Homo- and Hetero-dinuclear Complexes of Palladium and Platinum containing Phosphinoacetylene and/or Chloride as Bridging Ligands†

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Reactions between the diphenylacetylenephosphine complexes *cis*-[$M'Cl_2(PPh_2C{\equiv}CR)_2$] (M' = Pt or Pd, R = Ph or Bu^t) and *cis*-[$M(C_6F_5)_2(thf)_2$] (M = Pt or Pd; thf = tetrahydrofuran) in a 1 : 1 molar ratio have been studied. Three types of products have been obtained: (*a*) asymmetric homo- and hetero-dinuclear complexes *gem*-[$(C_6F_5)_2M(\mu\text{-}Cl)_2M'(PPh_2C{\equiv}CR)_2$], (*b*) symmetric *trans*-palladium derivatives [$\{Pd(\mu\text{-}Cl)(C_6F_5)(PPh_2C{\equiv}CR)\}_2$] and (*c*) the unusual chloride and diphenyl(phenylethynyl)phosphine bridged dinuclear compounds [$(C_6F_5)_2Pt(\mu\text{-}Cl)(\mu\text{-}PPh_2C{\equiv}CPh)M'Cl(PPh_2C{\equiv}CPh)$]. The complexes have been characterised by microanalysis, IR and NMR spectroscopy and the molecular structure of [$(C_6F_5)_2Pt(\mu\text{-}Cl)(\mu\text{-}PPh_2C{\equiv}CPh)PtCl(PPh_2C{\equiv}CPh)$]$\cdot OC_4H_8$. The NMR spectral data (^1H, ^{19}F and ^{31}P) indicate that, in solution, mixtures of isomers [$(C_6F_5)_2Pt(\mu\text{-}Cl)_2M'(PPh_2C{\equiv}CR)_2$] and [$(C_6F_5)_2Pt(\mu\text{-}Cl)(\mu\text{-}PPh_2C{\equiv}CPh)M'Cl(PPh_2C{\equiv}CPh)$] are present.

Phosphinoacetylene ligands, $PR_2C{\equiv}CR'$ (R = R' = alkyl or aryl), have received considerable attention in recent years.[1,2] These molecules can behave as simple P-donors,[3] as disubstituted acetylenes[4] or as polydentate ligands (P + 2π[5] or P + 4π[2d,4,6]), as well as undergo interesting and potentially useful transformations.[2] Thus, the cleavage of the P–C (alkyne) bond induced by thermolysis,[1d,7] photolysis[1a,b] or by chemical activation using Me_3NO,[1e,8] to yield phosphido PR_2 and $C{\equiv}CR'$ bridging fragments, seems to be a common feature of reactions involving phosphinoacetylenes and metal carbonyls. Although the detailed mechanism of P–C bond cleavage is unknown, it has been suggested[1a,b,8] that it proceeds through the formation of an intermediate with the acetylene π-interacting, followed by oxidative insertion into the P–C alkyne bond. On the other hand, activation of the unco-ordinated alkyne function, for example in *cis*-[$MX_2(PPh_2C{\equiv}CR)_2$] (M = Pd or Pt; X = halide, R = alkyl or aryl), towards such reactions as hydration,[9] hydrogen halide[10] or secondary phosphine[11] addition and intramolecular acetylene coupling[12] has also been observed.

Considering that *cis*-[$M(C_6F_5)_2(thf)_2$] (M = Pt or Pd; thf = tetrahydrofuran) has been shown to be an excellent precursor for the preparation of simple bis(η^2-alkyne) complexes,[13] as well as acetylide-bridged polynuclear complexes,[14] we thought it worthwhile to investigate its reactions with *cis*-[$MCl_2(PPh_2C{\equiv}CR)_2$] (M = Pt or Pd) derivatives. These reactions could be an alternative route for obtaining platinum acetylide complexes or could allow the synthesis of homo- and hetero-dinuclear derivatives with halide and/or phosphinoalkynyl bridges.

In this paper we report the results of this study which have enabled us to prepare three different types of binuclear derivatives: (*a*) the asymmetric homo- and hetero-dinuclear complexes *gem*-[$(C_6F_5)_2M(\mu\text{-}Cl)_2M'(PPh_2C{\equiv}CR)_2$] **1a**–**6a**, (*b*) the symmetric *trans*-palladium compounds [$\{Pd(\mu\text{-}Cl)(C_6F_5)(PPh_2C{\equiv}CR)\}_2$] **1b** and **2b** and (*c*) the unusual chloride and diphenyl(phenylethynyl)phosphine bridged dinuclear derivatives [$(C_6F_5)_2Pt(\mu\text{-}Cl)(\mu\text{-}PPh_2C{\equiv}CPh)M'Cl(PPh_2C{\equiv}CPh)$] (M' = Pd **7c** or Pt **8c**). The structure of **8c**$\cdot OC_4H_8$ has been established by single-crystal X-ray diffraction. The NMR data (^1H, ^{19}F and ^{31}P) indicate that complexes **6a** (M = M' = Pt, R = Bu^t), **7c** and **8c** exist in solution (**6a**, $CDCl_3$; **7c** and **8c**, CD_2Cl_2) as a mixture of both isomers (**a** and **c**).

Results and Discussion

Reactions with cis-[$Pd(C_6F_5)_2(thf)_2$].—The complexes *cis*-[$MCl_2(PPh_2C{\equiv}CR)_2$] (M = Pt or Pd, R = Ph or Bu^t) react with *cis*-[$Pd(C_6F_5)_2(thf)_2$] in CH_2Cl_2 (molar ratio 1 : 1) under mild conditions (room temperature, 15 min of stirring for R = Ph or 30 min for R = Bu^t) to give the corresponding homo- and hetero-dinuclear asymmetric *gem* derivatives [$(C_6F_5)_2Pd(\mu\text{-}Cl)_2M'(PPh_2C{\equiv}CR)_2$] **1a**–**4a** in good yields. Under these conditions the reactions proceed with retention of the original configuration around the metal centres and no rearrangement of ligands is observed. However, if the reactions between the palladium derivatives *cis*-[$PdCl_2(PPh_2C{\equiv}CR)_2$] and *cis*-[$Pd(C_6F_5)_2(thf)_2$] are carried out at room temperature in $CHCl_3$ for a longer reaction time (1 d), redistribution of ligands occurs and the respective geometrical isomers *sym-trans*-[$\{Pd(\mu\text{-}Cl)(C_6F_5)(PPh_2C{\equiv}CR)\}_2$] (R = Ph **1b** or Bu^t **2b**) are obtained in moderate yield.

The NMR spectra reveal that complexes **1a** and **2a** isomerise slowly (≈1 d) but cleanly to **1b** and **2b** indicating that the *gem* derivatives are the kinetic products of the reaction and the *sym-trans* ones the thermodynamic products.

The structural characterisation of complexes **1a**–**4a**, **1b** and **2b** is based on elemental analysis and spectroscopic methods (mass spectrometry, IR and ^1H, ^{19}F and ^{31}P NMR) (data are collected in Tables 1 and 2). The most useful information is obtained from the IR spectra. Thus, all complexes show only one (**1a**, **1b**, **3a** derivatives with $PPh_2C{\equiv}CPh$) or two (**2a**, **2b**, **4a**

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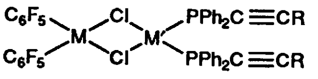
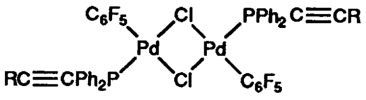
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.



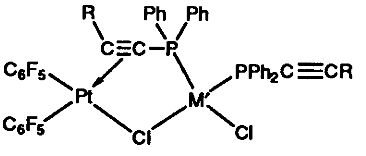
a

	M	M′	R
1a	Pd	Pd	Ph
2a	Pd	Pd	Bu^t
3a	Pd	Pt	Ph
4a	Pd	Pt	Bu^t
5a	Pt	Pd	Bu^t
6a	Pt	Pt	Bu^t



b

	R
1b	Ph
2b	Bu^t



c

	M′	R
7c	Pd	Ph
8c	Pt	Ph

derivatives with $PPh_2C\equiv CBu^t$) strong bands in the region 2166–2214 cm^{-1} assignable to ν(C≡C) of the phosphinoacetylene ligands which indicates that these molecules are only acting as P-donor ligands. On the other hand, they show typical absorptions for the C_6F_5 groups around 1500, 1050, 950 and 790 cm^{-1}; the latter, which is attributed to the X-sensitive mode of the C_6F_5 groups[15] and usually gives structural information, is obscured in the case of complexes **2a**, **2b** and **4a** by an internal absorption of *cis*-$[MCl_2(PPh_2C\equiv CBu^t)_2]$. However, the *gem* derivatives **1a** and **3a** exhibit two bands (**1a**, 797, 783; **3a**, 799, 787 cm^{-1}) indicating the presence of a *cis*-$Pd(C_6F_5)_2$ moiety in the respective complexes, while **1b** shows only one absorption (798 cm^{-1}, B_u) in good agreement with that expected for a compound of C_{2h} symmetry. Complexes **1b** and **2b** show two bands (2 B_u) [**1b**, 300m, 279m; **2b**, 286s, 275 (sh) cm^{-1}] associated with bridging ν(Pd–Cl) stretching vibrations, while the *gem* derivatives **1a**–**4a** show a more complex pattern of bands assignable to ν(M–Cl) vibrations of $Pd(\mu\text{-}Cl)_2M$ fragments (see Table 1).

The NMR spectra of complexes **1**–**4** indicate that both the two C_6F_5 groups and the two phosphinoacetylene ligands are equivalent. Moreover, the ^{31}P NMR spectra of **3a** and **4a** show signals with platinum satellites [**3a**, δ −11.45 (s), ^1J(Pt–P) = 4067; **4a**, δ −13.06 (s), ^1J(Pt–P) = 3946 Hz], while the ^{19}F NMR spectra of these complexes show that signals due to *o*-fluorine atoms of the C_6F_5 groups do not present platinum satellites. These facts necessarily imply that both phosphine ligands are bonded to the platinum while the two C_6F_5 groups are bonded to palladium centres: *i.e.* the reactions are stereospecific and no ligand rearrangement has taken place.

Interestingly, while for the *gem* derivatives **1a** and **2a** the ^{31}P NMR single resonance of the $PPh_2C\equiv CR$ ligands is only slightly deshielded (**1a**, δ 10.70; **2a**, δ 9.52) with respect to the corresponding one in the starting *cis*-$[PdCl_2(PPh_2C\equiv CR)_2]$ derivatives (R = Ph, δ 7.85; Bu^t, δ 7.27) the resonance observed for the isomers *sym-trans* **1b** and **2b** is considerably shielded (**1b**, δ 4.59; **2b**, δ 3.03).

Reactions with cis-$[Pt(C_6F_5)_2(thf)_2]$.—The reactions of *cis*-$[MCl_2(PPh_2C\equiv CR)_2]$ with *cis*-$[Pt(C_6F_5)_2(thf)_2]$ were carried out in toluene since the insolubility of the resulting products in this solvent precludes the isomerization processes which take place in solution (see below). The complexes *cis*-$[MCl_2(PPh_2C\equiv CR)_2]$ (M = Pd or Pt, R = Bu^t or Ph) react with *cis*-$[Pt(C_6F_5)_2(thf)_2]$ in toluene (molar ratio 1 : 1) yielding neutral homo- (**6a**, **8c**) and hetero-dinuclear derivatives (**5a**, **7c**) the nature of which is alkynylphosphine dependent. Thus, the reaction of *cis*-$[Pt(C_6F_5)_2(thf)_2]$ with suspensions of *cis*-$[MCl_2(PPh_2C\equiv CBu^t)_2]$ in toluene results in the formation of doubly chloride-bridged complexes **5a** and **6a**. However, suspensions of diphenyl(phenylethynyl)phosphine complexes *cis*-$[MCl_2(PPh_2C\equiv CPh)_2]$ give the unusual and sparingly soluble dinuclear species with μ-Cl and μ-η^3-$PPh_2C\equiv CPh$, **7c** and **8c**. The structural assignment is based on elemental analysis, IR and ^1H, ^{19}F and ^{31}P NMR spectroscopy (see Tables 1 and 2) and the crystal structure of **8c** (see below).

Complexes **5a** and **6a** display very similar IR spectra to those of the *gem* derivatives **2a** and **4a**, thus suggesting that they have an analogous structure; the most relevant data are the two absorptions observed at 2206 and 2164 for **5a** and at 2206 and 2167 cm^{-1} for **6a** typical of a terminal P-co-ordinated alkynylphosphine, $PPh_2C\equiv CBu^t$. By contrast, the IR spectra of **7c** and **8c** show two strong absorptions assignable to C≡C groups; the band at 2175 cm^{-1} (in both cases) is indicative of a terminal P-co-ordinated alkynylphosphine, as observed in the spectra of the dinuclear derivatives **1**–**6**, while a second absorption at 1949 (**7c**) or 1957 cm^{-1} (**8c**) clearly suggests co-ordination of the acetylene fragment to an adjacent metal atom.[5] Furthermore both complexes show two IR absorptions in the 809–797 cm^{-1} region due to the X-sensitive mode of the C_6F_5 groups, indicating that the *cis* geometry of the $Pt(C_6F_5)_2$ moiety is retained after the reaction.[15]

The ^{19}F, ^1H and ^{31}P NMR spectra of $[(C_6F_5)_2Pt(\mu\text{-}Cl)_2\text{-}Pd(PPh_2C\equiv CBu^t)_2]$ **5a**, which is in fact a geometrical isomer of $[(C_6F_5)_2Pd(\mu\text{-}Cl)_2Pt(PPh_2C\equiv CBu^t)_2]$ **4a**, are in good agreement with the proposed structure. Thus, the ^{31}P NMR spectrum shows a sharp singlet resonance [δ(P) 7.87] without platinum satellites indicating that both alkynylphosphine ligands are bound to palladium. The ^{19}F NMR spectrum exhibits the usual pattern of three signals (ratio 2 : 1 : 2) indicating that both C_6F_5 groups are equivalent but, as expected, the downfield resonance (δ −119.1) due to the *o*-fluorine atoms shows platinum satellites [$^3J(^{195}Pt\text{–}F_o)$ = 520 Hz], unequivocally showing that both C_6F_5 groups are bonded to the platinum centre.

The NMR (^{19}F, ^1H and ^{31}P) spectra of complex **6a** recorded immediately after dissolving the solid sample in $CDCl_3$ show that the isomers **6a** and $[(C_6F_5)_2Pt(\mu\text{-}Cl)(\mu\text{-}PPh_2C\equiv CBu^t)\text{-}PtCl(PPh_2C\equiv CBu^t)]$ **6c** are present in solution in an approximately 1 : 1.2 ratio. The ^1H NMR spectrum exhibits, besides multiplets (δ 7.76, 7.40 and 8.3–8.1) due to the phenyl protons, a singlet at δ 1.00 due to the equivalent Bu^t groups of **6a** and two additional singlet resonances of the same intensity at δ 0.89 and 0.79 which can readily be attributed to the expected two inequivalent Bu^t groups of **6c**. In accord the ^{31}P NMR spectrum shows the expected resonances for both isomers: a single resonance at δ −14.34 which appear as a pseudo-triplet (1 : 4 : 1) because of coupling with ^{195}Pt [^1J(Pt–P) = 3991 Hz] due to **6a** and two doublets [δ(P) 12.37, ^1J(Pt–P) = 3675, −19.96, ^1J(Pt–P) = 3990 Hz] with a ^2J(P–P) of 13.3 Hz as expected for the two inequivalent $PPh_2C\equiv CBu^t$ units (terminal and bridging) of **6c**. The presence of **6c** in solution is also confirmed by IR spectroscopy. Thus the spectrum in CD_2Cl_2 shows, besides the absorptions at 2209 and 2167 cm^{-1} due to

Table 1 Elemental analyses, yields, relevant IR absorptions and mass spectral data for the complexes

	Analysis (%)[a]			IR (cm^{-1})			
Compound	C	H	Yield (%)	$\nu(C{\equiv}C)$	$\nu(C_6F_5)$[b]	$\nu(M-Cl)$	*m/z*
1a $[(C_6F_5)_2Pd(\mu\text{-}Cl)_2Pd(PPh_2C{\equiv}CPh)_2]$	52.00 (52.45)	2.55 (2.55)	82	2171vs	797s, 783s	311m, 284m, 277m	[c] 1309 ($[M - C_6F_5 + PPh_2C{\equiv}CPh]^+$, 12), 1023 ($[M - C_6F_5]^+$, 9), 713 {$[PdCl(PPh_2C{\equiv}CPh)_2]^+$, 37%}
1b $[\{Pd(\mu\text{-}Cl)(C_6F_5)(PPh_2C{\equiv}CPh)\}_2]$	52.05 (52.45)	2.30 (2.55)	53	2176vs	798s	300m, 279m	1192 ($[M + 2H]^+$, 3.7), 453 {$[(PPh_2C{\equiv}CPh)(C_6F_5)]^+$, 100%}
2a $[(C_6F_5)_2Pd(\mu\text{-}Cl)_2Pd(PPh_2C{\equiv}CBu^t)_2]\cdot CH_2Cl_2$	47.85 (47.65)	3.10 (3.25)	66	2211s, 2166vs	796s, 782vs	310m, 285s, 276 (sh)	[c] 1249 ($[M - C_6F_5 + PPh_2C{\equiv}CBu^t]^+$, 13), 675 {$[PdCl(PPh_2C{\equiv}CBu^t)_2 + 2H]^+$, 32}, 638 {$[Pd(PPh_2C{\equiv}CBu^t)_2]^+$, 14%}
2b $[\{Pd(\mu\text{-}Cl)(C_6F_5)(PPh_2C{\equiv}CBu^t)\}_2]\cdot CH_2Cl_2$	47.50 (47.65)	2.95 (3.25)	45	2214s, 2172vs	795vs, 781vs	286s, 275 (sh)	[c] 433 {$[PPh_2C{\equiv}CBu^t)(C_6F_5)]^+$, 100%}
3a $[(C_6F_5)_2Pd(\mu\text{-}Cl)_2Pt(PPh_2C{\equiv}CPh)_2]$	48.75 (48.85)	2.45 (2.35)	54	2173vs	799s, 787s	309w, 389w, 279w, 266w, 248w	[c] 1243 ($[M - Cl]^+$, 8), 1113 ($[M - C_6F_5]^+$, 22), 803 {$[PtCl(PPh_2C{\equiv}CPh)_2]^+$, 100%}
4a $[(C_6F_5)_2Pd(\mu\text{-}Cl)_2Pt(PPh_2C{\equiv}CBu^t)_2]$	46.40 (46.55)	2.90 (3.10)	84	2214s, 2170vs	797s, 784vs	313 (sh), 303m, 277m	[c] 763 {$[PtCl(PPh_2C{\equiv}CBu^t)_2]^+$, 100}, 726 {$[Pt(PPh_2C{\equiv}CBu^t)_2 - H]^+$, 57%}
5a $[(C_6F_5)_2Pt(\mu\text{-}Cl)_2Pd(PPh_2C{\equiv}CBu^t)_2]$	46.45 (46.55)	2.85 (3.10)	82	2206m, 2164s	809vs, 798vs, 784s	286w, 279w, 270w	1238 ($[M]^+$, 5%)
6a $[(C_6F_5)_2Pt(\mu\text{-}Cl)_2Pt(PPh_2C{\equiv}CBu^t)_2]$	43.15 (43.40)	3.00 (2.90)	91	2206s, 2167vs	811vs, 800vs, 784vs	308m, 285m, 278m, 270m	1331 ($[M + 3H]^+$, 8), 764 {$[PtCl(PPh_2C{\equiv}CBu^t)_2]^+$, 100%}
7c $[(C_6F_5)_2Pt(\mu\text{-}Cl)(\mu\text{-}PPh_2C{\equiv}CPh)PdCl(PPh_2C{\equiv}CPh)]$	48.30 (48.85)	2.25 (2.35)	65	2175vs, 1949vs	806vs, 797vs	325m, 304m	1278 ($[M]^+$, 7), 1243 ($[M - Cl]^+$, 8%)
8c $[(C_6F_5)_2Pt(\mu\text{-}Cl)(\mu\text{-}PPh_2C{\equiv}CPh)PtCl(PPh_2C{\equiv}CPh)]$	44.95 (45.65)	2.15 (2.20)	91	2175vs, 1957vs	809vs, 798vs	334m, 279s	*c*

[a] Calculated values in parentheses. [b] X-Sensitive mode; an internal absorption of *cis*-$[MCl_2(PPh_2C{\equiv}CBu^t)_2]$ precludes an unambiguous assignment of these bands. For complexes **2a** and **4a** the band of very strong intensity could be the result of overlapping of one of the X-sensitive modes of the C_6F_5 groups, IR active, and this internal absorption. For complexes **2b**, **5a** and **6a** an additional band is observed. [c] Molecular peak not observed.

terminal P-co-ordinated alkynylphosphine ligands in both isomers **6a** and **6c**, a medium-intensity absorption at 1984 cm^{-1} which can be attributed to $\nu(C{\equiv}C)$ for the μ-$PPh_2C{\equiv}CBu^t$ ligand in **6c**. On standing the proportion of **6c** increases and after 24 h the two isomers are observed in approximately the intensity ratio 1 : 1.8. The isomerisation of **6a** to **6c** is slow in CD_3COCD_3 and thus the NMR spectrum of **6a** obtained just after dissolving it in CD_3COCD_3 (see Table 2) only shows small additional signals due to the presence of **6c** in very low concentration (molar ratio **6a**:**6c** ≈ 5:1). However after 4 h both isomers (**6a**, **6c**) are present, in approximately 2:1 ratio.

Similarly, although complexes **7c** and **8c** are sparingly soluble in common organic solvents they are soluble enough in CD_2Cl_2, immediately giving a mixture of the isomers $[(C_6F_5)_2Pt(\mu\text{-}Cl)_2Pd(PPh_2C{\equiv}CPh)_2]$ **7a** and $[(C_6F_5)_2Pt(\mu\text{-}Cl)(\mu\text{-}PPh_2C{\equiv}CPh)PdCl(PPh_2C{\equiv}CPh)]$ **7c** in 1 : 1.2 molar ratio and **8a** and **8c** in 1 : 3.5 molar ratio respectively, as observed by ^{19}F and ^{31}P NMR spectroscopy (see Table 2).

The ^{19}F and ^{31}P NMR spectra at room temperature in CD_2Cl_2 obtained for complex **7c** are shown in Fig. 1. As can be seen three phosphorus resonances without platinum satellites are observed. The more intense signal (δ 10.13) can be assigned to the two equivalent alkynylphosphine ligands bound to palladium in **7a** and the two others to phosphorus atoms of the two inequivalent alkynylphosphine ligands (terminal and bridging) in **7c**. The ^{19}F NMR spectrum also shows the expected pattern of three types of C_6F_5 groups as is clearly reflected by the presence of three triplets due to *p*-fluorine resonances; two triplets of the same intensity at δ −161.4 and −162.6 assigned to the two inequivalent C_6F_5 groups of the major isomer **7c** and a triplet at δ −164.6 which can be attributed to the two equivalent C_6F_5 groups of the minor isomer **7a**.

Structure of $[(C_6F_5)_2Pt(\mu\text{-}Cl)(\mu\text{-}\eta^3\text{-}PPh_2C{\equiv}CPh)PtCl(PPh_2C{\equiv}CPh)]\cdot OC_4H_8$.—Suitable crystals for an X-ray diffraction study were obtained by slow diffusion of hexane into a saturated tetrahydrofuran solution of complex **8c**. Fig. 2 shows a view of the molecule; selected bond distances and angles are listed in Table 3 and atomic coordinates in Table 4.

The most interesting feature of this complex is the simultaneous presence of a diphenyl(phenylethynyl)phosphine ligand and a chloride bridging two different platinum fragments *cis*-Pt(1)$(C_6F_5)_2$ and *cis*-Pt(2)Cl$(PPh_2C{\equiv}CPh)$. The phosphine bridge acts as a four-electron donor with the phosphorus atom bonded to Pt(2) and the triple bond to Pt(1). This indicates that the reaction between *cis*-$[Pt(C_6F_5)_2(thf)_2]$ and *cis*-$[PtCl_2(PPh_2C{\equiv}CPh)_2]$ proceeds with retention of the original configuration about the platinum centres. However, it should be noted that the formation of this compound is rather unexpected since complexes containing phosphinoacetylene bridging ligands are very rare.[5] Indeed the only examples known to us in which the phosphinoacetylene acts as a four-electron donor (P + 2π) are the dinuclear carbonyl complexes $[Ni_2(CO)_2(PPh_2C{\equiv}CBu^t)_2]$[5a] and $[Fe_2(CO)_6(PPh_2C{\equiv}CPh)_2]$[5a] in which both metal atoms are co-ordinated to the phosphorus atom of one phosphinoacetylene and the triple bond of the second phosphinoacetylene, and $[(OC)_4Fe(PPh_2C{\equiv}CBu^t)Fe(CO)_4]$.[5b] On the other hand it has been shown that the mutually *cis* phosphines in *cis*-$[PtCl_2(PPh_2C{\equiv}CPh)_2]$ adopt a configuration which places the less-demanding C≡CPh substituents 'across' one another (see A);[12] thus it is also noteworthy that the formation of complex **8c** requires a significant reorientation of one phosphinoalkynyl ligand, since the dinuclear doubly bridging chloride complex $[(C_6F_5)_2Pt(\mu\text{-}Cl)_2Pt(PPh_2C{\equiv}CPh)_2]$ **8a** could have been expected.

Table 2 Fluorine-19, ^{31}P and ^{1}H NMR data[a] for the complexes

	^{19}F			^{31}P		^{1}H	
Compound	F_o[b]	F_p	F_m	δ(P)	$^1J(^{195}Pt-^{31}P)$	δ(Ph)	δ(Bu^t)
1a	−115.7 (d)	−162.7 (t)	−165.4 (m)	10.70	—	—	—
1b	−118.8 (dd)	−159.9 (t)	−162.8 (m)	4.59	—	—	—
2a	−115.4 (dd)	−162.6 (t)	−165.2 (m)	9.52	—	7.72 (m, 8 H), 7.48 (m, 12 H)[c]	1.01 (s, 18 H)
2b	−118.8 (dd)	−160.4 (t)	−163.3 (m)	3.03	—	7.76 (m, 8 H), 7.42 (m, 12 H)[c]	1.16 (s, 18 H)
3a	−116.0 (dd)	−162.3 (t)	−165.3 (m)	−11.45	4067	—	—
4a	−115.7 (d)	−162.3 (t)	−165.1 (m)	−13.06	3946	7.75 (m, 8 H), 7.46 (m, 12 H)	0.99 (s, 18 H)
5a	−119.1 (d, 520)	−164.3 (t)	−166.4 (m)	7.87	—	7.78 (m, 8 H), 7.50 (m, 12 H)	1.02 (s, 18 H)
6a[d]	−117.9 (d, 518)	−164.1 (t)	−166.3 (m)	−8.24	3973	7.90 (m, 8 H), 7.63 (m, 12 H)	1.07 (s, 18 H)
6a[e]	−119.4	−161.0 (t),	−164.6 (m),	12.37 (d)[f]	3675	8.3–8.1 (vbr), 7.76 (m),	0.89 (s)
	(**6a** + **6c**)	−161.4 (t) **6c**	−166.3 (m)			7.40 (m) (**6a** + **6c**)	
		−163.9 **6a**	(**6a** + **6c**)		**6c**		**6c**
				−19.96 (d)[f]	3990		0.79 (s)
				−14.34 (s)	3991 **6a**		1.00 (s) **6a**
7c[g] **7c**	−119.0 (d, 396)	−161.4 (t),	−165.1 (m),	35.65 (s),	—	—	—
		−162.6 (t)	−165.7 (m)	4.21 (s)	—		
	−119.6 (d, 404)						
7a	−119.7 (d)	−164.6 (t)	−166.8 (m)	10.13 (s)	—		
8c[h]	−119.5 (m),	−161.3 (t),	−164.9 (m),	17.94 (d)[j]	3630	—	—
	−120.0 (d)	−162.6 (t) **8c**	−165.7 (m) **8c**		**8c**		
	(**8c** + **8a**)[i]	−164.2 (t) **8a**	−166.7 (m) **8a**				
				−17.35 (d)[j]	4037		
				−12.08 (s)	3984 **8a**		

[a] In $CDCl_3$ at 20 °C, chemical shifts are reported relative to $CFCl_3$, H_3PO_4 (85%) and $SiMe_3$ (as external references) respectively. [b] $^3J(^{195}Pt-F_o)$ in parentheses. [c] δ 5.30 (s, 1 CH_2Cl_2). [d] In CD_3COCD_3, the spectra showed small additional signals due to the presence of complex **6c** in low concentration (ratio **6a**:**6c** ≈ 5:1); after 4 h in acetone, both isomers **6a** and **6c** are observed in a molar ratio of *ca.* 2:1. [e] The complex dissolves in $CDCl_3$ giving immediately a mixture of **6a** and **6c** in *ca.* 1:1.2 mol ratio; after 24 h the ratio **6a**:**6c** was 1:1.8. [f] $^2J(P-P)$ = 13.3 Hz. [g] The complex is slightly soluble in $CDCl_3$ or CH_2Cl_2 giving immediately a mixture of **7a** and **7c** in solution, NMR in CD_2Cl_2 (**7a**:**7c** ratio observed 1:1.25). [h] The complex dissolves in CD_2Cl_2 yielding a mixture of **8a** and **8c** in a 1:3.5 molar ratio. [i] Platinum satellites are also observed but it is not possible to calculate individual $^3J(^{195}Pt-F_o)$ constants. [j] $^2J(P-P)$ are not well resolved.

Table 3 Selected bond lengths (Å) and angles (°) for $[(C_6F_5)_2Pt(\mu-Cl)(\mu-PPh_2C\equiv CPh)PtCl(PPh_2C\equiv CPh)]\cdot OC_4H_8$

Pt(1)–Cl(1)	2.380(4)	Pt(1)–C(1)	1.971(15)
Pt(1)–C(7)	2.046(11)	Pt(1)–C(13)	2.150(12)
Pt(1)–C(14)	2.200(12)	Pt(2)–Cl(1)	2.387(3)
Pt(2)–Cl(2)	2.320(4)	Pt(2)–P(1)	2.241(4)
Pt(2)–P(2)	2.227(4)	P(1)–C(13)	1.759(15)
P(1)–C(21)	1.786(15)	P(1)–C(27)	1.825(12)
P(2)–C(33)	1.751(15)	P(2)–C(41)	1.798(13)
P(2)–C(47)	1.810(15)	C(13)–C(14)	1.261(21)
C(14)–C(15)	1.396(21)	C(33)–C(34)	1.163(21)
C(34)–C(35)	1.478(20)		
Cl(1)–Pt(1)–C(1)	174.4(3)	Cl(1)–Pt(1)–C(7)	85.8(4)
C(1)–Pt(1)–C(7)	88.9(5)	Cl(1)–Pt(1)–C(13)	84.0(4)
C(1)–Pt(1)–C(13)	100.9(5)	C(7)–Pt(1)–C(13)	164.3(6)
Cl(1)–Pt(1)–C(14)	99.5(4)	C(1)–Pt(1)–C(14)	86.1(5)
C(7)–Pt(1)–C(14)	161.4(6)	Cl(1)–Pt(2)–Cl(2)	85.7(1)
Cl(1)–Pt(2)–P(1)	91.4(1)	Cl(2)–Pt(2)–P(1)	176.3(1)
Cl(1)–Pt(2)–P(2)	173.7(1)	Cl(2)–Pt(2)–P(2)	88.2(1)
P(1)–Pt(2)–P(2)	94.7(1)	Pt(1)–Cl(1)–Pt(2)	115.6(1)
Pt(2)–P(1)–C(13)	108.8(4)	Pt(2)–P(1)–C(21)	117.3(5)
C(13)–P(1)–C(21)	105.7(7)	Pt(2)–P(1)–C(27)	114.2(5)
C(13)–P(1)–C(27)	101.7(6)	C(21)–P(1)–C(27)	107.7(6)
Pt(2)–P(2)–C(33)	115.4(6)	Pt(2)–P(2)–C(41)	112.8(5)
C(33)–P(2)–C(41)	105.0(6)	Pt(2)–P(2)–C(47)	114.9(4)
C(33)–P(2)–C(47)	101.3(7)	C(41)–P(2)–C(47)	106.1(7)
P(1)–C(13)–C(14)	151.6(13)	C(13)–C(14)–C(15)	157.9(12)
P(2)–C(33)–C(34)	176.8(17)	C(33)–C(34)–C(35)	177.8(19)

Both platinum centres are located in distorted square-planar environments, with a *cis* arrangement of the C_6F_5 groups at Pt(1) and the chloride ligands (terminal and bridging) at Pt(2). The Pt–Cl(μ) bridging [Pt(2)–Cl(1) 2.387(3), Pt(1)–Cl(1) 2.380(4) Å] and the Pt–Cl terminal [Pt(2)–Cl(2) 2.320(4) Å] distances are similar to those of dinuclear $[\{PtCl(\mu-Cl)L\}_2]$ complexes.[16] The Pt–P distances are almost identical within experimental error [Pt(2)–P(1) 2.241(4), Pt(2)–P(2) 2.227(4) Å] and similar to those in the mononuclear complex *cis*-$[PtCl_2(PPh_2C\equiv CPh)_2]\cdot 2MeCN$[12] [2.235(2) and 2.237(2) Å]. The Pt(1)–C(C_6F_5) distances are perceptibly different [Pt(1)–C(1) 1.971(15) and Pt(1)–C(7) 2.046(11) Å] reflecting the presence of different *trans* ligands.

Both phosphinoacetylene ligands have comparable P–C(alkyne) bond distances [P(1)–C(13) 1.759(15), P(2)–C(33) 1.751(15) Å] and angles at the phosphorus atoms, but the C–C distances and angles at the acetylenic carbons differ markedly following the usual pattern observed for co-ordinated/unco-ordinated alkynes.[17] Thus, as expected, co-ordination of the C(13)–C(14) triple bond to Pt(1) has a perceptible effect both on the bond length and on the linearity of the acetylenic group [C(13)–C(14) 1.261(21) *versus* C(33)–C(34) 1.163(21) Å; P(1)–C(13)–C(14) 151.6(13) and C(13)–C(14)–C(15) 157.9(12) *versus* P(2)–C(33)–C(34) 176.8(17) and C(33)–C(34)–C(35) 177.8(19)°]. It should be noted that the C≡C bond length and angles at the acetylenic carbons of the phosphinoacetylene bridging ligand [P(1)PPh$_2$C(13)≡C(14)Ph] are rather similar to the corresponding parameters in the phosphine-stabilised low-valent metal complexes $[Ni_2(CO)_2(PPh_2C\equiv CBu^t)_2]$,[5a] $[Fe_2(CO)_6(PPh_2C\equiv CPh)_2]$[5a] and $[Fe_2(CO)_8(PPh_2C\equiv CBu^t)]$[5b] respectively for which a considerable distortion of the co-ordinated acetylenic fragment has been suggested. This fact suggests that the Pt(1)–π(acetylene) interaction is strong and accordingly the Pt(1)–C(alkyne) bond distances [Pt(1)–C(13) 2.150(12), Pt(1)–C(14) 2.200(12) Å] are considerably shorter than the corresponding Pt–C(alkyne) bond lengths found by us

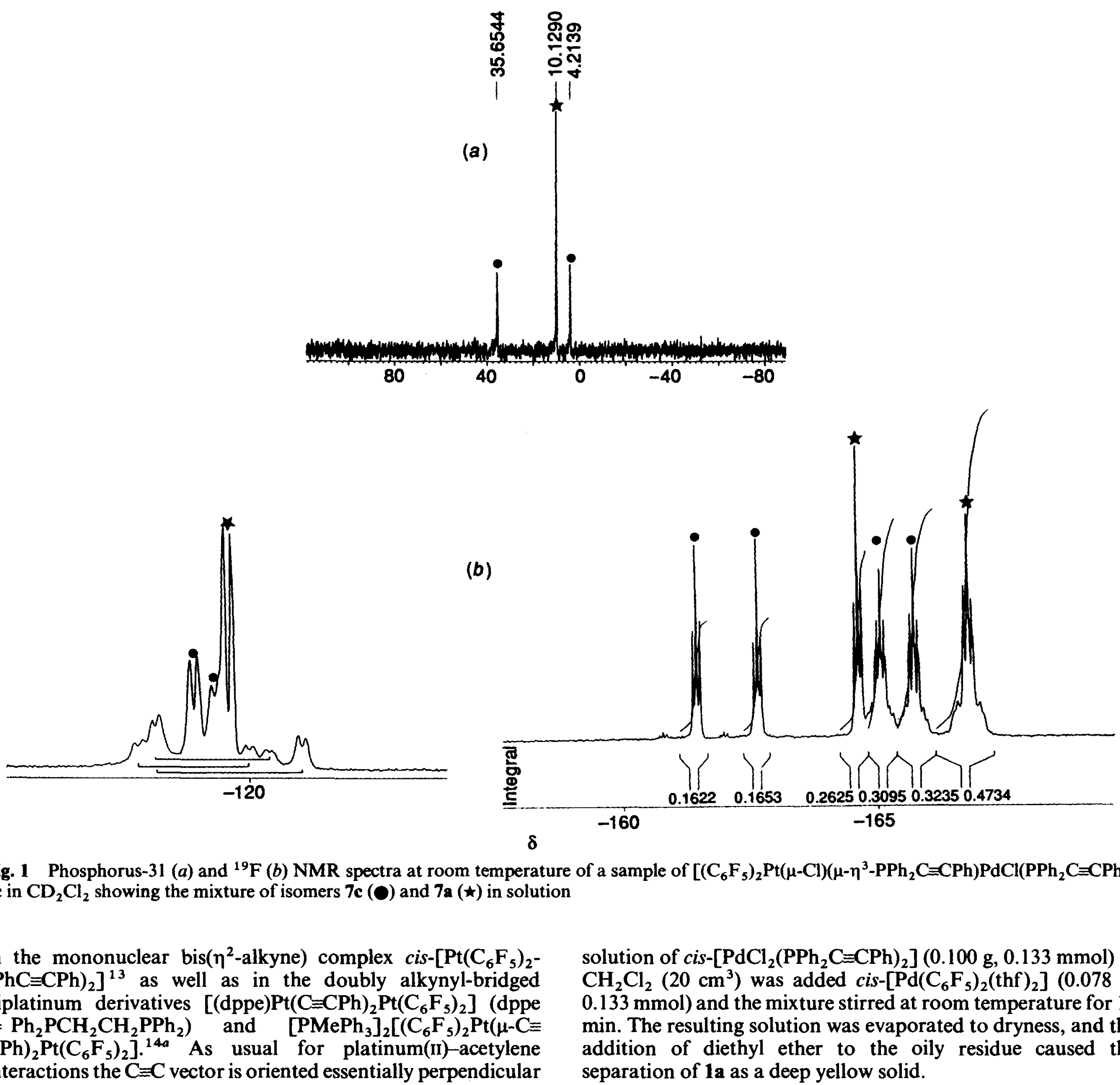


Fig. 1 Phosphorus-31 (*a*) and ^{19}F (*b*) NMR spectra at room temperature of a sample of $[(C_6F_5)_2Pt(\mu\text{-}Cl)(\mu\text{-}\eta^3\text{-}PPh_2C{\equiv}CPh)PdCl(PPh_2C{\equiv}CPh)]$ **7c** in CD_2Cl_2 showing the mixture of isomers **7c** (●) and **7a** (★) in solution

in the mononuclear bis(η^2-alkyne) complex *cis*-$[Pt(C_6F_5)_2(PhC{\equiv}CPh)_2]$[13] as well as in the doubly alkynyl-bridged diplatinum derivatives $[(dppe)Pt(C{\equiv}CPh)_2Pt(C_6F_5)_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) and $[PMePh_3]_2[(C_6F_5)_2Pt(\mu\text{-}C{\equiv}CPh)_2Pt(C_6F_5)_2]$.[14a] As usual for platinum(II)–acetylene interactions the C≡C vector is oriented essentially perpendicular to the local co-ordination plane of Pt(1) [the angle formed by the vector defined by Pt(1) and the midpoint of the C≡C bond and the C(13)–C(14) vector is 88.8(9)°] and is inclined by 27.7(8)° to the normal of this plane. As a consequence the central core is not planar and the best least-squares planes around Pt(1) and Pt(2) form a dihedral angle of 31.2(2)°.

The steric requirements of the bridging phosphinoacetylene ligand could be responsible for the large Pt(1)–Cl(1)–Pt(2) angle [115.6(1)°][16,18] and the long distance between the platinum atoms [4.033(2) Å].

Experimental

All manipulations were carried out under a nitrogen atmosphere. The C and H analyses and IR spectra were obtained as described elsewhere.[14] Proton, ^{19}F and ^{31}P NMR spectra were recorded on either a Varian Unity 300 or a Bruker ARX 300 instrument and the chemical shifts (ppm) are reported relative to $SiMe_3$, $CFCl_3$ and 85% H_3PO_4 (as external references) respectively. Literature methods were used to prepare *cis*-$[MCl_2(PPh_2C{\equiv}CR)_2]$[3d,f,12a] and *cis*-$[M(C_6F_5)_2(thf)_2]$[19] (M = Pt or Pd).

$[(C_6F_5)_2Pd(\mu\text{-}Cl)_2Pd(PPh_2C{\equiv}CPh)_2]$ **1a**.—To a yellow solution of *cis*-$[PdCl_2(PPh_2C{\equiv}CPh)_2]$ (0.100 g, 0.133 mmol) in CH_2Cl_2 (20 cm^3) was added *cis*-$[Pd(C_6F_5)_2(thf)_2]$ (0.078 g, 0.133 mmol) and the mixture stirred at room temperature for 15 min. The resulting solution was evaporated to dryness, and the addition of diethyl ether to the oily residue caused the separation of **1a** as a deep yellow solid.

$[\{Pd(\mu\text{-}Cl)(C_6F_5)(PPh_2C{\equiv}CPh)\}_2]$ **1b**.—The complex *cis*-$[Pd(C_6F_5)_2(thf)_2]$ (0.078 g, 0.133 mmol) was added to a yellow solution of *cis*-$[PdCl_2(PPh_2C{\equiv}CPh)_2]$ (0.100 g, 0.133 mmol) in chloroform (20 cm^3) and the mixture stirred at room temperature for 24 h. Concentration of the resulting dark orange solution (*ca.* 5 cm^3) produced complex **1b** as a very pale yellow solid.

$[(C_6F_5)_2Pd(\mu\text{-}Cl)_2Pd(PPh_2C{\equiv}CBu^t)_2]$ **2a**·CH_2Cl_2.—To a solution of *cis*-$[PdCl_2(PPh_2C{\equiv}CBu^t)_2]$ (0.100 g, 0.141 mmol) in CH_2Cl_2 (20 cm^3) was added *cis*-$[Pd(C_6F_5)_2(thf)_2]$ (0.082 g, 0.141 mmol) and the mixture was stirred at room temperature for 30 min. The resulting solution was filtered and the filtrate evaporated to ≈5 cm^3. Addition of hexane (≈1 cm^3) produced **2a** as a pale yellow solid.

$[\{Pd(\mu\text{-}Cl)(C_6F_5)(PPh_2C{\equiv}CBu^t\}_2]$ **2b**·CH_2Cl_2.—The synthesis was performed as described for complex **1b** starting from *cis*-$[PdCl_2(PPh_2C{\equiv}CBu^t)_2]$ (0.100 g, 0.141 mmol) and *cis*-$[Pd(C_6F_5)_2(thf)_2]$ (0.082 g, 0.141 mmol). In this case the resulting solution was treated with charcoal, filtered through Kieslguhr and then concentrated to ≈5 cm^3. Then, addition of

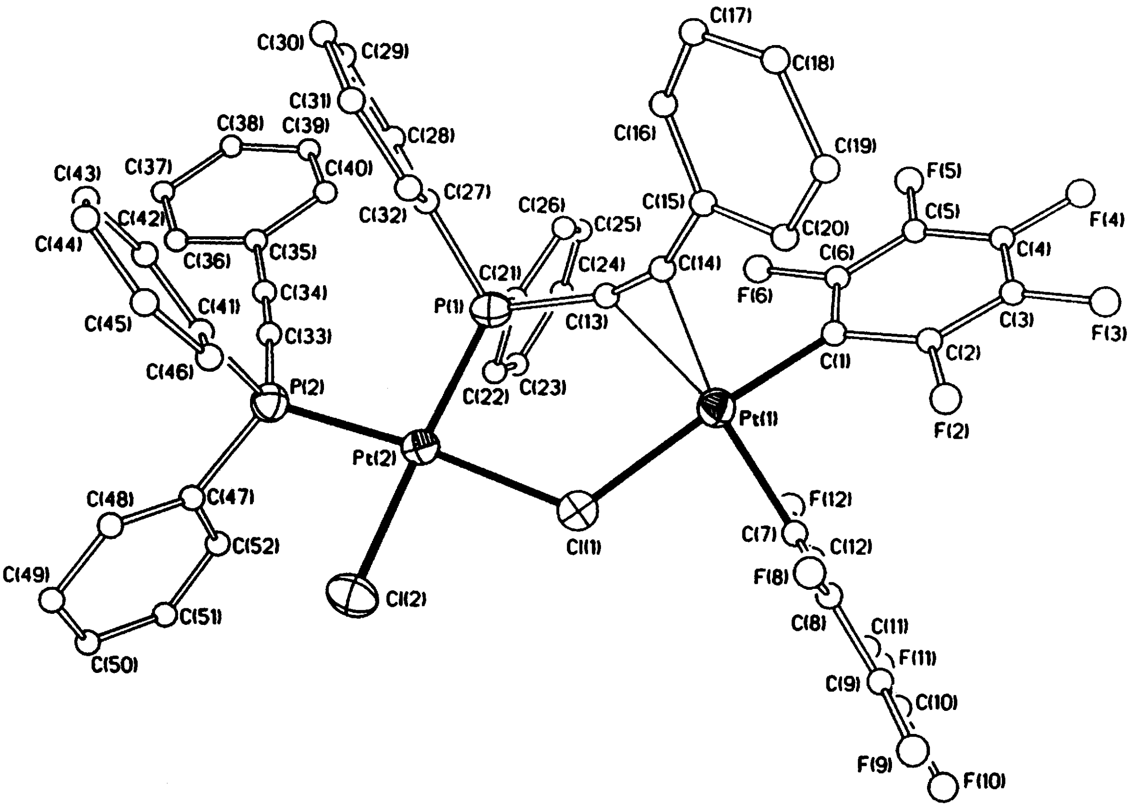
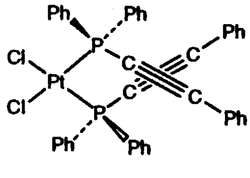


Fig. 2 Molecular structure of $[(C_6F_5)_2Pt(\mu\text{-}Cl)(\mu\text{-}\eta^3\text{-}PPh_2C{\equiv}CPh)PtCl(PPh_2C{\equiv}CPh)]\cdot OC_4H_8$ (**8c**·OC_4H_8) (non-hydrogen atoms only) showing the atom numbering scheme. The solvent of crystallisation is not shown



A

a few drops of hexane and cooling to −30 °C overnight gave **2b** as a yellow solid.

$[(C_6F_5)_2Pd(\mu\text{-}Cl)_2Pt(PPh_2C{\equiv}CPh)_2]$ **3a**.—To a colourless solution of *cis*-$[PtCl_2(PPh_2C{\equiv}CPh)_2]$ (0.100 g, 0.119 mmol) in CH_2Cl_2 (20 cm^3) was added *cis*-$[Pd(C_6F_5)_2(thf)_2]$ (0.070 g, 0.119 mmol). The solution immediately turned deep yellow, and after stirring for *ca.* 15 min it was concentrated to ≈5 cm^3. Then addition of a few drops of hexane and standing at −30 °C (2 d) precipitated **3a** as a pale yellow solid.

$[(C_6F_5)_2Pd(\mu\text{-}Cl)_2Pt(PPh_2C{\equiv}CBu^t)_2]$ **4a**.—To a colourless solution of *cis*-$[PtCl_2(PPh_2C{\equiv}CBu^t)_2]$ (0.100 g, 0.125 mmol) in CH_2Cl_2 (20 cm^3) was added *cis*-$[Pd(C_6F_5)_2(thf)_2]$ (0.073 g, 0.125 mmol) and the mixture stirred at room temperature for 30 min. The resulting yellow solution was concentrated until precipitation of **4a** as a pale yellow solid (*ca.* 5 cm^3) and then hexane was added to complete the precipitation.

$[(C_6F_5)_2Pt(\mu\text{-}Cl)_2Pd(PPh_2C{\equiv}CBu^t)_2]$ **5a**.—A yellow suspension of *cis*-$[PdCl_2(PPh_2C{\equiv}CBu^t)_2]$ (0.100 g, 0.141 mmol) in toluene (25 cm^3) was treated with *cis*-$[Pt(C_6F_5)_2(thf)_2]$ (0.095 g, 0.141 mmol). Immediate dissolution of the suspension took place yielding an orange-red solution, and after *ca.* 2–3 min an orange-yellow solid began to precipitate. The mixture was stirred for 1 h and then the orange-yellow solid **5a** which separated was filtered off.

$[(C_6F_5)_2Pt(\mu\text{-}Cl)_2Pt(PPh_2C{\equiv}CBu^t)_2]$ **6a**.—The complex *cis*-$[Pt(C_6F_5)_2(thf)_2]$ (0.084 g, 0.125 mmol) was added to a stirred suspension of *cis*-$[PtCl_2(PPh_2C{\equiv}CBu^t)_2]$ (0.100 g, 0.125 mmol) in toluene (30 cm^3). Immediately part of the initial suspension dissolved, but after a few (1–2) minutes a white product precipitated. The mixture was stirred for 1 h and then the white solid formed (**6a**) was filtered off.

$[(C_6F_5)_2Pt(\mu\text{-}Cl)(\mu\text{-}PPh_2C{\equiv}CPh)PdCl(PPh_2C{\equiv}CPh)]$ **7c**.—To a stirred yellow suspension of *cis*-$[PdCl_2(PPh_2C{\equiv}CPh)_2]$ (0.100 g, 0.133 mmol) in toluene (20 cm^3) was added *cis*-$[Pt(C_6F_5)_2(thf)_2]$ (0.090 g, 0.133 mmol) giving immediately an orange solution. After 15 min of stirring at room temperature a deep yellow solid began to precipitate. The mixture was stirred for 1 h and the resulting yellow solid (**7c**) was filtered off.

$[(C_6F_5)_2Pt(\mu\text{-}Cl)(\mu\text{-}PPh_2C{\equiv}CPh)PtCl(PPh_2C{\equiv}CPh)]$ **8c**.—To a stirred suspension of *cis*-$[PtCl_2(PPh_2C{\equiv}CPh)_2]$ (0.100 g, 0.119 mmol) in toluene (20 cm^3) was added *cis*-$[Pt(C_6F_5)_2(thf)_2]$ (0.080 g, 0.119 mmol) giving immediately a yellow solution. After a few (1–2) minutes a pale yellow solid was formed. The mixture was stirred for 1 h and then the solid (**8c**) was filtered off.

Crystal Structure Determination of $[(C_6F_5)_2Pt(\mu\text{-}Cl)(\mu\text{-}PPh_2C{\equiv}CPh)PtCl(PPh_2C{\equiv}CPh)]\cdot OC_4H_8$.—*Crystal data.* $C_{56}H_{38}Cl_2F_{10}OP_2Pt_2$, *M* 1439.9, monoclinic, space group $P2_1/n$, $a = 14.251(7)$, $b = 20.526(5)$, $c = 19.214(11)$ Å, $\beta = 110.66(4)°$, $U = 5259(4)$ Å^3, $Z = 4$, $D_c = 1.82$ g cm^{-3}, λ(Mo-Kα) = 0.710 73 Å, $\mu = 55.5$ cm^{-1}, $F(000) = 2768$, $T = 293 \pm 1$ K, crystal dimensions 0.3 × 0.3 × 0.25 mm.

Crystallographic data were collected on a CADY diffractometer, $3 < 2\theta < 44°$; 6433 independent reflections, 4592 with $I > 3\sigma(I)$ were used for all calculations. Cell constants were refined from 2θ values of 25 reflections including Friedel

Table 4 Atomic coordinates (× 10^4) for $[(C_6F_5)_2Pt(\mu\text{-}Cl)(\mu\text{-}PPh_2C{\equiv}CPh)PtCl(PPh_2C{\equiv}CPh)]\cdot OC_4H_8$

Atom	*x*	*y*	*z*
Pt(1)	1394(1)	2094(1)	2815(1)
Pt(2)	−647(1)	1444(1)	3665(1)
Cl(1)	911(2)	1985(2)	3875(2)
Cl(2)	−325(3)	1608(2)	4922(2)
P(1)	−919(3)	1350(2)	2447(2)
P(2)	−2091(3)	978(2)	3591(2)
C(1)	1923(9)	2150(6)	1997(7)
C(2)	2582(10)	2627(7)	1945(7)
C(3)	2996(10)	2673(8)	1391(8)
C(4)	2735(13)	2221(9)	850(9)
C(5)	2088(11)	1737(7)	859(8)
C(6)	1727(10)	1733(8)	1429(9)
F(2)	2867(6)	3120(4)	2461(4)
F(3)	3627(7)	3155(5)	1382(5)
F(4)	3130(7)	2251(5)	297(5)
F(5)	1860(8)	1295(5)	321(5)
F(6)	1132(7)	1204(5)	1410(5)
C(7)	2836(9)	2034(7)	3550(7)
C(8)	3294(10)	2526(7)	4012(8)
C(9)	4243(13)	2506(9)	4511(9)
C(10)	4803(11)	1955(10)	4585(9)
C(11)	4404(12)	1443(10)	4139(9)
C(12)	3376(11)	1483(9)	3610(8)
F(8)	2778(7)	3093(5)	3990(6)
F(9)	4655(8)	2994(6)	4994(6)
F(10)	5707(7)	1889(6)	5084(6)
F(11)	4917(7)	883(6)	4185(6)
F(12)	3047(6)	960(4)	3166(5)
C(13)	−170(9)	1923(7)	2204(7)
C(14)	−9(10)	2489(7)	2018(7)
C(15)	−197(11)	3071(8)	1615(8)
C(16)	−1077(13)	3170(9)	1044(9)
C(17)	−1336(19)	3725(12)	680(11)
C(18)	−680(20)	4250(14)	879(15)
C(19)	219(17)	4190(9)	1449(12)
C(20)	480(12)	3593(8)	1814(9)
C(21)	−645(10)	582(7)	2124(8)
C(22)	−254(11)	73(8)	2626(9)
C(23)	−15(15)	−475(10)	2392(13)
C(24)	−82(17)	−574(11)	1653(15)
C(25)	−420(16)	−106(11)	1197(12)
C(26)	−692(12)	512(9)	1407(9)
C(27)	−2176(10)	1590(8)	1844(7)
C(28)	−2828(10)	1169(8)	1315(8)
C(29)	−3756(14)	1396(11)	894(10)
C(30)	−4047(14)	2018(12)	990(11)
C(31)	−3422(13)	2429(11)	1515(11)
C(32)	−2478(12)	2228(7)	1947(8)
C(33)	−2491(11)	340(7)	2948(8)
C(34)	−2788(11)	−92(8)	2537(8)
C(35)	−3203(11)	−638(7)	2018(7)
C(36)	−3905(12)	−1016(8)	2125(9)
C(37)	−4357(14)	−1529(8)	1638(10)
C(38)	−4098(14)	−1605(8)	1027(10)
C(39)	−3383(17)	−1239(10)	938(10)
C(40)	−2944(13)	−714(8)	1404(9)
C(41)	−3121(10)	1542(6)	3337(7)
C(42)	−4053(10)	1375(9)	2866(8)
C(43)	−4828(11)	1818(9)	2705(9)
C(44)	−4660(12)	2440(11)	2991(10)
C(45)	−3744(12)	2617(9)	3454(9)
C(46)	−2964(11)	2185(8)	3609(8)
C(47)	−2083(9)	584(7)	4436(7)
C(48)	−2591(10)	829(8)	4852(8)
C(49)	−2580(13)	515(9)	5495(9)
C(50)	−1994(15)	−37(10)	5711(10)
C(51)	−1481(13)	−266(9)	5313(10)
C(52)	−1517(10)	22(8)	4679(9)
O	3545(21)	182(14)	1725(14)
C(53)	4124(26)	394(18)	1284(21)
C(54)	3878(27)	−75(20)	617(20)
C(55)	2884(27)	−366(19)	623(20)
C(56)	2757(25)	−283(18)	1393(21)

pairs (24 > 2θ > 22°). An empirical absorption correction (DIFABS[20]) was applied. Two standard reflections were measured every 500 but showed no decay. The structure was solved by direct methods and refined on $|F_o|$ to $R = 0.039$ and $R' = 0.054$ for 630 variables [weighting scheme $w^{-1} = \sigma^2(F_o) + 0.0007\,F_o^2$] using the SHELXTL PLUS[21] package. Highest shift : error ratio 0.001 : 1. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in calculated positions and refined as riding atoms (C–H 0.96 Å and $U = 0.0885$ Å^2). In the final stages of the refinement the presence of a molecule of tetrahydrofuran as crystallisation solvent was discovered. In this molecule the distances C–C and C–O were fixed at 1.54 and 1.46 Å respectively and the five atoms of the molecule were refined with a common thermal parameter. A difference map following convergence showed two peaks higher than 1 e Å^{-3} (maximum, minimum difference density 1.25, −0.81 e Å^{-3}) near the heavy atoms.

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

Acknowledgements

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