Journal of Organometallic Chemistry, 403 (1991) 253–267
Elsevier Sequoia S.A., Lausanne
JOM 21307

Synthesis of mono- and polynuclear perhalophenyl palladium–platinum acetylide complexes. Molecular structure of $(NBu_4)_2[Pt_2Ag_2(C_6F_5)_4(C\equiv CPh)_4] \cdot 4CH_2Cl_2$

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(Received July 25th, 1990)

Abstract

The reaction between $[Ag(C\equiv CR)]_n$ (R = ${}^tBu$, Ph) and the appropriate mononuclear palladium or platinum substrate affords mononuclear derivatives of the type $[M(C_6F_5)(C\equiv CR)L_2]$ (M = Pd, Pt; R = ${}^tBu$, Ph; L = PPh_3, dppe). Polynuclear $(NBu_4)_2[Pt_2Ag_2(C_6F_5)_4(C\equiv CPh)_4]$ (X = F, Cl; R = Ph, ${}^tBu$) complexes are obtained by reaction between $(NBu_4)_2[Pt_2(\mu\text{-}X')_2(C_6X_5)_4]$ (X′ = Cl, X = F; X′ = I, X = Cl) and $[Ag(C\equiv CR)]_n$ (Pt:Ag ratio 1:2). Similar heterometallic derivatives $Q_2[Pt_2M_2(C_6F_5)_4(C\equiv CR)_4]$ (Q = $PMePh_3$, NBu_4; M = Ag, Cu; R = Ph, ${}^tBu$) can be prepared by reaction of $Q_2[cis\text{-}Pt(C_6F_5)_2(C\equiv CR)_2]$ with AgCl or CuCl (Pt:M ratio 1:1). The structure of $(NBu_4)_2[Pt_2Ag_2(C_6F_5)_4(C\equiv CPh)_4] \cdot 4CH_2Cl_2$ has been determined by X-ray diffraction.

Introduction

It has recently been reported that phenylacetylide complexes of the type $[M(C\equiv CPh)_2]^-$ (M = Cu, Ag), $[AgCl(C\equiv CPh)]^-$ [1] and $[Au(C\equiv CPh)PPh_3]$ [2] are useful ethynylating agents towards some platinum(II) complexes. However it is known that when polymeric acetylide compounds $[M(C\equiv CR)]_x$ (M = Cu(I), Ag(I), Au(I)) are used as ethynylating agents, polynuclear derivatives can be obtained [3]. In particular, we recently found that the reaction between $[Ag(C\equiv CR)]_n$ (R = Ph, ${}^tBu$) and *trans*-$[PtCl_2(tht)_2]$ (tht = tetrahydrothiophene) produces hexanuclear derivatives of the type $[Pt_2Ag_4(C\equiv CR)_8]$ in high yields [4], and so we considered it of

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0022-328X/91/$03.50

interest to explore the behaviour of silver(I) acetylides towards other palladium or platinum(II) complexes.

Results and discussion

$[Ag(C{\equiv}CR)]_n$ (R = Ph, ^tBu) reacts slowly (see Experimental) with *cis*-$[PtI_2(PPh_3)_2]$(Ag : Pt, 2 : 1) in chloroform or acetone at room temperature to give the corresponding bis-acetylide complexes (eq. 1)

$$cis\text{-}[PtI_2(PPh_3)_2] + 2/n[Ag(C{\equiv}CR)]_n \rightarrow trans\text{-}[Pt(C{\equiv}CR)_2(PPh_3)_2] + 2AgI \quad (1)$$

trans-$[Pt(C{\equiv}CR)_2(PPh_3)_2]$ had been described previously [5] and the spectroscopic data of our product coincide with those previously reported. Details of analyses, yields and spectroscopic data for *trans*-$[Pt(C{\equiv}C^tBu)_2(PPh_3)_2]$ **1** are given in Tables 1 and 2. The presence of only one absorption due to $\nu(C{\equiv}C)$(2108 cm^{-1}) points to the *trans*-geometry of **1** (B_{2u}, D_{2h}); moreover the IR spectrum of **1** shows no absorptions in the 540–560 cm^{-1} region due to PPh_3, in accord with the *trans* structure [6]. It is noteworthy that the reaction between *cis*-$[PtCl_2(PPh_3)_2]$ and $(PPN)[Ag(C{\equiv}CPh)_2]$ [1] produces the *cis*-isomer (80%), whereas we obtained (eq. 1) only the *trans*-isomer, in moderate yield (65% R = Ph; 59% R = ^tBu).

We have also studied the reactivity of $[Ag(C{\equiv}CR)]_n$ towards pentafluorophenyl palladium or platinum complexes, and found that the outcome is strongly dependent on the nature of the substrate.

Reactions with $[M(C_6F_5)IL_2]$ (M = Pd, Pt; L = PPh_3, L_2 = dppe)

trans-$[Pd(C_6F_5)I(PPh_3)_2]$ reacts with a suspension of $[Ag(C{\equiv}CR)]_n$ (R = Ph, ^tBu) in dichloromethane or acetone (see Experimental), and from the mother liquors, after removal of the AgI formed, *trans*-$[Pd(C_6F_5)(C{\equiv}CPh)(PPh_3)_2]$ **2** or *trans*-$[Pd(C_6F_5)(C{\equiv}C^tBu)(PPh_3)_2]$ **3** can be isolated as colourless or pale yellow crystals, respectively. Attempts to prepare platinum derivatives similarly were unsuccessful since no reaction takes place when *trans*-$[Pt(C_6F_5)I(PPh_3)_2]$ is treated with $[Ag(C{\equiv}CR)]_n$ (R = Ph, ^tBu).

On the other hand, $[Pd(C_6F_5)I(dppe)]$ reacts with $[Ag(C{\equiv}C^tBu)]_n$ in acetone (eq. 2) to yield $[Pd(C_6F_5)(C{\equiv}C^tBu)(dppe)]$ **4** as very pale yellow crystals, but similar treatment with $[Ag(C{\equiv}CPh)]_n$ led to extensive decomposition to metallic palladium, and, under a variety of conditions, only small amounts of starting material were recovered. However, treatment of $[Pt(C_6F_5)I(dppe)]$ with $[Ag(C{\equiv}CR)]_n$ yields both $[Pt(C_6F_5)(C{\equiv}CPh)(dppe)] \cdot 0.25CH_2Cl_2$ **5** or $[Pt(C_6F_5)(C{\equiv}C^tBu)(dppe)]$ **6** (eq. 2), although in the case of **6** the reaction must be carried out at the reflux temperature to bring about complete replacement.

$$[M(C_6F_5)IL_2] + 1/n[Ag(C{\equiv}CR)]_n \rightarrow [M(C_6F_5)(C{\equiv}CR)L_2] + AgI \quad (2)$$

M = Pd, L = PPh_3, R = Ph **2**; R = ^tBu **3**

M = Pd, L_2 = dppe, R = ^tBu **4**

M = Pt, L_2 = dppe, R = Ph **5**; R = ^tBu **6**

Analyses, yields, molecular weights, and some relevant IR data for the products are listed in Table 1. NMR data are listed in Table 2. The IR spectra of complexes **2–6** show characteristic bands of coordinated L_2 or C_6F_5 [7] ligands. Complexes **2**

Table 1

Analytical results, molecular weights, conductivities and relevant IR data

Compound	Yield	Analysis (found (calc) (%))			M.w. [a]	Λ_M [b]	A [c]	IR (cm^{-1}) [d]	
		N	C	H	found (calc)			ν(C≡C)	ν-Xsens(C$_6$X$_5$)
1, *trans*-[Pt(C≡C^{t}Bu)$_2$(PPh$_3$)$_2$]	59	–	65.27 (65.37)	5.86 (5.49)	–	–	–	2108	–
2, *trans*-[Pd(C$_6$F$_5$)(C≡CPh)(PPh$_3$)$_2$]	85	–	66.39 (66.79)	4.26 (3.92)	896 (899)	–	–	2113	783
3, *trans*-[Pd(C$_6$F$_5$)(C≡C^{t}Bu)(PPh$_3$)$_2$]	47	–	65.20 (65.58)	4.20 (4.47)	771 (879)	–	–	[e]	778
4, [Pd((C$_6$F$_5$)(C≡C^{t}Bu)(dppe)]	58	–	60.30 (60.61)	4.40 (4.42)	820 (753)	–	–	[e]	773
5, [Pt(C$_6$F$_5$)(C≡CPh)(dppe)].0,25CH$_2$Cl$_2$	65	–	55.03 (54.75)	3.21 (3.37)	942 (862)	–	–	2116	785
6, [Pt(C$_6$F$_5$)(C≡C^{t}Bu)(dppe)]	45	–	54.29 (54.22)	4.19 (3.95)	797 (841)	–	–	[e]	787
7, (NBu$_4$)$_2$[Pt$_2$Ag$_2$(C$_6$F$_5$)$_4$(C≡CPh)$_4$]	76	1.31 (1.29)	48.68 (48.85)	4.49 (4.29)	–	178	880	2033	799, 779
8, (NBu$_4$)$_2$[Pt$_2$Ag$_2$(C$_6$F$_5$)$_4$(C≡C^{t}Bu)$_4$]	75	1.32 (1.34)	46.14 (46.12)	5.50 (5.22)	–	166	800	2033	785, 777
9, (NBu$_4$)$_2$[Pt$_2$Ag$_2$(C$_6$Cl$_5$)$_2$(C≡CPh)$_4$]	80	0.97 (1.12)	42.66 (42.40)	3.49 (3.72)	–	175	824	2030	833, 828
10, (NBu$_4$)$_2$[Pt$_2$Ag$_2$(C$_6$Cl$_5$)$_2$(C≡C^{t}Bu)$_4$]	75	1.14 (1.16)	39.52 (39.82)	4.31 (4.51)	–	167	863	2021	831, 825
11, (PMePh$_3$)$_2$[Pt$_2$Ag$_2$(C$_6$F$_5$)$_4$(C≡CPh)$_4$]	80	–	50.31 (50.55)	2.28 (2.53)	–	228	880	2029	796, 778
12, (PMePh$_3$)$_2$[Pt$_2$Cu$_2$(C$_6$F$_5$)$_4$(C≡CPh)$_4$]	73	–	52.41 (52.64)	2.68 (2.63)	–	208	940	2013, 2000(sh)	797, 779
13, (NBu$_4$)$_2$[Pt$_2$Cu$_2$(C$_6$F$_5$)$_4$(C≡C^{t}Bu)$_4$]	66	1.41 (1.40)	48.17 (48.16)	5.66 (5.46)	–	228	882	2001	785, 775
14, (PMePh$_3$)$_2$[cis-Pt(C$_6$F$_5$)$_2$(C≡CPh)$_2$]	70	–	61.25 (61.64)	3.90 93.60)	–	154	–	2096, 2083	775, 769
15, (NBu$_4$)$_2$[cis-Pt(C$_6$F$_5$)$_2$(C≡C^{t}Bu)$_2$]	63	2.51 (2.39)	56.89 (57.18)	7.93 (7.71)	–	152	–	2090(sh); 2085	777, 768

[a] In chloroform [b] in acetone solutions Ω^{-1} cm^2 mol^{-1} [c] equivalent conductivity measurements in acetone solutions, value of A in Onsager equation ($\Lambda_e = \Lambda_0 - A\sqrt{c}$) [d] For all the complexes with the C$_6$F$_5$ group, bands are observed at ca. (1630, 1500, 1060 and 950 cm^{-1}). In addition for the complexes with C≡C^{t}Bu group bands are observed at ca (1240 and 1200 cm^{-1}) and with C≡CPh group at ca (755 and 690 cm^{-1}). [e] Extremely weak.

Table 2

NMR data in $CDCl_3$

Compound [a]	$\delta(^1H)$/ppm [b]	$\delta(^{19}F)$/ppm [c] F(2), F(6)	 F(4)	 F(3), F(5)
1	0.86			
3	0.40			
4	0.96			
6	0.95			
7		−115.7 [404.8]	−166.8	−167.6 (19.95)
8	1.12	−114.0 [404.9]		−168.8
10	1.08			
13	1.11	−120.3 [521.65]	−165.7	−167.6 (19.95)
15	1.03	−114.8 [386.7]	−171.0	−170.0 (19.3)

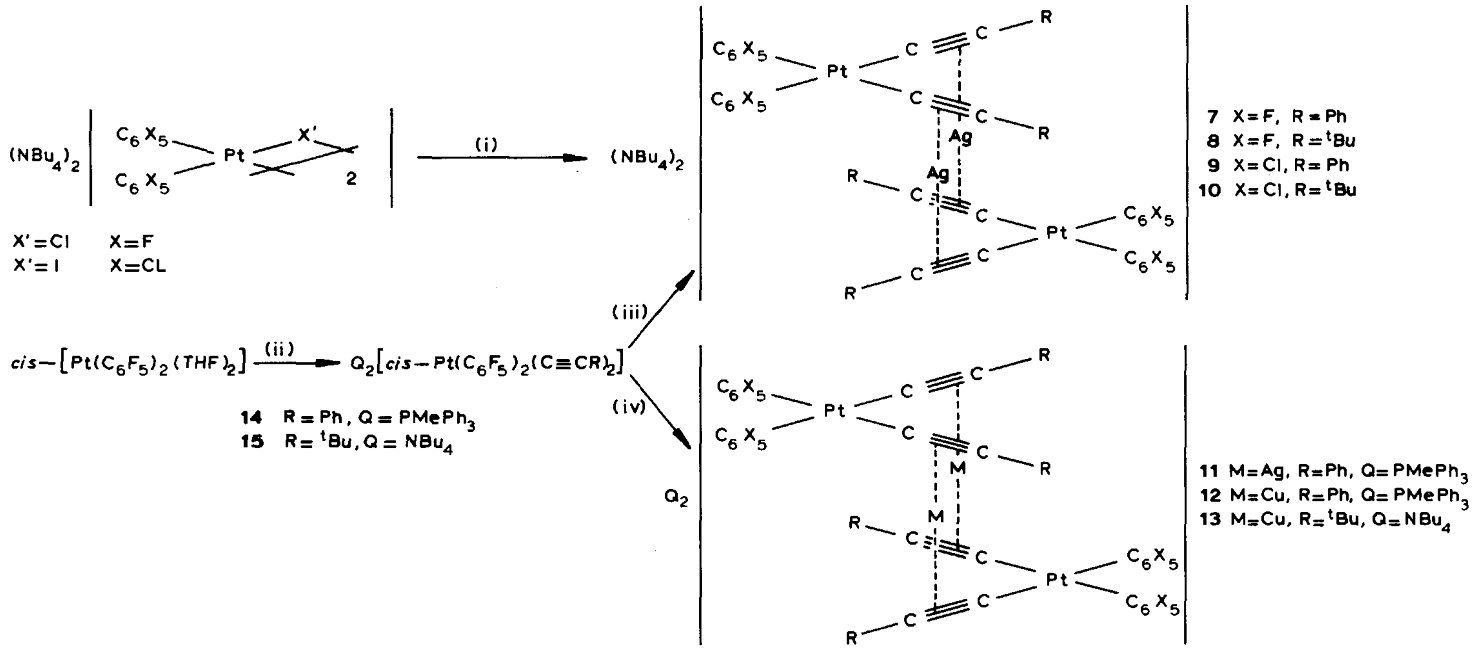
[a] Compounds **11**, **12** and **14** are not sufficiently soluble. [b] For the organic substituent on the acetylide; relative to internal $SiMe_4$. [c] $^3J(Pt-F_{ortho})$ (Hz) in brackets. $^3J(F(4)-F(3)) = {}^3J(F(4)-F(5))$ (Hz) in parentheses.

and **3** show no absorptions due to PPh_3, in the 540–560 cm^{-1} region, indicative of a *trans*-arrangement of both PPh_3 ligands [6]. The phenylacetylide complexes **2** and **5** show an absorption at 2113 and 2116 cm^{-1}, respectively, due to $\nu(C{\equiv}C)$, which indicates terminal coordination of the acetylide ligand [8]. Absorptions due to $\nu(C{\equiv}C)$ in the $C{\equiv}C^tBu$ complexes (**3**, **4**, **6**) were not observable in the IR spectra, but the ^1H NMR spectra showed singlets due to the $C(CH_3)_3$ group (see Table 2).

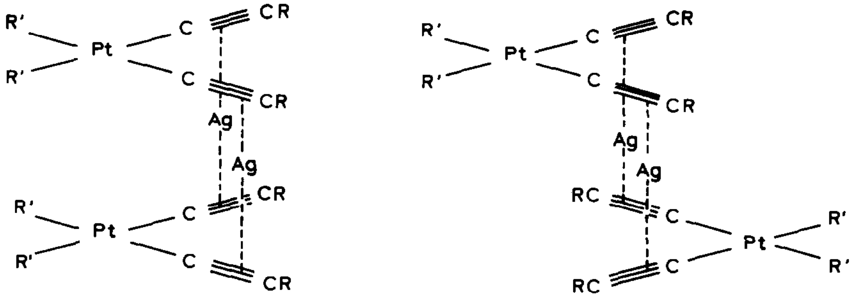
Reactions with $(NBu_4)_2[Pt_2(\mu\text{-}X')_2(C_6X_5)_4]$

The reaction between $(NBu_4)_2[Pt_2(\mu\text{-}Cl)_2(C_6F_5)_4]$ or $(NBu_4)_2[Pt_2(\mu\text{-}I)_2(C_6Cl_5)_4]$ and $[Ag(C{\equiv}CR)]_n$ (R = Ph, ^tBu) in chloroform (R = Ph) or acetone (R = ^tBu) (ratio Pt : Ag, 1 : 2) (see Experimental section for details) gives a precipitate of silver(I) halide, and the complexes $(NBu_4)_2[Pt_2Ag_2(C_6X_5)_4(C{\equiv}CR)_4]$ (X = F, R = Ph **7**, R = ^tBu **8**; X = Cl, R = Ph **9**, R = ^tBu **10**) can be isolated from the mother liquors as microcrystalline solids. The various syntheses and transformations are outlined in Scheme 1. When the reactions are carried out in a 1 : 1 Pt : Ag ratio, mixtures of the starting materials and the corresponding complex **7**–**10** are obtained.

The formulation of the anionic part of complexes **7**–**10** as tetrametallic species containig two $[cis\text{-}Pt(C_6X_5)_2(C{\equiv}CR)_2]$ units holding two Ag(I) cations was made on the basis of their analyses, conductivities (Table 1), IR spectra, and ^{19}F and ^1H NMR spectra (Table 2) and an X-ray diffraction study of complex **7**. Equivalent conductivity measurements in acetone solutions for complexes **7**–**10** over the 10^{-4}–10^{-3} mol dm^{-3} range show a values of A from the Onsager equation ($\Lambda_e = \Lambda_o - A\sqrt{C}$) characteristic of a 2 : 1 electrolyte (see Table 1) [9,10]. The IR spectra of complexes **7**–**10** in all cases show one absorption in the 2030–2000 cm^{-1} region, assignable to $\nu(C{\equiv}C)$ of the acetylide group and in the range expected for a σ–π coordination mode of these ligands.



Scheme 1. (i) $\frac{4}{n}$ $[Ag(C{\equiv}CR)]_n$ (R = Ph, chloroform; R = ^{t}Bu, acetone). (ii) LiC≡R, diethyl ether, 0 °C/(R = Ph, $PMePh_3Br$; R = ^{t}Bu, NBu_4Br), (iii) $AgClO_4$ or AgCl. For R = ^{t}Bu, acetone. (iv) AgCl (R = Ph, Q = $PMePh_3$) or CuCl (R = ^{t}Bu, Q = NBu_4), acetone.



A B

Fig. 1.

The ^{19}F NMR spectra of complexes **7** and **8** (see Table 2) indicate that the four C_6F_5 groups are equivalent. The ^{1}H NMR spectra of the tert-butylacetylide complexes **8** and **10** are very similar and, exhibit, besides resonances due to the NBu_4^+ ion, singlets for the methyl groups of the alkynyl ligand. Although both of the two posible orientations (Fig. 1, **A** and **B**) of the two platinum moieties around the silver atoms are compatible with these spectroscopic data, the molecular structure of **7** shows that **B**, the less sterically hindered, is adopted.

Syntheses of $Q_2[Pt_2Ag_2(C_6F_5)_4(C{\equiv}CR)_4]$ *by using* $Q_2[\text{cis-}Pt(C_6F_5)_2(C{\equiv}CR)_2]$ *as starting materials*

An alternative route for the syntheses of **8** involves the addition of $AgClO_4$ or AgCl to an acetone solution of $(NBu_4)_2[\textit{cis}\text{-}Pt(C_6F_5)_2(C{\equiv}C^tBu)_2]$ **15** at room temperature. Similar heterometallic platinum–silver $(PPh_3Me)_2[Pt_2Ag_2(C_6F_5)_4(C{\equiv}CPh)_4]$ **11** or platinum–copper complexes $Q_2[Pt_2Cu_2(C_6F_5)_4(C{\equiv}CR)_4]$ ($Q = PPh_3Me$, $R = Ph$ **12**; $Q = NBu_4$, $R = {}^tBu$ **13**) can also be synthesized by treating the corresponding anionic mononuclear derivatives $Q_2[\textit{cis}\text{-}Pt(C_6F_5)_2(C{\equiv}CR)_2]$ ($Q = PPh_3Me$, $R = Ph$ **14**, $Q = NBu_4$, $R = {}^tBu$ **15**) with AgCl or CuCl in acetone at room temperature (see Scheme 1 and Experimental for details). However, the reaction between $Q_2[\textit{cis}\text{-}Pt(C_6F_5)_2(C{\equiv}CR)_2]$ and [AuCl(tht)] yields (as indicated by the IR spectra mixtures of compounds, which we were unable to separate.

Analytical and other structural data for complexes **11**–**13** are shown in Table 1. The equivalent conductivities in acetone solutions (A in Onsager equation, see Table 1) indicate that they behave as 2 : 1 electrolytes. The IR spectra of these complexes have the $\nu(C{\equiv}C)$ vibrations at lower frequencies (2000–2029 cm^{-1}) than those observed for the mononuclear precursors **14** and **15**. This frequency lowering is similar to that observed for other alkynyl groups upon coordination to Cu^+ and Ag^+ [4,11]. The ^{1}H and ^{19}F NMR spectra are similar to those of complexes **7** and **8**. From all these data it is reasonable to assume that complexes **11**–**13** have a similar structure to that found for **7** (see below).

The anionic starting complexes $Q_2[\textit{cis}\text{-}Pt(C_6F_5)_2(C{\equiv}CR)_2]$ ($Q = PPh_3Me$, $R = Ph$ **14**; $Q = NBu_4$, $R = {}^tBu$ **15**) were prepared by alkynylation of $\textit{cis}\text{-}[Pt(C_6F_5)_2(THF)_2]$ (THF = tetrahydrofuran) [12] with $LiC{\equiv}CR$ in diethyl ether at 0 °C. Addition of NBu_4Br allows precipitation of $(NBu_4)_2[\textit{cis}\text{-}Pt(C_6F_5)_2(C{\equiv}C^tBu)_2]$ **15**, but the isolation of $[\textit{cis}\text{-}Pt(C_6F_5)_2(C{\equiv}CPh)_2]^{2-}$ required the use of PPh_3MeBr (affording **14**) since addition of NBu_4Br gave only an intractable oil. The analytical and structural data for **14** and **15** are listed in Table 1. The IR spectra of these complexes show two absorptions at ca. 800 cm^{-1} assigned to the X-sensitive mode of the C_6F_5 groups [7,12] and two bands due to $\nu(C{\equiv}C)$ (see Table 1) in accord with the expected results for the *cis* derivatives (C_{2v}). The ^{19}F NMR spectra show signals due to only one type of C_6F_5 group, and the ^1H NMR spectrum of **15** shows only one singlet for the methyl groups of the tert-butylacetylide ligands.

Structure of $(NBu_4)_2[Pt_2Ag_2(C_6F_5)_4(C{\equiv}CPh)_4] \cdot 4CH_2Cl_2$ *7*

The structure of complex **7** was determined by single-crytal X-ray diffaction. Single crystals were grown by slow diffusion of n-hexane into a CH_2Cl_2 solution of **7**.

General crystallographic information is given in Table 3. Positional parameters are listed in Table 4. Selected bond distances and bond angles are given in Table 5.

The structure of the anion is shown in Fig. 2, and consists of two square-planar platinum environments [*cis*-$Pt(C_6F_5)_2(C{\equiv}CPh)_2$] linked through two silver atoms, since the C≡C bonds of two acetylide groups (one associated with each platinum atom) are π-coordinated to the Ag atoms. The entire anion possesses an inversion centre, and because of this both square-planar platinum environment are parallel.

Each platinum atom is σ-bonded to two C_6F_5 groups mutually *cis* and to two C≡CPh groups in a slightly distorted square planar arrangement. The Pt–C distances to the C_6F_5 groups are Pt(1)–C(14) 2.060(9) Å and Pt(1)–C(20) 2.050(8) Å, in the range of distances found for other pentafluorophenyl-platinum derivatives [13,14]. The Pt–C(α) distances (Pt–acetylide) are 2.012(10) and 2.014(9) Å, similar to other Pt(II)–C(acetylide) distances [4,15–17], The C–Pt–C *cis* angles are in the range 87.5(3)–93.3(3).

The C≡C bonds of the acetylide groups are π-coordinated to the Ag atoms in such a way that two phenylacetylide units, one associated with each platinum atom, are asymmetrically π-bonded to each silver atom. The Ag–C(α) distances are

Table 3

Crystallographic data for the structural analysis of complex 7

formula	$Pt_2Ag_2F_{20}Cl_8N_2C_{92}H_{100}$	diffractometer	Enraf–Nonius CAD-4
fw	2503.32	temp, °C	0
space group	$P2_1/n$	scan method	ω–2θ
systematic absences	$h0l$, $h+1 \neq 2n$ $0k0$, $k \neq 2n$	data collection range, 2θ, deg	max 50
		no. of unique data, total with $F_o^2 > 6\sigma(F_o^2)$	8199, 5107
a, Å	15.697(3)	no. of parameters refined	541
b, Å	12.719(2)	transm. factors, max, min	1.19, 0.91
c, Å	23.601(6)	R	0.0378
β, deg	97.18(2)	R_w	0.0400
V, (Å^3)	4675(1)	largest shift/esd, final cycle	0.02
Z	2	largest peak, e/Å^3	0.63
d_{calcd}, g/cm^3	1.53		
μ (Mo-K_α), cm^{-1}	36.9		
radiation (monochromated incident beam)	Mo-K_α (λ = 0.71069 Å)		
orientation reflections, no.; range (2θ)	25; 26–30		

Table 4

Positional parameters for complex 7

Atom	*x*	*y*	*z*
Pt(1)	11672(1)	676(1)	−11(1)
Ag(1)	9983(1)	553(1)	545(1)
F(1)	10710(4)	2255(5)	−940(2)
F(2)	11005(5)	2795(5)	−1991(3)
F(3)	12329(6)	1954(7)	−2472(3)
F(4)	13402(6)	590(7)	−1851(3)
F(5)	13122(5)	14(7)	−804(3)
F(6)	10728(4)	2668(4)	510(3)
F(7)	11244(5)	4594(4)	807(3)
F(8)	12879(4)	5210(5)	696(3)
F(9)	13988(4)	3827(5)	318(3)
F(10)	13481(3)	1871(4)	31(3)
C(1)	11411(6)	346(7)	783(4)
C(2)	11213(5)	172(7)	1258(3)
C(4)	11790(3)	66(5)	2271(3)
C(5)	11694(3)	−159(5)	2838(3)
C(6)	10899(3)	−484(5)	2981(3)
C(7)	10201(3)	−584(5)	2557(3)
C(8)	10296(3)	−359(5)	1990(3)
C(3)	11091(3)	−34(5)	1847(3)
C(9)	12547(8)	693(9)	−1087(4)
C(10)	12736(8)	970(10)	−1627(5)
C(11)	12196(9)	1687(10)	−1934(5)
C(12)	11518(7)	2109(8)	−1697(4)
C(13)	11397(6)	1811(7)	−1144(4)
C(14)	11886(6)	1089(7)	−825(4)
C(15)	11548(5)	2915(7)	442(4)
C(16)	11792(7)	3902(7)	606(4)
C(17)	12604(7)	4240(8)	562(4)
C(18)	13167(6)	3523(8)	362(4)
C(19)	12876(6)	2527(8)	199(4)
C(20)	12051(5)	2167(7)	238(3)
C(21)	11416(5)	−799(7)	−293(4)
C(22)	11312(6)	−1691(7)	−465(4)
C(24)	11626(4)	−2955(5)	−1198(3)
C(25)	11608(4)	−3972(5)	−1420(3)
C(26)	11287(4)	−4798(5)	−1120(3)
C(27)	10984(4)	−4606(5)	−599(3)
C(28)	11002(4)	−3588(5)	−377(3)
C(23)	11323(4)	−2763(5)	−676(3)
N(1)	13900(4)	−1922(5)	809(3)
C(29)	14352(5)	−2962(7)	1002(4)
C(30)	15348(6)	−2900(7)	1020(4)
C(31)	15690(7)	−4022(10)	1177(6)
C(32)	16634(8)	−4034(11)	1269(7)
C(33)	14204(6)	−1099(7)	1261(4)
C(34)	13770(7)	−18(7)	1172(4)
C(35)	14093(8)	649(8)	1682(4)
C(36)	13652(8)	1763(8)	1628(4)
C(37)	12915(5)	−2089(7)	770(4)
C(38)	12599(6)	−2346(7)	1338(4)
C(39)	11633(6)	−2703(7)	1199(4)

Table 4 (continued)

Atom	x	y	z
C(40)	11289(7)	−3036(9)	1737(5)
C(41)	14125(6)	−1566(6)	223(4)
C(42)	13943(7)	−2391(9)	−246(4)
C(43)	14303(8)	−2003(9)	−779(4)
C(44)	14116(9)	−2786(11)	−1270(5)
Cl(1)	14910(3)	2557(4)	−2593(2)
Cl(2)	16502(3)	1806(4)	−2897(2)
C(45)	15488(8)	2240(11)	−3165(5)

2.257(9) and 2.225(7) Å, while the Ag–C(β) distances are respectively 2.483(9) and 2.445(8) Å. Similar Ag–C(α) and Ag–C(β) distances have been found in other Pt–Ag complexes in which the acetylide ligand is σ-bonded to platinum and π-bonded to the siver ion [4]. The C(α)–C(β) distances are equal within experimental error (C(1)–C(2) 1.221(13) Å and C(21)–C(22) 1.210(12) Å), and similar to C≡C distances in other σ, π phenyl acetylide polynuclear complexes [3c,18], although slightly longer than distances found, for instance, in $[Cu(C{\equiv}CPh)(PPh_3)]_4$, a tetranuclear complex containing four μ_3-bridging phenylacetylide ligands [19]. As a consequence of the π-Ag–acetylide interaction, the acetylide ligands are not linear, the angles Pt–C(α)–C(β) being 176.6(8) and 176.3(8)°, while the C(α)–C(β)–(phenyl) angles are 172.8(8) and 171.4(9)°. One of the acetylide groups, [C(1)≡C(2)], has a *trans*-bent arrangement whilst the other [C(21)≡C(22)], is *cis*-bent. *Cis*- and *trans*-bent arrangements have been found in acetylide polynuclear complexes containing σ- and π-acetylide bonds [18,20,21], whereas only *cis*-bent arrangements have been observed in acetylene–transition metal complexes [22]. Finally it should be noted that the C≡C bonds associated with each Ag atom are perpendicular to one another.

The Pt $\cdots$ Ag distances are 3.10 and 3.15 Å, respectively which excludes Pt $\cdots$ Ag bonding. However the Ag $\cdots$ Ag distance is 2.939(1) Å, near the high end of the range observed for other systems in which Ag–Ag bonding has been assumed to occur (2.740(2) to 3.085(2) Å), so that a weak Ag $\cdots$ Ag interaction could be present [23]. This notwithstanding, it seems sensible to assume that the π-Ag–acetylide bonds are the driving force in the formation of the compounds.

Experimental

C, N and H analyses were determined with a Perkin–Elmer 240-B microanalyzer. IR spectra were recorded (4000–200 cm^{-1}) on a Perkin–Elmer 883 spectrophotometer using Nujol mulls between polyethylene sheets. The ^1H and ^{19}F NMR were recorded on a Varian XL-200 spectrometer (200 MHz for ^1H) in $CDCl_3$ solutions. Molecular weights were determined in $CHCl_3$ solutions on a Knauer apparatus Conductivities of acetone solutions at various molarities were measured with a Philips PW 9509 conductimeter.

Literature methods were used for the preparation of the following starting materials $(NBu_4)_2[Pt_2(\mu\text{-}I)_2(C_6X_5)_4]$ (M = Pd, Pt) [24,25] *cis*-$[Pt(C_6F_5)_2(THF)_2]$

Table 5

Selected bond distances (Å) and bond angles (deg) for complex 7

Ag(1)-Pt(1)	3.106(0.001)	C(1)-Pt(1)	2.012(0.010)
C(14)-Pt(1)	2.060(0.009)	C(20)-Pt(1)	2.050(0.008)
C(21)-Pt(1)	2.014(0.009)	C(1)-Ag(1)	2.257(0.009)
C(2)-Ag(1)	2.445(0.008)	C(22)-Ag(1)	2.483(0.009)
C(21)-Ag(1)	2.225(0.007)	*Ag(1)-Ag(1)	2.939(0.001)
C(13)-F(1)	1.358(0.011)	C(12)-F(2)	1.323(0.012)
C(11)-F(3)	1.356(0.013)	C(10)-F(4)	1.320(0.016)
C(9)-F(5)	1.362(0.013)	C(15)-F(6)	1.353(0.010)
C(16)-F(7)	1.358(0.013)	C(17)-F(8)	1.331(0.011)
C(18)-F(9)	1.362(0.012)	C(19)-F(10)	1.359(0.011)
C(2)-C(1)	1.221(0.013)	C(3)-C(2)	1.449(0.011)
C(10)-C(9)	1.390(0.016)	C(14)-C(9)	1.368(0.015)
C(11)-C(10)	1.386(0.017)	C(12)-C(11)	1.371(0.018)
C(13)-C(12)	1.396(0.014)	C(14)-C(13)	1.361(0.012)
C(16)-C(15)	1.355(0.013)	C(20)-C(15)	1.363(0.012)
C(17)-C(16)	1.361(0.016)	C(18)-C(17)	1.393(0.015)
C(19)-C(18)	1.385(0.014)	C(20)-C(19)	1.387(0.013)
C(22)-C(21)	1.210(0.012)	C(23)-C(22)	1.453(0.011)
C(29)-N(1)	1.544(0.011)	C(33)-N(1)	1.528(0.011)
C(37)-N(1)	1.552(0.011)	C(41)-N(1)	1.537(0.011)
C(30)-C(29)	1.560(0.012)	C(31)-C(30)	1.554(0.015)
C(32)-C(31)	1.471(0.016)	C(34)-C(33)	1.537(0.013)
C(35)-C(34)	1.507(0.013)	C(36)-C(35)	1.575(0.015)
C(38)-C(37)	1.520(0.013)	C(39)-C(38)	1.578(0.013)
C(40)-C(39)	1.503(0.015)	C(42)-C(41)	1.526(0.013)
C(43)-C(42)	1.524(0.015)	C(44)-C(43)	1.527(0.017)
C(45)-Cl(1)	1.764(0.014)	C(45)-Cl(2)	1.729(0.013)

C(1)-Pt(1)-Ag(1)	46.5(0.3)	C(14)-Pt(1)-Ag(1)	130.9(0.2)
C(14)-Pt(1)-C(1)	176.5(0.3)	C(20)-Pt(1)-Ag(1)	99.1(0.2)
C(20)-Pt(1)-C(1)	90.7(0.3)	C(20)-Pt(1)-C(14)	87.5(0.3)
C(21)-Pt(1)-Ag(1)	86.9(0.3)	C(21)-Pt(1)-C(1)	93.3(0.3)
C(21)-Pt(1)-C(14)	88.8(0.3)	C(21)-Pt(1)-C(20)	173.9(0.3)
C(1)-Ag(1)-Pt(1)	40.3(0.3)	C(2)-Ag(1)-Pt(1)	70.0(0.2)
C(2)-Ag(1)-C(1)	29.8(0.3)	Ag(1)-C(1)-Pt(1)	93.2(0.4)
C(2)-C(1)-Pt(1)	176.6(0.8)	C(2)-C(1)-Ag(1)	83.7(0.6)
C(1)-C(2)-Ag(1)	66.6(0.5)	C(8)-C(3)-C(2)	121.0(0.5)
C(3)-C(2)-C(1)	172.8(0.8)	C(10)-C(9)-F(5)	114.0(1.0)
C(4)-C(3)-C(2)	119.0(0.6)	C(14)-C(9)-C(10)	125.5(1.0)
C(14)-C(9)-F(5)	120.4(0.9)	C(11)-C(10)-F(4)	119.8(1.1)
C(9)-C(10)-F(4)	123.0(1.1)	C(10)-C(11)-F(3)	119.8(1.2)
C(11)-C(10)-C(9)	117.3(1.2)	C(12)-C(11)-C(10)	120.1(1.0)
C(12)-C(11)-F(3)	120.1(1.1)	C(13)-C(12)-F(2)	121.7(1.0)
C(11)-C(12)-F(2)	119.8(1.0)	C(12)-C(13)-F(1)	115.2(0.8)
C(13)-C(12)-C(11)	118.5(0.9)	C(14)-C(13)-C(12)	124.6(0.9)
C(14)-C(13)-F(1)	120.2(0.8)	C(13)-C(14)-Pt(1)	122.8(0.7)
C(9)-C(14)-Pt(1)	123.2(0.7)	C(16)-C(15)-F(6)	114.9(0.8)
C(13)-C(14)-C(9)	114.0(0.9)	C(20)-C(15)-C(16)	126.3(0.9)
C(20)-C(15)-F(6)	118.8(0.7)	C(17)-C(16)-F(7)	117.5(0.8)
C(15)-C(16)-F(7)	122.1(1.0)	C(16)-C(17)-F(8)	123.6(0.9)
C(17)-C(16)-C(15)	120.4(1.0)	C(18)-C(17)-C(16)	117.3(0.9)
C(18)-C(17)-F(8)	119.2(1.0)	C(19)-C(18)-F(9)	121.4(0.9)
C(17)-C(18)-F(9)	119.1(0.9)	C(18)-C(19)-F(10)	115.1(0.8)
C(19)-C(18)-C(17)	119.5(0.9)	C(20)-C(19)-C(18)	124.2(0.9)

Table 5 (continued)

C(20)–C(19)–F(10)	120.6(0.8)	C(19)–C(20)–Pt(1)	121.8(0.6)
C(15)–C(20)–Pt(1)	125.9(0.6)	C(22)–C(21)–Pt(1)	176.3(0.8)
C(19)–C(20)–C(15)	112.3(0.8)	C(28)–C(23)–C(22)	120.7(0.7)
C(23)–C(22)–C(21)	171.4(0.9)	C(33)–N(1)–C(29)	106.8(0.6)
C(24)–C(23)–C(22)	119.2(0.7)	C(37)–N(1)–C(33)	110.9(0.6)
C(37)–N(1)–C(29)	108.5(0.6)	C(41)–N(1)–C(33)	109.9(0.6)
C(41)–N(1)–C(29)	111.7(0.6)	C(30)–C(29)–N(1)	112.7(0.7)
C(41)–N(1)–C(37)	109.1(0.6)	C(32)–C(31)–C(30)	110.9(1.0)
C(31)–C(30)–C(29)	106.0(0.8)	C(35)–C(34)–C(33)	107.2(0.7)
C(34)–C(33)–N(1)	115.1(0.7)	C(38)–C(37)–N(1)	114.3(0.7)
C(36)–C(35)–C(34)	109.9(0.8)	C(40)–C(39)–C(38)	110.1(0.8)
C(39)–C(38)–C(37)	106.9(0.7)	C(43)–C(42)–C(41)	108.8(0.8)
C(42)–C(41)–N(1)	114.1(0.7)	Cl(2)–C(45)–Cl(1)	109.4(0.7)
C(44)–C(43)–C(42)	111.0(1.0)		

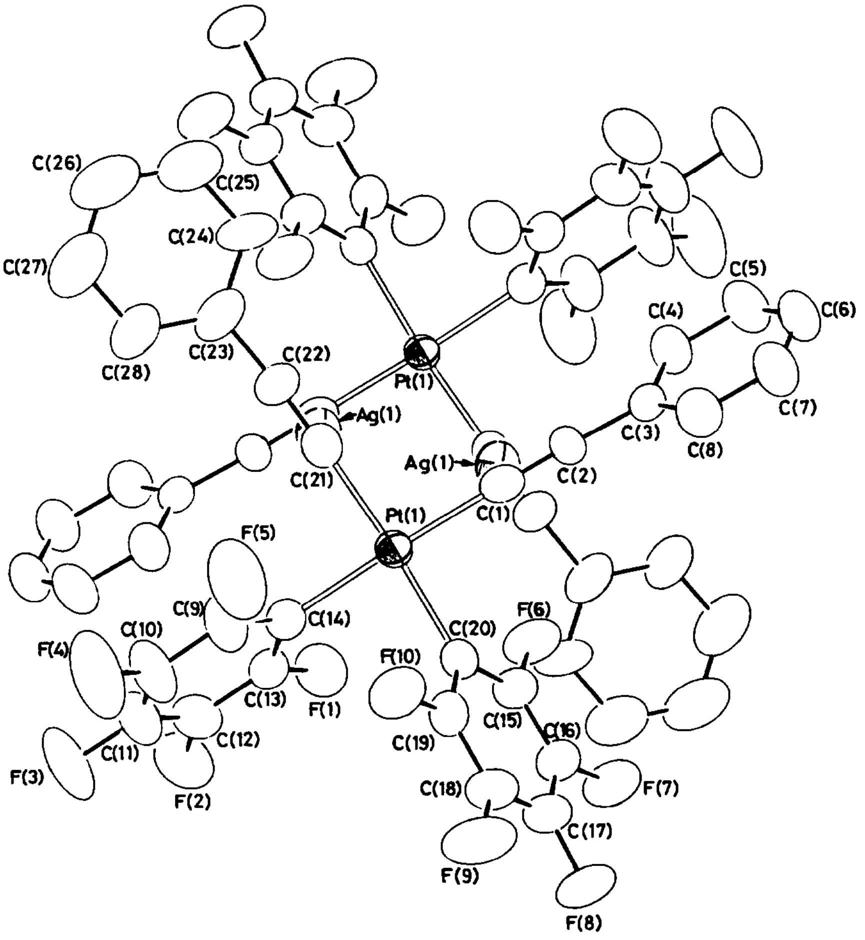


Fig. 2. Structure of the anion [Pt$_2$Ag$_2$(C$_6$F$_5$)$_4$(C≡CPh)$_4$]$^{2-}$, showing the atom labelling scheme.

[26], *trans*-$[PdI(C_6F_5)(PPh_3)_2]$ [27] and $[Ag(C{\equiv}CR)]_n$ [28]. Other starting materials were prepared as described below.

cis-*$[PtI_2(PPh_3)_2]$*. Potassium iodide (0.6743 g, 4.062 mmol) was added to a suspension of *cis*-$[PtCl_2(PPh_3)_2]$ [29] (0.4015 g, 0.509 mmol.) in 50 ml of acetone. After 10 h refluxing the yellow suspension was evaporated to dryness. The residue was extracted with hot chloroform and the extract was filtered and concentrated. Et_2O was added to precipitate the desired product, which was obtained in 80% yield. Analyses. Found C: 43.94; H: 3.17; calc. C: 44.42; H: 3.11%.

$[Pt_2(\mu\text{-}I)_2(C_6F_5)_2(tht)_2]$. Addition of KI (0.470 g, 2.831 mmol) to a solution of $[Pt_2(\mu\text{-}Cl)_2(C_6F_5)_2(tht)_2]$ [30] (0.6875 g, 0.708 mmol) in 30 ml. of acetone produced after a few minutes a deep yellow suspension. After 25 h stirring at room temperature the suspension was evaporated to dryness and the residue extracted with dichloromethane. The extract was filtered and concentrated, and n-hexane was added to precipitate the desired complex. 95% yield. Analyses. Found C: 20.86; H: 1.40; calc. C: 20.81; H: 1.40%.

$[M(C_6F_5)I(dppe)]M = Pd, Pt$. A solution of $[M_2(\mu\text{-}I)_2(C_6F_5)_2(tht)_2]$ ($M = Pt$ 0.1009 g, 0.087 mmol; $M = Pd$ [31] 0.312 g, 0.319 mmol) and 1,2-bis(diphenyl-phosphino)ethane (0.0696 g, 0.174 mmol for $M = Pt$ or 0.2545 g, 0.639 mmol for $M = Pd$) in 30 ml of CH_2Cl_2 was stirred at room temperature for 1 h. Concentration to ca. 2 ml and addition of n-hexane for $M = Pt$ or ethanol for $M = Pd$ led to precipitation of $[Pt(C_6F_5)I(dppe)]$ as a white solid or $[Pd(C_6F_5)I(dppe)]$ as yellow crystals.

$Pt(C_6F_5)I[(dppe)]$: 85% yield. Analyses. Found C: 43.26; H: 2.86; calc. C: 43.31; H: 2.73%.

$(Pd(C_6F_5)I(dppe)]$: 84% yield. Analyses. Found C: 48.06; H: 4.01; calc. 48.11; H: 4.29%.

Preparation of the complexes

trans-*$[Pt(C{\equiv}C^tBu)_2(PPh_3)_2]$ 1*. To a solution of cis-$[PtI_2(PPh_3)_2]$ (0.202 g, 0.208 mmol) in acetone (100 ml) was added $[Ag(C{\equiv}C^tBu)]_n$ (0.0784 g, 0.415 mmol). The mixture, protected from the light, was stirred at room temperature for 94 h, then choroform (25 ml) was added and the AgI filtered off. From the colourless solution **1** was isolated by partial evaporation (~ 3 ml, 59% yield).

trans-*$[Pd(C_6F_5)(C{\equiv}C^tBu)(PPh_3)_2](2\ R = Ph;\ 3\ R = {}^tBu)$*. A mixture of *trans*-$[Pd(C_6F_5)I(PPh_3)_2]$ (0.3 g, 0.324 mmol) and $[Ag(C{\equiv}CR)]_n$ ($R = Ph$ 0.0686 g or $R = {}^tBu$ 0.062 g, 0.328 mmol) in CH_2Cl_2 (50 ml, $R = Ph$) or acetone (50 ml, $R = {}^tBu$) was stirred for 20 h ($R = Ph$) or 48 h ($R = {}^tBu$) at room temperature with exclusion of the light. The AgI was then filtered off and the solution concentrated to ~ 2 ml. Addition of n-hexane (10 ml, $R = Ph$) or MeOH (10 ml, $R = {}^tBu$) gave **2** or **3** as white or pale yellow solids, respectively. [**2**, 85% yield; **3**, 47% yield].

$[M(C_6F_5)(C{\equiv}CR)(dppe)](M = Pd, R = {}^tBu$ 4; $M = Pt, R = Ph$ 5; $M = Pt, R = {}^tBu$ 6:). A typical preparation (complex **4**) was as follows: To a solution of $[M(C_6F_5)I(dppe)]$ ($M = Pd$ 0.2041 g, 0.256 mmol) in acetone (50 ml.) was added $[Ag(C{\equiv}CR)]_n$ ($R = {}^tBu$ 0.049 g, 0.259 mmol). The mixture, protected from the light, was stirred at room temperature for 40 h then filtered, and filtrate evaporated to ca. 2 ml. Subsequent slow addition of EtOH (~ 20 ml.) gave **4**, 58% yield.

Complexes **5** and **6** were obtained similarly. For **5** CH_2Cl_2 was used as solvent and the product was precipitated by adding diethyl ether, and for **6** the reaction was carried out at the reflux temperature (20 h) (**5**, 65% yield; **6**, 45% yield).

$(NBu_4)_2[Pt_2Ag_2(C_6F_5)_4(C\equiv CR)_4]$(R = Ph 7; R = ^{t}Bu 8). $[Ag(C\equiv CPh)]_n$ (0.5176 g, 2.478 mmol) or $[Ag(C\equiv C^tBu)]_n$ (0.4684 g, 2.478 mmol) was added to a solution of $(NBu_4)_2[Pt_2(\mu\text{-}Cl)_2(C_6F_5)_4]$ (1 g, 0.619 mmol) in chloroform (80 ml) or acetone (80 ml) respectively. The mixture was refluxed for 15 h and the AgCl then filtered off. Evaporation of the filtrate to ca. 1 cm^3 and addition of diethyl ether (20 ml) gave complexes **7** and **8** as a pale yelow or white microcrystals, respectively. Yields (76% for R = Ph, **7**; 75% for R = ^{t}Bu **8**).

$(NBu_4)_2[Pt_2Ag_2(C_6F_5)_4(C\equiv C^tBu)_4]$ **8** was also prepared by the following methods.

(a) By stirring $AgClO_4$ (0.0294 g, 0.1394 mmol) and $(NBu_4)_2[cis\text{-}Pt(C_6F_5)_2(C\equiv C^tBu)_2]$ **15** (0.1645 g, 0.1398 mmol) in acetone (20 ml) for 1 h at room temperature. Evaporation to dryness and addition of isopropanol (~ 10 ml) gave **8** (62% yield) as white crystals.

(b) Stirring AgCl (0.01218 g, 0.085 mmol) and **15** (0.1 g, 0.085 mmol) in acetone for 1 h at room temperature. Evaporation to dryness of the resulting colourless solution and addition of isopropanol gave **8** (76% yield) as white crystalline needles.

$(NBu_4)_2[Pt_2Ag_2(C_6Cl_5)_4(C\equiv CR)_4]$ (R = Ph 9; R = ^{t}Bu 10). $[Ag(C\equiv CPh)]_n$ (0.0791 g, 0.376 mmol) or $[Ag(C\equiv C^tBu)]_n$ (0.0711 g, 0.376 mmol) was added to a solution of $(NBu_4)_2[Pt_2(\mu\text{-}I)_2(C_6Cl_5)_4]$ (0.2 g, 0.094 mmol) in $CHCl_3$ (40 ml) or acetone (40 ml), respectively, and the mixture was stirred for 5 days at room temperature. The AgI was filtered off and the filtrate evaporated to dryness to give an oil, which was transformed into a yellow, **9**, or white, **10**, solid, by stirring with diethyl ether, **9** or n-hexane, **10**, respectively.

$(PMePh_3)_2[Pt_2Ag_2(C_6F_5)_4(C\equiv CPh)_4]$ 11. To a suspension of AgCl (0.0111 g, 0.0777 mmol) in acetone (20 ml) was added $(PMePh_3)_2[cis\text{-}Pt(C_6F_5)_2(C\equiv CPh)_2]$ **14** (0.1 g, 0.0777 mmol). The mixture was stirred for 1 h and rendered a colourless solution from which **11** was isolated as a white solid by evaporation to small volume (ca. 2 ml), addition of EtOH and filtration. 80% yield.

$(PMePh_3)_2[Pt_2Cu_2(C_6F_5)_4(C\equiv CPh)_4]$ 12. To a stirred suspension of CuCl (0.0092 g, 0.093 mmol) in acetone (20 ml) was added **14** (0.1186 g, 0.0922 mmol). The mixture was stirred for 1 h at room temperature and filtered. The resulting colourless solution was evaporated to ca. 1 cm^3 and EtOH (20 cm^3) was added. Evaporation to 5 cm^3 gave **12** as a white product. 73% yield.

$(NBu_4)_2[Pt_2Cu_2(C_6F_5)_4(C\equiv C^tBu)_4]$ 13. Complex **15** (0.150 g, 0.1275 mmol) was stirred with CuCl (0.0126 g. 0.1275 mmol) in acetone (30 cm^3) for 6 h. The resulting colourless solution was evaporated to dryness. Addition of isopropanol (10 cm^3) yielded **13** (66%).

$(PMePh_3)_2[$cis-$Pt(C_6F_5)_2(C\equiv CPh)_2]$ 14. A solution of $LiBu^n$ in hexane (2.54 mol dm^{-3}, 1.46 cm^3, 3.7 mmol) was added dropwise under N_2 during 5 min to an ethereal (20 cm^3) solution of $PhC\equiv CH$ (0.381 g, 3.73 mmol) at 0 °C. After 20 min *cis*-$[Pt(C_6F_5)_2(THF)_2]$ (0.5 g, 0.7425 mmol) was added. The resulting colourless solution was evaporated to dryness and deoxygenated water (50 cm^3) was added. The solution was filtered and added dropwise to a solution of $PMePh_3Br$ (0.530 g, 1.485 mmol) in isopropanol (30 cm^3), to yield a white solid. Recrystallization from CH_2Cl_2/isopropanol yielded (70%) **14** as a white solid.

$(NBu_4)_2[$cis-$Pt(C_6F_5)_2(C\equiv C^tBu)_2]$ 15. A solution of $LiBu^n$ in hexane (3.09 mol dm^{-3}, 0.94 cm^3, 2.90 mmol) was added dropwise under N_2 during 5 min to a diethyl ether (20 cm^3) solution of $^tBuC\equiv CH$ (0.236 g, 2.87 mmol) at 0 °C. After 20 min,

cis-$[Pt(C_6F_5)_2(THF)_2]$ (0.777 g, 1.1538 mmol) was added and the mixture was stirred at 0 °C for 30 min then evaporated to dryness. Deoxygenated H_2O (50 cm^3) was added, and the colourless solution obtained was added dropwise to an aqueous solution (10 cm^3) of NBu_4Br (0.744 g, 2.311 mmol). The resulting oil was washed with several portions of H_2O, extracted with CH_2Cl_2 (30 cm^3), dried with $MgSO_4$ and evaporated to dryness. Addition of diethyl ether (ca. 30 cm^3) gave small amount of a white solid, which was filtered off. The resulting solution was evaporated to dryness and the residue was treated dropwise with isopropyl alcohol with vigorous stirring to give **15**. 62% yield.

Preparation of crystals for X-ray structure determination

Crystals of $(NBu_4)_2[Pt_2(C_6F_5)_4(C{\equiv}C{-}C_6H_5)_4Ag_2]\cdot 4CH_2Cl_2$ were obtained by slow difussion of n-hexane into a dichloromethane solution.

Crystal structure analyses. A crystal of **7** was mounted on a glass fibre and covered with epoxy resin adhesive. The lattice dimensions and Laue group of the crystal were based on 25 reflections ($13° < \theta < 15°$). Important crystal and experimental parameters are given in Table 3. There was a 60% decay during the data collection time. The structure was solved by Patterson synthesis for (Pt) with further non-H atoms located by subsequent Fourier difference maps. An empirical absorption correction applied [32]. Full-matrix least-squares refinement with all non-hydrogen atoms allowed anisotropic thermal motion. Phenyl rings of the acetylide-groups were treated as rigid bodies and included in the refinement with idealised hexagonal symmetry (C–C 1.395 Å). In addition, four free CH_2Cl_2 molecules were located. The computer programs SHELX-76 [33] and SHELX-86 [34], CADABS, [35] DIFABS [32] were used. Geometrical calculations were carried out with the program PARST [36].

In the final convergent refinement, 541 parameters were fitted to 5107 data, for a data to parameter ratio of 9.4. The least-squares residuals are summarized in Table 3.

A complete list of bond lengths and angles, a table of thermal parameters, and a list of observed and calculated structure factors are available from the authors.

Acknowledgements

We thank the DGICYT (Spain) for financial support (Project PB89-0057), and M.T.M. thanks the Instituto de Estudios Riojanos for a grant.

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