Synthesis of Homo- and Hetero-dinuclear Complexes containing Alkynyl Bridges. Molecular Structure of *cis,trans*-$[(OC)(C_6F_5)_2Pt(\mu\text{-}\eta^2\text{-}C{\equiv}CPh)Pt(C{\equiv}CPh)(PPh_3)_2]$†

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Terminal organotransition-metal acetylides *trans*-$[Pt(C{\equiv}CR)_2L_2]$ (R = Ph or Bu^t, L = PPh_3 or PEt_3), *cis*-$[Pt(C{\equiv}CBu^t)_2L_2]$ (L = PPh_3 or PEt_3), $[Pt(C{\equiv}CR)_2(dppe)]$ (R = Bu^t or $SiMe_3$, dppe = $Ph_2PCH_2CH_2PPh_2$) and $[Au(C{\equiv}CR)(PPh_3)]$ (R = Ph or Bu^t) reacted with *cis*-$[Pt(C_6F_5)_2(CO)(thf)]$ (thf = tetrahydrofuran) to give, under alkynylation of the fragment $Pt(C_6F_5)_2(CO)$, the μ-η^2-acetylide-bridged dinuclear zwitterionic complexes $[(OC)(C_6F_5)_2Pt^-(\mu\text{-}\eta^2\text{-}C{\equiv}CR)M^+L_n]$. The phenylacetylide complex $[(OC)(C_6F_5)_2Pt^-(\mu\text{-}\eta^2\text{-}C{\equiv}CPh)Pt^+(C{\equiv}CPh)(PPh_3)_2]$ has been characterised by X-ray structural analysis.

Extensive studies have focused on the chemical behaviour of transition-metal complexes bearing a C≡C functional group, that is metal acetylides M–C≡CR and η^2-acetylene complexes.[1] The interest in this area is due principally to the wide variety of chemical processes undergone by the acetylenic group coordinated to mono- or poly-nuclear metal fragments[2] and to the richness of their co-ordination modes.[3]

Polynuclear μ-acetylide complexes[4] in which the acetylide ligand is σ bonded to one metal centre and η^2 bonded to the other have also attracted much attention as models for surface-bound species.[5h] However most studies have dealt with complexes which contain additional bridging ligands ($Ph_2PCH_2PPh_2$, SR, PR_2, *etc.*); very few monoacetylide dinuclear complexes without any additional bridging ligands are known.[5]

Following our recent work on alkyne- and acetylide-containing platinum complexes[6] we have shown that reactions of *cis*-$[Pt(C_6F_5)_2(thf)_2]$ (thf = tetrahydrofuran) with alkynes and bis(σ-alkynyl) derivatives yield a variety of products including the first bis(η^2-alkyne)platinum(II) complexes[6a,b] and several homo- and hetero-dinuclear doubly acetylide-bridged complexes.[6f–h] Since we have found in previous studies that mononuclear *cis*-$[Pt(C_6F_5)_2(CO)(thf)]$[7] reacts easily with alkynes RC≡CR (R = Ph or Et) giving rise to mono(η^2-alkyne)platinum(II) complexes[6b] it could be anticipated that its reactions with simple terminal organotransition-metal acetylides, L_nM–C≡CR, would provide an entry to dinuclear mono(μ-acetylide) complexes.

In this paper we describe the preparation and properties of several μ-η^2-acetylide dinuclear zwitterionic complexes $[(OC)(C_6F_5)_2Pt^-(\mu\text{-}\eta^2\text{-}C{\equiv}CR)M^+L_n]$ obtained by reaction between *cis*-$[Pt(C_6F_5)_2(CO)(thf)]$ and several metal alkynyl complexes $L_nMC{\equiv}CR$. The structure of *cis,trans*-$[(OC)(C_6F_5)_2Pt^-(\mu\text{-}\eta^2\text{-}C{\equiv}CPh)Pt^+(C{\equiv}CPh)(PPh_3)_2]$ **1** has been established by single-crystal X-ray diffraction. To the best of our knowledge, this is the first example of a diplatinum complex in which the metal centres are connected by only a μ-η^2-acetylide ligand.

Results and Discussion

Initial attempts to use mononuclear monoacetylide platinum complexes such as *trans*-$[PtX(C{\equiv}CR)(PPh_3)_2]$ (X = C_6F_5, R = Ph, Bu^t or $SiMe_3$; X = Cl, R = Ph) as building blocks for monoacetylide-bridged diplatinum compounds were unsuccessful. Thus, reactions with *cis*-$[Pt(C_6F_5)_2(CO)(thf)]$ afford a mixture of products which could not be separated by recrystallisation. We therefore turned our interest to bis(acetylide) mononuclear platinum complexes $[Pt(C{\equiv}CR)_2L_2]$. The reactions of these complexes with *cis*-$[Pt(C_6F_5)_2(CO)(thf)]$ are summarised in Scheme 1.

Reactions of trans-$[Pt(C{\equiv}CR)_2L_2]$ *with cis*-$[Pt(C_6F_5)_2(CO)(thf)]$.—The complexes *trans*-$[Pt(C{\equiv}CR)_2L_2]$ (R = Ph or Bu^t, L = PPh_3 or PEt_3) react with *cis*-$[Pt(C_6F_5)_2(CO)(thf)]$ in CH_2Cl_2 (molar ratio 1 : 1) to form, under alkynylation of the fragment '$Pt(C_6F_5)_2(CO)$', the μ-η^2-monoacetylide-bridged diplatinum zwitterionic complexes **1**–**4** shown in Scheme 1 (*i*). Owing to the presence of two terminal acetylide ligands in the starting materials and with the aim of obtaining trinuclear derivatives, similar reactions but using 2 equivalents of *cis*-$[Pt(C_6F_5)_2(CO)(thf)]$ were also carried out. However this does not result in incorporation of a second $Pt(C_6F_5)_2(CO)$ fragment and produces complexes **1**–**4**.

Complexes **1**–**4** were isolated as white solids, except for **1** which is pale yellow, and were characterised spectroscopically (see Experimental section and Table 1). Complex **1** was also fully characterised by single-crystal X-ray diffraction analysis which provided unambiguous structural assignment as illustrated in Fig. 1(*a*). Selected interatomic distances and angles are collected in Table 2.

This study confirms the presence of only one phenylacetylide ligand bridging two separated platinum moieties. The molecule consists of two organometallic moieties, $Pt(1)(C_6F_5)_2(CO)$ and $Pt(2)(C{\equiv}CPh)(PPh_3)_2$, connected by a μ-η^2-C≡CPh ligand

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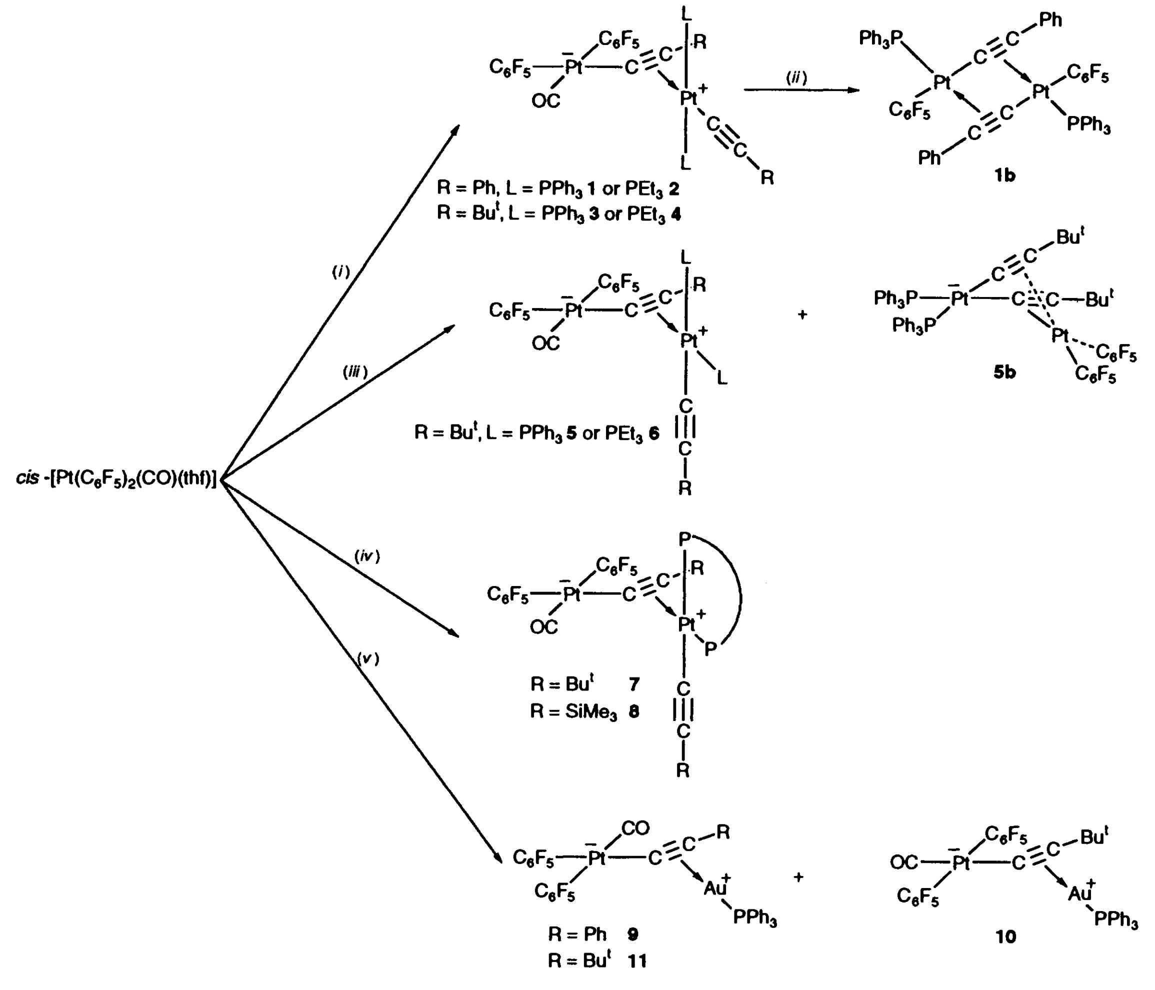
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

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

Complex	F_{ortho} [b]	F_{para}	F_{meta}	δ(P)	$^{1}J(^{195}Pt-^{31}P)$/Hz
1	−121.8 (377), −123.2 (335)	−166.7, −167.0	−169.8, −170.2	19.7	2462
2	−118.3 (324), −118.7 (376)	−160.9, −161.1	−164.2, −164.6	14.2	2213
3	−116.7 (370), −118.0 (330)	−161.9, −162.0	−164.8, −165.4	17.3	2537
4	−118.5[c] (≈330, ≈375)	−161.2, −162.0	−164.2, −165.0	10.5	2312
6[d]	−119.4[e] (2 F),	−161.1	−164.3	7.9	3263
	−114.9 (d, 1 F, 395), −116.7[e] (1 F)		−167.5[e], −165.2[e]	2.3	2234
7[f]	−112.9 (≈350), −116.1 (397)	−160.2, −161.2	−163.2	40.21	2284
					2577
8	−115.5 (≈365), −117.3 (413)	−161.7, −162.5	−164.8	40.04	2211
				39.8	2430
9	−117.4 (381), −118.12 (342)	−160.9	−164.2	35.9	—
10	−115.6 (291)	−160.9	−164.0	35.6	—

[a] In $CDCl_3$, chemical shifts are reported in ppm with external references to $CFCl_3$ and 85% H_3PO_4 respectively. [b] $^{3}J(^{195}Pt-F_o)$/Hz in parentheses. [c] Each F_{ortho} is isochronous. [d] Data at −56 °C; at room temperature: δ −118.0 [d, F_{ortho}, $^{3}J(^{195}Pt-F_o)$ = 330 Hz], −162.0 (m, F_{para}), −164.8, −165.5 (m, F_{meta}); both triplets corresponding to F_{para} signals are overlapped giving a multiplet. [e] Broad signal. [f] Data at −56 °C: δ −112.2 (m), −115.5 (d), −117 (m), −118.1 (m) (F_{ortho}); −160.4 (t), −161.7 (t) (F_{para}); −162.1 (m), −163.4 (m), −163.6 (m), −165.0 (m) (F_{meta}) (see Fig. 2).



Scheme 1 (*i*) *trans*-$[Pt(C\equiv CR)_2L_2]$ in CH_2Cl_2, room temperature, 1 h; (*ii*) in benzene, reflux, 1 h; (*iii*) *cis*-$[Pt(C\equiv CR)_2L_2]$ in benzene, room temperature, 2 min (mixture of **5** and **5b**) or 1 min (**6**); (*iv*) $[Pt(C\equiv CR)_2(dppe)]$ in Et_2O, −10 °C, 20 min; (*v*) $[Au(C\equiv CR)(PPh_3)]$ in CH_2Cl_2, room temperature, 5 min (**9**); in benzene, room temperature, immediate (**10**); in Et_2O, room temperature, 3 min (mixture of **10** and **11**)

which is σ bonded to the former and π bonded to the latter. Both platinum atoms are in approximately square-planar environments with the C_6F_5 groups mutually *cis* at Pt(1) and the PPh_3 ligands mutually *trans* at Pt(2). Thus, although the *cis* and *trans* geometries around the platinum centres have been preserved throughout the reaction, an unexpected alkynylation of the synthon $Pt(C_6F_5)_2(CO)$ has taken place yielding a more polar complex (in fact, **1** is formally zwitterionic) than would otherwise have been expected. This process is noteworthy, since the less-polar complex $[(Ph_3P)_2(PhC\equiv C)Pt(\mu-C\equiv CPh)Pt(C_6$-

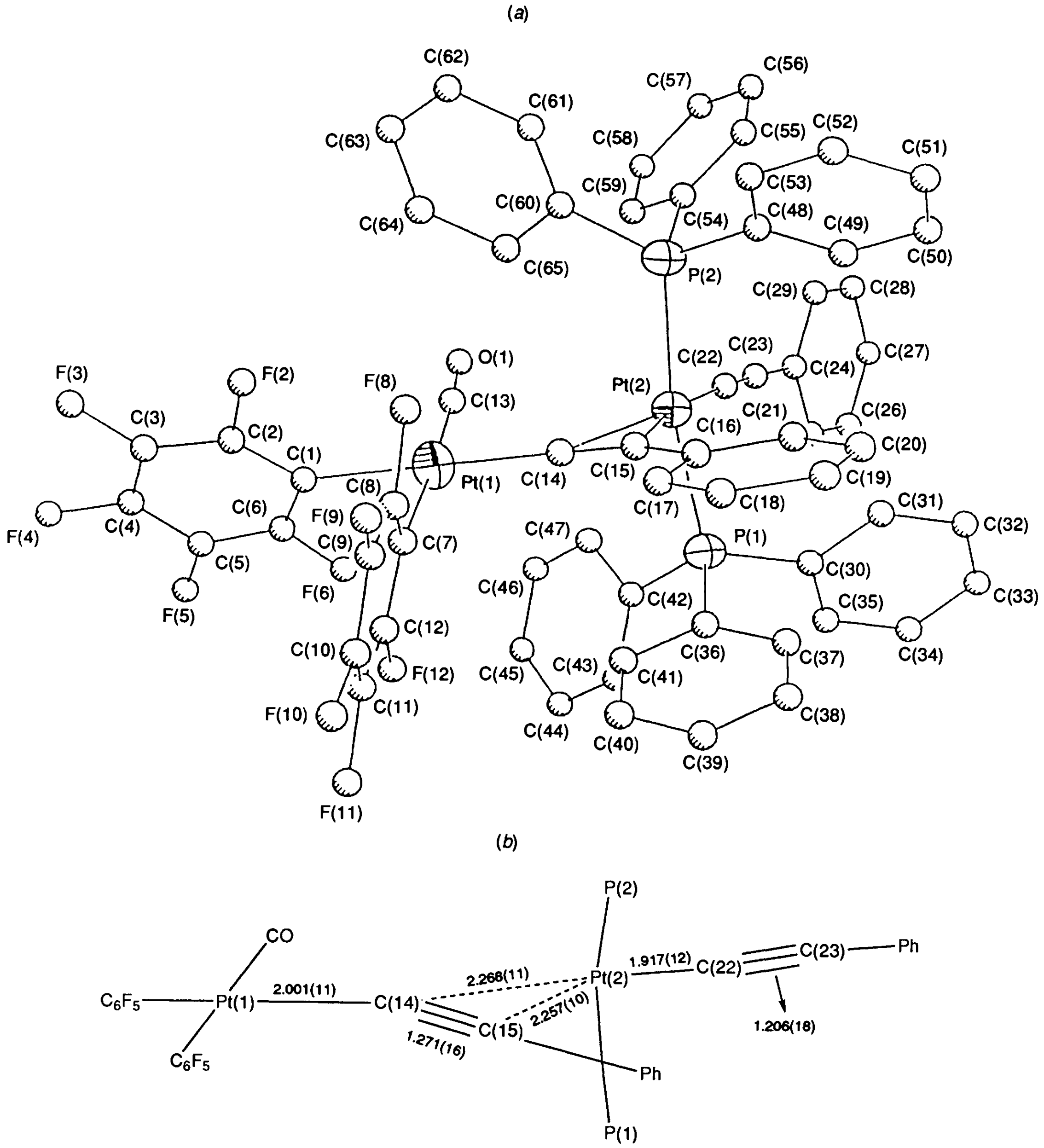


Fig. 1 (*a*) View of the structure of complex *cis,trans*-[(OC)$(C_6F_5)_2$Pt(μ-C≡CPh)Pt(C≡CPh)$(PPh_3)_2$] **1** with the atomic numbering scheme. (*b*) Schematic view of the μ-η^2-bonded acetylide group with bond lengths in Å

$F_5)_2$(CO)] could have been expected. However, the enhanced acidity of the metal centre in *cis*-[Pt$(C_6F_5)_2$(CO)(thf)], brought about by the electron-withdrawing nature of the C_6F_5 groups and by the good π-acceptor properties of the CO ligand, could be responsible for the formation of **1**.

Each of the two moieties shows the expected structural features. Thus, the Pt(1)–C pentafluorophenyl [Pt(1)–C(1) 2.048(11); Pt(1)–C(7) 2.035(13) Å] and carbonyl [Pt(1)–C(13) 1.839(15) Å] distances are similar to those found in [(η-C_5H_5)$(OC)_2$Rh→Pt$(C_6F_5)_2$(CO)][7] and *cis*-[Pt$(C_6F_5)_2$(CO)-{SC(S)P$(C_6H_{11})_3$}].[8]

The Pt(2)–P [Pt(2)–P(1) 2.324(3), Pt(2)–P(2) 2.350(3) Å] and Pt(2)–C (terminal acetylide) [Pt(2)–C(22) 1.917(12)] distances are typical for platinum(II) complexes.[9] The terminal phenylacetylide ligand has a C–C triple bond of length 1.207(18) Å which is similar to those found in other σ-alkynyl complexes of platinum.[9] The Pt(1)–C(13)–O(1) [176.5(11)], Pt(2)–C(22)–C(23) [176.7(12)] and C(22)–C(23)–C(24) [177.2(13)°] angles indicate nearly linear sp hybridisation at C(13), C(22) and C(23) respectively, as expected.

The skeleton of the bridging acetylide group [Fig. 1(*b*)] has the following structural features. (*i*) The Pt(1)–C≡CPh σ-bond length [Pt(1)–C(14) 2.001(11) Å] falls in the usual range but is slightly longer than Pt(2)–C≡CPh [Pt(2)–C(22) 1.917(12) Å]. (*ii*) The C–C triple bond C(14)–C(15) [1.271(16) Å] is slightly elongated due to co-ordination to Pt(2). (*iii*) The Pt(2)–C(acetylide bridging) distances [Pt(2)–C(14) 2.268(11), Pt(2)–C(15) 2.257(10) Å] are equal (within experimental error) indicating that the η^2 linkage is symmetric. (*iv*) The acetylenic skeleton Pt(1)–C(14)–C(15)–C(16) acquires a *cis*-bent arrangement such that the angles at C_α [Pt(1)–C(14)–C(15)] and at C_β [C(14)–C(15)–C(16)] are 165.0(9) and 157.9(10)° respectively and remains nearly planar [the torsion angle around the C(14)–C(15) bond is 17.4°]. (*v*) The C≡C [C(14)–C(15)] vector is oriented essentially perpendicular to the local co-ordination plane of Pt(2) [the angle formed by the vector defined by Pt(2)

Table 2 Bond lengths (Å) and angles (°) for complex **1**

Pt(1)–C(1)	2.048(11)	Pt(1)–C(7)	2.035(13)	F(8)–C(10)	1.416(21)	F(9)–C(11)	1.373(24)
Pt(1)–C(13)	1.839(15)	Pt(1)–C(14)	2.001(11)	F(10)–C(12)	1.349(17)	O(1)–C(13)	1.166(18)
Pt(2)–P(1)	2.324(3)	Pt(2)–P(2)	2.350(3)	C(1)–C(2)	1.356(17)	C(1)–C(6)	1.364(19)
Pt(2)–C(14)	2.268(11)	Pt(2)–C(15)	2.257(10)	C(2)–C(3)	1.367(19)	C(3)–C(4)	1.373(20)
Pt(2)–C(22)	1.917(12)	P(1)–C(30)	1.804(7)	C(4)–C(5)	1.367(23)	C(5)–C(6)	1.373(20)
P(1)–C(36)	1.827(7)	P(1)–C(42)	1.816(6)	C(7)–C(8)	1.381(19)	C(7)–C(12)	1.339(22)
P(2)–C(48)	1.814(7)	P(2)–C(54)	1.835(7)	C(8)–C(9)	1.384(24)	C(9)–C(10)	1.411(29)
P(2)–C(60)	1.828(8)	F(1)–C(2)	1.366(15)	C(10)–C(11)	1.367(29)	C(11)–C(12)	1.315(24)
F(2)–C(3)	1.349(16)	F(3)–C(4)	1.354(17)	C(14)–C(15)	1.271(16)	C(15)–C(16)	1.448(13)
F(4)–C(5)	1.326(17)	F(5)–C(6)	1.374(15)	C(22)–C(23)	1.206(18)	C(23)–C(24)	1.478(16)
F(6)–C(8)	1.382(19)	F(7)–C(9)	1.323(19)				
C(1)–Pt(1)–C(7)	87.9(5)	C(1)–Pt(1)–C(13)	88.9(6)	Pt(1)–C(7)–C(8)	122.5(11)	Pt(1)–C(7)–C(12)	124.0(10)
C(7)–Pt(1)–C(13)	176.8(6)	C(1)–Pt(1)–C(14)	174.8(4)	C(8)–C(7)–C(12)	113.4(13)	F(6)–C(8)–C(7)	120.5(13)
C(7)–Pt(1)–C(14)	87.4(5)	C(13)–Pt(1)–C(14)	95.8(5)	F(6)–C(8)–C(9)	112.9(13)	C(7)–C(8)–C(9)	126.6(16)
P(1)–Pt(2)–P(2)	170.4(1)	P(1)–Pt(2)–C(14)	90.1(3)	F(7)–C(9)–C(8)	124.4(17)	F(7)–C(9)–C(10)	122.2(17)
P(2)–Pt(2)–C(14)	97.8(3)	P(1)–Pt(2)–C(15)	90.2(3)	C(8)–C(9)–C(10)	113.3(15)	F(8)–C(10)–C(9)	114.9(17)
P(2)–Pt(2)–C(15)	93.5(3)	C(14)–Pt(2)–C(15)	32.6(4)	F(8)–C(10)–C(11)	123.6(18)	C(9)–C(10)–C(11)	121.5(17)
P(1)–Pt(2)–C(22)	85.8(4)	P(2)–Pt(2)–C(22)	88.7(4)	F(9)–C(11)–C(10)	117.0(16)	F(9)–C(11)–C(12)	124.0(17)
C(14)–Pt(2)–C(22)	159.0(5)	C(15)–Pt(2)–C(22)	167.3(5)	C(10)–C(11)–C(12)	118.9(19)	F(10)–C(12)–C(7)	119.6(13)
Pt(2)–P(1)–C(30)	112.4(3)	Pt(2)–P(1)–C(36)	112.8(3)	F(10)–C(12)–C(11)	114.1(15)	C(7)–C(12)–C(11)	126.3(15)
C(30)–P(1)–C(36)	105.3(4)	Pt(2)–P(1)–C(42)	113.0(3)	Pt(1)–C(13)–O(1)	176.5(11)	Pt(1)–C(14)–Pt(2)	121.5(5)
C(30)–P(1)–C(42)	107.0(4)	C(36)–P(1)–C(42)	105.9(4)	Pt(1)–C(14)–C(15)	165.0(9)	Pt(2)–C(14)–C(15)	73.2(7)
Pt(2)–P(2)–C(48)	105.8(3)	Pt(2)–P(2)–C(54)	115.6(3)	Pt(2)–C(15)–C(14)	74.2(7)	Pt(2)–C(15)–C(16)	127.7(7)
C(48)–P(2)–C(54)	103.0(4)	Pt(2)–P(2)–C(60)	120.9(4)	C(14)–C(15)–C(16)	157.9(10)	C(15)–C(16)–C(17)	121.1(5)
C(48)–P(2)–C(60)	107.5(4)	C(54)–P(2)–C(60)	102.5(4)	C(15)–C(16)–C(21)	118.9(5)	Pt(2)–C(22)–C(23)	176.7(12)
Pt(1)–C(1)–C(2)	123.7(9)	Pt(1)–C(1)–C(6)	124.1(9)	C(22)–C(23)–C(24)	177.2(13)	C(23)–C(24)–C(25)	119.5(6)
C(2)–C(1)–C(6)	112.2(11)	F(1)–C(2)–C(1)	119.1(11)	C(23)–C(24)–C(29)	120.5(6)	P(1)–C(30)–C(31)	118.1(3)
F(1)–C(2)–C(3)	115.0(11)	C(1)–C(2)–C(3)	125.9(12)	P(1)–C(30)–C(35)	121.8(3)	P(1)–C(36)–C(37)	119.5(3)
F(2)–C(3)–C(2)	122.7(12)	F(2)–C(3)–C(4)	119.6(13)	P(1)–C(36)–C(41)	120.2(3)	P(1)–C(42)–C(43)	122.5(3)
C(2)–C(3)–C(4)	117.8(13)	F(3)–C(4)–C(3)	120.3(13)	P(1)–C(42)–C(47)	117.5(3)	P(2)–C(48)–C(49)	116.5(3)
F(3)–C(4)–C(5)	118.9(13)	C(3)–C(4)–C(5)	120.8(13)	P(2)–C(48)–C(53)	123.5(3)	P(2)–C(54)–C(55)	121.9(3)
F(4)–C(5)–C(4)	119.3(13)	F(4)–C(5)–C(6)	124.4(14)	P(2)–C(54)–C(59)	118.0(3)	P(2)–C(60)–C(61)	119.7(3)
C(4)–C(5)–C(6)	116.2(13)	F(5)–C(6)–C(1)	119.7(11)	P(2)–C(60)–C(65)	120.1(3)		
F(5)–C(6)–C(5)	113.1(13)	C(1)–C(6)–C(5)	127.1(13)				

and the midpoint of the C≡C bond and the C(14)–C(15) vector is 90.54°] and is inclined by 4° to the normal to this plane.

The very long Pt(1)···Pt(2) distance (3.727 Å) clearly indicates that both metal centres are bound only through the μ-η^2 bridging phenylacetylide ligand.

The IR spectra of complexes **1**–**4** show ν(CO) at wavenumbers (2078 **1**, 2083 **2**, 2092 **3**, 2084 cm^{-1} **4**) lower than for the corresponding vibration of the precursor *cis*-[Pt(C_6F_5)$_2$(CO)(thf)] (2124 cm^{-1}).[7] This fact can be interpreted as a consequence of the alkynylation process of the fragment Pt(C_6F_5)$_2$(CO). The increase in electron density allows the Pt atom to be a better π donor towards CO in the resulting anionic unit Pt(C_6F_5)$_2$(C≡CR)(CO) than in the neutral *cis*-[Pt(C_6F_5)$_2$(CO)(thf)] derivative. On the other hand, there is a medium intensity ν(C≡C) band (1959 **1**, 1954 **2**, 1987 **3**, 1980 cm^{-1} **4**) in the expected region for side-on μ-η^2-C≡CR groups[6c–h] which can be assigned to the acetylide bridging ligand. Complexes **1** and **2** also display a weak absorption (2127 **1**, 2128 cm^{-1} **2**) due to the terminal C≡CPh group. For complexes **3** and **4** this absorption has not been observed. As expected, two strong absorptions around 800 cm^{-1}, due to the IR-active vibrations of the X-sensitive modes of the C_6F_5 groups, are observed for all complexes.[6a,b,f,7] The NMR data for all the complexes [^{1}H (Experimental section), ^{19}F and ^{31}P (Table 1)] are in good agreement with the molecular structure found for complex **1**. Thus, as expected, the two Bu^t groups for the *tert*-butylacetylide derivatives **3** and **4** are clearly inequivalent, while both phosphorus atoms of the phosphine ligands for all complexes are equivalent. Moreover the presence of a ^3J(Pt–P) coupling (29 Hz) for complex **1** suggests that the binuclear structure is retained in solution. On the other hand, the ^{19}F NMR spectra exhibit two sets of three signals (2:1:2) which can be assigned to two inequivalent C_6F_5 groups, thus confirming unequivocally a mutually *cis* disposition of these groups for all these compounds.

It should be noted that in these complexes the η^2-acetylenic interaction is quite stable. Thus, when a dichloromethane solution of *cis,trans*-[(OC)(C_6F_5)$_2$Pt(μ-C≡CPh)Pt(C≡CPh)(PPh$_3$)$_2$] **1** is treated at room temperature with PhC≡CPh, pyridine, CO, PPh$_3$ or HBF$_4$ (molar ratio 1:1) the starting material is recovered in all cases. Even when the reaction between **1** and PPh$_3$ (molar ratio 1:1) is carried out in CH_2Cl_2 at reflux (2.5 h) most of the starting complex (60%) is recovered, although in this case small amounts of *trans*-[Pt(C≡CPh)$_2$(PPh$_3$)$_2$] (3.2%) and *trans*-[Pt(C_6F_5)(C≡CPh)(PPh$_3$)$_2$][6h] (2.9%) are also obtained. Since we have recently communicated that treatment of the doubly bridged derivative [{Pt(C_6F_5)(μ-C≡CPh)(PPh$_3$)}$_2$] (**1b** in Scheme 1) with PPh$_3$ (molar ratio) renders *trans*-[Pt(C_6F_5)(C≡CPh)(PPh$_3$)$_2$] in quantitative yield, it seems sensible to assume that the formation of *trans*-[Pt(C_6F_5)(C≡CPh)(PPh$_3$)$_2$] in the above reaction takes place through **1b** as an intermediate. Moreover, **1b** was formed by refluxing **1** in benzene (1 h) in the absence of PPh$_3$ [Scheme 1(*ii*)].

Reactions of cis-[Pt(C≡CR)$_2$L$_2$] *with cis-*[Pt(C_6F_5)$_2$(CO)(thf)].—The *cis*-bis(σ-alkynyl) complexes *cis*-[Pt(C≡CBu^t)$_2$(PEt$_3$)$_2$] and [Pt(C≡CR)$_2$(dppe)] (R = Bu^t or SiMe$_3$, dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) react with *cis*-[Pt(C_6F_5)$_2$(CO)(thf)] [Scheme 1 (*iii*) and (*iv*)] forming the mono(μ-acetylide) diplatinum complexes **6**–**8**. However the similar reaction of *cis*-[Pt(C≡CBu^t)$_2$(PPh$_3$)$_2$] in benzene (2 min) leads to a mixture of the analogous mono(μ-acetylide) **5** and the already described bis(μ-acetylide) **5b**[6f] complexes in a 5:1 molar ratio. Although

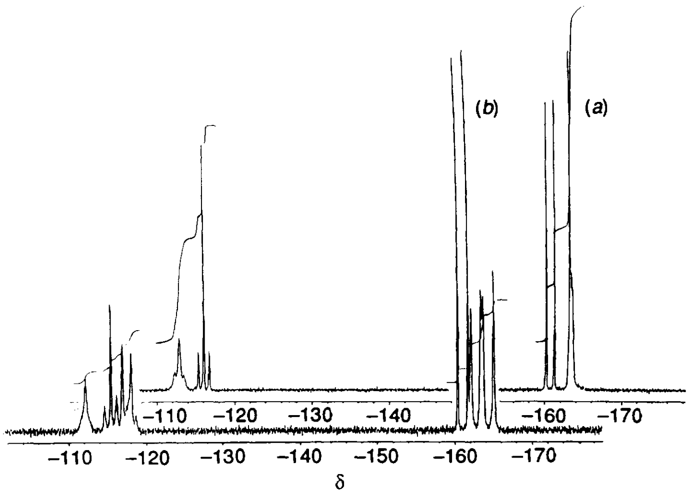


Fig. 2 The ^{19}F NMR spectra of the complex *cis*-$[(OC)(C_6F_5)_2Pt(\mu\text{-}C\equiv CBu^t)Pt(C\equiv CBu^t)(dppe)]$ **7**: at 20 (*a*) and −56 °C (*b*)

complex **5** can be fully characterised by IR, ^{1}H, ^{31}P and ^{19}F NMR spectroscopies (see below) it proved too unstable in solution to be isolated in a pure form. Moreover it was found that when the above **5**–**5b** mixture (5:1 ratio) was stirred in acetone only **5b** could be obtained (see Experimental section). This fact suggests that **5** is slowly transformed into **5b** presumably by displacement of a CO ligand caused by the terminal $C\equiv CBu^t$ and subsequent σ migration of the bridging $C\equiv CBu^t$ group.

Complexes **6**–**8** are moderately stable in the solid state, but their solutions slowly darken, yielding intractable dark solids. These solids are probably mixtures including complexes structurally related to **5b**. Spectroscopic data for complexes **5**–**8** (Experimental section, Table 1) are in accord with the structures depicted in Scheme 1, and consequently, these are tentatively proposed. Thus, the presence of a CO ligand and acetylide bridging ligand is inferred from the IR spectra. These show bands in the 2090–2099 and 1941–2007 cm^{-1} regions which are assigned to the ν(CO) and bridging ν(C≡C) vibrations respectively [for complexes **7** and **8** the spectra in Nujol exhibit two ν(CO) absorptions but, as expected, in benzene solution only one]. The positions of these bands compare well with those observed for complexes **1**–**4**. In particular, the ν(CO) band is substantially lower in energy than that of neutral *cis*-$[Pt(C_6F_5)_2(CO)(thf)]$ (2124 cm^{-1}) suggesting that the formation of the binuclear derivatives takes place with an increase in electron density [formal alkynylation of $Pt(C_6F_5)_2(CO)$] in accord with the proposed structures. Moreover, two absorptions of the same intensity are observed in the 792–802 cm^{-1} region due to the IR-active vibrations of the X-sensitive C_6F_5 modes which indicates that, as for the starting complex *cis*-$[Pt(C_6F_5)_2(CO)(thf)]$, the C_6F_5 groups are mutually *cis* (this fact is also confirmed by ^{19}F NMR spectroscopy).

The NMR data confirm the mutually *cis* disposition of both the C_6F_5 groups and phosphine ligands. The ^{31}P-{^{1}H} NMR spectra of complexes **5** and **6** exhibit two phosphorus resonances [singlets, ^{2}J(P–P) not resolved] showing different platinum–phosphorus coupling constants which indicate that the two phosphine ligands are inequivalent. The signal with the greater coupling constant could be tentatively assigned to the phosphine ligand *trans* to the η^2-acetylenic bond.[6h,10] Complex **8** exhibits a similar AB pattern in its ^{31}P NMR spectrum indicating that both phosphorus atoms of the dppe ligands are inequivalent. In contrast, the spectrum of **7** showed only one sharp resonance, but the pattern of the ^{195}Pt satellite peaks confirmed the expected AB nature, in which evidently the non-equivalent phosphorus nuclei have coincidental chemical shifts.

The ^{19}F NMR spectra are particularly informative. First, at room temperature, the spectra of all complexes (see Table 1 and Experimental section for **5**) imply the presence of two inequivalent C_6F_5 groups in each compound thus confirming the mutually *cis* disposition of these groups. On the other hand, the resonances due to *o*-fluorine atoms, which appear at low field, provide additional information on the behaviour of these complexes in solution. A representative ^{19}F NMR spectrum, corresponding to complex **7**, is given in Fig. 2. As can be seen two different (probably one associated with each C_6F_5 group) F_{ortho} resonances are clearly observed at room temperature; one appears as a sharp doublet and the other as a slightly broadened peak (the same pattern is observed for complex **8**), the latter suggesting a dynamic process. If it is assumed that both resonances are due to different C_6F_5 groups, the observed pattern suggests that at room temperature the co-ordination plane of the platinum centre containing the C_6F_5 groups is a time-averaged plane of symmetry. At −56 °C the F_{ortho} resonances and also the multiplet due to F_{meta} are split and the spectrum of **7** shows well separated signals for each of the five fluorine atoms in the two non-equivalent C_6F_5 ligands, as expected for a rigid conformation of the two C_6F_5 rings.

The observed spectrum of complex **7**, as well as that of **8**, at room temperature can be tentatively explained by assuming a rapid rotation of the C_6F_5 rings around the Pt–C_6F_5 bonds. Moreover, the broadening observed for the low-field signal in the F_{ortho} region suggests that the energy barrier for this process is different in each C_6F_5 ring. This is even more pronounced for complexes **5** and **6**. Thus, at low temperature both the latter showed five well separated signals for one C_6F_5 ring and only three (F_{ortho} as a broad singlet) for the other C_6F_5 group. At room temperature the two different F_{ortho} signals of the former C_6F_5 ring practically disappear into the baseline, only a sharp doublet remaining which probably arises from rapid rotation (on the NMR time-scale at this temperature) of the other C_6F_5 group. Unfortunately the poor stability of the compounds at higher temperature precluded the acquisition of spectra with high-temperature simplification.

Finally it was also decided to explore the reactivity of the complexes $[Au(C\equiv CR)(PPh_3)]$ (R = Ph or Bu^t) toward *cis*-$[Pt(C_6F_5)_2(CO)(thf)]$ with the aim of preparing heterodinuclear derivatives of platinum. The results of this study are shown in Scheme 1(*v*). The complex $[Au(C\equiv CPh)(PPh_3)]$ reacts in CH_2Cl_2 to give the mono(μ-phenylacetylide) binuclear complex *cis*-$[(OC)(C_6F_5)_2Pt(\mu\text{-}C\equiv CPh)Au(PPh_3)]$ **9** as a white microcrystalline product. Analytical data and the IR, ^{19}F and ^{31}P-{^{1}H} NMR spectra of this complex (see Experimental section and Table 1) are in accord with the structure shown in Scheme 1. In contrast, reaction of $[Au(C\equiv CBu^t)(PPh_3)]$ leads to a mixture of the unexpected *trans* (**10**) and *cis* (**11**) $[(OC)(C_6F_5)_2Pt(\mu\text{-}C\equiv CBu^t)Au(PPh_3)]$ (see Experimental section). Thus, complex **10** can be isolated as a white microcrystalline solid (38% yield) by recrystallisation of the first fraction of the reaction carried out in benzene. From the mother-liquors, only mixtures of **10** and **11** were obtained. The IR spectrum in Nujol of **10** exhibits two strong bands at 2105 and 2025 cm^{-1} which are easily assigned to ν(CO) and bridging ν(C≡C) vibrations respectively. These values compare well with those observed for this general family of mono(μ-acetylide) complexes. Only one strong absorption due to the X-sensitive mode of the C_6F_5 groups is observed at 780 cm^{-1}, suggesting a mutually *trans* disposition of these ligands.[11] This fact is unequivocally confirmed by ^{19}F NMR spectroscopy. The spectrum of **10** shows three signals in a 2:1:2 ratio due to F_{ortho} (isochronous), F_{para} and F_{meta} (isochronous) respectively, indicating that the two C_6F_5 groups are equivalent.

On the other hand, the treatment of a suspension of $[Au(C\equiv CBu^t)(PPh_3)]$ with *cis*-$[Pt(C_6F_5)_2(CO)(thf)]$ in diethyl ether renders, after 3 min of stirring, a dark solution. By treatment of this solution with charcoal, filtration, evaporation and subsequent addition of cold hexane to the residue, a white solid was obtained. The IR, ^{1}H, ^{31}P-{^{1}H} and ^{19}F (see

Experimental section) NMR spectra of this solid indicate that it is a mixture of complexes **10** and **11** in an approximately 1:2 molar ratio. The IR spectrum of the crude solid contains two strong bands at 2105 and 2016 cm^{-1}, characteristic of ν(CO) and ν(C≡C) bridging vibrations respectively. The ^1H and ^{31}P NMR spectra shows two singlets at δ 1.27 (**11**) and 1.17 (**10**) and at 35.3 (**11**) and 35.6 (**10**) for the Bu^t and PPh_3 groups.

Experimental

All manipulations were carried out under a nitrogen atmosphere. Solvents were dried by standard procedures and distilled under dry N_2 before use. The C, H and N analyses and IR spectra were obtained as described elsewhere.[6f] The NMR spectra were recorded on either a Varian XL 200 or a Unity 300 instrument, mass spectra on a V G Autospec.

The complexes *trans*-$[Pt(C{\equiv}CR)_2(PPh_3)_2]$[6h] (R = Ph or Bu^t), *cis*-$[Pt(C{\equiv}CBu^t)_2(PPh_3)_2]$,[6f] $[Pt(C{\equiv}CBu^t)_2(dppe)]$,[6f] $[Au(C{\equiv}CR)(PPh_3)]$ (R = Ph[12] or Bu^t)[13] and *cis*-$[Pt(C_6F_5)_2(CO)(thf)]$[7] were prepared by literature methods, *trans*-$[Pt(C{\equiv}CR)_2(PEt_3)_2]$ (R = Ph or Bu^t)[14] and $[Pt(C{\equiv}CSiMe_3)_2(dppe)]$[15] by treating *cis*-$[PtCl_2(PEt_3)_2]$ or $[PtCl_2(dppe)]$ with Li(C≡CR) in Et_2O and *cis*-$[Pt(C{\equiv}CBu^t)_2(PEt_3)_2]$ by treating $[Pt(C{\equiv}CBu^t)_2(cod)]$[6f] (cod = cycloocta-1,5-diene) with PEt_3 (molar ratio 1:2).

cis, trans-$[(OC)(C_6F_5)_2Pt(\mu\text{-}C{\equiv}CPh)Pt(C{\equiv}CPh)(PPh_3)_2]$ **1**.—To a solution of *trans*-$[Pt(C{\equiv}CPh)_2(PPh_3)_2]$ (0.103 g, 0.11 mmol) in CH_2Cl_2 (20 cm^3) was added *cis*-$[Pt(C_6F_5)_2(CO)(thf)]$ (0.081 g, 0.11 mmol) and the mixture stirred at room temperature for 1 h. The resulting yellow solution was evaporated under reduced pressure to *ca*. 1 cm^3. Slow addition of EtOH (4 cm^3) afforded a pale yellow microcrystalline solid **1**. Yield 73% [Found (Calc.): C, 53.2 (52.80); H, 2.65 (2.70%)]. IR (cm^{-1}): ν(CO) 2078s; ν(C≡C) 2127w and 1959m; $\nu(C_6F_5)_{X\text{-sens}}$ 802s and 795s. ^1H NMR ($CDCl_3$): δ 7.68 (m, 10 H), 7.36 (m, 20 H), 6.9 (m, 4 H), 6.74 (m, 2 H), 6.61 (m, 2 H) and 6.13 (d, 2 H). Electron impact (EI) mass spectrum: molecular peak not observed.

cis, trans-$[(OC)(C_6F_5)_2Pt(\mu\text{-}C{\equiv}CPh)Pt(C{\equiv}CPh)(PEt_3)_2]$ **2**.—The synthesis was performed as described for complex **1** starting from *trans*-$[Pt(C{\equiv}CPh)_2(PEt_3)_2]$ (0.165 g, 0.26 mmol) and *cis*-$[Pt(C_6F_5)_2(CO)(thf)]$ (0.164 g, 0.26 mmol). In this case **2** was precipitated as a white solid by adding diethyl ether and cooling to −30 °C overnight. Yield 50% [Found (Calc.): C, 41.40 (41.35); H, 3.70 (3.30%)]. IR (cm^{-1}): ν(CO) 2083s; ν(C≡C) 2128m and 1954m; the absorptions due to $\nu(C_6F_5)_{X\text{-sens}}$ could not be assigned unambiguously since the PEt_3 ligand shows internal absorptions in this region; the observed bands are 802s (sh), 770s and 760s. ^1H NMR ($CDCl_3$): δ 7.36, 7.2 (m, 10 H, Ph); 2.0 (m, 12 H, CH_2, PEt_3) and 1.2 (q, 18 H, CH_3, PEt_3). EI mass spectrum: m/z = 1192 (M^+ + 2 H) and 1163 (M^+ − CO + H).

cis, trans-$[(OC)(C_6F_5)_2Pt(\mu\text{-}C{\equiv}CBu^t)Pt(C{\equiv}CBu^t)(PPh_3)_2]$ **3**.—To a solution of *trans*-$[Pt(C{\equiv}CBu^t)_2(PPh_3)_2]$ (0.3 g, 0.34 mmol) in CH_2Cl_2 (20 cm^3) was added *cis*-$[Pt(C_6F_5)_2(CO)(thf)]$ (0.214 g, 0.34 mmol) and the mixture stirred at room temperature for 1 h. The resulting solution was filtered and the solution evaporated to ≈2 cm^3. Slow addition of hexane produced complex **3** as a white solid. Yield 52% [Found (Calc.): C, 51.70 (50.90); H, 3.65 (3.35%)]. IR (cm^{-1}): ν(CO) 2092s; ν(C≡C) 1987m; $\nu(C_6F_5)_{X\text{-sens}}$ 799s and 787s. ^1H NMR ($CDCl_3$): δ 7.78, 7.44 (m, 30 H, PPh_3); 0.3 (s, 9 H, Bu^t) and 0.18 (s, 9 H, Bu^t). EI mass spectrum: molecular peak not observed.

cis, trans-$[(OC)(C_6F_5)_2Pt(\mu\text{-}C{\equiv}CBu^t)Pt(C{\equiv}CBu^t)(PEt_3)_2]$ **4**.—This complex is prepared from *trans*-$[Pt(C{\equiv}CBu^t)_2(PEt_3)_2]$ (0.112 g, 0.18 mmol) and *cis*-$[Pt(C_6F_5)_2(CO)(thf)]$ (0.111 g, 0.18 mmol) in a similar fashion to that for **2**. Yield 30% [Found (Calc.): C, 37.85 (38.60); H, 4.45 (4.20%)]. IR (cm^{-1}): ν(CO) 2084s; ν(C≡C) 1980w; $\nu(C_6F_5)_{X\text{-sens}}$ 799s and 787s. ^1H NMR ($CDCl_3$): δ 2.08 (m, CH_2, PEt_3), 1.2 (CH_3, PEt_3), 1.17 (Bu^t) [partial overlapping of a quintuplet centred at 1.2 due to CH_3 (PEt_3) and a singlet at 1.17 due to Bu^t] and 1.07 (s, Bu^t).

Reaction of cis-$[Pt(C{\equiv}CBu^t)_2(PPh_3)_2]$ *with cis*-$[Pt(C_6F_5)_2(CO)(thf)]$ *to give a Mixture of cis,cis*-$[(OC)(C_6F_5)_2Pt(\mu\text{-}C{\equiv}CBu^t)Pt(C{\equiv}CBu^t)(PPh_3)_2]$ **5** *and* $[\{(Ph_3P)_2Pt(\mu\text{-}C{\equiv}CBu^t)_2\}Pt(C_6F_5)_2]$ **5b**.—A solid mixture of *cis*-$[Pt(C{\equiv}CBu^t)_2(PPh_3)_2]$ (0.15 g, 0.17 mmol) and *cis*-$[Pt(C_6F_5)_2(CO)(thf)]$ (0.107 g, 0.17 mmol) was dissolved in benzene (4 cm^3) and the resulting pale yellow solution stirred for 2 min. Evaporation of the solvent to *ca*. 1 cm^3, addition of hexane (3 cm^3) and cooling in a freezer (−30 °C) caused the precipitation of a white solid (100 mg, yield 41%). The NMR spectra of this solid showed it to be a mixture of complexes **5** and **5b** in 5:1 ratio. When using longer reaction times, the proportion of **5b** increases. IR (cm^{-1}) of **5**: ν(CO) 2090s; ν(C≡C) 1994w; $\nu(C_6F_5)_{X\text{-sens}}$ 802s and 794s. NMR ($CDCl_3$) of **5**: ^1H (at −56 °C) δ 7.4–7.1 (m, Ph, PPh_3), 0.88 (s, Bu^t), 0.29 (s, Bu^t); (at room temperature) 7.3–7.0 (m, Ph, PPh_3), 0.86 (br, s, Bu^t), 0.27 (s, br, Bu^t); ^{31}P NMR (at room temperature) δ 16.3 [br, s, $J(^{195}Pt-^{31}P)$ = 2392] and 12.8 [br, s, $J(^{195}Pt-^{31}P)$ = 2613 Hz]; ^{19}F NMR (at −56 °C) −111 (br, 1 F) and −115.7 (d, 1 F) (this signal partly overlapped with F_{ortho} signals due to **5b**) (F_{ortho} of one C_6F_5 group), −118.3 (s, br, 2 F, F_{ortho} of the other C_6F_5), −160.95 (1 F) and −161.4 (1 F) (two t, F_{para} of both C_6F_5), −164.0 (m, 2 F, F_{meta} of one C_6F_5), −161.1 (1 F) and −164.6 (1 F) [two m, F_{meta} of other C_6F_5 group]; (at room temperature) the F_{ortho} signals at δ −111 and −115.7 and the F_{meta} signals at −161.1 and −164.6 respectively practically disappear into the baseline; *ca*. −114 (broad hump), −117.9 [sharp d, 2 F, $^3J(Pt-F_{ortho})$ = 386 Hz], −161.6 and −162.4 (two t) and −164.6 (m).

A 0.14 g amount of the above mixture (5:1) was dissolved in acetone (10 cm^3) and stirred for 5 h. Evaporation of the resulting dark orange solution to *ca*. 1 cm^3 and addition of ethanol rendered complex **5b** (30 mg). On cooling (−30 °C) the filtrate, more **5b** (30 mg) was obtained.

cis, cis-$[(OC)(C_6F_5)_2Pt(\mu\text{-}C{\equiv}CBu^t)Pt(C{\equiv}CBu^t)(PEt_3)_2]$ **6**.—A mixture of *cis*-$[Pt(C{\equiv}CBu^t)_2(PEt_3)_2]$ (0.17 g, 0.29 mmol) and *cis*-$[Pt(C_6F_5)_2(CO)(thf)]$ (0.18 g, 0.29 mmol) was dissolved in benzene (4 cm^3). The resulting yellow solution was stirred for 1 min and evaporated to *ca*. 1 cm^3. By addition of diethyl ether (5 cm^3) a white solid, identified as complex **6**, separated. Yield 46% [Found (Calc.): C, 38.35 (38.60); H, 4.45 (4.20%)]. IR (cm^{-1}): ν(CO) 2093s; ν(C≡C) 2007m; $\nu(C_6F_5)_{X\text{-sens}}$ 798s and 790s. ^1H NMR ($CDCl_3$): (at 20 °C) δ 1.1, 2.1, 1.8 (very broad resonances due to unresolved overlapping of signals); (at −56 °C) 2.2, 1.8 (m, CH_2, PEt_3); 1.25 (s) and 1.12 (s) (Bu^t partly overlapped with a complex m due to the methyl resonances of the PEt_3 ligands). EI mass spectrum: m/z = 1122 (M^+ − CO) and 431 $[Pt(PEt_3)_2{}^+$, 100%].

cis-$[(OC)(C_6F_5)_2Pt(\mu\text{-}C{\equiv}CBu^t)Pt(C{\equiv}CBu^t)(dppe)]$ **7**.—The complex *cis*-$[Pt(C_6F_5)_2(CO)(thf)]$ (0.12 g, 0.19 mmol) was added to a suspension of *cis*-$[Pt(C{\equiv}CBu^t)_2(dppe)]$ (0.14 g, 0.19 mmol) in diethyl ether (20 cm^3) at −10 °C and the mixture stirred for 20 min at room temperature. The resulting pale yellow solution was then filtered and evaporated to small volume (≈1 cm^3). By addition of hexane (≈3 cm^3) and on standing at −30 °C (30 d), white crystals of complex **7** were obtained. Yield 63% [Found (Calc.): C, 46.90 (46.65); H, 3.20 (3.20%)]. IR (cm^{-1}): ν(CO) (solid) 2101s and 2091s, (in benzene) 2097s; ν(C≡C) 1997m; $\nu(C_6F_5)_{X\text{-sens}}$ 801s and 792s. ^1H NMR ($CDCl_3$): (at −50 °C) δ 8.3, 7.9, 7.45 (m, br, 20 H, Ph, dppe), ≈2.5 (m, br, 4 H, CH_2CH_2, dppe), 0.98 (s, 9 H, Bu^t) and 0.63 (s, 9 H, Bu^t); (at room temperature) same pattern but the Bu^t

Table 3 Fractional atomic coordinates (× 10^4) for complex **1**

Atom	*x*	*y*	*z*
Pt(1)	1080(1)	1214(1)	2894(1)
Pt(2)	380(1)	2577(1)	3991(1)
P(1)	1509(2)	3246(1)	3667(2)
P(2)	−802(2)	2042(2)	4451(2)
F(1)	763(6)	−302(3)	2588(4)
F(2)	664(6)	−1023(4)	1390(4)
F(3)	917(7)	−461(4)	122(4)
F(4)	1185(8)	817(4)	56(4)
F(5)	1214(7)	1556(4)	1229(4)
F(6)	1748(6)	154(4)	4129(4)
F(7)	3393(8)	−356(5)	4618(5)
F(8)	4865(7)	−46(6)	3990(7)
F(9)	4643(7)	830(6)	2850(7)
F(10)	3032(6)	1362(4)	2408(5)
O(1)	−774(8)	1743(5)	2285(6)
C(1)	1000(9)	662(5)	1977(6)
C(2)	868(9)	10(6)	1963(7)
C(3)	813(9)	−379(7)	1366(8)
C(4)	935(10)	−95(8)	725(7)
C(5)	1089(11)	557(8)	687(7)
C(6)	1086(10)	902(6)	1313(8)
C(7)	2323(9)	804(6)	3241(7)
C(8)	2465(11)	355(7)	3794(8)
C(9)	3280(14)	47(8)	4061(9)
C(10)	4011(12)	240(10)	3713(12)
C(11)	3886(13)	668(9)	3148(11)
C(12)	3071(11)	924(7)	2947(8)
C(13)	−50(11)	1554(7)	2536(8)
C(14)	1236(7)	1692(5)	3836(6)
C(15)	1457(7)	1866(5)	4492(7)
C(16)	1962(5)	1868(4)	5222(3)
C(17)	1823	2352	5713
C(18)	2335	2353	6407
C(19)	2985	1870	6611
C(20)	3123	1386	6119
C(21)	2612	1385	5425
C(22)	−428(8)	3298(6)	3746(7)
C(23)	−910(8)	3761(7)	3566(7)
C(24)	−1466(6)	4348(4)	3368(5)
C(25)	−1094	4863	3031
C(26)	−1602	5428	2863
C(27)	−2482	5477	3032
C(28)	−2854	4962	3369
C(29)	−2346	4397	3537
C(30)	1425(6)	4067(3)	3982(4)
C(31)	1172	4161	4660
C(32)	1150	4785	4943
C(33)	1381	5316	4548
C(34)	1634	5222	3870
C(35)	1656	4598	3587
C(36)	2662(4)	2980(4)	4050(4)
C(37)	3078	3224	4718
C(38)	3923	2982	5047
C(39)	4352	2495	4707
C(40)	3936	2251	4040
C(41)	3092	2494	3711
C(42)	1483(5)	3287(4)	2695(3)
C(43)	2255	3434	2389
C(44)	2193	3465	1639
C(45)	1358	3349	1195
C(46)	585	3202	1501
C(47)	648	3171	2251
C(48)	−571(5)	2164(4)	5422(3)
C(49)	−493	2805	5661
C(50)	−343	2941	6401
C(51)	−272	2435	6901
C(52)	−350	1794	6662
C(53)	−499	1658	5923
C(54)	−1947(4)	2392(4)	4194(4)
C(55)	−2486	2567	4708
C(56)	−3372	2798	4487
C(57)	−3719	2854	3752
C(58)	−3181	2680	3237
C(59)	−2295	2449	3458
C(60)	−1010(7)	1177(3)	4289(5)
C(61)	−1905	945	4145
C(62)	−2069	294	3966
C(63)	−1338	−125	3933
C(64)	−443	107	4077
C(65)	−279	758	4255

resonances are broader. EI mass spectrum: m/z = 1283 (M^+ − CO) and 593 [Pt(dppe)$^+$, 100%].

cis-[(OC)$(C_6F_5)_2$Pt(μ-C≡CSiMe$_3$)Pt(C≡CSiMe$_3$)(dppe)] **8**.—The synthesis was performed as described for complex **7**, starting from *cis*-[Pt(C≡CSiMe$_3$)$_2$(dppe)] (0.25 g, 0.32 mmol) and *cis*-[Pt$(C_6F_5)_2$(CO)(thf)] (0.2 g, 0.32 mmol). Yield 70% [Found (Calc.): C, 43.85 (43.75); H, 3.05 (3.15%)]. IR (cm^{-1}): ν(CO) (solid) 2101s and 2092s, (in benzene) 2099s; ν(C≡C) 2058s and 1946s; ν$(C_6F_5)_{\text{X-sens}}$ 802s and 793s. ^{1}H NMR (CDCl$_3$): δ 7.8, 7.5, 7.3 (m, 20 H, Ph, dppe), 2.4 (m, 4 H, CH$_2$CH$_2$, dppe), 0.03 (s, 9 H, SiMe$_3$) and −0.31 (s, 9 H, SiMe$_3$). EI mass spectrum: m/z = 1315 (M^+ − CO) and 593 [Pt(dppe)$^+$].

cis-[(OC)$(C_6F_5)_2$Pt(μ-C≡CPh)Au(PPh$_3$)] **9**.—To a CH$_2$Cl$_2$ (10 cm^3) solution of *cis*-[Pt$(C_6F_5)_2$(CO)(thf)] (0.175 g, 0.28 mmol) was added [Au(C≡CPh)(PPh$_3$)] (0.156 g, 0.28 mmol) and the mixture stirred at −10 °C for 5 min. The resulting dark solution was treated with charcoal and filtered through Kieselguhr. By concentrating the resulting orange solution to ≈2 cm^3, addition of hexane (5 cm^3) and standing overnight at −30 °C, a white microcrystalline solid, identified as complex **9**, separated. Yield 58% [Found (Calc.): C, 42.10 (41.90); H, 1.90 (1.80%)]. IR (cm^{-1}): ν(CO) 2097s; ν(C≡C) 2021m and ν$(C_6F_5)_{\text{X-sens}}$ 800s(br). ^{1}H NMR (CDCl$_3$): δ 7.5, 7.3 (m, Ph, PPh$_3$). EI mass spectrum: m/z = 1089 (M^+ − CO) and 459 [Au(PPh$_3$)$^+$, 100%].

Reaction of cis-[Pt$(C_6F_5)_2$(CO)(thf)] *with* [Au(C≡CBu^t)(PPh$_3$)].—To prepare complex **10**, [Au(C≡CBu^t)(PPh$_3$)] (0.17 g, 0.32 mmol) was added to a colourless solution of *cis*-[Pt$(C_6F_5)_2$(CO)(thf)] (0.2 g, 0.32 mmol) in benzene (4 cm^3). The resulting orange solution was immediately evaporated to small volume (≈1 cm^3), mixed with hexane (4 cm^3) and cooled to −30 °C yielding a white solid. Subsequent recrystallisation from C$_6$H$_6$–hexane at −30 °C gave complex **10** as a white crystalline solid (0.13 g, yield 38%). Evaporation of the mother-liquors to dryness and addition of hexane (15 cm^3) afforded a white solid (20 mg) identified by IR spectroscopy as a mixture of *cis* (**11**) and *trans* (**10**) isomers. By concentrating the hexane solution (to 5 cm^3) and cooling overnight at −30 °C an additional fraction of **10** and **11** was obtained.

Complex **10**. [Found (Calc.): C, 41.20 (40.50); H, 2.15 (2.20%)]: IR (cm^{-1}) ν(CO) 2105s, ν(C≡C) 2025s and ν$(C_6F_5)_{\text{X-sens}}$ 780s. ^{1}H NMR (CDCl$_3$) δ 7.5, 7.3 (m, 15 H, PPh$_3$) and 1.17 (s, 9 H, Bu^t). EI mass spectrum: m/z = 1072 (M^+ − CO + 3 H) and 460 [Au(PPh$_3$)$^+$ + H, 100%].

Preparation of a Mixture (2:1) *of cis-*[(OC)$(C_6F_5)_2$Pt(μ-C≡CBu^t)Au(PPh$_3$)] **11** *and Complex* **10**.—To a suspension of [Au(C≡CBu^t)(PPh$_3$)] (0.14 g, 0.26 mmol) in diethyl ether (10 cm^3) was added *cis*-[Pt$(C_6F_5)_2$(CO)(thf)] (0.163 g, 0.26 mmol) and the mixture stirred for 3 min during which time practically all the suspension dissolved. The resulting dark solution was treated with charcoal, filtered through Kieselguhr and evaporated to dryness. On treating the residue with cold hexane (20 cm^3) a white solid formed (90 mg, yield 31% based on Pt) which on the basis of IR, ^{1}H, ^{19}F and ^{31}P NMR spectra was found to be a mixture of complexes **11** and **10** in *ca.* 2:1 ratio (Found: C, 40.90; H, 2.20%). IR (cm^{-1}): ν(CO) 2105s; ν(C≡C) 2016m; $\nu(C_6F_5)_{X\text{-sens}}$ 800s, 790s cm^{-1} (probably due to the *cis* isomer **11**) and 780 (sh) (*trans* isomer **10**). NMR (CDCl$_3$): ^{1}H, δ 7.5, 7.4, 7.3 (complex m, Ph, PPh$_3$); 1.27 (s, **11**) and 1.17 (s, **10**) (2:1 ratio, Bu^t); ^{31}P NMR, 35.3 (s, major isomer **11**) and 35.6 (s, minor isomer **10**) (2:1 ratio), ^{19}F NMR (major isomer **11**), −117.6 [J(Pt–F$_o$) = 383], −118.2 [J(Pt–F$_o$) = 344] (F$_{ortho}$); −161.24, −161.32 (both t corresponding to F$_{para}$ signals are overlapped); −164.5 (m, F$_{meta}$); (minor isomer **10**), −115.6 [(F$_{ortho}$), J(Pt–F$_o$) = 291 Hz], −160.9 (t, F$_{para}$) and −164.0 (m, F$_{meta}$); ratio of isomers **11**:**10** 2:1.

A second fraction of a pure sample of complex **10** (40 mg) was collected when the hexane filtrate was concentrated and stored overnight at −30 °C.

Crystal Structure Determination.—Suitable crystals of complex **1** were obtained by slow diffusion of hexane into a CH$_2$Cl$_2$ solution of the corresponding crude product. Intensity data were recorded at room temperature using graphite-monochromated Mo-Kα X-radiation. An Enraf-Nonius CAD 4 diffractometer was employed ($4 \leqslant 2\theta \leqslant 44°$). Accurate lattice parameters were determined from the positions of 25 reflections ($18 < 2\theta < 20°$). Intensity data were collected by ω–2θ scans and were corrected for Lorentz and polarisation effects.

Crystal data. $C_{65}H_{40}F_{10}OP_2Pt_2$, $M = 1479.14$, monoclinic, space group $P2_1/n$, $a = 14.824(2)$, $b = 20.622(3)$, $c = 18.729(7)$ Å, $\beta = 99.36(2)°$, $U = 5649(2)$ Å^3, $Z = 4$, $D_c = 1.73$ g cm^{-3}, $F(000) = 2856$, $\mu = 50.8$ cm^{-1}, 6904 unique data, 5278 observed data [$F > 4\sigma(F)$] for the refinement of 625 parameters, $w = [1/\sigma^2(F) + 0.000\,68\,F^2]$, $R = 0.0424$. $R' = 0.049$, $\Delta/\sigma = 0.001$, largest difference peaks 0.75 and −0.61 e Å^{-3}.

Structure solution and refinement. The structure was solved by the use of Patterson and Fourier methods and refined by full-matrix least squares. All calculations were carried out with SHELXTL-PLUS.[16] An empirical absorption correction was applied.[17] All non-hydrogen atoms were refined using anisotropic thermal parameters. The carbon atoms of the Ph groups were refined as rigid rings. Hydrogen atoms were omitted. Calculations were performed on a Micro VAX 8300 computer. Final atomic coordinates are given in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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