Novel Heterotrinuclear, $PtAg_2$, and Hexanuclear, Pt_2Ag_4, Compounds containing Bridging Alkynyl Groups. Crystal Structure of $[Pt_2Ag_4(C_6F_5)_4(\mu_3\text{-}\eta^2\text{-}C{\equiv}CPh)_4(PPh_3)_2]\cdot 0.5CH_2Cl_2$†

Irene Ara,[a] **Juan Forniés,***[a] **Elena Lalinde,***[b] **M. Teresa Moreno**[b] **and Milagros Tomás**[a]
[a] *Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-Consejo Superior de Investigaciones Científicas, 50009 Zaragoza, Spain*
[b] *Universidad de La Rioja, Departamento de Química, 26001 Logroño, Spain*

Treatment of the polymeric derivatives $[\{PtAg_2(C_6F_5)_2(C{\equiv}CR)_2\}_n]$ (R = Ph or Bu^t) with 2 molar equivalents of neutral ligands L (Ag:L 1:1) afforded the new more soluble trinuclear mixed-ligand complexes $[PtAg_2(C_6F_5)_2(C{\equiv}CR)_2L_2]$ **1–8** (L = PPh$_3$, PEt$_3$, CNBu^t or C$_5$H$_5$N). Analogous reactions with 1 molar equivalent of L (Ag:L 2:1) produced, however, only a partial depolymerization of $[\{PtAg_2(C_6F_5)_2(C{\equiv}CR)_2\}_n]$ to give the hexanuclear complexes $[Pt_2Ag_4(C_6F_5)_4(C{\equiv}CR)_4L_2]$ **9–16**. Compounds **9–12** have also been obtained by treatment of the binuclear derivatives $[NBu_4][Pt(C_6F_5)_2(\mu\text{-}C{\equiv}CR)_2AgL]$ with AgClO$_4$ (1:1 molar ratio) in acetone. Similar reactions of $[\{PtAg_2(C_6F_5)_2(C{\equiv}CR)_2\}_n]$ with 1 or 0.5 equivalent of 1,2-bis(diphenylphosphino)ethane (dppe) yielded insoluble complexes of composition $[\{PtAg_2(C_6F_5)_2(C{\equiv}CR)_2(dppe)\}_n]$ **17**, **18** or $[\{Pt_2Ag_4(C_6F_5)_4(C{\equiv}CR)_4(dppe)\}_n]$ **19**, **20** which are thought to be polymeric. The crystal structure of $[Pt_2Ag_4(C_6F_5)_4(\mu_3\text{-}\eta^2\text{-}C{\equiv}CPh)_4(PPh_3)_2]\cdot 0.5CH_2Cl_2$ **9**·0.5CH$_2$Cl$_2$ has been determined by X-ray diffraction methods.

The chemistry of metal alkynyl complexes has undergone important development in recent years.[1] The interest in this area is due both to the versatile reactivity of the acetylenic fragment, which has been used for the generation of other hydrocarbyl ligands, and to the ability of the alkynyl groups to bond to transition metals displaying a great variety of bonding modes.

Recent efforts in our group have been focused on the synthesis of homo- and hetero-polynuclear complexes of platinum in which the metal centres are linked only by alkynyl groups. Thus, we have previously reported the preparation of several hexanuclear $[Pt_2M_4(C{\equiv}CR)_8]$ (M = Ag, Cu or Au)[2] and tetranuclear $Q_2[Pt_2M_2(C_6F_5)_4(C{\equiv}CR)_4]$[3] (Q = PMePh$_3$ or NBu$_4$, M = Ag or Cu, R = Ph or Bu^t) complexes by treating the homoleptic $[Pt(C{\equiv}CR)_4]^{2-}$ or mixed-ligand *cis*-$[Pt(C_6F_5)_2(C{\equiv}CR)_2]^{2-}$ σ-alkynyl substrates with adequate transition-metal Lewis acids. The tetranuclear complexes $[NBu_4]_2[Pt_2Ag_2(C_6F_5)_4(C{\equiv}CR)_4]$ also react with neutral ligands to give binuclear $[NBu_4][(C_6F_5)_2Pt(\mu\text{-}C{\equiv}CR)_2AgL]$ or tetranuclear $[NBu_4]_2[\{(C_6F_5)_2Pt(\mu\text{-}C{\equiv}CR)_2Ag\}_2(\mu\text{-dppe})]$ (dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) anionic complexes, depending on the ligand used.[4] Stable trinuclear $[Pt(C{\equiv}CPh)_4(MX)_2]^{2-}$ (M = Cu or Ag; X = Cl or Br) or hexanuclear $[Pt_2M_4(C{\equiv}CBu^t)_8X_2]^{2-}$ dianionic species can also be obtained by treatment of $[Pt_2M_4(C{\equiv}CR)_8]$ with NBu$_4$X, albeit the similar reactions with phosphine ligands L (PPh$_3$ or PEt$_3$) result in precipitation of the polymeric acetylides MC≡CR (Cu or Ag) and formation of *trans*-$[Pt(C{\equiv}CR)_2L_2]$.[5] The structures of some of the resulting complexes have revealed that the strength and the asymmetry of the silver–alkyne η linkages are strongly dependent on the presence or absence of other ligands on the silver centre.

Recently we reported the synthesis of polynuclear complexes $[\{PtAg_2(C_6F_5)_2(C{\equiv}CR)_2\}_n]$ (R = Ph or Bu^t) which, due to their low solubility in common non-donor solvents, were thought to display a polymeric structure, probably based on square-planar *cis*-$Pt(C_6F_5)_2(C{\equiv}CR)_2$ fragments connected by Ag atoms η^2 bonded to acetylide groups (Scheme 1, **A**).[6] We observed that only the *tert*-butylacetylide derivative reacts readily in acetone yielding the more soluble hexanuclear species $[Pt_2Ag_4(C_6F_5)_4(C{\equiv}CBu^t)_4(Me_2CO)_4]$,[6] the molecular structure of which shows it to be formed by two identical binuclear fragments $[(C_6F_5)_2Pt(\mu\text{-}C{\equiv}CBu^t)_2Ag(Me_2CO)_2]$ linked through two silver atoms (**B**), with the alkynyl groups acting as μ$_3$-η^2 bridging ligands. These findings prompted us to investigate the reactivity of the yellow polymeric material $[\{PtAg_2(C_6F_5)_2(C{\equiv}CR)_2\}_n]$ (R = Ph or Bu^t) towards other compounds in order to analyse the influence of the R group on the reactivity and on the stability of the polynuclear derivatives when formed. In this paper we present the results of the reactions between $[\{PtAg_2(C_6F_5)_2(C{\equiv}CR)_2\}_n]$ (R = Ph or Bu^t) and neutral donor ligands [L = PPh$_3$, PEt$_3$, CNBu^t or pyridine (py)] using two different molar ratios 1:2 (Ag:L 1:1) and 1:1 (Ag:L 2:1), which afford, respectively, two new types of polynuclear neutral complexes: (*a*) trinuclear $[PtAg_2(C_6F_5)_2(C{\equiv}CR)_2L_2]$ derivatives and (*b*) hexanuclear $[Pt_2Ag_4(C_6F_5)_4(C{\equiv}CR)_4L_2]$ compounds. The reactivity of the polynuclear complexes with 1,2-bis(diphenylphosphino)ethane and Br$^-$ has also been studied, and the results are reported. Part of these results have been published as a preliminary communication.[7]

Results and Discussion

The results of the reactions starting from $[\{PtAg_2(C_6F_5)_2(C{\equiv}CR)_2\}_n]$ are summarized in Scheme 2. Addition of 2 equivalents of neutral ligands (Ag:L 1:1) to a yellow (for R = Ph) or white (R = Bu^t) suspension of $[\{PtAg_2(C_6F_5)_2(C{\equiv}CR)_2\}_n]$ in acetone gave a clear solution, from which neutral trinuclear alkynyl bridged complexes $[PtAg_2(C_6F_5)_2(C{\equiv}CR)_2L_2]$ **1–8** can be isolated as yellow (R = Ph) or white (R = Bu^t) microcrystalline solids [Scheme 2(*i*)]. In contrast with the dimeric nature found for $[\{PtAg_2(C_6F_5)_2(C{\equiv}CBu^t)_2(Me_2CO)_2\}_2]$[6] (Scheme 1, **B**), analytical and molecular weight determinations (Table 1) indicate that complexes **1–8** are formed by monomeric $[PtAg_2(C_6F_5)_2(C{\equiv}CR)_2L_2]$ units, which

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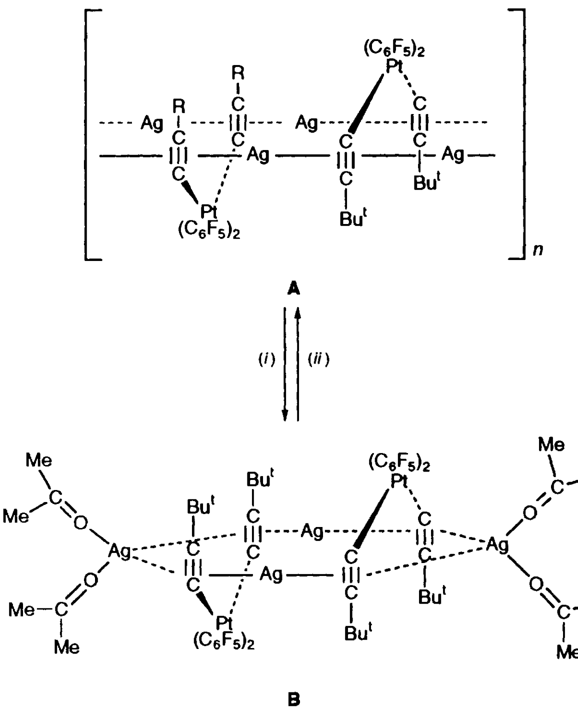
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

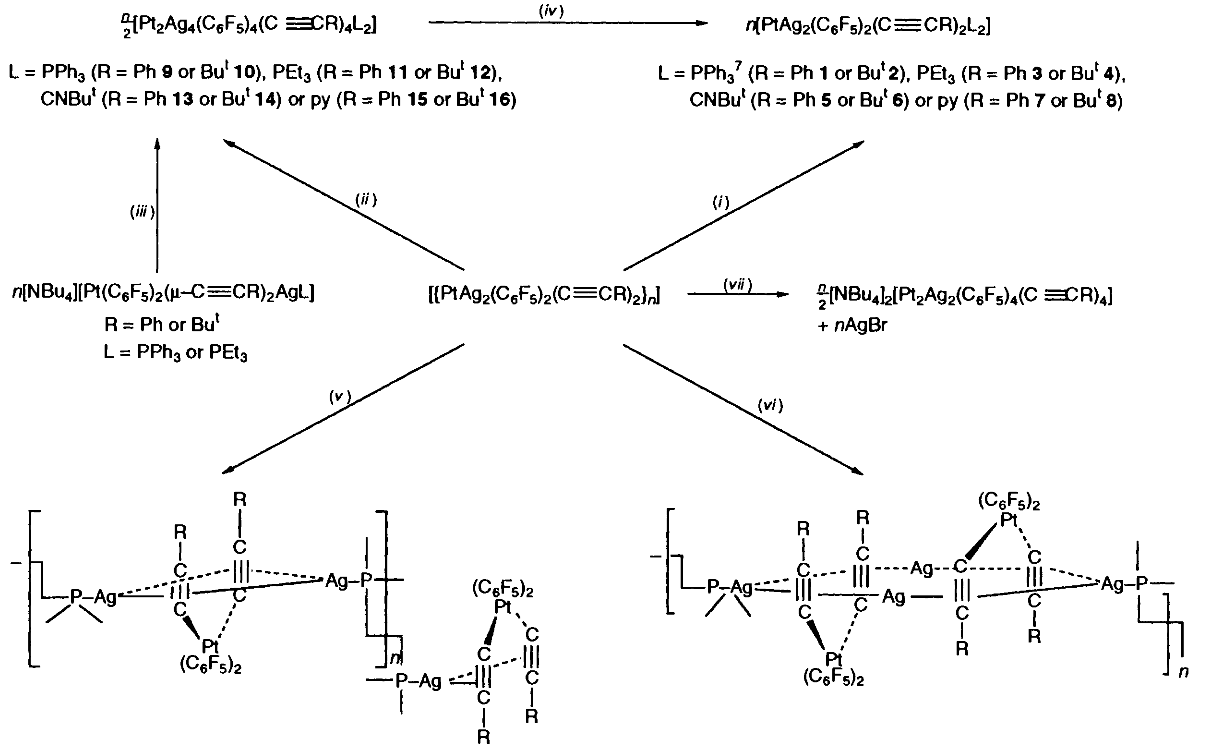
suggests that, with stronger ligands (PPh$_3$, PEt$_3$, CNBu^t or py), the polymeric derivatives are cleaved into the more soluble trinuclear species $[\mathrm{PtAg_2(C_6F_5)_2(C{\equiv}CR)_2L_2}]$. This fact has been confirmed by a single-crystal X-ray study of $[\mathrm{PtAg_2(C_6F_5)_2(C{\equiv}CPh)_2(PPh_3)_2}]$ **1** which has been previously communicated.[7]



Scheme 1 (*i*) Acetone; (*ii*) air dried

On the other hand, when complexes $[\{\mathrm{PtAg_2(C_6F_5)_2(C{\equiv}CR)_2}\}_n]$ are treated with only 1 equivalent of neutral ligands [Scheme 2(*ii*), see Experimental section] (Ag : L 2 : 1) a partial depolymerization takes place, yielding the hexanuclear tetraalkynyl complexes $[\mathrm{Pt_2Ag_4(C_6F_5)_4(C{\equiv}CR)_4L_2}]$ **9**–**16** as yellow (R = Ph **9**, **11**, **13** and **15**) or white (**10**, **12**, **14** and **16**) solids in good yields. Complexes **9**–**12** (L = PPh$_3$ or PEt$_3$) can be prepared equally well from the binuclear doubly acetylide bridged (σ-Pt, π-Ag) $[\mathrm{NBu_4}][\mathrm{Pt(C_6F_5)_2(\mu\text{-}C{\equiv}CR)_2AgL}]$[4] and AgClO$_4$ [1 : 1; Scheme 2(*iii*)] in acetone; under these conditions the sparingly soluble derivatives **9**–**11** precipitate immediately. As expected, the trinuclear complexes **1**–**4** can also be obtained stepwise from the hexanuclear derivatives **9**–**12**. Thus, the addition of an excess of PPh$_3$ or PEt$_3$ [ratio 2 : 1; Scheme 2(*iv*)] to a suspension of the dimeric derivatives **9**–**12** (solution for **11**) affords yellow (**9** and **11**) or colourless (**10** and **12**) solutions from which the corresponding monomeric trinuclear species $[\mathrm{PtAg_2(C_6F_5)_2(C{\equiv}CR)_2L_2}]$[7](L = PPh$_3$ **1** or **2**, PEt$_3$ **3** or **4**) can be isolated. All these facts, together with satisfactory molecular-weight determinations for **11** and **14**, suggest that complexes **9**–**16** are probably hexanuclear species formed by two anionic $[\mathrm{Pt(C_6F_5)_2(\mu\text{-}C{\equiv}CR)_2AgL}]^-$ units joined together through the two additional silver cations. Final proof of their hexanuclear nature is provided by the crystal structure of **9**, which is discussed later. Attempts to obtain anionic complexes related to **9**–**16**, but with the neutral ligand replaced by an anion (Br$^-$), were unsuccessful. Thus, when the polynuclear derivatives $[\{\mathrm{PtAg_2(C_6F_5)_2(C{\equiv}CR)_2}\}_n]$ are treated with 1 equivalent of NBu$_4$Br (Ag : Br$^-$ 2 : 1) in acetone [Scheme 2(*vii*)] a precipitate (AgBr) is formed and, after filtration, the tetranuclear derivatives $[\mathrm{NBu_4}]_2[\mathrm{Pt_2Ag_2(C_6F_5)_4(C{\equiv}CR)_4}]$[3] are isolated from the mother-liquors and identified by usual methods.

Finally, we have explored the reactivity of $[\{\mathrm{PtAg_2(C_6F_5)_2}$-



Scheme 2 (*i*) + L (molar ratio 1 : 2); (*ii*) + L (molar ratio 1 : 1); (*iii*) + AgClO$_4$ (ratio 1 : 1), acetone; (*iv*) as (*i*); (*v*) + dppe (molar ratio 1 : 1), acetone; (*vi*) + dppe (molar ratio 1 : 0.5), acetone; (*vii*) + NBu$_4$Br (molar ratio 1 : 1)

Table 1 Elemental analyses, yields, molecular weights and relevant IR absorptions for complexes **1**–**20**

	Analysis (%)[a]					IR (cm^{-1})		
Compound	C	H	N	$M^{a,b}$	Yield (%)	ν(C≡C)	ν(C≡N)	ν(X-sensitive C_6F_5)
1 $[\mathrm{PtAg_2(C_6F_5)_2(C{\equiv}CPh)_2(PPh_3)_2}]$	52.40 (52.20)	2.95 (2.75)	—	1567 (1472)	61	2051m, 2033 (sh)		799s, 790 (sh)
2 $[\mathrm{PtAg_2(C_6F_5)_2(C{\equiv}CBu^t)_2(PPh_3)_2}]$	50.35 (50.35)	3.65 (3.40)	—	1529 (1432)	87	2040m		793s, 784s
3 $[\mathrm{PtAg_2(C_6F_5)_2(C{\equiv}CPh)_2(PEt_3)_2}]$	40.75 (40.60)	3.70 (3.40)	—	1264 (1184)	70	2039s		800s, 779s
4 $[\mathrm{PtAg_2(C_6F_5)_2(C{\equiv}CBu^t)_2(PEt_3)_2}]$	37.85 (37.80)	4.60 (4.25)	—	1274 (1144)	75	2048m		793s, 784s
5 $[\mathrm{PtAg_2(C_6F_5)_2(C{\equiv}CPh)_2(CNBu^t)_2}]$	40.25 (41.00)	2.45 (2.55)	2.30 (2.50)	*c*	75	2038s	2212vs	799vs, 778s
6 $[\mathrm{PtAg_2(C_6F_5)_2(C{\equiv}CBu^t)_2(CNBu^t)_2}]$	37.75 (38.05)	3.05 (3.40)	2.55 (2.60)		68	2036m	2191vs	793vs, 785 (sh)
7 $[\mathrm{PtAg_2(C_6F_5)_2(C{\equiv}CPh)_2(py)_2}]$	41.35 (41.30)	2.05 (1.80)	2.55 (2.55)	1122 (1105)	71	2032m		797s, 790 (sh)
8 $[\mathrm{PtAg_2(C_6F_5)_2(C{\equiv}CBu^t)_2(py)_2}]$	37.89 (38.33)	2.45 (2.65)	2.51 (2.65)		84	2026w		795s, 786s
9 $[\mathrm{Pt_2Ag_4(C_6F_5)_4(C{\equiv}CPh)_4(PPh_3)_2}]$	45.85 (45.70)	2.30 (2.10)	—	*d*	87	2021m		799vs, 790 (sh)
10 $[\mathrm{Pt_2Ag_4(C_6F_5)_4(C{\equiv}CBu^t)_4(PPh_3)_2}]$	43.00 (43.15)	3.00 (2.85)	—	*d*	90	2022m		798vs, 789vs
11 $[\mathrm{Pt_2Ag_4(C_6F_5)_4(C{\equiv}CPh)_4(PEt_3)_2}]$	38.40 (38.35)	2.45 (2.35)	—	2014 (2131)	37	2026m		799vs, 792 (sh)
12 $[\mathrm{Pt_2Ag_4(C_6F_5)_4(C{\equiv}CBu^t)_4(PEt_3)_2}]$	34.60 (35.15)	3.45 (3.25)	—	*d*	75	2023m		796vs, 789 (sh)
13 $[\mathrm{Pt_2Ag_4(C_6F_5)_4(C{\equiv}CPh)_4(CNBu^t)_2}]$	38.65 (38.50)	1.40 (1.85)	1.55 (1.35)	*d*	83	2032w, 2017w	2214vs	799vs, 791 (sh)
14 $[\mathrm{Pt_2Ag_4(C_6F_5)_4(C{\equiv}CBu^t)_4(CNBu^t)_2}]$	34.85 (35.15)	2.75 (2.75)	1.45 (1.40)	1966 (1980)	73	2010w	2214vs	795vs, 790 (sh)
15 $[\mathrm{Pt_2Ag_4(C_6F_5)_4(C{\equiv}CPh)_4(py)_2}]$	38.90 (38.60)	1.10 (1.50)	1.20 (1.35)		64	2028m		795vs, 780 (sh)
16 $[\mathrm{Pt_2Ag_4(C_6F_5)_4(C{\equiv}CBu^t)_4(py)_2}]$	35.20 (35.30)	2.10 (2.30)	1.30 (1.40)		73	2006m		795vs, 781 (sh)
17 $[\{\mathrm{PtAg_2(C_6F_5)_2(C{\equiv}CPh)_2(dppe)}\}_n]$	48.55 (48.15)	2.75 (2.55)	—	*d*	86	2066m, 2034m		799vs (sh)
18 $[\{\mathrm{PtAg_2(C_6F_5)_2(C{\equiv}CBu^t)_2(dppe)}\}_n]$	46.15 (46.00)	2.95 (3.25)	—	*d*	75	2037w		793s, 785s
19 $[\{\mathrm{Pt_2Ag_4(C_6F_5)_4(C{\equiv}CPh)_4(dppe)}\}_n]$	42.85 (42.95)	1.90 (1.95)	—	*d*	88	2026w		801w, 798 (sh)
20 $[\{\mathrm{Pt_2Ag_4(C_6F_5)_4(C{\equiv}CBu^t)_4(dppe)}\}_n]$	40.40 (40.15)	2.45 (2.75)	—	*d*	80	2019w		796vs, 788 (sh)

[a] Calculated values in parentheses. [b] In $CHCl_3$ solution. [c] Decomposition in $CHCl_3$ precludes molecular weight determination. [d] Not soluble enough in $CHCl_3$.

$(C\equiv CR)_2\}_n]$ towards the didentate ligand dppe in similar molar ratios [*i.e.* 1:1 (Ag:L–L 2:1) and 2:1 (Ag:L–L 4:1)]. Treatment of $[\{PtAg_2(C_6F_5)_2(C\equiv CR)_2\}_n]$ with 1 or 0.5 equivalent of dppe affords yellow (R = Ph) or white (R = Bu^t) solids, which analyse as $[\{PtAg_2(C_6F_5)_2(C\equiv CR)_2(dppe)\}_n]$ (R = Ph **17** or Bu^t **18**) or $[\{Pt_2Ag_4(C_6F_5)_4(C\equiv CR)_4(dppe)\}_n]$ (R = Ph **19** or Bu^t **20**), respectively. The insolubility of these complexes has precluded molecular weight determinations or the use of some identification techniques (NMR spectroscopy). We suggest that the insolubility of **17** and **18** may be due to their polymeric structure $[\{cis\text{-}(C_6F_5)_2Pt(\mu_3\text{-}\eta^2\text{-}C\equiv CR)_2Ag_2\}_n(\mu\text{-dppe})_n]$, based on mononuclear anionic $cis\text{-}Pt(C_6F_5)_2(C\equiv CR)_2$ units linked by dicationic fragments Ag(μ-dppe)Ag through silver–acetylide π linkages as shown in Scheme 2. In the case of **19** and **20**, a similar polymeric structure $[\{Pt_2Ag_4(C_6F_5)_4(\mu_3\text{-}\eta^2\text{-}C\equiv CR)_4\}_n(\mu\text{-dppe})_n]$, based on tetranuclear dianionic $[Pt_2Ag_2(C_6F_5)_4(\mu_3\text{-}\eta^2\text{-}C\equiv CR)_4]^{2-}$ units joined by Ag(μ-dppe)Ag fragments (see Scheme 2), can be achieved. Probably, as is observed for the hexanuclear derivative **9**, the alkynyl groups in these complexes **17**–**20** are acting as $\mu_3\text{-}\eta^2$ (σ-Pt, π, π-Ag$_2$) bridging ligands.

Crystal Structure of $[Pt_2Ag_4(C_6F_5)_4(\mu_3\text{-}\eta^2\text{-}C\equiv CPh)_4(PPh_3)_2]\cdot 0.5CH_2Cl_2$ **9**$\cdot$0.5CH$_2$Cl$_2$.—Suitable crystals of complex **9**$\cdot$0.5CH$_2$Cl$_2$ were obtained by slow diffusion at −40 °C of hexane into a dichloromethane solution of the complex. The crystal structure reveals that this compound crystallizes with two crystallographically independent, but chemically very similar, hexanuclear $[Pt_2Ag_4(C_6F_5)_4(C\equiv CPh)_4(PPh_3)_2]$ molecules in the asymmetric unit. Discussion of the structure will therefore be limited to only one of the molecules. The complete molecular structure of **9** is shown in Fig. 1. Selected bond distances and angles are listed in Table 2.

The skeleton of complex **9**, which posesses an inversion centre, is similar to that previously found for the hexanuclear complex $[Pt_2Ag_4(C_6F_5)_4(C\equiv CBu^t)_4(Me_2CO)_4]$[6] (Scheme 1, **B**). Complex **9** consists of two identical units $cis\text{-}(C_6F_5)_2Pt(1)(\mu\text{-}C\equiv CPh)_2Ag(1)(PPh_3)$ joined together by two silver atoms [Ag(2) and Ag(2a)] through bridging C≡CPh groups. Therefore, there are two different types of silver atoms (terminal and bridging) in the molecule. Each unit consists of $cis\text{-}Pt(C_6F_5)_2(C\equiv CPh)_2$ and Ag(1)PPh$_3$ fragments bonded through the two alkynyl functions. The platinum atom Pt(1) is located in an approximately square-planar environment formed by four C atoms (the two C$_{ipso}$ of the two C$_6$F$_5$ *cis* and the two C$_\alpha$ of the two C$_\alpha$≡C$_\beta$Ph ligands), the Pt(1)–C distances (to C$_6$F$_5$ or C≡CPh groups) being similar to those found in other related complexes.[3,4,6] The silver atom Ag(1), located 1.340(1) Å down from the Pt(1) co-ordination plane, is in an approximately trigonal environment formed by the phosphorus atom, the midpoint of one of the acetylenic fragments [C(21)≡C(22)] and the C$_\alpha$ atom of the second alkynyl function C(13)–C(14). The Ag(1) ··· C(14) distance is extremely long [2.875(16) Å], which suggests that the interaction of Ag(1) with the C$_\beta$ atom of the acetylenic fragment C(13)–C(14) is negligible. The Ag(1)–P(1) bond length [2.395(4) Å] falls in the range of values found for other polynuclear complexes containing the Ag(PPh$_3$) unit[4,8] and the Pt(1) ··· Ag(1) distance [3.066(1) Å] is out of the range of values reported for Pt–Ag bond distances.[8a,b,9]

Both square-planar platinum environments are parallel and interconnected by the bridging silver atoms [Ag(2) and Ag(2a)] forming the hexanuclear molecule. The silver bridging atoms [Ag(2) and Ag(2a)] are unsymmetrically bonded to two alkynyl functions, one associated with each Pt atom, the acetylenic bonds being perpendicular to one another. Thus, Ag(2) is unsymmetrically bonded to both atoms C$_\alpha$ and C$_\beta$ of the C(13)–C(14) alkynyl ligand at Pt(1), but only to C$_\alpha$ of the C(21a)–C(22a) group at Pt(1a). The Ag(2) ··· C(22a) distance of 2.812(16) Å is well beyond the normal bonding range, suggesting again that the interaction with this C$_\beta$ atom is negligible. The distances of this Ag(2) atom to both platinum atoms are different. The shortest Ag(2) ··· Pt(1a) bond length [2.888(2) Å] associated with the small Ag(2)–C(21a)–Pt(1a) angle of 83.6(4)° suggests a weak Pt–Ag interaction.[9] However, the Ag(2)–C(13)–Pt(1) angle is 91.5(5)° and the resulting Ag(2) ··· Pt(1) distance is 3.105(2) Å, excluding any bonding interaction between these metals.

It is interesting that one of the two C$_6$F$_5$ groups associated with each platinum atom [C(7)$_{ipso}$ at Pt(1), see Fig. 1] is so positioned that one *o*-fluorine atom makes a short contact with each one of the silver bridging centres. The *o*-F(8) ··· Ag(2) distance [2.790(12) Å] falls in the range of distances found for similar *o*-F ··· Ag contacts in other (pentafluorophenyl)-platinum silver complexes,[9] implying a donation of electron density to the silver atom. This contact and the Ag(2) ··· Pt(1a) interaction are probably accentuating the unsymmetric co-ordination of the alkynyl groups. Considering the *o*-F ··· Ag and the Pt(1a) ··· Ag(2) interactions and also

Table 2 Selected interatomic distances (Å) and angles (°) for $[Pt_2Ag_4(C_6F_5)_4(C\equiv CPh)_4(PPh_3)_2]\cdot 0.5CH_2Cl_2$

Pt(1) ··· Ag(1)	3.066(1)	Pt(1) ··· Ag(2)	3.105(2)
Pt(1)–C(1)	2.053(12)	Pt(1)–C(7)	2.048(13)
Pt(1)–C(13)	2.042(14)	Pt(1)–C(21)	2.05(2)
Ag(1)–P(1)	2.395(4)	Ag(1)–C(13)	2.454(13)
Ag(2)–C(14)	2.568(13)	Ag(1)–C(21)	2.354(12)
Ag(1)–C(22)	2.68(2)	Ag(2)–C(13)	2.285(11)
Ag(2) ··· Pt(1a)	2.888(2)	Ag(2)–Ag(2a)	2.959(2)
Ag(2)–C(21a)	2.274(11)	C(13)–C(14)	1.24(2)
C(21)–C(22)	1.18(2)	*o*-F(8)–Ag(2)	2.790(12)
Ag(1)–Pt(1)–Ag(2)	84.08(4)	C(1)–Pt(1)–C(7)	86.6(5)
C(7)–Pt(1)–C(13)	91.5(5)	C(1)–Pt(1)–C(21)	88.4(5)
C(13)–Pt(1)–C(21)	93.6(5)	P(1)–Ag(1)–C(21)	142.1(4)
Pt(1)–C(13)–C(14)	177.7(12)	P(1)–Ag(1)–C(22)	115.9(3)
Pt(1)–C(13)–Ag(1)	85.5(5)	P(1)–Ag(1)–C(13)	138.8(3)
Pt(1)–C(21)–C(22)	170.4(12)	Ag(2)–C(13)–C(14)	88.3(9)
Pt(1)–C(21)–Ag(2a)	83.6(5)	Ag(2a)–C(21)–C(22)	104.3(10)
Pt(1)–Ag(1)–P(1)	172.28(10)	Ag(1)–C(21)–C(22)	92.2(10)
Pt(1)–C(13)–Ag(2)	91.5(5)	Ag(1)–C(13)–C(14)	96.6(10)
Pt(1)–C(21)–Ag(1)	87.9(5)	C(13)–C(14)–C(15)	175(2)
C(21)–C(22)–C(23)	172(2)		

Symmetry transformation used to generate equivalent atoms: $-x$, $-y$, $-z-1$.

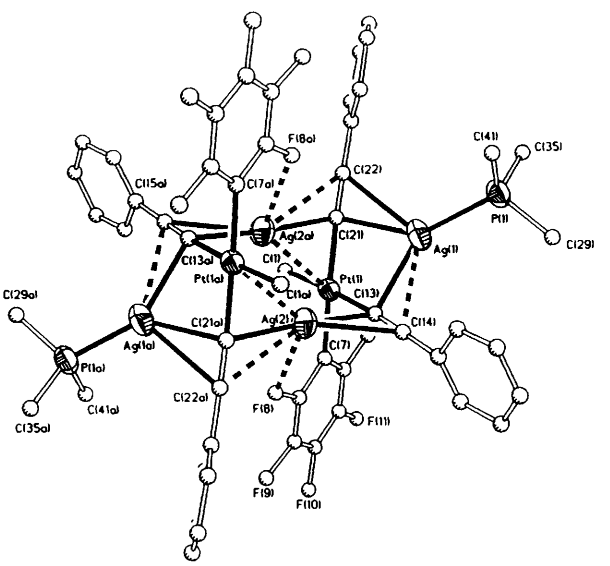


Fig. 1 Molecular structure of $[Pt_2Ag_4(C_6F_5)_4(\mu_3\text{-}\eta^2\text{-}C{\equiv}CPh)_4(PPh_3)_2]$ **9** showing the atom numbering scheme. Phenyl rings (except C_{ipso} atoms) of the PPh_3 ligands and the C(2)–C(6) and C(2a)–C(6a) C_6F_5 rings have been omitted for clarity. Symmetry transformation to generate equivalent atoms 'a': $-x, -y, -z-1$

the bonds to the two alkynyl functions, each silver bridging atom seems to be located in a distorted-tetrahedral environment (Fig. 1).

The co-ordination mode of the alkynyl ligands can be described as a very unsymmetric μ_3-η^2. In fact, the C(21)≡C(22)–Ph fragment is clearly σ bonded to Pt(1) [Pt(1)–C(21) 2.05(2) Å] and σ bonded as well to Ag(2a) [Ag(2a)–C(21) 2.274(11) Å, Ag(2a) ··· C(22) 2.812(16) Å], while the interaction with Ag(1) [Ag(1)–C(21) 2.354(12) Å, Ag(1)–C(22) 2.68(2) Å] seems to display a higher side-on character, the Ag–C(21) interaction being predominant. The other alkynyl ligand C(13)≡C(14)–Ph is bonded to the metal centres in a similar way, and displays two σ-C–M bonds [Pt(1)–C(13) 2.042(14) Å, Ag(1)–C(13) 2.454(13) Å, Ag(1) ··· C(14) 2.875(16) Å] while the interactions with Ag(2) show more π character [Ag(2)–C(13) 2.285(11) Å, Ag(2)–C(14) 2.568(13) Å]. All these structural facts suggest that the silver centres prefer bonding to the C_α atoms, which have higher electron density, and that the co-ordination mode of the alkynyl ligands is approximately halfway between the normal μ_3-η^2 manner and the μ_3-η^1 bridging mode. As a consequence, the alkynyl bending of the C≡CPh fragments is negligible (see Table 2) and significantly smaller than the bending found in symmetrical μ_3-η^2 alkynyl bridges.[10]

The molecular structure of $[PtAg_2(C_6F_5)_2(C{\equiv}CPh)_2(PPh_3)_2]$ **1** has been reported previously.[7] The most remarkable structural features are: (*a*) the significant asymmetry of the whole molecule; (*b*) one of the $Ag(PPh_3)$ units is bonded to the two alkynyl functions, while the second unit seems to be bonded to the platinum atom and only to one alkynyl group and (*c*) one of the alkynyl fragments is acting as a μ-η^2(σ–π) ligand and the other bridges the three metal atoms in a predominantly σ manner (μ_3-η^1).[7]

Infrared and NMR Spectra.—Selected IR absorptions are collected in Table 1. All complexes show one (or two in the cases of **13** and **17**) ν(C≡C) vibration in the expected region (2006–2066 cm^{-1}) for bridging alkynyl ligands[2–7] and two IR absorptions corresponding to the X-sensitive mode of the pentafluorophenyl ligands in the 801–778 cm^{-1} region, indicative of a *cis* disposition of C_6F_5 groups.[3,4,6,11] The adducts with *tert*-butyl isocyanide (**5**, **6** and **13**, **14**) exhibit also a strong, slightly broad band at 2191–2214 cm^{-1} assignable to the ν(C≡N) stretching vibration of terminal $CNBu^t$ ligands.

The NMR data for complexes **3**–**16** are given in Table 3. The room-temperature ^1H NMR spectra exhibit resonances due to the ligands (L) and the signals of the alkynyl groups (R = Ph or Bu^t) in the expected integration ratio. The complexes with R = Bu^t show only one single resonance for the methyl groups of the $C{\equiv}CBu^t$ ligands, thus indicating that, in solution, all $C{\equiv}CBu^t$ groups are equivalent.

The $^{31}P\text{-}\{^1H\}$ NMR spectra of the hexanuclear derivatives **9**–**12** at room temperature show the characteristic pattern of a pair of doublets, due to coupling of ^{31}P to both ^{107}Ag and ^{109}Ag isotopes, indicating that both phosphine ligands are equivalent and that the Ag–P bonds are retained in solution.[12]

The ^{19}F NMR spectra of the hexanuclear species are very similar and temperature dependent. At high temperature (50 °C), or even at room temperature in the case of complex **15**, they show only a set of three signals (ratio 2:1:2) corresponding to *o*-, *p*- and *m*-F, showing that all C_6F_5 groups are equivalent. The *o*-fluorine atoms occur as a sharp resonance (doublet or singlet) to low field along with the expected platinum satellites, indicating an effective equivalence of these atoms. Formal equivalence of the *m*-fluorine atoms, which appear as a multiplet at high field, is also observed. The *o*-fluorine signals broaden as the temperature is lowered and at −50 °C clearly split into two sharper resonances, each with the expected ^{195}Pt satellites (for **15** only two broad *o*-F resonances are observed). The *m*-fluorine signals also broaden when the system is cooled and for complexes **11**, **13**, **14** and **16** are also split into two different resonances at −50 °C. The presence of two different *o*- (and *m*-) fluorine environments at low temperature is consistent with stereochemically rigid molecules for which the co-ordination planes of the platinum centres are not symmetry planes. The observed pattern at high temperature is typical of AA'MXX' systems for which the co-ordination planes of the platinum centres are formal (time-averaged) symmetry planes.

The unsymmetric co-ordination of the two $Ag(PEt_3)$ fragments in the trinuclear derivatives **3** and **4** is not observed in solution. Thus, the room-temperature ^{31}P NMR spectrum of complex **4** exhibits a pair of doublets centred at δ 7.3, which are best resolved at low temperature [−50 °C, δ(P) 6.5; $^1J(^{109}Ag\text{–}P)$ = 699, $J(^{107}Ag\text{–}P)$ = 605] indicating that, in solution, the PEt_3 ligands are equivalent. For the analogous derivative **3** (R = Ph, L = PEt_3), the separate splitting due to the two isotopes of silver is not resolved at room temperature; the ^{31}P spectrum exhibits a broad doublet centred at δ 9.9 with a spacing of 667 Hz. However, at low temperature (−50 °C) the pair of doublets [δ(P) 9.1; $^1J(^{109}Ag\text{–}P)$ = 715 and $^1J(^{107}Ag\text{–}P)$ = 621 Hz] is clearly resolved. The ^{19}F NMR spectra of both complexes **3** and **4** (Table 3) show three sharp signals (ratio 2:1:2) corresponding to a single set of $F_{o,o'}$, F_p and $F_{m,m'}$, indicating that in solution the C_6F_5 groups are equivalent. The ^{19}F NMR spectrum of complex **3** at −50 °C shows the same sharp pattern as that at room temperature. These spectral patterns suggest that, even at low temperature, the platinum co-ordination plane and also the $PtAg_2$ plane are formal planes of symmetry in both complexes.

The ^1H NMR spectra of the isocyanide (**5**, **6**) and pyridine adducts (**7**, **8**) are not temperature dependent. At room temperature these adducts display only one signal pattern for both the C≡CR groups and the $CNBu^t$ or py ligands (see Table 3). By contrast, their ^{19}F NMR spectra are temperature dependent. Thus, at high temperature (50 °C) the spectra display a group of three sharp signals (for **6** and **8** the *o*-F resonances are broad) in a 2:1:2 ratio corresponding to a single set of *o*-, *p*- and *m*-fluorine atoms. When the solutions are cooled to room temperature the *p*-fluorine resonances remain sharp but the *o*-fluorine signals broaden, in the case of **5** and **7**, or decoalesce into two broad resonances for **6** and **8**. On further cooling to −50 °C the broad signal for **7** was resolved into two

Table 3 Fluorine-19, ^{31}P and ^{1}H NMR data^a for complexes **1**–**16**

		^{19}F			^{31}P		^{1}H	
Compd.	T/°C	$\delta(\mathrm{F}_o)^b$	$\delta(\mathrm{F}_p)$	$\delta(\mathrm{F}_m)$	δ(P)	$^1J(^{109,107}\mathrm{Ag–P})$	R	L
1	25	−117.9 (d, 399)	−165.5 (t)	−166.8 (m)	14.1	600		
	−60				14.28	721, 625		
2	25	−117.9 (d, 408)	−166.7 (t)	−167.8 (m)	12.5		0.86 (s) (Bu^t)	7.44, 7.6 (m, Ph)
	−60				12.95	701, 610		
3	20	−117.5 (d, 402)	−165.2 (t)	−166.3 (m)	9.9	667	7.21 (m), 7.31 (m) (Ph)	1.65 (m, CH$_2$), 1.12 [d, t, ^3J(P–H) = 18.5, CH$_3$]
	−50				9.1	715, 621		
4	20	−118.4 (d, 390)	−167.0 (t)	−167.9 (m)	7.3	694, 610	1.20 (s, Bu^t)	1.78 (m, CH$_2$), 1.26 [d, t, ^3J(P–H) = 18.4, CH$_3$]
	−50				6.5	699, 605		
5^{c,d}	50	−114.4 (d, 383)	−164.2 (t)	−165.5 (m)				
	20	−114.3 (br)^e	−164.1 (t)	−165.4 (m)			7.21 (m), 7.36 (m) (Ph)	1.40 (s, CNBu^t)
6	50	−113.8 (s, br)^e	−164.9 (t)	−165.3 (m)				
	20	−112.5, −115.3^f	−165.4 (t)	−166.6 (m)			1.13 (s, C≡CBu^t)	1.53 (s, CNBu^t)
	−50	−111.4 (s, 444), −116.1 (s, br)^e	−164.9 (t)	−165.9 (m)			1.1 (s, C≡CBu^t)	1.51 (s, CNBu^t)
7^d	50	−115.6 (d, 397)	−163.0 (t)	−164.6 (m)				
	20	−115.5 (s, br, 361)	−163.1 (t)	−164.7 (m)			7.26–7.03 (m, overlapping, Ph, py)	8.38 [d, H$_o$, py, J(H–H) = 4.4], 7.7 (t, H$_p$, py)
	−50	−113.0 (s, br, 451), −117.8 (s, br, 333)	−162.8 (t)	−164.1 (m), −164.4 (m)				
8	50	−115.3 (s, br)^e	−163.7 (t)	−165.2 (s)				
	20	≈ −114, −116^f	−163.6 (t)	−165.2 (s, br)			0.99 (s, Bu^t)	9.04 [d, H$_o$, py, J(H–H) = 4.2], 8.73 (t, H$_p$, py), 7.45 (m, H$_m$, py)
	−50	−112.7 (d, 456), −118.1 (dd, 364)	−163.1 (t)	−164.1 (m), −165.1 (m)				
9	50	−115.7 (d, 404)	−163.4 (t)	−165.0 (m)				
	20	−115.6 (s, br)^e	−163.1 (t)	−164.8 (m)	14.78	727, 630		
	−50	−112.6 (d, 459), −117.9 (d, 363)	−162.5 (t)	−164.1 (s, br)				
10	50	−115.1 (s, 415)	−164.0 (t)	−165.6 (m)				
	20	−114.9 (s, vbr)^e	−163.9 (t)	−165.4 (m)	14.9	728, 630	0.90 (s, Bu^t)	7.66 (m, Ph), 7.52 (m, Ph)
	−50	−113.3 (d, 448), −117.1 (d, 364)	−163.3 (t)	−165.0 (m)				
11	50	−115.6 (d, 364)	−163.2 (t)	−165.0 (m)				
	25	−115.9 (br)^e	−163.0 (t)	−164.8 (m)	11.3	732, 635	7.45 (m, Ph), 7.26 (m, Ph)	1.42 (m, CH$_2$), 0.92 [d, t, ^3J(P–H) = 19, CH$_3$]
	−50	−112.6 (d, 336), −118.1 (d, 343)	−162.3 (t)	−163.8 (s), −164.4 (s)				
12	50	−115.2 (s, 365)	−164.2 (t)	−165.8 (m)				
	25	−115.4^g	−164.0 (t)	−165.6 (m)	5.64	736, 638	1.18 (s, Bu^t)	1.86 (m, CH$_2$), 1.30 [d, t, ^3J(P–H) = 18.3, CH$_3$]
	−50	−112.9 (s, 423), −117.8 (s, 402)	−163.4 (t)	−165.1 (m)				
13	50	−115.2 (d, 411)	−163.2 (t)	−164.8 (m)				
	20	−115.2^g	−163.0 (t)	−164.6 (m)			7.24 (m, Ph), 7.36 (m, Ph)	1.37 (s, CNBu^t)
	−50	−112.6 (d, ≈440), −118.0 (d, 330)	−161.9 (t)	−163.1 (m), −163.3 (m)				
14	50	−114.4 (s, br)^e	−164.2 (t)	−165.7 (m)				
	20	−112.9, −116.3^f	−163.7 (t)	−165.3 (m)			1.17 (s, C≡CBu^t)	1.51 (s, CNBu^t)
	−50	−112.0 (d, 441), −117.7 (d, 357)	−162.9 (s)	−164.0 (s), −165.2 (s)				
15^h	20	−114.0 (d, 410)	−164.5 (t)	−165.4 (m)			7.30–7.13 (m, Ph)	8.64 [d, H$_o$, py, J(H–H) = 4.5], 7.98 (t, H$_p$, py), 7.48 (m, H$_m$, py)
	−50	≈ −108, −112^f	−159.8 (t)	−160.6 (s)				
16	50	−115.4 (s, br)^e	−163.5 (t)	−165.1 (s)				
	20	−115.5^g	−163.2 (t)	−164.8 (s, br)			1.02 (s, Bu^t)	8.76 [d, H$_o$, py, J(H–H) = 4.7], 7.95 (t, H$_p$, py), 7.57 (m, H$_m$, py)
	−50	−113.1 (d, 450), −118.4 (d, 348)	−162.5 (t)	−163.5 (m), −164.6 (m)				

[a] In CDCl$_3$, chemical shifts are reported relative to CFCl$_3$, H$_3$PO$_4$ (85%) and SiMe$_4$ (as external references) respectively; coupling constants J in Hz. [b] $^3J(^{195}\mathrm{Pt–F}_o)$/Hz in parentheses. [c] At −50 °C, the ^{19}F NMR spectrum of complex **5** shows three signals in the *o*-F region at δ −112.1, −115.2 and −118.5 with relative intensities 3:2:1 and in the *p*- and *m*-F region a complex multiplet centred at δ −164.1. [d] At −50 °C, the ^{1}H NMR spectrum exhibits the same pattern as that observed at 20 °C. [e] Satellites are observed but the $^3J(^{195}\mathrm{Pt–F}_o)$ is not well resolved. [f] Two broad humps. [g] Broad hump, platinum satellites are not observed. [h] In CD$_3$COCD$_3$.

separate *o*-fluorine resonances and for **6** and **8** the two broad resonances became sharper. For complex **7** even the *m*-fluorine multiplet was resolved into two separate multiplets. For these derivatives probably a restricted rotation of the C_6F_5 ring about the C–Pt bond causes the observed inequivalence in the fluorine atoms at low temperature.

Experimental

Elemental analyses were carried out with a Perkin-Elmer 240-B microanalyser. Infrared spectra were recorded on a Perkin-Elmer 883 spectrophotometer and NMR spectra with Varian XL-200 and Bruker ARX 300 spectrometers. The syntheses of $[\{PtAg_2(C_6F_5)_2(C{\equiv}CR)_2\}_n]$ (R = Ph or Bu^t)[6] and $[NBu_4][Pt(C_6F_5)_2(\mu\text{-}C{\equiv}CR)_2AgL]$ (R = Ph or Bu^t, L = PPh_3 or PEt_3)[4] have been described previously. All reactions were carried out at room temperature with exclusion of light. **CAUTION**: Some of the following preparations use $AgClO_4$, which is potentially explosive.

Syntheses.—$[PtAg_2(C_6F_5)_2(C{\equiv}CR)_2L_2]$ **1**–**7**. *Method* 1. The stoichiometric amount of L (Pt:L 1:2; Ag:L 1:1) was added to a suspension of $[\{PtAg_2(C_6F_5)_2(C{\equiv}CR)_2\}_n]$ (*ca*. 120 mg) in acetone ($\approx$5 cm^3), whereupon a solution (yellow for R = Ph **3**, **5**, **7** or colourless for R = Bu^t **4**, **6**) was formed. On evaporation to dryness, addition of EtOH ($\approx$5 cm^3) and stirring, a solid (yellow **3**, **5** and **7** or white **4** and **6**) was formed, which was washed with EtOH and air dried.

Method 2. The complexes $[PtAg_2(C_6F_5)_2(C{\equiv}CR)_2L_2]$ [L = PPh_3[7] (R = Ph **1** or Bu^t **2**) or PEt_3 (R = Ph **3** or Bu^t **4**)] can also be prepared by treating the corresponding hexanuclear derivatives $[Pt_2Ag_4(C_6F_5)_4(C{\equiv}CR)_4L_2]$ **9**–**12** with 2 additional equivalents of triphenylphosphine or triethylphosphine (Pt:L 1:1). A typical preparation (complex **3**) was as follows: PEt_3 (13.4 μl, 0.091 mmol) was added to a yellow solution of $[Pt_2Ag_4(C_6F_5)_4(C{\equiv}CPh)_4(PEt_3)_2]$ **11** (0.097 g, 0.045 mmol) in acetone (10 cm^3). The mixture was stirred for 20 min and then evaporated to dryness. Upon addition of ethanol (5 cm^3) to the residue, complex **3** was obtained as a yellow solid (70% yield). Complexes **1**, **2** and **4** were obtained similarly by using the appropriate starting material and phosphine. In all cases the yield was $\approx$80%.

$[PtAg_2(C_6F_5)_2(C{\equiv}CBu^t)_2(py)_2]$ **8**. A yellow suspension of $[\{PtAg_2(C_6F_5)_2(C{\equiv}CBu^t)_2\}_n]$ (0.100 g, 0.110 mmol) in CH_2Cl_2 (2 cm^3) was treated with pyridine (0.778 cm^3 of a solution 0.494 mol dm^{-3} in CH_2Cl_2, 0.386 mmol) giving immediately a colourless solution. Hexane (20 cm^3) was added and the mixture kept in a refrigerator overnight. The resulting white microcrystalline solid **8** was filtered off, washed with hexane and air dried.

$[Pt_2Ag_4(C_6F_5)_4(C{\equiv}CR)_4L_2]$ (L = PPh_3, R = Ph **9** *or* Bu^t **10**; L = PEt_3, R = Ph **11** *or* Bu^t **12**). *Method* 1. To a suspension of $[\{PtAg_2(C_6F_5)_2(C{\equiv}CR)_2\}_n]$ (*ca*. 120 mg, yellow R = Ph or colourless R = Bu^t) in acetone (*ca*. 10 cm^3) was added the stoichiometric amount of phosphine (Pt:L 1:1) and the mixture was stirred for 1 h. For R = Ph, L = PEt_3, the resulting yellow solution was evaporated to small volume (*ca*. 2 cm^3) and EtOH was added to give complex **11** as a yellow solid, which was filtered off and air dried. For complexes **9** (yellow), **10** (white) and **12** (white) the solids formed were filtered off and air dried.

Method 2. Complexes **9**–**12** can also be prepared by treating the previously described binuclear derivatives $[NBu_4][Pt(C_6F_5)_2(\mu\text{-}C{\equiv}CR)_2AgL]$[4] with $AgClO_4$. A typical preparation (complex **9**) was as follows: $AgClO_4$ (20 mg, 0.095 mmol) was added to a colourless solution of $[NBu_4][Pt(C_6F_5)_2(\mu\text{-}C{\equiv}CPh)_2Ag(PPh_3)]$ (0.128 g, 0.095 mmol) in acetone. The solution immediately turned yellow and, after stirring for a few (*ca*. 5) minutes, a yellow solid precipitated. The mixture was stirred for 1 h and then the yellow solid formed (**9**) was filtered off (yield 83%). Complexes **10** and **12** were obtained similarly by using the appropriate starting material. For complex **11** the resulting yellow solution was worked up in a similar way to the above general method. Yields: **10** (93), **11** (83) and **12** (90%).

$[Pt_2Ag_4(C_6F_5)_4(C{\equiv}CR)_4(CNBu^t)_2]$ (R = Ph **13** *or* Bu^t **14**). A yellow suspension of $[\{PtAg_2(C_6F_5)_2(C{\equiv}CPh)_2\}_n]$ (0.100 g, 0.106 mmol) in acetone (5 cm^3) was treated with CNBu^t (12 μl, 0.106 mmol) and the mixture stirred for 15 min. The resulting yellow solution was evaporated to dryness and the residue treated with EtOH (10 cm^3) to give complex **13** as a yellow solid which was filtered off, washed with EtOH and air dried.

The stoichiometric amount of CNBu^t (13 μl, 0.110 mmol) was added to a stirred white suspension of $[\{PtAg_2(C_6F_5)_2(C{\equiv}CBu^t)_2\}_n]$ (0.100 g, 0.110 mmol) in acetone (5 cm^3) giving immediately a colourless solution. The mixture was stirred for 15 min, concentrated until the precipitation of complex **14** as a white solid and then hexane was added to complete the precipitation. The product was filtered off, washed repeatedly with hexane and air dried.

$[Pt_2Ag_4(C_6F_5)_4(C{\equiv}CR)_4(py)_2]$ (R = Ph **15** *or* Bu^t **16**). The stoichiometric amount of pyridine (0.21 cm^3, 0.496 mol dm^{-3}, 0.106 mmol) was added to a yellow suspension of $[\{PtAg_2(C_6F_5)_2(C{\equiv}CPh)_2\}_n]$ (0.100 g, 0.106 mmol) in acetone (3 cm^3) and the mixture stirred for 15 min. The resulting turbid yellow solution was then filtered. Slow addition of hexane (5 cm^3) caused the precipitation of an orange gelatinous solid. After being cooled in a freezer overnight, the resulting orange solid was filtered off, washed with hexane and air dried.

To a suspension of $[\{PtAg_2(C_6F_5)_2(C{\equiv}CBu^t)_2\}_n]$ (0.10 g, 0.110 mmol) in CH_2Cl_2 (3 cm^3) was added pyridine (0.22 cm^3, 0.110 mmol, 0.496 mol dm^{-3} solution in CH_2Cl_2). After being stirred for 15 min, the resulting colourless solution was filtered and mixed with hexane (20 cm^3). The mixture was kept in a freezer (2 d) to render a white microcrystalline solid (**16**) which was filtered off, washed with hexane and air dried.

$[\{PtAg_2(C_6F_5)_2(C{\equiv}CR)_2(dppe)\}_n]$ (R = Ph **17** *or* Bu^t **18**). 1,2-Bis(diphenylphosphino)ethane (26 mg, 0.066 mmol for R = Ph or 44 mg, 0.110 mmol for R = Bu^t) was added to a suspension of $[PtAg_2(C_6F_5)_2(C{\equiv}CR)_2]$ (R = Ph, 0.063 g, 0.066 mmol; R = Bu^t, 0.100 g, 0.110 mmol) in acetone (20 cm^3). After being stirred for 1 h, the solution was filtered and concentrated to about 5 cm^3. For R = Ph, the addition of ethanol ($\approx$2 cm^3) gave a yellow precipitate (**17**) which was filtered off and washed with EtOH. For R = Bu^t, the resulting white precipitate (**18**) was filtered off, washed with acetone and air dried.

$[Pt_2Ag_4(C_6F_5)_4(C{\equiv}CR)_4(dppe)]$ (R = Ph **19** *or* Bu^t **20**). The diphosphine dppe (25 mg, 0.062 mmol for R = Ph; 22 mg, 0.055 mmol for R = Bu^t) was added to a suspension of $[\{PtAg_2(C_6F_5)_2(C{\equiv}CR)_2\}_n]$ (0.118 g, 0.124 mmol for R = Ph; 0.100 g, 0.110 mmol for R = Bu^t) in acetone (20 cm^3). The mixture was stirred for 24 h and then the yellow (R = Ph **19**) or white (R = Bu^t **20**) solid formed was filtered off, washed with acetone and air dried.

Reactions with NBu_4Br.—A suspension of $[\{PtAg_2(C_6F_5)_2(C{\equiv}CPh)_2\}_n]$ (0.089 g, 0.094 mmol) or $[\{PtAg_2(C_6F_5)_2(C{\equiv}CBu^t)_2\}_n]$ (0.090 g, 0.100 mmol) in acetone (20 cm^3) was treated with NBu_4Br [31 mg, 0.094 mmol, R = Ph; or 32 mg, 0.100 mmol, R = Bu^t; molar ratio Pt:Br 1:1] giving immediately a slightly turbid solution. The mixture was stirred for 6 h and then filtered. Evaporation of the filtrate to a small volume (*ca*. 1 cm^3) and addition of diethyl ether led to the precipitation of microcrystalline solids (yellow for R = Ph, white for R = Bu^t) which were filtered off and identified as the tetranuclear complexes $[NBu_4]_2[Pt_2Ag_2(C_6F_5)_4(C{\equiv}CR)_4]$[3] by comparison of their spectroscopic data with those of authentic samples. Yields: 80% for R = Ph and 72% for R = Bu^t.

Crystal Structure Determination of $[Pt_2Ag_4(C_6F_5)_4(C{\equiv}CPh)_4(PPh_3)_2]{\cdot}0.5CH_2Cl_2$.—*Crystal data*. $C_{92.5}H_{51}Ag_4$-

Table 4 Atomic coordinates (× 10^4) for $[Pt_2Ag_4(C_6F_5)_4(C{\equiv}CPh)_4(PPh_3)_2]\cdot0.5CH_2Cl_2$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pt(1)	−547(1)	−780(1)	−3730(1)	Pt(2)	−4606(1)	−3670(1)	−982(1)
Ag(1)	901(1)	31(1)	−3229(1)	Ag(3)	−6419(1)	−2959(1)	−480(1)
Ag(2)	696(1)	−660(1)	−5053(1)	Ag(4)	−4508(1)	−4704(1)	490(1)
P(1)	2005(2)	531(2)	−2685(2)	P(2)	−7757(2)	−2278(2)	−124(2)
F(2)	−1819(5)	−216(6)	−2532(4)	F(48)	−2752(5)	−4725(5)	−726(5)
F(3)	−3577(6)	41(9)	−2414(6)	F(49)	−1131(5)	−4340(5)	−575(5)
F(4)	−4608(6)	−194(10)	−3397(6)	F(50)	−845(5)	−2738(6)	−618(5)
F(5)	−3875(6)	−667(7)	−4522(5)	F(51)	−2224(6)	−1565(6)	−836(6)
F(6)	−2128(5)	−896(6)	−4669(4)	F(52)	−3838(5)	−1929(5)	−998(5)
F(8)	−339(9)	−1999(6)	−4753(5)	F(54)	−4153(7)	−5299(5)	−1555(5)
F(9)	−711(9)	−3552(6)	−4558(6)	F(55)	−3479(8)	−5491(7)	−2771(6)
F(10)	−1297(7)	−4455(5)	−3276(5)	F(56)	−3126(7)	−4118(8)	−3872(5)
F(11)	−1567(6)	−3751(5)	−2213(4)	F(57)	−3377(7)	−2588(7)	−3671(5)
F(12)	−1209(6)	−2176(5)	−2392(4)	F(58)	−4019(6)	−2390(5)	−2452(5)
C(1)	−1890(8)	−577(8)	−3625(6)	C(47)	−3363(7)	−3335(8)	−868(6)
C(2)	−2286(8)	−327(10)	−3045(7)	C(48)	−2661(8)	−3916(8)	−761(7)
C(3)	−3212(10)	−223(11)	−2971(8)	C(49)	−1830(8)	−3744(9)	−680(8)
C(4)	−3743(10)	−327(12)	−3457(9)	C(50)	−1679(9)	−2933(12)	−694(7)
C(5)	−3365(9)	−564(11)	−4012(8)	C(51)	−2378(10)	−2333(9)	−813(8)
C(6)	−2459(9)	−686(10)	−4092(7)	C(52)	−3191(8)	−2557(8)	−896(7)
C(7)	−742(8)	−2003(8)	−3582(6)	C(53)	−4144(7)	−3837(9)	−1944(6)
C(8)	−626(11)	−2412(9)	−4105(7)	C(54)	−3978(9)	−4596(10)	−2068(8)
C(9)	−813(12)	−3211(9)	−4014(9)	C(55)	−3642(11)	−4710(10)	−2716(9)
C(10)	−1116(10)	−3653(9)	−3370(9)	C(56)	−3463(11)	−4028(13)	−3235(8)
C(11)	−1247(9)	−3312(8)	−2830(7)	C(57)	−3575(9)	−3240(11)	−3150(7)
C(12)	−1069(8)	−2512(9)	−2930(7)	C(58)	−3917(8)	−3159(9)	−2516(7)
C(13)	783(9)	−1019(7)	−3852(6)	C(59)	−4964(7)	−3369(7)	−60(6)
C(14)	1587(9)	−1193(9)	−3926(7)	C(60)	−5084(8)	−3058(8)	407(7)
C(15)	2487(9)	−1454(10)	−3952(8)	C(61)	−5084(8)	−2579(9)	925(7)
C(16)	3104(10)	−875(12)	−4176(9)	C(62)	−5599(10)	−2736(11)	1537(9)
C(17)	3987(14)	−1054(19)	−4203(13)	C(63)	−5590(13)	−2312(13)	2013(9)
C(18)	4276(14)	−1829(20)	−3951(15)	C(64)	−5046(14)	−1695(14)	1871(11)
C(19)	3727(15)	−2460(16)	−3721(13)	C(65)	−4530(14)	−1517(12)	1277(10)
C(20)	2788(12)	−2219(13)	−3721(11)	C(66)	−4516(10)	−1952(10)	809(9)
C(21)	−461(8)	441(9)	−3779(6)	C(67)	−5838(7)	−3958(7)	−1112(6)
C(22)	−479(10)	1118(9)	−3710(7)	C(68)	−6593(7)	−4068(7)	−1200(6)
C(23)	−604(12)	1918(9)	−3547(8)	C(69)	−7502(8)	−4093(9)	−1361(7)
C(24)	−1310(16)	2026(13)	−3075(11)	C(70)	−8146(8)	−4303(9)	−830(8)
C(25)	−1463(17)	2786(16)	−2919(13)	C(71)	−9017(10)	−4274(10)	−1011(10)
C(26)	−824(18)	3351(18)	−3237(14)	C(72)	−9239(12)	−4029(15)	−1713(13)
C(27)	−130(17)	3280(16)	−3667(13)	C(73)	−8643(13)	−3790(15)	−2238(12)
C(28)	−29(16)	2520(11)	−3848(10)	C(74)	−7765(11)	−3818(12)	−2062(8)
C(29)	2925(8)	−243(9)	−2359(6)	C(75)	−8585(8)	−1737(8)	−770(7)
C(30)	3701(10)	−33(10)	−2159(9)	C(76)	−8715(9)	−2062(9)	−1311(7)
C(31)	4381(10)	−667(14)	−1895(9)	C(77)	−9393(10)	−1715(10)	−1786(7)
C(32)	4269(13)	−1470(13)	−1883(9)	C(78)	−9956(11)	−1059(12)	−1715(10)
C(33)	3520(12)	−1657(12)	−2096(9)	C(79)	−9820(11)	−738(11)	−1161(11)
C(34)	2871(9)	−1036(9)	−2347(7)	C(80)	−9144(10)	−1082(10)	−668(8)
C(35)	1625(9)	905(8)	−1940(7)	C(81)	−8354(8)	−3036(8)	540(7)
C(36)	901(11)	1481(11)	−2007(9)	C(82)	−9248(9)	−3163(9)	474(8)
C(37)	590(12)	1813(12)	−1430(10)	C(83)	−9655(11)	−3745(10)	978(10)
C(38)	971(13)	1527(13)	−817(9)	C(84)	−9222(13)	−4232(11)	1542(10)
C(39)	1659(13)	946(12)	−733(9)	C(85)	−8365(13)	−4114(10)	1603(9)
C(40)	1979(10)	643(10)	−1267(7)	C(86)	−7923(11)	−3533(9)	1120(8)
C(41)	2471(11)	1390(9)	−3299(7)	C(87)	−7490(9)	−1519(8)	320(7)
C(42)	2353(23)	1524(22)	−3990(18)	C(88)	−7987(11)	−1356(10)	880(8)
C(43)	2697(24)	2181(22)	−4527(18)	C(89)	−7777(16)	−767(11)	1175(9)
C(44)	3148(22)	2762(20)	−4334(17)	C(90)	−7039(17)	−337(10)	901(11)
C(45)	3029(24)	2796(22)	−3653(20)	C(91)	−6535(16)	−486(12)	368(12)
C(46)	2575(26)	2088(27)	−3113(22)	C(92)	−6768(10)	−1062(10)	62(9)
C(42′)	2689(51)	1289(49)	−3938(42)	Cl(1)	2638(14)	3561(13)	8904(12)
C(43′)	3224(33)	2041(31)	−4446(25)	Cl(2)	1775(21)	3831(20)	7702(17)
C(45′)	3500(33)	2576(30)	−3526(25)	Cl(2′)	3500(22)	4124(21)	7886(18)
C(44′)	3625(50)	2582(48)	−4171(42)	C(94)	2634(30)	3563(34)	8090(23)
C(46′)	3004(23)	1959(21)	−3064(17)				

$ClF_{20}P_2Pt_2$, M = 2461.315, triclinic, space group $P\bar{1}$, a = 15.265(3), b = 16.866(4), c = 19.759(4) Å, α = 106.66(2), β = 86.48(2), γ = 95.86(2)°, U = 4843.65 Å^3, Z = 2, D_c = 1.688 g cm^{-3}, λ(Mo-Kα) = 0.710 73 Å, F(000) = 2354.0, pale yellow prismatic parallelepiped, dimensions 0.30 × 0.30 × 0.72 mm, μ(Mo-Kα) = 3.81 mm^{-1}. The asymmetric unit contains two molecules, each with a centre of symmetry.

Data collection, structure analysis and refinement. Data were obtained by Crystalytics Co. (Lincoln, NE). A crystal was sealed into a thin-walled glass capillary with epoxy. Measurements were made on a four-circle Nicolet (Siemens) Autodiffractometer with graphite-monochromated Mo-Kα radiation. Data were collected at 20 ± 1 °C using the ω-scan technique with 2θ ranging from 3 to 45.8°. Of the 13 782 reflections collected 13 316 were unique (absorption correction, minimum and maximum transmissions factors = 0.732, 1.000). The structure was solved by the Patterson method[13] and refined by full-matrix least squares on F^2 for all reflections (SHELXL 93).[14] Non-hydrogen atoms were refined anisotropically, except for the C atoms corresponding to a phenyl ring disordered over two positions at 0.65 and 0.35 occupancy, respectively, with the common C$_{ipso}$ atom [C(41)–C(46) for one phenyl ring and C(41), C(42′)–C(46′) for the other], and three C atoms of a phenyl ring [C(25)–C(27)] which showed large thermal parameters, probably due to some static and/or dynamic disorder. Hydrogen atoms were located at fixed positions, with the isotropic parameter being 1.2 times larger than that of the corresponding C atom. Some residual electron density was modelled as interstitial solvent (0.5 molecule of CH_2Cl_2 per formula unit, with one of the Cl atoms disordered over two positions at half occupancy). The final wR_2 factor was 0.146 for all non-negative data ($R_1 = 0.053$ and $wR_2 = 0.127$ for 9240 reflections with $F > 4\sigma F_o$). The weighting scheme was $w = 1/\sigma^2(F_o)^2 + (0.0754\ P)^2$, where $P = [(F_o^2, 0) + 2F_c^2]_{max}/3$. The highest residual peak of 1.22 e Å^{-3} is thought to belong to some additional disordered solvent.

All calculations were performed on a Local Area VAX cluster (VAX/VMS V5.5) with the Siemens SHELXTL PLUS and SHELXL 93 software packages.[13,14] Atomic coordinates are given in Table 4.

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

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