Rings and linear polymers formed by addition of silver perchlorate to *trans*-$[Pt(C{\equiv}CR)_2(PMe_2Ph)_2]$ (R = Bu^t, H)

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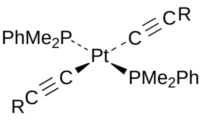
Addition of $AgClO_4$ to *trans*-$[Pt(C{\equiv}CR)_2(PMe_2Ph)_2]$ (R = Bu^t, H) gives 1 : 1 adducts of the general formula *trans*-$[PtAg(ClO_4)(\mu\text{-}C{\equiv}CR)_2(PMe_2Ph)_2]$ which are cyclic dimers when R = Bu^t (ClO_4^- not coordinated) or linear polymers when R = H (ClO_4^- coordinated to silver).

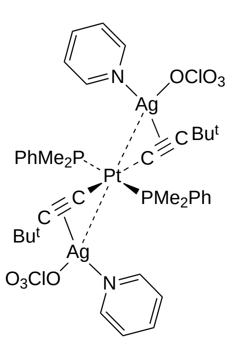
cis-Dialkynyl complexes of platinum behave as chelating bidentate ligands at copper(i) and silver(i). *cis*-$[Pt(CuCl)(C{\equiv}CBu^t)_2(PMe_2Ph)_2]$ **1** contains Cu coordinated to two alkynes and a chloride ligand and the complexes $[Pt_2M(C{\equiv}CPh)_4(dppe)_2][BF_4]$ (M = Cu[1], Ag[2]) and *cis*-$[Pt_2Ag(C{\equiv}CPh)_4(PPh_3)_4][ClO_4]$[3] contain Ag or Cu atoms coordinated tetrahedrally to four alkyne groups. Some recent examples of coordination of Pt alkynyl complexes to silver(i)[1–4] and a review by Forniés and Lalinde have appeared.[5]

Attempting to form linear polymers containing M(μ-C≡CR)M′ components, we coupled CuCl with *trans*-$[Pt(C{\equiv}CBu^t)_2(PMe_2Ph)_2]$. Since the alkynyl ligands are *trans* at platinum, chelation is not possible and the linear polymer $[\{PtCu_2Cl_2(C{\equiv}CBu^t)_2(PMe_2Ph)_2\}_n]$ with the polymer backbone $\cdots Pt[(\mu\text{-}C{\equiv}CR)CuCl_2Cu(\mu\text{-}RC{\equiv}C)Pt]_n(\mu\text{-}C{\equiv}CR)\cdots$ was obtained.[6] This paper describes our preparation of halide-free polymers with the backbone $\cdots Pt(\mu\text{-}C{\equiv}CR)[Ag(\mu\text{-}RC{\equiv}C)Pt(\mu\text{-}C{\equiv}CR)]_nAg\cdots$ composed only of metal and bridging alkynyl ligands.

The complex *trans*-$[Pt(C{\equiv}CBu^t)_2(PMe_2Ph)_2]$ **1a** reacts with $AgClO_4$ (2 mol/mol Pt) in acetonitrile to give *trans*-$[PtAg_2(MeCN)_x(\mu\text{-}C{\equiv}CBu^t)_2(PMe_2Ph)_2][ClO_4]_2$ **2** (x is probably 4) and we have determined the X-ray structure of the corresponding copper complex with $x = 4$.[2] Treatment of **2** with pyridine gave the neutral derivative *trans*-$[PtAg_2(ClO_4)_2(py)_2(\mu\text{-}C{\equiv}CBu^t)_2(PMe_2Ph)_2]$ **3** which was characterised by single-crystal X-ray diffraction.[2] In **3** one silver ion coordinates to each of the two alkynyl ligands and polymerisation is prevented. However, with restricted addition of $AgClO_4$ (1 mol/mol Pt complex) to *trans*-$[Pt(C{\equiv}CBu^t)_2(PMe_2Ph)_2]$ **1a**, a complex is formed which crystallised from benzene as *trans*-$[Pt_2Ag_2(\mu\text{-}C{\equiv}CBu^t)_4(PMe_2Ph)_4][ClO_4]_2\cdot 2C_6H_6$ **4**$\cdot 2C_6H_6$.† The stoichiometry fits a linear polymer but in this case an alternative cyclic dimer is formed. The X-ray structure was determined at 150(2) K because of crystal degradation at 293 K (see Fig. 1).‡ In contrast to compound **3**, the silver atoms in **4** coordinate on the same face of the Pt coordination plane allowing two square-planar Pt complexes to be glued parallel to each other by two



1a R = Bu^t
b R = H



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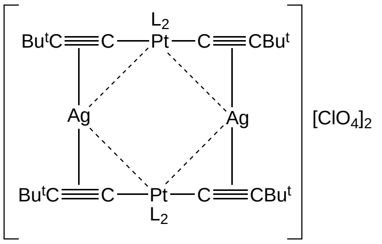


4 (L = PMe_2Ph)

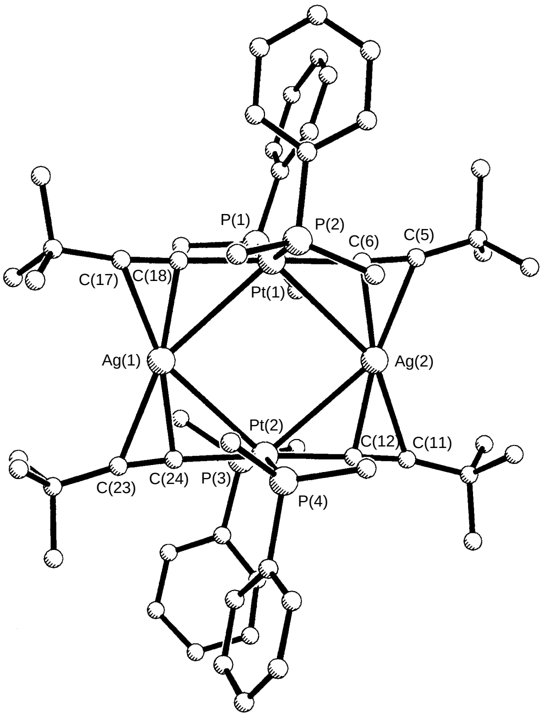


Fig. 1 Structure of the square dicationic complex in *trans*-$[Pt_2Ag_2(\mu\text{-}C{\equiv}CBu^t)_4(PMe_2Ph)_4][ClO_4]_2\cdot 2C_6H_6$ **4**$\cdot 2C_6H_6$. The non-coordinated perchlorate ions and the benzene molecule are not shown.

Ag^+ ions. The perchlorate ions are not coordinated. The Pt_2Ag_2 set of atoms is closely planar and approximately square [Pt–Ag distances 3.1960(10), 3.2161(9), 3.2080(9), 3.2683(10) Å; Pt–Ag–Pt angles 86.51(2), 85.44(2)°; Ag–Pt–Ag angles 93.26(2), 94.79(2)°; Pt···Pt 4.3938(9) Å and Ag···Ag 4.7138(9) Å]. The Ag atoms appear to be pulled in towards the centre of the square resulting in shorter contacts with the α than the β alkynyl carbon atoms [av. Ag–C^α 2.236 Å, av. Ag–C^β 2.448 Å] (Fig. 2). Pt···Ag distances up to 2.95 Å have been considered to indicate donor interactions from Pt to Ag but in this case the average Pt···Ag distance of 3.22 Å shows that such interactions must be extremely weak.[7]

The Bu^t groups in **4** are bent away from each other [av. $C^\alpha C^\beta C(Bu^t)$ 169.1°], as are the tertiary phosphines [P–Pt–P 160.06(8), 163.95(8)°], suggesting that replacement of the Bu^t groups by smaller substituents would allow the cyclic molecules to relax into a tighter configuration. However, addition of $AgClO_4$ (1 mol/mol Pt) to *trans*-$[Pt(C{\equiv}CH)_2(PMe_2Ph)_2]$ gives crystals of *trans*-$[PtAg(ClO_4)(\mu\text{-}C{\equiv}CH)_2(PMe_2Ph)_2]$ **5**† which, rather than forming a cyclic dimer, gives a linear polymer (X-ray structure, Fig. 3).‡ Relaxation of crowding around Ag has allowed the perchlorate to coordinate to it and the *trans* PMe_2Ph ligands to become closely linear [P–Pt–P 177.2(1)°]. The Ag^+ ions still coordinate on the same face of each Pt coordination plane (as in **4** but not **3**) forming a zigzag chain with a perchlorate ion in each cavity along the chain. In addition to the short coordinated Ag–O distance [Ag(1)–O(1) 2.65(1) Å], there are number of ClO_4^--to-chain contacts which might help to stabilize this arrangement. The shortest C≡CH···O contact is too long to be considered a hydrogen bond. [C^β···O 3.56 Å]. Fig. 2 shows the differences in the geometries of Ag^+ coordination in compounds **4** and **5**. The Ag^+ ion is more closely coordinated to C^α than C^β in **5**, the reverse of the situation in **4**, and Pt···Ag distance are much longer in **5** than in **4**.

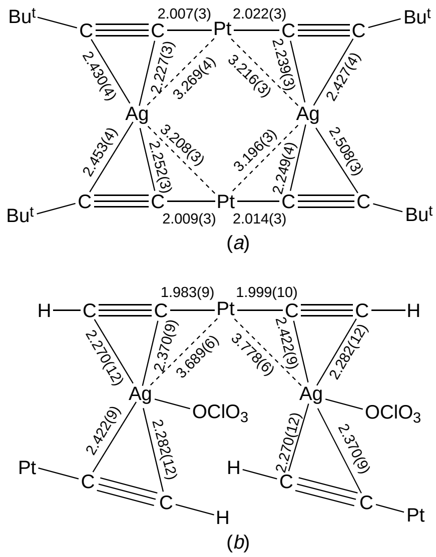
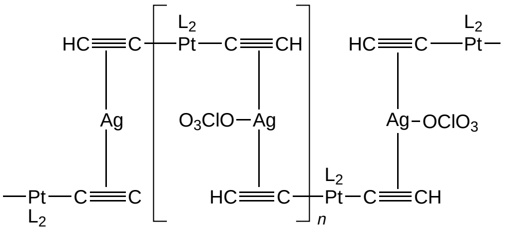


Fig. 2 Details of the Ag/Pt/alkynyl ligand geometries in **4**·$2C_6H_6$ (*a*) and in **5** (*b*); distances in Å



5 (L = PMe_2Ph)

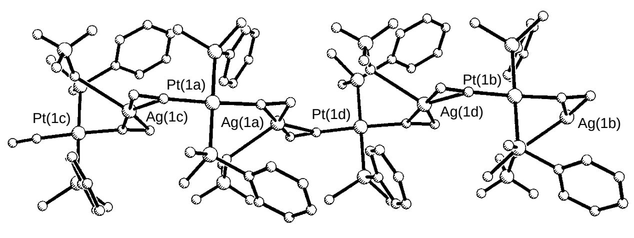


Fig. 3 Structure of the linear polymer $[\{PtAg(ClO_4)(C{\equiv}CH)_2(PMe_2Ph)_2\}_n]$ **5**; in this case the coordinated perchlorate ions are shown

We have tried to synthesise analogues of **5** with other counter ions such as BPh_4^- which are too big to fit the cavities or unlikely to coordinate but no crystalline products could be obtained. We have still to assess properly the factors that control the mode of aggregation of $[PtAg(ClO_4)(C{\equiv}CR)_2(PMe_2Ph)_2]$ units in complexes of this type.

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Footnotes

† *Synthesis and spectra* of Ag–Pt complexes. Compound **4**: a solution of **1a** (0.223 g) in acetonitrile was treated with $AgClO_4$ (0.081 g). Addition of benzene and slow evaporation at room temp. gave pale yellow crystals of **4**·$2C_6H_6$ (0.240 g, 98%); ν(C≡C) (Nujol), 2031w cm^{-1}; ^1H NMR (CD_3CN): δ 1.17 (s, Bu^t), 2.02 [t, *J*(PH) 7.4, *J*(PtH) 30.8 Hz, PMe_2Ph], 7.37 (s, C_6H_6), 7.4–8.0 (PMe_2Ph); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 15.08 [t, *J*(PC) 39.1 Hz, PMe_2Ph], 30.82 (CMe_3), 32.55 (CMe_3); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ −14.79 [*J*(PtP) 2109 Hz].

Compound **5**: a solution of **1b** {prepared from *cis*-$[PtCl_2(PMe_2Ph)_2]$ and NaC_2H in liquid NH_3} (0.20 g) in acetonitrile was treated with $AgClO_4$ (0.088 g). Addition of benzene led to the gradual crystallization of pale yellow crystals (0.11 g, 40%), ν(C≡C) (Nujol), 1914 cm^{-1}; ^1H NMR spectra (CD_3CN) show a mixture, FABMS (NOBA matrix) showed $[Pt_2Ag(C_2H)_4(PMe_2Ph)_4]^+$ and $[PtAg(C_2H)_2(PMe_2Ph)_2]^+$ as the highest mass ions.

‡ *Crystal data*. Compound **4**·$2C_6H_6$: $C_{68}H_{92}Ag_2Cl_2O_8P_4Pt_2$, pale yellow crystals from benzene, 0.40 × 0.20 × 0.15 mm, M = 1838.12, triclinic, space group $P\bar{1}$, a = 14.608(2), b = 16.338(2), c = 16.356(3) Å, α = 87.28(1), β = 75.02(1), γ = 76.43(1)°, U = 3665.3(13) Å^3, Z = 2, D_c = 1.66 g cm^{-3}, 9854 unique data, 9854 used, 723 parameters, R_1 = 0.0522, wR_2 = 0.0916. Compound **5**: $C_{20}H_{24}AgClO_4P_2Pt$, pale yellow crystals from acetonitrile–benzene, 0.09 × 0.22 × 0.40 mm, M = 728.29, monoclinic, space group $P2_1/c$, a = 10.481(2), b = 12.236(2), c = 18.868(3) Å, β = 101.53(1)°, U = 2371.3(6) Å^3, Z = 4, D_c = 2.04 g cm^{-3}, 4173 unique data, 3163 used [$I_o > 3\sigma(I_o)$], 262 parameters, R = 0.0387, R_w = 0.0428.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/324.

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