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Synthesis and structures of novel types of heteronuclear Pt–M (M = Ag, Sn or Pb) neutral or anionic organometallic complexes

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Abstract

Donor–acceptor Pt→Ag bonds formed by reactions between anionic platinum complexes and silver salts or complexes are the subject of this review. We discuss their structural features and the role played by the charge of the anions and by *o*-X...Ag interactions in the stability and spatial arrangement of the resulting heteronuclear complexes. The extension of these studies to other M→M′ systems is briefly commented.

1. Introduction

During recent years (from 1980 onwards), we have developed high-yield synthetic procedures for the preparation of anionic palladium(II) or platinum(II) complexes, containing perhalophenyl groups (C_6X_5, X = F, Cl), which are air- and moisture-stable as solids and also stable in solution and can, thereafter, comfortably be used as reagents in a variety of ways [1]. Owing to their anionic nature, the metal centre must have an excess of electron density and could act as a Lewis base towards suitable Lewis acids, for instance, the Ag^+ cation in silver salts or complexes, to form heteronuclear derivatives displaying Pt→Ag bonds.

In fact, this is the case for most of the reactions discussed in the following. We consider separately (i) the cases where the Pt(II) atom is the only basic centre, and (ii) other situations where other donor atoms are also forming bonds with the silver centres. Moreover, the pentahalophenyl rings are frequently positioned in such a way that one of the *ortho*-halogen atoms in the C_6X_5 groups makes a short contact with the silver atom, thereby increasing the stability of the cluster (see for instance Fig. 10). This question shall be considered separately.

2. The platinum atom as the only acting basic centre

2.1. Anionic *monomeric* platinum(II) complexes of the types $(NBu_4)[Pt(C_6F_5)_{3-x}(C_6Cl_5)_xL]$ or $(NBu_4)_2[Pt(C_6F_5)_{4-x}(C_6Cl_5)_x]$ (x = 0, 2) react with silver complexes $O_3ClOAgL'$ to afford (eqns. (1) or (2)) heterobinuclear complexes of type **A** [2, 3] or **B** [3], with the platinum atom acting as a monodentate terminal ligand forming Pt→Ag donor–acceptor bonds, otherwise unsupported by any covalent bridge.

$$(NBu_4)[Pt(C_6F_5)_{3-x}(C_6Cl_5)_xL] + O_3ClOAgL' \longrightarrow (NBu_4)ClO_4 + \underset{\mathbf{A}}{[L(C_6F_5)_{3-x}(C_6Cl_5)_xPtAgL']} \quad (1)$$

(x = 0, 1, 2, 3; L = S, N, P donors; L′ = PPh_3, PEt_3)

$$(NBu_4)_2[Pt(C_6F_5)_{4-x}(C_6Cl_5)_x] + O_3ClOAg(tht) \longrightarrow (NBu_4)ClO_4 + \underset{\mathbf{B}}{(NBu_4)[(C_6F_5)_{4-x}(C_6Cl_5)_xPt \longrightarrow Ag(tht)]} \quad (2)$$

(x = 0, 2; tht = tetrahydrothiophene, SC_4H_8)

The structures of two (type **A**) complexes are given in Figs. 1 and 2. It is also noteworthy that the Pt centre is the preferred donor atom, despite the presence of the SC_4H_8 ligand, which could form a Pt–S–Ag bridging system.

The structures of two (type **B**) complexes are given in Figs. 3 and 4 and show the Pt atoms also acting as monodentate terminal ligands directly attached to the silver centre.

2.2. Anionic *dimeric* platinum(II) complexes containing C_6F_5 groups behave as bidentate chelate ligands whilst similar C_6Cl_5 complexes (when existent) act as bidentate bridging ones.

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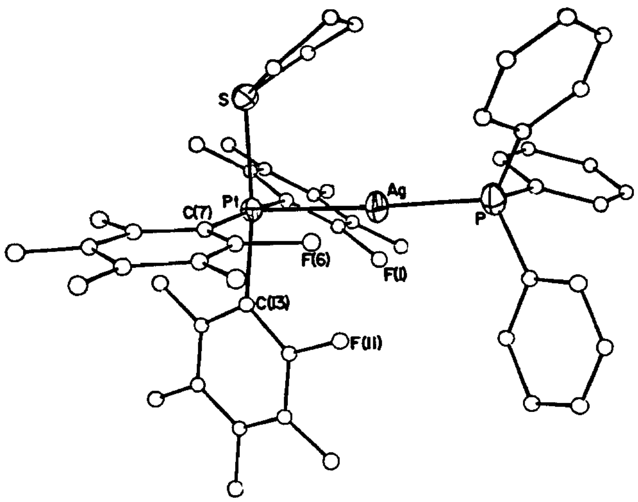

Fig. 1. Structure of $(C_6F_5)_3(SC_4H_8)PtAgPPh_3$ (**A1**). Pt–Ag: 2.637(1) Å [2].

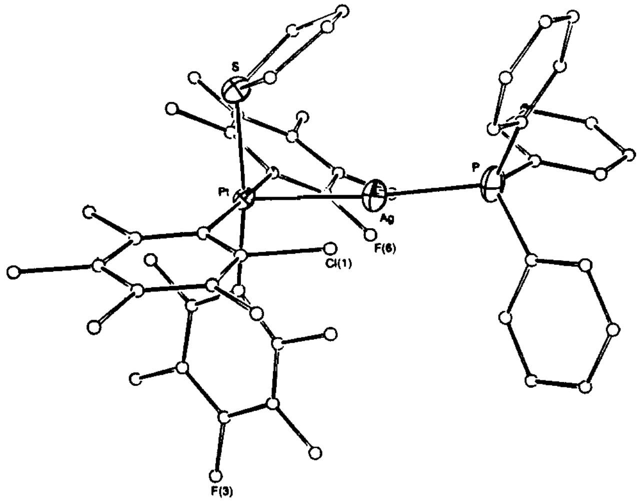

Fig. 2. Structure of $(C_6F_5)_2(C_6Cl_5)(SC_4H_8)PtAgPPh_3$ (**A2**). Pt–Ag: 2.650(2) Å [3].

In the first case (eqn. (3)), we obtain trinuclear complexes [4, 5].

$$(NBu_4)_2[Pt_2(\mu\text{-}X)_2(C_6F_5)_4] + AgClO_4 \xrightarrow{CH_2Cl_2/OEt_2} (NBu_4)ClO_4 + \underset{\textbf{C}}{(NBu_4)[Pt_2Ag(\mu\text{-}X)_2(C_6F_5)_4L]} \quad (3)$$

$X = Cl, Br, C_6F_5;\ L = OEt_2$

The structures of the anion for μ-X = Cl (**C1**) or C_6F_5 (**C2**) and L = OEt_2* are shown in Figs. 5 and 6, respectively. Figures 7 and 8 show the structures of the anions in the starting Pt(II) complexes. Minor changes can be observed as a consequence of coordination to the Ag^+.

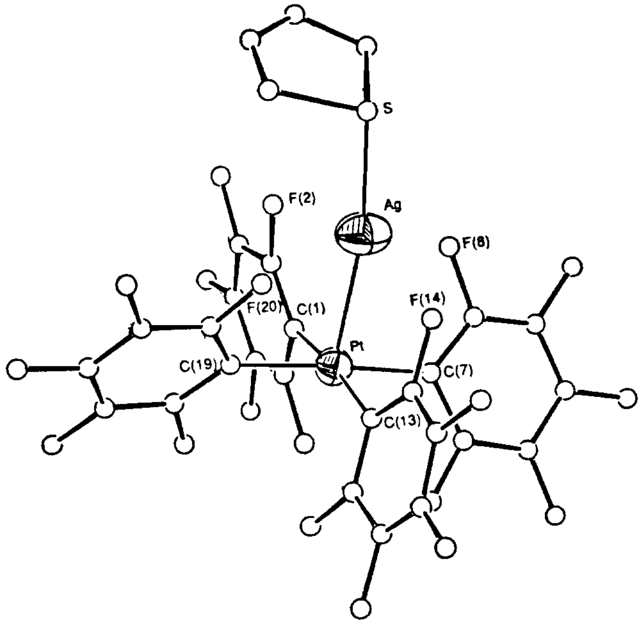

Fig. 3. Structure of $[(C_6F_5)_4PtAg(SC_4H_8)]^-$ (**B1**). Pt–Ag: 2.641(1) Å [3].

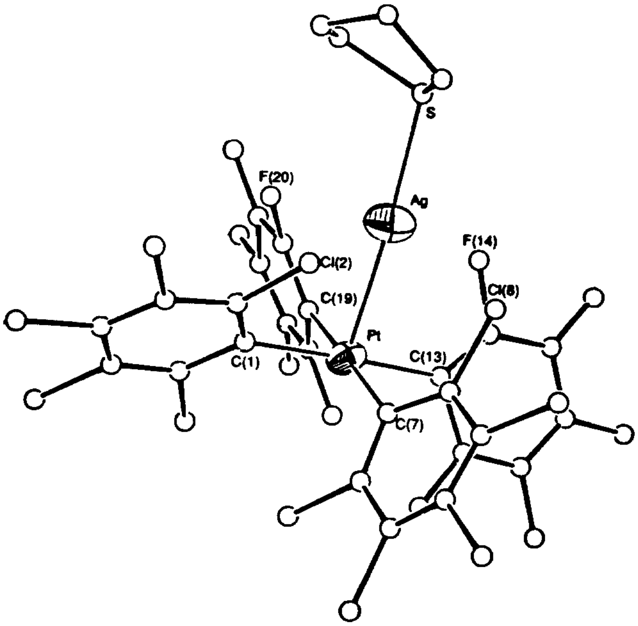

Fig. 4. Structure of [*cis*-$(C_6F_5)_2(C_6Cl_5)_2PtAg(SC_4H_8)]^-$ (**B2**). Pt–Ag: 2.692(2) Å [3].

The most remarkable difference is the loss of the planarity of the $Pt(\mu\text{-}Cl)_2Pt$ core in the chloro compound which forms in **C1** a dihedral angle of 132.5° or the decrease of the dihedral angle from 151.9 to 142.2° in the cases of complexes containing the $Pt(\mu\text{-}C_6F_5)_2Pt$ moiety. Similar complexes with L = phosphines can be prepared by using $O_3ClOAgPR_3$ reagents or also by displacing the OEt_2 molecule by addition of phosphines to CH_2Cl_2 solutions of the diethyl ether complexes, at

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*Diethyl ether is a common solvent used in many of these reactions in order to separate $(NBu_4)ClO_4$ which is insoluble in it. Usually the anionic Pt–Ag complexes are soluble in this solvent.

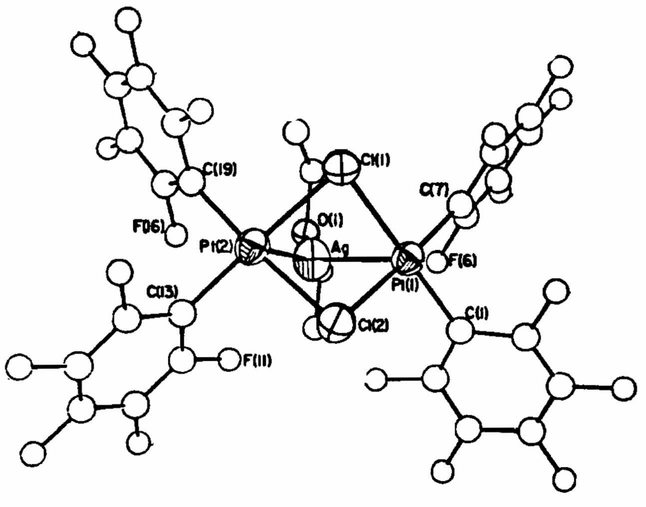


Fig. 5. Structure of $[Pt_2Ag(\mu\text{-}Cl)_2(C_6F_5)_4OEt_2]^-$ (C1). Pt(1)–Ag: 2.782(1) Å, Pt(2)–Ag: 2.759(1) Å [4].

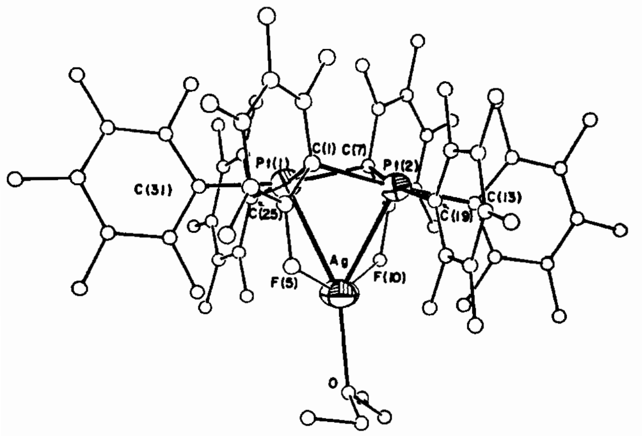


Fig. 6. Structure of $[Pt_2Ag(\mu\text{-}C_6F_5)_2(C_6F_5)_4OEt_2]^-$ (C2). Pt(1)–Ag: 2.815(1) Å, Pt(2)–Ag: 2.804(1) Å [5].

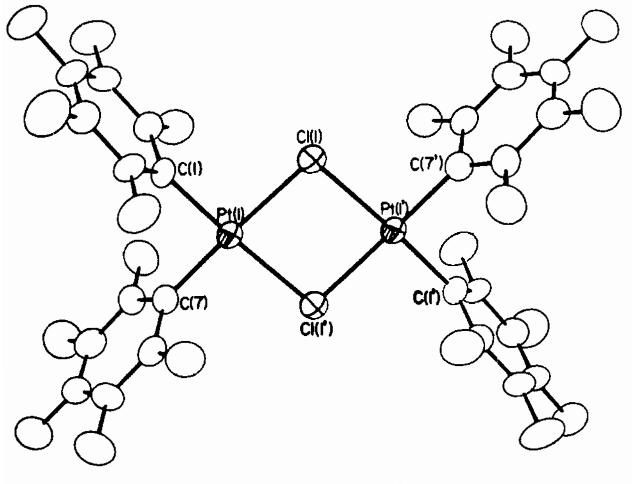


Fig. 7. Structure of $[Pt_2(\mu\text{-}Cl)_2(C_6F_5)_4]^{2-}$ [4].

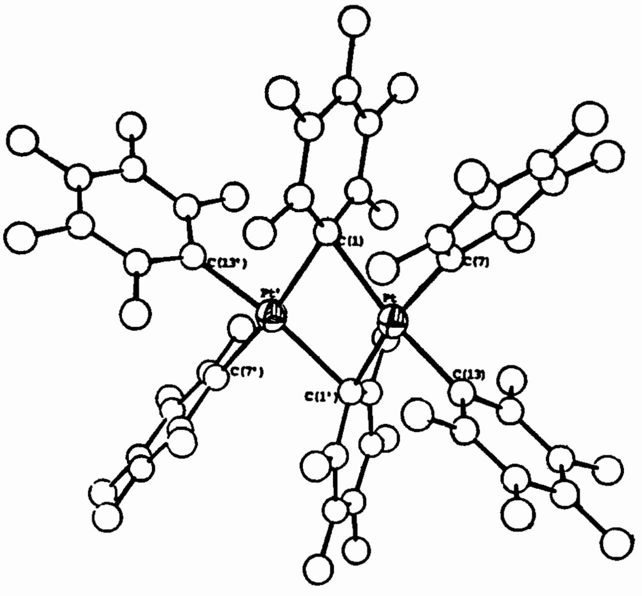


Fig. 8. Structure of $[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4H_2O]^{2-}$ [5].

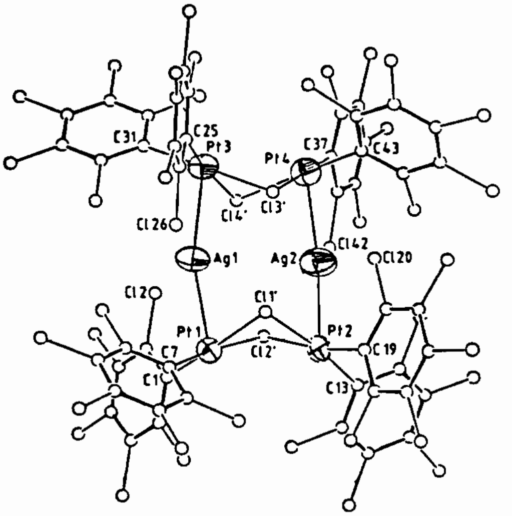


Fig. 9. Structure of $[Pt_4Ag_2(\mu\text{-}Cl)_4(C_6Cl_5)_8]$ (**D**). Pt(1)–Ag(1): 2.766(4); Pt(3)–Ag(1): 2.755(4); Pt(2)–Ag(2): 2.781(4); Pt(4)–Ag(2): 2.748(4) Å [6].

−30 °C. It seems of interest that, no cleavage of the Pt→Ag bonds takes place.

$(NBu_4)_2[Pt_2(\mu\text{-}X)_2(C_6Cl_5)_4]$ behave, however, as bridging ligands [6] and their reactions with $AgClO_4$ (eqn. (4)) lead to hexanuclear Pt_4Ag_2 complexes. The structure (X=Cl) (Fig. 9) shows two dicoordinated Ag(1) atoms embraced by two $[Pt_2(\mu\text{-}Cl)_2(C_6Cl_5)_4]^{2-}$ bridging units, each Ag^+ being linked to two Pt atoms in a nearly linear arrangement.

$$2(NBu_4)_2[Pt_2(\mu\text{-}X)_2(C_6Cl_5)_4] + 2AgClO_4 \xrightarrow{CH_2Cl_2/OEt_2} 2(NBu_4)ClO_4 + \underset{\mathbf{D}}{(NBu_4)_2[Pt_2Ag(\mu\text{-}X)_2(C_6Cl_5)_4]_2} \qquad (4)$$

X=Cl, Br

Additionally, each silver atom displays several Ag...Cl contacts, not only with *o*-Cl atoms of the C_6Cl_5 groups but also with the bridging chloride ligands.

The decisive role played by the solvent should not be ignored: if the processes represented in eqns. (3) or (4) are carried out in tetrahydrofuran, silver halide precipitates and *cis*-$Pt(C_6X_5)_2(THF)_2$ can be isolated [7] from the filtered solution. These complexes are very versatile synthons, since the two THF molecules seem to be loosely bonded and undergo, therefore, facile substitution by a variety of both neutral and anionic ligands [8–10].

3. Platinum and other donor atoms are acting as basic centres

A number of processes lead to complexes displaying Pt → Ag bonds assisted by other covalent interactions, for instance by bridging $Pt(\mu\text{-}X)Ag$ systems. As expected, such interactions have a perceptible influence upon the strength of the Pt → Ag bonds which can eventually become impossible or unnecessary.

3.1. For instance, the mononuclear $(NBu_4)_2[$*trans*-$PtCl_2(C_6X_5)_2]$ (X = F, Cl) react with either $AgClO_4$ or $AgNO_3$ to give (eqn. (5)) complexes of the same general formula [11, 12] which however are structurally very different

$$(NBu_4)_2[\textit{trans}\text{-}PtCl_2(C_6X_5)_2] + 2AgClO_4 \longrightarrow$$
$$2(NBu_4)ClO_4 + (NBu_4)[PtAgCl_2(C_6X_5)_2]_n \quad (5)$$
$$\mathbf{E,\ F}$$

X = F, $n = 2$ (**E**); X = Cl, $n = \infty$ (**F**)

Thus, the anion of the pentafluorophenyl complex (**E**) is tetranuclear (Fig. 10), with two square planar *trans*-$PtCl_2(C_6F_5)_2$ fragments linked to a central Ag_2 group by Pt–Ag and Cl–Ag bonds [11].

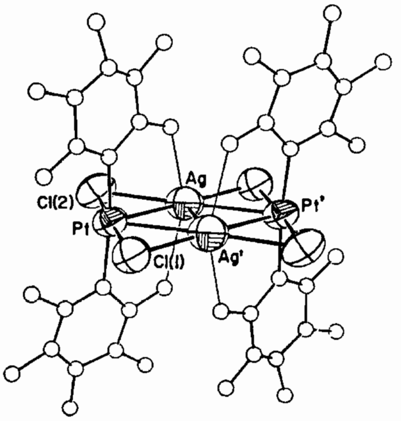


Fig. 10. Structure of $[\{PtAgCl_2(C_6F_5)_2\}^-]_2$ (**E**). Pt–Ag: 3.063(3); Pt–Ag': 2.772(3); Ag–Ag: 2.994(6); Cl(2)–Ag: 2.408(8); Ag'–Cl(1): 2.724(8) Å [11].

For X = C_6Cl_5 the polymeric anion (**F**) (Fig. 11), however, consists of alternating parallel *trans*-$PtCl_2(C_6Cl_5)_2$ fragments and the silver atoms are connecting the platinum fragments through Cl–Ag–Cl bridges. No Pt → Ag bonds are present, the silver atom has additional unsymmetric contacts with four *o*-Cl atoms of the C_6Cl_5 groups. The environment of the Ag atoms is a rhombically distorted octahedron of six Cl atoms and a Pt → Ag bonding interaction is thereby precluded [12].

3.2. Attempts to prepare another polynuclear compound, simultaneously containing Pt → Ag and $Pt(\mu\text{-}Cl)Ag$ bonds, by reacting $(NBu_4)_2[Pt(C_6F_5)_3Cl]$ with $AgClO_4$ (CH_2Cl_2 as a solvent) failed, owing to the precipitation of AgCl. The binuclear homoleptic $(NBu_4)2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$ (Fig. 8) was isolated [5].

3.3. This goal can however be achieved by the reaction [11] between $(NBu_4)_2[Pt_2Ag_2(\mu\text{-}Cl)_4(C_6F_5)_4]$ (**E**) (Fig. 10) and L = PPh_3, which leads to $(NBu_4)[(C_6F_5)_2ClPt(\mu\text{-}Cl)AgPPh_3]$ (**G1**) (Fig. 12) albeit the similar reactions with L = $AsPh_3$ or $SbPh_3$ result in the precipitation of AgCl and formation of *trans*-$Pt(C_6F_5)_2L_2$, whereas with L = CO the anionic $(NBu_4)[Pt(C_6F_5)_3Cl(CO)]$ can be recovered after filtering off the precipitated AgCl.

The pentachlorophenyl derivative [12] of analogous stoichiometry **F** (Fig. 11) also reacts with neutral ligands to give binuclear **G** (eqn. (6)) or trinuclear **H** (eqn. (7)) complexes depending on the used ligand.

$$(NBu_4)_x[PtAg(\mu\text{-}Cl)_2(C_6Cl_5)_2]_x + xL \longrightarrow$$
$$x(NBu_4)[(C_6Cl_5)_2PtAgCl_2(C_6X_5)_2L] \quad (6)$$
$$\mathbf{G}$$

L = PPh_3, PEt_3, $AsPh_3$, $SbPh_3$

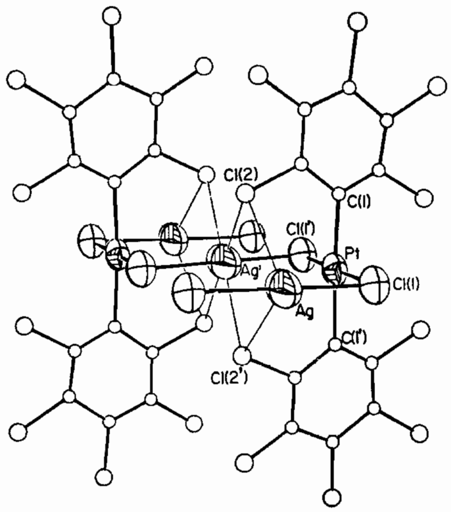


Fig. 11. Structure of $[\{PtAgCl_2(C_6Cl_5)_2\}^-]_\infty$ (**F**). Cl(1)–Ag: 2.477(5) Å [12].

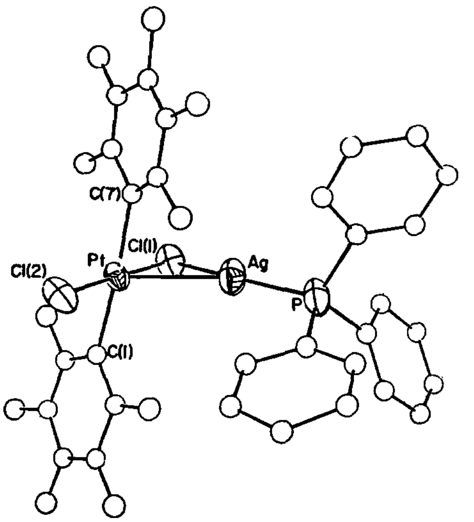


Fig. 12. Structure of $[PtAgCl_2(C_6F_5)_2(PPh_3)]^-$ (**G1**). Pt–Ag: 2.796(2); Cl(1)–Ag: 2.473(5); Ag–P: 2.350(6) Å [11].

$$\begin{aligned}(NBu_4)_x[PtAg(\mu\text{-}Cl)_2(C_6Cl_5)_2]_x + xL &\longrightarrow \\ x/2(NBu_4)_2[\textit{trans}\text{-}PtCl_2(C_6Cl_5)_2]& \\ +x/2[Pt(C_6Cl_5)_2\{(\mu\text{-}Cl)AgL\}_2]& \qquad (7)\\ \mathbf{H}&\end{aligned}$$

The formation of the binuclear complexes **G** is the result of a symmetric partial cleavage of the Pt(μ-Cl)Ag bridging system by the L ligand whereas the trinuclear complexes **H** owe their formation to the splitting of the bridge in an asymmetric way (see Scheme 1 (a) and (b)), two adjacent silver atoms remain bonded to a Pt atom and, as a consequence, the mononuclear fragment $(NBu_4)[\textit{trans}\text{-}PtCl_2(C_6Cl_5)_2]$ is formed in equimolar amounts.

The structure of a complex of each type is given in Figs. 13 (**G2**) and 14 (**H1**). The first has a Pt→Ag bond (2.782(1) Å) and *o*-Cl...Ag contacts whereas the similar pentafluorophenyl derivative (**G1**) (Fig. 12) does not display similar *o*-F...Ag contacts. The trinuclear complex **H1** (Fig. 14) does not have any Pt→Ag bonds, both metals being linked through strong Pt(μ-Cl)Ag bonds.

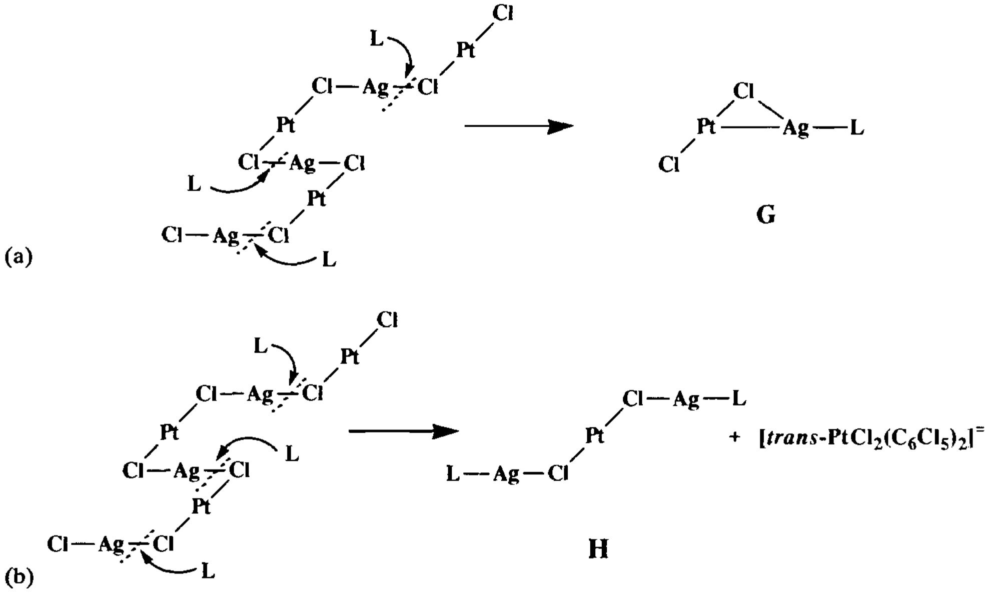
Attempts to synthesize binuclear complexes of the **G** or **H** type by reactions between $(NBu_4)[\textit{trans}\text{-}PtCl_2(C_6X_5)_2]$ and $O_3ClOAgL$ (in 1:1 or 1:2 ratio, respectively) worked satisfactorily only with the C_6Cl_5 derivatives; with the C_6F_5 ones, AgCl is precipitated in all cases.

4. Miscellaneous basic centres

4.1. The NBu_4 salts of the mononegative anions $[\textit{trans}\text{-}PtCl_2(C_6Cl_5)L]^-$ react with $O_3ClOAgL'$ either in 1:1 or 1:2 molar ratio to give tetranuclear complexes **J** (eqn. (8))

$$\begin{aligned}(NBu_4)[PtCl_2(C_6Cl_5)L] + O_3ClOAgL' &\longrightarrow \\ (NBu_4)ClO_4 + [LCl(C_6Cl_5)Pt(\mu\text{-}Cl)AgL']_2& \qquad (8)\\ \mathbf{J}&\end{aligned}$$

$L' = PPh_3$, $L = PPh_3$, SC_4H_8, NC_5H_5; $L' = PPh_2Me$, $L = PPh_3$



Scheme 1.

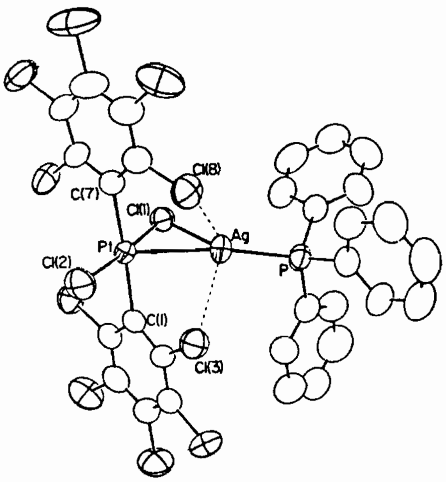


Fig. 13. Structure of $[PtAgCl_2(C_6Cl_5)_2(PPh_3)]^-$ (**G2**). Pt–Ag: 2.782(1); Cl(1)–Ag: 2.667(3); Ag–P: 2.395(2) Å [12].

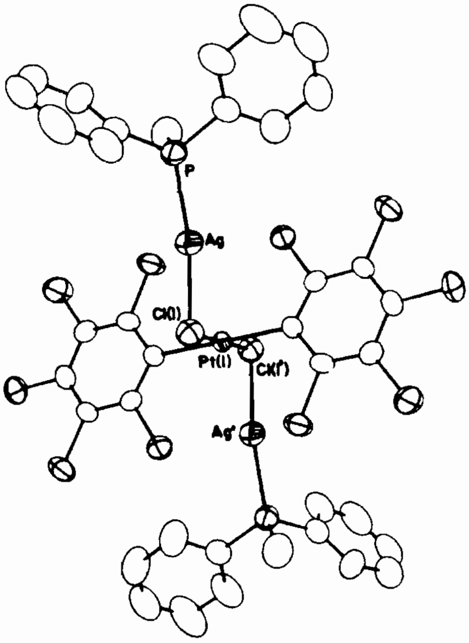


Fig. 14. Structure of [*trans*-$Pt(C_6Cl_5)_2\{\mu$-Cl-$Ag(PPh_2Me)\}_2$] (**H1**). Cl(1)–Ag: 2.418(2); Ag–P: 2.370(2) Å [12].

The structure of an example of **J** type complexes is presented in Fig. 15, and shows two $(Ph_3P)(C_6Cl_5)ClPt(\mu$-$Cl)Ag(PPh_3)$ units interconnected through weak (3.023(2) Å) Ag′...Cl(1) interactions. Each unit consists of $PtCl_2(C_6Cl_5)PPh_3$ and $AgPPh_3$ fragments bonded by a single chloride bridge Pt(μ-Cl)Ag and possibly by a weak Pt→Ag bond (2.945(1) Å) [13].

The bromide derivative $(NBu_4)[LBr(C_6Cl_5)Pt(\mu$-$Br)AgL']$ (L = L′ = PPh_3) has also been synthesized [14] and shows a similar structure (Fig. 16)

4.2. By treating $(NBu_4)_2$[*trans*-$PtX_2\{(\mu$-$SC_4H_8)Pt(C_6F_5)_3\}_2$] (X = Cl, Br) [15] with $AgClO_4$ (molar ratio 1:*n*, *n* = 1–4) in dichloromethane–toluene solutions, neutral pentametallic *trans*-[$PtX_2\{(\mu$-$SC_4H_8)(C_6F_5)_3PtAg(\eta^2$-$C_6H_5Me)\}_2$] can be obtained [16]. The structure of one of the anionic Pt_3 precursors (X = Cl) is shown in Fig. 17, while that of the neutral Pt_3Ag_2 complex (X = Cl) appears in Fig. 18. In spite of the great excess (*n* = 4) used in some syntheses, the central Pt atom is unable to form a bond to the silver atom, probably

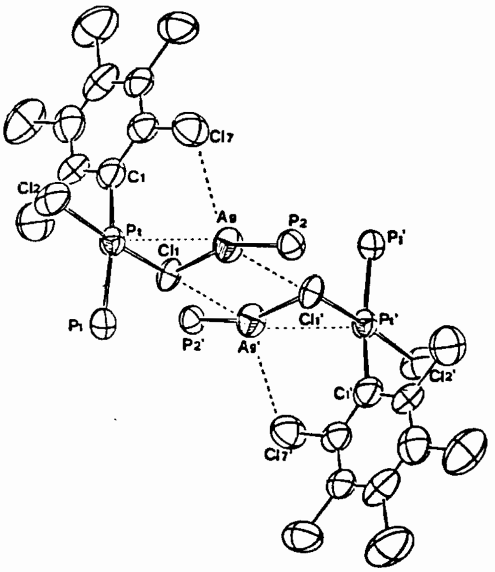


Fig. 15. Structure of $[(PPh_3)(C_6Cl_5)ClPt(\mu$-$Cl)Ag(PPh_3)]_2$ (**J1**). Pt–Ag: 2.945(1); Cl(1)–Ag: 2.514(2); Cl(1)–Ag′: 3.023(2) Å [13].

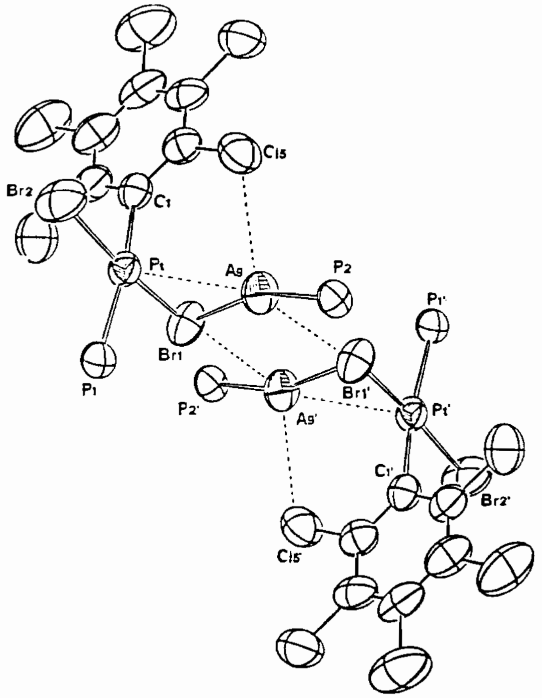


Fig. 16. Structure of $[(PPh_3)(C_6Cl_5)BrPt(\mu$-$Br)Ag(PPh_3)]_2$ (**J2**). Pt–Ag: 2.918(1); Br(1)–Ag: 2.606(1); Br(1)–Ag′: 3.109(2) Å [14].

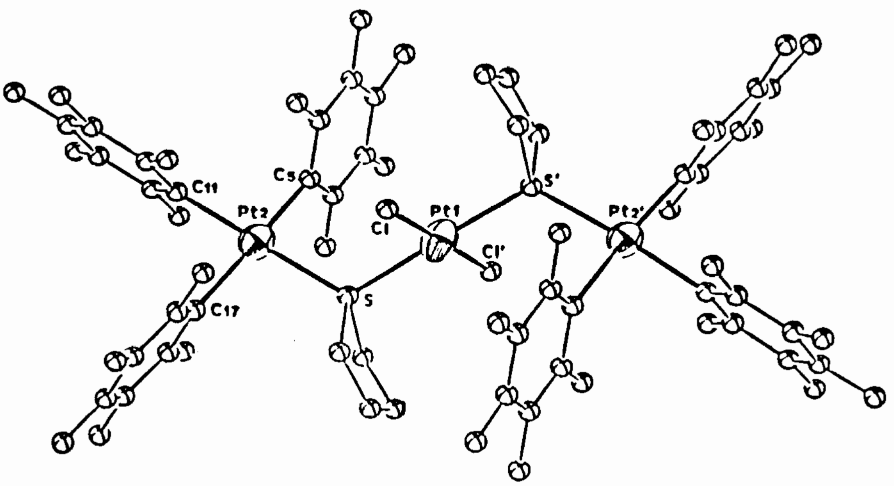


Fig. 17. Structure of $[\textit{trans}\text{-}PtCl_2\{\mu\text{-}SC_4H_8)Pt(C_6F_5)_3\}_2]^{2-}$ [15].

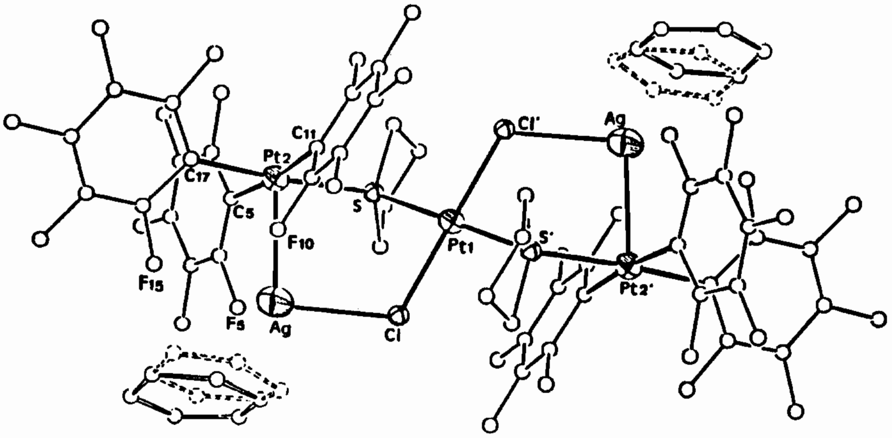


Fig. 18. Structure of $[\textit{trans}\text{-}PtCl_2\{(\mu\text{-}SC_4H_8)(C_6F_5)_3PtAg(\eta^2\text{-}C_6H_5Me)\}_2]$ (K). Pt(2)–Ag: 2.818(2); Cl–Ag: 2.637(4) Å [16].

because its environment (two Cl^- and two S atoms) does not supply it with the necessary excess of electron density. On the contrary, each of the two terminal Pt atoms (environment: three anionic C_6F_5 groups, one neutral tetrahydrothiophene) is bonded to a $Ag(C_6H_5\text{–}CH_3)$ fragment. The skeleton of the whole molecule is formed by two five-membered rings, sharing the central Pt(1) atom, and the silver atom of each $Ag(C_6H_5\text{–}CH_3)$ fragment is linked to a platinum atom, a chloride of the central *trans*-$PtCl_2$ moiety and has also three short contacts to *o*-F atoms of the three C_6F_5 groups.

5. The role of the *o*-X...Ag short contacts

In most of the discussed platinum–silver complexes, the perhalophenyl rings are so positioned that *o*-X...Ag (X = F, Cl) contacts result (see Figs. 1–4, 6, 9, 10, 11, 13, 15, 16, 18). We think that the *o*-X atom is donating some electron density to the silver centre, thereby being responsible for the adopted structure and the stability of the complexes. Since the ^{19}F NMR spectra of the hitherto studied complexes do not show any evidence of coupling between the F and Ag nuclei, even at low temperature, we conclude that such interaction does not subsist in solution.

5.1. *The o-X...Ag distances*

The experimental values are collected in Table 1 (for comparative purposes, we use a parameter ρ (in brackets), defined as experimental distances/sum of the covalent radii $r(Ag)+r(X)$ [8]), which also includes examples from the work of other authors with different types of complexes.

ρ values for the *o*-F...Ag contacts are in the range 1.34–1.47 whilst *o*-Cl...Ag contacts have lower ρ (1.19–1.33) values, which in the second case seems to point to stronger interactions. This seems reasonable since the higher electronegativity of the fluorine atom

TABLE 1. Ag...X contact distances and ρ values ($\rho = d(\text{Ag–X})/S$ covalent radii)

[(tht)(C_6F_5)$_3$PtAg(PPh_3)] **(A1)**	2.763(8) 2.757(7) 2.791(7)	1.40 1.39 1.41
[(tht)(C_6F_5)$_2$(C_6Cl_5)PtAg(PPh_3)] **(A2)**	2.921(13(F) 2.763(14)(F) 2.822(7)(Cl)	1.47 1.40 1.21
(NBu_4)[(C_6F_5)$_4$PtAg(tht)] **(B1)**	2.738(9) 2.712(12) 2.704(10) 2.722(14)	1.38 1.37 1.37 1.37
(NBu_4)[*cis*-(C_6F_5)$_2$(C_6Cl_5)$_2$PtAg(tht)] **(B2)**	2.671(12)(F) 2.778(12)(F) 2.827(7)(Cl) 2.827(6)(Cl)	1.34 1.37 1.21 1.21
(NBu_4)$_2$[(C_6F_5)$_4$(μ-C_6F_5)$_2$$Pt_2$Ag($OEt_2$)] **(C2)**	2.651(10) 2.663(10)	1.34 1.34
(NBu_4)$_2$[(C_6Cl_5)$_8$(μ-Cl)$_4$$Pt_4Ag_2$] **(D)**	2.783(14) 2.788(13) 2.821(13) 2.867(14)	1.19 1.19 1.21 1.23
(NBu_4)$_2$[(C_6F_5)$_4$$Cl_2Pt_2Ag_2$] **(E)**	2.60(1) 2.69(1)	1.31 1.36
{(NBu_4)[Pt(C_6Cl_5)$_2$$Cl_2$Ag]}$_x$ **(F)**	3.010(8) 3.092(8)	1.29 1.33
(NBu_4)[PtAgCl_2(C_6Cl_5)$_2$$PPh_3$] **(G2)**	2.951(3) 3.012(3)	1.27 1.29
[(PPh_3)(C_6Cl_5)ClPt(μ-Cl)AgPPh_3]$_2$ **(J1)**	3.041(4) 3.023(2)	1.30 1.30
[(PPh_3)(C_6Cl_5)BrPt(μ-Br)AgPPh_3]$_2$ **(J2)**	3.007(3) 3.109(2)	1.29 1.25
[*trans*-PtCl_2{(μ-SC_4H_8)(C_6F_5)$_3$PtAg(η^2-C_6H_5Me)}$_2$] **(K)**	2.686(11) 2.732(9) 2.733(9)	1.36 1.38 1.38
[Ag(1,2-$C_2H_4Cl_2$)$OTeF_5$]$_2$ [17]	2.705(3) 2.640(3) 2.915(3) 3.000(3) 2.626(3)	1.16 1.13 1.25 1.28 1.12
[Ag_2(CH_2Cl_2)$_4$Pd($OTeF_5$)$_4$] [17]	2.775(2) 2.811(2) 2.859(2) 2.882(2)	1.19 1.21 1.23 1.23
[Ag_2(1,2-$C_2H_4Cl_2$)$_4$Pd($OTeF_5$)$_4$] [17]	2.840(1) 2.655(1) 2.645(1) 2.928(1)	1.22 1.14 1.13 1.26
[Ag_2(Ph_2S_2)$_4$](AsF_6) [18]	2.824 2.841	1.42 1.43
[Ag(2,4,6-t-$Bu_3C_6H_2NC$)$_2$](PF_6) [19]	2.668	1.34
[C_6H_6Ag]($AlCl_4$) [20]	2.77 2.80 3.04	1.18 1.20 1.30

should make it more reluctant to donate electron density to the silver centre.

The tetranuclear complexes (**J1** and **J2**) represented in Figs. 15 and 16 also deserve some comment. The former displays two different types of Ag...Cl contacts: *o*-Cl...Ag and another Cl...Ag contact, the latter being responsible for the formation of a tetranuclear cluster from two binuclear Pt–Ag units. Despite the different nature of both Cl atoms (one is bonded to an organic group, while the other has inorganic character) both Ag...Cl contacts are of the same strength. In the second complex **J2** (Fig. 16), there are also two Ag...X contacts, an *o*-Cl...Ag and a Br...Ag interaction and the second one seems to be perceptibly stronger than expected from the lower electronegativity of the Br atom.

Data from other authors, which have also invoked the existence of Ag...X (X = F, Cl) contacts, are given in Table 1, the calculated ρ values being similar to ours [17–20].

We think it may be assumed that the perhalophenyl groups in our compounds adopt in each case the precise orientation which enables the close proximity of the *o*-X atoms to the silver centre in order to donate electron density, according to the higher or lower acidity of each silver centre, which will depend on the nature of the other ligands attached to the silver atom or shared with the platinum centres. The interplay of all the interactions is very complicated: for instance the structures of complexes **G1** and **G2** illustrated in Figs. 12 and 13 are very similar. Both show a $[\mathrm{AgPPh_3}]^+$ moiety connected to a $[trans\text{-}\mathrm{PtCl_2(C_6X_5)_2}]^{2-}$ fragment through a direct $\mathrm{Pt \rightarrow Ag}$ and a $\mathrm{Pt(\mu\text{-}Cl)Ag}$ bond. No *o*-F...Ag contacts are present in **G1** (Fig. 12) whilst two *o*-Cl...Ag contacts exist in the $\mathrm{C_6Cl_5}$ derivatives **G2** (Fig. 13). This does not seem to have any perceptible influence on the $\mathrm{Pt \rightarrow Ag}$ bonds, which are of similar strength (2.796(2) and 2.781(1) Å) in both complexes but the Ag–P and especially the Ag–Cl bonds are longer in the pentachlorophenyl complex than in the pentafluorophenyl one (2.350(6) and 2.395(2) Å; 2.473(5) and 2.667(3) Å, respectively), because in the latter the acidity of its silver centre is reduced by the two *o*-Cl...Ag contacts.

In the same way, the slightly shorter Pt–Ag distances in $[\mathrm{Pt_2Ag(\mu\text{-}Cl)_2(C_6F_5)_4OEt_2}]^-$ (**C1**, Fig. 5) (2.759(1), 2.782(1) Å) compared to $[\mathrm{Pt_2Ag(\mu\text{-}C_6F_5)_2(C_6F_5)_4OEt_2}]^-$ (**C2**, Fig. 7) (2.815(2), 2.827(2) Å) must be related to the absence of *o*-F...Ag contacts in the former and the presence of such contacts in the latter.

6. The strength of the Pt–Ag bonds

Taking into account the donor–acceptor nature of the Pt–Ag bonds, the most marked effect on their strength will result from the excess of available electron density on the platinum centres in the precursors, which will be related to the negative charge of the complexes. So far, we have not been able to synthesize Pt–Ag complexes by starting from neutral precursors, despite repeated attempts. Other authors have described a small number of Pt–Ag complexes formed from neutral platinum precursors. The stable ones [21, 22] contain an additional hydride bridge while the others [23] could not be isolated but only detected spectroscopically (NMR) due to lack of stability.

TABLE 2.

Complex	Pt–Ag (Å)	Figure
$\mathrm{(NBu_4)[(C_6F_5)_4Pt{-}Ag(tht)]}$	2.641(1)	3
$\mathrm{(NBu_4)[}cis\mathrm{\text{-}(C_6F_5)_2(C_6Cl_5)_2Pt{-}Ag(tht)]}$	2.692(1)	4
$\mathrm{[(tht)(C_6F_5)_3Pt{-}Ag(PPh_3)]}$	2.637(1)	1
$\mathrm{[(tht)(C_6F_5)_2(C_6Cl_5)Pt{-}Ag(PPh_3)]}$	2.650(2)	2

The Pt–Ag distances (Table 2) in anionic complexes (obtained from dianionic Pt precursors) or neutral complexes (from monoanionic precursors) do not permit any correlation to be established, though the neutral complexes are readily cleaved by the weak donor acetone, whilst neither donor solvents nor powerful ligands ($\mathrm{PPh_3}$, $\mathrm{NC_5H_5}$) cleave the Pt–Ag bonds in the anionic complexes.

On the other hand, it is clearly impossible to have the same mono or dianionic platinum complexes, i.e. strictly containing the same class and number of ligands, but by appropriate choice of suitable precursors it is possible to start from a dianionic complex and react it stepwise with a silver complex to synthesize a monoanionic complex and subsequently a neutral one, both displaying the same type of platinum–silver bonding [24]. For instance, the reaction between $[trans\text{-}\mathrm{PtCl_2(C_6Cl_5)_2}]^{2-}$ and $\mathrm{O_3ClOAgPPh_3}$ (with a very readily displaceable perchlorato ligand) may proceed (Scheme 2) via step (a) followed by (b).

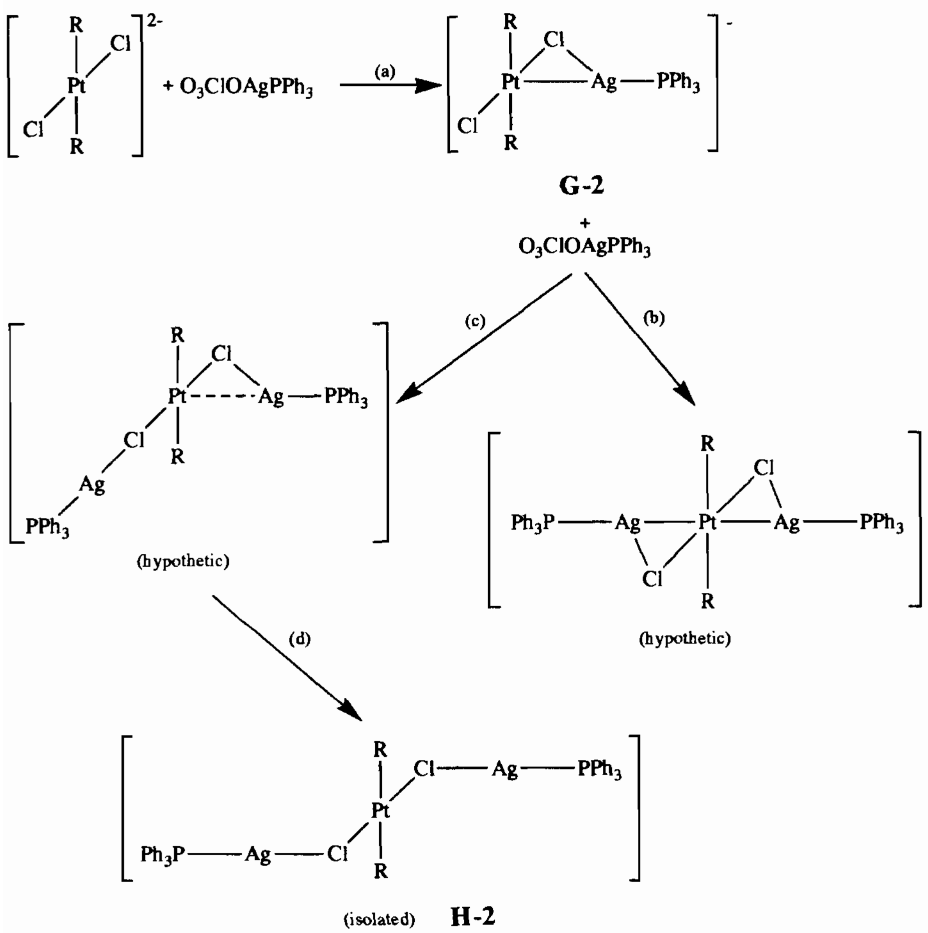
Step (a) is feasible and the monoanionic $\mathrm{(NBu_4)}[trans\text{-}\mathrm{Cl(C_6Cl_5)_2Pt}\overset{\diagup\mathrm{Cl}\diagdown}{\rule{2em}{0.4pt}}\mathrm{Ag{-}PPh_3}]$ (**G2**) can be isolated and structurally characterized (Fig. 13). In this complex, the platinum atom is not any longer the stronger donor centre and upon addition of one mole of $\mathrm{O_3ClOAgPPh_3}$ to **G2** reaction (b) does not take place but the terminal Cl ligand forms a bridge to the $\mathrm{AgPPh_3}$ fragment (c) which further decreases the electron density of the platinum centre: consequently the former Pt–Ag bond in **G2** is destabilized and the isolated neutral trinuclear complex (**H2**, Fig. 19 does not contain any Pt–Ag bond (d).

7. Other synthetic possibilities

The above results can be extended in two possible directions, either by using similar anionic complexes of a different central atom or by reacting the above described platinum complexes with other acidic metal complexes.

7.1. Reactions using anionic palladium complexes

Similar anionic palladium complexes prepared in our laboratory were the first choice. As a general law in comparative palladium and platinum chemistry, the palladium complexes are more labile than the homol-



Scheme 2. R = C_6Cl_5.

ogous platinum derivatives and it is therefore not surprising that our highly perarylated palladium complexes act as arylating agents upon the silver complex. Thus, the reactions between $(NBu_4)_2[Pd(C_6F_5)_4]$ or $(NBu_4)[Pd(C_6F_5)_3(tht)]$ and $O_3ClOAg(tht)$ or $O_3ClOAgPPh_3$ do not lead to heteronuclear complexes but to AgC_6F_5 and $(NBu_4)[Pd(C_6F_5)_3(tht)]$ or, [*cis*-$Pd(C_6F_5)_2(PPh_3)(tht)$], respectively [3].

After these results, we used less arylated anionic Pd(II) complexes, which contain one anionic chelating ligand in order to block two coordination sites thereby decreasing the number of undesirable reaction pathways. For instance, $(NBu_4)[M(C_6F_5)_2(acac)]$ (M = Pd, Pt) react (2:1) with $AgClO_4$ [25], yielding (eqn. (9)) complexes of Pd or Pt of the same stoicheiometry which are however structurally very different:

$$2(NBu_4)[M(C_6F_5)_2(acac)] + AgClO_4 \longrightarrow NBu_4ClO_4 + (NBu_4)[M(C_6F_5)_2(acac)]_2Ag \qquad (9)$$

M = Pd, Pt

For M = Pt (Fig. 20 a trinuclear complex results with a naked Ag atom linearly bonded to the platinum centres of two $[Pt(C_6F_5)_2(acac)]^-$ fragments, whereas the palladium derivative (Fig. 21) does not show any Pd–Ag bonds, though its silver atom is also linearly linked to the C^3 donor atom of the (acac) ligands. This illustrates again the lower tendency of palladium to engage in the formation of metal–metal bonds [26].

7.2. Reactions with other acidic metal centres

Anionic platinum complexes containing along with C_6F_5 other competitive donor ligands, such as acetylide ligands, react with Cu, Ag or Au complexes, to afford polynuclear complexes [27, 28] without metal–metal bonds (eqn. (10))

$$2Q_2[cis\text{-}Pt(C_6F_5)_2(C{\equiv}CR)_2] + 2MX \longrightarrow Q_2[Pt_2M_2(C_6F_5)_2(C{\equiv}CR)_4] + QX \qquad (10)$$

Q = $PMePh_3$, R = Ph; Q = NBu_4, R = ^tBu; MX = $AgClO_4$, AgCl or CuCl

The structure of the complex with M = Ag is shown in Fig. 22 and consists of two square planar [*cis*-$Pt(C_6F_5)_2(C{\equiv}CPh)_2$] moieties interconnected by two

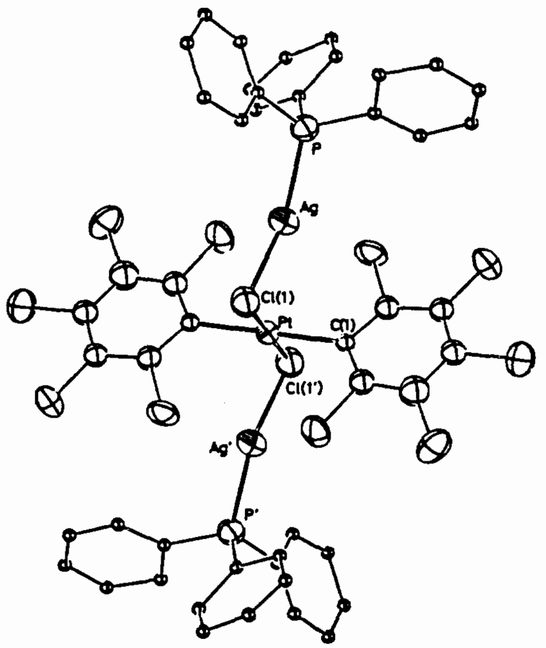


Fig. 19. Structure of [*trans*-$Pt(C_6Cl_5)_2\{\mu\text{-}Cl\text{-}Ag(PPh_3)\}_2$] (**H2**). Cl(1)–Ag: 2.447(8) Å [24].

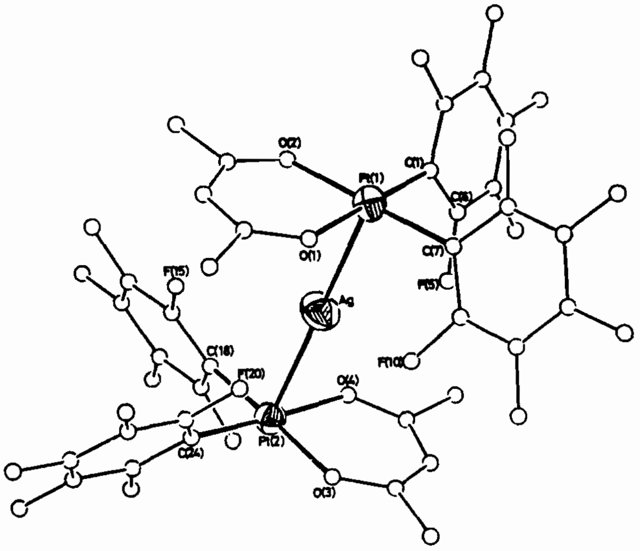


Fig. 20. Structure of $\{[Pt(C_6F_5)_2(acac)]_2Ag\}^-$ (**L**). Pt(1)–Ag: 2.681(1); Pt(2)–Ag: 2.667(1) Å [25].

silver atoms, which are asymmetrically bonded to the acetylide groups [28].

Exclusion of competitive ligands in the coordination sphere of the platinum precursors leads to complexes with Pt→M bonds, when M = Sn or Pb. For instance, $(NBu_4)_2[Pt_2(\mu\text{-}Cl)_2(C_6F_5)_4]$ reacts with $SnCl_2$ and $AgClO_4$ in THF solution to afford [29] the tetranuclear $(NBu_4)[Sn\{Pt(\mu\text{-}Cl)(C_6F_5)_2\}_3]$. The structure of the anion (Fig. 23) shows a naked Sn atom, bonded to the three Pt atoms in a Pt_3Cl_3 puckered ring. There are also *o*-F...Sn short contacts.

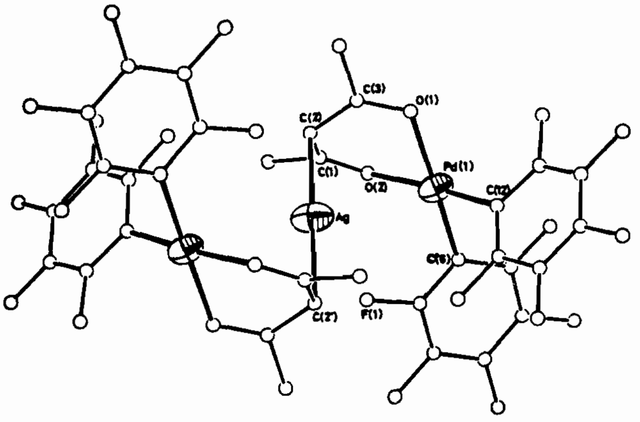


Fig. 21. Structure of $\{[Pd(C_6F_5)_2(acac)]_2Ag\}^-$ (**M**). C(2)–Ag: 2.241(7) Å [25].

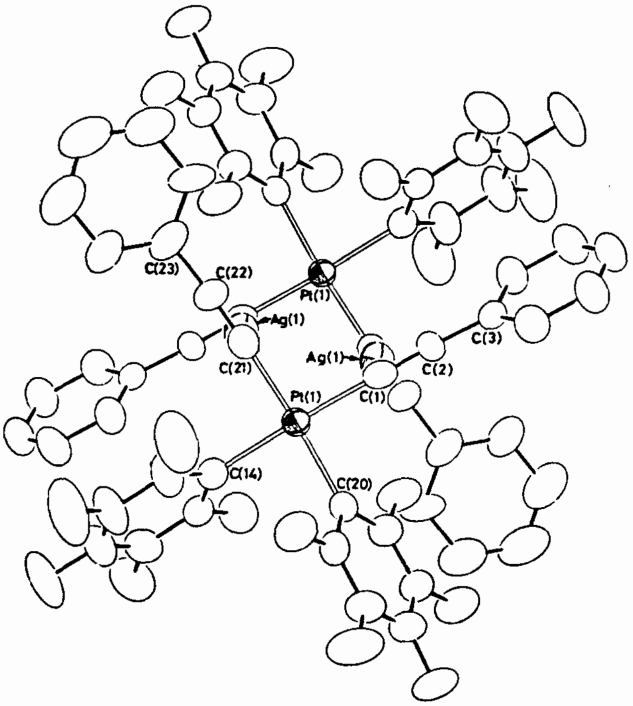


Fig. 22. Structure of $[Pt_2Ag_2(C_6F_5)_4(C{\equiv}CPh)_4]^{2-}$ (**N**) [28].

A presumably similar Pt–Pb complex is being structurally studied at present.

Finally, $(NBu_4)_2[Pt(C_6F_5)_4]$ reacts (2:1) with $Pb(NO_3)_2$ (in MeOH) to give the yellow $(NBu_4)_2[Pb\{Pt(C_6F_5)_4\}_2]$ which displays (Fig. 24) a singular structure [30]. The lead atom in the trinuclear anion is linearly bonded to the central Pt atoms in the square planar $Pt(C_6F_5)_4$ fragments. The two Pt–Pb distances are 2.769(2) and 2.793(2) Å suggesting the presence of single bonds. This is the first example of a complex with the central Pb(II) atom linearly coordinated to two metal atoms, the lone pair being stereochemically inactive. The C_6F_5 groups are so positioned that eight *o*-F...Pb short

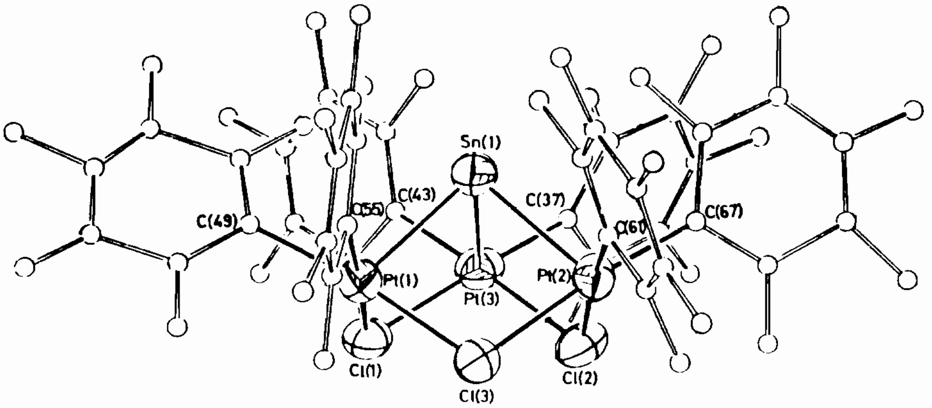


Fig. 23. Structure of $[Sn\{Pt(\mu\text{-}Cl)(C_6F_5)_2\}_3]^-$ (O). Sn(1)–Pt(1): 2.732(2); Sn(1)–Pt(2): 2.742(3); Sn(1)–Pt(3): 2.704(2) Å [29].

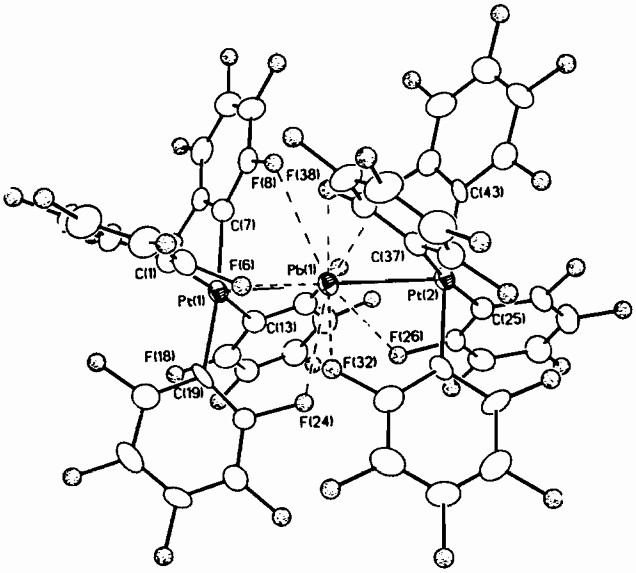


Fig. 24. Structure of $[Pb\{Pt(C_6F_5)_4\}_2]^{2-}$ (P). Pb(1)–Pt(1): 2.769(2); Pb(1)–Pt(2): 2.793(2) Å [30].

contacts (the eight *o*-F atoms are forming a compressed Archimedean antiprism) are present and are probably determinant for the adopted structure.

At present, we are engaged in the study of reactions between other aryl platinate complexes and suitable compounds of post-transition metals.

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References

1 R. Usón and J. Forniés, in F. G. A. Stone and R. West (eds.) *Advances in Organometallic Chemistry*, Vol. 28, Academic Press, San Diego, CA, 1988, p. 219.
2 F. A. Cotton, L. R. Falvello, R. Usón, J. Forniés, M. Tomás, J. M. Casas and I. Ara, *Inorg. Chem., 26* (1987) 1366.
3 R. Usón, J. Forniés, M. Tomás, I. Ara, J. M. Casas and A. Martín, *J. Chem. Soc., Dalton Trans.,* (1991) 2253.
4 R. Usón, J. Forniés, M. Tomás, J. M. Casas, F. A. Cotton and L. R. Falvello, *Inorg. Chem., 26* (1987) 3482.
5 R. Usón, J. Forniés, M. Tomás, J. M. Casas, F. A. Cotton, L. R. Falvello and R. Llusar, *Organometallics, 7* (1988) 2279.
6 R. Usón, J. Forniés, M. Tomás and J. M. Casas, *Angew. Chem., Int. Ed. Engl.,* (1989) 748.
7 R. Usón, J. Forniés, M. Tomás and B. Menjón, *Organometallics, 5* (1986) 1581.
8 R. Usón, J. Forniés and M. Tomás, *J. Organomet. Chem., 358* (1988) 525, and refs. therein.
9 L. R. Falvello, J. Forniés, R. Navarro, V. Sicilia and M. Tomás, *Angew. Chem., Int. Ed. Engl., 29* (1990) 891.
10 J. Forniés, C. Fortuño, R. Navarro, F. Martínez and A. J. Welch, *J. Organomet. Chem., 394* (1990) 643.
11 R. Usón, J. Forniés, B. Menjón, F. A. Cotton, L. R. Falvello and M. Tomás, *Inorg. Chem., 24* (1985) 4651.
12 R. Usón, J. Forniés, M. Tomás, J. M. Casas, F. A. Cotton and L. R. Falvello, *Inorg. Chem., 25* (1986) 4519.
13 R. Usón, J. Forniés, M. Tomás, I. Ara and J. M. Casas, *Inorg. Chem., 28* (1989) 2388.
14 R. Usón, J. Forniés, M. Tomás and I. Ara, *Inorg. Chim. Acta, 186* (1991) 67.
15 R. Usón, J. Forniés, M. Tomás and I. Ara, *J. Chem. Soc., Dalton Trans.,* (1989) 1011.
16 R. Usón, J. Forniés, M. Tomás and I. Ara, *J. Chem. Soc., Dalton Trans.,* (1990) 3151.
17 M. R. Colsman, T. D. Newbound, L. S. Marshall, M. D. Noirot, N. M. Miller, G. P. Wulfsberg, J. S. Frye, O. P. Anderson and S. H. Strauss, *J. Am. Chem. Soc., 112* (1990) 2349.
18 H. W. Roesky, T. Gries, P. G. Jones, K. L. Weber and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.,* (1984) 1781.

19 Y. Yamamoto, K. Aoki and A. Yamazaki, *Inorg. Chim. Acta, 68* (1983) 75.

20 R. W. Turner and E. L. Amma, *J. Am. Chem. Soc., 88* (1966) 3243.

21 A. Albinati, H. Lehner, L. M. Venanzi and M. Wolfer, *Inorg. Chem., 26* (1987) 3933.

22 A. Albinati, F. Demartin, L. M. Venanzi and M. K. Wolfer, *Angew. Chem., Int. Ed. Engl., 27* (1988) 563.

23 G. J. Arsenault, G. M. Anderson and R. J. Puddephatt, *Organometallics, 7* (1988) 2094.

24 R. Usón, J. Forniés, M. Tomás, J. M. Casas and I. Ara, unpublished results.

25 E. Urriolabeitia, *Ph.D. Thesis,* University of Zaragoza, 1991.

26 D. L. Kepert and K. Vrieze, in J. C. Bailar and A. F. Trotman-Dickenson (eds.), *Comprehensive Inorganic Chemistry,* Vol. 4, Pergamon, Oxford, 1973, p. 224 and refs. therein.

27 P. Espinet, J. Forniés, F. Martínez, M. Tomás, E. Lalinde, M. T. Moreno, A. Ruiz and A. J. Welch, *J. Chem. Soc., Dalton Trans.,* (1990) 791.

28 P. Espinet, J. Forniés, F. Martínez, M. Sotés, E. Lalinde, M. T. Moreno, A. Ruiz and A. J. Welch, *J. Organomet. Chem., 403* (1991) 253.

29 R. Usón, J. Forniés, M. Tomás and I. Usón, *Angew. Chem., Int. Ed. Engl., 29* (1990) 1449.

30 R. Usón, J. Forniés, L. R. Falvello, M. A. Usón and I. Usón, unpublished results.