Review

Anionic perhaloaryl-palladium and -platinum complexes as sources of unusual homo- and hetero-nuclear compounds

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Introduction

As we began our work in the field of organometallic chemistry our choice of perhaloaryl groups (C_6X_5, X = F, Cl) as the organic ligands was determined by the expectation they would give rise to stronger M_T–C_{aryl} bonds. In the late 1960's only a few perhaloaryl derivatives of palladium and platinum (of the types $MX(C_6X_5)L_2$, $M(C_6X_5)_2L_2$) had been reported, but several authors had noted that transition metal–perfluorocarbon (M–R_F) bonds were stronger than the corresponding metal–hydrocarbon (M–R_H) bonds, for the following reasons: (a) the higher electronegativity of R_F relative to R_H, which makes the former a more ionic ligand; (b) the decrease in the electron density on the metal, which leads to contraction of its filled d orbitals and so a decrease in the repulsion between them and the group attached to the α-carbon atom; (c) the contraction of the metal orbital forming the metal–carbon σ-bond, and thus an increase in the strength of this bond in R_F as opposed to R_H complexes; (d) the possibility of back donation of electron density from filled d orbitals to π^*-orbitals on the aryl ligands; (e) the *ortho*-effect in 2,6-substituted aryl groups; and, possibly, (f) a greater inertness of the M–R_F bond, involving a greater kinetic stability of the perhalo derivatives [1].

Since our aim was the synthesis of organometallic compounds stable enough for the study of the reactions at the metal centres, strong or inert M_T–C bonds were a requisite if the organometallic character was to be preserved throughout the reactions.

To date there has been no direct proof of the greater strength of M–C_6X_5 (M = Pd, Pt) relative to M–C_6H_5 bonds; for instance, the M–C distances are very similar (~ 2.06 Å) in aryl and perfluoroaryl complexes [2], although only few comparable cases have been studied. It is a fact, however, that the perhaloaryl derivatives, whatever the reason, are more stable: time and again we have attempted the preparation of the corresponding aryl derivatives only to find that the synthetic procedures that allowed isolation of C_6X_5 stable derivatives in good yield led to decomposition to metallic powders if C_6H_5 groups were present instead C_6X_5 in the precursor. Furthermore, we have seen our initial expectations generally confirmed,

since the M–C$_6$X$_5$ bonds remained unaltered during reactions at the metal centres, except in a few reactions, namely cleavage by HCl [3,4,5], C$_6$X$_5$ transfers between two metal centres [3,6–8], and insertion of isocyanides into the M–C bonds [9–11] which, are not, however, decomposition processes.

A further observation we made during our early work was that the presence of group 15 neutral ligands on the metal hindered the introduction of more than two C$_6$X$_5$ groups. Since we were interested in the synthesis of more highly arylated, i.e. anionic, complexes, in the mid-1970's we began to use precursors containing either more weakly coordinating ligands or no ligands at all, and by arylating with (C$_6$X$_5$)MgX$'$ or C$_6$X$_5$Li we duly obtained stable anionic complexes of several types, which provided the starting point for development of a different chemistry, as will be seen from the account below.

A comprehensive review of our work [12] and a discussion of the preparative routes to bi- or poly-nuclear complexes [13] have appeared recently. Here, we focus on the synthesis of the homoleptic (NBu$_4$)$_2$[M(C$_6$X$_5$)$_4$] complexes (M = Pd, Pt; X = F, Cl) and the special chemistry that has emerged through their use as precursors.

## 1. The way to (NBu$_4$)$_2$[M(C$_6$X$_5$)$_4$]

As mentioned above, if the starting complexes are of the type MCl$_2$(PR$_3$)$_2$, only mono- or bis-arylated complexes can be obtained, irrespective of the extent of the excess of the arylating agent used, but complexes containing sulphur donors behave differently. For instance, reaction of *trans*-PdCl$_2$(tht)$_2$ (tht = tetrahydrothiophen) with C$_6$F$_5$Li (1/6 molar ratio) gives (70% isolated yield) of (NBu$_4$)$_2$[Pd(C$_6$F$_5$)$_4$], while a mixture of *cis*- and *trans*-PtCl$_2$(tht)$_2$ gives (56%) (NBu$_4$)[Pt(C$_6$F$_5$)$_3$(tht)], and the use of a greater excess of C$_6$F$_5$Li (1/13) leads to formation of non-crystallisable oils. Arylation of PtCl$_2$ with C$_6$F$_5$Li (1/2.3) gives (NBu$_4$)$_2$[*trans*-PtCl$_2$(C$_6$F$_5$)$_2$] (60%), but with a greater excess of the arylating agent (1/8 ratio), (NBu$_4$)$_2$[Pt(C$_6$F$_5$)$_4$] is the major product (66%). The same method leads to isolation (47% yield) of (NBu$_4$)$_2$[Pt(C$_6$Cl$_5$)$_4$], whereas the attempted arylation of PdCl$_2$ causes violent decomposition and precipitation of metallic Pd [7]. Arylation of PdCl$_2$(tht)$_2$ with C$_6$Cl$_5$Li (1/6) does not proceed beyond the neutral Pd(C$_6$Cl$_5$)$_2$(tht)$_2$, but the homoleptic (NBu$_4$)$_2$[Pd(C$_6$Cl$_5$)$_4$] can be obtained (64%) along with some (9%) (NBu$_4$)$_2$[Pd$_2$(μ-Br$_2$)(C$_6$Cl$_5$)$_4$] by arylating (NBu$_4$)$_2$[Pd$_2$(μ-Br)$_2$Br$_4$] with C$_6$Cl$_5$Li (1/4 ratio) [3].

2. (NBu$_4$)$_2$[M(C$_6$X$_5$)$_4$] as precursors for other anionic complexes

The homoleptic tetrakis-aryl derivatives are excellent precursors for the synthesis of other anionic, monomeric, or dimeric arylcomplexes.

(a) Synthesis of (NBu$_4$)$_2$[M$_2$(μ-Cl)$_2$(C$_6$X$_5$)$_4$]

Arylation of PdCl$_2$ with [Pd(C$_6$X$_5$)$_4$]$^{2-}$ gives binuclear chloride-bridged anionic complexes [7] (eq. 1), two C$_6$X$_5$ groups migrating from one Pd atom to the other.

$$(NBu_4)_2[Pd(C_6X_5)_4] + PdCl_2 \rightarrow (NBu_4)_2[Pd_2(\mu\text{-}Cl)_2(C_6X_5)_4] \qquad (1)$$
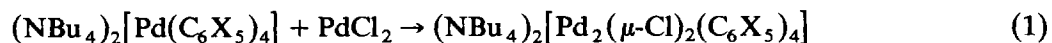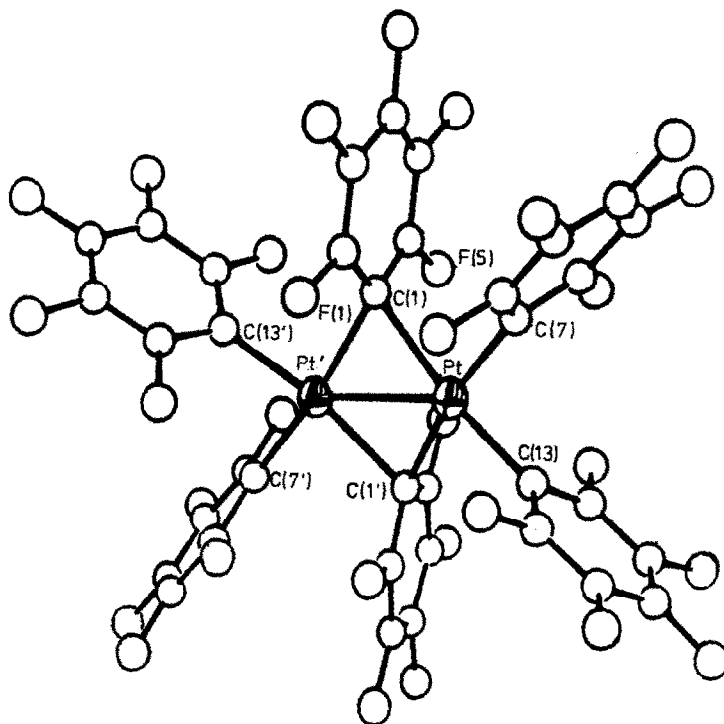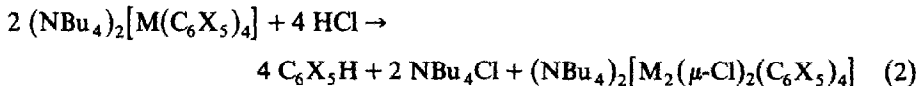
The reaction does not take place with the corresponding Pt compounds in keeping

Fig. 1. Structure of $[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]^{2-}$ (15).

with their generally more inert character. At higher temperatures (toluene, reflux) decomposition to metallic platinum is observed.
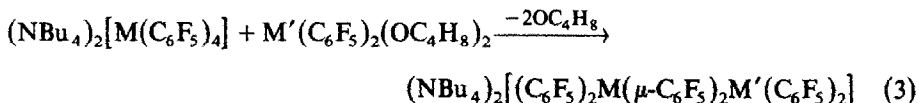
A general process (eq. 2) allows synthesis of all the possible binuclear complexes:

$$2\,(NBu_4)_2\big[M(C_6X_5)_4\big] + 4\,HCl \rightarrow$$

$$4\,C_6X_5H + 2\,NBu_4Cl + (NBu_4)_2\big[M_2(\mu\text{-}Cl)_2(C_6X_5)_4\big] \quad (2)$$

Since in all the four cases, the yields are > 85%, this is a good preparative method (and the only one leading to the platinum complexes) despite the fact that half of the C_6X_5 groups are lost in the form of C_6X_5H [3,4].

(b) Synthesis of $(NBu_4)_2[MM'(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$

A reaction reminiscent of that of eq. 1 leads [14] to homo- or hetero-binuclear (M = Pd, Pt; M' = Pd, Pt) anionic homoleptic C_6F_5 complexes (eq. 3)

$$(NBu_4)_2\big[M(C_6F_5)_4\big] + M'(C_6F_5)_2(OC_4H_8)_2 \xrightarrow{-2OC_4H_8}$$

$$(NBu_4)_2\big[(C_6F_5)_2M(\mu\text{-}C_6F_5)_2M'(C_6F_5)_2\big] \quad (3)$$

The structure of one of these complexes (M = M' = Pt) has been determined by X-ray methods [15] and shows (Fig. 1) a bent (dihedral angle 151.9°) central $>Pt(\mu\text{-}C_6F_5)_2Pt<$ moiety, with two C_6F_5 bridging groups and four terminal ones. These complexes are the first reported binuclear homoleptic derivatives doubly bridged by two pentafluorophenyl ligands. The ^{19}F NMR spectra of all these

compounds show signals assigned to F_o of the bridging C_6F_5 groups at lower fields than from F_o of the terminal groups, which could be of value in diagnosing the presence of bridging C_6F_5 groups in new species. If the same reaction (eq. 3) is attempted with the corresponding pentachlorophenyl derivatives the starting products are recovered unchanged.

(c) Synthesis of $(NBu_4)_2[M(C_6X_5)_3Cl]$ and $(NBu_4)[M(C_6X_5)_3L]$

The (1/1) reaction between $(NBu_4)_2[Pt(C_6F_5)_4]$ and HCl gives (76%) $(NBu_4)_2[Pt(C_6F_5)_3Cl]$, whilst related compounds $(NBu_4)_2[M(C_6X_5)_4]$ (M = Pd, X = F, Cl; M = Pt, X = Cl) give the anionic binuclear $(NBu_4)_2[M_2(\mu\text{-}Cl)_2(C_6X_5)_4]$.

In the presence of a one molar proportion of a neutral ligand [5] the action of HCl (1/1) leads to the cleavage of only one M–C bond (eq. 4), but for M = Pd,

$$(NBu_4)_2[M(C_6X_5)_4] + HCl + L \rightarrow (NBu_4)[M(C_6X_5)_3L] + NBu_4Cl + C_6X_5H$$

$$(4)$$
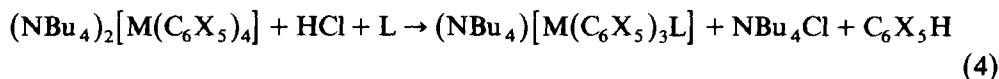
(M = Pd, X = F; M = Pt, X = Cl)

X = Cl, a mixture of the starting complex and the neutral *cis*-$Pd(C_6Cl_5)_2L_2$ is obtained [16]. Seemingly, in this reaction two Pd–C bonds are cleaved and the formed binuclear complex reacts with the neutral ligand, which cleaves the Cl-bridges and displaces a chloride ion, as is normally for these binuclear complexes [3.7].

More recently, the synthesis of $(NBu_4)_2[M_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$ has made available to us a different precursor, which reacts with NBu_4Br or neutral ligands L to give respectively $(NBu_4)_2[M(C_6F_5)_3Br]$ and $(NBu_4)[M(C_6F_5)_3L]$ in > 75% yields (M = Pd, Pt; L = N, P, As donor ligand) [14].

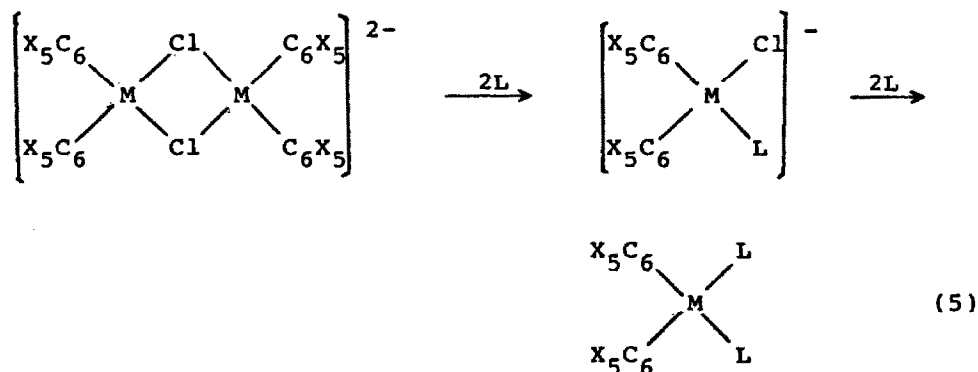*(d) Synthesis of a mononuclear platinum(III) complex: $(NBu_4)[Pt(C_6Cl_5)_4]$*

The $[Pt(C_6Cl_5)_4]^{2-}$ anion can be oxidized by a variety of chemical systems (Cl_2, Br_2, I_2, $TlCl_3$, [p-$MeC_6H_4N_2$]BF_4) or electrochemically (ϵ_0 0.54 V) to give a deep blue solution from which $(NBu_4)[Pt(C_6Cl_5)_4]$ can be readily isolated as an air- and moisture-stable blue solid. It is the first mononuclear platinum(III) compound to have been fully structurally characterized. The values of μ_{eff} vary between 2.42 BM (80 K) and 2.57 BM (260 K), somewhat higher than expected for a $\frac{1}{2}$ spin system. The structure [17] of the anion is practically the same as that of the platinum(II) precursor (Figs. 2, 3); both are square planar, and the Pt–C, C–C and C–Cl distances and the sizes of the angles between the C_6Cl_5 planes and the central PtC_4 plane coincide within experimental error.

Moreover, the platinum(III) complex reacts with NO to give $(NBu_4)[Pt(C_6Cl_5)_4$-NO], in which the structure of the anion is a somewhat distorted square pyramid with a linear Pt–N–O linkage (Fig. 4).

(e) Preparation of cis-$M(C_6X_5)_2(OC_4H_8)_2$: useful precursors for unusual complexes

The anionic binuclear derivatives $(NBu_4)_2[M_2(\mu\text{-}Cl)_2(C_6X_5)_4]$ (M = Pd, Pt; X = F, Cl) react stepwise and with stereoretention to give anionic or neutral complexes (eq. 5) upon addition of neutral ligands.

We have used this process [18] to prepare *cis*-complexes of palladium that are inert towards isomerisation.

$$(NBu_4)_2[M_2(\mu\text{-}X')_2(C_6X_5)_4] + 2\ AgClO_4 \xrightarrow{OC_4H_8}$$

$$2\ AgX' + 2\ NBu_4ClO_4 + 2\ cis\text{-}M(C_6X_5)_2(OC_4H_8)_2 \quad (6)$$

$(M = Pd, Pt; X' = Cl, Br; X = F, Cl)$

Another type of reaction of the binuclear derivatives yields complexes of the formula $cis\text{-}M(C_6X_5)_2(OC_4H_8)_2$ (eq. 6).
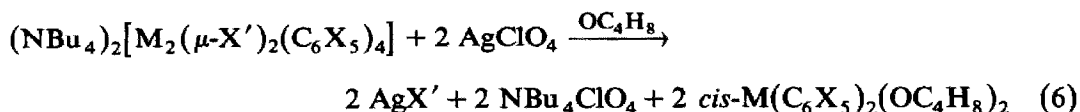
The complexes are air- and moisture-stable solids, and the two neutral ligands can be readily displaced by a variety of ligands to give otherwise unaccessible compounds.

(a) Bubbling of CO(NTP) through dichloromethane solutions of $cis\text{-}M(C_6X_5)_2$-$(OC_4H_8)_2$ gives $cis\text{-}M(C_6X_5)_2(CO)_2$ [19,20]. The palladium compounds are the first monomeric dicarbonyls reported so far; they show ν(CO) at 2186 and 2163 cm^{-1} (X = F); 2173 and 2152 cm^{-1} (X = Cl), pointing to negligible, if any, π-back-bond-
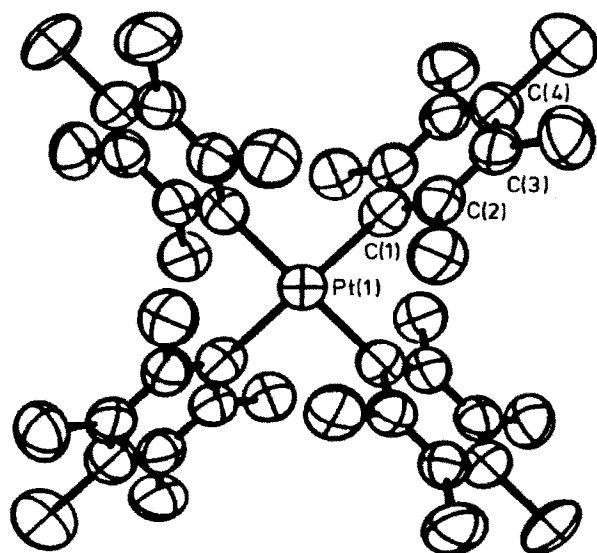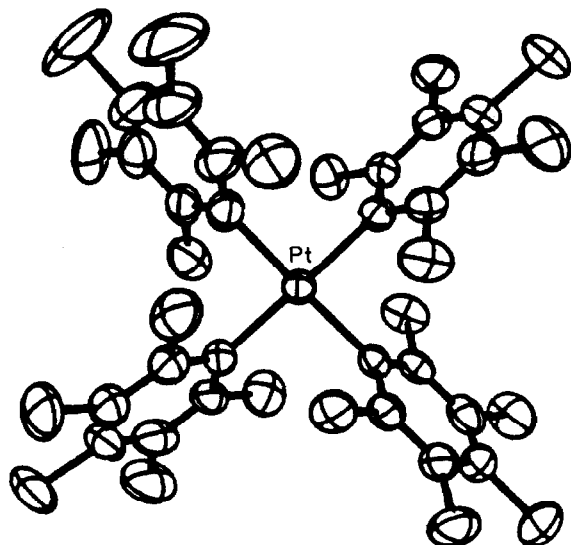

Fig. 2. Structure of $[Pt(C_6Cl_5)_4]^{2-}$ (17).

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Fig. 3. Structure of $[Pt(C_6Cl_5)_4]^-$ (**17**).
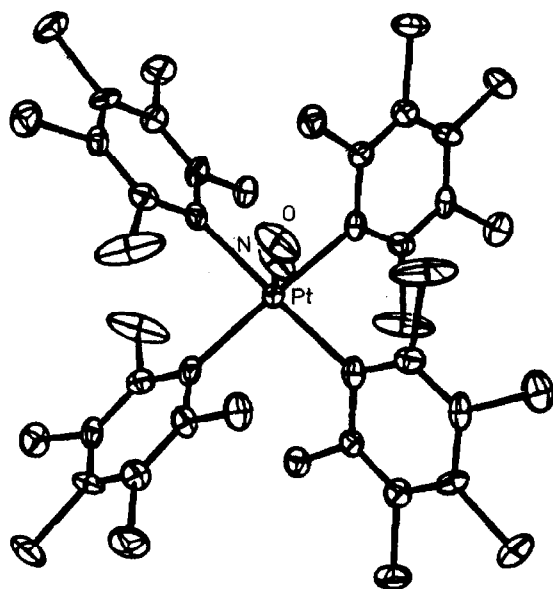
Fig. 4. Structure of $[Pt(C_6Cl_5)_4NO]^-$ (**17**).

ing. The platinum compounds are air- and moisture-stable; cis-$Pt(C_6F_5)_2(CO)_2$ can be sublimed at 205°C without decomposition.

(b) From C_2Ph_2, bis-acetylene derivatives can be obtained. The structure of cis-$Pt(C_6F_5)_2(PhC\equiv CPh)_2$ has been determined [21]. The platinum atom lies in a slightly distorted square planar environment (Fig. 5) and the acetylene ligands remain almost unchanged upon coordination (C≡C distance 1.197(6) Å, compared with 1.19 Å in the free C_2Ph_2), and almost linear, pointing to negligible π-back bonding.
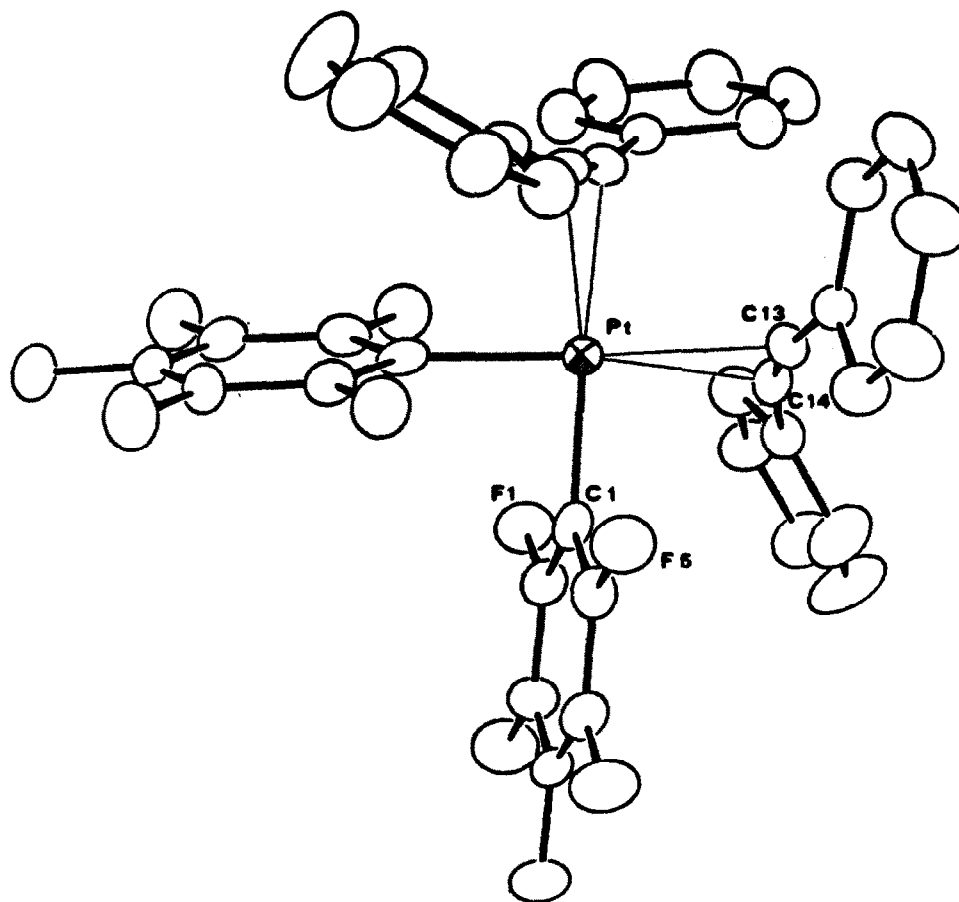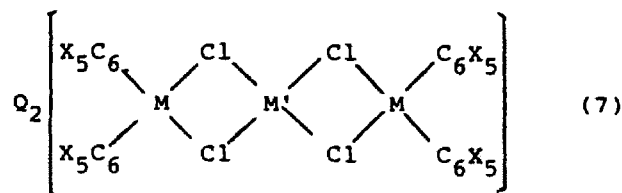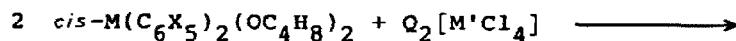
Fig. 5. Structure of cis-Pt$(C_6F_5)_2$(dpa)$_2$ (21).

(c) With complexes containing other uncoordinated donor atoms (Pd(η^2-S$_2$CS)(dppe) polynuclear complexes can be obtained [22].

(d) Mono- or bi-nuclear halo complexes ([MCl$_4$]$^{2-}$, [M$_2(\mu$-Br)$_2$Br$_4$]$^{2-}$) react (eq. 7) to give homo- or hetero-tri- and tetra-nuclear derivatives [23].

$$2 \quad cis-M(C_6X_5)_2(OC_4H_8)_2 + Q_2[M'Cl_4] \longrightarrow$$

$$Q_2 \begin{bmatrix} X_5C_6 & Cl & Cl & C_6X_5 \\ & \diagdown M \diagdown & \diagdown M' \diagdown & \diagdown M \diagdown \\ X_5C_6 & Cl & Cl & C_6X_5 \end{bmatrix} \qquad (7)$$

The structure of the trinuclear platinum(II) complex (Fig. 6) shows that the square-planar anion [PtCl$_4$]$^{2-}$ is acting as a tetradentate, doubly chelating ligand to bridge two "Pt$(C_6X_5)_2$" moieties. When Q$_2$[M$_2'(\mu$-Br)$_2$Br$_4$] is used instead of Q$_2$[M'Cl$_4$] in the reaction of eq. 7, the tetranuclear Q$_2$[(X$_5$C$_6$)$_2$M$(\mu$-Br)$_2$M'(μ-Br)$_2$M'(μ-Br)$_2$M$(C_6X_5)_2$] was obtained, but attempts to grow suitable crystals for X-ray studies failed owing to precipitation of M'Br$_2$ and formation of the trinuclear complex.
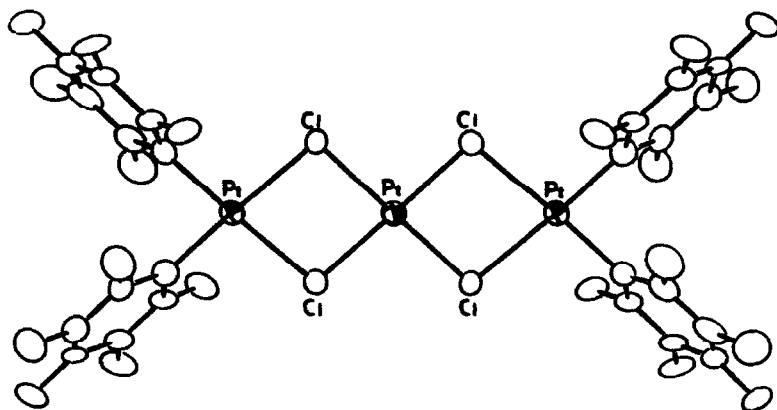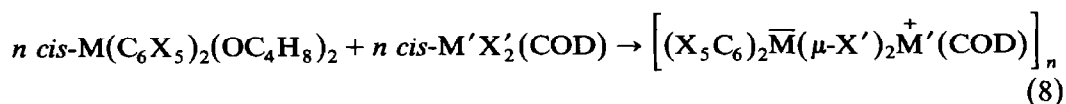
Fig. 6. Structure of $[(C_6F_5)_2Pt(\mu\text{-Cl})_2Pt(C_6F_5)_2]^{2-}$ (**23**).

(e) With neutral *cis*-dihalide complexes $M'X'_2(COD)$ (COD = 1,5-cycloocta-diene) homo- or hetero-metallic binuclear geminal complexes are obtained [24] (eq. 8),

$$n\,\textit{cis-}M(C_6X_5)_2(OC_4H_8)_2 + n\,\textit{cis-}M'X'_2(COD) \rightarrow \left[(X_5C_6)_2\overline{M}(\mu\text{-X'})_2\overset{+}{M}'(COD)\right]_n$$
$$(8)$$

$(M = Pd, Pt; X = F, Cl; M' = Pd, Pt; X' = Cl, Br, I)$

They exhibit an interesting behaviour in that the n value is 1 in solution but 2 in the solid state, and the transformation binuclear (solution) $\rightleftharpoons$ tetranuclear (solid
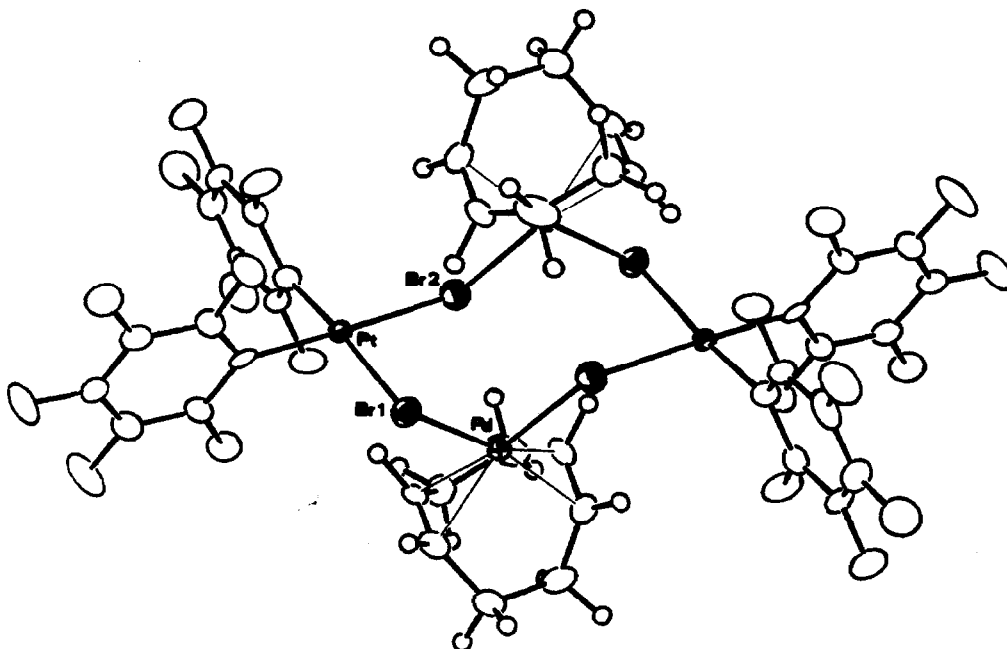

Fig. 7. Structure of $[\overline{Pt(C_6F_5)_2(\mu\text{-Br})Pd(COD)(\mu\text{-Br})Pt(C_6F_5)_2(\mu\text{-Br})Pd(COD)(\mu\text{-Br})}]$ (**24**).

state) is reversible, i.e. the single bridge system present in the solid state changes to a double bridge system in the solutes, and the former is reformed upon evaporation. The structure of the heteronuclear complex where M = Pt, M′ = Pd, X = F, X′ = Br has been determined (Fig. 7), and shows that the four metal centres are singly bridged by four Br atoms to give a puckered eight-membered ring with two terminal C_6F_5 groups attached to each Pt atom and a chelating diolefin linked to each Pd atom. Moreover, the overall neutral complexes are formally zwitter-ionic, with a half of the metal atoms (formal charge −1) bonded to two carbanionic ligands and sharing the two halide groups, and the other half of the metal atoms (formal charge +1) simply sharing the two bridging halide ligands.

3. Basic behaviour of anionic platinum complexes

The types of anionic complexes described have an excess of electron density on the metal centres and therefore show basic properties, which can be illustrated by their behaviour towards Lewis acids, such as silver(I) cations. Polynuclear complexes containing Pt–Ag bonds are formed, and in most of them *ortho*-X substituents of the C_6X_5 groups are so positioned as to interact with the silver atoms, possibly donating some electron density and thus increasing the stability of the clusters. We discuss these effects below in some detail. The environment of the platinum centre influences its basic behaviour, and several different situations have been observed so far:

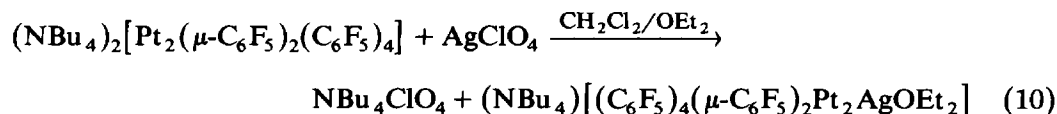### (a) Anionic (non halide-containing) platinum complexes

Anionic monomeric platinum complexes of the type $(NBu_4)[Pt(C_6F_5)_3L]$ react with $O_3ClOAgL′$ to give (eq. 9) heterobinuclear complexes containing a Pt–Ag bond unsupported by any covalent bridge [25].

$$(NBu_4)\left[Pt(C_6F_5)_3L\right] + O_3ClOAgL′ \rightarrow NBu_4ClO_4 + \left[L(C_6F_5)_3Pt \rightarrow AgL′\right] \qquad (9)$$

$$(L = SC_4H_8, PPh_3, PEt_3, PEtPh_2, NC_5H_5; L′ = PPh_3, PEt_3)$$

The structure of the complex with L = SC_4H_8 and L′ = PPh_3 is shown in Fig. 8. The structural rôle played by the pentafluoroaryl groups is discussed below, but it is noteworthy that the platinum centre is the preferred donor atom despite the presence of the potentially bridging SC_4H_8, which could form a Pt–S–Ag bridge system.

The anionic binuclear platinum complex [15] $(NBu_4)_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$ reacts with uncomplexed $AgClO_4$ to give a trinuclear Pt_2Ag complex (Fig. 9) with two unsupported Pt–Ag bonds (eq. 10), i.e. the Ag^+ bridging the two platinum(II) donor centres in the binuclear starting complex.

$$(NBu_4)_2\left[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4\right] + AgClO_4 \xrightarrow{CH_2Cl_2/OEt_2}$$

$$NBu_4ClO_4 + (NBu_4)\left[(C_6F_5)_4(\mu\text{-}C_6F_5)_2Pt_2AgOEt_2\right] \qquad (10)$$

(b) Anionic halide-containing platinum complexes

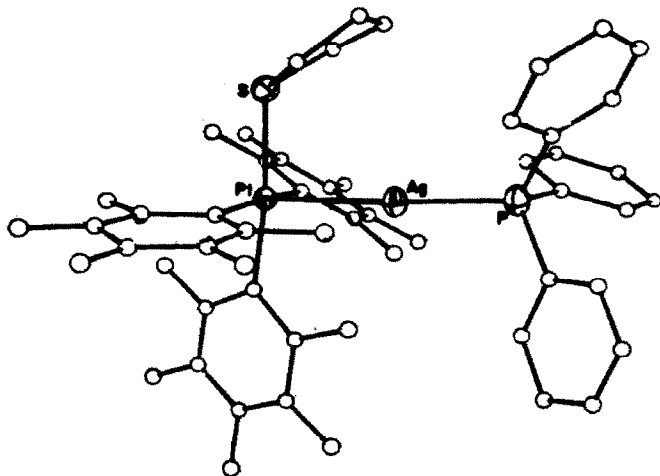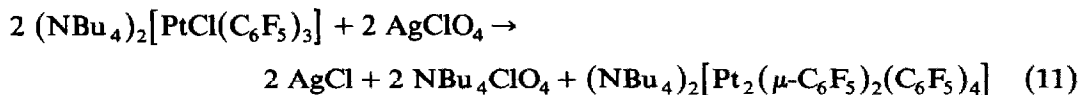Three different types of behaviour have so far been observed:

Fig. 8. Structure of $[(SC_4H_8)(C_6F_5)_3Pt \rightarrow AgPPh_3]$ (25).

(i) The halide ligands are not involved in the process. $(NBu_4)_2[Pt_2(\mu\text{-}X)_2(C_6F_5)_2]$ reacts [26] with $AgClO_4$ or $O_3ClOAgL$ to give heterotrinuclear Pt_2Ag derivatives $(NBu_4)_2[(C_6F_5)_4(\mu\text{-}X)_2Pt_2AgL]$ (X = Cl, Br; L = OEt_2, PPh_3, $PMePh_2$). The structure of the complex with X = Cl, L = OEt_2 is shown in Fig. 10, and is very similar to that shown in Fig. 9.

(ii) Silver halide separates out. Because of the insolubility of AgX, in some cases the halide ligands can be removed (eq. 11)

$$2 (NBu_4)_2[PtCl(C_6F_5)_3] + 2 AgClO_4 \rightarrow$$

$$2 AgCl + 2 NBu_4ClO_4 + (NBu_4)_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4] \quad (11)$$

The binuclear complex can be isolated, and treated with $AgClO_4$ to give the
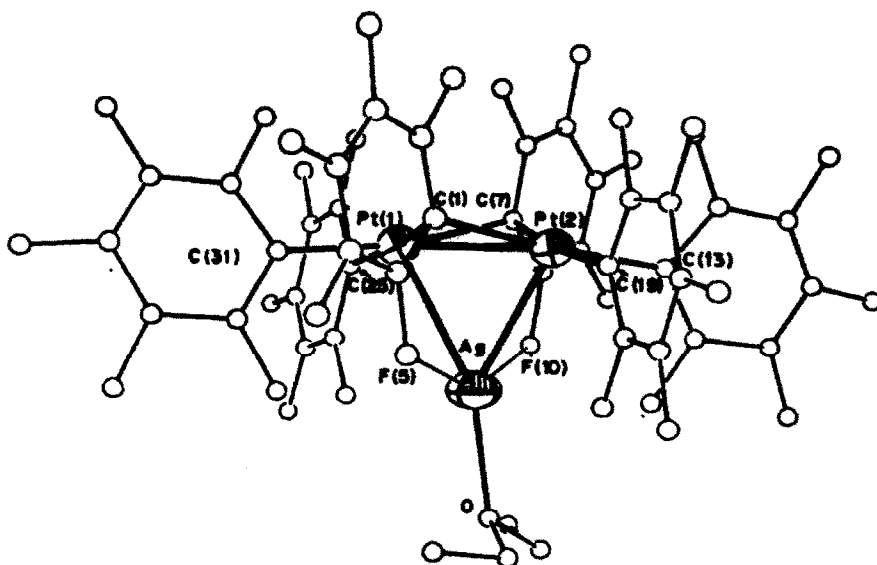
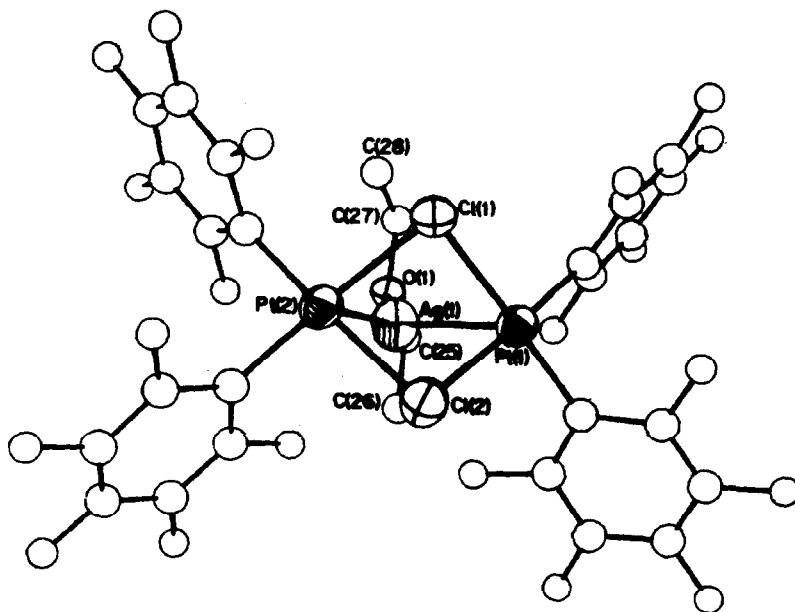Fig. 9. Structure of $[(C_6F_5)_4(\mu\text{-}C_6F_5)_2Pt_2Ag(OEt_2)]^-$ (15).

Fig. 10. Structure of $[(C_6F_5)_4(\mu\text{-Cl})_2Pt_2Ag(OEt_2)]^-$ (26).

trinuclear $(NBu_4)_2[(C_6F_5)_4(\mu\text{-}C_6F_5)_2Pt_2AgOEt_2]$ (see Section 3a), which can also be obtained directly by using an excess of $AgClO_4$ in the reaction of eq. 11 [15].

(iii) The product contains Pt–Ag as well as Cl–Ag bonds. In methanol or acetone solution, $(NBu_4)_2[trans\text{-}PtCl_2(C_6F_5)_2]$ reacts (eq. 12) with silver salts ($AgClO_4$ or
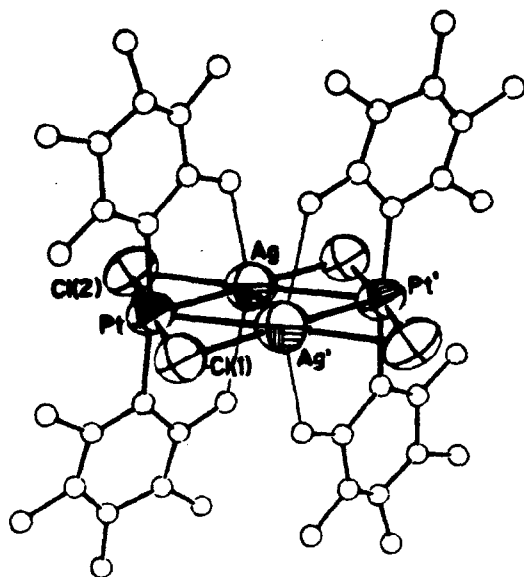
$$(NBu_4)_2[trans\text{-}PtCl_2(C_6F_5)_2] + 2\,AgClO_4$$
$$\rightarrow 2\,NBu_4ClO_4 + (NBu_4)_2[Pt_2Ag_2Cl_4(C_6F_5)_4] \quad (12)$$
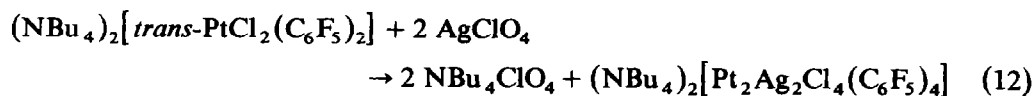
Fig. 11. Structure of $[Pt_2Ag_2Cl_4(C_6F_5)_4]^{2-}$ (27).
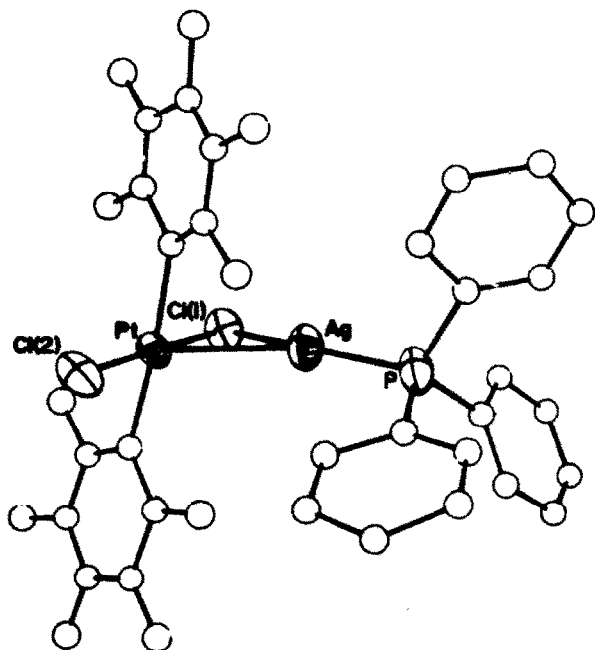
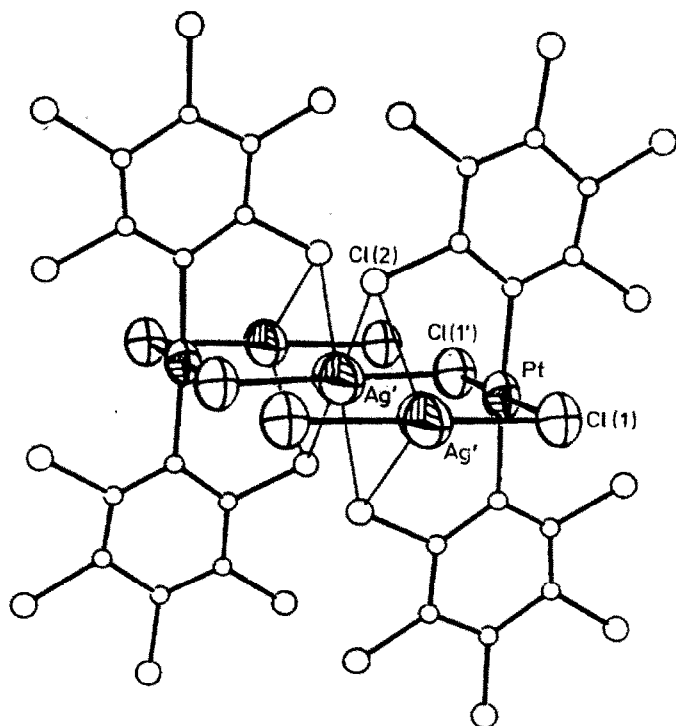Fig. 12. Structure of $[(C_6F_5)_2ClPt(\mu\text{-}Cl)AgPPh_3]^-$ (27).

Fig. 13. Structure of a fragment of the polymeric anion $[Pt(C_6Cl_5)_2(\mu\text{-}Cl)_2Ag]_x^{x-}$ (28).
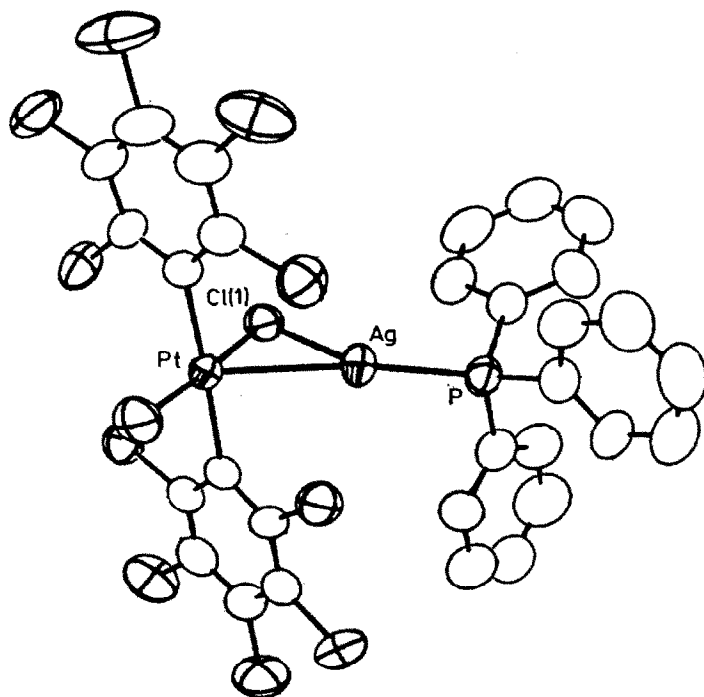
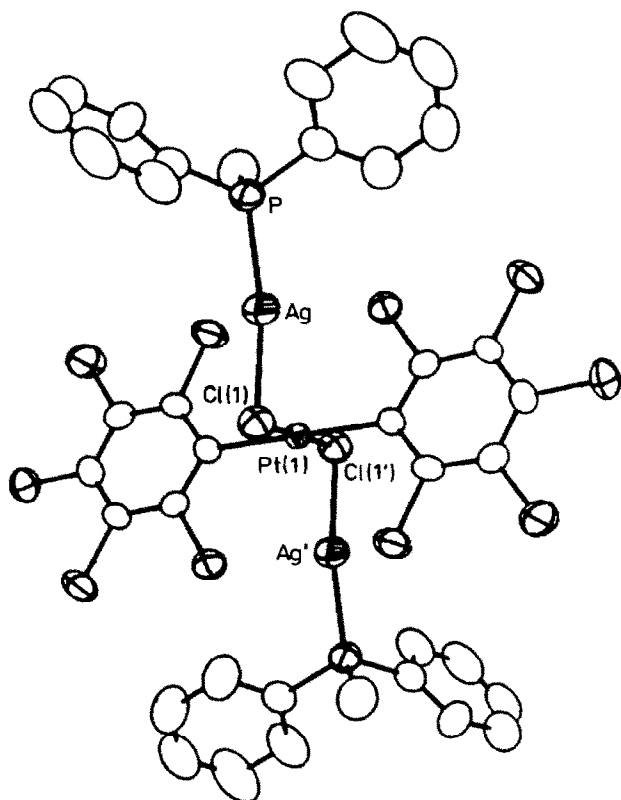Fig. 14. Structure of $[(C_6Cl_5)_2ClPt(\mu\text{-}Cl)AgPPh_3]^-$ (**28**).

Fig. 15. Structure of $[(C_6Cl_5)_2Pt(\mu\text{-}Cl)_2(AgPPh_2Me)_2]$ (**28**).

AgNO$_3$) (1/1) to give an anionic tetranuclear complex, which contain (see structure in Fig. 11) both Pt–Ag and Cl–Ag bonds. Addition of PPh$_3$ to the tetranuclear cluster gives the binuclear (NBu$_4$)[(C$_6$F$_5$)$_2$ClPt(μ-Cl)AgPPh$_3$] (Fig. 12) containing tri-coordinated silver bonded to platinum, triphenylphosphine, and a bridging chlorine atom [27].

(iv) The product contains halide-silver, but no Pt → Ag bonds. The use of (NBu$_4$)$_2$[*trans*-PtCl$_2$(C$_6$Cl$_5$)$_2$] instead of the pentafluorophenyl complex in a reaction analogous to that in eq. 12 leads to {(NBu$_4$)[PtCl$_2$(C$_6$Cl$_5$)$_2$Ag]}$_x$, which has the same stoichiometry but is structurally very different (Fig. 13), consisting of NBu$_4^+$ cations and polymeric anions. In the anion, each Pt atom lies in a *trans*-square planar PtCl$_2$(C$_6$Cl$_5$)$_2$ unit and each Ag atom is in a linear Cl–Ag–Cl unit, each chlorine atom bridging the silver atom to a different Pt atom. Moreover, the silver atoms, display short contacts to four *o*-Cl atoms, and are therefore in the centre of a rhombically distorted octahedron of chlorine atoms, but do not interact with the platinum atoms (Ag–Pt distance > 3.2 Å) [28].

Dichloromethane suspensions of the polynuclear {(NBu$_4$)[PtCl$_2$(C$_6$Cl$_5$)$_2$Ag]}$_x$ react with group 15 donors to give bi- or tri-nuclear complexes, depending on the neutral ligand L. For L = PPh$_3$, PEt$_3$, AsPh$_3$, SbPh$_3$, the binuclear complexes (NBu$_4$)[(C$_6$Cl$_5$)$_2$ClPt(μ-Cl)AgPPh$_3$] are obtained, whereas for L = PPh$_2$Me, PPh$_2$Et, PPhMe$_2$, trinuclear complexes [(C$_6$Cl$_5$)$_2$Pt(μ-Cl)$_2$(AgL)$_2$] are obtained. The structure (Fig. 14) of the former (L = PPh$_3$) shows the *trans*-PtCl$_2$(C$_6$Cl$_5$)$_2$ moiety to be bonded to the [AgPPh$_3$]$^+$ cation by a strong Pt–Ag bond, singly bridged by a Cl atom. The trinuclear complexes (L = PPh$_2$Me) (see Fig. 15) have the platinum and silver centres singly bridged by a Cl atom. There is no platinum–silver interaction.

4. The structural rôle of the C$_6$X$_5$ groups

In most of the known pentahalophenyl complexes, the C$_6$X$_5$ groups are well described as σ-bonded terminal ligands. Some of the complexes which we have recently studied and structurally characterized have very different and previously unknown structural features.

(a) C$_6$F$_5$ as a C-donor bridging ligand between two metal atoms
In the complex (NBu$_4$)$_2$[Pt$_2$(μ-C$_6$F$_5$)$_2$(C$_6$F$_5$)$_4$] [15], the binuclear anion (Fig. 1) contains two kinds of C$_6$F$_5$ ligands: two C$_6$F$_5$ groups act as bridging C-ligands, and the Pt–C(bridge) distances (2.246(11) and 2.166(11) Å) are longer than the Pt–C(terminal) ones (2.010(11) Å), as observed in few other compounds (see Al$_2$Ph$_6$ [29]). Recently we have prepared a palladium(II) complex of the same stoichiometry (NBu$_4$)$_2$[Pd$_2$(C$_6$F$_5$)$_6$] [14] which can be expected to have a similar structure of the anion, [Pt$_2$(μ-C$_6$F$_5$)$_2$(C$_6$F$_5$)$_4$]$^{2-}$. No analogous complexes containing C$_6$Cl$_5$ groups have so far been reported.

(b) Interactions between o-X substituents in coordinated C$_6$X$_5$ groups and Ag atoms
In most of the heteronuclear Pt–Ag complexes discussed above, *ortho*-X substituents of the C$_6$X$_5$ groups attached to the platinum atoms are positioned so as to interact with the silver atoms.

Table 1 lists structural data for pentafluorophenyl (complexes **1–4**), pentachloro-

Table 1

Structural data for some polynuclear pentahalophenyl Pt–Ag complexes

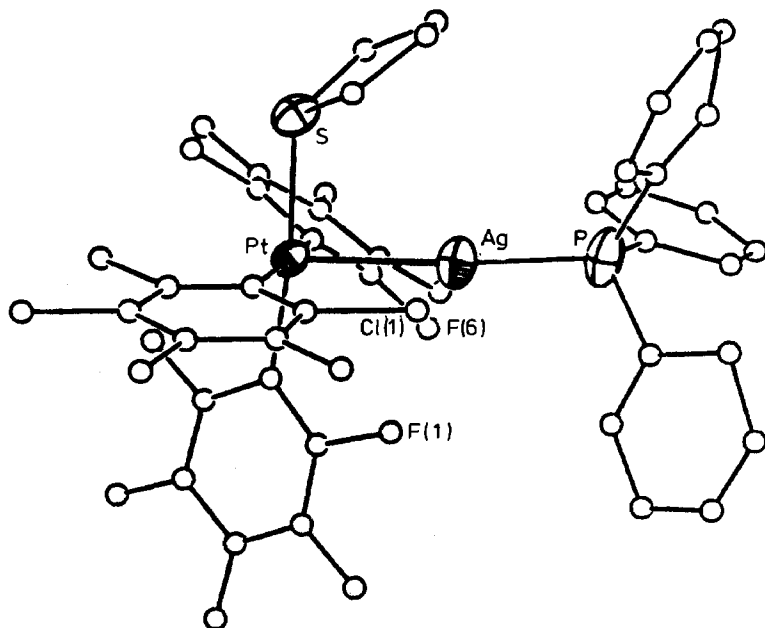| I	II	III	IV	V	VI		
					Other distances		
Compound	Fig.	$o\text{-}X\ldots Ag$	$\rho = \dfrac{\text{Exp. distances}}{\text{sum. cov. radii}}$	Ag–P	Ag–Pt	Pt–Cl [a]	Ag–Cl [a]
(NBu$_4$)$_2$[Pt$_2$Ag$_2$Cl$_4$(C$_6$F$_5$)$_4$] (1)	11	2.60(1) 2.69(1)	1.31 1.36	–	2.772(3) 3.063(3)	2.341(7) 2.322(7)	2.408(8) 2.724(8)
(NBu$_4$)[(C$_6$F$_5$)$_2$ClPt(μ-Cl)AgPPh$_3$] (2)	12	–	–	2.350(6)	2.796(2)	2.339(5) [b] 2.296(5) '	2.473(5) [b]
(NBu$_4$)$_2$[(C$_6$F$_5$)$_4$(μ-C$_6$F$_5$)$_4$Pt$_2$OEt$_2$] (3)	9	2.651(10) 2.663(10)	1.34 1.34	–	2.816(2) 2.804(2)		
[(tht)(C$_6$F$_5$)$_2$PtAgPPh$_3$] (4)	8	2.763(8) 2.757(7) 2.791(7)	1.40 1.39 1.41	2.358(3)	2.637(1)		
[(NBu$_4$)[Pt(C$_6$Cl$_5$)$_2$Cl$_2$AgI]]$_x$ (5)	13	3.010(8) 3.092(8)	1.29 1.33	–	–	2.325(5)	2.477(5)
(NBu$_4$)[(C$_6$Cl$_5$)$_2$ClPt(μ-Cl)AgPPh$_3$] (6)	14	2.951(3) 3.012(3)	1.27 1.29	2.395(2)	2.782(1)	2.331(2) 2.295(2)	2.667(3)
[(C$_6$Cl$_5$)$_2$Pt(μ-Cl)$_2$(AgPPh$_2$Me)$_2$] (7)	15	–	–	2.370(2)	–	2.323(1)	2.418(2)
[(tht)(C$_6$F$_5$)$_2$(C$_6$Cl$_5$)PtAgPPh$_3$] (8)	16	2.921(13)(F) 2.763(14)(F) 2.822(7)(Cl)	1.47 1.40 1.21	2.362(8)	2.649(2)		

[a] b: bridging and t: terminal.

Fig. 16. Structure of [cis-(SC₄H₈)(C₆F₅)₂(C₆Cl₅)Pt→AgPPh₃] (35).

phenyl (complexes 5–7), and mixed (complex 8) derivatives (column I). The o-X...Ag distances are given in column III, and column IV gives the same values expressed in units of covalent distance (i.e. the sum of covalent radii [30] (0.64(F) + 1.34(Ag) = 1.98 Å or, respectively, 0.99(Cl) + 1.34(Ag) = 2.33 Å), which may be regarded as a relative measure of the strength of the o-X...Ag interaction. Column V shows the experimental Ag–P, and column VI other relevant distances.

Since we first pointed out the presence of the non-bonded o-X...Ag interaction in pentahalophenyl derivatives, F...Ag "short contacts" have been observed by others in different kinds of compounds viz.: [Ag₂(Ph₂S₂)₄](AsF₆) (2.824 (ρ = 1.42); 2.841 (ρ = 1.43) [31]); [Ag(2.4.6-t-Bu₃C₆H₂NC)₂](PF₆) (2.668 (ρ = 1.34) [32]); [Ag(S₃N₂O)₂](AsF₆) (2.844 (ρ = 1.43) [33]). Analogous Cl...Ag contacts have been noticed for [C₆H₆Ag(AlCl₄)] (2.77, 2.80, 3.04 Å (ρ = 1.18, 1.20 or 1.30, respectively [34]).

As may be seen from Table 1, the o-Cl...Ag are generally stronger than the o-F...Ag interactions, the higher electronegativity of the F atom making it more reluctant to donate electron density than the less electronegative Cl atom. The mixed compound 8 (Fig. 16), with two C₆F₅ groups and one C₆Cl₅ group bonded to the Pt atom, confirms this point: the o-Cl atom of the C₆Cl₅ group interacts more strongly with the silver atom (ρ = 1.21) than do the o-F atoms of the two C₆F₅ groups (ρ = 1.48, 1.40) [35]. However, a closer examination of complexes 2 and 6 (Fig. 17 and 18) in comparison with seemingly similar structures, is worthwhile.

The presence of two o-Cl...Ag contacts and the implied donation of electron density to the silver atom reduces the strength of the other interactions to the P and (bridging) Cl ligands. From the X-ray data, we have calculated in which way the C₆F₅ rings in complex 2 must be rotated in order to bring one o-F atom in each ring to the usual distances found in o-F...Ag contacts, and have found that it is not possible to achieve this without distorting the rest of the structural frame. That

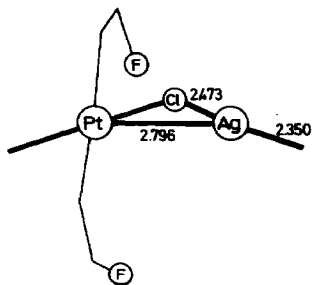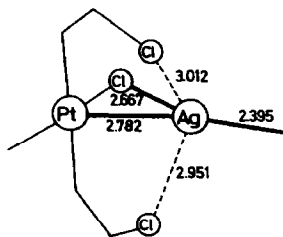Fig. 17. Central core of the structure of complex 2 (Fig. 12): No o-F…Ag contacts, short Ag–P and Ag–Cl bonds.

Fig. 18. Central core of the structure of complex 6 (Fig. 14): o-Cl…Ag contacts, large Ag–P and Ag–Cl bonds.

means, as could be expected, that the adopted structure is in each case the more acceptable and despite their apparent similarity they are not interconvertible.

Looking at another aspect, we note that the reactions of $[trans\text{-}PtCl_2(C_6F_5)_2]^{2-}$ or $[trans\text{-}PtCl_2(C_6Cl_5)_2]^{2-}$ with $AgClO_4$ lead to complexes **1** (Fig. 11) and **5** (Fig. 13) which have the same stoichiometry $\{(NBu_4)[PtCl_2(C_6X_5)_2Ag]\}_x$ but are structurally very different ($x = 2$, for X = F; $x = \infty$, for X = Cl).

In the pentafluorophenyl compound, the resulting Pt_2Ag_2 anionic cluster is rigorously centrosymmetric and essentially planar: two *trans*-planar $PtCl_2(C_6F_5)_2$ units enfold a central Ag_2 unit (Ag–Ag 2.994(6) Å). Each silver atom forms a bond of considerable strength (2.772 Å) to a Pt atom as well as a longer interaction with the other Pt atom. Each Ag atom also has contacts to Cl atoms at distances of 2.408(8) and 2.724(8) Å. Two o-F atoms closely approach each Ag atom, above and below the central plane, at distances of 2.60(1) and 2.69(1) Å (Fig. 11).

The polymeric anion in the pentachlorophenyl derivative has each Pt atom in a *trans*-planar $PtCl_2(C_6Cl_5)_2$ unit, similar to that described above, but each Ag atom is in a linear Cl–Ag–Cl unit. Moreover, in view of the long distances there is unlikely to be any significant Pt–Ag or Ag–Ag bond. An important additional stabilizing factor is provided by interactions between the silver atoms and the Cl(2) atoms; the latter are so positioned as to bridge adjacent silver atoms, thus completing a rhombically distorted octahedron of Cl atoms around each silver atom.

The question of the possible causes of the marked differences between the products formed from analogous precursors in similar reactions can be addressed in two ways:

(a) What prevents the pentachlorophenyl derivative adopting the structure taken up by the pentafluorophenyl species?

Since steric factors would not prevent the C_6Cl_5 groups from adopting the same orientations as the C_6F_5 groups (Fig. 19), the difference in structure (Fig. 20) may be due to electronic factors: since in the C_6Cl_5 derivatives an excess of electron density would be concentrated around the silver atoms in view of the better donor properties of the o-chlorine atoms.

On the other hand, it is also reasonable to ask:

(b) What prevents the pentafluorophenyl derivative adopting the polymeric structure?
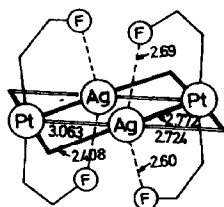
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Fig. 19. Central core of the structure of complex 1 (Fig. 11). The poorer donor character of the *o*-F atoms makes Ag–Pt and Ag–Cl bonds necessary.
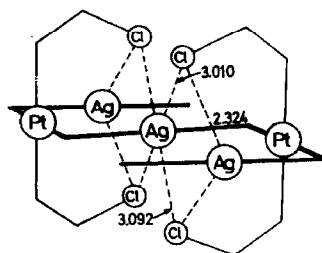
Fig. 20. Central core of the structure of complex 5 (Fig. 13). Each silver atom contacts six chlorine atoms, and no silver–silver nor silver–platinum bonds are necessary.

For the structural framework of the polymeric pentachlorophenyl derivative to be substantially retained, two requirements must be fulfilled: (i) the *o*-F atoms must form a bent bridge to two adjacent Ag atoms, and they may be unable to do so, and (ii) owing to the absence in the polymeric structure of any Pt–Pt and Ag–Pt bonds, the *o*-F atoms would have to provide the additional electron density necessary, and, as we have seen above, they are less able than the *o*-Cl atoms of the C_6Cl_5 groups to perform this rôle. In the C_6Cl_5 complex, the Ag atoms receive electron density from six Cl atoms (two strong Ag–Cl bonds, four *o*-Cl...Ag contacts) thus making Pt–Ag bonding unnecessary.

As we have seen above (section 3 (iv)), the polymeric pentachlorophenyl compound reacts with group 15 ligands to give two types of oligomeric derivatives, the anionic binuclear $(NBu_4)[(C_6Cl_5)_2ClPt(\mu\text{-}Cl)AgL]$, and the neutral trimeric $[(C_6Cl_5)_2Pt(\mu\text{-}Cl)_2(AgL)_2]$. The latter contains no Pt–Ag bonds or *o*-Cl...Ag contacts, and so stronger Ag–Cl (2.428(Å) and Ag–P (2.370(3) Å) bonds are present. In the former, a Pt–Ag bond, a bridging Cl atom, and, in addition two *o*-Cl...Ag short contacts are present, and consequently there are weaker bonds to both Cl (Ag–Cl(bridged) 2.667(3) Å) and P (Ag–P 2.395(2) Å).

We can conclude that from a structural point of view the C_6X_5 groups can act as: (a) terminal groups displaying *o*-X...Ag contacts to only one Ag atom; (b) terminal groups with *o*-Cl...Ag contacts to two Ag atoms; and (c) bridging C_6F_5 groups (between Pt atoms) with additional *o*-F...Ag contacts.

Our current work is focused on the preparation and structural studies of related complexes containing at least one different ligand with the aim of elucidating the influence of the latter on the Pt–Ag bonds and/or the *o*-X...Ag contacts.

References

1 P.M. Maitlis, P. Espinet and J.H. Russell, in G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Pergamon Press, Oxford, 8 (1982) 549 and ref. therein.
2 N. Bresciani-Pahor, M. Plazzota, L. Randaccio, G. Bruno, V. Ricevuto, R. Romeo and U. Belluco, Inorg. Chim. Acta, 31 (1978) 171.
3 R. Usón, J. Forniés, F. Martínez, M. Tomás and I. Reoyo, Organometallics, 2 (1983) 1386.
4 R. Usón, J. Forniés, M. Tomás and R. Fandos, J. Organomet. Chem., 263 (1984) 253.
5 R. Usón, J. Forniés, M. Tomás, I. Ara and B. Menjón, J. Organomet. Chem., 336 (1987) 129.
6 R. Usón, J. Forniés, R. Navarro and M.P. García, Inorg. Chim. Acta, 33 (1979) 69.
7 R. Usón, J. Forniés, F. Martínez and M. Tomás, J. Chem. Soc., Dalton Trans., (1980) 888.
8 R. Usón, J. Forniés, P. Espinet and G. Alfranca, Synth. React. Inorg. Metal-org. Chem., 10 (1980) 579.
9 R. Usón, J. Forniés, P. Espinet, E. Lalinde, P.G. Jones and G.M. Sheldrick, J. Chem. Soc., Dalton Trans., (1982) 2389.
10 R. Usón, J. Forniés, P. Espinet and E. Lalinde, J. Organomet. Chem., 254 (1983) 371.
11 R. Usón, J. Forniés, P. Espinet, L. Pueyo and E. Lalinde, J. Organomet. Chem., 299 (1986) 251.
12 R. Usón and J. Forniés, in F.G.A. Stone and R. West (Eds.), Adv. Organomet. Chem., Academic Press, San Diego, 28 (1988) 219.
13 R. Usón and J. Forniés, in R.B. King and J.J. Eisch (Eds.), Organometallic Synthesis, Elsevier, Amsterdam, New York, 3 (1986) 161.
14 R. Usón, J. Forniés, M. Tomás and J.M. Casas, J. Chem. Soc., Dalton Trans., in press.
15 (a) R. Usón, J. Forniés, M. Tomás, J.M. Casas, F.A. Cotton and L.R. Falvello, J. Am. Chem. Soc., 107 (1985) 2556; (b) R. Usón, J. Forniés, M. Tomás, J.M. Casas, F.A. Cotton, L.R. Falvello and R. Llusar, Organometallics, in print.
16 R. Usón, J. Forniés and C. Fortuño, unpublished results.
17 R. Usón, J. Forniés, M. Tomás, B. Menjón, R. Bau, K. Sünkel and E. Kuwabara, Organometallics, 5 (1986) 1576.
18 R. Usón, J. Forniés, P. Espinet, F. Martínez and M. Tomás, J. Chem. Soc., Dalton Trans., (1981) 463.
19 R. Usón, J. Forniés, M. Tomás and B. Menjón, Organometallics, 4 (1985) 1912.
20 R. Usón, J. Forniés, M. Tomás and B. Menjón, Organometallics, 5 (1985) 1986.
21 R. Usón, J. Forniés, M. Tomás, B. Menjón and A.J. Welch, J. Organomet. Chem., 304 (1986) C24.
22 J. Forniés, M.A. Usón, J.I. Gil and P.G. Jones, J. Organomet. Chem., 311 (1986) 243.
23 R. Usón, J. Forniés, M. Tomás, B. Menjón, J. Carnicer and A.J. Welch, unpublished results.
24 R. Usón, J. Forniés, M. Tomás, B. Menjón and A.J. Welch, Organometallics, 7 (1988) 1318.
25 F.A. Cotton, L.R. Falvello, R. Usón, J. Forniés, M. Tomás, J.M. Casas and I. Ara, Inorg. Chem., 26 (1987) 1366.
26 R. Usón, J. Forniés, M. Tomás, J.M. Casas, F.A. Cotton and L.R. Falvello, Inorg. Chem., 26 (1987) 3482.
27 R. Usón, J. Forniés, B. Menjón, F.A. Cotton, L.R. Falvello and M. Tomás, Inorg. Chem., 24 (1985) 4651.
28 R. Usön, J. Forniés, M. Tomás, J.M. Casas, F.A. Cotton and L.R. Falvello, Inorg. Chem., 25 (1986) 4519.
29 J.F. Malone and W.S. McDonald, J. Chem. Soc., Dalton Trans., (1972) 2646.
30 L. Pauling, The Nature of the Chemical Bond, 3rd edit.; Cornell University Press; Ithaca, NY, 1960, p. 403.
31 H.W. Roesky, T. Gries, P.G. Jones, K.L. Weber and G.M. Sheldrick, J. Chem. Soc., Dalton Trans., (1984) 1781.
32 Y. Yamamoto, K. Aoki and A. Yamazaki, Inorg. Chim. Acta, 68 (1983) 75.
33 H.W. Roesky, M. Thomas, J. Schimkowiak, M. Schmidt, M. Noltemeyer and G.M. Sheldrick, J. Chem. Soc., Chem. Commun., (1982) 791.
34 R.W. Turner and E.L. Amma, J. Am. Chem. Soc., (1967) 3243.
35 R. Usón, J. Forniés, M. Tomás and I. Ara, unpublished results.