Asymmetric Homo- and Hetero-bimetallic Complexes of the Nickel Group Elements. Crystal Structure of $[(C_6F_5)_2Pd(\mu\text{-}Cl)_2Pt(PEt_3)_2]$†

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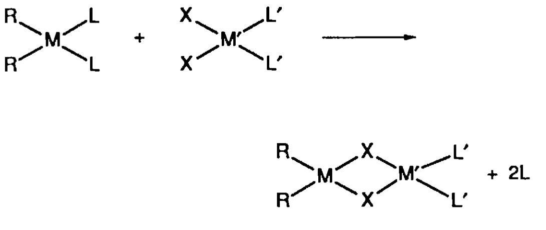
By reaction between *cis*-$[Pd(C_6F_5)_2(PhCN)_2]$ and *cis*-$[MX_2L_2]$ in dichloromethane, the asymmetric homo- and hetero-bimetallic complexes $[R_2Pd(\mu\text{-}X)_2ML_2]$ are formed (M = Ni, Pd or Pt; X = Cl, Br, I or SCN; R = C_6F_5 or $C_6H_2F_3$-2,4,6; L = PEt_3, PBu_3, PPh_2Me or C_5H_5N; L_2 = $Ph_2PCH_2CH_2PPh_2$). In chloroform solution all the *gem* derivatives are binuclear. The crystal structure of $[(C_6F_5)_2Pd(\mu\text{-}Cl)_2Pt(PEt_3)_2]$ has been solved and refined to *R* = 0.042 for 4241 observed reflections, confirming the existence of binuclear molecules where the Pd and Pt atoms have square-planar co-ordination [Pd–Cl 2.449(2) and 2.402(2) and Pt–Cl 2.430(2) and 2.386(2) Å].

Neutral binuclear palladium(II) complexes of the type $[(L)RPd(\mu\text{-}Cl)_2PdR(L)]$ (R = C_6F_5 or C_6Cl_5, L = neutral ligand) can be prepared by the reaction between $[PdR_2L_2]$ and $PdCl_2$.[1] However, the synthesis of neutral binuclear organometallic complexes in which the metal atoms have different co-ordination environments has been reported only recently.[2–4]

A general method for the preparation of asymmetric binuclear complexes is based on the reaction of a labile complex *cis*-$[MR_2L_2]$ with a halogeno complex *cis*-$[M'X_2L'_2]$ according to equation (1). Appropriate choice of the reagents should allow the synthesis of homo- or hetero-nuclear complexes. Complexes such as $[Pd(C_6F_5)_2(diox)]$,[5,6] $[MR_2(thf)_2]$ [R = C_6F_5 (M = Ni,[7] Pd[4] or Pt[8]) or C_6Cl_5 (M = Pd[4] or Pt[8]); diox = dioxane, thf = tetrahydrofuran], or $[MR_2(PhCN)_2]$ [R = C_6F_5 (M = Ni or Pd[9,10]) or $C_6H_2F_3$-2,4,6 (M = Pd[11])] have shown to be excellent precursors for the synthesis of other halogenophenyl derivatives. Thus, *cis*-$[MR_2(thf)_2]$ have been used[4] to synthesise $[\{R_2M(\mu\text{-}X)_2M'(cod)\}_n]$ (cod = cycloocta-1,5-diene) and in a preliminary communication[2] we showed that $[(C_6F_5)_2Pd(\mu\text{-}X)_2ML_2]$-type complexes can be prepared starting from the benzonitrile adduct *cis*-$[Pd(C_6F_5)_2(PhCN)_2]$.


(1)

Here the preparation and structural study of a number of new asymmetric homo- and hetero-bimetallic complexes of general formula $[R_2Pd(\mu\text{-}X)_2ML_2]$ (R = C_6F_5 or $C_6H_2F_3$-2,4,6; X = halide or SCN; M = Ni, Pd or Pt; L = phosphine or pyridine) are described.

Results and Discussion

In dichloromethane, *cis*-$[PdR_2(PhCN)_2]$ (R = C_6F_5 or $C_6H_2F_3$-2,4,6) reacts with *cis*-$[MX_2L_2]$ (M = Ni, Pd or Pt; X = Cl, Br, I or SCN; L = phosphine or py) under mild conditions to give the corresponding asymmetric binuclear complexes listed in Table 1, according to equation (2).

$$cis\text{-}[PdR_2(PhCN)_2] + cis\text{-}[MX_2L_2] \longrightarrow [R_2Pd(\mu\text{-}X)_2ML_2] + 2PhCN \quad (2)$$

Complexes **1**, **3** and **6** were isolated as dichloromethane-solvated species, but the solvent was readily removed by heating at 125–130 °C. The substitution reactions (2) are stereospecific and no ligand rearrangement of L has been observed in any case. Moreover, when *trans*-$[PdCl_2(PEt_3)_2]$ was used as reactant the *gem* derivative **5** was also the reaction product, indicating that *trans* to *cis* isomerization of the chloro complex had taken place.

Analytical data, colours, yields and decomposition temperatures for the *gem* derivatives are collected in Table 1. Their acetone solutions are non-conducting and molecular weight determinations in chloroform or acetone solutions (Table 1) are in agreement with the proposed binuclear structures. The acetone and chloroform solutions show the same colour as the solids and a X-ray diffraction study carried out with a single crystal of $[(C_6F_5)_2Pd(\mu\text{-}Cl)_2Pt(PEt_3)_2]$ confirmed its binuclearity in the solid state.

The chloro-bridged complexes give in their infrared spectra bands assignable to the $Pd(\mu\text{-}Cl)_2M$ fragment (Table 1), which are about 10 cm⁻¹ lower than for the starting halogeno complex *cis*-$[PdCl_2L_2]$. The absorptions found at 2160 and 2130 cm⁻¹ for complex **11** are consistent with the presence of bridging thiocyanate.[12] The pentafluorophenyl derivatives show bands (1630, 1490, 1460, 1050 and 950 cm⁻¹) assignable to the C_6F_5 groups[13] as well as the split band at 800–780 cm⁻¹ (X-sensitive mode of C_6F_5)[14] which is characteristic of the *cis*-$Pd(C_6F_5)_2$ moiety.[15] Similarly, the infrared spectra of the trifluorophenyl

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† Di-μ-chloro-bis(pentafluorophenyl)-$2\kappa^2C^1$-bis(triethylphosphine)-$1\kappa^2P$-palladiumplatinum.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Relevant data for the binuclear complexes

Complex[a]	Colour	Yield (%)	Analysis (%)[b]		M.p.[c] (θ/°C)	M^b	ν(M–Cl)/cm^{-1}
			C	H			
1 $[(C_6F_5)_2Pd(\mu\text{-}Cl)_2Ni(dppe)]$	Orange	85	46.9 (47.1)	2.5 (2.5)	170	939[d] (968.1)	330, 310
2 $[(C_6H_2F_3)_2Pd(\mu\text{-}Cl)_2Ni(dppe)]$	Orange	89	50.6 (50.9)	3.3 (3.1)	160	874[d] (896.1)	325, 310
3 $[(C_6F_5)_2Pd(\mu\text{-}Cl)_2Pd(dppe)]$	Pale yellow	79	44.5 (44.9)	2.2 (2.4)	163	1030[d] (1015.8)	280, 255
4 $[(C_6H_2F_3)_2Pd(\mu\text{-}Cl)_2Pd(dppe)]$	Pale yellow	81	47.8 (48.3)	3.2 (3.0)	170	951[d] (943.8)	285, 255
5 $[(C_6F_5)_2Pd(\mu\text{-}Cl)_2Pd(PEt_3)_2]$	Pale yellow	63	32.8 (33.7)	3.7 (3.5)	178	870[e] (853.8)	290, 260
6 $[(C_6F_5)_2Pd(\mu\text{-}Cl)_2Pt(dppe)]$	White	74	41.0 (41.3)	2.3 (2.2)	178	1125[d] (1104.5)	280, 260
7 $[C_6H_2F_3)_2Pd(\mu\text{-}Cl)_2Pt(dppe)]$	White	84	43.6 (44.2)	2.8 (2.7)	166	1047[d] (1032.5)	290, 270
8 $[(C_6F_5)_2Pd(\mu\text{-}Cl)_2Pt(PEt_3)_2]$	Pale yellow	80	30.2 (30.6)	3.0 (3.2)	188	983[e] (942.5)	285, 260
9 $[(C_6F_5)_2Pd(\mu\text{-}Br)_2Pt(PEt_3)_2]$	Yellow	73	28.0 (27.9)	2.7 (2.9)	149	998[e] (1031.3)	
10 $[(C_6F_5)_2Pd(\mu\text{-}I)_2Pt(PEt_3)_2]$	Yellow-orange	75	25.5 (25.6)	2.7 (2.7)	164	1086[e] (1125.3)	
11 $[(C_6F_5)_2Pd(\mu\text{-}SCN)_2Pt(PEt_3)_2]$[f]	White	76	31.0 (31.6)	3.2 (3.0)	182	971[d] (987.5)	
12 $[(C_6F_5)_2Pd(\mu\text{-}Cl)_2Pt(PBu^n{}_3)_2]$	White	60	38.9 (38.9)	4.9 (4.9)	128	1152[e] (1110.5)	285, 265
13 $[(C_6F_5)_2Pd(\mu\text{-}Cl)_2Pt(PPh_2Me)_2]$	White	70	41.9 (41.2)	2.8 (2.4)	178	1148[e] (1106.5)	290, 270
14 $[(C_6F_5)_2Pd(\mu\text{-}Cl)_2Pt(py)_2]$[g]	Yellow	68	31.0 (30.6)	1.1 (1.1)	195	832[d] (864.5)	335, 315

[a] dppe = $Ph_2PCH_2CH_2PPh_2$, py = C_5H_5N. [b] Calculated values in parentheses. [c] Decomposition temperatures from thermogravimetry. [d] In Me_2CO. [e] In $CHCl_3$. [f] N 3.0 (2.8%). [g] N 3.1 (3.2%).

Table 2 NMR data (J in Hz) for the asymmetric binuclear complexes

Complex	^1H, δ($SiMe_4$)	^{19}F, δ($CFCl_3$) F_o	F_p	F_m	^{31}P-{^1H}, δ(H_3PO_4)
1[a]	7.3 (20 H, m, Ph) 2.4 (4 H, d, J_{PH} 17, CH_2)	−113.7	−161.4	−163.3	64.9
2[a]	8.1 (8 H, m, Ph) 7.7 (12 H, m, Ph) 6.3 (4 H, m, $C_6H_2F_3$) 2.7 (4 H, d, J_{PH} 18, CH_2)	−82.2	−119.0		62.1
3[a]	7.6 (20 H, m, Ph) 2.8 (4 H, d, J_{PH} 17, CH_2)	−115.3	−160.3	−163.5	74.1
4[a]	8.0 (8 H, m, Ph) 7.6 (12 H, m, Ph) 6.3 (4 H, m, $C_6H_2F_3$) 3.1 (4 H, d, J_{PH} 12, CH_2)	−82.0	−119.2		69.8
5[b]	1.8–1.0 (m, Et)	−117.4	−159.3	−162.5	38.6
6[a]	7.7 (20 H, m, Ph) 2.7 (4 H, d, J_{PH} 16, CH_2)	−115.1	−160.5	−163.5	46.0 (J_{PtP} 3746)
7[a]	8.0 (8 H, m, Ph) 7.6 (12 H, m, Ph) 6.3 (4 H, m, $C_6H_2F_3$) 2.7 (4 H, d, J_{PH} 12, CH_2)	−82.4	−118.8		43.2 (J_{PtP} 3732)
8[b]	2.0 (12 H, dq, $J_{PH} \approx J_{HH}$ 8, CH_2) 1.3 (18 H, dt, J_{PH} 18, J_{HH} 8, CH_3)	−116.1	−162.0	−164.9	11.6 (J_{PtP} 3615)
9[b]	2.1 (12 H, dq, J_{PH} 8.2, J_{HH} 7.5, CH_2) 1.3 (18 H, dt, J_{PH} 18, J_{HH} 7.5, CH_3)	−115.4	−162.0	−164.9	11.8 (J_{PtP} 3572)
10[b]	2.1 (12 H, dq, J_{PH} 8.8, J_{HH} 6.9, CH_2) 1.3 (18 H, dt, J_{PH} 17.6, J_{HH} 7.5, CH_3)	−114.4	−162.2	−164.7	8.9 (J_{PtP} 3420)
11[a]	2.1 (12 H, m, CH_2) 1.3 (18 H, m, CH_3)	−112.8 −113.9	−161.7	−164.3	−0.5 (J_{PtP} 3086)
12[b]	1.5 [36 H, br, $(CH_2)_3$] 1.0 (18 H, t, J_{HH} 6, CH_3)	−116.2	−162.3	−165.1	−3.5 (J_{PtP} 3622)
13[b]	7.4 (20 H, m, Ph) 1.9 (6 H, d, J_{PH} 10.8, CH_3; with satellites, J_{PtH} 36)	−115.9	−162.0	−164.9	−1.7 (J_{PtP} 3755)
14[a]	8.5 (4 H, m, py) 8.0 (2 H, m, py) 7.3 (4 H, m, py)	−115.1	−160.3	−163.5	

[a] In $(CD_3)_2CO$. [b] In $CDCl_3$.

derivatives show strong bands at 1580, ~~1395~~, 1090, 990 and 730 cm^{-1} due to internal vibrational modes of the $C_6H_2F_3$-2,4,6 groups,[11] and a split band at *ca.* 830 cm^{-1} which appears to be related to the *cis* geometry of the $Pd(C_6H_2F_3)_2$ group.[11,16]

The ^1H, ^{19}F and ^{31}P-{^1H} NMR data for the binuclear complexes are collected in Table 2. Except for complex **11**, the ^{19}F NMR spectra show the expected patterns of three (C_6F_5) or two ($C_6H_2F_3$) resonance signals corresponding to two equivalent fluorophenyl groups freely rotating around the Pd–C bonds. Two signals for the *o*-F atoms in the spectrum of complex **11** are attributed to a structure of the type $[(C_6F_5)_2Pd(\mu\text{-}SCN)(\mu\text{-}NCS)Pt(PEt_3)_2]$. A similar spectrum was observed for the anionic species $[(C_6H_2F_3)_2Pd(\mu\text{-}SCN)(\mu\text{-}NCS)Pd(C_6H_2F_3)_2]^{2-}$, for which an X-ray diffraction study confirmed the centrosymmetric structure.[11] The ^{31}P-{^1H} NMR spectrum of complex **11** also supports the above

Table 3 Fractional atomic coordinates (× 10^4) for complex **8**

Atom	*X/a*	*Y/b*	*Z/c*
Pt	327.1(3)	2875.9(2)	495.8(2)
Pd	1203.8(6)	2566.6(4)	−1895.0(4)
Cl(1)	2626(2)	2714(2)	5(2)
Cl(2)	−737(3)	3193(2)	−1317(2)
P(1)	−1888(2)	3127(1)	786(1)
P(2)	1641(2)	2468(2)	2130(1)
F(2)	−480(7)	667(4)	−3488(4)
F(3)	−2535(9)	491(5)	−5427(5)
F(4)	−3350(8)	2121(5)	−6452(4)
F(5)	−2075(10)	3945(5)	−5441(5)
F(6)	−33(8)	4141(4)	−3488(4)
F(8)	3384(7)	3541(4)	−3216(5)
F(9)	5556(8)	2812(5)	−3840(5)
F(10)	6165(7)	959(5)	−3369(5)
F(11)	4562(7)	−173(4)	−2303(5)
F(12)	2393(6)	535(4)	−1661(5)
C(1)	−141(9)	2425(6)	−3394(6)
C(2)	−816(9)	1485(6)	−3948(6)
C(3)	−1874(10)	1403(7)	−4951(7)
C(4)	−2275(12)	2232(8)	−5435(7)
C(5)	−1645(10)	3148(7)	−4943(6)
C(6)	−577(11)	3229(6)	−3925(7)
C(7)	2814(8)	2073(6)	−2397(6)
C(8)	3657(9)	2611(6)	−2946(6)
C(9)	4772(9)	2246(7)	−3276(7)
C(10)	5065(10)	1296(8)	−3052(7)
C(11)	4279(8)	756(6)	−2533(6)
C(12)	3147(9)	1128(6)	−2197(6)
C(13)	−3318(9)	3511(6)	−356(6)
C(14)	−2910(13)	4607(7)	−606(9)
C(15)	−3013(9)	1995(6)	1038(6)
C(16)	−3342(15)	1194(6)	172(8)
C(17)	−1617(9)	4075(6)	1842(7)
C(18)	−3075(12)	4288(8)	2003(8)
C(19)	613(10)	2113(7)	3085(6)
C(20)	1667(13)	1938(8)	4186(7)
C(21)	3266(9)	3432(7)	2807(6)
C(22)	2772(11)	4363(7)	3192(9)
C(23)	2597(10)	1408(6)	2029(6)
C(24)	1421(13)	489(7)	1366(9)
H(141)	−1934(13)	4676(7)	−903(9)
H(142)	−2612(13)	5099(7)	98(9)
H(143)	−3917(13)	4803(7)	−1200(9)
H(161)	−2263(15)	985(6)	139(8)
H(162)	−3945(15)	1741(6)	−572(8)
H(163)	−4072(15)	554(6)	318(8)
H(201)	1688(13)	1152(8)	4237(7)
H(202)	1229(13)	2208(8)	4783(7)
H(203)	2837(13)	2326(8)	4311(7)
H(221)	2171(11)	4175(7)	3755(9)
H(222)	2001(11)	4659(7)	2520(9)
H(223)	3798(11)	4913(7)	3559(9)
H(231)	3096(10)	1169(6)	2811(6)
H(232)	3516(10)	1634(6)	1696(6)
H(241)	2047(13)	−117(7)	1335(9)
H(242)	920(13)	715(7)	578(9)
H(243)	500(13)	250(7)	1693(9)

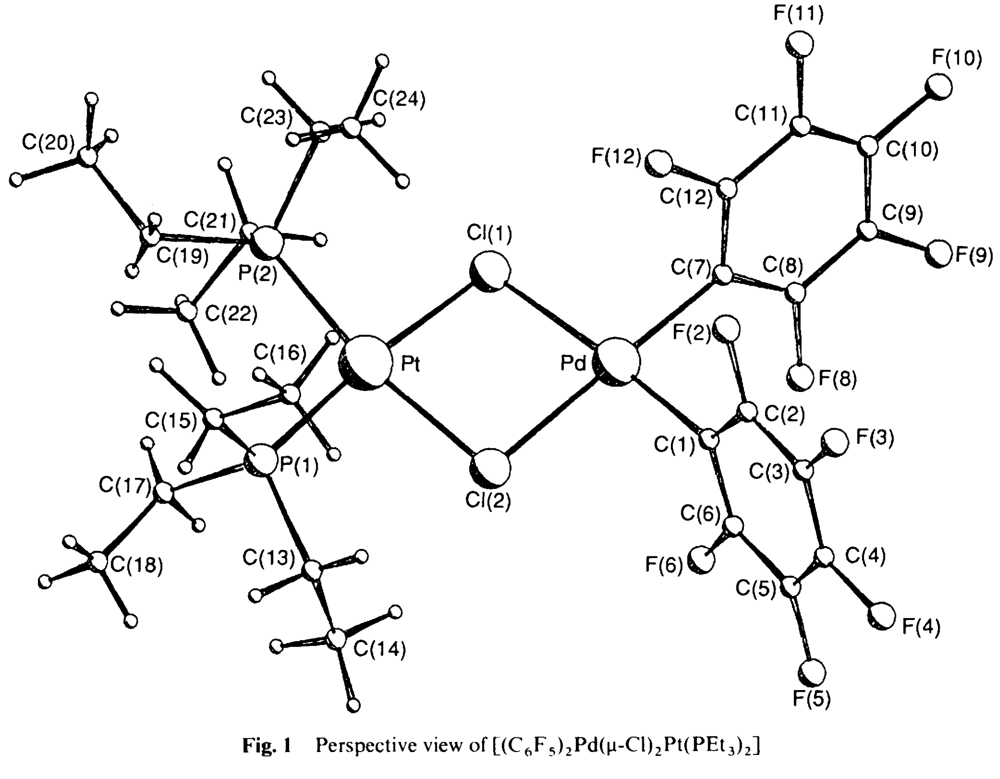

Fig. 1 Perspective view of $[(C_6F_5)_2Pd(\mu\text{-}Cl)_2Pt(PEt_3)_2]$

assignment, since it consists of a central doublet flanked by the expected satellites by coupling to ^{195}Pt.

X-Ray Crystal Structure of $[(C_6F_5)_2Pd(\mu\text{-}Cl)_2Pt(PEt_3)_2]$ **8**.—Fig. 1 represents a perspective view of the molecule with the atom numbering. Fractional atomic coordinates are listed in Table 3, and Table 4 shows bond lengths and angles. The molecule shows a planar skeleton with two metal atoms (Pd, Pt) in a square-planar configuration, apart from phosphine substituents and C_6F_5 groups, bridged by two chlorine atoms. Two phosphine and two C_6F_5 groups are linked terminally around platinum and palladium respectively, completing the co-ordination of each metal atom. The bond angles have expected values and give no indication of steric strain.[17] The phosphine has a strong *trans* influence, lengthening the bonds Pt–Cl *trans* to it. So, the Pt–Cl bridging distances are 2.430(2) and 2.386(2) Å, giving a weighted mean distance of 2.408(2) Å, significantly longer than the previously reported distance of 2.34(1) Å.[18]

Table 4 Bond lengths (Å) and angles (°) with their estimated standard deviations

Cl(1)–Pt	2.430(2)	C(10)–F(10)	1.342(9)
Cl(2)–Pt	2.386(2)	C(11)–F(11)	1.353(8)
P(1)–Pt	2.251(2)	C(12)–F(12)	1.350(8)
P(2)–Pt	2.263(2)	C(2)–C(1)	1.417(10)
Cl(1)–Pd	2.449(2)	C(6)–C(1)	1.361(11)
Cl(2)–Pd	2.402(2)	C(3)–C(2)	1.373(11)
C(1)–Pd	1.980(7)	C(4)–C(3)	1.357(13)
C(7)–Pd	1.992(7)	C(5)–C(4)	1.355(12)
C(13)–P(1)	1.814(7)	C(6)–C(5)	1.392(11)
C(15)–P(1)	1.826(7)	C(8)–C(7)	1.376(10)
C(17)–P(1)	1.825(7)	C(12)–C(7)	1.380(10)
C(19)–P(2)	1.846(8)	C(9)–C(8)	1.381(11)
C(21)–P(2)	1.809(8)	C(10)–C(9)	1.381(12)
C(23)–P(2)	1.820(7)	C(11)–C(10)	1.315(11)
C(2)–F(2)	1.316(9)	C(12)–C(11)	1.404(10)
C(3)–F(3)	1.348(10)	C(14)–C(13)	1.556(12)
C(4)–F(4)	1.392(10)	C(16)–C(15)	1.501(12)
C(5)–F(5)	1.332(10)	C(18)–C(17)	1.483(12)
C(6)–F(6)	1.318(9)	C(20)–C(19)	1.529(12)
C(8)–F(8)	1.364(9)	C(22)–C(21)	1.540(12)
C(9)–F(9)	1.374(9)	C(24)–C(23)	1.568(12)
Cl(2)–Pt–Cl(1)	83.1(1)	C(4)–C(3)–C(2)	119.9(8)
P(1)–Pt–Cl(1)	173.4(1)	C(3)–C(4)–F(4)	118.4(8)
P(1)–Pt–Cl(2)	90.8(1)	C(5)–C(4)–F(4)	120.7(9)
P(2)–Pt–Cl(1)	87.8(1)	C(5)–C(4)–C(3)	120.9(7)
P(2)–Pt–Cl(2)	170.4(1)	C(4)–C(5)–F(5)	119.2(7)
P(2)–Pt–P(1)	98.5(1)	C(6)–C(5)–F(5)	121.8(8)
Cl(2)–Pd–Cl(1)	82.3(1)	C(6)–C(5)–C(4)	119.0(8)
C(1)–Pd–Cl(1)	174.3(2)	C(1)–C(6)–F(6)	121.5(7)
C(1)–Pd–Cl(2)	92.6(2)	C(5)–C(6)–F(6)	115.7(7)
C(7)–Pd–Cl(1)	98.4(2)	C(5)–C(6)–C(1)	122.8(8)
C(7)–Pd–Cl(2)	178.6(2)	C(8)–C(7)–Pd	124.7(5)
C(7)–Pd–C(1)	86.6(3)	C(12)–C(7)–Pd	119.9(5)
Pd–Cl(1)–Pt	94.0(1)	C(12)–C(7)–C(8)	115.4(6)
Pd–Cl(2)–Pt	96.4(1)	C(7)–C(8)–F(8)	120.2(6)
C(13)–P(1)–Pt	113.6(2)	C(9)–C(8)–F(8)	116.7(7)
C(15)–P(1)–Pt	113.4(3)	C(9)–C(8)–C(7)	123.1(7)
C(15)–P(1)–C(13)	100.7(4)	C(8)–C(9)–F(9)	120.3(8)
C(17)–P(1)–Pt	114.8(2)	C(10)–C(9)–F(9)	120.4(7)
C(17)–P(1)–C(13)	104.7(4)	C(10)–C(9)–C(8)	119.2(7)
C(17)–P(1)–C(15)	108.4(4)	C(9)–C(10)–F(10)	118.3(8)
C(19)–P(2)–Pt	121.0(3)	C(11)–C(10)–F(10)	122.0(8)
C(21)–P(2)–Pt	111.3(3)	C(11)–C(10)–C(9)	119.6(7)
C(21)–P(2)–C(19)	106.5(4)	C(10)–C(11)–F(11)	120.2(7)
C(23)–P(2)–Pt	109.9(2)	C(12)–C(11)–F(11)	118.7(7)
C(23)–P(2)–C(19)	103.6(4)	C(12)–C(11)–C(10)	121.1(7)
C(23)–P(2)–C(21)	102.9(4)	C(7)–C(12)–F(12)	120.5(6)
C(2)–C(1)–Pd	122.3(5)	C(11)–C(12)–F(12)	117.9(6)
C(6)–C(1)–Pd	121.5(6)	C(11)–C(12)–C(7)	121.6(7)
C(6)–C(1)–C(2)	116.0(7)	C(14)–C(13)–P(1)	114.4(6)
C(1)–C(2)–F(2)	120.1(6)	C(16)–C(15)–P(1)	111.2(6)
C(3)–C(2)–F(2)	118.5(7)	C(18)–C(17)–P(1)	115.4(6)
C(3)–C(2)–C(1)	121.3(7)	C(20)–C(19)–P(2)	115.2(6)
C(2)–C(3)–F(3)	119.1(8)	C(22)–C(21)–P(2)	113.8(6)
C(4)–C(3)–F(3)	121.0(7)	C(24)–C(23)–P(2)	112.6(6)

In the same way, the Pd–Cl distances [2.449(2) and 2.402(2) Å] are longer than the value expected for a bridging Pd–Cl distance.[19,20] The CH_2 group of the phosphine lies on the side of the phosphorus atom remote from the terminal CH_3 group of the other phosphine, in order to minimize steric interaction between them. The distances C–F, C–C, Pd–C and Pt–P are similar to values in the literature.

The shortest intermolecular contact between non-hydrogen atoms is F(11)$\cdots$F(4^{i}) (2.971 Å; i $-x$, $-y$, -1 $-z$). The crystal packing may be regarded as a three-dimensional array of planar molecules stabilized by van der Waals interactions.

Experimental

Carbon, H and N analyses were carried out with a Perkin-Elmer 240C instrument. Infrared spectra were recorded on a Perkin-Elmer 1430 spectrophotometer using Nujol mulls between polyethylene sheets, proton, ^{19}F, and ^{31}P NMR spectra on a Varian FT 80A or a Bruker AC 200E spectrometer. Molecular weights were determined with a Knauer 11.00 vapour-pressure osmometer. Conductance measurements were performed with a Crison 525 conductimeter (in acetone, $c \approx 5 \times 10^{-4}$ mol dm^{-3}). Decomposition temperatures were determined under a nitrogen atmosphere with a Mettler TG 50 thermobalance (heating rate 10 °C min^{-1}). All the solvents were dried by conventional methods. The complex *cis*-$[PdR_2(PhCN)_2]$ (R = C_6F_5[10] or $C_6H_2F_3$-2,4,6[11]) and the halogeno complexes *cis*-$[MX_2L_2]$[21] were prepared as described elsewhere.

Preparation of the Complexes.—$[R_2Pd(\mu\text{-}X)_2ML_2]$ **1**–**14** (*see* Table 1). Complexes **1**–**14** were obtained by treating *cis*-$[PdR_2(PhCN)_2]$ with *cis*-$[MX_2L_2]$ (molar ratio 1:1) in CH_2Cl_2 according to the following general method. To a dichloromethane (10 cm^3) solution of the *cis*-$[PdR_2(PhCN)_2]$ (0.174 mmol) was added *cis*-$[MX_2L_2]$ (0.174 mmol), and the solution was stirred at room temperature for 30 min. It was then concentrated under reduced pressure to *ca*. one fifth of the initial volume, and hexane was added to precipitate the binuclear complexes, which were filtered off, washed with hexane and air-dried. The individual yields are listed in Table 1. NMR spectra of complexes **1**, **3** and **6** gave evidence of the presence of one dichloromethane molecule (δ 5.7) which was removed by heating at *ca*. 130 °C.

X-Ray Structure Determination of Complex **8**.—*Crystal data*. $C_{24}H_{30}Cl_2F_{10}P_2PdPt$, M = 942.5, triclinic, space group $P\bar{1}$, a = 9.141(7), b = 13.646(3), c = 13.384(5) Å, α = 91.29(2), β = 108.53(3), γ = 98.48(4)°, U = 1561.2(6) Å^3, Z = 2, D_c = 1.874 g cm^{-3}, λ(Mo-Kα) = 0.710 69 Å, μ = 53.9 cm^{-1}, F(000) = 896, T = 298 K.

Data collection and processing. A single crystal with approximate dimensions of 0.25 × 0.4 × 0.8 mm was mounted on a Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator for Mo-Kα radiation. Accurate cell parameters were obtained by least-squares refinement of the setting angles of 25 reflections with $6 \leqslant \theta \leqslant 13$. The ω–2θ scan method was used with scan width (1.0 + 0.35 tanθ)°. Three orientation and three intensity-control reflections were checked every 50 reflections and every hour respectively and showed no significant variation.

Structure analysis and refinement. The structure was solved by direct methods[22] and refined by full-matrix least-squares techniques.[23] Anisotropic thermal parameters were used for non-H atoms and a global isotropic thermal parameter was applied to H atoms. From 4610 independent reflections, 4241 [$> 2.5\sigma(I)$] were included in the final refinement cycle giving R 0.042 and R' = 0.046 with $w = [\sigma^2(F) + 0.004\,177F^2]^{-1}$. The residual peaks in the final Fourier difference synthesis were located close to the metal atoms. Scattering factors were taken from ref. 24. Molecular drawings were made with the PLUTO program.[25]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

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