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# Electron-rich metal centres (Au, Pt) as sources of organometallic complexes with unusual features

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## Abstract

The central gold(I) atoms in binuclear complexes of the type $[AuR_2]^+$ (R = $C_6F_5$, $C_6Cl_5$, $CH_2PR_3$) are able to donate electron density to silver(I) cations to form polymeric or oligomeric compounds containing the cyclic $Au_2Ag_2$ moiety, with direct Au–Ag bonds unsupported by any other bridging ligand. One of the gold atoms in binuclear $\mu,\mu'$-bis(diphenylphosphinium)bis(methylido)digold(I) also donates electron density to the gold(III) atom in $Au(C_6F_5)_3$ to form the first unbridged direct $Au^I$–$Au^{III}$ bond.

Anionic $Pt^{II}$ complexes $[PtR_4]^{2-}$, $[PtX_2R_2]^{2-}$, $[Pt_2(\mu\text{-}X)_2R_4]^{2-}$, $[Pt_2(\mu\text{-}R_2)_2R_4]^{2-}$, etc. (R = $C_6F_5$ or $C_6Cl_5$) react with silver salts or complexes to form a variety of unusual heteronuclear derivatives, most of which display *o*-X... Ag short contacts, which seem to be responsible for the stability of the clusters. The homoleptic anion $[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]^-$ containing Pt in the average oxidation state of +2.5 can also be prepared by oxidation of the electron-rich binuclear $Pt^{II}$ precursor.

## Introduction

In comparison with other $M_T$–R bonds ($M_T$ = transition metal, R = alkyl or aryl group) the $M_T$–$C_6X_5$ (X = F, Cl) seem to be very stable either from a thermodynamic or kinetic point of view. It is possible to take advantage of this fact to synthesise not only the usual mono- or bi-arylated complexes (with the other coordination sites occupied by halide or neutral ancillary ligands), but also more heavily arylated or even homoleptic anionic complexes, which are stable enough for the study of the reactivity of the metal centres without loss of aryl ligands, i.e. preserving the organometallic character of the precursors.

From 1981, we have been engaged in the study of the nucleophilic behaviour of gold and platinum metal centres in a variety of pentahalophenyl derivatives. Using silver(I) or gold(III) as electrophilic metal centres we have synthesised quite a few novel compounds. These show very unusual features: (a) direct unbridged metal–metal bonds, (b) homoleptic, $C_6F_5$-bridged bi- or poly-nuclear complexes, (c) compounds containing $Au_2Ag_2$ rings, (d) $Au^I$–$Au^{III}$ or perhaps $Au^{II}$–$Au^{II}$ unsupported bonds, and so on.

I should like to discuss here some of our recent results in this field.

## A. Gold(I) as a donor centre

Despite the +1 oxidation state, several gold(I) complexes (neutral, anionic and even cationic ones) behave as if the gold atoms are able to donate electron density to other electrophilic metal centres. For instance, the gold(I) atom in $Q[AuR_2]$ ($Q = NBu_4$, $R = C_6F_5$, $C_6Cl_5$, $C_6F_3H_2$) appears to have excess electron density which can be donated to the silver cation $Ag^+$; subsequent addition of neutral donors L (eq. 1) precipitates yellow or red neutral insoluble complexes [1].

$$[AuR_2] + AgClO_4 \xrightarrow[+L]{-QClO_4} 1/x\ [AuR_2AgL]_x \qquad (1)$$

(L = N,P,O,S donors, olefin, acetylene, arene)

The structures of two of these complexes ($L = SC_4H_8$, $\mu_2$-$C_6H_6$) have been established by X-ray crystallography and are shown in Fig. 1. They are polymeric chains formed by repetition of the $R_2Au(\mu\text{-}AgL)_2AuR_2$ unit through Au...Au short contacts (2.889 and respectively, 3.013 Å) and some striking features may be noticed: (a) the complexes present direct Au–Ag bonds unsupported by any other bridging ligand, (b) the $Au_2Ag_2$ ring is almost regular in the $SC_4H_8$ derivative (Au–Ag distances: 2.726, 2.717 Å) but more asymmetric (2.702, 2.792 Å) in the $\eta^2$-$C_6H_6$ one. In the latter, one of the *ortho*-fluorine atom of a $C_6F_5$ group displays a short contact (Ag...*o*-F distance: 2.84 Å) with the nearest silver atom thus contributing both to the observed distortion and to the stability of the cluster.

The $AuR_2$ groups in both complexes are only very slightly distorted in comparison with the free $[AuR_2]^-$ anion, despite the fact that the gold atom donates electron density to two $Ag^+$ cations, as indicated by the $^{197}$Au Mössbauer spectrum [2].

Halide containing aurate(I) anions, $[AuRX]^-$ or $[AuX_2]^-$ do not give similar complexes, since the gold–halide bond is not inert and silver halide precipitates.

But even cationic gold(I) complexes are able to give similar $Au_2Ag_2$ rings if the gold atom is coordinated to two strong donating ylide ligands. Possibly, despite the overall positive charge, the gold atom has an excess of electron density, the partial positive charge being delocalised on the two P atoms: $[R_3\overset{+}{P}\text{–}\overset{-}{C}H_2\text{–}\overset{+}{Au}\text{–}\overset{-}{C}H_2\text{–}\overset{+}{P}R_3]^+$. Be that as it may, reaction (eq. 2) of the above cation with $AgClO_4$ affords neutral complexes containing the tetranuclear $Au_2Ag_2$ ring moiety:

$$2\ [Au(CH_2\text{–}PR_3)_2]ClO_4 + AgClO_4 \rightarrow$$
$$[(R_3P\text{–}CH_2)_2Au(\mu\text{-}Ag(OClO_3)_2)_2Au(CH_2\text{–}PR_3)] \qquad (2)$$

($PR_3 = PPh_3$, $PPh_2Me$, $PPhMe_2$)

The structure [3] of the complex with $PR_3 = PPh_3$ (Fig. 2) is centro-symmetric and the Au–Ag distances (2.783–2.760(2) Å) in the central $Au_2Ag_2$ ring are within the previously observed range (2.70–2.79 Å). The silver atoms are bonded to two gold atoms and two oxygen atoms (of two $OClO_3$ ligands) at 2.47 and 2.26 Å.

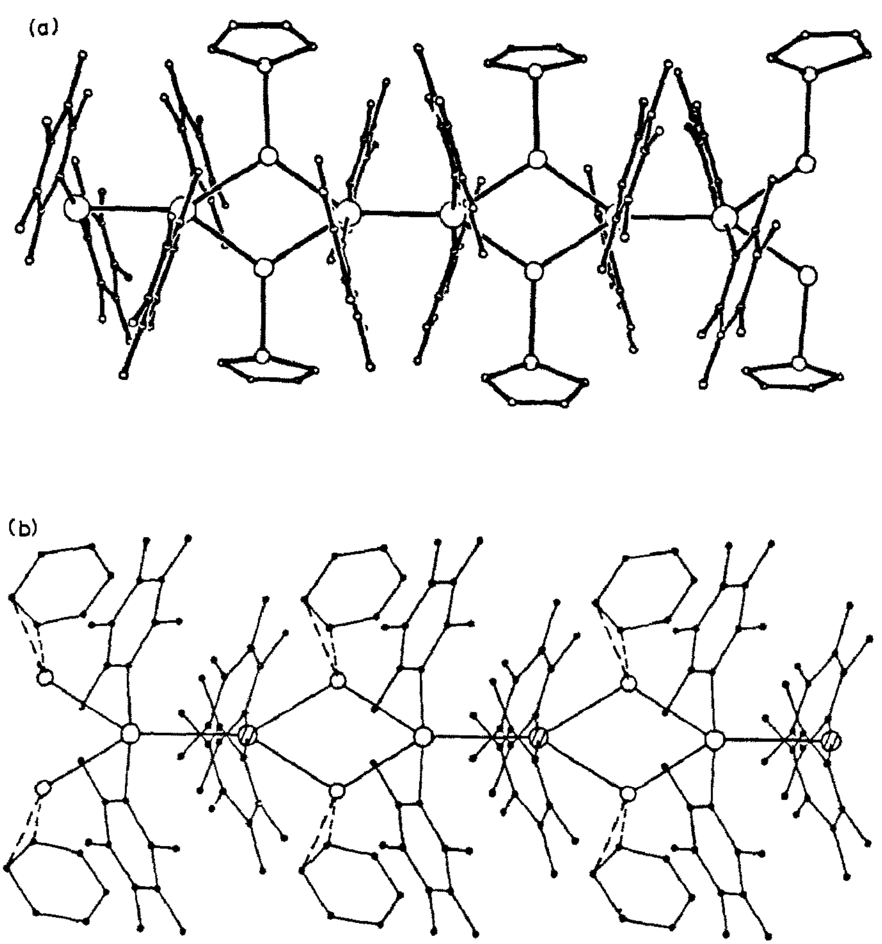


Fig. 1. Structure of polymeric $[AuAg(C_6F_5)_2 \cdot L]_x$. (a) $L = SC_4H_8$, Au–Ag: 2.726 and 2.717 Å, Au...Au: 2.889 Å. (b) $L = \eta^2\text{-}C_6H_6$, Au–Ag: 2.702 and 2.792 Å, Au...Au: 3.013 Å.

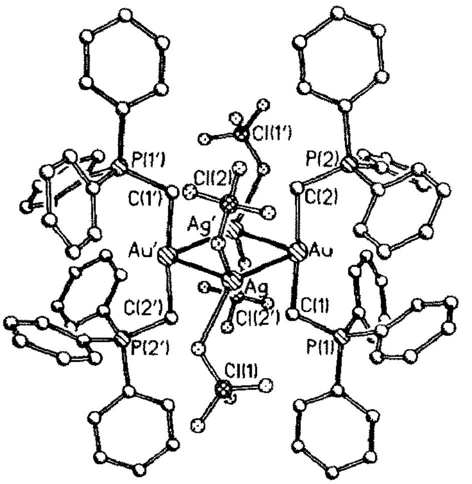
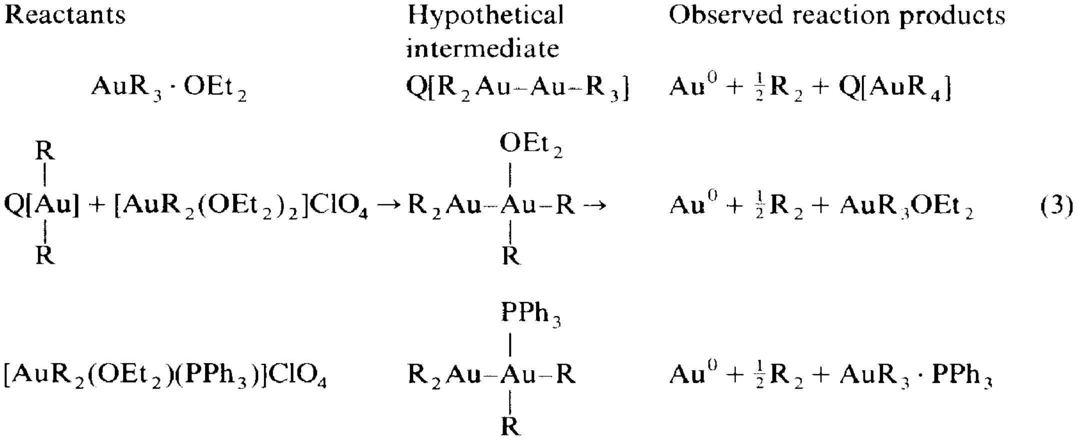


Fig. 2. Structure of $[AuAg(CH_2PPh_3)_2(OClO_3)_2]_2$.

Au...Au contacts are not observed, probably because of the barrier formed by the six phenyl groups of the ylide ligands.

Attempts to use neutral or cationic electrophilic gold(III) complexes instead of $Ag^+$ cations, in order to form direct unbridged $Au^I$–$Au^{III}$ bonds failed because of transfer reactions of R groups from the $[AuR_2]^-$ anion to the $Au^{III}$ reagent, giving [4] metallic gold and more arylated gold(III) complexes (see Scheme 1, eq. 3).



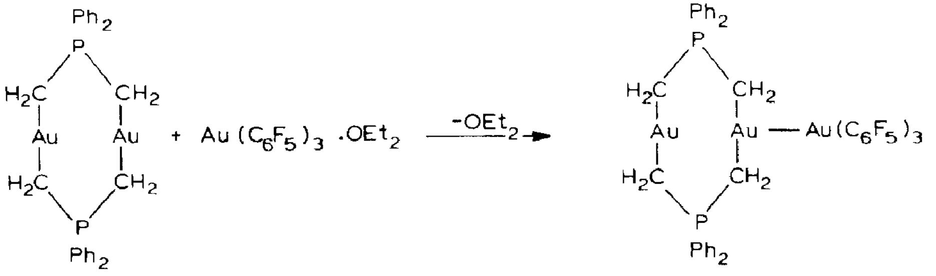
$$AuR_3 \cdot OEt_2 \qquad Q[R_2Au{-}Au{-}R_3] \qquad Au^0 + \tfrac{1}{2}R_2 + Q[AuR_4]$$

$$Q[\overset{R}{\underset{R}{Au}}] + [AuR_2(OEt_2)_2]ClO_4 \rightarrow R_2Au{-}\overset{OEt_2}{\underset{R}{Au}}{-}R \rightarrow \qquad Au^0 + \tfrac{1}{2}R_2 + AuR_3OEt_2 \qquad (3)$$

$$[AuR_2(OEt_2)(PPh_3)]ClO_4 \qquad R_2Au{-}\overset{PPh_3}{\underset{R}{Au}}{-}R \qquad Au^0 + \tfrac{1}{2}R_2 + AuR_3 \cdot PPh_3$$

Scheme 1. Transfer reactions of R groups in reactions between $[AuR_2]^-$ and neutral or cationic $Au^{III}$ complexes.

We therefore selected a different starting complex, $\mu,\mu'$-bis(diphenylphosphinium)bis(methylido)digold(I) (A), which has been structurally characterized by Fackler et al. [5] and fully described by Schmidbaur et al. [6]. The complex contains two gold(I) centres doubly bridged by the strong anionic $[Ph_2P(CH_2)_2]^-$ ligand and it should therefore possess excess electron density at the gold atoms without being too prone to ligand migration. In fact, it reacts (1/1) with silver salts to give insoluble solids of the correct stoichiometry. Substituting $Au(C_6F_5)_3 \cdot OEt_2$ for the silver salts gives a more soluble reaction product (eq. 4), which can be isolated and studied [7] by structural methods (Fig. 3).



(4)

(A)

The two $Au^I$ centres, which were 2.977(1) Å apart [5] in the precursor, approach to 2.769(1) Å in the trinuclear complex, a distance which is between the shortest (2.672(1) Å) [8a] and the second shortest (2.776 Å) [8b] $Au^I$...$Au^I$ contact previously known, and not much longer than the longest $Au^{II}$–$Au^{II}$ bonds. One of the $Au^I$ centres is bonded to the $Au^{III}$ of the $AuR_3$ group with a very short bond of 2.672(1) Å, comparable to the shortest $Au^{II}$–$Au^{II}$ bonds. The shortest Au–Au bond of 2.553(1) Å has been observed in the $Au^{II}$ species $[Au(CH_2PPh_2S)_2Cl_2]$ [9].

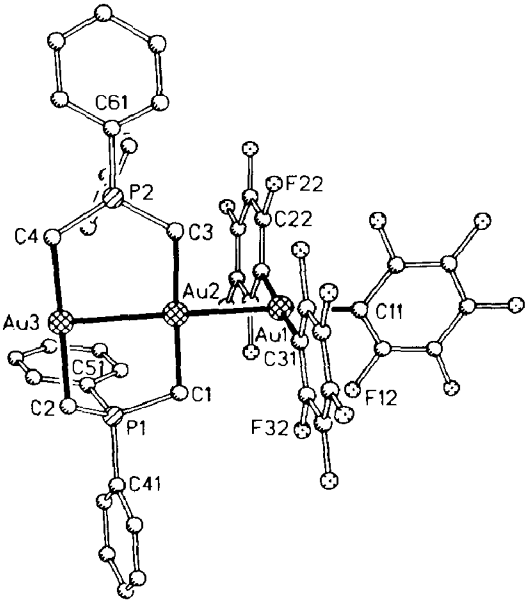


Fig. 3. Structure of a trinuclear gold complex with a direct $Au^I$–$Au^{III}$ bond.

The assignment of oxidation states to the gold atoms in the complex is to some extent a matter of taste. If the original oxidation states are retained this is the first direct $Au^I$–$Au^{III}$ bond. If the bonding interaction between Au(1) and Au(2) is associated with substantial transfer of electron density from Au(2) to Au(1), this bonding system could be described as $Au^{II}$–$Au^{II}$ and would be the first such system without a supporting bridging ligand. Mössbauer spectroscopy might provide useful information as to the "true" oxidation states.

The $^1H$ NMR spectra show 8 equivalent hydrogen atoms in the four methylene groups of the precursor, but two sets of signals of 4H atoms in the product.

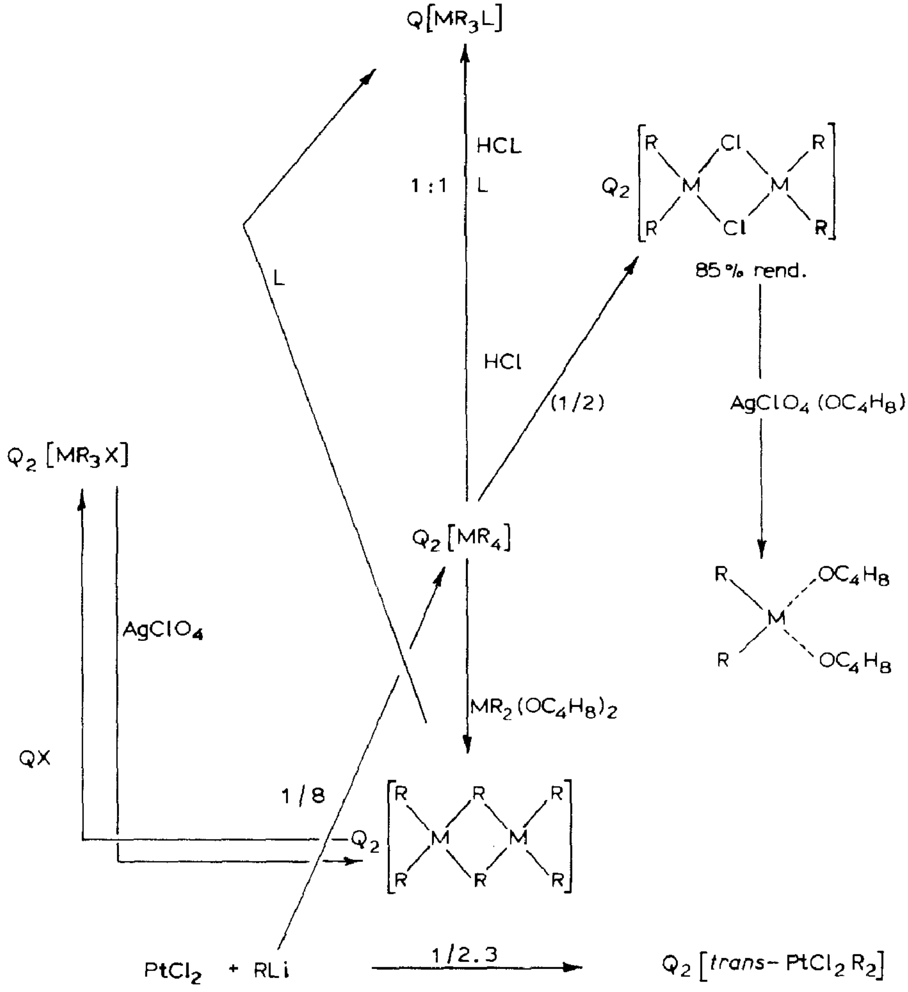
It is naturally tempting to add another $AuR_3$ moiety to the free $Au^I$ atom. Deep red solutions are formed, from which a red-brown solid is obtained which gives correct analyses. Its $^1H$ NMR spectrum is incompatible with a symmetric structure ($\delta$ 1.42, 4H; $\delta$ 1.87, 4H) but unfortunately we have not yet been able to obtain crystals suitable for X-ray studies.

## B. Platinum(II) as donor centre

As a result from our work [10] between 1976 and 1982, anionic pentahalophenyl platinate(II) derivatives are now easily accessible as summarized in Scheme 2.

The starting product $(NBu_4)_2[Pt(C_6X_5)_4]$ can be obtained by the direct arylation of $PtCl_2$ with an excess of $C_6X_5Li$, whilst with a 1/2.3 $PtCl_2/C_6X_5Li$ ratio $(NBu_4)_2[trans\text{-}PtCl_2(C_6X_5)_2]$ is obtained [11].

The (1/2) reaction of $(NBu_4)_2[Pt(C_6X_5)_4]$ with HCl leads to binuclear complexes [1]; $(NBu_4)_2[Pt_2(\mu\text{-}Cl)_2(C_6X_5)_4]$. This is not only an excellent synthetic method ($>$ 85% yield) but it is the only one for obtaining $Pt^{II}$ compounds. If a (1/1) molar ratio is used, the same binuclear complexes are obtained while half of the starting complex remains unreacted. However, in the presence of one mole of a neutral ligand, complexes $(NBu_4)_2[Pt(C_6X_5)_3L]$ are obtained [12].



Scheme 2. Synthetic ways to anionic $Pt^{II}$ complexes.

The binuclear complexes react with $AgClO_4$ in $OC_4H_8$ solution to give neutral *cis*-$Pt(C_6X_5)_2(OC_4H_8)_2$ derivatives [13], where the two $OC_4H_8$ ligands can easily be displaced by a variety of stronger nucleophiles, for instance, $[Pt(C_6F_5)_4]^{2-}$ to give the anionic binuclear complex $(NBu_4)_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$, containing bridging and terminal $C_6F_5$ groups [14].

The last complex reacts with anionic $X^-$ or neutral L ligands to give monomeric $Q_2[PtR_3X]$ or $Q\{PtR_3L]$ derivatives.

In all of these anionic platinum(II) complexes, the platinum(II) acts as an electron-rich metal centre and reacts with silver salts or complexes to afford new types of complexes with unusual features:

$$\text{(i)}\quad Q\big[Pt(C_6F_5)_3(SC_4H_8)\big] + (O_3ClO)AgPPh_3 \xrightarrow{-QClO_4} \big[(SC_4H_8)R_3Pt\text{–}Ag\text{–}PPh_3\big] \qquad (5)$$

The resulting neutral complex [15] shows (Fig. 4) a direct unbridged Pt–Ag bond which, at 2.637 Å is shorter than any previously known one. One *ortho*-F atom of

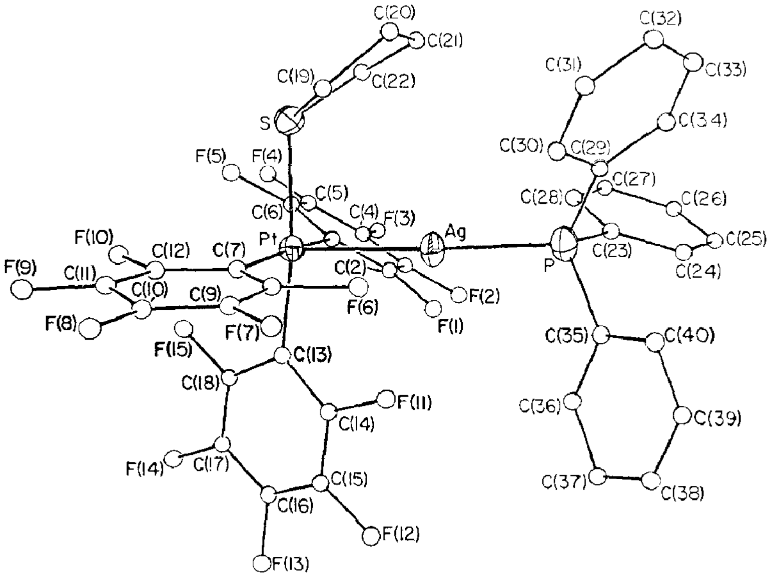


Fig. 4. Structure of the neutral binuclear $(SC_4H_8)(C_6F_5)_3Pt-AgPPh_3$.

each $C_6F_5$group makes a short contact with the silver atom (2.757, 2.763, 2.791(7) Å) possibly donating some electron density, thus contributing to the stability of the molecule. The ring which contains F(1) is tilted in 39° from the Ag–Pt–C(1) plane, thereby avoiding a series of unacceptable contacts.

(ii) $Q_2[Pt_2(\mu\text{-}X)_2(C_6F_5)_4] + AgClO_4 \xrightarrow{-QClO_4}$

$$Q[Pt_2Ag(\mu\text{-}X)_2(C_6F_5)_4 \cdot OEt_2] \quad (6)$$

The centro-symmetric anion in the starting complex loses its planarity upon reaction (eq. 6, Fig. 5) and the dihedral angle between the planes Pt(1)–Cl(1)–Cl(2) and Pt(2)–Cl(1)–Cl(2) is now 132°. The long Pt–Pt distances (3.263(1) Å) excludes any bonding interaction. There are two Pt–Ag bonds unsupported by any bridging ligand (Pt–Ag: 2.782, 2.759(1) Å), which are not cleaved by addition of neutral ligands; these merely substitute the $OEt_2$ molecule [16].

(iii) $2\,Q_2[Pt(C_6F_5)_3Cl] + 3\,AgClO_4 \xrightarrow[-2AgCl]{-3QClO_4} Q[Pt_2Ag(C_6F_5)_6 \cdot OEt_2]$ (7)

This compound (Fig. 6) is the first example of two $C_6F_5$ groups acting as bridging ligands [17]. The two Pt atoms are only 2.698(1) Å apart: there should either exist a Pt–Pt bond or this distance is forced by the spread of the bridging $C_6F_5$ groups (PtCPt angles: 74.1°). The Pt–Ag distances (2.827, 2815(2) Å) and the lack of any bridging ligand across the Pt–Ag edges imply the existence of Pt–Ag bonds. Moreover, there are close approaches of two *o*-F atoms (from the bridging groups) to the silver atom (2.66, 2.65(1) Å). The cluster is bent: dihedral angle: 152°.

(iv) $2\,Q_2[\textit{trans}\text{-}PtCl_2(C_6F_5)_2] + 2\,AgClO_4 \xrightarrow{-QClO_4} Q_2[Pt_2Ag_2Cl_4(C_6F_5)_4]$ (8)

This cluster [18] is rigorously centrosymmetric (Fig. 7) and essentially planar. Two *trans*-planar $PtCl_2(C_6F_5)_2$ units embrace a central $Ag_2$ unit (Ag–Ag: 2.994(6)

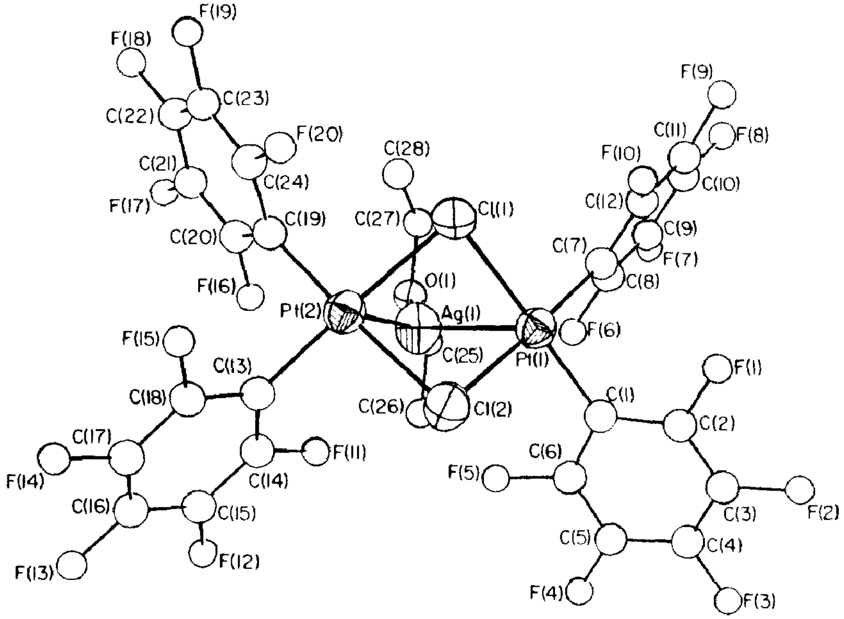


Fig. 5. Structure of the anion in $(NBu_4)[Pt_2Ag(\mu\text{-}Cl)_2(C_6F_5)_4 \cdot OEt_2]$.

Å). Each Ag atom forms a bond of considerable strength (2.772 Å) to one of the Pt atoms as well as a larger contact to the other Pt atom. Each Ag atom also has contacts to Cl atoms at 2.408 and 2.724 Å. One of the most remarkable features of this structure is again the close approach of two *o*-F atoms to each Ag atom, at distances 2.60 and 2.69(1) Å.

(v) $$Q_2[\textit{trans}\text{-}PtCl_2(C_6Cl_5)_2] + AgClO_4 \xrightarrow{-QClO_4} \tfrac{1}{x}Q[Pt(C_6Cl_5)_2(\mu\text{-}Cl)_2Ag)]_x \qquad (9)$$

The result of this reaction (Fig. 8) is similar in stoichiometry to that of reaction (iv)

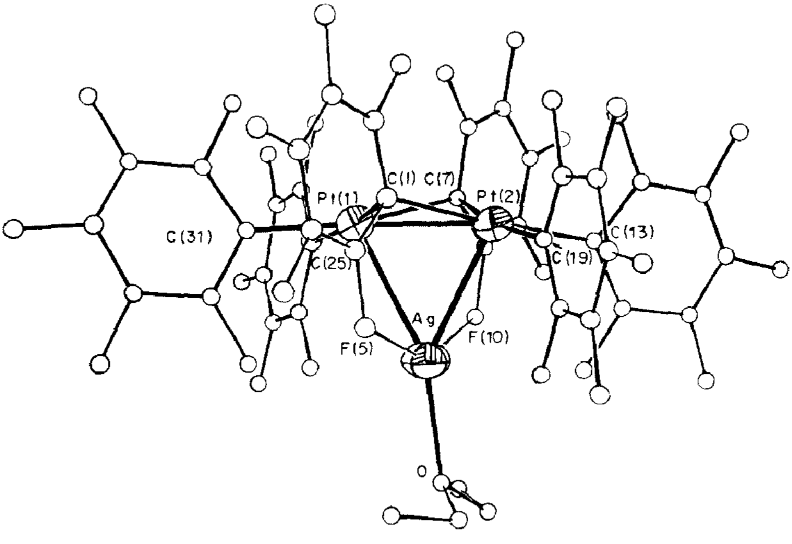


Fig. 6. Structure of the anion in $(NBu_4)[Pt_2Ag(C_6F_5)_6 \cdot OEt_2]$.

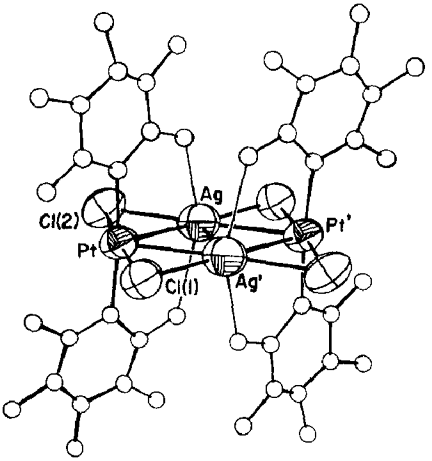


Fig. 7. Structure of the anionic tetranuclear $[Pt_2Ag_2Cl_4(C_6F_5)_4]^{2-}$.

but the structure of the $C_6Cl_5$ derivative is very different [19] and consists of Q cations and polymeric anions, a representative fragment of the latter is shown in the figure. Each Pt atom is in a *trans*-planar $PtCl_2(C_6Cl_5)_2$ unit with normal distances and each Ag atom is in a linear Cl–Ag–Cl unit. In view of the long distances, significant Pt–Ag or Ag–Ag bonding is unlikely.

An important additional stabilizing factor is a set of interactions between the silver atoms and the Cl(2) atoms; the latter are so positioned to bridge adjacent silver atoms, thus completing around each silver atom a rhombically distorted octahedron of Cl atoms.

We think it possible that electronic factors cause the marked differences found in the results of reactions iv and v. *o*-F atoms are more reluctant to donate electron

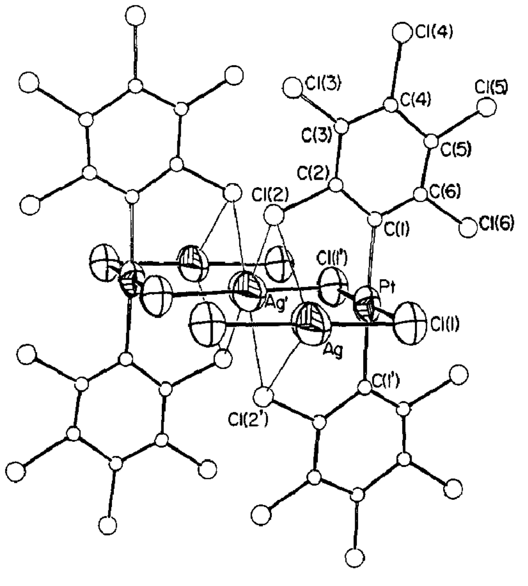


Fig. 8. Structure of the polymeric anion $[Pt(C_6Cl_5)_2(\mu\text{-}Cl)_2Ag]_x^{-}$.

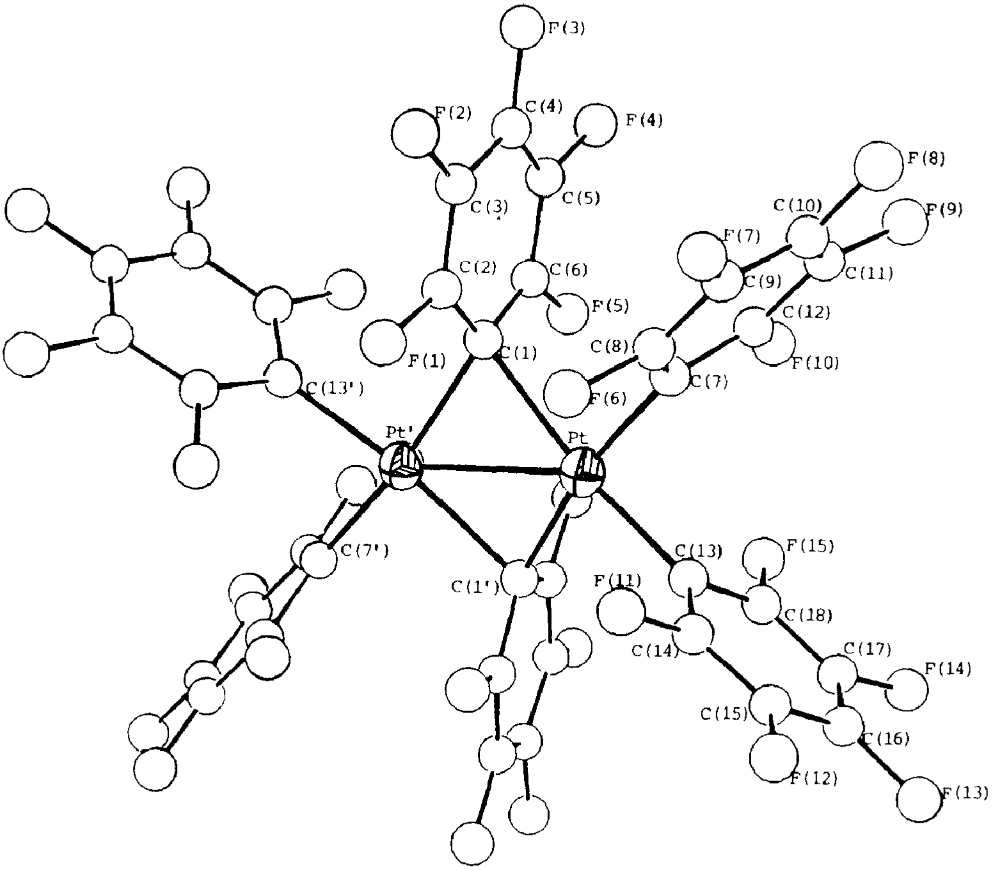


Fig. 9. Structure of the homoleptic $[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]^{2-}$.

density than *o*-Cl atoms owing to the higher electronegativity of fluorine. Therefore, if the $C_6Cl_5$ derivative has the same structure as the $C_6F_5$ derivative, an excess of electron density should concentrate around the silver atoms. On the other hand, if the $C_6F_5$ derivative has he same polymeric structure as the $C_6Cl_5$ derivative, the *o*-F atoms should form a bent bridge (to two adjacent Ag atoms) and would be the only additional source of electron density, since the polymeric structure excludes Pt–Pt and Pt–Ag bonds.

$$\text{(vi)}\quad Q_2[Pt(C_6F_5)_4] + cis\text{-}Pt(C_6F_5)_2(OC_4H_8)_2 \xrightarrow{-2OC_4H_8} Q_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4] \qquad (10)$$

The anion $[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]^{2-}$ in the yellow complex is the first reported binuclear homoleptic derivative, which is doubly bridged by two $C_6F_5$ groups. The structure [20] is represented in Fig. 9. The dihedral angle at the C(1)–C(1′) edge is 151.9°; the Pt–P distance is 2.714 and the Pt–C(bridge) distances 2.24 and 2.17(1) Å are longer than the Pt–C(terminal) distance (2.01(1) Å).

The complex reacts with $AgClO_4$ to give the same trinuclear $Pt_2Ag$ cluster discussed above (iii) which can be oxidised with $I_2$ to give an interesting $Pt^{II}$–$Pt^{III}$ complex.

$$\text{(vii)}\quad Q[Pt_2Ag(C_6F_5)_6 \cdot OEt_2] + \tfrac{1}{2}I_2 \xrightarrow{-AgI} Q[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4] \qquad (11)$$

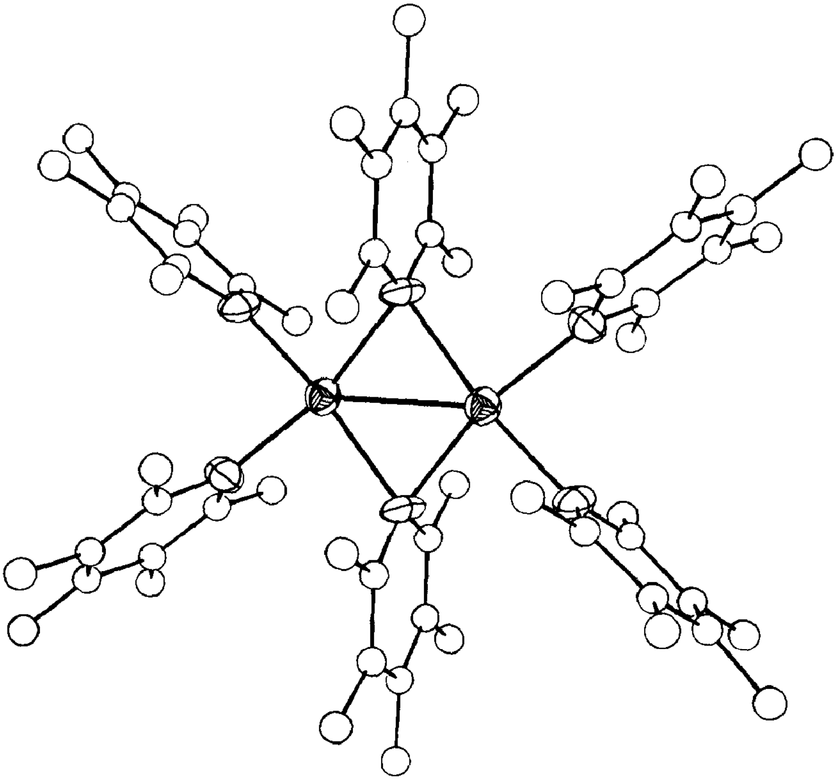


Fig. 10. Structure of the $Pt^{II}$–$Pt^{III}$ binuclear $[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]^-$.

The structure of the anion in the black complex [20] is represented in Fig. 10.

The entire anion is centrosymmetric and displays the following important features. The two Pt atoms are in identical environments, and should be assigned an average oxidation state of +2.5 rather than separate $Pt^{2+}$ and $Pt^{3+}$ states. The "$Pt_2(\mu\text{-}C)_2$" fragment is rigorously planar, as required by the inversion centre. The Pt–Pt distance (2.611(1) Å) is shorter than other Pt–Pt distances either in polynuclear complexes with +2.5Pt or in binuclear $Pt^{3+}$ complexes in which a Pt–Pt bond has been postulated.

The EPR spectrum of a powdered sample (taken in liquid $N_2$ using a VARIAN E-112 spectrometer working in the X band) shows an anisotropic signal with $g_x = 1.16$, $g_y = 2.10$ and $g_z = 1.93$.

## Acknowledgements

The work described here was done by a team of active co-workers, whose name are given in the references and to whom I wish to express my appreciation. Support of this research by the Comisión Asesora de Investigación Científica y Técnica (CAICYT, Spain) is gratefully acknowledged.

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