shift is to high frequency; coupling constants (J) are in Hz. [b] $N = |J(P_AP_B) + J(P_AP_{B'})|$.

Table 4. Hydrogen-1 n.m.r. data for the mixed platinum–palladium 'A-frames' and (1c) [a]

Complex	$\delta(H_a)$/p.p.m.	$\delta(H_e)$/p.p.m.	$^2J(H_aH_e)$/Hz	$^3J(PtH_a)$/Hz	$^3J(PtH_e)$/Hz
(3) $[ClPt(\mu-SO_2)(\mu-dppm)_2PdCl]$	4.15	2.60	12.9	<8	27.0
(5) $[ClPt(\mu-MeO_2CC{\equiv}CCO_2Me)(\mu-dppm)_2PdCl]$	3.92	2.90	12.5	<8	65.0
(6)/(7) $[ClPt(\mu-CS_2)(\mu-dppm)_2PdCl]$	3.73 [b]	3.19	13.2	<8	42.3
	4.19 [c]	3.13	12.7	n.r.	n.r.
(1c) $[ClPt(\mu-dppm)_2PdCl]$	4.27			69.8	

[a] Spectra measured in $CDCl_3$; chemical shifts (δ) in p.p.m. (±0.01 p.p.m.) relative to $\delta(SiMe_4)$ = 0.00 p.p.m.; coupling constants (J) in Hz (±0.1 Hz); n.r. = not resolved. H_a and H_e are defined in structure (3). [b] Major isomer. [c] Minor isomer.

(3) by N_2 or Ar to regenerate the metal–metal bonded species (1c); in this respect the mixed-metal SO_2 adduct resembles the dipalladium analogue [20] rather than the diplatinum analogue.[21] The mixed-metal SO_2 adduct (3) is less stable in solution than the metal–metal bonded species (1c). A dichloromethane solution of (3) decomposes to give a complex mixture of products if left to stand for a few days.

Insertion of CO. When carbon monoxide is bubbled through a dichloromethane or chloroform solution of (1c) a deep red solid precipitates rapidly and quantitatively. The insolubility of this material precluded any ^1H or ^{31}P n.m.r. studies or molecular weight determination. Hence, the only characterizing data are from microanalysis (Table 1) and i.r. spectroscopy which both agree with the formulation as the bridging carbonyl adduct (4). The value of ν(CO) in (4) (1 680 cm^{-1}) is almost the average of ν(CO) in $[Pt_2Cl_2(\mu-CO)(\mu-dppm)_2]$

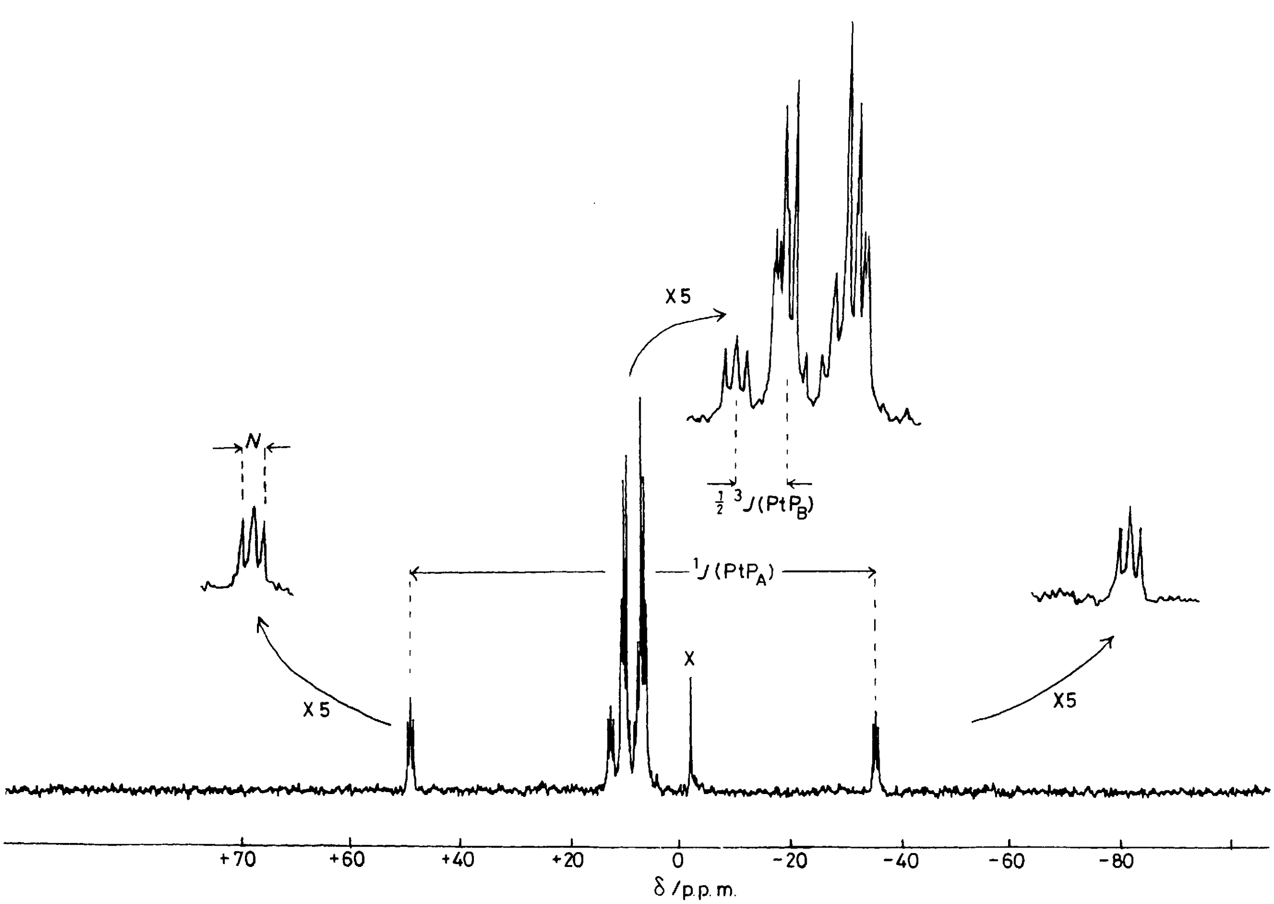


Figure 4. ^{31}P-{^{1}H} n.m.r. spectrum of the product(s) obtained by adding an excess of CS_2 to a $CDCl_3$ solution of [ClPt(μ-dppm)$_2$PdCl] (1c) at *ca.* 21 °C

(1 638 cm^{-1})[13] and [Pd_2Cl_2(μ-CO)(μ-dppm)$_2$] (1 705 cm^{-1})[6] and all three absorptions occur in the ketonic part of the ν(CO) region. The crystal structures of the bis(diphenylarsino)methane (dpam) analogues, [Pt_2Cl_2(μ-CO)(μ-dpam)$_2$][27] and [Pd_2Cl_2(μ-CO)(μ-dpam)$_2$],[28] show that the M–C–O bond angle is close to 120°. These results have led to the suggestion[29] that these and related compounds should be considered as ' dimetallated ketones '.

The mixed-metal complex [ClPt(μ-CO)(μ-dppm)$_2$PdCl] (4) does not lose its CO as readily as does the dipalladium analogue [Pd_2Cl_2(μ-CO)(μ-dppm)$_2$] but probably more readily than the diplatinum analogue [Pt_2Cl_2(μ-CO)(μ-dppm)$_2$].[13] Substantial decomposition occurs when (4) is boiled in chlorinated solvents. However, the CO is readily displaced by SO_2 which in turn can be readily and completely displaced by N_2 or Ar, or by CO to regenerate the μ-CO complex (4). Hence a small amount of SO_2 could probably be used to catalyse the reversible uptake of CO by (1c). We could find no evidence for the formation of an ionic terminal carbonyl complex [(CO)Pt(μ-dppm)$_2$PdCl]$^+$Cl$^-$ and no dissolution of a suspension of (1c) occurred on bubbling CO through its suspension in methanol for 48 h. The dipalladium analogue of [(CO)Pt(μ-dppm)$_2$PtCl]$^+$Cl$^-$ has not been reported and it seems that the formation of such a terminal-carbonyl cation is peculiar to the diplatinum complex.

Insertion of $MeO_2CC{\equiv}CCO_2Me$. When a dichloromethane solution of (1c) was treated with an excess of $MeO_2CC{\equiv}CCO_2Me$, a yellow solid separated which was collected after the mixture had stood for 24 h. Elemental analysis and molecular weight determination (Table 1) agree with the compound being a 1 : 1 adduct, [$PdPtCl_2$($MeO_2CC{\equiv}CCO_2Me$)(dppm)$_2$]. The i.r. spectrum (Nujol) showed ν(C=O) at 1 695 cm^{-1} and ν(M–Cl) at 288 cm^{-1}. The ^{31}P-{^{1}H} n.m.r. spectrum (Table 3) shows the characteristic AA′BB′ pattern with both ^1J(PtP$_A$) and ^3J(PtP$_B$) being larger than for (1c), as expected from the above discussion of the ^{31}P n.m.r. spectrum of the SO_2 adduct (3). The ^{1}H and ^{1}H-{^{31}P} n.m.r. spectra (Table 4) also show the characteristic AB pattern for the CH_2 resonance. Singlet resonances at δ 2.20 and 2.76 are assigned to the methyl protons of the methoxy groups. Acetylenes bearing the electronegative substituents $-CO_2Me$ and $-CF_3$ have been shown to insert into the metal–metal bonds of [Pd_2Cl_2(μ-dppm)$_2$],[30,31] [Pt_2Cl_2(μ-dppm)$_2$],[32] and [Rh_2Cl_2(μ-CO)(μ-dppm)$_2$][33] to give the 1 : 1 adducts. The crystal structure of the palladium complex [Pd_2Cl_2(μ-$F_3CC{\equiv}CCF_3$)(μ-dppm)$_2$][30] and the related dirhodium complex [Rh_2Cl_2(μ-$F_3CC{\equiv}CCF_3$)(μ-dppm)$_2$][33] show that the acetylene adopts a '*cis*-dimetallated olefin' mode rather than the more usual perpendicular bridging mode. Fluorine-19 n.m.r. spectroscopic evidence favours a similar 'A-frame' structure for the diplatinum compound.[32] We therefore assign the mixed palladium–platinum adduct the 'A-frame' structure (5). Hoffman and Hoffmann[34] have discussed the electronic factors involved in the mode of acetylene bridging in these complexes.

The metal–metal distance in the dipalladium–$CF_3C{\equiv}CCF_3$ compound is the longest reported for a M_2(μ-dppm)$_2$ species (3.49 Å) which shows how flexible the M_2(μ-dppm)$_2$ skeleton is in accommodating a wide range of metal–metal separations.

Insertion of CS_2. When a few drops of carbon disulphide were added to a dichloromethane solution of (1c) the solution darkened to deep red and the $^{31}P-\{^1H\}$ n.m.r. spectrum suggested that the CS_2 had inserted into the metal–metal bond. The spectrum (Figure 4) shows large shifts to high frequency for both P_A and P_B and accompanying increases in $^1J(PtP_A)$ and $^3J(PtP_B)$ with respect to the parameters for (1c). These results are consistent with insertion into the platinum–palladium bond as discussed above for the SO_2 adduct (3) (see Table 3 for $^{31}P-\{^1H\}$ n.m.r. data).

The $^1H-\{^{31}P\}$ n.m.r. spectrum of the mixed-metal CS_2 adduct prepared *in situ* shows that two species are present in solution in the ratio *ca.* 4 : 1. From the ^1H n.m.r. parameters for the two species (given in Table 4) they appear to be similar and may well be the two linkage isomers (6) and (7). Although the ^{31}P n.m.r. spectrum of this CS_2 addition product (see Figure 4) does not appear to be that of a mixture we can only explain these results if it is assumed that the ^{31}P n.m.r. parameters for the isomers (6) and (7) are so closely similar that they are not resolved. We were unable to isolate the solid CS_2 adduct(s). It seems that the CS_2 in this complex is labile; it is readily displaced by bubbling N_2 or Ar through the solution to regenerate the metal–metal bonded species. When CO or SO_2 are bubbled through a solution of the CS_2 adduct, the CO adduct (4) or the SO_2 adduct (3) respectively were readily formed. Slow evaporation of a solution of the CS_2 adduct(s) gave only the palladium–platinum starting material (1c) in high yield. A CS_2 adduct of the diplatinum complex (1a) has been prepared.[35]

We have tried to make other mixed platinum–palladium 'A-frames' but without success. In an attempt to make a hydrido-bridged 'A-frame' we treated $[ClPt(\mu\text{-dppm})_2PdCl]$ (1c) with sodium tetrahydroborate under similar conditions to those used to form hydrido-diplatinum 'A-frames'.[7] We obtained a very insoluble red material which had an i.r. spectrum very similar to the starting material but could not be further characterized due to its insolubility. Treatment of $[ClPt(\mu\text{-dppm})_2PdCl]$ (1c) with elemental sulphur under similar conditions to those used to make sulphido-bridged 'A-frames' of platinum [21] and palladium [20] led to substantial decomposition and a complex mixture of products formed.

Experimental

The general techniques and apparatus used were the same as in other recent papers from this laboratory.[36]

Preparation of $[Pd_2Cl_2(\eta^3\text{-}C_3H_5)_2(\mu\text{-dppm})]$.—Solid dppm (0.11 g, 0.27 mmol) was added to a yellow solution of $[Pd_2(\mu\text{-Cl})_2(\eta^3\text{-}C_3H_5)_2]$ (0.10 g, 0.27 mmol) in acetonitrile (5 cm^3). The mixture was warmed (to *ca.* 60 °C) on a steam bath for 1 min to give a yellow solid product which was filtered off and washed with methanol (5 cm^3) and dried *in vacuo*. Yield, 0.18 g (86%). The product could be recrystallized from dichloromethane–acetone as diamond-shaped prisms, m.p. 192—194 °C (Found: C, 49.45; H, 4.2; *M*, 763. $C_{28}H_{25}Cl_2P_2Pd_2$ requires C, 49.65; H, 4.15%; *M*, 749). The complex was non-conducting in acetone.

Preparation of $[Pd_2Cl_2(\mu\text{-dppm})_2]$ *from* $[Pd_2(\mu\text{-Cl})_2(\eta^3\text{-}C_3H_5)_2]$.—Solid dppm (0.44 g, 1.15 mmol) was added to a suspension of $[Pd_2(\mu\text{-Cl})_2(\eta^3\text{-}C_3H_5)_2]$ (0.70 g, 0.27 mmol) in ethanol (5 cm^3). The mixture was warmed gently (to *ca.* 50 °C) on a steam bath for *ca.* 2 min and then put aside for 1 h. The bright orange crystalline product was then filtered off, washed with methanol, and dried *in vacuo*. Yield, 0.14 g (45%).

Preparation of $[Pd_2Cl_2(\mu\text{-dppm})_2]$ (1b) *from* $[Pd(PPh_3)_4]$ *and* $[PdCl_2(NCPh)_2]$.—$[Pd(PPh_3)_4]$ (0.3 g, 0.26 mmol) and dppm (0.20 g, 0.52 mmol) were dissolved in dry benzene (15 cm^3) under nitrogen to give an orange-red solution. Addition of $[PdCl_2(NCPh)_2]$ (0.10 g, 0.26 mmol) gave a dark red solution which was then heated under reflux for 20 min. When the mixture had cooled, the orange solid product was filtered off, washed with benzene (10 cm^3) and dried *in vacuo*. Yield, 0.23 g (84%).

Formation of $[Pt_2Cl_2(\mu\text{-dppm})_2]$ (1a) *from* $[Pt(PPh_3)_4]$ *and* $[PtCl_2(NCBu^t)_2]$.—Solid dppm (0.31 g, 0.80 mmol) was added to a slight excess of $[Pt(PPh_3)_4]$ (0.55 g, 0.44 mmol) in dry benzene (20 cm^3) under nitrogen. $[PtCl_2(NCBu^t)_2]$ (0.17 g, 0.40 mmol) was added and the mixture was then heated under reflux for 1 h. When the mixture had cooled, the yellow solid product was filtered off, washed with benzene (10 cm^3) and dried *in vacuo*. Yield, 0.34 g (70%). The product was contaminated with *ca.* 10% $[PtCl_2(dppm)]$ (from the $^{31}P-\{^1H\}$ n.m.r. spectrum; see Discussion section).

Preparation of $[ClPt(\mu\text{-dppm})_2PdCl]\cdot C_6H_6$ (1c).—$[Pd(PPh_3)_4]$ (4.90 g, 4.25 mmol) and dppm (3.25 g, 8.46 mmol) were dissolved in dry benzene (300 cm^3) under nitrogen, to give a deep red solution, $[PtCl_2(NCBu^t)_2]$ (1.84 g, 4.25 mmol) was then added in one portion. The resultant mixture was heated under reflux for 3 h and then allowed to cool to room temperature. The orange microcrystalline product was filtered off, washed with benzene (10 cm^3) and pentane (20 cm^3) and dried *in vacuo*. Yield, 4.65 g (89%). The product, which was a benzene solvate, could be recrystallized from dichloromethane–hexane to give the corresponding dichloromethane solvate.

Preparation of $[BrPt(\mu\text{-dppm})_2PdBr]$ (1d).—$[ClPt(\mu\text{-dppm})_2PdCl]\cdot C_6H_6$ (0.15 g, 0.12 mmol) and lithium bromide (0.50 g, 6.0 mmol) were suspended in acetonitrile (20 cm^3) and heated under reflux for 2 h. The resultant red-orange solid was then filtered off, washed with small portions of acetonitrile, water, and methanol and dried *in vacuo*. Yield, 0.14 g (95%). It formed microprisms from dichloromethane–hexane.

Preparation of $[IPt(\mu\text{-dppm})_2PdI]$ (1e).—$[ClPt(\mu\text{-dppm})_2PdCl]\cdot C_6H_6$ (0.15 g, 0.12 mmol) and sodium iodide were suspended in acetone (20 cm^3) and the mixture was heated under reflux for 3 h. The resultant red solid was washed with small portions of water and acetone and dried *in vacuo*. Yield, 0.15 g (94%). The product formed red microprisms from dichloromethane-hexane.

Preparation of $[(NCS)Pt(\mu\text{-dppm})_2Pd(SCN)]$ (1f).—This was prepared and isolated in a similar fashion to the di-iodo-complex above, using K(SCN). Yield, 64%.

Preparation of $[ClPt(\mu\text{-}SO_2)(\mu\text{-dppm})_2PdCl]\cdot 0.5CH_2Cl_2$ (3).—Sulphur dioxide was gently bubbled through a solution of $[ClPt(\mu\text{-dppm})_2PdCl]$ (0.200 g, 0.16 mmol) in dichloromethane (20 cm^3) for 5 min to give a deep red solution. Methanol (40 cm^3) was added and the solution cooled to −30 °C for 2 h. The maroon crystals were then filtered off, washed with methanol (5 cm^3) and dried. Yield, 0.18 g (88%).

Preparation of $[ClPt(\mu\text{-}CO)(\mu\text{-dppm})_2PdCl]\cdot CHCl_3$ (4).—$[ClPt(\mu\text{-dppm})_2PdCl]\cdot C_6H_6$ (0.200 g, 0.16 mmol) was dissolved in chloroform (20 cm^3) and carbon monoxide was bubbled through this solution for 5 min. The red precipitate which had formed was then filtered off, washed with dichloromethane (2 cm^3) and dried. Yield, 0.20 g (97%).

Preparation of $[ClPt(\mu\text{-}MeO_2CC{\equiv}CCO_2Me)(\mu\text{-dppm})_2PdCl]$ (5).—$MeO_2CC{\equiv}CCO_2Me$ (0.2 cm^3) was added to a solution of $[ClPt(\mu\text{-dppm})_2PdCl]\cdot C_6H_6$ (0.400 g, 0.33 mmol) in dichloromethane (10 cm^3) and the mixture was then set aside for 24 h. The yellow precipitate was filtered off, washed with dichloromethane (1 cm^3) and dried. Yield, 0.20 g (48%).

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