

Synthesis of novel platinum–silver and platinum–copper complexes with bridging alkynyl ligands

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Abstract

The study of the reactivity of $[\text{Pt}_2\text{M}_4(\text{C}\equiv\text{CR})_8]$ ($\text{M} = \text{Ag}$ or Cu ; $\text{R} = \text{Ph}$ or ^tBu) towards different neutral and anionic ligands is reported. This study reveals that reactions of the phenylacetylide derivatives $[\text{Pt}_2\text{M}_4(\text{C}\equiv\text{CPh})_8]$ with anionic, X^- ($\text{X} = \text{Cl}$ or Br) or neutral donors (CN^tBu or py) in a molar ratio 1:4 (M/donor ratio 1:1) yield the trinuclear anionic $(\text{NBu}_4)_2[\{\text{Pt}(\text{C}\equiv\text{CPh})_4\}(\text{MX})_2]$ ($\text{M} = \text{Ag}$ or Cu , $\text{X} = \text{Cl}$ or Br) or neutral $[\{\text{Pt}(\text{C}\equiv\text{CPh})_4\}(\text{AgL})_2]$ ($\text{L} = \text{CN}^t\text{Bu}$ or py) complexes, respectively. The crystal structure of $(\text{NBu}_4)_2[\{\text{Pt}(\text{C}\equiv\text{CPh})_4\}(\text{CuBr})_2]$ (**4**) shows that the anion is formed by a dianionic $\text{Pt}(\text{C}\equiv\text{CPh})_4$ fragment and two neutral CuBr units joined through bridging alkynyl ligands. All the alkynyl groups are σ bonded to Pt and η^2 -coordinated to a Cu atom which have an approximately trigonal-planar geometry. By contrast, similar reactions with $[\text{Pt}_2\text{M}_4(\text{C}\equiv\text{C}^t\text{Bu})_8]$ (molar ratio M/donor 1:1) afford hexanuclear dianionic $(\text{NBu}_4)_2[\text{Pt}_2\text{M}_4(\text{C}\equiv\text{C}^t\text{Bu})_8\text{X}_2]$ or neutral $[\text{Pt}_2\text{Ag}_4(\text{C}\equiv\text{C}^t\text{Bu})_8\text{Py}_2]$. Only by treatment with a large excess of Br^- (molar ratio M/ Br^- 1:2) are the trinuclear complexes $(\text{NBu}_4)_2[\{\text{Pt}(\text{C}\equiv\text{C}^t\text{Bu})_4\}(\text{MBr})_2]$ ($\text{M} = \text{Ag}$, Cu) obtained. Attempted preparations of analogous complexes with phosphines ($\text{L}' = \text{PPh}_3$ or PEt_3) by reactions of $[\text{Pt}_2\text{M}_4(\text{C}\equiv\text{CR})_8]$ with L' leads to displacement of alkynyl ligands from platinum and formation of neutral mononuclear complexes $[\text{trans-Pt}(\text{C}\equiv\text{CR})_2\text{L}'_2]$.

Keywords: Platinum; Silver; Alkynyl; Copper; Polynuclear; X-ray diffraction

1. Introduction

The synthesis of heteropolynuclear complexes of platinum in which the metal centres are linked only by alkynyl ligands is the subject of our current interest [1–4]. In this context, we have recently reported the synthesis of hexanuclear complexes $[\text{Pt}_2\text{M}_4(\text{C}\equiv\text{CR})_8]$ ($\text{M} = \text{Ag}$ or Cu ; $\text{R} = \text{Ph}$ or ^tBu) [1], the structure of $[\text{Pt}_2\text{Ag}_4(\text{C}\equiv\text{C}^t\text{Bu})_8]$ has been determined, and it has been shown that two staggered square-planar ' $\text{Pt}(\text{C}\equiv\text{CR})_4$ ' fragments are connected by four silver atoms which are π bonded to two acetylide groups, one associated with each platinum environment. As far as we know, these are the only reported heteropolynuclear complexes of platinum containing only bridging alkynyls and therefore we considered it of interest to

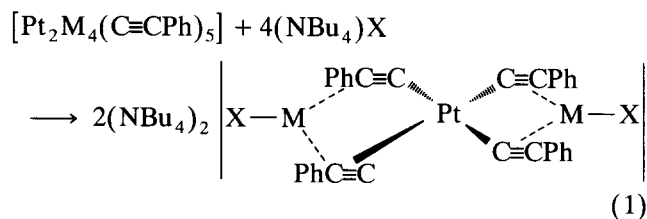
explore their reactivity. In this paper, we report the results of the reactivity towards some neutral and anionic ligands.

2. Results and discussion

The hexanuclear complexes $[\text{Pt}_2\text{M}_4(\text{C}\equiv\text{CPh})_8]$ ($\text{M} = \text{Ag}$ or Cu) react with $(\text{NBu}_4)\text{Cl}$ or $(\text{NBu}_4)\text{Br}$ in a 1:4 molar ratio (M/ Cl^- or Br^- ratio 1:1) in acetone to give yellow solutions, from which anionic trinuclear bridging alkynyl complexes $(\text{NBu}_4)_2[\{\text{Pt}(\text{C}\equiv\text{CPh})_4\}(\text{MX})_2]$ ($\text{M} = \text{Ag}$, $\text{X} = \text{Cl}$ **1**, $\text{X} = \text{Br}$ **2**; $\text{M} = \text{Cu}$, $\text{X} = \text{Cl}$ **3**, $\text{X} = \text{Br}$ **4**) can be isolated as microcrystalline yellow solids (Eq. 1). Analogous results are obtained by treating $[\text{Pt}_2\text{M}_4(\text{C}\equiv\text{CPh})_8]$ with $(\text{NBu}_4)\text{Br}$ in a 1:8 molar ratio (M/ Br^- ratio 1:2). The polynuclear complexes **1–3** can also be prepared by treating the anionic mononuclear derivative $(\text{NBu}_4)_2[\text{Pt}(\text{C}\equiv\text{CPh})_4]$ [1] with

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MX. Thus AgCl, AgBr and CuCl dissolve almost instantly in acetone solutions of $(\text{NBu}_4)_2[\text{Pt}(\text{C}\equiv\text{CPh})_4]$ (molar ratio 2:1) giving yellow solutions from which the yellow products **1–3** are obtained (see Experimental details).



M	X
Ag	Cl 1 ; Br 2
Cu	Cl 3 ; Br 4

The formulation of the anions of these complexes **1–4** as trinuclear species with the dianionic 'Pt(C≡CPh)₄' fragment chelating two neutral MX units is supported by their analyses, conductivities, IR and ¹H NMR spectra (see Experimental details). Their conductivities in acetone solutions are as expected for 1:2 electrolytes [5] and their IR spectra show one strong ν(C≡C) band (with a shoulder in the cases of **3** and **4**) significantly shifted to lower wavelengths, compared with that observed for [Pt(C≡CPh)₄]²⁻ [1], indicating side-on π-coordination of the C≡CPh groups [1]. It should be noted that the ν(C≡C) absorptions for the platinum–copper complexes are at lower frequencies than those of platinum–silver derivatives, suggesting that the former have stronger M–π acetylide interactions. Similar trends have been observed for the polymeric complexes [(M(C₂Ph))_n(Cu or Ag)] [6] and also for acetylide containing clusters of Group IB metals [7]. The ¹H NMR spectra exhibit signals due to the aromatic protons and to the NBu₄⁺ cation in the expected integration ratio (4:2).

Table 1
Selected bond lengths (in Å) and bond angles (in °)

Pt(1)...Cu(1)	2.945(2)	Cu(1)–C(1)	2.157(11)
Pt(1)–C(1)	2.020(8)	Cu(1)–C(2)	2.338(10)
Pt(1)–C(9)	2.015(11)	Cu(1)–C(9)	2.141(8)
C(1)–C(2)	1.200(12)	Cu(1)–C(10)	2.326(9)
C(9)–C(10)	1.209(15)	Cu(1)–X(1)	2.168(11)
C(2)–C(3)	1.438(12)	Cu(1)–X(2)	2.147(8)
C(10)–C(11)	1.455(16)	Cu(1)–Br(1)	2.298(2)
C(1)–Pt(1)–C(9)	87.5(4)	C(1)–C(2)–C(3)	167.9(12)
Pt(1)–C(1)–C(2)	172.4(10)	C(9)–C(10)–C(11)	167.1(9)
Pt(1)–C(9)–C(10)	172.7(7)	Pt(1)–Cu(1)–Br(1)	147.4(1)
X(1)–Cu(1)–X(2)	108.9(3)	Br(1)–Cu(1)–X(2)	126.3(3)
		Br(1)–Cu(1)–X(1)	124.6(3)

X(1) is defined as the C(1)–C(2) midpoint. X(2) is defined as the C(9)–C(10) midpoint.

It is evident from all these data that new heterometallic species stabilized by bridging acetylide ligands have been formed. However, in order to obtain structural information on the acetylide bonding mode in this family of complexes, an X-ray study of **4** has been carried out. Two views of the anion in complex **4** are presented in Fig. 1, and selected bond distances and bond angles are collected in Table 1. The compound crystallizes with two crystallographically independent, but chemically very similar, anions in the unit cell. Discussion of the structure will therefore be limited to only one of these anions.

The anion is a centrosymmetric trinuclear (Cu, Pt, Cu) species in which a dianionic 'Pt(C≡CPh)₄' fragment is chelating two neutral CuBr units through bridging alkynyl ligands ($\mu\text{-}\eta^1:\eta^2$). Each CuBr unit is bonded to two of the four alkyne groups in a similar fashion to that found in [PtCuCl(C≡C^tBu)₂(PMe₂Ph)₂] [8] which contains a CuCl group linked to the two *cis*-C≡C^tBu ligands at platinum. The platinum atom is in an approximately square-planar environment formed by the

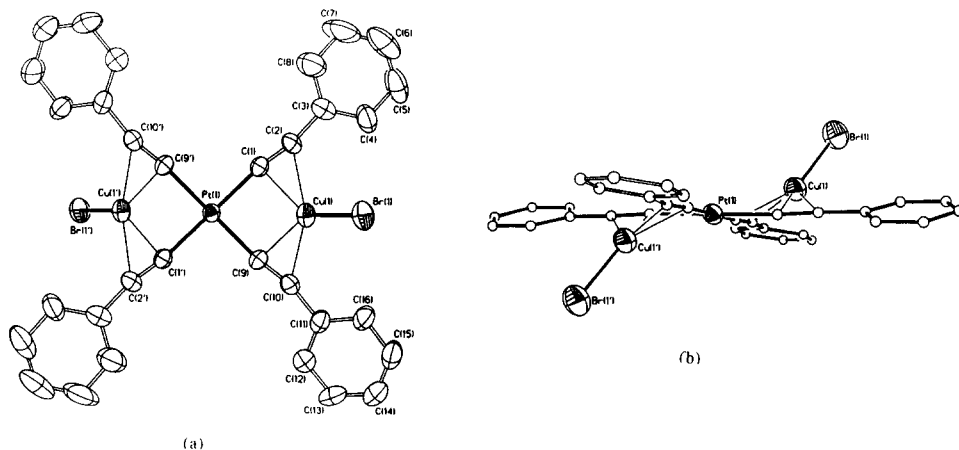


Fig. 1. (a) Drawing of the anion $[\{\text{Pt}(\text{C}\equiv\text{CPh})_4\}(\text{CuBr})_2]^{2-}$ in complex **4** showing the atom-labelling scheme; (b) perspective showing the displacement of the CuBr groups out of the platinum coordination plane.

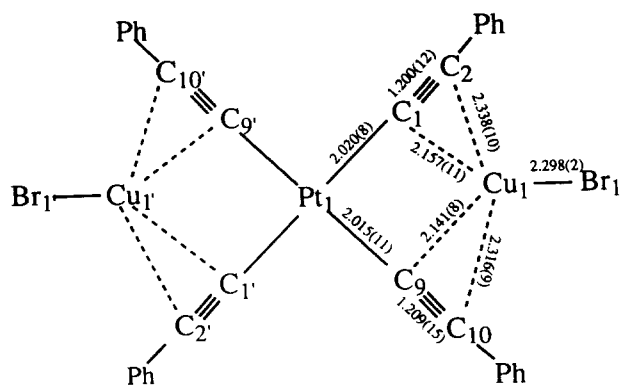


Fig. 2. Schematic view of the two metallo-cycles formed in the anion $[\{Pt(C\equiv CPh)_4\}(CuBr)_2]^{2-}$ of complex (4) with bond lengths in Å.

four C_α atoms of the $C_\alpha\equiv C_\beta Ph$ groups. On the other hand, the copper atoms are in planar trigonal environments formed by the bromine atom and the midpoints of two acetylenic fragments.

As is observed in Fig. 1(b), the anion is not planar, because the copper atoms Cu(1) and Cu(1') are displaced [0.905(2) Å] up and down respectively from the Pt(1) coordination plane. The dihedral angle formed by the coordination planes of the platinum [PtC(1)C(9)-C(1')C(9')] and copper [(best least squares plane formed by Cu(1), Br(1), midpoint C(1)-C(2) and midpoint C(9)-C(10)] atoms is 50.0°. A similar structural feature has been previously found in $[PtCuCl(C\equiv C^tBu)_2(PMe_2Ph)_2]$ in which the Cu atom lies out (0.526 Å) of the PtP_2 plane [8]. However, the related system $[(C_5H_4SiMe_3)_2Ti(C\equiv CSiMe_3)_2]CuCl$ displays a central planar TiC_4Cu core [9].

The bonding of the $C_\alpha\equiv C_\beta Ph$ groups ($\mu-\eta^1:\eta^2$) and the bond lengths of the resulting metallo-cycles are schematized in Fig. 2. The Pt- C_α bond lengths [Pt(1)-C(1) 2.020(8); Pt(1)-C(9) 2.015(11) Å] and $C_\alpha\equiv C_\beta$ distances [C(1)-C(2) 1.200(12) Å and C(9)-C(10) 1.209(15)] and the angles at C_α [Pt(1)C(1)C(2) 172.4(10); Pt(1)C(9)C(10) 172.7(7)°] and at C_β [C(1)C(2)C(3) 167.9(12)° and C(9)C(10)C(11) 167.1(9)°]

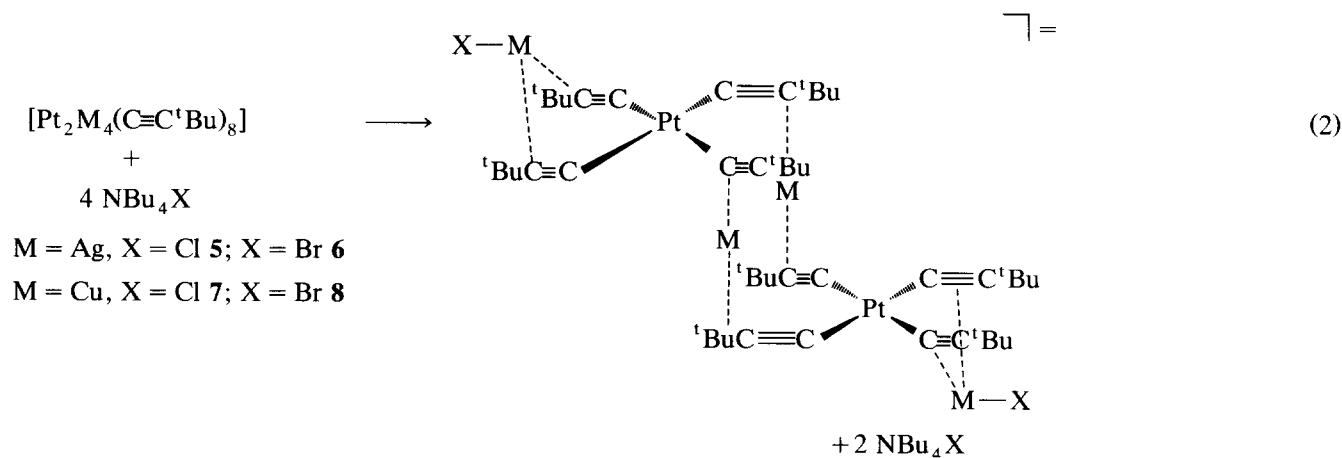
atoms are similar to the corresponding ones found in $[PtCuCl(C\equiv C^tBu)_2(PMe_2Ph)_2]$ [8]. The C_β atoms [C(2) and C(10)] are, as in $[PtCuCl(C\equiv C^tBu)_2(PMe_2Ph)_2]$, slightly farther from Cu(1) [2.338(10) and 2.326(9) Å] than C_α [C(1) and C(9)] [2.157(11) and 2.141(8) Å] so that the interaction between the acetylides and the copper atoms is asymmetric. The distance between the Cu atoms and the midpoints of the $C\equiv C$ triple bonds [Cu-C(1), (2) 2.168(11) and Cu-C(9), (10) 2.147(8) Å] are identical within experimental error.

Finally, the Pt...Cu distance [2.942(5)] is slightly shorter than that found in $[PtCuCl(C\equiv C^tBu)_2(PMe_2Ph)_2]$ [3.129(2) Å] [8], and a metal-metal bond interaction can be excluded.

Surprisingly, the analogous *t*-butylacetylide derivatives $[Pt_2M_4(C\equiv C^tBu)_8]$ ($M = Ag$ or Cu) exhibit a different behaviour towards X^- , and the products depend upon the amount of $(NBu_4)X$ used. Thus, when the reactions between $[Pt_2M_4(C\equiv C^tBu)_8]$ and $(NBu_4)X$ ($X = Cl$ or Br) in acetone are carried out using a 1:4 molar ratio (M/X ratio 1:1) pale yellow solutions are obtained and from these solutions, the anionic $(NBu_4)_2[Pt_2M_4(C\equiv C^tBu)_8X_2]$ ($M = Ag$, $X = Cl$ 5, Br 6; $M = Cu$ Cl 7 Br 8) species can be isolated as white microcrystalline solids. Similar results can be obtained starting from $(NBu_4)_2[Pt(C\equiv C^tBu)_4]\cdot 2H_2O$ and MX . By mixing $(NBu_4)_2[Pt(C\equiv C^tBu)_4]\cdot 2H_2O$ with $AgCl$, $AgBr$ or $CuCl$ in a 1:2 molar ratio in acetone, complexes 5–7 are obtained in similar yields.

We have formulated these complexes as hexametal species (Eq. 2) on the basis of their analytical and conductance data, and FAB mass, IR and 1H NMR spectra. Analytical data and 1H NMR spectra of complexes 5–8 are in accord with the proposed stoichiometry. In the IR spectra of 5–8 there is only one strong absorption (2042 cm^{-1} 5, 6; 2012 cm^{-1} 7 and 2014 cm^{-1} 8) assignable to $\nu(C\equiv C)$, suggesting that all the acetylide ligands are engaged in π bonding.

Unfortunately we have not been able to obtain suitable crystals for X-ray studies, but a plausible structure compatible with all these data is the one shown

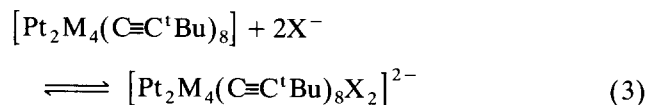


in Eq. 2 with the anionic part formed by two $[\text{Pt}(\text{C}\equiv\text{C}^t\text{Bu})_2(\mu\text{-C}\equiv\text{C}^t\text{Bu})_2\text{MX}]$ units holding by two $\text{M}(\text{I})$ cations. Thus, two of $\text{M}(\text{I})$ cations retain linear coordination being π bonded only by two alkyne groups, and the other two M centres are probably three-coordinate. The presence of two different environments for silver centres has been found previously in the hexanuclear derivative $[\text{Pt}_2\text{Ag}_4(\text{C}_6\text{F}_5)_4(\text{C}\equiv\text{C}^t\text{Bu})_4(\text{CH}_3\text{COCH}_3)_4]$ [3] which displays a similar structure.

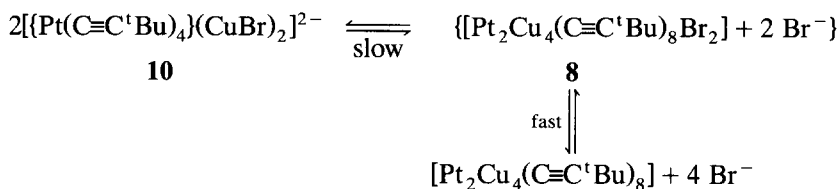
The ^1H NMR spectra of complexes **5–8**, at room temperature are very similar and exhibit only a single resonance for the methyl groups of the $\text{C}\equiv\text{C}^t\text{Bu}$ ligands besides resonances due to the NBu_4^+ ions. This indicates that in solution all $\text{C}\equiv\text{C}^t\text{Bu}$ groups are equivalent. In order to confirm the proposed structure, for which two different alkynyl environments should be observed, the spectra of complexes **6** and **8** were registered at low temperature, but both complexes in CDCl_3 at -55°C (see Experimental details) display similar patterns to those observed at room temperature.

In contrast, the reactions with Br^- have been also explored in 1:2 and 1:8 molar ratios and we found a lower proportion of halide (1:2), as required by Eq. (2), produces mixtures of $[\text{Pt}_2\text{M}_4(\text{C}\equiv\text{C}^t\text{Bu})_8]$ and the expected hexanuclear complexes **6** and **8**, although in lower yield. This, and the fact that the white platinum–copper compounds **7** and **8** give deep-yellow solutions in solvents such as CHCl_3 , CH_2Cl_2 and acetone, seems to indicate that in solution these com-

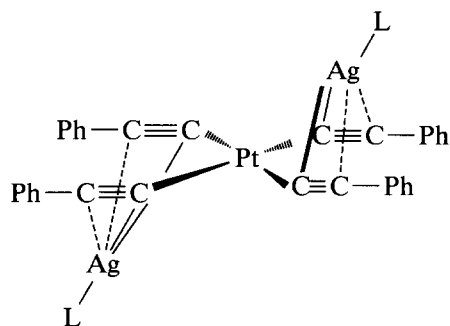
plexes (and probably also **5** and **6**) are in equilibrium with Cl^- or Br^- and the starting yellow hexanuclear derivative $[\text{Pt}_2\text{Cu}_4(\text{C}\equiv\text{C}^t\text{Bu})_8]$ (Eq. 3).



An excess of Br^- , with molar ratio 1:4, shifts the equilibrium to the right and the anionic hexanuclear complexes can be separated in high yields. With a molar ratio 1:2, the equilibrium is not shifted so far and a mixture of $[\text{Pt}_2\text{M}_4(\text{C}\equiv\text{C}^t\text{Bu})_8]$ and complex **6** or **8**, respectively, is then obtained. Unexpectedly, the use of a larger excess of Br^- (molar ratio 1:8) leads to the *t*-butylacetylide trinuclear derivatives $(\text{NBu}_4)_2\{[\text{Pt}(\text{C}\equiv\text{C}^t\text{Bu})_4(\text{MBr})_2]\}$ ($\text{M} = \text{Ag}$ **9**, $\text{M} = \text{Cu}$ **10**), analogous to **2** and **4**. Thus, when the hexanuclear derivatives $[\text{Pt}_2\text{M}_4(\text{C}\equiv\text{C}^t\text{Bu})_8]$ ($\text{M} = \text{Ag}$, Cu) are treated in acetone with $(\text{NBu}_4)\text{Br}$ (molar ratio 1:8; M/Br^- ratio 1:2) white microcrystalline precipitates of $(\text{NBu}_4)_2\{[\text{Pt}(\text{C}\equiv\text{C}^t\text{Bu})_4(\text{AgBr})_2]\}$ **9** and $(\text{NBu}_4)_2\{[\text{Pt}(\text{C}\equiv\text{C}^t\text{Bu})_4(\text{CuBr})_2]\}$ **10** are formed quickly. Based on the spectroscopic properties, the structure of these complexes is assumed to be analogous to that of **4** in which a dianionic $\text{Pt}(\text{C}\equiv\text{C}^t\text{Bu})_4$ unit is coordinated to two MBr ($\text{M} = \text{Ag}$, Cu) fragments in a side-on fashion. Thus, analytical and conductance data for **9** and **10** are consistent with the proposed formulae and their IR spectra show only one strong absorption (2056 cm^{-1} **9**; 2024 cm^{-1} **10**) assignable to coordinated $\nu(\text{C}\equiv\text{C})$.

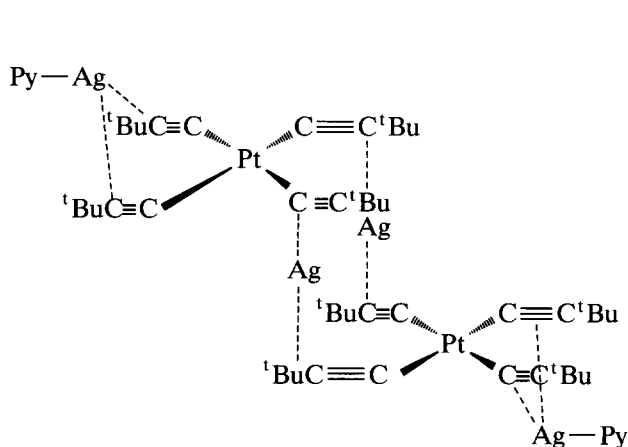


Scheme 1.



11 L = Py

12 L = CNBu^t



13

Scheme 2.

The ^1H NMR spectrum of the mixed platinum–silver complex **9** exhibits the typical resonances of the NBu_4^+ ion (3.36 m; 1.64 m; 1.41 m and 0.97 t) and a singlet at 1.27 ppm due to $\text{C}\equiv\text{C}^t\text{Bu}$ groups of the expected intensity ratio. The ^1H NMR spectrum in CDCl_3 for the mixed platinum–copper complex **10** reveals that in solution several species are present. The deep-yellow solution displays two different singlet signals for the $\text{C}\equiv\text{C}^t\text{Bu}$ groups, at 1.30 and 1.23 ppm in a 1,1:1 ratio in addition to the NBu_4^+ resonances. In the presence of an excess of Br^- (molar ratio **10**/ Br^- 1:8) both ^tBu signals are slightly shifted (1.24, 1.17 ppm respectively) and have relative intensities of (1:2.6). All these facts can be explained as consequence of the equilibria (see Scheme 1).

We have also explored the reactivity of $[\text{Pt}_2\text{M}_4(\text{C}\equiv\text{CR})_8]$ towards different neutral donors. Thus, trinuclear platinum silver complexes $[\{\text{Pt}(\text{C}\equiv\text{CPh})_4\}(\text{AgPy})_2]$ (**11**) and $[\{\text{Pt}(\text{C}\equiv\text{CPh})_4\}(\text{AgCN}^t\text{Bu})_2]$ (**12**) (Scheme 2) analogues of the anionic trinuclear compounds **1–4** have been obtained by reaction of $\text{Pt}_2\text{Ag}_4(\text{C}\equiv\text{CPh})_8$ with pyridine or CN^tBu in 1:4 molar ratio in CH_2Cl_2 . On the basis of the spectroscopic properties (see Section 3) we infer these complexes to be isostructural to **1–4**. In both complexes, the $\nu(\text{C}\equiv\text{C})$ band is shifted towards higher frequencies (2066 cm^{-1} **11**, 2077 cm^{-1} **12**) than for $[\text{Pt}_2\text{Ag}_4(\text{C}\equiv\text{CPh})_8]$ (2043 cm^{-1}). These frequencies are very similar to that observed for the homoleptic anion $[\text{Pt}(\text{C}\equiv\text{CPh})_4]^{2-}$ (2075 cm^{-1}) suggesting that the interaction of the silver centres with the π bonds of the acetylenic fragments is presumably weak.

Notwithstanding, these $\nu(\text{C}\equiv\text{C})$ vibrations can be compared to those observed in the clusters $[\text{Au}_3\text{Ag}_2(\text{C}_2\text{Ph})_6]^-$ (2082 cm^{-1}) [10] or $[\text{Au}_2\text{Ag}_2(\text{C}_2\text{Ph})_4(\text{PPh}_3)_2]$ (2075 cm^{-1}) [11] as a result of asymmetric π -bonding of silver [12]. The different behaviour of the *t*-butylacetylide derivative is also reflected in its reactivity with pyridine. Thus, $[\text{Pt}_2\text{Ag}_4(\text{C}\equiv\text{C}^t\text{Bu})_8]$ reacts with Py in a molar ratio of ca. 1:4 to give also the selective formation of the 1:2 adduct $[\text{Pt}_2\text{Ag}_4(\text{C}\equiv\text{C}^t\text{Bu})_8\text{Py}_2]$ (**13**) which is presumably similar (Scheme 2) to the anionic hexanuclear derivatives **5–8**.

In contrast, the reactivity of all derivatives $[\text{Pt}_2\text{M}_4(\text{C}\equiv\text{CR})_8]$ ($\text{M} = \text{Ag}$ or Cu ; $\text{R} = \text{Ph}$ or ^tBu) with phosphines (PEt_3 , PPh_3) is very similar, but displacement of the alkynyl groups from platinum atoms occurs, and only the mononuclear complexes *trans*- $[\text{Pt}(\text{C}\equiv\text{CR})_2\text{L}_2]$ ($\text{L} = \text{PEt}_3$ [13], PPh_3 [14,15]) are obtained instead of the expected heteronuclear derivatives.

Thus, when the hexanuclear complexes $[\text{Pt}_2\text{M}_4(\text{C}\equiv\text{CR})_8]$ ($\text{M} = \text{Ag}$, $\text{R} = \text{Ph}$ or ^tBu ; $\text{M} = \text{Cu}$, $\text{R} = \text{Ph}$) are treated with four equivalents of PEt_3 in acetone, a precipitate [white $\{\text{Ag}(\text{C}\equiv\text{CR})_n\}$ or yellow-lemon $\{\text{Cu}(\text{C}\equiv\text{CPh})_n\}$] is quickly formed and after filtration, the corresponding mononuclear complexes *trans*-

$[\text{Pt}(\text{C}\equiv\text{CR})_2(\text{PEt}_3)_2]$ [13] ($\text{R} = \text{Ph}$ or ^tBu) are isolated. Surprisingly, PEt_3 does not react with $[\text{Pt}_2\text{Cu}_4(\text{C}\equiv\text{C}^t\text{Bu})_8]$ and the analogous reactions with PPh_3 allow the isolation of *trans*- $[\text{Pt}(\text{C}\equiv\text{CR})_2(\text{PPh}_3)_2]$ [$\text{R} = ^t\text{Bu}$ [14], $\text{R} = \text{Ph}$ [15] (see Experimental details).

However, although the polynuclear phosphine complexes $[\text{Pt}_2\text{M}_2(\text{C}\equiv\text{CR})_4\text{L}_2]$ have never been isolated, the formation of such derivatives, analogues of **11** and **12**, as transient species which evolve to $\{\text{M}(\text{C}\equiv\text{CR})_n\}$ and *trans*- $[\text{Pt}(\text{C}\equiv\text{CR})_2\text{L}_2]$ cannot be ruled out.

Finally, these reactions contrast with the stability observed previously by us for the binuclear anionic derivatives $(\text{NBu}_4)_2[\text{Pt}(\text{C}_6\text{F}_5)_2(\mu\text{-}\eta^2\text{-C}\equiv\text{CR})_2\text{AgL}]$ ($\text{R} = \text{Ph}$ or ^tBu ; $\text{L} = \text{PPh}_3$, PEt_3) which have been obtained by treating the anionic tetranuclear platinum-silver compounds $(\text{NBu}_4)_2[\text{Pt}_2\text{Ag}_2(\text{C}_6\text{F}_5)_4(\text{C}\equiv\text{CR})_4]$ with PPh_3 or PEt_3 [4]. These tetranuclear anionic species $[\text{Pt}_2\text{Ag}_2(\text{C}_6\text{F}_5)_4(\text{C}\equiv\text{CR})_4]^{2-}$ can be readily formed by reaction of $[\text{Pt}(\text{C}_6\text{F}_5)_2(\text{C}\equiv\text{CR})_2]^{2-}$ and AgCl in acetone [2], suggesting that the liberated chloride ion does not react with such species once they are formed.

3. Experimental details

Elemental analyses (C, H and N) were carried out on a Perkin-Elmer 240-B microanalyzer. Conductivities were measured in ca. 5×10^{-4} mol dm^{-3} acetone or nitromethane solutions with a Philips PW P501/01 conductimeter. ^1H NMR spectra were recorded on a Varian XL-200 or Unity-300 spectrometer, and IR spectra were measured (4000–200 cm^{-1}) on a Perkin-Elmer 883 spectrophotometer. The synthesis of $[\text{Pt}_2\text{M}_4(\text{C}\equiv\text{CR})_8]$ ($\text{M} = \text{Ag}$, Cu ; $\text{R} = \text{Ph}$ or ^tBu) and $(\text{NBu}_4)_2[\text{Pt}(\text{C}\equiv\text{CR})_4] \cdot n\text{H}_2\text{O}$ ($\text{R} = \text{Ph}$, $n = 0$, ^tBu , $n = 2$) has been reported previously [1]. The reactions with silver compounds were carried out in the dark.

3.1. Preparation of the complexes

3.1.1. $(\text{NBu}_4)_2[\{\text{Pt}(\text{C}\equiv\text{CPh})_4\}(\text{MX})_2]$ ($\text{M} = \text{Ag}$, $\text{X} = \text{Cl}$ **1**, Br **2**; $\text{M} = \text{Cu}$, $\text{X} = \text{Cl}$ **3**, Br **4**)

Method (a).

A typical preparation (complex **1**) was as follows. A yellow suspension of $[\text{Pt}_2\text{Ag}_4(\text{C}\equiv\text{CPh})_8]$ (0.087 g, 0.053 mmol) in 20 ml of acetone was treated with $(\text{NBu}_4)\text{Cl}$ (0.059 g, 0.213 mmol) (1:4 ratio) and, almost immediately, a yellow solution was formed. After stirring for 30 min, the solution was evaporated to ca. 1 ml and stored at -30°C overnight. Pale yellow crystals of **1** were formed. They were filtered off, washed with two portions of cold acetone (1 ml each) and air-dried.

Complexes **2–4** were prepared, as yellow crystals, using a similar procedure.

$(\text{NBu}_4)_2[\text{Pt}(\text{C}\equiv\text{CPh})_4(\text{AgCl})_2]$ (**1**). Yield 55%. Anal. Found (Calc.): N, 1.99 (2.04); C, 55.80 (56.06); H, 6.86 (6.76)% Λ_M (in acetone solution): $251 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. IR (cm^{-1}): $\nu(\text{C}\equiv\text{C})$ 2045 (s). $^1\text{H NMR}$ (CDCl_3): δ 0.92 [t, $-\text{CH}_3(^n\text{Bu})$], 1.41 [m, $-\text{CH}_2(^n\text{Bu})$], 1.59 [m, $-\text{CH}_2(^n\text{Bu})$], 3.35 [m, $\text{NCH}_2(^n\text{Bu})$], 7.04, 7.28 (m, Ph). EI-MS: m/z 886 $[\text{PtAg}_2(\text{C}\equiv\text{CPh})_4\text{Cl}_2]^{2-}$ (37%); m/z 1522 $[\text{Pt}_2\text{Ag}_3(\text{C}\equiv\text{CPh})_8]^-$ (100%).

$(\text{NBu}_4)_2[\{\text{Pt}(\text{C}\equiv\text{CPh})_4\}(\text{AgBr})_2]$ (**2**). $[\text{Pt}_2\text{Ag}_4(\text{C}\equiv\text{CPh})_8]$: 0.116 g, 0.071 mmol; $(\text{NBu}_4)\text{Br}$: 0.092 g, 0.284 mmol. Yield 75%. Anal. Found (Calc.): N, 2.15 (1.92); C, 52.54 (52.65); H, 6.76 (6.35)%. Λ_M (in acetone solution): $247 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. IR (cm^{-1}): $\nu(\text{C}\equiv\text{C})$ 2048 (s). $^1\text{H NMR}$ (CDCl_3): δ 0.80 [t, $-\text{CH}_3(^n\text{Bu})$], 1.45 [m, $-\text{CH}_2(^n\text{Bu})$], 1.60 [m, $-\text{CH}_2(^n\text{Bu})$], 3.35 [m, $\text{NCH}_2(^n\text{Bu})$], 7.06, 7.31 (m, Ph). EI-MS: m/z molecular peak of the anion not observed; m/z 2525 $[\text{Pt}_3\text{Ag}_6(\text{C}\equiv\text{CPh})_{12}\text{Br}]^-$ (65%); m/z 1711 $[\text{Pt}_2\text{Ag}_4(\text{C}\equiv\text{CPh})_8\text{Br}]^-$ (52%); m/z 1523 $[\text{Pt}_2\text{Ag}_3(\text{C}\equiv\text{CPh})_8]^-$ (72%).

$(\text{NBu}_4)_2[\{\text{Pt}(\text{C}\equiv\text{CPh})_4\}(\text{CuCl})_2]$ (**3**). $[\text{Pt}_2\text{Cu}_4(\text{C}\equiv\text{CPh})_8]$: 0.100 g, 0.069 mmol; $(\text{NBu}_4)\text{Cl}$: 0.076 g, 0.276 mmol. Yield 70%. Anal. Found (Calc.): N, 2.17 (2.18); C, 59.34 (59.94); H, 7.35 (7.23)% Λ_M (in acetone solution): $192 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. IR (cm^{-1}): $\nu(\text{C}\equiv\text{C})$ 2021 (s), 1985 (sh). $^1\text{H NMR}$ (CDCl_3): δ 0.89 [t, $-\text{CH}_3(^n\text{Bu})$], 1.42 [m, $-\text{CH}_2(^n\text{Bu})$], 1.67 [m, $-\text{CH}_2(^n\text{Bu})$], 3.46 [m, $\text{NCH}_2(^n\text{Bu})$], 7.23, 7.64 (m, Ph). EI-MS: m/z molecular peak of the anion not observed; m/z 2213 $[\text{Pt}_3\text{Cu}_6(\text{C}\equiv\text{CPh})_{12}\text{Cl}]^-$ (5%).

$(\text{NBu}_4)_2[\{\text{Pt}(\text{C}\equiv\text{CPh})_4\}(\text{CuBr})_2]$ (**4**). $[\text{Pt}_2\text{Cu}_4(\text{C}\equiv\text{CPh})_8]$: 0.100 g, 0.069 mmol; $(\text{NBu}_4)\text{Br}$: 0.089 g, 0.276 mmol. Yield 76%. Anal. Found (Calc.): N, 1.97 (2.04); C, 55.54 (56.05); H, 6.94 (6.76)% Λ_M (in acetone solution): $243 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. IR (cm^{-1}): $\nu(\text{C}\equiv\text{C})$ 2034 (s), 1988 (sh). $^1\text{H NMR}$ (CDCl_3): δ 0.91 [t, $-\text{CH}_3(^n\text{Bu})$], 1.42 [m, $-\text{CH}_2(^n\text{Bu})$], 1.68 [m, $-\text{CH}_2(^n\text{Bu})$], 3.44 [m, $\text{NCH}_2(^n\text{Bu})$], 7.18, 7.66 (m, Ph). EI-MS: m/z 2260 $[\text{Pt}_3\text{Cu}_6(\text{C}\equiv\text{CPh})_{12}\text{Br}]^-$ (18%); m/z 1532 $[\text{Pt}_2\text{Cu}_4(\text{C}\equiv\text{CPh})_8\text{Br}]^-$ (27%); m/z 1389 $[\text{Pt}_2\text{Cu}_3(\text{C}\equiv\text{CPh})_8]^-$ (50%).

The reactions between $[\text{Pt}_2\text{M}_4(\text{C}\equiv\text{CPh})_8]$ ($\text{M} = \text{Ag}$ or Cu) and $(\text{NBu}_4)\text{Br}$ were also carried out in a 1:8 molar ratio compounds. **2** or **4** were also obtained; yields 70 and 75%, respectively.

Method (b).

Alternatively complexes **1**, **2**, and **3** were prepared by reaction of $(\text{NBu}_4)_2[\text{Pt}(\text{C}\equiv\text{CPh})_4]$ with MX ($\text{M} = \text{Ag}$, Cu , $\text{X} = \text{Cl}$; $\text{M} = \text{Ag}$, $\text{X} = \text{Br}$). A typical preparation (complex **1**) was as follows: to a colourless solution of $(\text{NBu}_4)_2[\text{Pt}(\text{C}\equiv\text{CPh})_4]$ (0.152 g, 0.140 mmol) in 20 ml of acetone was added 0.040 g (0.281 mmol) of AgCl . Immediately the silver chloride dissolved and the solution became deep yellow. The mixture was stirred for 30 min and then evaporated to small volume (ca. 1 ml).

By cooling at -30°C overnight yellow crystals of **1** were obtained (yield 41%). Complexes **2**: $(\text{NBu}_4)_2[\text{Pt}(\text{C}\equiv\text{CPh})_4]$: 0.100 g, 0.092 mmol; AgBr : 0.035 g, 0.184 mmol (78% yield) and **3** $(\text{NBu}_4)_2[\text{Pt}(\text{C}\equiv\text{CPh})_4]$: 0.100 g, 0.092 mmol; CuCl : 0.018 g, 0.184 mmol (yield 78%) were prepared similarly.

3.1.2. $(\text{NBu}_4)_2[\text{Pt}_2\text{M}_4(\text{C}\equiv\text{C}^t\text{Bu})_8\text{X}_2]$ ($\text{M} = \text{Ag}$, $\text{X} = \text{Cl}$ **5**, Br **6**; $\text{M} = \text{Cu}$ $\text{X} = \text{Cl}$ **7**, Br **8**)

Method (a).

5: A yellow solution of $[\text{Pt}_2\text{Ag}_4(\text{C}\equiv\text{C}^t\text{Bu})_8]$ (0.071 g, 0.048 mmol) in 30 ml of acetone was treated with $(\text{NBu}_4)\text{Cl}$ (0.054 g, 0.193 mmol) (1:4 molar ratio) for 30 min at room temperature. The evaporation of the solution (ca. 2 ml) rendered white crystals which were filtered off, washed with cold acetone and air-dried (yield 77%).

Complexes **6–8** were obtained similarly as white crystals.

$(\text{NBu}_4)_2[\text{Pt}_2\text{Ag}_4(\text{C}\equiv\text{C}^t\text{Bu})_8\text{Cl}_2]$ (**5**). Anal. Found (Calc.): N, 1.39 (1.38); C, 47.27 (47.41); H, 7.34 (7.16)% Λ_M (in acetone solution): $289 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. IR (cm^{-1}): $\nu(\text{C}\equiv\text{C})$ 2042 (s). $^1\text{H NMR}$ (CDCl_3): δ 1.00 [t, $-\text{CH}_3(^n\text{Bu})$], 1.30 (s, ^tBu), 1.44 [m, $-\text{CH}_2(^n\text{Bu})$], 1.66 [m, $-\text{CH}_2(^n\text{Bu})$], 3.39 [m, $\text{NCH}_2(^n\text{Bu})$]. EI-MS: m/z 1506 $[\text{Pt}_2\text{Ag}_4(\text{C}\equiv\text{C}^t\text{Bu})_8\text{Cl}]^-$ (3%); m/z 1362 $[\text{Pt}_2\text{Ag}_3(\text{C}\equiv\text{C}^t\text{Bu})_8]^-$ (2%).

$(\text{NBu}_4)_2[\text{Pt}_2\text{Ag}_4(\text{C}\equiv\text{C}^t\text{Bu})_8\text{Br}_2]$ (**6**). $[\text{Pt}_2\text{Ag}_4(\text{C}\equiv\text{C}^t\text{Bu})_8]$ (0.094 g, 0.064 mmol; $(\text{NBu}_4)\text{Br}$: 0.082 g, 0.256 mmol. Yield: 72%. Anal. Found (Calc.): N, 1.67 (1.32); C, 45.22 (45.42); H, 7.52 (6.86). Λ_M (in acetone solution): $267 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. IR (cm^{-1}): $\nu(\text{C}\equiv\text{C})$ 2042 (s). $^1\text{H NMR}$ (CDCl_3): at 20°C , δ 1.00 [t, $-\text{CH}_3(^n\text{Bu})$], 1.30 (s, ^tBu), 1.46 [m, $-\text{CH}_2(^n\text{Bu})$], 1.66 [m, $-\text{CH}_2(^n\text{Bu})$], 3.37 [m, $\text{NCH}_2(^n\text{Bu})$]; at -55°C , δ 0.99 [t, $-\text{CH}_3(^n\text{Bu})$], 1.28 (s, ^tBu), 1.42 [m, $-\text{CH}_2(^n\text{Bu})$], 1.64 [m, $-\text{CH}_2(^n\text{Bu})$], 3.34 [m, $\text{NCH}_2(^n\text{Bu})$] EI-MS: m/z 1551, $[\text{Pt}_2\text{Ag}_4(\text{C}\equiv\text{C}^t\text{Bu})_8\text{Br}]^-$ (5%); 1362, $[\text{Pt}_2\text{Ag}_3(\text{C}\equiv\text{C}^t\text{Bu})_8]^-$ (4%).

$(\text{NBu}_4)_2[\text{Pt}_2\text{Cu}_4(\text{C}\equiv\text{C}^t\text{Bu})_8\text{Cl}_2]$ (**7**). $[\text{Pt}_2\text{Cu}_4(\text{C}\equiv\text{C}^t\text{Bu})_8]$ (0.090 g, 0.069 mmol; $(\text{NBu}_4)\text{Cl}$: 0.077 g, 0.278 mmol. Yield: 88%. Anal. Found (Calc.): N, 1.65 (1.51); C, 51.98 (51.96); H, 8.54 (7.85). Λ_M (in acetone solution): $276 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. IR (cm^{-1}): $\nu(\text{C}\equiv\text{C})$ 2012 (s). $^1\text{H NMR}$ (CDCl_3): δ 1.00 [t, $-\text{CH}_3(^n\text{Bu})$], 1.31 (s, ^tBu), 1.48 [m, $-\text{CH}_2(^n\text{Bu})$], 1.65 [m, $-\text{CH}_2(^n\text{Bu})$], 3.35 [m, $\text{NCH}_2(^n\text{Bu})$]. EI-MS: m/z 1328, $[\text{Pt}_2\text{Cu}_4(\text{C}\equiv\text{C}^t\text{Bu})_8\text{Cl}]^-$ (10%).

$(\text{NBu}_4)_2[\text{Pt}_2\text{Cu}_4(\text{C}\equiv\text{C}^t\text{Bu})_8\text{Br}_2]$ (**8**). $[\text{Pt}_2\text{Cu}_4(\text{C}\equiv\text{C}^t\text{Bu})_8]$ (0.090 g, 0.069 mmol; $(\text{NBu}_4)\text{Br}$: 0.090 g, 0.278 mmol. Yield 62%. Anal. Found (Calc.): N, 1.74 (1.45); C, 49.31 (49.58); H, 8.49 (7.49)%. Λ_M (in acetone solution): $289 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. IR (cm^{-1}): $\nu(\text{C}\equiv\text{C})$ 2014 (s). $^1\text{H NMR}$ (CDCl_3): at 20°C : δ 1.00 [t, $-\text{CH}_3(^n\text{Bu})$], 1.31 (s, ^tBu), 1.46 [m, $-\text{CH}_2(^n\text{Bu})$], 1.80

Table 2
Atomic coordinates ($\times 10^4$) for $(\text{NBu}_4)_2[\text{Pt}(\text{C}\equiv\text{CPh})_4(\text{CuBr})_2]$ (**4**)

	x	y	z
Pt(1)	0	0	0
Pt(2)	5000	5000	5000
Cu(1)	-241(1)	1660(1)	863(1)
Cu(2)	4146(1)	6103(1)	3748(1)
Br(1)	-99(1)	2150(1)	1902(1)
Br(2)	4410(1)	6618(1)	2618(1)
N(1)	1037(7)	-1237(6)	2000(4)
N(2)	2093(7)	5342(6)	6668(4)
C(1)	-1384(8)	983(7)	466(4)
C(2)	-2119(8)	1628(7)	753(4)
C(3)	-3163(8)	2299(8)	1052(5)
C(4)	-3219(11)	3276(10)	1161(7)
C(5)	-4252(13)	3916(11)	1442(8)
C(6)	-5205(13)	3584(15)	1613(8)
C(7)	-5202(13)	2649(15)	1513(10)
C(8)	-4175(11)	2002(10)	1231(7)
C(9)	890(8)	1029(7)	-8(4)
C(10)	1342(8)	1678(7)	52(5)
C(11)	2099(9)	2335(7)	19(5)
C(12)	3108(10)	2178(9)	-451(6)
C(13)	3823(11)	2817(11)	-498(8)
C(14)	3591(12)	3577(11)	-85(8)
C(15)	2600(13)	3732(10)	367(7)
C(16)	1839(11)	3118(9)	420(6)
C(17)	4491(7)	6443(7)	4707(4)
C(18)	4196(9)	7279(8)	4470(5)
C(19)	3969(11)	8355(8)	4339(6)
C(20)	4102(11)	8796(8)	3702(6)
C(21)	3897(14)	9838(10)	3607(8)
C(22)	3224(37)	10422(23)	4166(20)
C(23)	2966(38)	9978(26)	4784(21)
C(24)	3242(34)	8962(27)	4891(20)
C(22')	4018(40)	10395(30)	4096(29)
C(23')	4012(59)	9935(30)	4742(27)
C(24')	4061(42)	8897(31)	4889(26)
C(25)	4058(8)	4740(7)	4333(4)
C(26)	3503(8)	4661(7)	3905(5)
C(27)	2875(8)	4318(7)	3451(5)
C(28)	2833(10)	3328(9)	3493(6)
C(29)	2267(11)	2987(10)	3065(7)
C(30)	1725(10)	3589(13)	2592(7)
C(31)	1750(9)	4568(12)	2546(5)
C(32)	2315(9)	4947(9)	2969(5)
C(33)	1799(9)	-593(8)	1599(5)
C(34)	3080(10)	-909(10)	1649(7)
C(35)	3708(22)	-305(15)	1101(11)
C(35')	3643(35)	-83(23)	1310(14)
C(36)	3441(23)	701(18)	1424(13)
C(36')	3761(28)	-292(24)	559(16)
C(37)	1495(9)	-2319(7)	1797(5)
C(38)	1465(11)	-2476(8)	1057(6)
C(39)	2107(12)	-3517(9)	857(7)
C(40)	3385(12)	-3729(11)	788(7)
C(41)	1094(11)	-1258(8)	2758(5)
C(42)	694(14)	-243(10)	3053(6)
C(43)	540(18)	-284(12)	3793(8)
C(44)	170(19)	742(12)	4084(8)
C(45)	-199(8)	-802(8)	1842(5)
C(46)	-1100(9)	-1288(9)	2177(5)
C(47)	-2229(10)	-792(10)	1909(6)
C(48)	-3233(11)	-1177(12)	2238(7)
C(49)	1489(9)	5272(8)	7401(5)

Table 2 (continued)

C(50)	2261(9)	4694(10)	7913(5)
C(51)	1549(14)	4813(13)	8630(7)
C(51')	1577(40)	4144(26)	8460(23)
C(52)	781(16)	4087(14)	8695(11)
C(52')	545(32)	4824(29)	8881(19)
C(53)	2655(8)	4310(7)	6397(5)
C(54)	1841(10)	3642(9)	6412(7)
C(55)	2460(13)	2649(10)	6095(6)
C(56)	2715(13)	2773(11)	5387(8)
C(57)	1127(8)	5936(8)	6257(5)
C(58)	1548(9)	6103(9)	5514(5)
C(59)	544(11)	6626(10)	5150(6)
C(60)	836(13)	6853(12)	4428(7)
C(61)	3067(8)	5859(8)	6621(5)
C(62)	2710(10)	6926(8)	6821(6)
C(63)	3769(11)	7333(9)	6714(6)
C(64)	3434(14)	8393(11)	6909(8)

[m, $-\text{CH}_2(^n\text{Bu})$], 3.30 [m, $\text{NCH}_2(^n\text{Bu})$]; at -55°C : δ 0.91 [t, $-\text{CH}_3(^n\text{Bu})$], 1.21 (s, ^tBu), 1.30 [m, $-\text{CH}_2(^n\text{Bu})$], 1.35 [m, $-\text{CH}_2(^n\text{Bu})$], 3.27 [m, $\text{NCH}_2(^n\text{Bu})$] EI-MS: m/z 1373, $[\text{Pt}_2\text{Cu}_4(\text{C}\equiv\text{C}^t\text{Bu})_8\text{Br}]^-$ (12%); m/z 367 $[\text{Cu}_2(\text{C}\equiv\text{C}^t\text{Bu})_2\text{Br}]^-$ (100%).

Method (b).

Alternatively, complexes **5–7** can be prepared by reactions of $(\text{NBu}_4)_2[\text{Pt}(\text{C}\equiv\text{C}^t\text{Bu})_4] \cdot 2\text{H}_2\text{O}$ with MX (M = Ag, X = Cl, Br; M = Cu, X = Cl).

5: AgCl (0.027 g, 0.192 mmol) was added to a colourless solution of $(\text{NBu}_4)_2[\text{Pt}(\text{C}\equiv\text{C}^t\text{Bu})_4] \cdot 2\text{H}_2\text{O}$ (0.100 g, 0.096 mmol) in acetone solution (30 ml) and the mixture was stirred at room temperature for 30 min. The resulting pale yellow solution was concentrated to ca. 1 ml yielding **5** (yield 74%). Complexes **6**: $(\text{NBu}_4)_2[\text{Pt}(\text{C}\equiv\text{C}^t\text{Bu})_4] \cdot 2\text{H}_2\text{O}$: 0.100 g, 0.096 mmol; AgBr: 0.036 g, 0.192 mmol (75% yield) and **7** $(\text{NBu}_4)_2[\text{Pt}(\text{C}\equiv\text{C}^t\text{Bu})_4] \cdot 2\text{H}_2\text{O}$: 0.100 g, 0.096 mmol; CuCl: 0.019 g, 0.192 mmol (60% yield) were prepared similarly.

The reactions of $[\text{Pt}_2\text{M}_4(\text{C}\equiv\text{C}^t\text{Bu})_8]$ (M = Ag, Cu) with $(\text{NBu}_4)\text{Br}$ were also carried out in molar ratios 1:2 and 1:8. The reactions between $[\text{Pt}_2\text{M}_4(\text{C}\equiv\text{C}^t\text{Bu})_8]$ (M = Ag, Cu) and $(\text{NBu}_4)\text{Br}$ in a 1:2 molar ratio afforded the complexes **6** and **8** but in lower yields (**6**, 40%; **8** 50%) than when the reactions were carried out in a 1:4 molar ratio. Moreover, in these conditions small amounts of the starting materials $[\text{Pt}_2\text{M}_4(\text{C}\equiv\text{C}^t\text{Bu})_8]$ (20% for M = Ag and 15% for M = Cu) were recovered as second fractions. By using a large excess of Br^- (molar ratio $[\text{Pt}_2\text{M}_4(\text{C}\equiv\text{C}^t\text{Bu})_8]/(\text{NBu}_4\text{Br})$ of 1:8) the trinuclear derivatives $(\text{NBu}_4)_2[\text{PtM}_2(\text{C}\equiv\text{C}^t\text{Bu})_4\text{Br}_2]$ (M = Ag **9** and M = Cu **10**) were obtained.

3.1.3. $(\text{NBu}_4)_2[\{\text{Pt}(\text{C}\equiv\text{C}^t\text{Bu})_4\}(\text{MBr})_2]$ (M = Ag **9**; M = Cu **10**)

$(\text{NBu}_4)_2[\{\text{Pt}(\text{C}\equiv\text{C}^t\text{Bu})_4\}(\text{AgBr})_2]$ (**9**). A yellow suspension of $[\text{Pt}_2\text{Ag}_4(\text{C}\equiv\text{C}^t\text{Bu})_8]$ (0.144 g, 0.098 mmol) in

acetone (10 ml) was treated with 0.253 g (0.784 mmol) of $(\text{NBu}_4)\text{Br}$ (molar ratio 1:8) resulting in an almost immediate change to white. After stirring for 1 h the white precipitate was removed by filtration, washed with acetone (2 ml) and air-dried (yield 50%). Evaporation of the filtrate to small volume (1 ml) causes the precipitation of a white solid which was identified by IR spectroscopy as the hexanuclear derivative $(\text{NBu}_4)_2[\text{Pt}_2\text{Ag}_4(\text{C}\equiv\text{C}^t\text{Bu})_8\text{Br}_2]$ (**6**). Anal. Found (Calc.): N, 1.89 (2.03); C, 48.59 (48.74); H, 8.85 (7.89)% Λ_M (in nitromethane solution): $167 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$. IR (cm^{-1}): $\nu(\text{C}\equiv\text{C})$ 2056 (s). ^1H NMR (CDCl_3) (20°C): δ 0.97 [t, $-\text{CH}_3(^n\text{Bu})$], 1.27 (s, ^tBu), 1.41 [m, $-\text{CH}_2(^n\text{Bu})$], 1.64 [m, $-\text{CH}_2(^n\text{Bu})$], 3.36 [m, $\text{NCH}_2(^n\text{Bu})$]. EI-MS: m/z 1363 $[\text{Pt}_2\text{Ag}_3(\text{C}\equiv\text{C}^t\text{Bu})_8]^-$ (12%); m/z 1551 $[\text{Pt}_2\text{Ag}_4(\text{C}\equiv\text{C}^t\text{Bu})_8\text{Br}]^-$ (15%); m/z 457 $[\text{Ag}_2(\text{C}\equiv\text{C}^t\text{Bu})_2\text{Br}]^-$ (96%).

$(\text{NBu}_4)_2[\text{Pt}(\text{C}\equiv\text{C}^t\text{Bu})_4(\text{CuBr})_2]$ (**10**) was prepared similarly from a yellow solution of $[\text{Pt}_2\text{Cu}_4(\text{C}\equiv\text{C}^t\text{Bu})_8]$ (0.120 g, 0.093 mmol) and NBu_4Br (0.239 g, 0.741 mmol) in acetone. In this case the yield of the resulting white precipitate was of 68%. By evaporation of the filtrate a second fraction of **10** was obtained (15%). Anal. Found (Calc.): N, 1.96 (2.17); C, 52.37 (52.08); H, 8.25 (8.43). Λ_M (in nitromethane solution): $160 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$. IR (cm^{-1}): $\nu(\text{C}\equiv\text{C})$ 2024 (s). ^1H NMR (CDCl_3): at 25°C: δ 0.99 [t, $-\text{CH}_3(^n\text{Bu})$], 1.23 (s, ^tBu), 1.30 (s, ^tBu), 1.50 [m, $-\text{CH}_2(^n\text{Bu})$], 1.70 [m, $-\text{CH}_2(^n\text{Bu})$], 3.47 [m, $\text{NCH}_2(^n\text{Bu})$]. EI-MS: m/z 1373 $[\text{Pt}_2\text{Cu}_4(\text{C}\equiv\text{C}^t\text{Bu})_8\text{Br}]^-$ (20%); m/z 367 $[\text{Cu}_2(\text{C}\equiv\text{C}^t\text{Bu})_2\text{Br}]^-$ (100%).

3.1.4. $[\{\text{Pt}(\text{C}\equiv\text{CPh})_4\}(\text{AgPy})_2]$ (**11**)

Pyridine (19 μl , 0.235 mmol) was added to a yellow solution of $[\text{Pt}_2\text{Ag}_4(\text{C}\equiv\text{CPh})_8]$ (0.092 g, 0.056 mmol) in 10 ml of CH_2Cl_2 . Immediately the solution changed to deep yellow. After 2 h, the solution was evaporated to ca. 3 ml, producing a bright yellow precipitate, which was collected by filtration, washed with cold CH_2Cl_2 and air-dried. Yield 72%. Anal. Found (Calc.): N, 2.88 (2.88); C, 51.46 (51.82); H, 2.89 (3.11)%. IR (cm^{-1}): $\nu(\text{C}\equiv\text{C})$ 2066 (vs). ^1H NMR (CDCl_3): δ 7.05–7.32 (m, 20H Ph and 4H Py), 7.65 (t, 2H, py), 8.65 (d, 4H, py). EI-MS: m/z peak molecular not observed.

3.1.5. $[\{\text{Pt}(\text{C}\equiv\text{CPh})_4\}(\text{AgCN}^t\text{Bu})_2]$ (**12**)

To an orange-yellow solution of $[\text{Pt}_2\text{Ag}_4(\text{C}\equiv\text{CPh})_8]$ (0.120 g, 0.074 mmol) in 10 ml of CH_2Cl_2 was added CN^tBu (34 μl , 0.296 mmol) (1:4 molar ratio). Immediately the solution turned lemon-yellow. After stirring for 10 min at room temperature, the reaction mixture was concentrated to ca. 2 ml. Addition of diethyl ether (5 ml) caused the precipitation of **12** as a yellow microcrystalline solid, which was filtered off, washed with diethyl ether and air-dried (yield 68%). Anal. Found

(Calc.): N, 2.91 (2.85); C, 51.12 (51.39); H, 3.75 (3.90)% IR (cm^{-1}): $\nu(\text{C}\equiv\text{N})$ 2184 (vs); $\nu(\text{C}\equiv\text{C})$ 2077 (s). ^1H NMR (CD_3COCD_3): δ 1.23 (s, 18H, Bu^t), 7.04, 7.32 (m, 20H, Ph). EI-MS: m/z molecular peak not observed.

3.1.6. $[\text{Pt}_2\text{Ag}_4(\text{C}\equiv\text{C}^t\text{Bu})_8(\text{Py})_2]$ (**13**)

To a yellow solution of $[\text{Pt}_2\text{Ag}_4(\text{C}\equiv\text{C}^t\text{Bu})_8]$ (0.096 g, 0.065 mmol) in acetone (10 ml) was added pyridine (22 μl , 0.274 mmol). Immediately the solution turned pale-yellow. The mixture was stirred for 2 h at room temperature, and then evaporated to ca. (\approx 3 ml). Addition of hexane (2 ml) and cooling to -30°C for 24 h rendered **13** as a yellow microcrystalline solid, which was filtered, washed with n-hexane and air-dried (yield 50%). Anal. Found (Calc.): N, 1.51 (1.72); C, 42.28 (42.77); H, 5.07 (5.07). IR (cm^{-1}): $\nu(\text{C}\equiv\text{C})$ 2048 (s). ^1H NMR (CDCl_3): δ 1.29 (s, 72H, ^tBu), 7.60 (m, 4H, py), 8.05 (m, 2H, py), 8.70 (m, 4H, py). EI-MS: m/z molecular peak not observed.

3.2. Reactions of $[\text{Pt}_2\text{M}_4(\text{C}\equiv\text{CR})_8]$ with L (L = PEt_3 , PPh_3)

3.2.1. Reactions with PEt_3

PEt_3 was added to a suspension (R = Ph) or a solution (R = ^tBu) of $[\text{Pt}_2\text{M}_4(\text{C}\equiv\text{CR})_8]$ (M = Ag or R = Ph or ^tBu ; M = Cu, R = Ph) in 20 ml of acetone (molar ratio 4:1) and the mixture was stirred at room temperature for 1 h. In all cases, the corresponding polymeric acetylide $\{\text{Ag}(\text{C}\equiv\text{CR})\}_n$ (white; R = Ph, 50%, R = ^tBu , 75%) or $\{\text{Cu}(\text{C}\equiv\text{CR})\}_n$ (yellow-green; R = Ph, 50%) precipitated (confirmed by IR spectra). After filtration, the mother liquors (R = ^tBu) were evaporated to dryness and the residue treated with water to give a white solid identified as *trans*- $[\text{Pt}(\text{C}\equiv\text{C}^t\text{Bu})_2(\text{PEt}_3)_2]$ [**10**] (yield 40%). For R = Ph, evaporation of the mother liquors to ca. 3 ml gave pale yellow crystals which were identified (analyses, IR and ^{31}P NMR) as *trans*- $[\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{PEt}_3)_2]$ [**13**] (yield 40%).

To a yellow solution of $[\text{Pt}_2\text{Cu}_4(\text{C}\equiv\text{C}^t\text{Bu})_8]$ (0.082 g, 0.063 mmol) in acetone (20 ml) were added 39 μl (0.265 mmol) of PEt_3 and the mixture was stirred at room temperature for 1 h. The resulting solution was evaporated to ca. 3 ml and cooled at -20°C for 2 days; 50% of the starting material precipitated and was recovered.

3.2.2. Reactions with PPh_3

To a yellow solution of $[\text{Pt}_2\text{Cu}_4(\text{C}\equiv\text{C}^t\text{Bu})_8]$ (0.065 g, 0.050 mmol) in 20 ml of acetone was added PPh_3 (0.053 g, 0.201 mmol), and the mixture was stirred for 1 h. The white precipitate was filtered off. Recrystallization from CHCl_3 /acetone gave colourless crystals of *trans*- $[\text{Pt}(\text{C}\equiv\text{C}^t\text{Bu})_2(\text{PPh}_3)_2]$ [**14**] (yield 45%). A similar result was obtained with $[\text{Pt}_2\text{Ag}_4(\text{C}\equiv\text{C}^t\text{Bu})_8]$ (0.1 g,

0.068 mmol; PPh₃: 0.071 g, 0.272 mmol), which rendered *trans*-[Pt(C≡C^tBu)₂(PPh₃)₂] (yield 66%).

A dark-garnet suspension of [Pt₂Cu₄(C≡CPh)₈] (0.101 g, 0.069 mmol) was treated with 0.073 g (0.278 mmol) of PPh₃ resulting in an immediate change to yellow. The mixture was stirred for 12 h, and the resulting yellow solid was filtered off, washed with acetone and air-dried. The IR spectrum of this solid is identical to that of *trans*-[Pt(C≡CPh)₂(PPh₃)₂]. However, it analyses as [Pt(C≡CPh)₂(PPh₃)₂] · 2(CuC≡CPh). Found: C, 65.38; H, 4.37. Calc.: C, 65.27, H, 4.03%. This solid was dissolved in chloroform (15 ml) and stirred. Immediately a yellow green precipitate of {Cu(C≡CPh)}_n separates. The mixture was stirred for 3 days and then filtered. Evaporation of the filtrate to dryness and addition of 3 ml of acetone yields lemon-yellow crystals of *trans*-[Pt(C≡CPh)₂(PPh₃)₂] [15] (IR, analyses, ³¹P NMR) (yield 68%).

If the reaction is carried out in CHCl₃ (3 days) only CuC≡CPh precipitate (IR). From the mother liquors, *trans*-[Pt(C≡CPh)₂(PPh₃)₂] can be obtained in very high yield (81%).

To a yellow suspension of 0.103 g (0.063 mmol) of [Pt₂Ag₄(C≡CPh)₈] in 30 ml of acetone was added PPh₃ (0.066 g, 0.253 mmol) at room temperature, immediately giving a yellow solution. After a few minutes, a yellow precipitate was formed. The mixture was stirred for 30 min and then the solid was filtered off, washed with acetone and air-dried. The IR spectrum of this solid is identical to that *trans*-[Pt(C≡CPh)₂(PPh₃)₂], but it analyses as [Pt(C≡CPh)₂(PPh₃)₂] · 2(AgC≡CPh). C, 61.20 (60.95); H, 4.11 (3.76). This solid was dissolved in CHCl₃ (15 ml) giving a yellow turbid solution. The mixture was stirred for 2 days and then filtered. Evaporation of the filtrate to small volume (c. 1 ml) gave crystals of *trans*-[Pt(C≡CPh)₂(PPh₃)₂] (yield 17%) (IR, analyses, ³¹P NMR). From the filtrate only mixtures of uncharacterized complexes were obtained.

3.3. Crystal structure analysis of 4

Yellow crystals of 4 were grown by slow evaporation of an acetone solution of the complex at room temperature.

(NBu₄)₂[(Pt(C≡CPh)₄)(CuBr)₂]: C₆₄H₉₂Br₂Cu₂N₂Pt, M = 1371.4, triclinic, space group P1 (No. 2), *a* = 12.148(4), *b* = 13.977(5), *c* = 20.053(4) Å, α = 84.71(2)°, β = 80.81(2)°, γ = 74.38(3)°, V = 3232.7(17) Å³, Z = 2, ρ_{calc} = 1.409 g cm⁻³, λ = 0.71073 Å, μ = 4.083 mm⁻¹, F(000) = 1392, T = 293 K.

Diffraction measurements were made with a Nicolet (Siemens) four-circle Autodiffractometer (Crystalytics, Co.) using graphite monochromated Mo Kα X-radiation on a single crystal (approximate dimensions 0.50 × 0.50 × 0.65 mm) mounted in a thin-walled glass capil-

lary sealed with epoxy. Cell dimensions were determined from the setting angle values of 15 centred reflections. A total of 9445 diffracted intensities (including checks) were measured in a unique hemisphere of reciprocal space for 3.0 < 2θ < 45.8° by ω scans. Six check reflections remeasured after every 300 ordinary data showed no decay and ca. 3% variation over the period of data collection. Of the non-check intensity data collected, 8887 unique observations remained after averaging of duplicate and equivalent measurements; of these 6016 with I > 2σ(I) were retained for use in structure solution and refinement. An absorption correction was applied in the basis of 252 azimuthal scan data, maximum and minimum transmission coefficients were 0.682 and 1.000, respectively. Lorentz and polarization corrections were applied. All calculations were made with programs of the SHELXTL-PLUS system package [16]. Complex neutral-atom scattering factors were taken from Ref. [17]. The structure was solved by heavy atom (Patterson and difference Fourier) methods, and refined by full-matrix least-squares against F. Three carbon atoms of one of the phenyl rings show disorder over two positions and were refined with partial occupancies of 0.54 [C(22), C(23) and C(24)] and 0.46 [C(22'), C(23') and C(24')]. In each NBu₄⁺ cation there are also two carbon atoms (one terminal methyl carbon atom and the methylene carbon bonded to it) disordered over two positions. These atoms were refined with the following partial occupancies: 0.56 [C(35) and C(36)] and 0.44 [C(35') and C(36')] for the tetrabutylammonium group containing the N(1) atom, and 0.73 [C(51) and C(52)] and 0.27 [C(51') and C(52')] for the tetrabutylammonium group containing the N(2) atom. All non-hydrogen atoms, except for the disordered ones in the tetrabutylammonium groups, were assigned anisotropic displacement parameters and refined without positional constraints. For the disordered atoms in the NBu₄⁺ cations, the C–C bond distance were restrained to 1.54(1) Å. Hydrogen atoms were constrained to idealized geometries (C–H 0.96 Å) (except for the carbon atoms of the whole phenyl ring in the anion, and the butyl chains of the cations containing disordered atoms) and a common refined isotropic displacement parameter was assigned. Refinement of the 667 least-squares variables converged smoothly to residual indices R = 0.042, wR = 0.049, S = 1.07 [18]. Weights, w, were set equal [σ_c²(F_o) + gF_o²]⁻¹ where σ_c²(F_o) is the variance in F_o due to counting statistics and g = 0.0010 was chosen to minimize the variation in S as a function of F_o. Final difference electron density maps showed no features outside the range +0.59 to -0.90 e Å⁻³. Table 2 reports the atomic positional parameters. A complete list of bond lengths and angles, atomic coordinates and hydrogen atoms parameters are available from the Cambridge Crystallographic Data Center.

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