Dalton Communications

Neutral $PtAg_2$ Clusters containing Unsymmetrical μ_3-σ and μ-η^2,σ Alkynyl Groups. Crystal Structure of $[PtAg_2(C_6F_5)_2(\mu\text{-}\eta^2,\sigma\text{-}C{\equiv}CPh)(\mu_3\text{-}\sigma\text{-}C{\equiv}CPh)(PPh_3)_2]\cdot 0.25CH_2Cl_2$

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The reaction between $[\{PtAg_2(C_6F_5)_2(C{\equiv}CR)_2\}_n]$ and triphenylphosphine in a molar ratio of 1:2 has resulted in a good yield of the trinuclear mixed-metal complexes $[PtAg_2(C_6F_5)_2(\mu\text{-}\eta^2,\sigma\text{-}C{\equiv}CR)(\mu_3\text{-}\sigma\text{-}C{\equiv}CR)(PPh_3)_2]$ (R = Ph **3** or Bu^t **4**), and the crystal structure of **3** revealed that they contain two different types of unsymmetrical μ_3-σ and μ-η^2,σ-edge-bridging alkynyl ligands.

The chemistry of transition-metal alkynyl complexes is of increasing interest due to the wide-ranging reactivity patterns and possible bonding modes of alkynyl ligands.[1] We have recently reported[2] the preparation of the polynuclear complexes $[\{PtAg_2(C_6F_5)_2(C{\equiv}CR)_2\}_n]$ (R = Ph **1** or Bu^t **2a**) which, due to their low solubility in common non-donor solvents, were thought to be polymeric, probably based on square-planar *cis*-$Pt(C_6F_5)_2(C{\equiv}CR)_2$ fragments connected by Ag atoms η^2-bonded to acetylide groups. We observed that only the *tert*-butylacetylide derivative **2a** dissolved readily in acetone yielding the more soluble hexanuclear species $[\{PtAg_2(C_6F_5)_2(C{\equiv}CBu^t)_2(Me_2CO)_2\}_2]$ **2b**. This prompted us to investigate the reactivity of the polymeric materials **1** and **2a** towards other donor ligands and we report here the reaction of $[\{PtAg_2(C_6F_5)_2(C{\equiv}CR)_2\}_n]$ (R = Ph **1** or Bu^t **2a**) with triphenylphosphine (Ag:PPh_3 1:1) which affords the unexpected trinuclear complexes $[PtAg_2(C_6F_5)_2(\mu\text{-}\eta^2,\sigma\text{-}C{\equiv}CR)(\mu_3\text{-}\sigma\text{-}C{\equiv}CR)(PPh_3)_2]$ (R = Ph **3** or Bu^t **4**). These compounds are the first examples of heterometallic trinuclear complexes containing two alkynyl groups, one bonded only to two metal atoms (Pt and Ag) in the usual μ-η^2,σ manner and the other one bonded to all three metal atoms in a very unsymmetrical μ_3-bonding mode.

Compounds **3** and **4** are obtained as a pale yellow (**3**) or white (**4**) air-stable solid when two equivalents of PPh_3 are added to a suspension of **1** or **2a** respectively in acetone.[†] Analytical and molecular weight determinations are in accord with this formulation. The IR spectra show medium $\nu(C{\equiv}C)$ absorptions at 2051, with a shoulder at 2033, (**3**) and 2040 cm^{-1} (**4**) which are consistent with the presence of bridging acetylide ligands. The ^{19}F NMR spectra display the characteristic (2:1:2) pattern indicating that, in solution, both C_6F_5 groups are equivalent. The ^{31}P NMR spectra of both complexes are very similar and show, at low temperature (−60 °C), the typical pair of doublets due to coupling of ^{31}P to both ^{107}Ag and ^{109}Ag isotopes [centred at δ 14.28 ($J_{^{107}Ag\text{-}P}$ = 625, $J_{^{109}Ag\text{-}P}$ = 721 Hz) (**3**) and at δ 12.95 ($J_{^{107}Ag\text{-}P}$ = 610, $J_{^{109}Ag\text{-}P}$ = 701 Hz) (**4**)], indicating that at low temperature the Ag–P bonds are retained in solution, and also the chemical equivalence of the two phosphorus atoms. However, as the temperature is raised, broadening and collapse of the phosphorus resonances in both complexes is evident. At room temperature (25 °C) for complex **4** and at 55 °C for complex **3** only one broad resonance [centred at δ 12.5 (**4**) and 14.2 (**3**)] is observed, which probably indicates rapid exchange of PPh_3 on the NMR time scale. This behaviour is not surprising, since in solution fast phosphine exchange processes have been previously found for phosphine complexes of silver(I).[3]

In order to establish the bonding features of the alkynyl ligands in the complexes, a single crystal X-ray study of **3** has been carried out.[‡] The structure of **3** is shown in Fig. 1(*a*). The

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[†] To a stirred suspension of $[\{PtAg_2(C_6F_5)_2(C{\equiv}CR)_2\}_n]$ [0.082 g, 0.086 mmol (R = Ph); 0.150 g, 0.116 mmol (R = Bu^t)] in acetone (10 cm^3) was added triphenylphosphine [0.045 g, 0.172 mmol (R = Ph); 0.061 g, 0.231 mmol (R = Bu^t)]. Immediately, a yellow (R = Ph) or colourless (R = Bu^t) solution was formed. The mixture was stirred for 30 min, evaporated to a small volume (1 cm^3) and ethanol (10 cm^3) was added, to give **3** or **4** as a pale yellow or white solid respectively, which were filtered off, washed with ethanol and air dried (yield: 61 **3**, 87% **4**). Compound **3** (Found: C, 52.40; H, 2.95. Calc. for $C_{64}H_{40}Ag_2F_{10}P_2Pt$: C, 52.20; H, 2.75%), M_w in $CHCl_3$: 1567 (calc. 1472). IR: $\nu(C{\equiv}C)$ 2051m, 2033 (sh) cm^{-1}. NMR ($CDCl_3$): ^{19}F (188.22 MHz, reference $CFCl_3$), δ −117.9 (d, F_o, $^3J_{Pt\text{-}F_o}$ = 399 Hz), −165.5 (t, F_p), −166.8 (m, F_m); ^{31}P (80.984 MHz, 85% H_3PO_4), at −60 °C, δ 14.28 (dd, sp, $J_{^{107}Ag\text{-}P}$ = 625, $J_{^{109}Ag\text{-}P}$ = 721); at −30 °C, δ 14.26 (dd, less sharp than at −60 °C); at 25 °C, δ 14.1 (d, br, $J_{^{107,109}Ag\text{-}P}$ = 600 Hz); at 55 °C, δ 14.2 (s, br). Compound **4** (Found: C, 50.35; H, 3.65. Calc. for $C_{60}H_{48}Ag_2F_{10}P_2Pt$: C, 50.35; H, 3.40%), M_w in $CHCl_3$: 1529 (calc. 1432). IR: $\nu(C{\equiv}C)$ 2040m cm^{-1}. NMR ($CDCl_3$): ^1H (200.057 MHz, $SiMe_4$), δ 0.86 (s, Bu^t), 7.47, 7.6 (m, Ph); ^{19}F, δ − 117.9 (d, F_o, $^3J_{Pt\text{-}F_o}$ = 408 Hz), − 166.7 (t, F_p), −167.8 (m, F_m); ^{31}P, at −60 °C, δ 12.95 (dd, sp, $J_{^{107}Ag\text{-}^{31}P}$ = 610, $J_{^{109}Ag\text{-}^{31}P}$ =701); at −30 °C, δ 12.86 (d, br, $J_{^{107,109}Ag\text{-}^{31}P} \approx$ 626 Hz); at 25 °C, δ 12.5 (s, br); T_c = *ca.* 0 °C.

[‡] Crystal data. $C_{64}H_{40}Ag_2F_{10}P_2Pt\cdot 0.25CH_2Cl_2$, M_r = 1487.42, monoclinic, space group $P2_1/c$, a = 22.650(6), b = 13.800(3), c = 19.619(5) Å, β = 95.55(2)°, U = 6101(3) Å^3, Z = 4, D_c = 1.625 Mg m^{-3}, λ(Mo-Kα) = 0.710 73 Å, μ = 3.065 mm^{-1}, F(000) = 2906, T = 298 K, crystal dimensions = 0.38 × 0.40 × 0.50 mm, Nicolet autodiffractometer, ω scan technique. Standard Patterson method. Refinement on F^2 for all reflections (SHELXL 93[4]). Anisotropic thermal parameters for all non-hydrogen atoms, except for a phenyl group, which was modelled as equally disordered in two positions. Hydrogen atoms added at fixed positions (C–H = 0.96 Å). Crystal contains $\frac{1}{4}$ molecule of CH_2Cl_2 per formula unit. The final $wR(F^2)$ was 0.143, conventional $R(F)$ was 0.068 for 4678 data with $F > 4\sigma F_o$ and 728 parameters. Weighting scheme, $w = 1/\sigma^2(F_o)^2 + (0.0710\ \ P)^2$, where $P = [(F_o{}^2,\ \ 0) + 2F_c{}^2]_{max}/3$. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

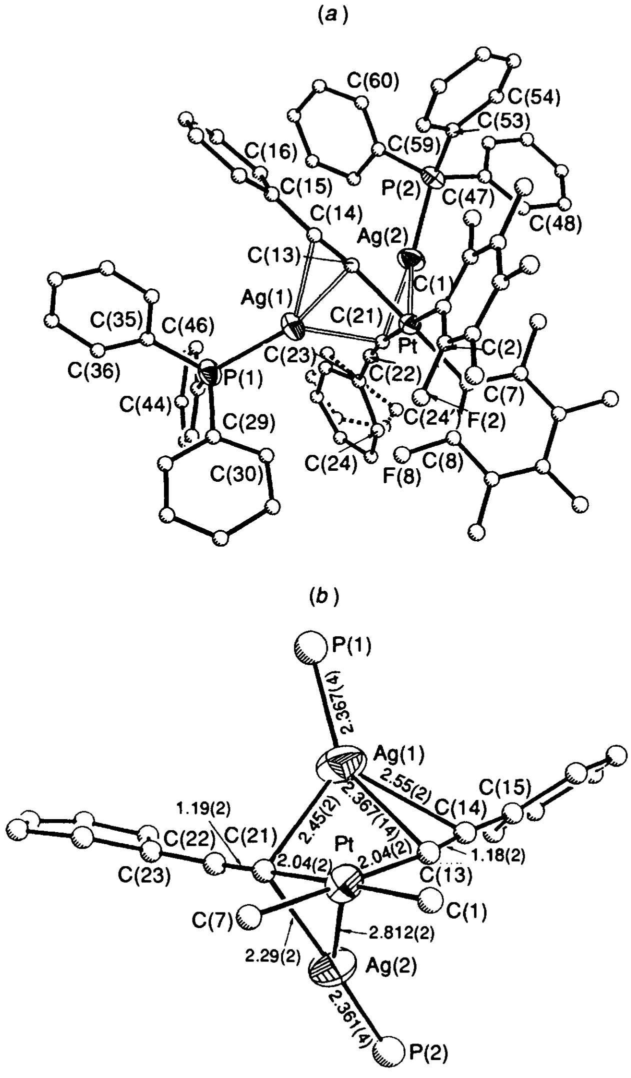

Fig. 1 (*a*) View of complex **3** with the atom numbering scheme. The alternative orientations of the two disordered phenyl ligands are indicated by atoms with dashed bonds. (*b*) Schematic view of the asymmetrical μ_3-σ and μ-η^2,σ bonding alkynyl groups; bond lengths in Å; bond angles (°): Pt–C(13)–C(14) 169.9(14), C(13)–C(14)–C(15) 175(2), Pt–C(21)–C(22) 173.1(14), C(21)–C(22)–C(23) 170(2), Pt–C(21)–Ag(1) 83.8(6), Pt–C(21)–Ag(2) 80.7(5)

whole molecule, which consists of one platinum Pt(C_6F_5)$_2$(C$\equiv$CPh)$_2$ and two silver Ag(PPh$_3$) fragments, is very unsymmetric. This situation can be observed in more detail in Fig. 1(*b*), which shows a skeletal view of the molecule. The most remarkable feature is that one of the Ag(PPh$_3$) units [Ag(1)–PPh$_3$] is bonded to both alkynyl groups, while the other [Ag(2)–PPh$_3$] unit is bonded to the platinum atom and to one alkynyl function. As a consequence, the two C$\equiv$CPh fragments co-ordinate differently. The alkynyl C(13)C(14)Ph moiety co-ordinates in the usual μ-η^2,σ manner, being σ bonded to Pt [Pt–C(13) 2.04(2) Å] and asymmetrically η^2 bonded to Ag(1) [Ag(1)–C(13) 2.367(14) *vs.* Ag(1)–C(14) 2.55(2) Å]. The other alkynyl group, C(21)C(22)Ph, is positioned so that C_α [C(21)] interacts with the three metal atoms with a σ bond to the platinum centre [Pt–C(21) 2.04(2) Å] and two asymmetric bonds to the silver atoms [Ag(2)–C(21) 2.29(2) *vs.* Ag(1)–C(21) 2.45(2) Å]. The interactions of C(22) (C_β) with Ag(1) and Ag(2) can be considered to be negligible [2.90(2) and 2.83(2) Å, respectively] suggesting that the C(21)C(22)Ph ligand is essentially co-ordinated through C(21). In spite of such a different bonding mode for both alkynyl functions, the two very short C$\equiv$C bond lengths observed are identical within experimental error [C(13)–C(14) 1.18(2) and C(21)–C(22) 1.19(2) Å, respectively] and comparable to that found in free acetylene (1.189 Å).[5] The acetylenic fragments are not significantly distorted from linearity [see Fig. 1(*b*)]. Finally, the two platinum–silver distances are different, probably reflecting the bridging characteristics of both alkynyl ligands. The shortest bond length [Pt–Ag(2) 2.812(2) Å] which is close to those reported for other platinum–silver bonds,[6] is associated with the acute Pt–C(21)–Ag(2) bond angle [80.7(5)°] subtended at the C_α of the asymmetric μ_3-σ acetylide ligand. The Pt–Ag(1) distance of 3.014(2) Å is longer, excluding any kind of metal–metal bonding interaction.

Acknowledgements

We thank the Comisión Interministerial de Ciencia y Tecnología (Spain, Project PB 92–0364) and the Instituto de Estudios Riojanos (Spain) for financial support.

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Received 22*nd June* 1994; *Communication* 4/03805C