Synthesis, Molecular Structure (M = Pd, X = OH) and Reactivity of Trinuclear Asymmetric Complexes $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2M(\mu\text{-}X)_2Pt(PPh_3)_2]$ (M = Pd or Pt; X = Cl or OH)†

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The tetranuclear complexes $[NBu_4]_2[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2M(\mu\text{-}Cl)_2M(\mu\text{-}PPh_2)_2Pt(C_6F_5)_2]$ (M = Pd or Pt) reacted with $AgClO_4$ and *cis*-$[PtCl_2(PPh_3)_2]$ in dichloromethane–acetone affording the neutral homo- or hetero-metallic asymmetric species $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2M(\mu\text{-}Cl)_2Pt(PPh_3)_2]$ **1** and **2**. Treatment of their CH_2Cl_2 solutions with KOH in methanol rendered the corresponding μ-hydroxo derivatives **3** and **4** which reacted with HX′ (X′ = Cl, Br, SPh, NHC_6H_4Me-*p* or PPh_2) to afford $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2M(\mu\text{-}X)(\mu\text{-}X')Pt(PPh_3)_2]$ (X = X′ = Cl **1**, **2**; Br **5**, **6**; SPh **7**, **8**; X = OH, X′ = NHC_6H_4Me-*p* **9**, **10**; X = OH, X′ = PPh_2 **11**, **12**). The structure of **3** has been determined by single-crystal X-ray diffraction.

Phosphido groups have proven to be excellent bridging ligands which due to their flexibility are able to support a wide range of bonding and non-bonding M–M distances. Thus, this type of ligand has been widely used as building blocks in the preparation of a great variety of interesting polynuclear complexes.[2–9] In addition, the stability of the bridging system $M(\mu\text{-}PR_2)_xM'$ allows, in most of cases, the retention of the polynuclear framework during chemical reactions.[10–13]

In the last few years we have prepared some polynuclear homo- or hetero-metallic palladium(II) or platinum(II) pentafluorophenyl complexes containing bridging diphenylphosphide ligands and the tetranuclear derivatives $[NBu_4]_2[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2M(\mu\text{-}Cl)_2M(\mu\text{-}PPh_2)_2Pt(C_6F_5)_2]$ (M = Pd or Pt)[14] **A** have been used for the syntheses of dinuclear complexes with donor–acceptor Pt–M bonds $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2M(PPh_3)]$ (M = Pd or Pt).[1] Tri- or tetranuclear palladium or platinum complexes containing a linear array of metal centres joined together by a double bridging system are rather infrequent;[14–18] they are usually symmetrical.

In this paper we describe the syntheses, structural characterization and some reactions of trinuclear asymmetric complexes of general formula $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2M(\mu\text{-}X)_2Pt(PPh_3)_2]$ (X = Cl or OH) which have been prepared from the tetranuclear anionic derivatives **A** and which do not contain metal–metal bonds. As expected, in all cases the fragment '$Pt(\mu\text{-}PPh_2)_2M$' is preserved during the reaction processes.

Results and Discussion

Synthesis of Complexes **1**–**4**.—The synthetic strategy for the preparation of the neutral, trinuclear and asymmetric complexes $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2M(\mu\text{-}Cl)_2Pt(PPh_3)_2]$ (M = Pd **1** or Pt **2**) involves reaction of the tetranuclear derivatives $[NBu_4]_2[\{(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2M(\mu\text{-}Cl)\}_2]$ (M = Pd or Pt)[14] with *cis*-$[PtCl_2(PPh_3)_2]$ and $AgClO_4$ (molar ratio 1 : 2 : 2) in CH_2Cl_2-acetone which results in the precipitation of AgCl and the isolation of complexes **1** or **2** as yellow solids. The $AgClO_4$ was used as an halide scavenger and, considering the well known lability of the '$M(\mu\text{-}Cl)_2Pt$' bridging system in the tetranuclear phosphido complexes **A**,[1,14] a plausible pathway is: (*a*) initial formation of the binuclear solvento complexes [equation (1)] and (*b*) displacement of the acetone in these neutral solvento complexes by the metalloligand *cis*-$[PtCl_2(PPh_3)_2]$ [equation (2)] (M = Pd **1** or Pt **2**). Since **1** and **2** are non-conducting in acetone solution, an ionic formulation such as $[\{Pt(\mu\text{-}Cl)(PPh_3)_2\}_2][\{(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2M(\mu\text{-}Cl)\}_2]$ for these complexes {as a result of the reaction of *cis*-$[PtCl_2(PPh_3)_2]$ with $AgClO_4$} can be ruled out.

$$[NBu_4]_2[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2M(\mu\text{-}Cl)_2M(\mu\text{-}PPh_2)_2Pt(C_6F_5)_2] + 2AgClO_4 \longrightarrow \downarrow 2AgCl + 2NBu_4ClO_4 + 2[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2M(Me_2CO)_2] \quad (1)$$

$$[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2M(Me_2CO)_2] + cis\text{-}[PtCl_2(PPh_3)_2] \longrightarrow [(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2M(\mu\text{-}Cl)_2Pt(PPh_3)_2] \quad (2)$$

On the other hand, if dichloromethane solutions of complexes **1** and **2** are treated with KOH in methanol (molar ratio 1 : 2) a substitution reaction takes place and the unusual mixed phosphide hydroxide-bridged complexes are obtained [equation (3)] (M = Pd **3** or Pt **4**).

$$[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2M(\mu\text{-}Cl)_2Pt(PPh_3)_2] + 2\,KOH \longrightarrow [(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2M(\mu\text{-}OH)_2Pt(PPh_3)_2] + 2\,KCl \quad (3)$$

Spectroscopic Characterization of Complexes **1**–**4**.—The IR spectra of complexes **1**–**4** show characteristic absorptions of the pentafluorophenyl group[19,20] near 1500, 1050, 950 and 800 cm^{-1}. The ones due to the X-sensitive mode of the C_6F_5 groups ($\approx 800\ cm^{-1}$) appear in all cases as two bands of similar intensities, as expected for complexes containing two C_6F_5 groups bonded to the same metal centre and in *cis* position.[19,20] The IR spectra show also, in all cases, a strong absorption near 550 cm^{-1} (assigned as the first overtone of the asymmetric PC_3 deformation mode) which according to Mastin[21] can be indicative of the presence of two PPh_3 ligands bonded to the same metal centre in *cis* position; however since internal absorptions of the PPh_2 group also appear in this region, this absorption cannot be used in these cases as the basis of a

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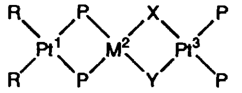
† Polynuclear Homo- or Hetero-metallic Palladium(II)–Platinum(II) Pentafluorophenyl Complexes containing Bridging Diphenylphosphido Ligands. Part 3.[1]

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Table 1 $^{31}P-\{^1H\}$ NMR data for complexes **1–6**, **9**, **10**, **13** and **14**



Complex	PPh$_2$ region				PPh$_3$ region		
	δ_P	J(PP)	J(Pt^{1}P)	J(Pt^{2}P)	δ_P	J(PP)	J(Pt^{3}P)
1 M = Pd, X = Y = Cl	−127.40		1780.13		14.13		3767.12
2 M = Pt, X = Y = Cl	−135.61		1942.16	2582.06	15.10		3780.36
3 M = Pd, X = Y = OH	−126.76		1776.06		10.67		3565.36
4 M = Pt, X = Y = OH	−147.98		1935.01	2548.92	5.52		3625.97
5 M = Pd, X = Y = Br	−125.09		1770.97		14.71		3682.54
6 M = Pt, X = Y = Br	−134.97		1920.86	2521.05	15.23		3680.13
9 M = Pd, X = OH, Y = NHR′	−110.74	200.34	*a*		13.88	15.34	2954.67
	−116.42				5.02		3713.37
10 M = Pt, X = OH, Y = NHR′	−133.03	144.26	*b*	*b*	13.42	16.07	3235.17
	−134.42				3.94		3760.87
13 M = Pd, X = OH, Y = Br	−124.57	214.98	*c*		18.11	15.98	3990.20
	−130.11				4.46		3306.79
14 M = Pt, X = OH, Y = Cl	−131.91	156.63	1967.00	2659.10	16.51	17.67	4045.06
	−145.11		1899.01	2527.96	5.43		3401.50

R = C_6F_5, R′ = C_6H_4Me-*p*. [a] $\frac{1}{2}[J(AX) + J(BX)]$ = 1756.22 Hz. [b] Platinum satellites appear as very complex overlapped multiplets and J(PtP) cannot be extracted. [c] $\frac{1}{2}[J(AX) + J(BX)]$ = 1760.26 Hz.

Table 2 Selected bond lengths (Å) and angles (°)

Pt(1)–P(1)	2.226(3)	Pt(1)–P(2)	2.238(3)
Pt(1)–O(1)	2.045(6)	Pt(1)–O(2)	2.089(6)
Pt(2)–P(3)	2.281(3)	Pt(2)–P(4)	2.316(3)
Pt(2)–C(1)	2.080(10)	Pt(2)–C(7)	2.065(11)
Pd–P(3)	2.226(3)	Pd–P(4)	2.259(3)
Pd–O(1)	2.128(6)	Pd–O(2)	2.194(6)
P(1)–Pt(1)–P(2)	97.9(1)	P(1)–Pt(1)–O(1)	92.5(2)
P(2)–Pt(1)–O(1)	169.2(2)	P(1)–Pt(1)–O(2)	171.8(2)
P(2)–Pt(1)–O(2)	90.3(2)	O(1)–Pt(1)–O(2)	79.3(3)
P(3)–Pt(2)–P(4)	74.1(1)	P(3)–Pt(2)–C(1)	175.1(3)
P(4)–Pt(2)–C(1)	101.2(3)	P(3)–Pt(2)–C(7)	94.5(3)
P(4)–Pt(2)–C(7)	166.6(3)	C(1)–Pt(2)–C(7)	90.3(4)
P(3)–Pd–P(4)	76.3(1)	P(3)–Pd–O(1)	99.1(2)
P(4)–Pd–O(1)	173.3(2)	P(3)–Pd–O(2)	174.0(2)
P(4)–Pd–O(2)	109.2(2)	O(1)–Pd–O(2)	75.2(2)
Pt(2)–P(3)–Pd	104.4(1)	Pt(2)–P(4)–Pd	102.3(1)
Pt(1)–O(1)–Pd	103.3(3)	Pt(1)–O(2)–Pd	99.6(3)

conclusive structural assignment. Complexes **1** and **2** show absorptions near 270 cm^{-1} which can be assigned to the bridging 'Pt(μ-Cl)$_2$M' skeleton and **3** and **4** show an absorption at *ca.* 3600 cm^{-1} which is due to ν(OH).[22–25]

The ^1H NMR spectra of complexes **3** and **4** in CD_2Cl_2 show high-field resonances (δ −1.37 **3**, −0.87 **4**) assigned to the OH groups and, as in other cases,[25–27] no platinum satellites are observed. Complexes **1–4**, which contain two equivalent C_6F_5 groups, should display ^{19}F NMR spectra corresponding to an AA′MXX′ system. However (see Experimental section) signals due to *m*- and *p*-F appear, in all cases, overlapped and a full assignment cannot be made. For the *o*-F atoms a unique signal with platinum satellites is observed in all cases and the relative intensities of the *o*- and *m*- + *p*-F signals (4 : 6) are in accord with the proposed structure.

The ^{31}P NMR spectral data (in CD_2Cl_2) have been collected in Table 1. Complexes **1–4** show two signals in very different regions. The signal due to the P atoms of the PPh$_3$ ligands, which are equivalent, appears as a singlet (δ *ca.* 14–5) with platinum satellites, the ^1J(PtP) values being in the range found for other platinum(II) phosphine complexes.[28] Signals due to the equivalent bridging PPh$_2$ ligands appear, in all cases, as an upfield singlet; **1** and **3** show only one pair of platinum satellites, while **2** and **4** show two pairs. In the last two cases, because of the large *trans* influence of the pentafluorophenyl groups,[29] the lower ^1J(PtP) values are due to coupling with the ^{195}Pt atom which is bonded to these groups. Similar ^1J(PtP) values have been found for **1** and **3**. The position of the signals due to the PPh$_2$ ligands suggests[1,14,30,31] that the metal atoms that are bridged by the phosphido groups are not bonded to each other. This is in accord with the structure of **3**, which is described below.

Crystal Structure of [(C_6F_5)$_2$Pt(μ-PPh$_2$)$_2$Pd(μ-OH)$_2$Pt(PPh$_3$)$_2$] **3**.—The structure of complex **3** has been determined by a single-crystal X-ray diffraction study and confirms the spectroscopic data. Selected bond distances and angles are listed in Table 2. As can be seen in Fig. 1, **3** is a trinuclear asymmetric compound formed by three slightly distorted square-planar environments which are held together by (μ-OH)$_2$ and (μ-PPh$_2$)$_2$ bridging ligands.

Complex **3** can also be considered as formed by the co-ordination of the distorted square-planar *cis*-(OH)$_2$Pt(PPh$_3$)$_2$ and *cis*-(C_6F_5)$_2$Pt(μ-PPh$_2$)$_2$ units to a palladium(II) centre which also results in a distorted square-planar environment. The Pt(1) ··· Pd [3.273(1) Å] and the Pt(2) ··· Pd [3.562(1) Å] distances are long enough to indicate that no metal–metal bonds are present in this compound. This is in accord with qualitative molecular-orbital calculations, carried out for systems of this type, which indicate that no through-ring metal–metal interactions are expected.[32] The long Pt ··· Pd distances imply large Pt–O–Pd [99.6(3), 103.3(3)°] and Pd–P–Pt angles [102.3(1), 104.4(1)°]. In addition, the small O–Pt–O [79.3(3)°], O–Pd–O [75.2(2)°] and P–Pd–P [76.3(1)°] and P–Pt–P [74.1(1)°] angles are also a consequence of the long Pt ··· Pd distances. The bridging M–P [Pt(2)–P(4) 2.316(3), Pt(2)–P(3) 2.281(3), Pd–P(4) 2.259(3), Pd–P(3) 2.226(3) Å] and M–O [Pd–O(2) 2.194(6), Pd–O(1) 2.128(6), Pt(1)–O(1) 2.045(6), Pt(1)–O(2) 2.089(6) Å] distances are in the range found in other phosphido[1,14,31,33–36] or hydroxo[24,37–39] palladium and platinum complexes. The Pt(2)–C distances are similar to those found in [(C_6F_5)$_2$Pt(μ-PPh$_2$)$_2$Pt(phen)][14] (phen = 1,10-phenanthroline) and the Pt(1)–P$_{terminal}$ distances are similar to the corresponding distances found in platinum phosphine complexes.[40]

Each metal centre is located in a practically planar environment and the whole molecule displays a boat structure (Fig. 2) and the dihedral angles between the co-ordination plane

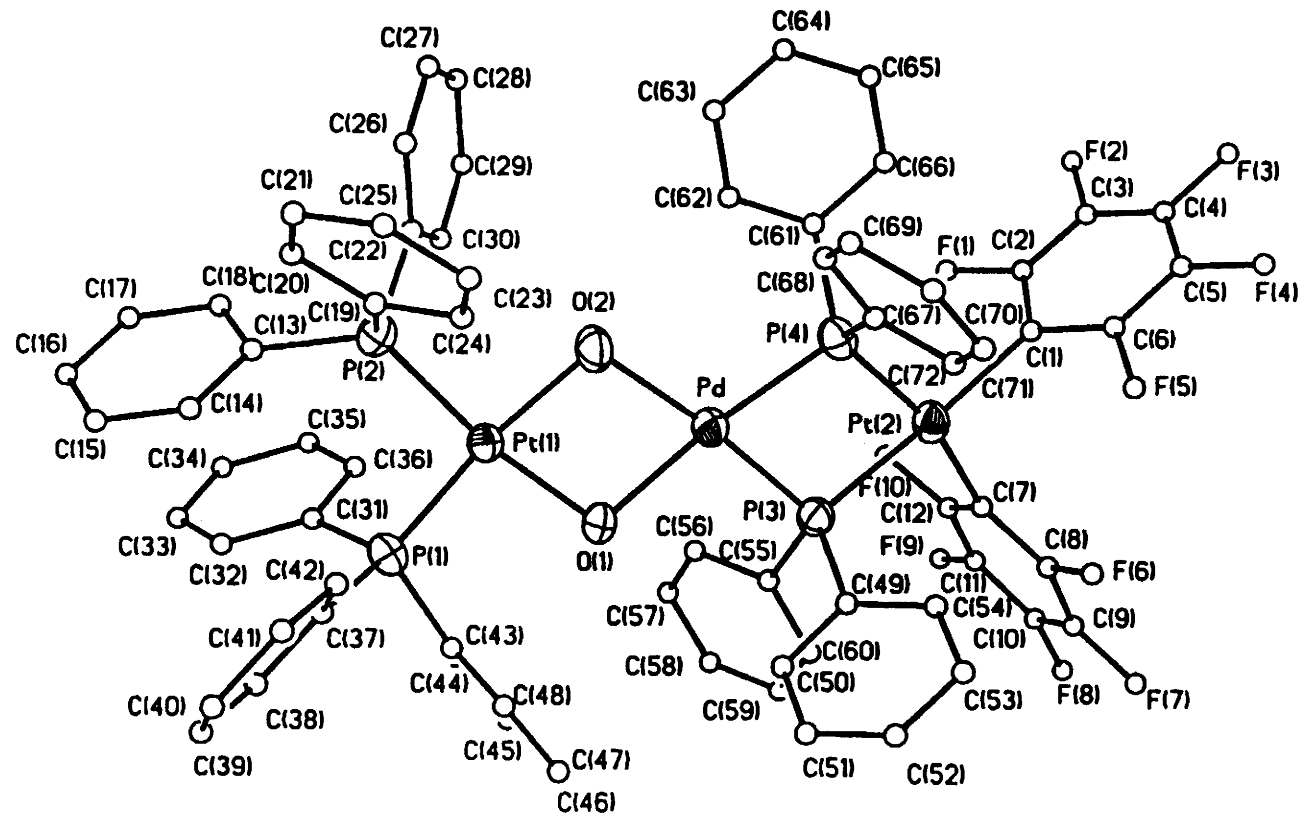


Fig. 1 Structure of $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pd(\mu\text{-}OH)_2Pt(PPh_3)_2]$ **3** with the atomic numbering scheme

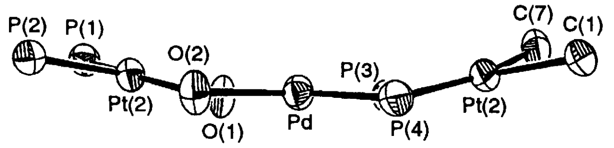
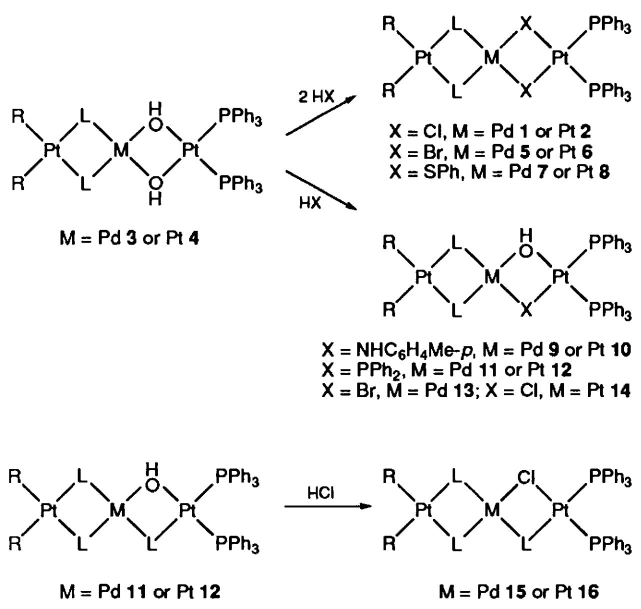


Fig. 2 Skeletal side-on view of the molecule **3**



Scheme 1 R = C_6F_5, L = PPh_2

of palladium and the co-ordination planes of Pt(1) and Pt(2) respectively are 12.3 and 16.2°.

Reactivity of Complexes **3** *and* **4** *towards some Protic Reagents*.—The well recognised reactivity of hydroxo complexes,[24,39,41-44] which have been used as intermediates for the synthesis of other transition-metal complexes,[41] prompted us to study the reactions of **3** and **4** with some protic reagents, HX (see Scheme 1). So, when dichloromethane solutions of **3** or **4** were treated with aqueous HCl, HBr (needs an excess over that stoichiometrically required) or with HSPh, the corresponding $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2M(\mu\text{-}X)_2Pt(PPh_3)_2]$ (X = Cl, M = Pd **1** or Pt **2**; X = Br, M = Pd **5** or Pt **6**; X = SPh, M = Pd **7** or Pt **8**) are obtained.

If less acidic reagents are used a partial substitution of the $M(\mu\text{-}OH)_2Pt$ bridging system takes place and complexes containing the $M(\mu\text{-}OH)(\mu\text{-}X)Pt$ moiety are formed even if an excess of HX is used. Complexes **3** and **4** react with *p*-toluidine in CH_2Cl_2 (molar ratio 1:2) giving the trinuclear complexes $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2M(\mu\text{-}NHC_6H_4Me\text{-}p)(\mu\text{-}OH)Pt(PPh_3)_2]$ (M = Pd **9** or Pt **10**). This is in contrast with the facile conversion of the '$Pt(\mu\text{-}OH)_2Pt$' species, in cationic platinum complexes, into the corresponding '$Pt(\mu\text{-}NH_2)_2Pt$' ones by treating the former with ammonia,[44] although a similar behaviour has been observed in neutral dinuclear palladium(II) derivatives.[42]

The reactions of complexes **3** and **4** with $PHPh_2$ in CH_2Cl_2 (molar ratio 1:2) render a mixture from which the trinuclear derivatives $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2M(\mu\text{-}OH)(\mu\text{-}PPh_2)Pt(PPh_3)_2]$ (M = Pd **11** or Pt **12**) are isolated in very low yields (12 and 10% respectively). If the reactions are carried out in 1:1 molar ratio **11** and **12** are obtained in higher yields (44 and 32% respectively). On the other hand, attempts to achieve complete substitution of the $(\mu\text{-}OH)_2$ bridging system by increasing the amount of $PHPh_2$ (molar ratio 1:3) did not give the expected results since, in both cases, a mixture of complexes which have not been separated is formed. The ^{31}P NMR spectrum of the resulting mixture from **4** shows several resonances of which those corresponding to **12** and $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(PHPh_2)_2]$[45] can be identified.

Similar complexes containing the bridging '$M(\mu\text{-}OH)(\mu\text{-}X)Pt$' system can also be prepared by treating **3** or **4** with stronger acids in adequate (1 : 1) molar ratio. Thus trinuclear complexes $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2M(\mu\text{-}OH)(\mu\text{-}X)Pt(PPh_3)_2]$ (M = Pd, X = Br **13**; M = Pt, X = Cl **14**) have been prepared through the reaction of **3** or **4** in CH_2Cl_2 with, respectively, HBr or HCl in 1 : 1 molar ratio.

Finally, when the trinuclear complexes $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2M(\mu\text{-}OH)(\mu\text{-}PPh_2)Pt(PPh_3)_2]$ (M = Pd **11** or Pt **12**) are treated with an aqueous methanol solution of HCl (molar ratio 1 : 1) substitution of the bridging OH ligand takes place and the mixed halide–phosphide complexes $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2M(\mu\text{-}Cl)(\mu\text{-}PPh_2)Pt(PPh_3)_2]$ (M = Pd **15** or Pt **16**) are obtained.

The IR spectra of complexes **5**–**16** show characteristic absorptions of the C_6F_5, PPh_2 and PPh_3 ligands. All the hydroxo complexes show an absorption near 3600 cm^{-1} due to ν(OH)[22–25] and **9** and **10** show, in addition, a weak absorption near 3300 cm^{-1} which can be assigned to ν(NH).[42]

Although all these complexes are scarcely soluble in common organic solvents, their ^{19}F, ^{31}P and occasionally ^1H NMR spectra, in dichloromethane solution, have been taken and the relevant data presented in the Experimental section (^1H, ^{19}F) or Tables 1 and 3 (^{31}P). Unfortunately, the thiolato derivatives **7** and **8** are not soluble enough for NMR studies, although their analytical data and IR spectra allow a structural assignment by comparison with the rest of the complexes. The ^1H NMR spectra of **9**–**14** show a signal due to the hydrogen of the OH group (see Experimental section) without platinum satellites, however no resonance from the amide NH is detected[42] in the spectra of **9** and **10**. The ^{19}F NMR spectra of **5**–**16** do not provide any structural information. In all cases both C_6F_5 groups are inequivalent, but signals due to *p*-F appear overlapped with the ones due to *m*-F and signals due to *o*-F appear as one (**5**–**6**, **11**–**14**) or two (**9**, **10**, **15**, **16**) broad multiplets with platinum satellites (see Experimental section).

Complexes **9**, **10**, **13** and **14** contain two inequivalent PPh_2 and two inequivalent PPh_3 ligands and their ^{31}P NMR spectra show signals due to both type of ligands in well differentiated regions. In all cases the signal due to the P atoms of the PPh_3 ligands appears as a first-order spin system. The analysis of the resonances due to the P atoms of the PPh_2 groups for complexes **9**, **10** and **13** shows a high value of J/δ and their spectra must be analysed as an AB spin system.[46,47] The platinum satellites of **10** appear as complex multiplets which cannot be analysed and for **9** and **13** only the values of $\frac{1}{2}[J(AX) + J(BX)]$ (see Table 1) can be obtained from the spectra. For complex **14** the value of J/δ is small and the spectrum can be analysed as a first-order spin system (see Table 3). As in other cases, the *J*(PtP) corresponding to the Pt–P bonds *trans* to C_6F_5 and *trans* to Cl or OH are well differentiated.

Complexes **11**, **12**, **15** and **16**, which contain five inequivalent P atoms, show, in their ^{31}P NMR spectra, the corresponding signals (see Table 3). Signals due to PPh_3 (P^4 and P^5) appear in the expected range. Those due to P^1 and P^2 appear in the high-field region (from δ −105.19 to −159.09) while the resonance due to P^3 (a phosphide group which bridges two metal centres which are also bridged by OH or Cl ligands) appear at lower field, as in other cases.[48] The spectra of **11**, **15** and **16** show signals which can be analysed as first-order spin systems. That of **12** has not well separated signals corresponding to P^1 and P^2 and this part of the spectrum must be analysed[46,47] as the AB part of an ABX spin system (P^1 and P^2 coupled to P^3); *J*(AX), *J*(BX) and |*J*(AB)| can be calculated from the two AB quartets observed. The signals due to P^4 and P^5 can be analysed in terms of a first-order spin system. Platinum satellites are observed for all signals, nevertheless in some cases these satellites appear overlapped and *J*(PtP) values cannot be evaluated.

Finally, it has to be remarked that for all the complexes described the resonances due to the phosphide groups appear in the high-field region, as usual for phosphide groups which are not bridging metal–metal bonds.[1,14,30–32]

Conclusion

The synthesis of the unusual trinuclear (homo- or hetero-metallic) asymmetric complexes $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2M(\mu\text{-}Cl)_2Pt(PPh_3)_2]$ has been achieved through a synthetic strategy consisting in the formation of solvento (solv) complexes $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2M(solv)_2]$ which selectively react with *cis*-$[PtCl_2(PPh_3)_2]$, the latter acting as a metalloligand. The well recognised stability of bridging phosphide ligands is clearly reflected in the behaviour of these trinuclear complexes in which the $(\mu\text{-}X)_2$ (X = Cl or OH) bridging system reacts easily while the phosphide bridging system remains in all cases intact.

Experimental

General Methods.—The C, H and N analyses and IR spectroscopy were performed as described elsewhere.[14] Proton, ^{19}F and ^{31}P NMR spectra were recorded on a Varian Unity 300 or a Bruker 300 AXR spectrometer in CD_2Cl_2 solutions. The complexes $[NBu_4]_2[\{(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2M(\mu\text{-}Cl)\}_2]$ (M = Pd or Pt)[14] and *cis*-$[PtCl_2(PPh_3)_2]$[49] were prepared by literature methods. All complexes described below are initially obtained as dichloromethane solvates. The CH_2Cl_2 was eliminated by heating the samples in an oven at *ca.* 80 °C for 2–3 d.

Syntheses.—$[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2M(\mu\text{-}Cl)_2Pt(PPh_3)_2]$ (M = Pd **1** *or* Pt **2**). To a CH_2Cl_2 solution (15 cm^3) of $[NBu_4]_2[\{(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pd(\mu\text{-}Cl)\}_2]$ (0.150 g, 0.058 mmol) was added *cis*-$[PtCl_2(PPh_3)_2]$ (0.092 g, 0.116 mmol) and the solution was stirred for 15 min. An acetone solution (3 cm^3) of $AgClO_4$ (0.024 g, 0.116 mmol) was added and the mixture stirred for 1.5 h. Then the solvent was evaporated to dryness and the residue extracted with CH_2Cl_2 (30 cm^3). The orange solution was passed through a silica gel column (1 cm^2 × 10 cm) and concentrated to *ca.* 1.5 cm^3 so that an orange solid began to crystallise. After addition of Et_2O (5 cm^3) the solid **1** was filtered off, washed with Et_2O (2 × 2 cm^3) and vacuum dried (0.165 g, 79% yield) (Found: C, 47.9; H, 2.85. $C_{72}H_{50}Cl_2F_{10}P_4PdPt_2$ requires C, 48.1; H, 2.8%); $\tilde{\nu}_{max}/cm^{-1}$ (Nujol) 784s and 775s (C_6F_5), 256w and 296w (MCl); δ_F −116.20 [4 F, m, *J*(PtF) 334.82 Hz, *o*-F] and −165.48 (6 F, m, *m*- + *p*-F).

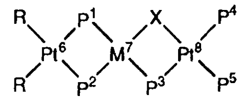
A similar procedure was used for the preparation of complex **2**; *i.e.* using $[NBu_4]_2[\{(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(\mu\text{-}Cl)\}_2]$ (0.200 g, 0.073 mmol), *cis*-$[PtCl_2(PPh_3)_2]$ (0.115 g, 0.146 mmol) and $AgClO_4$ (0.031 g, 0.147 mmol): 0.192 g, 70% yield (Found: C, 45.5; H, 2.7. $C_{72}H_{50}Cl_2F_{10}P_4Pt_3$ requires C, 45.9; H, 2.7%); $\tilde{\nu}_{max}/cm^{-1}$ (Nujol) 782s and 773s (C_6F_5), 259w and 297w (MCl); δ_F −116.30 [4 F, m, *J*(PtF) 336.19 Hz, *o*-F] and −165.65 (6 F, m, *m*- + *p*-F).

$[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2M(\mu\text{-}OH)_2Pt(PPh_3)_2]$ (M = Pd **3** *or* Pt **4**). To a solution of complex **1** (0.100 g, 0.055 mmol) in CH_2Cl_2 (20 cm^3) was added a solution of KOH (0.111 mmol) in MeOH. After 15 min stirring the mixture was evaporated to dryness and the residue extracted with CH_2Cl_2 (30 cm^3). The yellow solution was concentrated to *ca.* 1.5 cm^3 and a yellow solid began to crystallise. After 2 h at −18 °C solid **3** was filtered off, washed with cold CH_2Cl_2 (2 × 0.5 cm^3) and dried in vacuum (0.060 g, 62% yield) (Found: C, 49.0; H, 2.5. $C_{72}H_{52}F_{10}O_2P_4PdPt_2$ requires C, 49.1; H, 3.0%); $\tilde{\nu}_{max}/cm^{-1}$ (Nujol) 783s and 775s (C_6F_5), 3596s (OH); δ_H −1.37 (1 H, s, OH); δ_F −115.11 [4 F, m, *J*(PtF) 336.20 Hz, *o*-F] and −164.78 (6 F, m, *m*- + *p*-F).

Complex **4** was obtained similarly from **2** (0.100 g, 0.053 mmol) and a solution of KOH (0.106 mmol) in MeOH, 34% yield (Found: C, 46.7; H, 2.65. $C_{72}H_{52}F_{10}O_2P_4Pt_3$ requires C, 46.8; H, 2.8%); $\tilde{\nu}_{max}/cm^{-1}$ (Nujol) 781s and 773s (C_6F_5), 3588s (OH); δ_H −0.87 (1 H, s, OH); δ_F −116.02 [4 F, m, *J*(PtF) 334.12 Hz, *o*-F] and −165.84 (6 F, m, *m*- + *p*-F).

$[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2M(\mu\text{-}Br)_2Pt(PPh_3)_2]$ (M = Pd **5** *or* Pt **6**). To a solution of complex **3** (0.150 g, 0.085 mmol) in CH_2Cl_2 (20 cm^3) was added HBr (0.170 mmol) in MeOH solution.

Table 3 $^{31}P\text{-}\{^1H\}$ NMR data for complexes **11**, **12**, **15** and **16**



Complex			δ					J/Hz									
	M	X	P^1	P^2	P^3	P^4	P^5	P^1P^2	P^1P^3	PtP^1	P^2P^3	Pt^6P^2	P^3P^4	Pt^8P^3	P^4P^5	Pt^8P^4	Pt^8P^5
11[a]	Pd	OH	−127.23	−105.19	−30.17	26.98	4.97	194.39	307.39	1664.50	29.40	1804.22	253.93	1972.49	20.10	1942.80	3835.76
12	Pt	OH	−123.49	−127.60	−31.42	29.88	4.25	142.76[b]	287.24	*c*	−10.97	*c*	268.18	*d*	12.17	1924.97	3911.06
15	Pd	Cl	−159.09	−129.95	2.37	25.97	12.81	213.54	315.47	1698.45	35.74	1860.54	252.32	1641.09	15.36	2020.08	4410.55
16[e]	Pt	Cl	−153.55	−136.96	1.39	28.36	11.23	159.14	283.12	*f*	*g*	1980.28	262.77	*h*	16.56	2031.13	4488.09

[a] $J(P^3P^5)$ 8.63 Hz. [b] $|J(P^1P^2)|$. [c] Signals due to P^1 and P^2 (AB part of an ABX spin system) show platinum satellites as very complex multiplets and J(PtP) values cannot be extracted. [d] Signal due to P^3 shows two pairs of platinum satellites with J(PtP) = 1837.96 and 2009.3 Hz. Nevertheless an unambiguous assignment of these couplings to $J(Pt^7P^3)$ or $J(Pt^8P^3)$ cannot be made. [e] $J(Pt^7P^2)$ 2852.23 Hz. [f] Low-field satellites of signal due to P^1 appear overlapped with high-field ones due to P^2. Moreover the two upfield satellites due to P^1 appear overlapped too. So, $J(Pt^6P^1)$ and $J(Pt^7P^1)$ cannot be measured. [g] Signals due to P^2 and P^3 are broad and $J(P^2P^3)$ cannot be measured. [h] See footnote *d*. Here the two J(PtP) values are 1564.21 and 1792.82 Hz.

After 1 h stirring the solution was evaporated to dryness and the residue treated with CH_2Cl_2 (*ca.* 1 cm^3). The resulting solid **5** was filtered off, washed with CH_2Cl_2 (2 × 0.5 cm^3) and dried *in vacuo* (0.055 g, 34% yield) (Found: C, 45.7; H, 2.5. $C_{72}H_{50}Br_2F_{10}P_4PdPt_2$ requires C, 45.9; H, 2.7%); $\tilde{\nu}_{max}/cm^{-1}$ 784s and 775s (C_6F_5); δ_F −116.07 [4 F, m, *J*(PtF) 324.00 Hz, *o*-F] and −165.58 (6 F, m, *m*- + *p*-F).

To a solution of complex **4** (0.200 g, 0.108 mmol) in CH_2Cl_2 (40 cm^3) was added HBr (0.433 mmol) in MeOH. After 2.5 h stirring the solution was evaporated to dryness and the residue treated with CH_2Cl_2 (8 cm^3). The resulting solid **6** was filtered off and dried *in vacuo* (0.090 g, 42% yield) (Found: C, 43.4; H, 2.3. $C_{72}H_{50}Br_2F_{10}P_4Pt_3$ requires C, 43.9; H, 2.55%); $\tilde{\nu}_{max}/cm^{-1}$ 784s and 774s (C_6F_5); δ_F −116.70 [4 F, m, *J*(PtF) 295.10 Hz, *o*-F] and −165.99 (6 F, m, *m*- + *p*-F).

$[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2M(\mu\text{-}SPh)_2Pt(PPh_3)_2]$ (M = Pd **7** *or* Pt **8**). To a suspension of complex **3** (0.150 g, 0.085 mmol) in CH_2Cl_2 (5 cm^3) was added PhSH (18 μl, 0.170 mmol). Instantly an orange solution was formed and **7** began to crystallise. After 30 min stirring the mixture was evaporated to *ca.* 2 cm^3, cooled to −18 °C for 3 h and the solid thus obtained was filtered off, washed with cold CH_2Cl_2 and dried *in vacuo* (0.140 g, 85% yield) (Found: C, 51.6; H, 3.2; S, 3.3. $C_{84}H_{60}F_{10}P_4PdPt_2S_2$ requires C, 51.9; H, 3.1; S, 3.3%); $\tilde{\nu}_{max}/cm^{-1}$ 784s and 776s (C_6F_5).

A similar procedure was used for the preparation of complex **8** from **4** (0.150 g, 0.081 mmol) and PhSH (17 μl, 0.162 mmol): 0.125 g, 72% yield (Found: C, 49.5; H, 2.6; S, 2.8. $C_{84}H_{60}F_{10}P_4Pt_3S_2$ requires C, 49.6; H, 3.0; S, 3.15%); $\tilde{\nu}_{max}/cm^{-1}$ 784s and 776s (C_6F_5).

$[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2M(\mu\text{-}NHC_6H_4Me\text{-}p)(\mu\text{-}OH)Pt(PPh_3)_2]$ (M = Pd **9** *or* Pt **10**). To a solution of complex **3** (0.100 g, 0.056 mmol) in CH_2Cl_2 (25 cm^3) was added *p*-toluidine (0.018 g, 0.167 mmol). After 2.5 h stirring the solution was partially evaporated and cooled to −18 °C. The resulting yellow solid **9** was filtered off, washed with cold CH_2Cl_2 and dried *in vacuo* (0.070 g, 67% yield) (Found: C, 50.9; H, 3.3; N, 0.7. $C_{79}H_{59}F_{10}NOP_4PdPt_2$ requires C, 51.3; H, 3.7; N, 0.7%); $\tilde{\nu}_{max}/cm^{-1}$ (Nujol) 784s and 773s (C_6F_5), 3584w (OH), 3322w (NH); δ_H 6.61 [2 H, d, *J*(HH) 7.11, *p*-MeC$_6$*H*$_4$NH], 6.01 [2 H, d, *J*(HH) 7.11 Hz, *p*-MeC$_6$*H*$_4$NH], 2.28 (3 H, s, *p*-C*H*$_3$C$_6$H$_4$NH) and −1.39 (1 H, s, OH); δ_F −115.67 (2 F, m, *o*-F), −116.49 (2 F, m, *o*-F) and −166.17 (6 F, m, *m*- + *p*-F).

Complex **10** was prepared similarly from **4** (0.100 g, 0.054 mmol) and *p*-toluidine (0.015 g, 0.140 mmol): 0.080 g, 87% yield (Found: C, 48.55; H, 2.7; N, 0.8. $C_{79}H_{59}F_{10}NOP_4Pt_3$ requires C, 49.0; H, 3.1; N, 0.8%); $\tilde{\nu}_{max}/cm^{-1}$ (Nujol) 782s and 772s (C_6F_5), 3573w (OH), 3317w (NH); δ_H 6.65 [2 H, d, *J*(HH) 7.33, *p*-MeC$_6$*H*$_4$NH], 6.07 [2 H, d, *J*(HH) 7.33, *p*-MeC$_6$*H*$_4$NH], 2.30 (3 H, s, *p*-C*H*$_3$C$_6$H$_4$NH) and −0.84 (1 H, s, OH); δ_F −115.62 [2 F, m, *J*(PtF) 337.47, *o*-F), −115.92 [2 F, m, *J*(PtF) 341.55 Hz, *o*-F) and −166.08 (6 F, m, *m*- + *p*-F).

$[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pd(\mu\text{-}OH)(\mu\text{-}PPh_2)Pt(PPh_3)_2]$ **11**. To a suspension of complex **3** (0.500 g, 0.285 mmol) in CH_2Cl_2 (10 cm^3) was added $PHPh_2$ (50 μl, 0.285 mmol). After 1 h stirring the solution was evaporated to dryness, $CHCl_3$ (4 cm^3) was added and stirred for 15 min. After 3 h at −18 °C the resulting orange solid **11** was filtered off, washed with cold $CHCl_3$ (2 × 0.5 cm^3) and dried *in vacuo* (0.240 g, 44% yield) (Found: C, 52.1; H, 3.4. $C_{84}H_{61}F_{10}OP_5PdPt_2$ requires C, 52.3; H, 3.2%); $\tilde{\nu}_{max}/cm^{-1}$ (Nujol) 784s and 776s (C_6F_5), 3572w (OH); δ_H −1.88 (1 H, br s, OH); δ_F −115.62 [4 F, m, *J*(PtF) 312.35 Hz, *o*-F] and −166.60 (6 F, m, *m*- + *p*-F).

$[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(\mu\text{-}OH)(\mu\text{-}PPh_2)Pt(PPh_3)_2]$ **12**. To a suspension of complex **4** (0.200 g, 0.108 mmol) in CH_2Cl_2 (10 cm^3) was added $PHPh_2$ (20 μl, 0.117 mmol). After 1 h stirring the orange solution was evaporated to *ca.* 1 cm^3 and $CHCl_3$ (10 cm^3) was added. The yellow solid **12** was filtered off and dried *in vacuo* (32% yield) (Found: C, 50.1; H, 2.6. $C_{84}H_{61}F_{10}OP_5Pt_3$ requires C, 50.0; H, 3.05%); $\tilde{\nu}_{max}/cm^{-1}$ (Nujol) 783s and 775s (C_6F_5), 3564w (OH); δ_H −1.53 (1 H, br s, OH); δ_F −115.81 [4 F, m, *J*(PtF) 330.47 Hz, *o*-F] and −166.70 (6 F, m, *m*- + *p*-F).

$[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pd(\mu\text{-}Br)(\mu\text{-}OH)Pt(PPh_3)_2]$ **13**. The reaction between complex **3** (0.085 g, 0.048 mmol) and HBr (0.048 mmol) in MeOH and similar work-up as for **5** rendered **13** (0.035 g, 40% yield) (Found: C, 47.0; H, 2.8. $C_{72}H_{51}BrF_{10}OP_4PdPt_2$ requires C, 47.45; H, 2.8%); $\tilde{\nu}_{max}/cm^{-1}$ (Nujol) 783s and 775s (C_6F_5), 3582w (OH); δ_H −1.41 (1 H, s, OH); δ_F −116.38 [4 F, m, *J*(PtF) 333.44 Hz, *o*-F] and −165.68 (6 F, m, *m*- + *p*-F).

$[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(\mu\text{-}Cl)(\mu\text{-}OH)Pt(PPh_3)_2]$ **14**. This complex was prepared similarly to **13** from **4** (0.100 g, 0.054 mmol) and HCl (0.054 mmol) in MeOH: (0.060 g, 59% yield) (Found: C, 45.8; H, 2.8. $C_{72}H_{51}ClF_{10}OP_4Pt_3$ requires C, 46.3; H, 2.9%); $\tilde{\nu}_{max}/cm^{-1}$ (Nujol) 781s and 772s (C_6F_5), 3573w (OH); δ_H −1.20 (1 H, s, OH); δ_F −116.43 [4 F, m, *J*(PtF) 347.11 Hz, *o*-F] and −165.79 (6 F, m, *m*- + *p*-F).

$[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2M(\mu\text{-}Cl)(\mu\text{-}PPh_2)Pt(PPh_3)_2]$ (M = Pd **15** *or* Pt **16**). To a solution of complex **11** (0.100 g, 0.0518 mmol) in CH_2Cl_2 (10 cm^3) was added a solution (0.12 cm^3) of HCl (0.0518 mmol) in MeOH. After 1 h stirring the solution was evaporated to dryness and the residue treated with CH_2Cl_2 (3 cm^3). The resulting orange solid **15** was filtered off and dried in vacuum (0.040 g, 40% yield) (Found: C, 51.5; H, 3.1. $C_{84}H_{60}ClF_{10}P_5PdPt_2$ requires C, 51.8; H, 3.1%); $\tilde{\nu}_{max}/cm^{-1}$ (Nujol) 783s and 774s (C_6F_5); δ_F −116.09 [2 F, m, *J*(PtF) 289.25, *o*-F], −116.53 [2 F, m, *J*(PtF) 277.17 Hz, *o*-F] and −166.42 (6 F, m, *m*- + *p*-F).

To a solution of complex **12** (0.060 g, 0.0297 mmol) in CH_2Cl_2 (10 cm^3) was added HCl (0.0297 mmol) in MeOH. After 1 h stirring the solution was evaporated to *ca.* 1 cm^3 and Et_2O (3 cm^3) was added. The resulting yellow solid was filtered off and dried *in vacuo* (0.051 g, 84% yield) (Found: C, 49.25; H, 2.6. $C_{84}H_{60}ClF_{10}P_5Pt_3$ requires C, 49.6; H, 3.0%); $\tilde{\nu}_{max}/cm^{-1}$ (Nujol) 782s and 774s (C_6F_5); δ_F −116.43 [2 F, m, *J*(PtF) 329.33, *o*-F], −116.73 [2 F, m, *J*(PtF) 290.89 Hz, *o*-F] and −166.40 (6 F, m, *m*- + *p*-F).

Reactions of $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2M(\mu\text{-}OH)_2Pt(PPh_3)_2]$ (M = Pd **3** *or* Pt **4**) *with* HCl (*molar ratio* 1:2).—(*a*) To a solution of $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pd(\mu\text{-}OH)_2Pt(PPh_3)_2]$ **3** (0.100 g, 0.057 mmol) in CH_2Cl_2 (20 cm^3) was added an aqueous solution of HCl (0.1136 mmol) and the mixture was stirred for 30 min. The solution was evaporated to dryness and the residue treated with CH_2Cl_2 (5 cm^3) to give a deep yellow solid, **1** (0.071 g, 70% yield).

(*b*) The complex $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(\mu\text{-}OH)_2Pt(PPh_3)_2]$ **4** (0.087 g, 0.047 mmol) reacted with aqueous HCl (0.095 mmol) in a similar way, rendering **2** (0.055 g, 63% yield).

Crystallography.—Crystals of complex **3** were obtained by slow diffusion of hexane into a dichloromethane solution of it at room temperature.

Crystal data. $C_{73}H_{54}Cl_2F_{10}O_2P_4PdPt_2$, *M* = 1844.5, monoclinic, space group *C*2/*c*, *a* = 19.092(2), *b* = 22.742(2), *c* = 31.810(2) Å, β = 93.48(1)°, *U* = 13 786(2) Å^3 (by least-squares refinement on diffractometer angles for 48 automatically centred reflections, λ = 0.710 73 Å), *Z* = 8, D_c = 1.78 g cm^{-3}, *F*(000) = 7152. Yellow crystal (approximate dimensions 0.10 × 0.15 × 0.30 mm), μ(Mo-Kα) = 45.5 cm^{-1}.

Data collection and processing. Siemens/Stoe AED2 diffractometer, graphite-monochromated Mo-Kα radiation; 12 874 reflections measured ($2 \leqslant \theta \leqslant 25°$, $+h$, $+k$, $\pm l$), ω scan technique with the learned-profile mode.[50] 12 127 Unique (merging R_{int} = 0.0418), giving 7275 with $F > 6.0\sigma(F)$. No decay. Data reduction included an absorption correction (ψ-scan method, 10 reflections). Maximum and minimum transmission factors 0.290 and 0.234 respectively. No extinction correction was applied.

Structure analysis and refinement. The positions of the heavy atoms were determined from the Patterson map. The remaining

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

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pt(1)	1101(1)	2123(1)	812(1)	C(31)	−317(3)	2824(3)	370(2)
Pt(2)	2606(1)	2361(1)	2795(1)	C(32)	−734	2972	11
Pd	1980(1)	2149(1)	1728(1)	C(33)	−1463	2970	21
P(1)	635(2)	2853(1)	422(1)	C(34)	−1776	2821	392
P(2)	633(1)	1372(1)	437(1)	C(35)	−1359	2673	752
P(3)	2378(1)	2845(1)	2174(1)	C(36)	−630	2675	741
P(4)	2447(1)	1638(1)	2285(1)	C(37)	1006(3)	2941(3)	−86(2)
O(1)	1649(3)	2691(3)	1207(2)	C(38)	766	3378	−366
O(2)	1596(4)	1532(3)	1237(2)	C(39)	1057	3435	−756
C(1)	2832(6)	1856(5)	3331(3)	C(40)	1590	3055	−865
C(2)	2336(6)	1602(5)	3568(3)	C(41)	1831	2618	−585
C(3)	2484(7)	1276(6)	3923(4)	C(42)	1539	2561	−195
C(4)	3161(8)	1173(5)	4044(4)	C(43)	827(5)	3568(3)	672(2)
C(5)	3680(7)	1399(6)	3830(4)	C(44)	324	3869	888
C(6)	3514(6)	1736(6)	3475(3)	C(45)	507	4384	1107
F(1)	1647(3)	1697(3)	3449(2)	C(46)	1192	4597	1109
F(2)	1968(4)	1046(4)	4139(3)	C(47)	1695	4295	893
F(3)	3319(4)	838(3)	4396(2)	C(48)	1512	3780	674
F(4)	4349(4)	1297(4)	3961(3)	C(49)	3152(6)	3155(5)	1949(3)
F(5)	4055(3)	1967(4)	3272(3)	C(50)	3116(7)	3439(5)	1570(3)
C(7)	2578(6)	3111(5)	3160(3)	C(51)	3715(8)	3637(6)	1395(4)
C(8)	3150(8)	3454(7)	3274(4)	C(52)	4351(8)	3545(6)	1586(5)
C(9)	3108(10)	3990(7)	3488(5)	C(53)	4406(7)	3282(8)	1968(6)
C(10)	2462(13)	4170(7)	3612(5)	C(54)	3791(7)	3085(7)	2150(5)
C(11)	1894(9)	3840(7)	3517(5)	C(55)	1774(6)	3461(5)	2175(3)
C(12)	1953(8)	3325(5)	3292(4)	C(56)	1059(6)	3387(6)	2062(3)
F(6)	3803(4)	3286(4)	3173(3)	C(57)	595(8)	3835(8)	2098(5)
F(7)	3687(6)	4298(4)	3579(4)	C(58)	827(9)	4374(8)	2251(5)
F(8)	2452(6)	4676(4)	3833(3)	C(59)	1504(10)	4449(6)	2370(5)
F(9)	1269(6)	4031(4)	3629(3)	C(60)	1985(7)	4005(5)	2332(3)
F(10)	1353(4)	3044(3)	3195(3)	C(61)	1919(6)	1001(5)	2421(3)
C(13)	−63(3)	1474(3)	25(2)	C(62)	1299(7)	863(6)	2211(4)
C(14)	87	1695	−368	C(63)	937(8)	355(7)	2309(5)
C(15)	−454	1789	−676	C(64)	1191(9)	−9(6)	2626(5)
C(16)	−1146	1661	−589	C(65)	1796(9)	139(6)	2854(5)
C(17)	−1296	1440	−195	C(66)	2161(6)	630(5)	2745(4)
C(18)	−754	1347	112	C(67)	3227(6)	1277(6)	2091(3)
C(19)	1295(4)	951(3)	186(2)	C(68)	3178(7)	814(6)	1825(4)
C(20)	1099	566	−142	C(69)	3750(9)	561(6)	1665(5)
C(21)	1591	181	−296	C(70)	4403(9)	766(9)	1775(5)
C(22)	2280	181	−122	C(71)	4451(9)	1205(12)	2046(6)
C(23)	2477	566	205	C(72)	3882(7)	1472(8)	2204(5)
C(24)	1984	951	360	C(73)	423(7)	2193(11)	2630(3)
C(25)	266(3)	859(3)	803(2)	Cl(1)	26(5)	2093(4)	3123(2)
C(26)	350	252	762	Cl(2)	−119(6)	2020(5)	2163(2)
C(27)	35	−130	1037	C(74)	441(14)	5305(14)	4901(20)
C(28)	−363	94	1353	Cl(3)	917(7)	4770(7)	4615(5)
C(29)	−448	701	1395	Cl(4)	−454(6)	5127(7)	4994(4)
C(30)	−133	1083	1120				

atoms were located in successive Fourier syntheses. The phenyl rings of the PPh_3 ligands were regarded as idealised rigid groups with C–C distances of 1.395 Å. Hydrogen atoms were incorporated at calculated positions through the use of a riding model in which the C–H distance was fixed at 0.96 Å, with a common isotropic displacement parameter refining to 0.093(6) Å^2.

Two sites in the crystallographic asymmetric unit were found to be occupied by disordered CH_2Cl_2 moieties. Both were near symmetry centres; therefore the highest possible occupancy was 0.5. Loose geometrical restraints were applied to the C–Cl and Cl ··· Cl distances. All non-hydrogen atoms save those of the solvent molecules were refined with anisotropic displacement parameters. There was only one peak higher than 1 e Å^{-3} (1.37 e Å^{-3}) on the final Fourier-difference map located close to Pt(2), without any chemical meaning. The structure refinement was based on $|F_o|$. Final R and R' were 0.044 and 0.047 $\{R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$; $w^{-1} = [\sigma^2(|F_o|) + g|F_o|^2]$; $g = 0.0003\}$. Calculations were carried out on a local area VAX cluster (VAX/VMS V5.5) with the program REDU4 Rev. 7.03 (Stoe) for data reduction and with SHELXTL PLUS.[51] Final atomic coordinates are given in Table 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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