Bis(dialkylphosphino)methane Complexes of Palladium(II) and the Molecular Structure of $[Pd_2Cl_3(\mu\text{-}Pr^iPCH_2PPr^i_2)(\mu\text{-}Pr^i_2PCH_2PHPr^i)]\cdot 2CHCl_3$† containing an Unusual Phosphidophosphine Bridging Ligand

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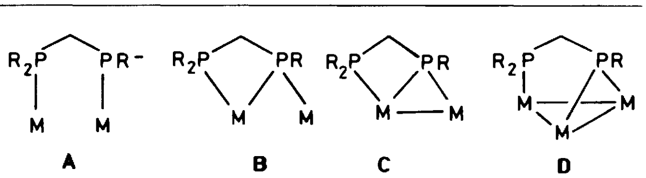
The mononuclear chelate complexes $[PdX_2(R_2PCH_2PR_2)]$ ($X = CF_3CO_2$ or Cl; R = Me, Et, or Pr^i) have been prepared and characterized spectroscopically. Reaction of $[PdCl_2(PhCN)_2]$ with $Pr^i_2PCH_2PHPr^i$ gave a novel binuclear complex, $[Pd_2Cl_3(\mu\text{-}Pr^iPCH_2PPr^i_2)(\mu\text{-}Pr^i_2PCH_2PHPr^i)]$, with the phosphidophosphine ligand in an unusual bridging mode. This complex was characterized by ^1H and ^{31}P n.m.r. spectroscopy and by *X*-ray crystal-structure analysis of its trichloromethane solvate [triclinic, space group $P\bar{1}$, $a = 8.744(2)$, $b = 11.483(1)$, $c = 20.108(4)$ Å, $\alpha = 103.49(1)$, $\beta = 97.15(2)$, $\gamma = 91.11(2)°$, $Z = 2$, $R = 0.035$ for 5 918 symmetry-independent reflections with $I \geqslant 3\sigma(I)$].

The ligands $R_2PCH_2PR_2$ and R_2P^- (R = alkyl or aryl) are both used to form bridges between two metal centres and hence to reduce the tendency towards fragmentation of binuclear complexes to mononuclear species.[1,2] It is therefore reasonable to expect that phosphidophosphines $R_2PCH_2PR^-$ should be particularly versatile bridging ligands. Some of their possible bridging modes involving two or three metal centres (M) are represented by **A**—**D**.



Little work has been reported on transition metal complexes of these ligands. Co-ordination mode **C** has been recently observed in the compound $[RuRh(Ph)(C_8H_{12})(\mu\text{-}H)(\mu\text{-}PhPCH_2PPh_2)(Ph_2PCH_2PPh_2)]\cdot 0.5PhMe$, where the phosphidophosphine ligand was formed by cleavage of a C–P bond of $Ph_2PCH_2PPh_2$.[3] Mode **D** has been found in $[Ru_3(CO)_6(\mu\text{-}H)_2(\mu\text{-}PhPCH_2PPh_2)_2]$[4] and in the complexes $[Fe_3(CO)_9(\mu\text{-}H)(\mu\text{-}Pr^iPCH_2PRPr^i)]$ (R = H or Pr^i), which were prepared in a more systematic way by reaction of $[Fe_2(CO)_9]$ with the appropriate ligand $Pr^iRPCH_2PHPr^i$.[5]

In this paper, the mononuclear complexes of the ligands $R_2PCH_2PR_2$ (R = Me, Et, or Pr^i) with palladium(II), and the synthesis and structure of an unusual binuclear complex derived from the unsymmetrical diphosphinomethane $Pr^i_2PCH_2PHPr^i$ are described.

Results and Discussion

Reaction of either palladium(II) acetate, in the presence of excess trifluoroacetic acid, or of $[PdCl_2(PhCN)_2]$ with the ligands $R_2PCH_2PR_2$ gave the corresponding complexes $[PdX_2(R_2PCH_2PR_2)]$ (**1a**, $X = CF_3CO_2$, R = Me; **1b**, X = Cl, R = Me; **2a**, $X = CF_3CO_2$, R = Et; **2b**, X = Cl, R = Et; **3a**, $X = CF_3CO_2$, R = Pr^i; **3b**, X = Cl, R = Pr^i). In most cases, these complexes were readily identified as chelate monomeric species by the ^1H and ^{31}P n.m.r. spectra. Thus, the ^{31}P chemical shifts were to high field of the free ligand, which is characteristic of complexes with a four-membered chelate ring.[6] In addition, the CH_2P_2 resonance in the ^1H n.m.r. spectrum appeared as a triplet with $^2J(PH) = 10$—14 Hz, as is usually observed for chelate complexes of these ligands; binuclear complexes with bridging $R_2PCH_2PR_2$ ligands give more complex signals with much lower values of $^2J(PH)$.[7]

The only difficulty in characterization was found with the product, (**1b**), of reaction of $[PdCl_2(PhCN)_2]$ with $Me_2PCH_2PMe_2$. This complex was extremely insoluble in common organic solvents, and hence was difficult to purify and impossible to characterize by n.m.r. spectroscopy. The structure of this complex could not be determined.

A more interesting compound, in the forms (**4a**) and (**4b**), was obtained by reaction of $[PdCl_2(PhCN)_2]$ with $Pr^i_2PCH_2PHPr^i$. The reaction products were initially difficult to characterize spectroscopically and the trichloromethane solvate of the major form, (**4a**), was identified by *X*-ray diffraction as $[Pd_2Cl_3(\mu\text{-}Pr^iPCH_2PPr^i_2)(\mu\text{-}Pr^i_2PCH_2PHPr^i)]\cdot 2CHCl_3$. The phosphidophosphine ligand, $Pr^i_2PCH_2PPr^{i-}$, was therefore formed by cleavage of the P–H bond of the diphosphinomethane, which was only partially retained in this reaction.

In the crystal structure of (**4a**)·$2CHCl_3$ the molecules are separated by van der Waals contacts, except for the Cl(3)···H(21) distance [2.63(5) Å], which may indicate a weak intermolecular hydrogen-bonding interaction of (**4a**) and $C(21)HCl_3$ [Cl(3)···C(21) 3.507(5) Å, Cl(3)···H(21)–C(21) 158(4)°]. The geometry of the two crystallographically independent solvent molecules is as expected (Figure 1).

The molecular structure of (**4a**) is illustrated in Figure 2. The metal centres of the PdCl and $PdCl_2$ fragments are spanned by the diphosphinomethane ligand and bridged by the phosphidophosphine, which also acts as a *cis*-bidentate chelating ligand to the Pd(1) atom. The molecular core therefore consists of fused four-membered and six-membered heterocycles in which both metal centres lie in square-planar environments. Severe deformations of the co-ordination geometry of the metal centres are obvious from angular distortions (Table 1) and from displacements of the constituent atoms from the $Pd(1)ClP_3$ and

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† 1,1,2-Trichloro-μ-[(di-isopropylphosphino)isopropylphosphinomethane-*PP'*]-μ-[di-isopropylphosphinomethyl(isopropyl)phosphido-*P*(Pd¹,Pd²)*P'*(Pd²)]dipalladium(II)–chloroform (1/2).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Pd(2)Cl$_2$P$_2$ planes; these displacements lie within $\pm$0.096(1) and $\pm$0.148(1) Å, respectively.

The conformation of the phosphidophosphine ligand is practically eclipsed about both P–CH$_2$ bonds, and that of the diphosphinomethane is staggered about the P(1)–CH$_2$ bond and half-way between eclipsed and staggered about the P(2)–CH$_2$ bond, as is evident from the torsion angles listed in

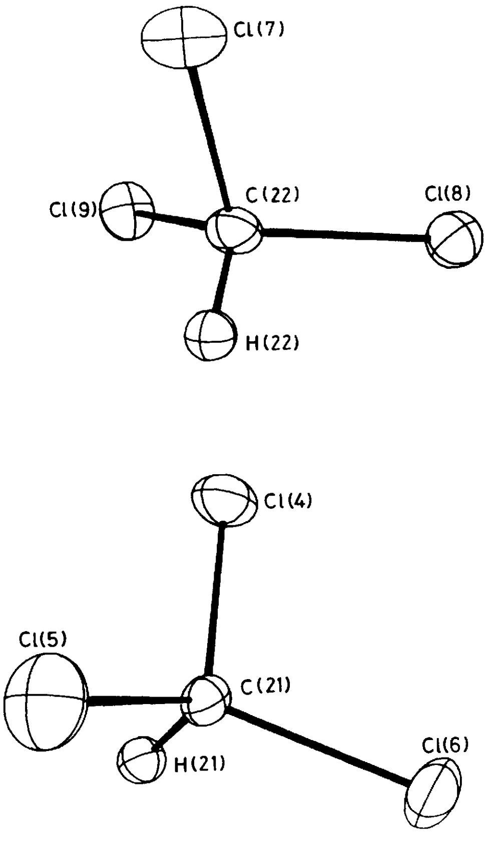

Figure 1. Geometry of the symmetry-independent solvent molecules in the crystal structure of (**4a**)·2CHCl$_3$, showing the atomic numbering scheme employed in Table 2. The bond lengths and angles are: C–H 0.92(5) and 0.92(5), C–Cl 1.736(6)—1.759(6) Å; H–C–Cl 105(3)—115(3), Cl–C–Cl 109.2(3)—111.6(3)°

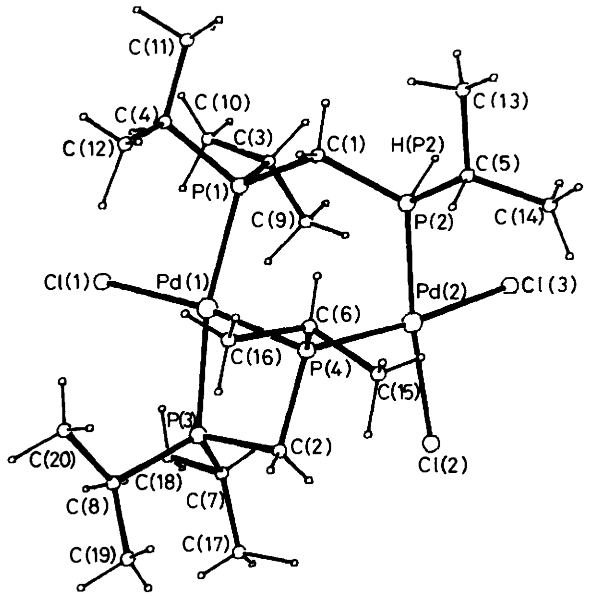

Figure 2. The molecular structure of [Pd$_2$Cl$_3$(μ-Pr^{i}PCH$_2$PPr$^i_2$)(μ-Pr$^i_2$PCH$_2$PHPr^i)] (**4a**) with hydrogen atoms not labelled, for clarity. Here, and in the numbering scheme used in Table 2, atom H(*n*) [or atoms H(*n*A), H(*n*B), and H(*n*C)] is attached to C(*n*)

Table 1. Selected parameters of the molecular structure of (**4a**)

Bond lengths (Å)

Pd(1)–Cl(1)	2.390(2)	Pd(1)–P(4)	2.259(1)	P(1)–C(4)	1.836(4)	P(3)–C(7)	1.832(5)
Pd(2)–Cl(2)	2.354(1)	Pd(2)–P(4)	2.257(1)	P(2)–C(1)	1.824(4)	P(3)–C(8)	1.844(4)
Pd(2)–Cl(3)	2.388(2)	Pd(2)–P(2)	2.245(1)	P(2)–C(5)	1.844(5)	P(4)–C(2)	1.851(5)
Pd(1)–P(1)	2.322(1)	P(1)–C(1)	1.829(4)	P(2)–H(P2)	1.36(4)	P(4)–C(6)	1.850(5)
Pd(1)–P(3)	2.307(1)	P(1)–C(3)	1.853(4)	P(3)–C(2)	1.830(5)		

Non-bonding distances (Å)

Pd(1) · · · Pd(2)	3.738(1)	Pd(1) · · · C(2)	3.070(4)	P(1) · · · P(2)	3.134(1)	P(3) · · · P(4)	2.720(1)

Bond angles (°)

Cl(1)–Pd(1)–P(1)	89.5(1)	Cl(2)–Pd(2)–P(4)	93.6(1)	Pd(1)–P(1)–C(4)	113.3(2)	Pd(1)–P(4)–Pd(2)	111.7(1)
Cl(1)–Pd(1)–P(3)	100.1(1)	Cl(3)–Pd(2)–P(2)	86.0(1)	Pd(2)–P(2)–C(1)	122.1(2)	Pd(1)–P(4)–C(2)	96.1(2)
P(1)–Pd(1)–P(4)	97.4(1)	P(2)–Pd(2)–P(4)	90.8(1)	Pd(2)–P(2)–C(5)	114.5(2)	Pd(1)–P(4)–C(6)	115.6(2)
P(3)–Pd(1)–P(4)	73.1(1)	Cl(2)–Pd(2)–P(2)	174.0(1)	Pd(2)–P(2)–H(P2)	113(2)	Pd(2)–P(4)–C(2)	115.6(2)
Cl(1)–Pd(1)–P(4)	173.1(1)	Cl(3)–Pd(2)–P(4)	173.6(1)	Pd(1)–P(3)–C(2)	95.1(2)	Pd(2)–P(4)–C(6)	113.4(2)
P(1)–Pd(1)–P(3)	169.4(1)	Pd(1)–P(1)–C(1)	115.5(2)	Pd(1)–P(3)–C(7)	112.8(2)	P(1)–C(1)–P(2)	118.2(3)
Cl(2)–Pd(2)–Cl(3)	90.1(1)	Pd(1)–P(1)–C(3)	113.0(2)	Pd(1)–P(3)–C(8)	121.0(2)	P(3)–C(2)–P(4)	95.3(2)

Torsion angles (°)

P(4)–Pd(1)–P(1)–C(1)	−10.9(2)	P(2)–Pd(2)–P(4)–Pd(1)	76.7(1)	Pd(1)–P(4)–C(2)–P(3)	4.7(2)
Pd(1)–P(1)–C(1)–P(2)	58.1(2)	P(1)–Pd(1)–P(4)–Pd(2)	−58.1(1)	Pd(1)–P(3)–C(2)–P(4)	−4.6(2)
Pd(2)–P(2)–C(1)–P(1)	−32.8(2)	P(3)–Pd(1)–P(4)–C(2)	−3.8(2)	P(4)–Pd(1)–P(3)–C(2)	3.9(2)
P(4)–Pd(2)–P(2)–C(1)	−31.2(2)				

Table 1. Such conformations of the two ligands afford an essentially planar PdP$_2$C ring and a distorted boat conformation of the Pd$_2$P$_3$C dimetallacycle (Table 1, Figure 3), resulting in a dihedral angle of 65.1° between the Pd(1)ClP$_3$ and Pd(2)Cl$_2$P$_2$ planes.

Closure of the four-membered PdP$_2$C chelate ring leads to severe distortions of the ring angles [P(3)–Pd(1)–P(4) 73.1(1), P(3)–C(2)–P(4) 95.3(2)°] and to very short transannular non-bonding distances [P(3)$\cdots$P(4) 2.720(1), Pd(1)$\cdots$C(2) 3.070(4) Å]. The geometrical constraints of the PdP$_2$C ring are therefore similar to those usually found in the mononuclear chelate complexes of the diphosphinomethane Ph$_2$PCH$_2$PPh$_2$.[8]

In the Pd$_2$P$_3$C ring, large openings of the bond angles from 90° at palladium and 109.5° at phosphorus and carbon (Table 1) permit a remarkably large Pd$\cdots$Pd separation [3.738(1) Å]. The absence of metal–metal bonding distinguishes structural features of (**4a**) (mode **B**) from those (mode **C**) of [RuRh(Ph)(C$_8$H$_{12}$)(μ-H)(μ-PhPCH$_2$PPh$_2$)(Ph$_2$PCH$_2$PPh$_2$)]·0.5PhMe, where a phosphidophosphine ligand, Ph$_2$PCH$_2$PPh$^-$, chelates a Ru centre while bridging a Ru–Rh bond of 2.941 3(8) Å.[3] The bond lengths in (**4a**) are unexceptional, and the palladium–chlorine and palladium–phosphorus bonds are sensitive to the *trans*-influencing capabilities of the *trans* ligand (Table 1).

Complex (4) could exist as four geometrical isomers, **I**—**IV**, each of which is chiral, as shown in Figure 4. In (**4a**)·2CHCl$_3$ the diphosphinomethane ligand co-ordinates PdCl and PdCl$_2$ fragments through the PPr$^i_2$ and PHPr^i groups, respectively, and the P–H bond is *anti* with respect to the P(4)–C(6) bond (Figure 2). Thus the *X*-ray structure analysis identifies (**4a**) as isomer **III** of Figure 4.

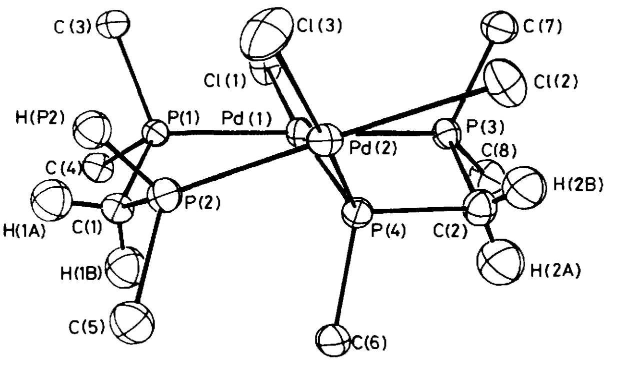

Figure 3. A view of the molecular core of (**4a**), showing the conformation of the Pd$_2$P$_3$C heterocycle and the mutual orientation of the Pd(1)ClP$_3$ and Pd(2)Cl$_2$P$_2$ fragments

The ^{31}P n.m.r. spectrum of (**4a**) gave four resonances of approximately equal intensity, which were assigned as follows. By comparison of the proton-coupled and -decoupled ^{31}P n.m.r. spectra (Figure 5), the secondary phosphine centre P^b with ^1J(P^{b}H) = 405 Hz could be positively assigned. Next the resonance for P^c, which has no *trans* phosphorus and hence no large ^2J(PP) coupling, could be assigned. Phosphorus P^d is part of a strained four-membered chelate ring and is therefore upfield from the other Pr$^i_2$P$^-$ phosphorus centre, P^a;[6] these assignments are fully consistent with the pattern of smaller PP couplings. The ^{1}H n.m.r. spectrum of (**4a**) contained a resonance due to the PH group at δ 4.98, ^1J(PH) = 400, ^2J(PH) = 13 Hz, as well as the expected complex resonances due to CH$_2$P and (CH$_3$)$_2$CH protons (see Experimental section).

The second isomer, (**4b**), could not be completely separated from (**4a**), but its structure could be deduced from the n.m.r. spectra. Using the methods of assignment given above, the secondary phosphine centre in (**4b**) was shown to be *trans* to the tertiary phosphine centre in the four-membered chelate ring. This isomer therefore adopts the structure **I** or **II** (Figure 4), but, on the basis of lower steric hindrance, **II** is considered more probable. The structure **II**, (**4b**), can be derived from **III**, (**4a**), by exchanging the R$_2$P and RPH groups of the bridging diphosphinomethane ligand.

The isomers (**4a**) and (**4b**) appear to be the first examples of compounds in which the R$_2$PCH$_2$PR$^-$ ligand adopts co-ordination mode **B**; Meek and co-workers,[9–11] however, have prepared related complexes with the ligands R$_2$PCH$_2$CH$_2$CH$_2$-PPh$^-$ (R = Ph or *cyclo*-C$_6$H$_{11}$).

Experimental

Hydrogen-1 n.m.r. and ^{1}H-{^{31}P} n.m.r. spectra were recorded using a Varian XL100 n.m.r. spectrometer; ^{31}P-{^{1}H} and ^{31}P n.m.r. spectra were recorded using Varian XL200 and XL300 n.m.r. spectrometers; δ values are in p.p.m., *J* values in Hz.

All reactions involving phosphine ligands were carried out under an atmosphere of nitrogen.

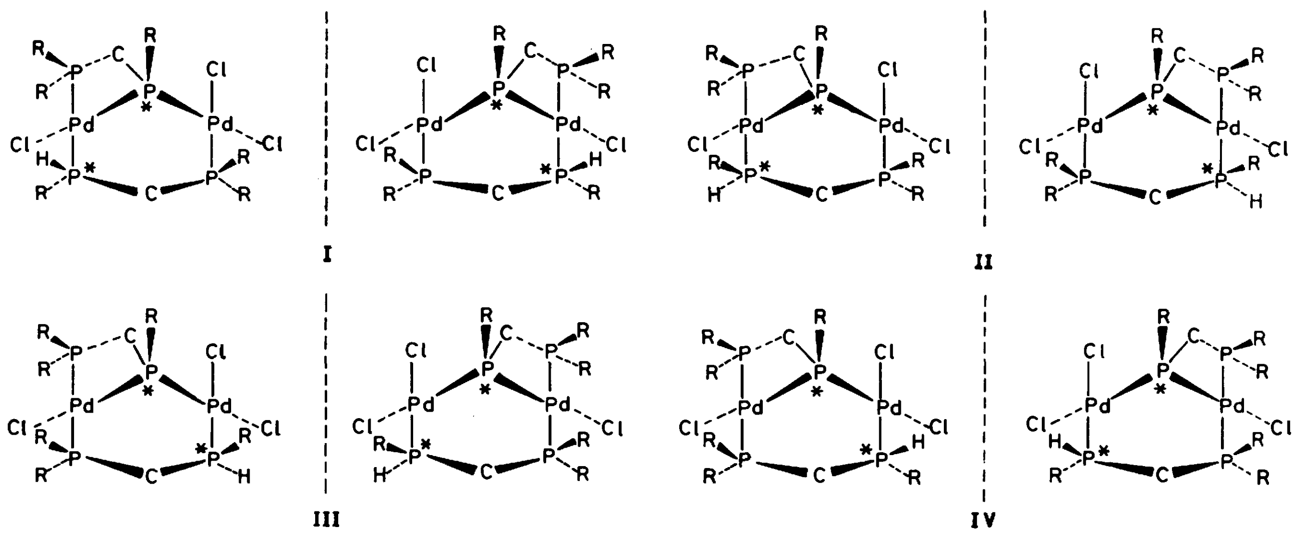

Figure 4. The possible isomeric forms of [Pd$_2$Cl$_3$(μ-RPCH$_2$PR$_2$)(μ-R$_2$PCH$_2$PHR)]

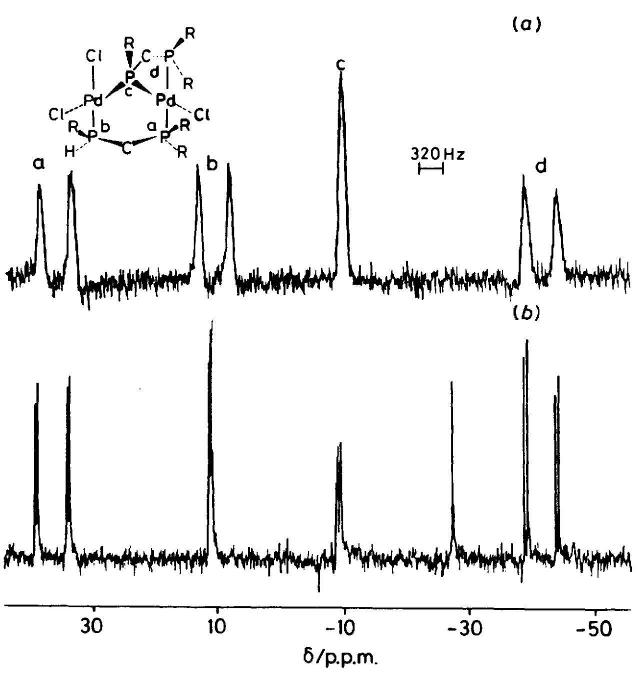

Figure 5. N.m.r. spectra of (**4a**): (*a*) ^{31}P-{^{1}H}, (*b*) ^{31}P. Assignments for phosphorus atoms P^a, P^b, P^c, and P^d are indicated

$[Pd(CF_3CO_2)_2(dmpm)]$.—Palladium(II) acetate (0.822 mmol) was dissolved in acetone–trifluoroacetic acid (9:1 v/v, 50 cm^3) and a solution of bis(dimethylphosphino)methane (dmpm) (0.799 mmol) in acetone (5 cm^3) was added. A yellow solution resulted. After 3 h the solvent was evaporated under vacuum to yield a yellow solid. Recrystallization of a small sample from acetone–pentane gave a white crystalline solid, which was sparingly soluble in organic solvents (Found: C, 23.1; H, 2.65. Calc. for $C_9H_{14}F_6O_4P_2Pd$: C, 23.1; H, 3.0%). N.m.r. ([$^2H_6$]acetone): ^{31}P, δ −66.4 [s, PdP, $\Delta\delta = \delta_{complex} - \delta_{free} = -9.2$]; ^{1}H, δ 3.49 [t, ^2J(PH) = 11, CH_2P_2], 1.97 [m, ^2J(PH) + ^4J(PH) = 13.5, CH_3P].

The following compounds were prepared similarly. $[Pd(CF_3CO_2)_2(depm)]$ [depm = bis(diethylphosphino)methane], yield 49% (Found: C, 29.5; H, 4.2. Calc. for $C_{13}H_{22}F_6O_4P_2Pd$: C, 29.8; H, 4.2%). N.m.r. ([$^2H_6$]acetone): ^{31}P, δ −42.9 [s, PdP, Δδ = −12.5]; ^{1}H, δ 3.45 [t, ^2J(PH) = 11, CH_2P_2], 2.34 [m, ^3J(HH) = 7.5, ^2J(PH) = 10.5, CH_2C], 1.35 [m, ^3J(HH) = 7.5, ^3J(PH) = 22, CH_3C]. $[Pd(CF_3CO_2)_2(dippm)]$ [dippm = bis(di-isopropylphosphino)methane], yield 20%. N.m.r. ([$^2H_6$]acetone): ^{31}P, δ −25.1 [s, PdP, Δδ = −21.1]; ^{1}H, δ 3.35 [t, ^2J(PH) = 11, CH_2P_2], 2.70 [septet, ^3J(HH) = 7], 1.46 [dd, ^3J(HH) = 7, ^3J(PH) = 6, CH_3C], 1.42 [dd, ^3J(HH) = 7, ^3J(PH) = 4, CH_3C]. $[Pd(CF_3CO_2)_2(dppm)]$ [dppm = bis(diphenylphosphino)methane], yield 73% (Found: C, 48.7; H, 3.1. Calc. for $C_{29}H_{22}F_6O_4P_2Pd$: C, 48.6; H, 3.1%). N.m.r. ([$^2H_6$]acetone): ^{31}P, δ −48.2 [s, PdP, Δδ = −23.4]; ^{1}H, δ 4.69 [t, ^2J(PH) = 10.8, CH_2P_2].

$[PdCl_2(depm)]$.—A solution of $[PdCl_2(PhCN)_2]$ (5.69 mmol) in acetone (10 cm^3) was added to a solution of depm (6.66 mmol) in acetone (40 cm^3). A white solid precipitated immediately. This was isolated by filtration, and dried *in vacuo*; yield 88% (Found: C, 29.25; H, 6.2. Calc. for $C_9H_{22}Cl_2P_2Pd$: C, 29.25; H, 6.0%). N.m.r. (CD_2Cl_2): ^{31}P, δ −44.0 [s, PdP, Δδ = −14.4]; ^{1}H, δ 3.03 [t, ^2J(PH) = 11, CH_2P_2], 2.22 [m, ^3J(HH) = 8, ^2J(PH) = 7, CH_2C], 2.19 [m, ^3J(HH) = 7, ^2J(HH) = 7, ^2J(PH) = 7, CH_2C], 1.45 [m, ^3J(HH) = 7, 8, ^3J(PH) = 21, CH_3C].

$[PdCl_2(dippm)]$ was prepared similarly; yield 50% (Found: C, 36.8; H, 7.2. Calc. for $C_{13}H_{30}Cl_2P_2Pd$: C, 36.7; H, 7.1%). N.m.r. (CD_2Cl_2): ^{31}P, δ −27.4 [s, PdP, Δδ = −23.4]; ^{1}H, δ 2.86 [t, ^2J(PH) = 10.3, CH_2P_2], 2.52 [septet, ^3J(HH) = 6.5, $CHMe_2$], 1.45 [dd, ^3J(HH) = 6.5, ^3J(PH) = 18, CH_3C], 1.39 [dd, ^3J(HH) = 6.5, ^3J(PH) = 18, CH_3C].

An attempt to prepare $[PdCl_2(dmpm)]$ by this method gave an insoluble yellow solid (Found: C, 24.3; H, 3.7. Calc. for $C_5H_{14}Cl_2P_2Pd$: C, 19.2; H, 4.5%).

$[Pd_2Cl_3(\mu\text{-}Pr^iPCH_2PPr^i{}_2)(\mu\text{-}Pr^i{}_2PCH_2PHPr^i)]$.—To a solution of $[PdCl_2(PhCN)_2]$ (1.54 mmol) in acetone (50 cm^3), was added a mixture of dippm and $Pr^i{}_2PCH_2PHPr^i$ (1.6 mmol, 1:1 mixture) in acetone (10 cm^3). A white precipitate of $[PdCl_2(dippm)]$ formed immediately (yield 50%) and was removed by filtration. The yellow filtrate was evaporated to give a yellow oil, which was recrystallized from chloroform to give pure (**4a**) (Found: C, 32.3; H, 6.5. Calc. for $C_{20}H_{47}Cl_3P_4Pd_2$: C, 32.9; H, 6.5%). N.m.r. ([$^2H_6$]acetone): ^{31}P, δ −42.4 [m, $^2J(P^aP^d)$ = 414, $^2J(P^cP^d)$ = 45, P^d], −8.7 [m, $^2J(P^aP^c)$ = 8, $^2J(P^bP^c)$ = 13, $^2J(P^cP^d)$ = 45, P^c], +13.5 [m, $^2J(P^aP^b)$ = 32, $^2J(P^bP^c)$ = 13, P^b], +39.9 [m, $^2J(P^aP^b)$ = 32, $^2J(P^bP^c)$ = 8, $^2J(P^aP^d)$ = 414, P^a]; ^{1}H, δ 4.98 [dd, ^1J(PH) = 400, ^3J(PH) = 13, PH]; 0.88 [m, ^2J(HH) = 14, ^2J(PH) = 25.8, $CH_2P^cP^d$], 1.70 [m, ^2J(HH) = 14, ^2J(PH) = 25, $CH_2P^cP^d$], 2.75 [m, ^2J(HH) = 16, ^2J(PH) = 10,12, $CH_2P^aP^b$], 4.85 [m, ^2J(HH) = 16, ^2J(PH) = 8, 8, $CH_2P^aP^b$], 2.17, 2.48, 3.32 (m, C*H*Me$_2$), 1.22—1.58 [complex m, CH*Me*$_2$].

The filtrate from this recrystallization was shown to contain a mixture of (**4a**) and (**4b**). N.m.r. of (**4b**) ([$^2H_6$]acetone): ^{31}P, δ −38.0 [m, $^2J(P^bP^d)$ = 422, $^2J(P^cP^d)$ = 40, P^d], −11.0 [m, $^2J(P^aP^c)$ = 10, $^2J(P^bP^c)$ = 13, $^2J(P^cP^d)$ = 40, P^c], −3.6 [m, $^2J(P^aP^b)$ = 28, $^2J(P^bP^d)$ = 422, $^2J(P^bP^c)$ = 13, $^1J(P^bH)$ = 355, P^b], +56.5 [m, $^2J(P^aP^b)$ = 28, $^2J(P^aP^c)$ = 10, P^a]; ^{1}H, δ 4.52 [m, ^1J(PH) = 355, ^2J(PH) = 13,13,6, P^{b}H].

X-*Ray Crystal Structure Analysis of* (**4a**)·$2CHCl_3$.—Transparent, platy yellow crystals were obtained from trichloromethane solution.

Crystal data. $C_{22}H_{49}Cl_9P_4Pd_2$, M = 969.4, triclinic, space group $P\bar{1}$, a = 8.744(2), b = 11.483(1), c = 20.108(4) Å, α = 103.49(1), β = 97.15(2), γ = 91.11(2)°, U = 1 945.6 Å^3, Z = 2, D_c = 1.655 g cm^{-3}, $F(000)$ = 972, μ(Mo-K_α) = 17.15 cm^{-1}, λ = 0.710 69 Å, T = 20.5 °C.

Measurements. A crystal of approximate dimensions 0.25 × 0.50 × 0.80 mm was mounted on an Enraf-Nonius CAD4 diffractometer and exposed to graphite-monochromated Mo-K_α radiation. The unit-cell dimensions were determined by a least-squares treatment of diffractometric angles of 25 high-angle reflections. Intensities of 7 326 reflections with $2 \leqslant \theta \leqslant 25°$ were measured by continuous θ/2θ scans. The scan widths in θ were (0.74 + 0.35tanθ)°, and the scan speeds were adjusted to give $\sigma(I)/I < 0.02$, subject to a time limit of 100 s. Two strong reflections were remeasured every 2 h, but their intensities displayed no significant changes.

The integrated intensities of reflections, derived in the usual manner,[12] were corrected for Lorentz, polarization and absorption effects. The latter correction, made by an empirical method,[13] yielded absorption factors (on F^2) of 0.80—1.19. Averaging 980 symmetry-related structure amplitudes to obtain 490 unique ones gave R (internal) of 0.026. Rejection of 918 reflections with $I < 3\sigma(I)$ yielded 5 918 unique structure amplitudes and only these were used in further analysis.

Structure solution and refinement. The positions of the palladium atoms were determined from a Patterson function and those of the remaining atoms, including hydrogens, from

Table 2. Fractional atomic co-ordinates of (**4a**)·$2CHCl_3$, with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Pd(1)	−0.065 58(3)	0.046 74(2)	0.306 53(1)
Pd(2)	0.101 93(3)	0.182 16(2)	0.177 97(1)
Cl(1)	−0.099 18(15)	−0.122 04(10)	0.354 80(6)
Cl(2)	0.340 27(11)	0.268 22(10)	0.238 90(5)
Cl(3)	0.219 69(14)	0.122 05(10)	0.075 13(6)
Cl(4)	0.526 60(19)	0.474 09(14)	0.135 62(11)
Cl(5)	0.306 2(3)	0.415 7(2)	0.013 1(1)
Cl(6)	0.210 1(2)	0.518 3(2)	0.144 9(1)
Cl(7)	0.601 6(2)	0.453 1(1)	0.584 4(1)
Cl(8)	0.780 7(2)	0.329 6(2)	0.673 3(1)
Cl(9)	0.448 4(2)	0.326 2(2)	0.665 4(1)
P(1)	−0.212 63(10)	−0.056 21(7)	0.204 84(4)
P(2)	−0.120 86(11)	0.110 38(8)	0.111 44(4)
P(3)	0.101 33(11)	0.167 57(8)	0.394 55(4)
P(4)	−0.018 08(10)	0.217 31(7)	0.273 29(4)
C(1)	−0.271 3(4)	0.033 4(3)	0.142 7(2)
C(2)	0.102 1(5)	0.295 2(4)	0.354 5(2)
C(3)	−0.110 8(4)	−0.180 5(3)	0.155 1(2)
C(4)	−0.396 8(4)	−0.120 5(3)	0.218 5(2)
C(5)	−0.224 9(5)	0.220 9(4)	0.072 0(2)
C(6)	−0.182 9(5)	0.315 0(3)	0.268 7(2)
C(7)	0.298 8(5)	0.116 5(4)	0.398 5(2)
C(8)	0.049 6(5)	0.212 9(4)	0.482 8(2)
C(9)	0.060 9(5)	−0.149 2(4)	0.163 2(3)
C(10)	−0.136 6(7)	−0.299 6(4)	0.175 7(3)
C(11)	−0.502 9(5)	−0.177 4(5)	0.152 1(3)
C(12)	−0.478 5(7)	−0.027 0(6)	0.266 9(3)
C(13)	−0.372 9(7)	0.168 4(6)	0.027 5(3)
C(14)	−0.115 9(12)	0.280 6(13)	0.035 6(8)
C(15)	−0.125 6(7)	0.435 3(4)	0.258 7(3)
C(16)	−0.273 0(6)	0.330 6(5)	0.330 5(3)
C(17)	0.418 8(6)	0.211 5(5)	0.439 7(4)
C(18)	0.309 9(7)	0.001 3(5)	0.422 6(4)
C(19)	0.105 8(12)	0.338 8(7)	0.520 8(4)
C(20)	−0.123 5(8)	0.194 7(9)	0.482 6(3)
C(21)	0.337 6(6)	0.424 8(4)	0.101 2(3)
C(22)	0.615 6(7)	0.411 8(4)	0.662 9(3)
H(P2)	−0.100(5)	0.024(3)	0.054(2)
H(1A)	−0.330(5)	−0.022(4)	0.103(2)
H(1B)	−0.347(6)	0.084(4)	0.162(2)
H(2A)	0.059(6)	0.358(5)	0.375(3)
H(2B)	0.188(6)	0.320(4)	0.352(2)
H(3)	−0.153(6)	−0.188(4)	0.104(2)
H(4)	−0.354(5)	−0.186(4)	0.240(2)
H(5)	−0.244(5)	0.287(4)	0.108(2)
H(6)	−0.242(4)	0.272(3)	0.233(2)
H(7)	0.308(5)	0.096(4)	0.355(2)
H(8)	0.097(6)	0.153(5)	0.504(3)
H(9A)	0.075(6)	−0.076(5)	0.149(2)
H(9B)	0.102(5)	−0.208(4)	0.130(2)
H(9C)	0.097(8)	−0.138(6)	0.217(3)
H(10A)	−0.077(10)	−0.380(7)	0.139(4)
H(10B)	−0.265(9)	−0.315(6)	0.170(3)
H(10C)	−0.067(7)	−0.280(5)	0.227(3)
H(11A)	−0.558(7)	−0.120(5)	0.125(3)
H(11B)	−0.587(6)	−0.230(4)	0.166(2)
H(11C)	−0.453(6)	−0.239(4)	0.119(2)
H(12A)	−0.521(8)	0.032(6)	0.262(3)
H(12B)	−0.404(8)	0.010(6)	0.319(3)
H(12C)	−0.561(7)	−0.058(5)	0.278(3)
H(13A)	−0.390(8)	0.096(6)	0.002(3)
H(13B)	−0.425(6)	0.230(5)	0.012(3)
H(13C)	−0.442(8)	0.155(6)	0.058(4)
H(14A)	−0.099(10)	0.231(7)	0.009(4)
H(14B)	−0.03(2)	0.33(2)	0.05(1)
H(14C)	−0.181(14)	0.333(10)	0.018(6)
H(15A)	−0.095(7)	0.425(5)	0.221(3)
H(15B)	−0.047(6)	0.476(4)	0.300(2)
H(15C)	−0.195(8)	0.475(5)	0.255(3)
H(16A)	−0.221(6)	0.377(4)	0.368(3)
H(16B)	−0.305(5)	0.255(4)	0.340(2)
H(16C)	−0.361(7)	0.373(5)	0.318(3)
H(17A)	0.411(8)	0.303(6)	0.410(3)
H(17B)	0.511(6)	0.183(4)	0.437(2)
H(17C)	0.406(6)	0.226(4)	0.482(3)
H(18A)	0.294(6)	0.017(4)	0.472(2)
H(18B)	0.245(7)	−0.060(5)	0.394(3)
H(18C)	0.409(8)	−0.036(5)	0.419(3)
H(19A)	0.057(9)	0.381(6)	0.501(4)
H(19B)	0.092(7)	0.355(5)	0.569(3)
H(19C)	0.193(9)	0.352(6)	0.526(3)
H(20A)	−0.143(7)	0.211(5)	0.534(3)
H(20B)	−0.160(8)	0.252(6)	0.466(3)
H(20C)	−0.141(12)	0.100(9)	0.453(5)
H(21)	0.327(5)	0.346(4)	0.105(2)
H(22)	0.634(5)	0.481(4)	0.697(2)

difference electron-density maps. The structure was refined by least-squares methods, using a two-large-blocks approximation to the normal matrix. The weighting scheme $w = [\sigma^2(|F_o|)]^{-1}$ was shown adequate by analysis of $w = (|F_o| - |F_c|)^2$ values. The atomic scattering factors and the anomalous dispersion corrections were taken from ref. 14. All non-hydrogen atoms were allowed anisotropic, and hydrogen atoms isotropic, thermal vibrations. Refinement of 530 structural parameters converged at $R = 0.035$ and $R' = 0.049$ $\{R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R' = [\Sigma w(|F_o| - |F_c|)^2/w|F_o|^2]^{\frac{1}{2}}\}$. In the final difference electron-density map the function values ranged from −0.84 to +1.06 e $Å^{-3}$, and the extreme values were associated with positions of Pd and Cl atoms. The final atomic co-ordinates are given in Table 2. Relatively high thermal parameters of the C(14), H(14C), and H(14B) may suggest some disorder of this methyl group.

All calculations were performed on a GOULD SEL 32/27 superminicomputer, using the locally developed GX program package.[15]

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