Neutral Pentanuclear Pt_3Ag_2 Complexes: Crystal Structure of *trans*-$[PtCl_2\{(\mu\text{-}SC_4H_8)Pt(C_6F_5)_3(\eta^2\text{-}C_6H_5Me)\}_2]$ *

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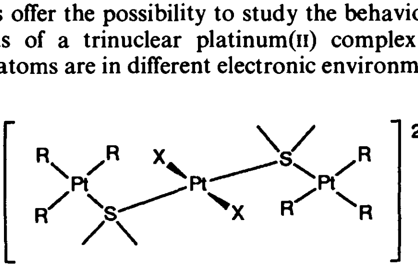
By treating $[NBu_4]_2[$*trans*-$PtX_2\{(\mu\text{-}SC_4H_8)Pt(C_6F_5)_3\}_2]$ (X = Cl or Br) with $AgClO_4$ (molar ratio 1 : *n*, where *n* = 1—4) in dichloromethane–toluene solution the neutral pentametallic complexes *trans*-$[PtX_2\{(\mu\text{-}SC_4H_8)(C_6F_5)_3PtAg(\eta^2\text{-}C_6H_5Me)\}_2]$ [X = Cl, (1); or Br, (2)] have been obtained. The structure of (1) has been established by *X*-ray diffraction and shows that two new Pt–Ag bonds have been formed as the result of the addition of two $Ag(\eta^2\text{-}C_6H_5Me)$ fragments to the terminal platinum atoms of the trinuclear starting complex.

During the last few years we have prepared a variety of heteropolynuclear complexes, most of which display Pt–Ag bonds[1,2] by treating silver salts ($AgClO_4$ or $AgNO_3$) or silver complexes $\{[Ag(ClO_4)L]$, L = PPh_3, $PMePh_2$, or $PEt_3\}$ with monomeric or dimeric anionic platinum(II) complexes, containing pentahalogenophenyl ligands C_6X_5 (X = F or Cl). Although the nature of each product is dependent on the platinum precursor and on the silver compound, we think that a general feature is the enhanced electron density on the platinum atoms of the anionic complexes, which can be donated to the electrophilic silver centres to give the polynuclear complexes. Polynuclear Pt–Ag complexes have also been synthesized by using neutral $[PtMe_2(bipy)]$ (bipy = 2,2′-bipyridine) as a basic centre but the stability of these derivatives is much lower.[3]

We have recently synthesized anionic trimetallic complexes of the type $[NBu_4]_2[$*trans*-$PtX_2\{(\mu\text{-}SC_4H_8)Pt(C_6F_5)_3\}_2]$ (X = Cl, Br, or I; SC_4H_8 = tetrahydrothiophene)[4] containing two terminal 'anionic' $Pt(C_6F_5)_3$ fragments linked to a 'neutral' *trans*-$PtX_2(\mu\text{-}SC_4H_8)_2$ central moiety through the bridging S atoms of the two SC_4H_8 ligands. For the first time these complexes offer the possibility to study the behaviour towards silver salts of a trinuclear platinum(II) complex where the platinum atoms are in different electronic environments.



Results and Discussion

The reaction between $[NBu_4]_2[$*trans*-$PtCl_2\{(\mu\text{-}SC_4H_8)Pt(C_6F_5)_3\}_2]$ and $AgClO_4$ in CH_2Cl_2–toluene has been carried out in different trinuclear complex/$AgClO_4$ ratios from 1 : 1 to 1 : 4, the same polymetallic Pt_3Ag_2 compound *trans*-$[PtX_2\{(\mu\text{-}SC_4H_8)(C_6F_5)_3PtAg(\eta\text{-}C_6H_5Me)\}_2]$ (1) was always obtained albeit in different yields, the highest for the 1 : 4 ratio. As will be seen from the *X*-ray structure of (1), only the more external and anionic platinum centres are able to react with $AgClO_4$. It seems noteworthy that the tetranuclear Pt_3Ag compound could not be obtained since the reaction in a 1 : 1 molar ratio renders only complex (1) (albeit in lower yield, 28%), along with unreacted starting material.

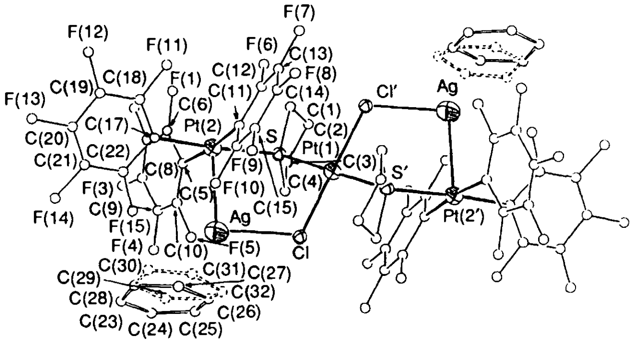


Figure. Molecular structure of complex (1). All non-metallic atoms are represented by arbitrarily small circles for clarity. Dotted rings are used for toluene molecules in position B. The methyl group in the toluene molecule is not shown owing to positional disorder

The corresponding bromo derivative (2) is obtained in a similar way, whilst the iodo compound could not be obtained since the reaction between $[NBu_4]_2[$*trans*-$PtI_2\{(\mu\text{-}SC_4H_8)Pt(C_6F_5)_3\}_2]$ and $AgClO_4$, under similar conditions results in precipitation of AgI. Analytical and i.r. data are given in the Experimental section.

The structure of complex (1) has been established by single-crystal *X*-ray diffraction and is shown in the Figure. The atomic co-ordinates are presented in Table 1, selected bond distances and angles in Table 2. The pentametallic complex is formed by addition of two $Ag(\eta^2\text{-}C_6H_5Me)^+$ fragments to the terminal Pt atoms of the trimetallic starting anion. The central Pt(1) atom lies on a symmetry centre and has a square-planar environment formed by two *trans*-chloride and two *trans*-SC_4H_8 ligands, whilst the two terminal Pt(2) and Pt(2′) atoms have a slightly distorted square-pyramidal co-ordination with apical silver. The Pt atoms are only 0.076 Å from the best least-squares basal

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* *trans*-Di-μ-chloro-2:3κ²*Cl*; 3:4κ²*Cl*-hexakis(pentafluorophenyl)-1κ³*C*¹,5κ³*C*¹-bis(μ-tetrahydrothiophene)-1:3κ²*S*; 3:5κ²*S*-bis[2,4(η²)-toluene]-1,3,5-triplatinum-2,4-disilver.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. Fractional atomic co-ordinates (× 10^4) and their estimated standard deviations for complex (**1**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pt(1)	0	0	0	C(22)	4 571(15)	2 343(19)	3 994(11)
Pt(2)	3 398(1)	1 350(1)	1 939(1)	F(1)	6 300(9)	2 064(9)	1 708(7)
Ag	1 375(1)	2 449(1)	2 667(1)	F(2)	7 919(10)	4 392(12)	1 918(9)
Cl(1)	−486(4)	1 693(4)	1 074(3)	F(3)	7 128(11)	6 790(10)	2 433(8)
S	2 152(3)	1 252(3)	464(2)	F(4)	4 573(11)	6 844(9)	2 638(7)
C(1)	3 202(14)	767(17)	−353(10)	F(5)	2 965(8)	4 578(8)	2 465(6)
C(2)	3 009(26)	1 717(22)	−945(14)	F(6)	3 429(10)	−1 469(9)	626(6)
C(3)	2 929(25)	3 056(21)	−376(15)	F(7)	2 265(13)	−3 997(10)	393(8)
C(4)	1 917(16)	2 862(13)	197(11)	F(8)	594(12)	−4 532(10)	1 416(10)
C(5)	4 553(13)	3 189(13)	2 106(8)	F(9)	166(11)	−2 479(11)	2 704(10)
C(6)	5 814(16)	3 241(15)	1 963(10)	F(10)	1 325(11)	14(10)	2 969(7)
C(7)	6 696(16)	4 438(18)	2 087(13)	F(11)	5 445(9)	−488(10)	2 532(7)
C(8)	6 287(18)	5 613(18)	2 310(11)	F(12)	6 926(12)	−505(13)	4 197(10)
C(9)	5 012(16)	5 652(13)	2 415(10)	F(13)	6 862(14)	1 355(17)	5 750(9)
C(10)	4 195(13)	4 459(13)	2 339(10)	F(14)	5 308(14)	3 280(15)	5 609(7)
C(11)	2 409(14)	−592(13)	1 792(10)	F(15)	3 804(11)	3 287(12)	3 977(6)
C(12)	2 587(14)	−1 703(14)	1 141(11)	C(23)	2 002(43)	4 626(33)	5 029(24)
C(13)	2 033(16)	−2 965(14)	1 028(12)	C(24)	1 515(27)	5 148(21)	4 300(20)
C(14)	1 182(18)	−3 272(17)	1 531(16)	C(25)	447(33)	4 386(27)	3 560(19)
C(15)	987(15)	−2 219(18)	2 185(14)	C(27)	328(30)	2 601(25)	4 288(19)
C(16)	1 588(15)	−911(17)	2 298(12)	C(26)	−157(25)	3 121(23)	3 558(15)
C(17)	4 530(14)	1 335(15)	3 168(11)	C(28)	1 457(26)	3 324(27)	4 997(16)
C(18)	5 364(15)	470(17)	3 298(11)	C(29)	951(34)	3 848(29)	4 270(22)
C(19)	6 106(20)	427(21)	4 150(16)	C(30)	893(37)	2 031(31)	4 972(25)
C(20)	6 072(21)	1 400(27)	4 909(14)	C(31)	−289(45)	1 350(34)	4 299(31)
C(21)	5 290(21)	2 294(24)	4 824(14)	C(32)	−877(26)	1 938(26)	3 631(21)

Table 2. Selected bond distances (Å) and angles (°) for *trans*-$[PtCl_2\{(\mu\text{-}SC_4H_8)(C_6F_5)_3PtAg(\eta^2\text{-}C_6H_5Me\}_2]$

Cl–Pt(1)	2.297(4)	S–Pt(1)	2.301(3)
Ag–Pt(2)	2.818(2)	S–Pt(2)	2.328(4)
C(5)–Pt(2)	2.061(13)	C(11)–Pt(2)	2.092(14)
C(17)–Pt(2)	2.004(15)	Cl–Ag	2.637(4)
C(25)–Ag	2.565(31)	C(26)–Ag	2.388(27)
C(29)–Ag	2.718(33)		
S–Pt(1)–Cl	85.8(1)	S–Pt(2)–Ag	89.9(1)
C(5)–Pt(2)–Ag	95.1(4)	C(5)–Pt(2)–S	92.7(4)
C(11)–Pt(2)–Ag	89.9(4)	C(11)–Pt(2)–S	90.3(4)
C(11)–Pt(2)–C(5)	174.2(6)	C(17)–Pt(2)–Ag	93.6(5)
C(17)–Pt(2)–S	176.1(5)	C(17)–Pt(2)–C(5)	88.5(6)
C(17)–Pt(2)–C(11)	88.1(6)	Cl–Ag–Pt(2)	94.5(1)
Pt(2)–S–Pt(1)	115.2(2)	Ag–Cl–Pt(1)	113.0(2)

plane (formed by a C atom of each C_6F_5 group and the S bridging atom). Moreover, the dihedral angle between the Pt(2), C(5), C(17) and Pt(2), S, C(11) planes is 173.96° and the Pt(2)–Ag bond deviates by 2.6° from perpendicularity to the basal plane.[5]

The silver atom receives electron density from Pt(2), one toluene molecule, one Cl atom from the central $Pt(1)Cl_2S_2$ fragment, and three *o*-F atoms, one from each C_6F_5 group bonded to Pt(2). The Pt(2)–Ag distance [2.818(2) Å] is longer than most distances found in other complexes containing Pt^{II}–Ag bonds.[1] The toluene molecule is disordered, with 55% in position A and 45% in B (Figure). Both types of positions share the C(26) and C(28) atoms (100% occupancy): C(26) shows the shorter C–Ag distance 2.388(27) Å followed by a contiguous C atom on each toluene molecule, C(25)–Ag 2.565(31) or C(29)–Ag 2.718(33) Å. Despite the disorder, the toluene molecule can be considered as η^2 bonded to the silver atoms, as usual in silver–arene complexes.[6]

On the other hand, each chloride ligand of the central square-planar Pt(1) is located at 2.637(4) Å from a silver atom. This distance is longer than several other Ag–Cl distances found in cases where the chloride ligand is acting as a bridge between two metal atoms, *e.g.* *trans*$[Pt(C_6Cl_5)_2\{(\mu\text{-}Cl)Ag(PMePh_2)\}_2]$ 2.418(2) Å, $[NBu_4][$*trans*$\text{-}Pt(C_6F_5)_2Cl\{(\mu\text{-}Cl)Ag(PPh_3)\}_2]$ 2.473(8) Å, and $\{[NBu_4][Pt(C_6Cl_5)_2Cl_2Ag]\}_x$ 2.477(5) Å.[1] However there are also examples where similar or longer μ-Ag–Cl distances have been found: $[NBu_4][$*trans*$\text{-}Pt(C_6Cl_5)_2Cl(\mu\text{-}Cl)Ag(PPh_3)]$ 2.667 Å,[1] $[\{AgCl(C_9H_7N)\cdot0.25(C_9H_7N)\}_n]$ (C_9H_7N = quinoline) with distances ranging from 2.600(4) to 2.725(4) Å,[7] or in the cubane-like $[\{AgCl(PPh_3)\}_4]$[8] and $[\{AgCl(PEt_3)\}_4]$[9] with distances of 2.656(3) and, 2.6475 (av.) Å. Although none of these examples is completely similar to the present complex, it seems sensible to assign a bridging role to the Cl atoms in (**1**), in which the skeleton can be considered as formed by two five-membered rings, each containing three metal atoms and with Pt(1) shared by the two rings.

Moreover, the three C_6F_5 groups bonded to each terminal Pt atom are so positioned that one *o*-F atom of each group lies at a short distance from the silver atom [F(5) ··· Ag 2.732(9), F(10) ··· Ag 2.686(11), and F(15) ··· Ag 2.733(9) Å].

It is interesting that the structural data for the $(C_6F_5)_3Pt(\mu\text{-}SC_4H_8)PtCl_2(\mu\text{-}SC_4H_8)Pt(C_6F_5)_3$ fragment in (**1**) are very similar to those found for the structure of the starting material; even the Pt–Cl distances are equal within experimental error [2.295(4) and 2.297(4) Å, respectively] although in (**1**) the Cl is acting as a bridging ligand. The main difference between both structures is the orientation of the C_6F_5 group *trans* to the SC_4H_8 ligand which in (**1**) is rotated by 43.3° with respect to the situation in the starting material, this being necessary for the short F(15) ··· Ag contact.

The bromide derivative (**2**) is likely to have a similar structure, but is less stable. Acetone solutions of (**1**) are non-conducting, whilst (**2**) is non-conducting in CH_2Cl_2 but conducting in acetone, possibly owing to cleavage of the donor–acceptor Pt–Ag bonds because of the donor nature of the solvent. Similar cleavage of Pt–Ag bonds has previously been observed in other Pt–Ag complexes.[1]

Experimental

Preparation of $trans$-$[\mathrm{PtX_2\{(\mu\text{-}SC_4H_8)(C_5F_6)_3PtAg(\eta^2\text{-}C_6H_5Me)\}_2}]$ [X = Cl, (**1**) *or* Br, (**2**)].—To a solution of $\mathrm{AgClO_4}$ (0.0715 g, 0.345 mmol) in toluene (3 $\mathrm{cm^3}$) was added $\mathrm{CH_2Cl_2}$ (30 $\mathrm{cm^3}$): the mixture was cooled to 0 °C and then $[\mathrm{NBu_4}]_2[trans\text{-}\mathrm{PtCl_2\{(\mu\text{-}SC_4H_8)Pt(C_6F_5)_3\}_2}]$[4] (0.2 g, 0.0862 mmol) was added. The resulting pale yellow solution was magnetically stirred and after 10 min a pale yellow solid began to precipitate. After stirring for 1 h the solid was filtered off and washed with toluene and n-hexane [Found: C, 31.25; H, 1.50. Calc. for (**1**): C, 31.15; H, 1.45%], yield 78%, decomp. 240 °C, Λ_M (acetone, *ca.* 5×10^{-4} mol $\mathrm{dm^{-3}}$) 7 $\mathrm{ohm^{-1}\ cm^2\ mol^{-1}}$. I.r. (Nujol): $\mathrm{C_6F_5}$ groups, 958vs, 950vs, 804s, 792m, and 775s; $\mathrm{SC_4H_8}$ groups, 1 270m, 1 257m, and 880 m; ν(Pt–Cl) 340m; toluene, 752s, and 694m $\mathrm{cm^{-1}}$.

Complex (**2**) was similarly prepared in 84% yield from $\mathrm{AgClO_4}$ (0.0723 g, 0.35 mmol) and $[\mathrm{NBu_4}]_2[trans\text{-}\mathrm{PtBr_2\{(\mu\text{-}SC_4H_8)Pt(C_6F_5)_3\}_2}]$ (0.21 g, 0.0875 mmol). [Found: C, 29.65; H, 1.15. Calc. for (**2**): C, 29.95: H, 1.35%], decomp. 210 °C, Λ_M (acetone, *ca.* 5×10^{-4} mol $\mathrm{dm^{-3}}$) 98 $\mathrm{ohm^{-1}\ cm^2\ mol^{-1}}$, (dichloromethane, *ca.* 5×10^{-4} mol $\mathrm{dm^{-3}}$) 4 $\mathrm{ohm^{-1}\ cm^2\ mol^{-1}}$. I.r. (Nujol): $\mathrm{C_6F_5}$ groups, 960vs, 953vs, 804s, 792m, and 775s; $\mathrm{SC_4H_8}$ groups, 1 270m, 1 258m, and 880m; toluene, 750s and 694m $\mathrm{cm^{-1}}$. In absence of toluene no reaction takes place and the starting products are recovered. Synthesis and isolation of the complexes were carried out with the exclusion of light.

X-*Ray Crystallographic Analysis of Complex* (**1**).—Yellow crystals of complex (**1**) suitable for crystal-structure investigation were obtained by slow diffusion (*ca.* 3 weeks at −30 °C) of n-hexane into a dichloromethane solution of the complex.

Crystal data. $\mathrm{C_{58}H_{32}Ag_2Cl_2F_{30}Pt_3S_2}$, M = 2 235, triclinic, space group $P\bar{1}$, a = 10.323(3), b = 10.404(3), c = 15.572(4) Å, α = 104.35(2), β = 103.38(2), γ = 96.46(2)°, U = 1 550 $\mathrm{Å^3}$, Z = 1, crystal dimensions 0.06 × 0.11 × 0.27 mm, $\mu(\text{Mo-}K_\alpha)$ = 73.36 $\mathrm{cm^{-1}}$, $F(000)$ = 1 044.

An empirical absorption correction[10] was applied (minimum and maximum transmission factors 0.253 and 0.460). Siemens/Stoe AED2 four-circle diffractometer. Data collection range $4 \leqslant 2\theta \leqslant 50°$. Scan method: ω—2θ. Total data: 5 800. Number of unique data with $F_o \geqslant 6\sigma(F_o)$: 2 593. The structure was solved by Patterson techniques and refined to R = 0.0346 and R' = 0.0349.[11] The weighting scheme was $w^{-1} = \sigma^2(F) + 0.001\,06\ F^2$. Toluene molecule disordered in two different orientations with two carbons C(26) and C(28) at full occupancy. A single variable was refined to describe the occupancies (α and 1 − α) of the non-shared carbons. The final occupancies were 0.55 for orientation A and 0.45 for **B**. All atoms, except those of the disordered toluene, were refined with anisotropic displacement parameters.

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

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