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# Synthesis of anionic pentafluorophenyl platinum–silver acetylide complexes. Molecular structures of $(NBu_4)[Pt(C_6F_5)_2(\mu\text{-}C{\equiv}CPh)_2Ag(PPh_3)]$ and $(NBu_4)_2[\{Pt(C_6F_5)_2(\mu\text{-}C{\equiv}CPh)_2Ag\}_2(\mu\text{-dppe})]$

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**Abstract**

Heterobinuclear alkynyl-bridged complexes $(NBu_4)[Pt(C_6F_5)_2(\mu\text{-}C{\equiv}CR)_2AgL]$ (R = Ph or $^t$Bu; L = $PPh_3$ or $PEt_3$) (**1–4**) are obtained by treating the anionic tetranuclear platinum-silver derivatives $(NBu_4)_2[Pt_2Ag_2(C_6F_5)_4(C{\equiv}CR)_4]$ (R = Ph or $^t$Bu) with $PPh_3$ or $PEt_3$ (molar ratio 1:2 or 1:4), whereas treatment with the bidentate 1,2-bis(diphenylphosphino)ethane (dppe) (molar ratio 1:1) gives tetranuclear complexes $(NBu_4)_2[\{Pt(C_6F_5)_2(\mu\text{-}C{\equiv}CR)_2Ag\}_2(\mu\text{-dppe})]$ (R = Ph **5**; R = $^t$Bu **6**). The structures of $(NBu_4)[Pt(C_6F_5)_2(\mu\text{-}C{\equiv}CPh)_2AgPPh_3]$ (**1**) and $(NBu_4)_2[\{Pt(C_6F_5)_2(\mu\text{-}C{\equiv}CPh)_2Ag\}_2(\mu\text{-dppe})]$ (**5**) have been established by single-crystal X-ray diffraction studies. In the solid state, the structure of the anion of complex **1** reveals that the two metal atoms [Pt ··· Ag 3.059(1) Å] are asymmetrically bridged by two phenylacetylide groups, each of which forms a $\sigma$-bond to platinum and a side-on $\pi$-bond to silver. The anion of compound **5**, which possesses an inversion centre, is formed by two identical $\{Pt(C_6F_5)_2(\mu\text{-}C{\equiv}CPh)_2Ag\}$ units connected through a dppe ligand. Each silver atom is asymmetrically $\pi$-bonded to each acetylide group and completes their trigonal coordination by bonding to a phosphorus atom of the dppe. $^1$H, $^{19}$F, $^{31}$P NMR data indicate that all complexes exhibit dynamic behaviour in solution.

## 1. Introduction

There is a rich and extensive chemistry derived from metal acetylide compounds. Since the preparation of the first metal acetylide complex in the 1950s, a wide variety of acetylide complexes of transition metals and metal clusters displaying a range of coordination types have been isolated [1–4]. On the other hand acetylide ligands bound to more than one site are susceptible to both nucleophilic and electrophilic attack, and such reactivity has been used to form new hydrocarbon ligands in polynuclear complexes [2–5]. This work deals with the chemical reactivity of platinum acetylide complexes.

We have recently described the preparation of anionic tetranuclear platinum–silver acetylide complexes $Q_2[Pt_2Ag_2(C_6F_5)_4(C{\equiv}CR)_4]$ (R = Ph or $^t$Bu; Q = $PMePh_3$ or $NBu_4$) consisting of two square-planar *cis*-$Pt(C_6F_5)_2(C{\equiv}CR)_2$ fragments connected by two silver atoms which are $\pi$-bonded to two acetylide groups, one associated with each platinum environment [6]. Such complexes were readily obtained by reaction of $Q_2[Pt(C_6F_5)_2(C{\equiv}CR)_2]$ and AgCl in acetone, suggesting that in these anionic systems the alkynyl ligands have a higher coordinating ability towards $Ag^+$ than the chloride ion. The opposite has been observed by Riera *et al.* [7] in the cationic silver compound $[Mn_2Ag(\mu\text{-}C{\equiv}C^tBu)_2(CO)_6(dppe)_2]BF_4$ which reacts with $[NMe_3(CH_2Ph)]Cl$ producing AgCl and $[Mn(C{\equiv}C^tBu)(CO)_3(dppe)]$. This fact suggests a remarkable stability for these anionic tetranuclear platinum–silver complexes and we therefore considered it of interest to explore their reactivity. In the present paper, we report the reactivity of $(NBu_4)_2[Pt_2Ag_2(C_6F_5)_4(C{\equiv}CR)_4]$ (R = Ph or $^t$Bu) towards different phosphines, to give anionic polynuclear platinum–silver acetylide complexes with two

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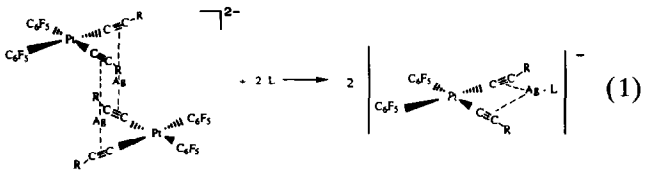
acetylide groups acting as $\mu-\eta^2$ ($\sigma-$Pt, $\pi-$Ag) bridges between the platinum and the silver.

## 2. Results and discussion

### 2.1. Reactions with monophosphines: binuclear complexes

Treatment of pale yellow solutions of $(NBu_4)_2[Pt_2Ag_2(C_6F_5)_4(C{\equiv}CR)_4]$ (R = Ph or $^t$Bu) with $PPh_3$ or $PEt_3$, independent of the molar ratio used (1:2 or 1:4 ratio, Ag/L 1:1 or 1:2, respectively), leads to the formation of binuclear derivatives $(NBu_4)[Pt(C_6F_5)_2(\mu\text{-}C{\equiv}CR)_2AgL]$ (**1–4**) according to eqn. (1).



(1)

R = Ph L = $PPh_3$ **1**
R = $^t$Bu L = $PPh_3$ **2**
R = Ph L = $PEt_3$ **3**
R = $^t$Bu L = $PEt_3$ **4**

The formulation of the anions in complexes **1–4** as dimetal species with *cis*-$Pt(C_6F_5)_2(C{\equiv}CR)_2$ units chelating the "AgL" fragment (eqn. (1)) was made on the basis of their analyses, conductivities, IR spectra, $^1$H NMR spectra (see Experimental section), $^{19}$F and $^{31}$P NMR spectra (Table 1) and an X-ray diffraction study of complex **1**. Their conductivities in acetone solutions are as expected for 1:1 electrolytes [8]. The IR spectra of all complexes show $\nu$(C≡C) vibrations (two in the case of **1**, **3** and one, broadened for **2**, **4**) significantly shifted to higher wavenumbers compared to those of the tetranuclear precursors (R = Ph, 2038 $cm^{-1}$ and, R = $^t$Bu, 2033 $cm^{-1}$) but in the range expected for $\sigma-\pi$ coordination of the acetylide [6,9,10]. Moreover, two IR absorptions corresponding to the X-sensitive mode of $C_6F_5$ were found in the 800–770 $cm^{-1}$ region, confirming that the *cis* disposition of $C_6F_5$ groups is retained [11]. It should be noted that although complexes **1–4** are formed by the action of phosphine (L) on the $\pi$-Ag(C≡C) bonds of the starting materials, the use of further amounts of L does not produce breaking of the $\pi$-Ag(C≡C) bonds in **1–4**.

### 2.2. Structure of $(NBu_4)[Pt(C_6F_5)_2(\mu\text{-}C{\equiv}CPh)_2Ag(PPh_3)]$ (1)

In order to characterise the acetylide bridges, the structure of one complex of this family (**1**) has been established by X-ray diffraction. Suitable crystals were obtained by slow diffusion of hexane through a chloroform solution of **1** at room temperature.

An drawing of the anion is presented in Fig. 1. Selected bond distances and angles are listed in Table 2. The anion is a non-planar platinum–silver dinuclear species with two acetylide ligands bridging between them in unusual fashion, each forming a $\sigma$-bond to platinum and a side-on $\pi$-bond to silver.

TABLE 1. $^{19}$F and $^{31}$P NMR data of the complexes at different temperatures

| Complex | $^{19}$F NMR | | | | $^{31}$P NMR | | | |
|---|---|---|---|---|---|---|---|---|
| | $T$ (°C) | $F_{oo'}$ [c] | $F_p$ | $F_{mm'}$ | $T$ (°C) | (P) | $J(^{109}Ag-P)$ (Hz) | $J(^{107}Ag-P)$ (Hz) |
| **1** $(NBu_4)[Pt(C_6F_5)_2(\mu\text{-}C{\equiv}CPh)_2Ag(PPh_3)]$ [a] | 20 [d] | −117.1 [403] | −167.8 [e] | | −60 [f] | 12.6 | 657 | 570 |
| **2** $(NBu_4)[Pt(C_6F_5)_2(\mu\text{-}C{\equiv}C^tBu)_2Ag(PPh_3)]$ [b] | −60 [g] | −113.9 [418] | −167.9 | −167.1 | −85 [h] | 13.1 | 604 [i] | |
| **3** $(NBu_4)[Pt(C_6F_5)_2(\mu\text{-}C{\equiv}CPh)_2Ag(PEt_3)]$ [a] | 20 [d] | −117.1 [405] | −168.0 [e] | | −60 [j] | 6.0 | 675 | 584 |
| **4** $(NBu_4)[Pt(C_6F_5)_2(\mu\text{-}C{\equiv}C^tBu)_2Ag(PEt_3)]$ [a] | 20 [d] | −116.1 [≈ 400] | −168.4 [e] | | 20 | 3.6 | 686 | 592 |
| **5** $(NBu_4)_2[\{Pt(C_6F_5)_2(\mu\text{-}C{\equiv}CPh)_2Ag\}_2(dppe)]$ [b] | −60 [k] | −114.3 [403] | −166.5 [e] | | −60 [l] | 10.8 | 610 [i] | |
| **6** $(NBu_4)_2[\{Pt(C_6F_5)_2(\mu\text{-}C{\equiv}C^tBu)_2Ag\}_2(dppe)]$ [b] | −60 [m] | −113.8 [420] | −167.9 | −167.0 | −85 [n] | 9.4 | 603 [i] | |

[a] in $CDCl_3$. [b] in $CD_3COCD_3$. [c] $^3J$(Pt–$F_o$) values (Hz) are given in brackets. [d] The same pattern is found at −60°C (see text). [e] Overlapping of signals due to $F_p$ and $F_{mm'}$. [f] At −30°C two broad resonances ($\delta$(P) = 13.0, $^1J(^{109,107}Ag-P)$ = 618 Hz); at 20°C no $^{31}$P signal is observed; at 50°C one broad signal centred at 10.5 ppm. [g] See Fig. 3 for the spectra at 20°C and 50°C. [h] At −60°C two broad resonances centred at 11.6 ppm (14.38 and 8.80 ppm, respectively); at −30°C one broad resonance at 10.26 ppm; at 50°C one signal at 5.4 ppm which is sharper than that observed at −30°C. [i] $^1J(^{109,107}Ag-P)$. [j] At 20°C two broad signals ($\delta$(P) = 8.1, $^1J(^{109,107}Ag-P)$ = 642 Hz). [k] At 25°C the spectrum showed two resonances in the $F_o$ region; one at −114.3 ppm which is assigned to **5** and other at −112.7 ppm corresponding to starting complex (see text) (ratio 9:1). In addition, two multiplets at −167.0 and −167.6 ppm due to unresolved overlapping of $F_m$ and $F_p$ signals. [l] At −30°C two multiplets centred at 10.9 ppm and separated at 627 Hz; at 25°C two broad multiplets at 14.08 and 7.26 ppm, respectively; at 50°C coalescence of the signals. [m] At 25°C $\delta(F_{oo'})$ = −113.8; $\delta(F_p)$ = −169.1; $\delta(F_{mm'})$ = −167.95; other signals corresponding to $(NBu_4)_2[PtAg_2(C_6F_5)_4(C{\equiv}C^tBu)_2]$ are also observed. $\delta F_{oo'}$ = −111.87; $\delta(F_p)$ = −168.8 (ratio 5.6:1); at 50°C $\delta(F_{oo'})$ = −113.8, $\delta(F_p)$ = −169.5, $\delta(F_{mm'})$ = −168.4; signals due to $(NBu_4)_2[PtAg_2(C_6F_5)_4(C{\equiv}C^tBu)_2]$ $\delta$(F)) = −111.8; $\delta(F_p)$ = −169.15, ($F_{mm'}$ overlapping with those of **6**) (ratio 2.9:1). [n] At −60°C two multiplets centred at 9.4 ppm and separated at 603 Hz; at −30°C two broad signals at 5.4 and 13.29 ppm, respectively, and at 20°C coalescence of the signals is observed.

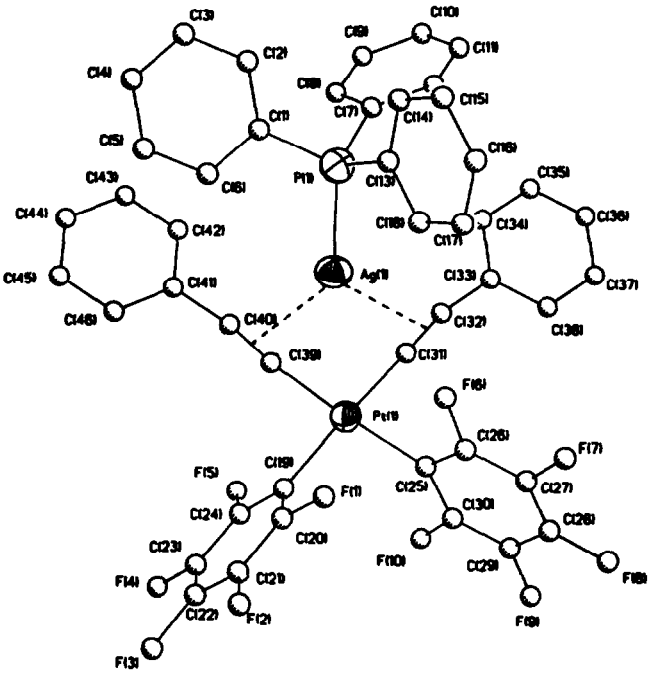


Fig. 1. View of the structure of the anion $[Pt(C_6F_5)_2(\mu\text{-}C{\equiv}CPh)_2AgPPh_3]^-$ in complex **1** with the atomic numbering scheme.

TABLE 2. Selected bond distances (Å) and bond angles (°) for complex **1**

| | | | |
|---|---|---|---|
| Ag(1)–Pt(1) | 3.059(1) | C(19)–Pt(1) | 2.054(6) |
| C(25)–Pt(1) | 2.033(7) | C(31)–Pt(1) | 1.990(6) |
| C(39)–Pt(1) | 2.012(7) | P(1)–Ag(1) | 2.370(2) |
| C(31)–Ag(1) | 2.379(7) | C(32)–Ag(1) | 2.679(7) |
| C(39)–Ag(1) | 2.367(6) | C(40)–Ag(1) | 2.545(7) |
| C(1)–P(1) | 1.816(5) | C(7)–P(1) | 1.803(6) |
| C(13)–P(1) | 1.815(6) | C(32)–C(31) | 1.240(9) |
| C(33)–C(32) | 1.437(8) | C(40)–C(39) | 1.226(10) |
| C(41)–C(40) | 1.437(9) | | |
| C(19)–Pt(1)–Ag(1) | 131.9(2) | C(25)–Pt(1)–Ag(1) | 125.2(2) |
| C(25)–Pt(1)–C(19) | 92.4(3) | C(31)–Pt(1)–Ag(1) | 51.0(2) |
| C(31)–Pt(1)–C(19) | 176.8(3) | C(31)–Pt(1)–C(25) | 86.0(3) |
| C(39)–Pt(1)–Ag(1) | 50.7(2) | C(39)–Pt(1)–C(19) | 89.7(3) |
| C(39)–Pt(1)–C(25) | 175.0(3) | C(39)–Pt(1)–C(31) | 92.1(3) |
| P(1)–Ag(1)–Pt(1) | 151.5(1) | C(31)–Ag(1)–Pt(1) | 40.6(2) |
| C(31)–Ag(1)–P(1) | 137.1(2) | C(32)–Ag(1)–Pt(1) | 68.1(1) |
| C(32)–Ag(1)–P(1) | 115.2(1) | C(32)–Ag(1)–C(31) | 27.6(2) |
| C(39)–Ag(1)–Pt(1) | 41.1(2) | C(39)–Ag(1)–P(1) | 145.7(2) |
| C(39)–Ag(1)–C(31) | 74.8(2) | C(39)–Ag(1)–C(32) | 99.0(2) |
| C(40)–Ag(1)–Pt(1) | 69.7(2) | C(40)–Ag(1)–P(1) | 121.6(2) |
| C(40)–Ag(1)–C(31) | 101.2(2) | C(40)–Ag(1)–C(32) | 121.2(2) |
| C(40)–Ag(1)–C(39) | 28.6(2) | C(1)–P(1)–Ag(1) | 116.0(2) |
| C(7)–P(1)–Ag(1) | 115.5(2) | C(7)–P(1)–C(1) | 104.7(2) |
| C(13)–P(1)–Ag(1) | 110.1(2) | C(13)–P(1)–C(1) | 103.7(3) |
| C(13)–P(1)–C(7) | 105.7(2) | Ag(1)–C(31)–Pt(1) | 88.4(3) |
| C(32)–C(31)–Pt(1) | 177.8(6) | C(32)–C(31)–Ag(1) | 89.8(5) |
| C(31)–C(32)–Ag(1) | 62.6(4) | C(33)–C(32)–Ag(1) | 129.9(4) |
| C(33)–C(32)–C(31) | 167.0(7) | Ag(1)–C(39)–Pt(1) | 88.2(3) |
| C(40)–C(39)–Pt(1) | 170.9(6) | C(40)–C(39)–Ag(1) | 83.8(4) |
| C(39)–C(40)–Ag(1) | 67.6(4) | C(41)–C(40)–Ag(1) | 120.6(4) |
| C(41)–C(40)–C(39) | 170.5(7) | | |

The Pt atom is in an approximately square planar environment formed by the two C-*ipso* atoms of $C_6F_5$ groups (mutually *cis*) and one carbon atom of each C≡CPh ligand. The Pt–C distances (to $C_6F_5$ or C≡CPh groups) are similar to those found in the tetranuclear precursor $(NBu_4)_2[Pt_2Ag_2(C_6F_5)_4(C{\equiv}CPh)_4]$ [6]. The silver atom is linked to one $PPh_3$ and participates in asymmetric $\pi$ linkages to the triple bonds of the two acetylides. The silver–phosphorus bond length (Ag–P = 2.370(2) Å) closely matches those values reported for other polynuclear complexes containing the $Ag(PPh_3)$ unit [12–14]. The bonding mode between the C≡CPh groups and the Ag is shown schematically in Fig. 2(a). The Ag–$C_\beta$ distances are significantly longer than the Ag–$C_\alpha$ distances so that the interaction between the acetylides and the Ag centre is very asymmetric. This has been previously observed in other polynuclear complexes containing Ag $\pi$-coordinated to acetylide groups [14–17]. Moreover the distance between the silver and the midpoints of the C≡C triple bonds (Ag–$C_{39,40}$ 2.379 Å; Ag–$C_{31,32}$ 2.452 Å) are somewhat different, with Ag appearing unexpectedly closer to that

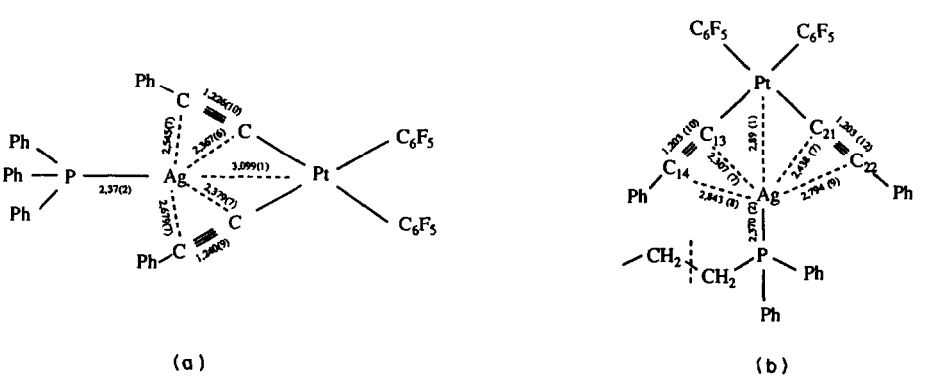
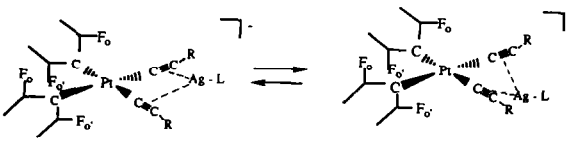


Fig. 2. Schematic view of the $\mu$-$\eta^2$ bonded acetylide groups for the complexes (a) $(NBu_4)$ $[Pt(C_6F_5)_2(\mu\text{-}C{\equiv}CPh)_2AgPPh_3]$ (**1**) and (b) $(NBu_4)_2[\{Pt(C_6F_5)_2(\mu\text{-}C{\equiv}CPh)_2Ag\}_2(\mu\text{-dppe})]$ (**5**) with bond lengths in Ångstroms.

acetylide whose C≡C distance is the shorter (C(39)–C(40) 1.226(10) Å; C(31)–C(32) 1.240(9) Å). The midpoints of the C≡C triple bonds and the phosphorus atom form an almost planar trigonal environment around the silver. The dihedral angle formed by the coordination planes of the platinum atom (best least squares plane containing Pt(1), C(19), C(25), C(31), C(39)) and silver atom (best least squares plane formed by Ag(1), P(1), midpoint C(39)–C(40), midpoint C(31)–C(32)) is 126.81(13)°. The Ag–C distances are longer than those observed in the starting material, $[Pt_2Ag_2(C_6F_5)_4(C{\equiv}CPh)_4]^{2-}$, indicating slightly stronger Ag-$\pi$ acetylide interactions in the latter case. The $C_\alpha$–$C_\beta$ distances are similar to C≡C distances in other $\sigma$, $\pi$ phenylacetylide polynuclear complexes [6,9,10,14,15]. Both acetylene skeletons Pt–$C_{39}$–$C_{40}$–$C_{41}$ and Pt–$C_{31}$–$C_{32}$–$C_{33}$ are slightly distorted from linearity with a *trans*-bent geometry. The angles at $C_\alpha$ (Pt–$C_{39}$–$C_{40}$, 170.9(6)°; Pt–$C_{31}$–$C_{32}$, 177.8°) and at $C_\beta$ ($C_{39}$–$C_{40}$–$C_{41}$, 170.5(7)°; $C_{31}$–$C_{32}$–$C_{33}$, 167.0(7)°) lie within the usual range for $\mu$-$\eta^2$-acetylide ligands [6,9,10,18]. Finally, although the Pt ··· Ag distance is slightly shorter than those found in $[Pt_2Ag_2(C_6F_5)_4(C{\equiv}CPh)_4]^{2-}$ (3.10 and 3.15 Å), it is considerably longer than those reported for platinum–silver bonds [12].

### 2.3. NMR spectra

Complexes **1–4** display dynamic behaviour in solution. Although $^1H$ NMR spectra of these complexes at room temperature are consistent with static molecules (see Experimental section) the $^{19}F$ and $^{31}P\{^1H\}$ NMR spectra (see Table 1) are not. The $^{31}P$ NMR spectrum at room temperature of complex **4** (R = $^t$Bu, L = $PEt_3$) shows the expected typical pair of doublets centred at 3.6 ppm due to coupling of $^{31}P$ to both $^{107}Ag$ and $^{109}Ag$ isotopes. The magnitudes of the coupling constants, $J(^{107}Ag–P) = 592$ and $J(^{109}Ag–P) = 686$ Hz, are consistent with direct Ag–P bonding [19] and their ratio satisfies the gyromagnetic ratio $^1J(^{109}Ag–P)/{}^1J(^{107}Ag–P) = \gamma^{109}Ag/\gamma^{107}Ag$) [19]. In the analogous derivative **3** (R = Ph, L = $PEt_3$), the separate splittings due to the two isotopes of silver are not resolved at room temperature; the $^{31}P$ NMR spectrum exhibits a broad doublet centred at 8.1 ppm with a spacing of 642 Hz ($^1J(^{109,107}Ag–P) = 642$ Hz). However, at low temperature (−50°C) the pair of doublets ($\delta(P) = 6.0$ ppm, $^1J(^{109}Ag–P) = 675$ Hz, $^1J(^{107}Ag–P) = 584$ Hz) are clearly observed. If it is assumed that **3** and **4** have a non-planar structure similar to **1** and that the two *cis*-$C_6F_5$ groups in square-planar platinum or palladium environments [20] are not free to rotate about their M–C bonds, then one should expect five distinct signals corresponding to the five fluorine atoms of the equivalent $C_6F_5$ ligands in the $^{19}F$ NMR spectrum. However, the room temperature $^{19}F$ NMR spectrum of either complex (**3** or **4**) shows only two signals in a ratio 2:3 corresponding to the $F_{oo'}$ and $F_{mm'} + F_p$, respectively (see Table 1). This suggests that a dynamic process, probably a rapid intramolecular exchange of the AgL unit as depicted in eqn. (2), produces a time-averaged plane of symmetry at room temperature which renders the two halves of each $C_6F_5$ group equivalent. The spectra of both complexes (**3** and **4**) at −60°C show the same sharp pattern as at room temperature, indicating that the dynamic process is very rapid, even at low temperature.




(2)

The dynamic behaviour of the triphenylphosphine derivatives $(NBu_4)[Pt(C_6F_5)_2(\mu\text{-}C{\equiv}CR)_2Ag(PPh_3)]$ (R = Ph, **1**, R = $^t$Bu, **2**) is more complex since both display lability of the $PPh_3$ ligand at room temperature. We measured the $^{31}P$ and $^{19}F$ NMR spectra at several temperatures. At 50°C, the $^{31}P$ NMR spectrum of complex **1** exhibits one broad resonance centred at 10.5 ppm, suggesting a fast exchange of the $PPh_3$ on the NMR time scale. No $^{31}P$ signal is observed at room temperature, but when the spectrum is recorded at −30°C, two broad signals centred at 13.0 ppm and separated by 618 Hz are observed. Finally, at −60°C the expected two doublets arising from $^{109}Ag$–P and $^{107}Ag$–P spin-spin coupling ($\delta(P) = 12.6$ ppm; $J(^{109}Ag–P) = 657$, $J(^{107}Ag–P) = 570$ Hz) are clearly observed. At −60°C the $^{19}F$ NMR spectrum of **1** shows only two signals in a 2:3 ratio ($\delta F_{oo'} = -116.4$ ppm and $F_{mm'} + F_p = -166.4$ ppm) again suggesting a time-averaged plane of symmetry in the complex. A similar pattern is observed at room temperature (see Table 1).

For complex **2**, even at −85°C, the $^{31}P$ NMR spectrum exhibits only two broad signals centred at 13.1 ppm and separated by 604 Hz. At −60°C, there are two broader resonances, but now centred at 11.6 ppm. At about −30°C, both signals converge to one broad resonance at 10.26 ppm, which by 50°C is sharper and shifted upfield to 5.4 ppm. However, no resonance corresponding to uncoordinated phosphine is observed. Only at −60°C does the $^{19}F$ NMR spectrum of **2** display pattern (three signals in a 2:2:1 ratio; $\delta F_{oo'} = -113.95$, $\delta F_{mm'} = -167.13$, $\delta F_p = -167.92$ ppm (see Fig. 3)) similar to those found at room and low temperature for **1**, **3** and **4**. In addition, at −60°C there appears downfield of the resonance of the *ortho*-fluorine atoms one small additional signal, indicating the presence of some other product in low concentration. When the temperature is raised to ambient, a more

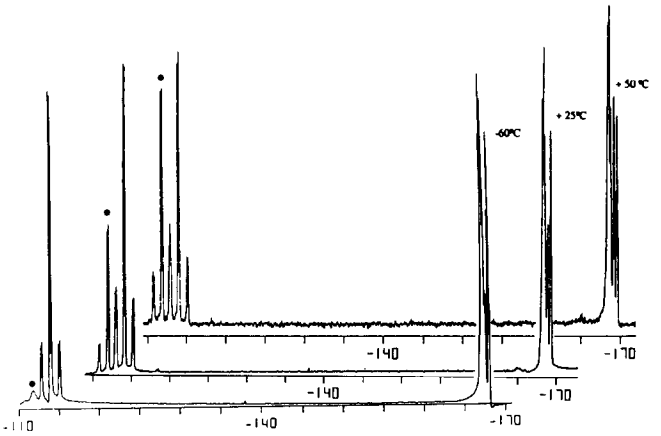


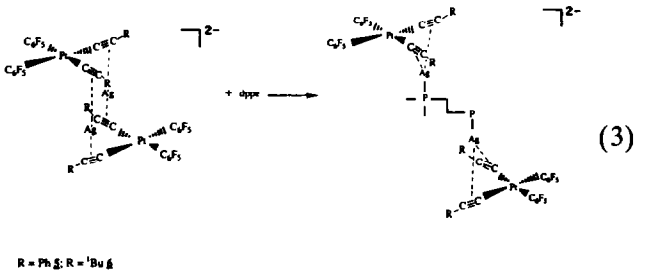

Fig. 3. $^{19}F$ NMR spectra of complex $(NBu_4)[Pt(C_6F_5)_2(\mu\text{-}C{\equiv}C^tBu)_2AgPPh_3]$ (2) at different temperatures.

complicated spectrum appears. This shows two sets of signals corresponding to two types of $C_6F_5$ groups in approximate ratio 1:2.1. The signals of the minor component of both sets (denoted with * in Fig. 3) are easily assigned to the tetranuclear starting material $(NBu_4)_2[Pt_2Ag_2(C_6F_5)_4(C{\equiv}C^tBu)_4]$ by comparison of its $^{19}F$ NMR data in the same solvent ($CD_3COCD_3$). When the temperature is increased to 50°C the signal intensities of both species are similar, indicating an approximate 1:1 ratio.

The $^1H$ NMR spectrum of complex **2** at room temperature in $CD_3COCD_3$ displays two singlet $^t$Bu resonances at 1.17 and 0.94 ppm (approximate ratio 1:2.1) and again the downfield signal ($\delta = 1.17$ ppm) coincides with the $^t$Bu group resonance of $(NBu_4)_2[Pt_2Ag_2(C_6F_5)_4(C{\equiv}C^tBu)_4]$ in the same solvent. Besides a rapid intramolecular exchange of the $AgPPh_3$ unit, which also seems to be operating at low temperature, all this suggests the occurrence of a second temperature-dependent dynamic process involving a rapid exchange of $PPh_3$. Similar fast phosphine exchange processes have been previously found in phosphine silver(I) complexes [21]. In the case of **1** and **2**, the less basic character of $PPh_3$ compared with the $PEt_3$ in **3** and **4** may account for this behaviour. Moreover, for complex **2**, the $^{19}F$ NMR spectra indicate that an additional slow (on the NMR time scale) equilibrium with $(NBu_4)_2[Pt_2Ag_2(C_6F_5)_4(C{\equiv}C^tBu)_4]$ is established. We suggest that the equilibria shown in Scheme 1 accounts for all these observations.

### 2.4. Synthesis and characterization of the tetranuclear derivatives $(NBu_4)_2[\{Pt(C_6F_5)_2(\mu\text{-}C{\equiv}CR)_2Ag\}_2(\mu\text{-dppe})]$

Tetranuclear platinum–silver derivatives $(NBu_4)_2[\{Pt(C_6F_5)_2(\mu\text{-}C{\equiv}CR)_2Ag\}_2(\mu\text{-dppe})]$ (R = Ph **5**, R = $^t$Bu **6**) were obtained as white solids in good yield by the reaction of $(NBu_4)_2[Pt_2Ag_2(C_6F_5)_4(C{\equiv}CR)_4]$ with 1 equiv. of dppe [1,2-bis(diphenylphosphino)ethane] according to eqn. (3).



R = Ph **5**; R = $^t$Bu **6**

(3)

With the aim of obtaining binuclear derivatives related to **1–4**, similar reactions but using an excess of dppe were also carried out. Treatment of $(NBu_4)_2[Pt_2Ag_2(C_6F_5)_4(C{\equiv}C^tBu)_4]$ with 2 mol of dppe produces only complex **6**. The reaction between $(NBu_4)_2[Pt_2Ag_2(C_6F_5)_4(C{\equiv}CPh)_4]$ and 2 equiv. of dppe seems to be more complex, giving a mixture of products that we have not been able to resolve.

The structure of complex **5** has been characterized by an X-ray diffraction study, the results of which are presented in Fig. 4 and Table 3. Analytical, conductivities and selected IR data are reported in the Experimental section. The behaviour of the new species in solution was investigated by $^1H$ (see Experimental section), $^{19}F$ and $^{31}P$ NMR (Table 1) spectroscopies.

Analytical data and conductivities, the latter of which are as expected for 1:2 electrolytes, suggest that both **5** and **6** are tetranuclear species, as confirmed by the crystallographic structure of complex **5**.

$$[Pt(C_6F_5)_2(\mu\text{-}C{\equiv}CR)_2AgPPh_3]^- \underset{(i)}{\overset{fast}{\rightleftharpoons}} \{[Pt(C_6F_5)_2(\mu\text{-}C{\equiv}CR)_2Ag]^- + PPh_3\}$$

$$\text{(ii)} \downarrow \text{slow}$$

$$1/2[Pt_2Ag_2(C_6F_5)_4(C{\equiv}CR)_4]^{2-}$$

(i) for **1** and **2**; R = Ph, $^t$Bu
(ii) for **2**; R = $^t$Bu

Scheme 1.

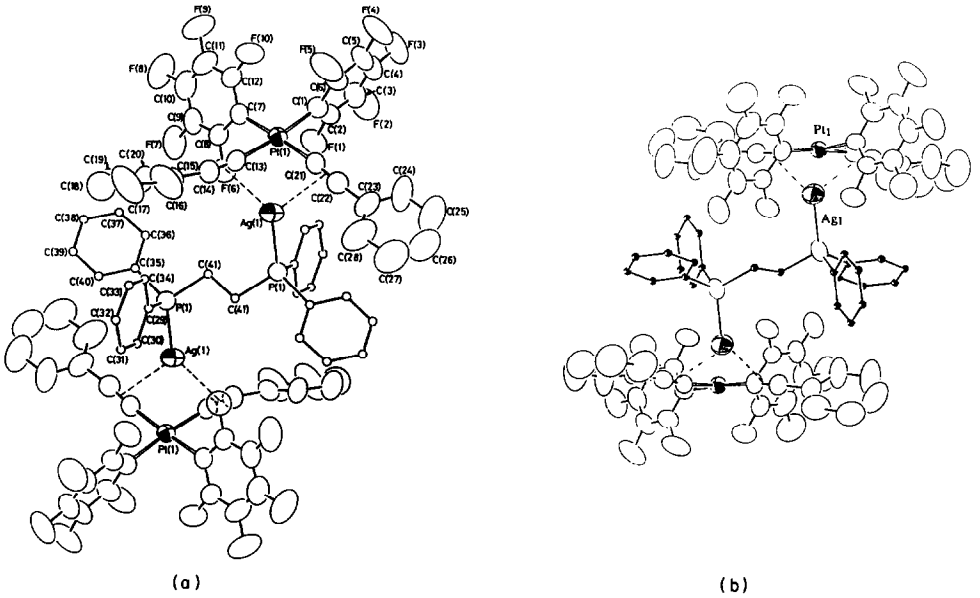



Fig. 4. ORTEP drawing of the anion $[\{Pt(C_6F_5)_2(\mu\text{-}C{\equiv}CPh)_2Ag\}_2(\mu\text{-dppe})]^{2-}$ in complex **5** showing (a) the atomic numbering scheme and (b) the parallel alignment of the platinum square-planar environments.

### 2.5. *Molecular structure of* $(NBu_4)_2[\{Pt(C_6F_5)_2(\mu\text{-}C{\equiv}CPh)_2Ag\}_2(\mu\text{-dppe})]$ (5)

In the crystal, heterobimetal tetranuclear $[\{Pt(C_6F_5)_2(\mu\text{-}C{\equiv}CR)_2Ag\}_2(\mu\text{-dppe})]^{2-}$ anions and $NBu_4^+$ cations are present. Figure 4 presents two ORTEP drawings of the anion, one showing the atom numbering scheme and the other showing the parallel alignment of the two platinum environments as required by symmetry. Selected bond distances and angles are given in Table 3.

TABLE 3. Selected bond distances (Å) and bond angles (°) for complex **5**

| | | | |
|---|---|---|---|
| Ag(1)–Pt(1) | 2.891(1) | C(1)–Pt(1) | 2.049(6) |
| C(7)–Pt(1) | 2.045(8) | C(13)–Pt(1) | 2.006(7) |
| C(21)–Pt(1) | 2.006(8) | P(1)–Ag(1) | 2.370(2) |
| C(13)–Ag(1) | 2.307(7) | C(21)–Ag(1) | 2.438(7) |
| C(29)–P(1) | 1.804(9) | C(35)–P(1) | 1.814(9) |
| C(41)–P(1) | 1.862(9) | C(14)–C(13) | 1.203(10) |
| C(15)–C(14) | 1.446(10) | C(22)–C(21) | 1.203(12) |
| C(23)–C(22) | 1.458(13) | *C(41)–C(41) | 1.586(20) |
| C(1)–Pt(1)–Ag(1) | 133.0(2) | C(7)–Pt(1)–Ag(1) | 119.4(2) |
| C(7)–Pt(1)–C(1) | 90.6(3) | C(13)–Pt(1)–Ag(1) | 52.5(2) |
| C(13)–Pt(1)–C(1) | 174.4(3) | C(13)–Pt(1)–C(7) | 86.4(2) |
| C(21)–Pt(1)–Ag(1) | 56.3(2) | C(21)–Pt(1)–C(1) | 91.0(3) |
| C(21)–Pt(1)–C(7) | 174.8(3) | C(21)–Pt(1)–C(13) | 92.3(3) |
| P(1)–Ag(1)–Pt(1) | 140.1(1) | C(13)–Ag(1)–Pt(1) | 43.6(2) |
| C(13)–Ag(1)–P(1) | 147.2(2) | C(21)–Ag(1)–Pt(1) | 43.2(2) |
| C(21)–Ag(1)–P(1) | 132.2(2) | C(21)–Ag(1)–C(13) | 75.1(3) |
| C(29)–P(1)–Ag(1) | 107.1(3) | C(35)–P(1)–Ag(1) | 120.6(3) |
| C(35)–P(1)–C(29) | 102.6(4) | C(41)–P(1)–Ag(1) | 115.7(3) |
| C(41)–P(1)–C(29) | 106.7(5) | C(41)–P(1)–C(35) | 102.7(4) |
| Ag(1)–C(13)–Pt(1) | 83.9(3) | C(14)–C(13)–Pt(1) | 172.3(7) |
| C(14)–C(13)–Ag(1) | 103.7(6) | C(15)–C(14)–C(13) | 167.0(9) |
| Ag(1)–C(21)–Pt(1) | 80.5(3) | C(22)–C(21)–Pt(1) | 172.6(7) |
| C(22)–C(21)–Ag(1) | 94.2(6) | C(23)–C(22)–C(21) | 174.0(7) |

The tetranuclear anion is formed by two heterobimetal "$Pt(C_6F_5)_2(\mu\text{-}C{\equiv}CPh)_2Ag$" units linked through a dppe which is coordinated to the two silver atoms. In each unit, the platinum atom is $\sigma$-bonded to two $C_6F_5$ groups mutually *cis* and to two C≡CPh groups in an approximately square planar environment. The silver atom is asymmetrically $\pi$-bonded to the two C≡C triple bonds of the phenylacetylides. One of the phosphorus atoms of the bridging dppe completes the coordination sphere of the silver atom. Because of the inversion centre, both square-planar platinum environments are parallel and mutually *trans*. The structure of complex **1** is similar to that of each of the two symmetry-related halves of the tetranuclear anion.

The Pt–C bond lengths (to $C_6F_5$ and C≡CPh) and the Ag–P (2.370 (2) Å) distance are similar to those observed in complex **1**. The dihedral angle formed by the coordination planes around the platinum and silver centres is 110.62(13)°.

In order to compare some parameters of the silver acetylide $\eta^2$-linkages of this complex with those found in **1**, the bonding of the C≡CPh groups to platinum and silver for both derivatives is schematized in Fig. 2. When the structural parameters of the doubly bridging parts of **1** and **5** are compared, the following features are evident: (i) the difference in distances from silver to $C_\alpha$ and $C_\beta$ for complex **5** (0.536; 0.356 Å) are longer

than those found in **1** (0.178; 0.293 Å), indicating that the silver acetylide $\pi$-linkages are more asymmetric in **5**; (ii) the Ag–C distances (to $C_\alpha$ and $C_\beta$) and Ag–(midpoints of C≡C triple bonds) distances (Ag–$C_{13}$, $C_{14}$ = 2.5183 Å; Ag–$C_{21}$, $C_{22}$ = 2.5518 Å) in **5** are longer than the similar distances in **1**, suggesting that the latter has slightly stronger Ag-$\pi$ acetylide interactions; (iii) no significant difference is observed in the acetylene skeletons, as the $C_\alpha$–$C_\beta$ distances (see Fig. 2) and angles at $C_\alpha$ (172.3(7)°, 172.6(7)°) and $C_\beta$ (167.0(9)°, 174.0(7)°) in **5** are similar to those in **1**; (iv) the platinum–silver distance (2.891(1) Å) in **5** is slightly shorter than that in **1** but too long for any metal–metal bond to be considered.

*2.6. IR and NMR spectra*

The infrared spectra of both **5** and **6** show a strong band at 2059 $cm^{-1}$ which is consistent with the presence of bridging acetylide [6,9,10], as well as a double band at *ca.* 780 $cm^{-1}$ corresponding to the X-sensitive mode of $C_6F_5$, characteristic of the *cis*-$Pt(C_6F_5)_2$ moiety [11]. The $^{19}F$ and $^{31}P$ spectra at several temperatures indicate that both complexes are dynamic in solution. The $^{31}P$ NMR spectra at low temperature (in $CD_3COCD_3$) shows two symmetrical multiplets centred at 10.84 (for **5** at −60°C) and 9.35 ppm (**6** at −85°C) and separated by 610 (**5**) and 603 Hz (**6**), respectively. This suggests that the Ag–P bonds are retained in solution. The appearance of a multiplet probably arises from the superposition of the three different spin systems AA'XX', BB'YY' and ABXY attributable to the isotopomers $(NBu_4)_2[\{Pt(C_6F_5)_2(\mu\text{-}C{\equiv}CR)_2{}^{107}Ag\}2(\mu\text{-dppe})]$ (abundance 26.87%); $(NBu_4)_2[\{Pt(C_6F_5)_2(\mu\text{-}C{\equiv}CR)_2{}^{109}Ag\}_2(\mu\text{-dppe})]$ (23.19%) and $(NBu_4)_2[\{Pt(C_6F_5)_2(\mu\text{-}C{\equiv}CR)_2{}^{107}Ag\}(\mu\text{-dppe})\{Pt(C_6F_5)_2(\mu\text{-}C{\equiv}CR)_2{}^{109}Ag\}]$ (49.93%). However, the $^{19}F$ NMR spectra at −60°C exhibit three well-resolved signals in a ratio 2:2:1 corresponding to four equivalent $C_6F_5$ groups. This indicates that a very fast dynamic process which cannot be frozen at low temperature equalizes the two halves of each $C_6F_5$.

As the temperature is raised, broadening and collapse of the phosphorus resonances in both complexes (**5** and **6**) is evident (see Table 1). Qualitatively, the spectra are similar to those obtained for **2** but the rate of exchange is probably smaller (for example, the temperature at which Ag–P coupling is no longer observed is *ca.* +50°C for **5** and 20°C for **6** whereas for **2** it is *ca.* −30°C). As we have suggested for **2**, the absence of Ag–P coupling indicates a second temperature-dependent process involving rapid exchange between free and coordinated dppe.

In contrast, when the temperature is increased, the $^{19}F$ NMR spectra bear some resemblance to those observed for complex **2**. At room temperature, the $^{19}F$ NMR spectra contain a second set of $C_6F_5$ signals corresponding to the tetranuclear precursors $(NBu_4)_2[Pt_2Ag_2(C_6F_5)_4(C{\equiv}CR)_4]$ with relative intensity of 5.6:1 for complex **6**, and 9:1 for **5**. For complex **6** at 50°C, both sets of signals have a relative intensity of 2.9:1. These spectra can be interpreted in terms of the occurrence of an additional slow equilibrium with complexes $(NBu_4)_2[Pt_2Ag_2(C_6F_5)_4(C{\equiv}CR)_4]$ which is favoured at higher temperatures. These data are comparable to those for complex **2**, where similar conclusions were reached.

## 3. Experimental details

The C, H and N analyses were carried out on a Perkin-Elmer 240-B microanalyzer. Conductivities of acetone solutions at several molarities for **3** and in *ca.* $5 \times 10^{-4}$ mol $dm^{-3}$ solutions for **1**, **2** and **4**–**6** were measured with a Philips PW 9509 conductimeter. The IR spectra were recorded (4000–200 $cm^{-1}$) on a Perkin-Elmer 883 spectrophotometer using Nujol mulls between polyethylene sheets. Proton, $^{19}F$ and $^{31}P$ NMR spectra were recorded on a Varian XL-200 spectrometer operating at 200.057, 188.220 and 80.984 MHz, respectively; chemical shifts (ppm) are reported relative to $SiMe_4$, $CFCl_3$ and 85% $H_3PO_4$ (as external references). The synthesis of $(NBu_4)_2[Pt_2Ag_2(C_6F_5)_4(C{\equiv}CR)_4]$ (R = Ph or $^tBu$) has been described previously [6]. All the reactions were carried out with exclusion of light.

*3.1. Preparation of the complexes*

*3.1.1. $(NBu_4)[Pt(C_6F_5)_2(\mu\text{-}C{\equiv}CR)_2Ag(PPh_3)]$ (R = Ph 1, R = $^tBu$ 2)*

Triphenylphosphine (0.03648 g, 0.1428 mmol) was added to a solution of $(NBu_4)_2[Pt_2Ag_2(C_6F_5)_4(C{\equiv}C\text{-}Ph)_4]$ (0.1505 g, 0.0714 mmol) in $CH_2Cl_2$ (20 ml) and the mixture was stirred at room temperature for 1 h. Evaporation of the solution (~3 ml) and addition of EtOH (10 ml) gave white crystals of **1**, 90% yield. Complex **2** was obtained similarly by using the appropriate starting material and acetone as a solvent, 81% yield.

Similar results were obtained by using a $(NBu_4)_2[Pt_2Ag_2(C_6F_5)_4(C{\equiv}CR)_4]/PPh_3$ ratio of 1:4.

**1**: Anal. Found (calcd.): N, 1.01 (1.04); C, 55.57 (55.40); H, 4.84 (4.57)%. $\Lambda_M$ (in acetone solution) 81 $ohm^{-1}$ $cm^2$ $mol^{-1}$. IR: $\nu$(C≡C) 2057m, 2041m; $\nu$(X-sens)($C_6F_5$): 799m, 776s $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ 0.84 (t, $-CH_3-(^nBu)$); 1.33 (m, $-CH_2-(^nBu)$); 1.56 [m, $-CH_2-(^nBu)$); 3.3 (m, $N-CH_2-(^nBu)$); 7.38, 7.00 (m, Ph) ppm.

**2**: Anal. Found (calcd.): N, 0.95 (1.07); C, 53.33 (53.42); H, 5.47 (5.23)%. $\Lambda_M$ (in acetone solution) 91 $ohm^{-1}$ $cm^2$ $mol^{-1}$. IR: $\nu$(C≡C) 2063m; $\nu$(X-sens)($C_6F_5$): 786s, 778s $cm^{-1}$. $^1H$ NMR ($CD_3COCD_3$): $\delta$ 0.93 (s, $^tBu$); 0.97 (t, $-CH_3-(^nBu)$); 1.17 (s, corresponding to $^tBu$ of $(NBu_4)_2[Pt_2Ag_2(C_6F_5)_4(C{\equiv}C^tBu)_4]$); 1.44 [m, $-CH_2-(^nBu)$); 1.74 (m, $-CH_2-(^nBu)$); 3.47 (m, $N-CH_2-(^nBu)$); 7.64, 7.48 (m, Ph) ppm.

*3.1.2. $(NBu_4)[Pt(C_6F_5)_2(\mu\text{-}C{\equiv}CR)_2Ag(PEt_3)]$ (R = Ph 3; R = $^tBu$ 4)*

To a solution of $(NBu_4)_2[Pt_2Ag_2(C_6F_5)_4(C{\equiv}CR)_4]$ (0.1508 g, 0.0697 mmol for R = Ph; 0.1 g, 0.048 mmol for R = $^tBu$) in $CH_2Cl_2$ (~ 3 ml) (R = Ph) or diethyl ether (~ 2 ml) (R = $^tBu$) was added $PEt_3$ (20 $\mu$l, 0.1394 mmol for R = Ph; 14 $\mu$l, 0.0959 mmol for R = $^tBu$) and the mixture was stirred at room temperature for 30 min. Addition of EtOH (10 ml) for R = Ph or n-hexane (10 ml) for R = $^tBu$ and cooling to −25°C for 48 h gave white crystals of **3** or **4** in 68% and 67% yields, respectively.

Similar results were obtained if a $(NBu_4)_2[Pt_2Ag_2(C_6F_5)_4(C{\equiv}CR)_4]/PEt_3$ ratio of 1:4 was used.

**3**: Anal. Found (calcd.): N, 1.12 (1.17); C, 50.26 (50.05); H, 5.38 (5.12)%. Equivalent conductivity measurements in acetone solutions show a value of $A$ from the Onsager equation ($\Lambda_e = \Lambda_o - AVc$) of 552 characteristic of a 1:1 electrolyte. IR: $\nu$(C≡C) 2053sh, 2051s; $\nu$(X-sens)($C_6F_5$): 798s, 773s $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ 0.86 (t, $-CH_3-(^nBu)$); 1.08 (d, t, $CH_3$ ($PEt_3$), $^3J$(P–H) = 18 Hz); 1.34 (m, $-CH_2-(^nBu)$); 1.52 (m, $-CH_2-(^nBu)$, $P-CH_2-(PEt_3)$, overlap); 3.34 (m, $N-CH_2-(^nBu)$); 7.19 (m, Ph) ppm.

**4**: Anal. Found (calcd.): N, 1.21 (1.21); C, 47.95 (47.63); H, 6.53 (6.00)%. $\Lambda_M$ (in acetone solution) 103 $ohm^{-1}$ $cm^2$ $mol^{-1}$. IR: $\nu$(C≡C) 2066m; $\nu$(X-sens)($C_6F_5$): 786s, 776s $cm^{-1}$. $^1H$ NMR ($CD_3COCD_3$): $\delta$ 0.86 (t, $CH_3-(^nBu)$); 1.1 (s, $^tBu$); 1.24 (d, t, $CH_3(PEt_3)$, $^3J$(P–H) = 17.8 Hz); 1.37 (m, $-CH_2-(^nBu)$); 1.71 (m, $-CH_2-(^nBu)$, $P-CH_2-(PEt_3)$, overlap); 3.37 (m, $N-CH_2-(^nBu)$ ppm.

*3.1.3. $(NBu_4)_2[\{Pt(C_6F_5)_2(\mu\text{-}C{\equiv}CPh)_2Ag\}_2(\mu\text{-}dppe)]$ (5)*

1,2-Bis(diphenylphosphino)ethane (0.0256 g, 0.0697 mmol) was added to a solution of $(NBu_4)_2[Pt_2Ag_2(C_6$-

TABLE 4. Crystallographic data for the structural analysis of complexes **1** and **5**

| | | |
|---|---|---|
| Formula | $PtAgF_{10}PNC_{58}H_{61}$ (1) | $Pt_2Ag_2F_{20}P_2N_2C_{114}H_{116}$ (5) |
| FW | 1343.88 | 2609.65 |
| Space group | $P2_1/c$ | $P\bar{1}$ |
| Systematic absences | $0k0$, $k \neq n$<br>$h0l$, $l \neq n$ | – |
| $a$ (Å) | 21.240(4) | 11.377(2) |
| $b$ (Å) | 10.861(2) | 16.212(4) |
| $c$ (Å) | 25.094(6) | 15.483(4) |
| $\alpha$ (°) | | 91.444(21) |
| $\beta$ (°) | 97.106(17) | 109.087(19) |
| $\gamma$ (°) | | 89.118(16) |
| $V$ (Å$^3$) | 5744.3 | 2687.9 |
| $Z$ | 4 | 1 |
| $d_{calc}$ (g $cm^{-3}$) | 1.55 | 1.61 |
| $\mu$(Mo K$\alpha$) ($cm^{-1}$) | 29.5 | 31.5 |
| Radiation (monochromated incident beam) | Mo K$\alpha$ ($\lambda$ = 0.71069 Å) | Mo K$\alpha$ ($\lambda$ = 0.71069 Å) |
| Orientation reflections no; range ($2\theta$) | 25; 28–30 | 25; 26–30 |
| Diffractometer | Enraf-Nonius CAD-4 | Enraf-Nonius CAD-4 |
| Temperature | Room temperature | Room temperature |
| Data collection range, $2\theta$ (°) | 2–44 | 2–44 |
| No. of unique data, total with $F_o^2 > 6\sigma(F_o^2)$ | 7017, 5599 | 6572, 5224 |
| $g$ | 0.000192 | 0.001748 |
| No. of parameters refined | 775 | 640 |
| Transmission factors, max, min | 1.12, 0.82 | 1.15, 0.82 |
| $R$ | 0.0325 | 0.0349 |
| $R_w$ | 0.0343 | 0.0385 |
| Largest shift/e.s.d. final cycle | 0.009 | 0.025 |
| Largest peak (e Å$^{-3}$) | 0.51 | 0.62 |

TABLE 5. Positional parameters for complex **1**

| | x | y | z | $B_{eq}$ |
|---|---|---|---|---|
| Pt1 | 2667(1) | 4254(1) | 6210(1) | 3.32(1) |
| Ag1 | 2461(1) | 3815(1) | 4996(1) | 4.41(3) |
| P1 | 2125(1) | 2568(2) | 4240(1) | 3.87(9) |
| C2 | 2681 | 1256 | 3444 | 5.37(45) |
| C3 | 3157 | 527 | 3271 | 6.44(56) |
| C4 | 3693 | 228 | 3627 | 6.75(58) |
| C5 | 3753 | 657 | 4155 | 7.04(60) |
| C6 | 3276 | 1385 | 4327 | 5.35(45) |
| C1 | 2740(2) | 1685(5) | 3972(2) | 4.43(40) |
| C8 | 2076 | 4134 | 3375 | 7.92(64) |
| C9 | 1773 | 4865 | 2963 | 10.91(88) |
| C10 | 1115 | 4827 | 2843 | 8.53(69) |
| C11 | 758 | 4057 | 3135 | 7.26(61) |
| C12 | 1060 | 3327 | 3547 | 5.62(47) |
| C7 | 1719(2) | 3365(6) | 3667(3) | 4.46(40) |
| C14 | 1315 | 517 | 4050 | 6.13(52) |
| C15 | 896 | −364 | 4207 | 7.72(64) |
| C16 | 737 | −359 | 4730 | 6.89(59) |
| C17 | 996 | 527 | 5095 | 6.46(56) |
| C18 | 1414 | 1408 | 4939 | 4.78(42) |
| C13 | 1574(3) | 1403(5) | 4416(2) | 4.21(39) |
| F1 | 2840(2) | 1852(4) | 7003(2) | 5.87(25) |
| F2 | 3739(3) | 1226(4) | 7783(2) | 8.00(32) |
| F3 | 4790(2) | 2647(5) | 8014(2) | 8.18(32) |
| F4 | 4910(2) | 4743(5) | 7450(2) | 7.06(28) |
| F5 | 4012(2) | 5425(4) | 6676(2) | 5.21(23) |
| F6 | 1571(2) | 2262(5) | 6291(2) | 7.17(30) |
| F7 | 614(2) | 2177(7) | 6874(2) | 10.41(41) |
| F8 | 470(3) | 3960(7) | 7623(2) | 12.02(49) |
| F9 | 1324(3) | 5785(6) | 7773(2) | 11.13(46) |
| F10 | 2288(3) | 5921(4) | 7207(2) | 6.96(30) |
| C19 | 3367(3) | 3684(6) | 6796(2) | 3.46(34) |
| C20 | 3340(3) | 2633(6) | 7092(3) | 4.20(38) |
| C21 | 3808(4) | 2276(7) | 7500(3) | 5.21(45) |
| C22 | 4329(4) | 2962(8) | 7615(3) | 5.26(46) |
| C23 | 4395(3) | 4038(7) | 7331(3) | 4.61(43) |
| C24 | 3914(3) | 4350(6) | 6934(2) | 3.80(36) |
| C25 | 1986(3) | 4107(7) | 6709(3) | 4.31(39) |
| C26 | 1536(3) | 3186(9) | 6661(3) | 5.31(46) |
| C27 | 1033(4) | 3127(11) | 6966(4) | 7.23(61) |
| C28 | 951(5) | 4012(12) | 7333(4) | 7.44(69) |
| C29 | 1389(5) | 4922(10) | 7400(3) | 6.96(62) |
| C30 | 1883(4) | 4968(8) | 7110(3) | 5.13(47) |
| C31 | 1979(3) | 4883(6) | 5668(3) | 3.75(36) |
| C32 | 1565(3) | 5278(6) | 5317(3) | 3.68(35) |
| C34 | 963 | 5900 | 4455 | 4.86(41) |
| C35 | 413 | 6381 | 4168 | 6.00(49) |
| C36 | −86 | 6774 | 4439 | 6.11(52) |
| C37 | −35 | 6685 | 4998 | 5.50(47) |
| C38 | 515 | 6204 | 5285 | 4.54(40) |
| C33 | 1013(2) | 5812(4) | 5014(2) | 3.87(35) |
| C39 | 3301(3) | 4280(6) | 5677(3) | 4.11(37) |
| C40 | 3631(3) | 4180(6) | 5311(3) | 4.18(38) |
| C42 | 3968 | 4287 | 4407 | 5.50(45) |
| C43 | 4425 | 4083 | 4063 | 7.00(60) |
| C44 | 5014 | 3591 | 4262 | 6.97(61) |
| C45 | 5145 | 3302 | 4807 | 6.67(56) |
| C46 | 4688 | 3506 | 5151 | 5.27(46) |
| C41 | 4099(2) | 3998(5) | 4951(2) | 4.25(40) |
| N1 | 7086(3) | 1383(5) | 3931(2) | 4.78(33) |
| C47 | 6683(4) | 219(7) | 4017(3) | 6.03(48) |

TABLE 5 (continued)

| | x | y | z | $B_{eq}$ |
|---|---|---|---|---|
| C48 | 6022(5) | 552(8) | 4173(4) | 7.84(64) |
| C49 | 5624(5) | −674(8) | 4226(4) | 8.01(65) |
| C50 | 5426(5) | −1248(11) | 3687(4) | 9.03(72) |
| C51 | 6781(4) | 2129(7) | 3458(3) | 5.66(46) |
| C52 | 6703(5) | 1431(8) | 2911(3) | 7.23(57) |
| C53 | 6384(5) | 2336(9) | 2479(4) | 7.68(60) |
| C54 | 6299(6) | 1741(10) | 1932(4) | 9.88(76) |
| C55 | 7739(4) | 870(7) | 3842(3) | 5.64(47) |
| C56 | 8192(4) | 1874(9) | 3703(4) | 7.63(60) |
| C57 | 8800(5) | 1263(11) | 3572(4) | 8.82(68) |
| C58 | 9270(5) | 2138(11) | 3362(5) | 10.30(79) |
| C59 | 7129(4) | 2272(7) | 4415(3) | 5.10(42) |
| C60 | 7431(4) | 1709(8) | 4953(3) | 6.47(52) |
| C61 | 7299(5) | 2672(9) | 5388(4) | 7.84(62) |
| C62 | 7591(6) | 2218(11) | 5945(5) | 9.77(78) |

$F_5)_4(C{\equiv}CPh)_4]$ (0.1509 g, 0.0697 mmol) in 30 ml of $CH_2Cl_2$. After 30 min stirring at room temperature the solvent was removed and the residue treated with 10 ml of EtOH to give **5** in 89% yield.

**5**: Anal. Found (calcd.): N, 1.03 (1.11); C, 53.01 (53.15); H, 4.88 (4.62)%. $\Lambda_M$ (in acetone solution) 166 $ohm^{-1}$ $cm^2$ $mol^{-1}$. IR: $\nu$(C≡C) 2059s; $\nu$(X-sens)($C_6F_5$): 798s, 777s $cm^{-1}$. $^1H$ NMR ($CD_3COCD_3$): $\delta$ 0.86 (t, $-CH_3$–($^n$Bu)); 1.31 (m, $-CH_2$–($^n$Bu)); 1.35 (m, $-CH_2$–($^n$Bu)); 2.29 (m, $-CH_2-CH_2$); 3.26 (m, N–$CH_2$–($^n$Bu)); 7.30, 7.11, 6.98 (m, Ph) ppm.

### *3.1.4. $(NBu_4)_2[\{Pt(C_6F_5)_2(\mu\text{-}C{\equiv}C^tBu)_2Ag\}_2(\mu\text{-}dppe)]$ (6)*

Dppe (0.02805 g, 0.0704 mmol) was added to a solution of $(NBu_4)_2[Pt_2Ag_2(C_6F_5)_4(C{\equiv}C^tBu)_4]$ (0.1467 g, 0.7704 mmol) in 30 ml of $CH_2Cl_2$ at room temperature. After a few minutes, a white precipitate formed. The mixture was stirred for 1 h and then the solid **6**, was filtered off, washed with $CH_2Cl_2$ and air dried; 80% yield.

Similar results were obtained using a $(NBu_4)_2[Pt_2Ag_2(C_6F_5)_4(C{\equiv}C^tBu)_4]$/dppe ratio of 1:2.

**6**: Anal. Found (calcd.): N, 1.04 (1.13); C, 51.55 (51.29); H, 5.57 (4.95)%. $\Lambda_M$ (in acetone solution) 223 $ohm^{-1}$ $cm^2$ $mol^{-1}$. IR: $\nu$(C≡C) 2059s; $\nu$(X-sens)($C_6F_5$): 784s, 777s $cm^{-1}$. $^1H$ NMR ($CD_3COCD_3$): $\delta$ 0.95 (s, $^t$Bu); 0.98 (t, $-CH_3$–($^n$Bu)); 1.17 (s, corresponding to $^t$Bu of $(NBu_4)_2[Pt_2Ag_2(C_6F_5)_4(C{\equiv}C^tBu)_4]$); 1.44 (m, $-CH_2$–($^n$Bu)); 1.85 (m, $-CH_2$–($^n$Bu)), $\delta$ 2.65 (m, $-CH_2-CH_2$]; 3.48 (m, N–$CH_2$–($^n$Bu)); $\delta$ 7.37 (m, Ph) ppm.

### *3.2. Crystal structure analyses*

Crystals of $(NBu_4)[Pt(C_6F_5)_2(\mu\text{-}C{\equiv}CPh)_2Ag(PPh_3)]$ (**1**) and $(NBu_4)_2[\{Pt(C_6F_5)_2(\mu\text{-}C{\equiv}CPh)_2Ag\}_2(\mu\text{-}dppe)]$

TABLE 6. Positional parameters for complex **5**

| | x | y | z | $B_{eq}$ |
|---|---|---|---|---|
| Pt1 | 616(1) | 2298(1) | 2526(1) | 3.88(2) |
| Ag1 | 1168(1) | 3918(1) | 3377(1) | 6.22(4) |
| P1 | 129(2) | 5140(1) | 3612(1) | 5.78(15) |
| F1 | −2340(4) | 2449(3) | 1383(3) | 6.74(32) |
| F2 | −3694(4) | 1934(4) | −301(3) | 9.05(41) |
| F3 | −2605(5) | 1073(4) | −1356(3) | 8.86(39) |
| F4 | −106(5) | 767(4) | −726(3) | 9.34(45) |
| F5 | 1251(4) | 1263(4) | 930(3) | 8.31(38) |
| F6 | −1050(5) | 2455(3) | 3851(3) | 7.01(36) |
| F7 | −2016(5) | 1356(4) | 4651(3) | 8.81(43) |
| F8 | −1742(6) | −280(4) | 4382(5) | 11.12(54) |
| F9 | −430(7) | −793(3) | 3284(5) | 11.43(61) |
| F10 | 551(5) | 287(3) | 2447(4) | 7.97(40) |
| C1 | −454(6) | 1899(4) | 1248(5) | 4.51(45) |
| C2 | −1724(7) | 2027(5) | 872(5) | 4.66(47) |
| C3 | −2436(7) | 1775(5) | 24(5) | 5.47(52) |
| C4 | −1915(8) | 1359(6) | −529(5) | 5.89(56) |
| C5 | −676(9) | 1189(6) | −217(5) | 6.21(61) |
| C6 | 25(7) | 1482(5) | 659(5) | 5.37(51) |
| C7 | −167(7) | 1436(5) | 3110(4) | 4.66(44) |
| C8 | −861(7) | 1649(5) | 3681(5) | 4.79(48) |
| C9 | −1375(8) | 1099(6) | 4106(5) | 5.83(57) |
| C10 | −1238(10) | 275(7) | 3986(7) | 7.43(73) |
| C11 | −570(10) | 15(6) | 3422(7) | 7.62(73) |
| C12 | −70(8) | 596(5) | 2991(5) | 5.66(55) |
| C13 | 1728(8) | 2576(5) | 3799(5) | 5.02(51) |
| C14 | 2410(7) | 2645(5) | 4576(5) | 5.36(52) |
| C15 | 3120(9) | 2546(5) | 5532(5) | 6.48(61) |
| C16 | 4387(11) | 2689(9) | 5837(7) | 11.23(97) |
| C17 | 5106(17) | 2499(13) | 6794(9) | 15.17(152) |
| C18 | 4447(19) | 2268(10) | 7338(10) | 12.22(133) |
| C19 | 3159(19) | 2155(8) | 7049(9) | 11.89(125) |
| C20 | 2477(12) | 2286(6) | 6134(6) | 8.79(82) |
| C21 | 1294(6) | 3222(5) | 1995(5) | 4.34(44) |
| C22 | 1604(7) | 3832(5) | 1701(5) | 4.88(49) |
| C23 | 1897(8) | 4541(5) | 1249(7) | 6.25(63) |
| C24 | 1439(14) | 4561(8) | 310(8) | 11.37(112) |
| C25 | 1691(19) | 5271(11) | −149(12) | 14.69(172) |
| C26 | 2431(14) | 5888(9) | 378(12) | 10.53(125) |
| C27 | 2860(15) | 5886(9) | 1265(13) | 11.88(137) |
| C28 | 2634(11) | 5177(7) | 1784(10) | 10.77(106) |
| C29 | −1510(9) | 5007(5) | 2991(6) | 6.04(62) |
| C30 | −1927(9) | 4328(6) | 2396(6) | 6.41(66) |
| C31 | −3145(10) | 4252(7) | 1878(8) | 8.04(84) |
| C32 | −4024(11) | 4849(7) | 1927(9) | 8.95(95) |
| C33 | −3649(15) | 5503(8) | 2539(10) | 10.39(120) |
| C34 | −2384(14) | 5603(7) | 3062(9) | 9.41(101) |
| C35 | 461(9) | 6121(5) | 3205(5) | 5.91(58) |
| C36 | 1009(13) | 6778(7) | 3772(7) | 9.84(91) |
| C37 | 1197(15) | 7510(7) | 3382(9) | 11.71(121) |
| C38 | 874(12) | 7608(7) | 2468(8) | 8.89(96) |
| C39 | 342(13) | 6961(8) | 1901(8) | 10.09(102) |
| C40 | 140(14) | 6216(7) | 2266(7) | 10.64(104) |
| C41 | 256(12) | 5390(5) | 4819(5) | 8.17(76) |
| N1 | 5280(6) | 8336(4) | 7606(4) | 5.68(43) |
| C42 | 4342(8) | 8959(6) | 7790(6) | 6.97(64) |
| C43 | 4952(10) | 9658(8) | 8435(9) | 9.92(95) |
| C44 | 3886(14) | 10289(8) | 8481(9) | 10.93(114) |
| C45 | 3026(12) | 10018(8) | 8909(10) | 10.81(111) |
| C46 | 6201(7) | 8000(6) | 8494(5) | 6.14(54) |
| C47 | 5611(9) | 7477(7) | 9038(6) | 7.95(69) |
| C48 | 6613(10) | 7291(8) | 9970(7) | 9.34(87) |
| C49 | 6201(13) | 6654(10) | 10507(8) | 12.51(121) |
| C50 | 6144(8) | 8731(5) | 7135(6) | 6.18(56) |
| C51 | 5449(9) | 9039(6) | 6167(6) | 7.44(66) |
| C52 | 6441(10) | 9509(6) | 5852(6) | 7.70(73) |
| C53 | 6681(11) | 10371(6) | 6287(8) | 9.19(88) |
| C54 | 4434(8) | 7677(6) | 6977(6) | 7.02(65) |
| C55 | 5181(11) | 6954(7) | 6729(7) | 8.28(83) |
| C56 | 4070(13) | 6454(8) | 6005(9) | 10.88(112) |
| C57 | 4635(18) | 5670(11) | 5735(13) | 15.85(192) |

(**5**) were obtained by slow diffusion of hexane into a chloroform or dichloromethane solution, respectively.

General crystallographic information is given in Table 4. Positional parameters are given in Tables 5 and 6. In both cases, the structure was solved by Patterson synthesis for Pt with further non-H atoms located by subsequent Fourier difference maps. An empirical absorption correction was applied [22]. Full-matrix least squares refinement with all non-hydrogen atoms allowed anisotropic thermal motion. For **1**, phenyl rings (not the $C_6F_5$ groups) were treated as rigid bodies and included in the refinement with idealized hexagonal symmetry (C–C 1.395 Å). Data were weighted according to $\omega^{-1} = [\sigma^2(F) + gF^2]$. The computer programs SHELX-76 [23], CADABS [24], and DIFABS [22] were used. Geometrical calculations were carried out with the program PARST [25].

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

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