# Some new developments in aryl-gold and aryl-platinum chemistry

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Abstract.- The enhanced stability of the metal-to-carbon bond M-R (M= Au, Pt) when R is a polyhalophenyl group (R= $C_6F_5$, $C_6F_3H_2$, $C_6Cl_5$) allows the isolation of neutral, cationic or anionic aryl derivatives of both metals, which are excellent precursors for the synthesis of polynuclear compounds or mixed clusters with unusual structures and properties. On the other hand, stable solutions of the neutral complexes $MR_2L_2$ (M= Pd, Pt; R= $C_6F_5$, $C_6Cl_5$; L= $OC_4H_8$) are a suitable source for the preparation of otherwise inaccessible compounds.

## INTRODUCTION

Following arguments (ref. 1) advanced by Chatt and Shaw (1959-60) many stable complexes of the types $MR_2L_2$ and $MRXL_2$ (L= π-acid ligand) were prepared. From 1969 to 1976 we synthesized several hundreds of stable gold, palladium and platinum derivatives, both neutral and cationic with R= $C_6X_5$ (X= F, Cl), and began to wonder whether (1) the π-acid ligands were at all necessary to achieve the observed stability and if (2) the presence of these neutral ligands effectively hindered further arylation of the metal centres.

We also began to use starting materials containing either weaker coordinating ligands (such as tetrahydrothiophen, $SC_4H_8$) or ligand-free compounds ($PdCl_2$, $PtCl_2$) which react with RLi or RMgX to give anionic homoleptic or more arylated complexes (Scheme 1).

Some of these novel anionic complexes provided the startingpoint of a new chemistry, where the presence of the polyhalophenyl groups is a critical factor, as may be seen from the following selected examples.

### Scheme 1

Types of anionic* complexes (1976-1982)

| Au derivatives | Pd and Pt derivatives |
|---|---|
| $\|AuRX\|^-$ | $\|MR_3(SC_4H_8)\|^-$ |
| $\|AuR_2\|^-$ | $\|MR_2Cl_2\|^{2-}$ |
| $\|AuRX_3\|^-$ | $\|MR_3Cl\|^{2-}$ |
| $\|AuR_2X_2\|^-$ | $\|MR_4\|^{2-}$ |
| $\|AuR_3X\|^-$ | $\|M(\mu-X)R_2\|_2^{2-}$ |
| $\|AuR_4\|^-$ | |

*Isolated as salts of bulky cations ($NBu_4$, PPN, etc)

## POLYNUCLEAR GOLD-SILVER COMPLEXES

There is much evidence that metal centres M can act as Lewis bases towards other metal centres M', thus forming M $\rightarrow$ M' donor bonds. The stability of such compounds is dependent upon the respective M and M', the most important stabilizing factor being a large electron density on M. (ref. 2).

We have therefore chosen the anions $\|AuR_2\|^-$ as metal centre M and have tried to form a M $\rightarrow$ M' metal bond, Ag being selected as M' centre. (Equation 1) (ref. 3)
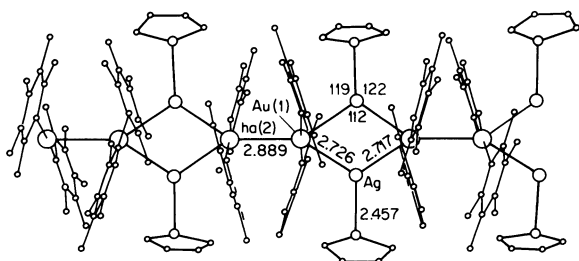
$$(NBu_4)\|AuR_2\| + AgClO_4 \xrightarrow[CH_2Cl_2]{Et_2O \text{ or}} (NBu_4)ClO_4 + \|AuAgR_2\|_n \quad \text{(yellow solutions)}$$

R= $C_6F_3H_2$, $C_6F_5$, $C_6Cl_5$

$$\|AuArR_2 \cdot L\|_n$$

L= O-, N-, S-, P-donor, alkene, alkyne, arene  (1)

+L
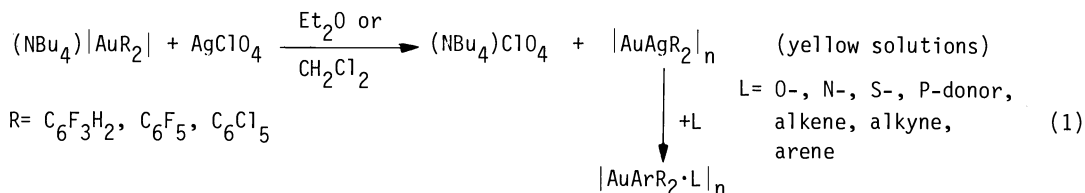
Fig. 1. Structure of the polymeric

$|AuAgR_2(SC_4H_8)|_x$



$R = C_6F_5$
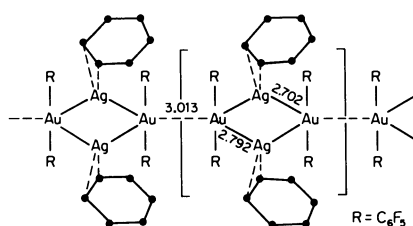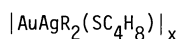
Fig. 2. Structure of the polymeric
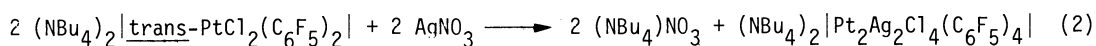
$|AuAgR_2(C_6H_6)|_x$. Note the asymmetric $Au_2Ag_2$ unit, due to contacts of the silver atoms to ortho-fluorine atoms of the $C_6F_5$ groups (Ag...F, 2.84 Å)

Despite the general lack of solubility, single crystals of the compounds with L= $SC_4H_8$ (tetrahydrothiophen) and L= $C_6H_6$ (benzene) could be obtained and their structure was solved by X-ray crystallography (Fig. 1 and 2). (ref. 3).

Though both structures are similar there are some striking differences. The two compounds form polymeric chains by repetition of the structural unit — $R_2Au_2Ag_2L_2$ — through short Au...Au contacts. The $(AuAg)_2$ rings involve short Au-Ag distances and there are no ligands serving as bridges across the Au-Ag edges of the $Au_2Ag_2$ moiety, which implies that there are also Au-Ag bonds. A feasible bonding model is that the silver atoms are $sp^2$ hybridized, electron density being withdrawn from the gold atoms. A remarkable difference is to be noticed: the $Au_2Ag_2$ rings are approximately square-planar in Fig. 1 whilst in Fig. 2 they adopt a planar-rectangular disposition.

## POLYNUCLEAR PLATINUM-SILVER COMPLEXES

On the other hand, by reaction of equimolar quantities of $(NBu_4)_2|\underline{trans}\text{-}PtCl_2(C_6F_5)_2|$ and $AgNO_3$ in methanol, (ref. 4) according to eqn (2)

$$2\ (NBu_4)_2|\underline{trans}\text{-}PtCl_2(C_6F_5)_2| + 2\ AgNO_3 \longrightarrow 2\ (NBu_4)NO_3 + (NBu_4)_2|Pt_2Ag_2Cl_4(C_6F_5)_4|\quad (2)$$
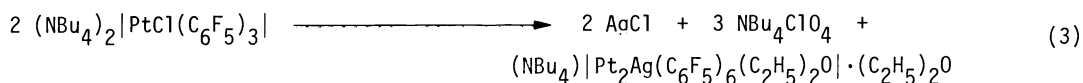
an unstable yellow solid is precipitated. Its instability made it very difficult to obtain single crystals, but by slow diffusion of i-$C_3H_7OH$ into an acetone solution at -25°C this could be accomplished and the structure was solved by X-ray crystallography.

The entire molecular structure of the anion $|Pt_2Ag_2Cl_4(C_6F_5)_4|^{2-}$ and that of the central, essentially planar $Pt_2Ag_2Cl_4$ unit are shown in the following Figures 3 and 4. The molecule is rigorously centro symmetric. Considering first the central $Pt_2Ag_2Cl_4$ unit, each Pt atom is linked to an essentially $\underline{trans}$-planar set of Cl and C atoms with normal bond lengths. The two $PtCl_2(C_6F_5)_2$ units then embrace a central $Ag_2$ unit (Ag-Ag distance: 2.994(6) Å). Each silver atom has a close contact with one Pt atom (2.772(2)Å) which surely represents a Pt-Ag bond of considerable strength as well as a longer contact (3.063(3) Å), with the other Pt-atom.
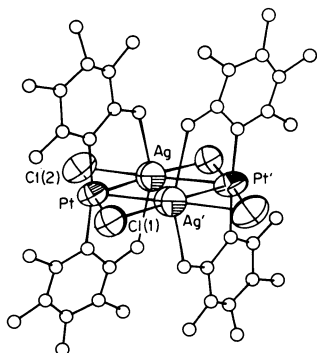


Fig. 3. Structure of the $|Pt_2Ag_2Cl_4(C_6F_5)_4|^{2-}$ ion.
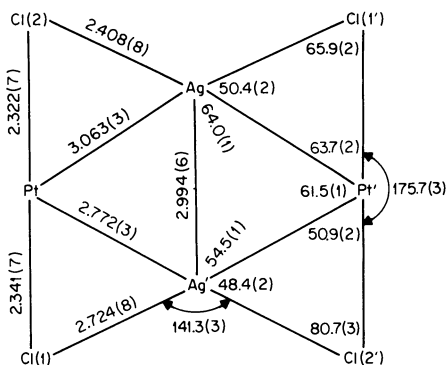


Fig. 4. Drawing of the central $Ag_2Pt_2Cl_4$ unit.

One of the most remarkable features of this structure is the close approach of two ortho fluorine to each Ag atom, at distances 2.60(1) and 2.69(1) Å, longer than the expected (1.98 Å) distance for a Ag-F bond. Despite this fact, these contacts must contribute to the stability of the cluster.

A different type of cluster, (ref. 5) arises from the reaction between $|PtCl(C_6F_5)_3|^-$ and $AgClO_4$ (eqn. 3)

$$2 \ (NBu_4)_2|PtCl(C_6F_5)_3| \longrightarrow 2 \ AgCl \ + \ 3 \ NBu_4ClO_4 \ + \qquad (3)$$
$$(NBu_4)|Pt_2Ag(C_6F_5)_6(C_2H_5)_2O|\cdot(C_2H_5)_2O$$

The structure of the trinuclear anion Fig. 5 displays unusual features. Thus, pairs of $|Pt(C_6F_5)_3|^-$ units are linked through bridging $C_6F_5$ groups, the two Pt atoms being only 2.698(1)Å apart, either because there is a Pt-Pt bond or because the spread of the bridging $C_6F_5$ groups forces the two Pt atoms to this distance. This is the first case in which $C_6F_5$ groups have been proved to act as bridging ligands. Moreover, the Pt-Ag distances 2.827(2) and 2.815(2) Å together with the absence of bridging ligands across the Pt-Ag edges, imply that there are also Pt-Ag bonds. We again find close approaches of ortho-fluorine atoms (from the bridging groups) to the silver atom Ag-F(5), 2.66(1); Ag-F(10), 2.67(1) Å. Each $C_6F_5$ bridging group is practically perpendicular to the $Pt_2Ag$ plane, with dihedral angles of 96.7° and 98.3°. The dihedral angle between Pt(1)-C(1)-Pt(2) and Pt(1)-C(7)-Pt(2) is 30.0°.
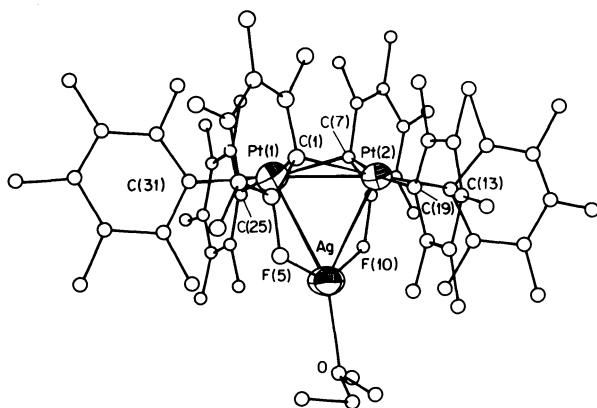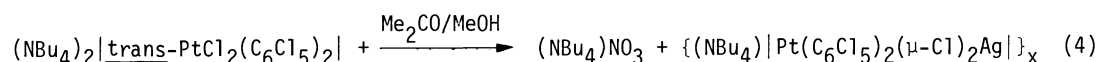


Fig. 5. The structure of the $|Pt_2Ag(C_6F_5)_6(Et_2O)|^-$ ion

As we have seen, the presence of perfluoroaryl groups seems to be a necessary condition for the stability of the above described Pt-Ag clusters. Therefore, we have studied the process of eqn. 2, substituting the $C_6Cl_5$ group for the $C_6F_5$ one (eqn. 4)

$$(NBu_4)_2|\underline{trans}\text{-}PtCl_2(C_6Cl_5)_2| \ + \ \xrightarrow{Me_2CO/MeOH} \ (NBu_4)NO_3 \ + \ \{(NBu_4)|Pt(C_6Cl_5)_2(\mu\text{-}Cl)_2Ag|\}_x \quad (4)$$

adapting the silver salts and the used solvent to the solubility requirements of the starting Pt complex (ref. 6). The obtained (eqn. 4) yellow polymeric heteronuclear complex is insoluble in all common solvents. Suitable crystals for X-ray diffraction studies could, however, be obtained by underlaying a dichloromethane solution of $(NBu_4)_2|PtCl_2(C_6Cl_5)_2|$, an inert layer of 1,2-dichloroethane and an acetone solution of $AgClO_4$ (1:1 molar ratio) and allowing to very slowly diffuse at -25°C.
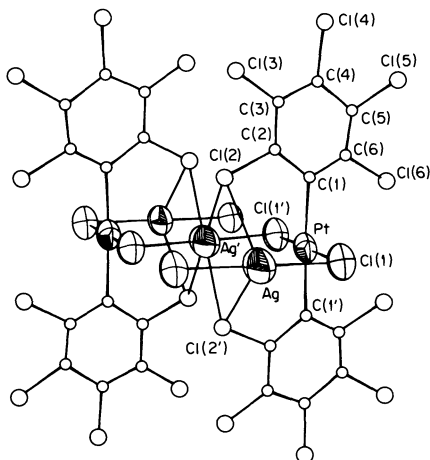


Fig. 6. The polymeric $|Pt(C_6Cl_5)_2(\mu\text{-}Cl)_2Ag|_x^-$ anion

The structure consists of $|NBu_4|^+$ cations and polymeric anions; a representative segment of the latter is shown in Fig. 6. The Pt atoms are located on two-fold axes and the Ag atoms on inversion centres.

Each Pt atom is in a planar $\underline{trans}\text{-}PtCl_2(C_6Cl_5)_2$ unit with normal Pt-Cl distances (2.323(5)Å) and each Ag atom is in a linear Cl-Ag-Cl unit (Ag-Cl distances 2.477(5) Å. There is unlikely to be any significant Pt-Ag or Ag-Ag bonding, in view of the long distances.

An important stabilizing factor for this structure is a set of interactions between the Ag atoms and the Cl(2) atoms. The latter are positioned so as to bridge (not quite symmetrically) adjacent Ag atoms, thus completing about each Ag atom a rhombically distorted octahedron of Cl atoms. The role of the ortho chlorine atoms of the $C_6Cl_5$ groups in this structure is reminiscent of that played by ortho fluorine atoms in the above described complexes, but differs in important ways. It seems likely that the greater size of the Cl atom militates against coplanarity of an entire Ag...Pt-C-C-Cl unit, which could be analogous to what occurs with the $C_6F_5$ groups. The fact that the Ag atoms receive electron density from six Cl atoms makes Pt $\longrightarrow$ Ag bonding unnecessary as well as sterically infeasible.

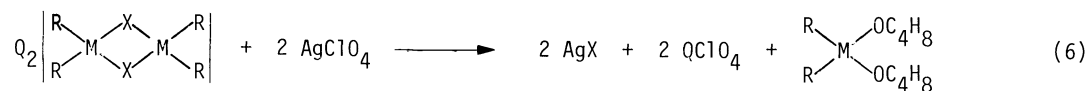## UNUSUAL NEUTRAL PLATINUM(II) COMPLEXES

In the preceding sections we have shown that the presence of $C_6X_5$ groups stabilizes some new types of gold and platinum complexes through "contacts" between o-halogen atoms of these groups and metallic centres.

Moreover, the presence of $C_6X_5$ groups in some anionic binuclear complexes causes new reaction paths to take place and so permits the preparation of unusual stable precursors which open routes for new syntheses.

For instance, the reaction of $AgClO_4$ with inorganic binuclear complexes $Q_2|M(\mu-X)X_2|_2$ (X= halogen), takes place, according to eqn. 5

$$Q_2|M(\mu-X)R_2|_2 + 2 AgClO_4 \longrightarrow Ag_2|M(\mu-X)R_2|_2 + 2 QClO_4 \qquad (5)$$
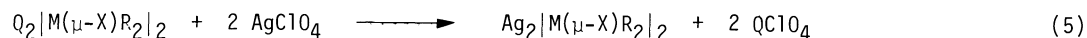
This is an old-fashioned metathetical reaction which gives the silver salt of the binuclear anion. However, a seemingly similar reaction using a salt of the binuclear anion containing four terminal $C_6X_5$ groups leads (ref. 7) to a very different outcome (eqn. 6)

$$Q_2 \left| \begin{array}{c} R \\ R \end{array} \!\!\! M \!\!\! \begin{array}{c} X \\ X \end{array} \!\!\! M \!\!\! \begin{array}{c} R \\ R \end{array} \right| + 2 AgClO_4 \longrightarrow 2 AgX + 2 QClO_4 + \begin{array}{c} R \\ R \end{array} \!\!\! M \!\!\! \begin{array}{c} OC_4H_8 \\ OC_4H_8 \end{array} \qquad (6)$$

Q= $NBu_4$; R= $C_6F_5$, $C_6Cl_5$; M= Pd or Pt

and after some working-up the four neutral $MR_2(OC_4H_8)_2$ can be isolated as white stable solids. Under mild conditions the two weakly coordinated $OC_4H_8$ molecules undergo ready displacement by other ligands. Scheme 2 collects a selection of syntheses carried out in our Laboratory.

(i) Normal pressure carbonylation of the cis-$|M(C_6X_5)_2(OC_4H_8)_2|$ in dichloromethane solution leads to precipitation of the corresponding dicarbonyl derivatives (50-91% yield) (ref. 7). The platinum complexes are much more stable even in moist air, as also are their solutions in non-coordinating solvents. The palladium(II) complexes are, however, only moderately stable under CO at -30°C (they turn grey after 10 hours (R= $C_6F_5$) or, respectively, several days (R= $C_6Cl_5$)). All the complexes show two $\nu$(C-O) absorptions (see Scheme 3). The high frequencies of the first $\nu$(C-O) band are noteworthy and seem to indicate a very low degree of metal-to-carbon $\pi$-back bonding which must be negligible in the palladium complexes.

(ii) Addition of $PPh_3$ to solution of cis-$|Pt(C_6X_5)_2(CO)_2|$ (both in 1:1 ratio or in excess) causes the displacement of only one of the CO groups, inmediately for X= F, more slowly for X= Cl. (ref. 8). Only one band due to $\nu$(C-O) is observed in the IR spectra of the solids, sharply decreased in energy as expected.
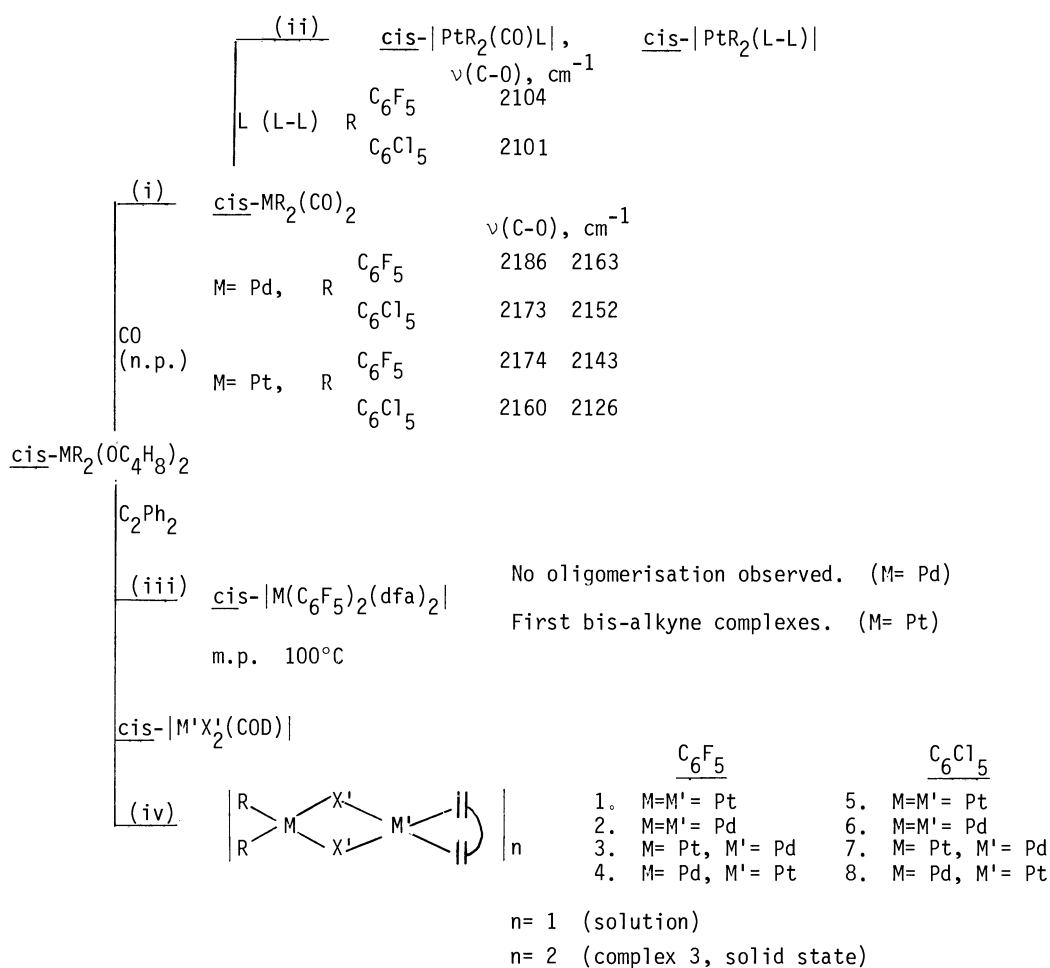
Addition of a chelating ligand (L-L= 2,2'-bipyridine) causes the substitution of both CO groups. IR monitoring of the reaction shows that the intensity of the $\nu$(C-O) bands of the starting product slowly decreases until disappearance. Any other $\nu$(C-O) band (assignable to a monocarbonyl intermediate) cannot be observed.

(iii) Addition of $C_2Ph_2$ (2:1 ratio) to dichloromethane solutions of cis-$|Pt(C_6F_5)_2(OC_4H_8)|$ causes no perceptible change, but upon vacuum evaporation of the solutions the cis-$|M(C_6F_5)_2(dfa)_2|$ (M= Pd, Pt) can be obtained (ref. 9).

Since their IR spectra give no useful information (no band assignable to $\nu$(C≡C) could be observed), the structure of the platinum compound has been solved by single crystal

*Scheme 2*

cis-$|MR_2(OC_4H_8)_2|$ as starting products for new syntheses

| | | (ii) | cis-$|PtR_2(CO)L|$, | cis-$|PtR_2(L-L)|$ |
|---|---|---|---|---|
| | | | $\nu(C-O)$, cm$^{-1}$ | |
| | | L (L-L) R | $C_6F_5$ 2104 | |
| | | | $C_6Cl_5$ 2101 | |

(i)　cis-$MR_2(CO)_2$

$\nu(C-O)$, cm$^{-1}$

| | | | | |
|---|---|---|---|---|
| M= Pd, R | $C_6F_5$ | 2186 | 2163 |
| | $C_6Cl_5$ | 2173 | 2152 |
| M= Pt, R | $C_6F_5$ | 2174 | 2143 |
| | $C_6Cl_5$ | 2160 | 2126 |

CO
(n.p.)

cis-$MR_2(OC_4H_8)_2$

$C_2Ph_2$

(iii)　cis-$|M(C_6F_5)_2(dfa)_2|$

m.p.　100°C

No oligomerisation observed.　(M= Pd)

First bis-alkyne complexes.　(M= Pt)

cis-$|M'X_2'(COD)|$

(iv)　$\left| \begin{array}{c} R \\ R \end{array} \hspace{-2mm} \begin{array}{c} X' \\ M \\ X' \end{array} \hspace{-2mm} M' \hspace{-2mm} \begin{array}{c} || \\ || \end{array} \right|_n$

| | $C_6F_5$ | | $C_6Cl_5$ |
|---|---|---|---|
| 1. | M=M'= Pt | 5. | M=M'= Pt |
| 2. | M=M'= Pd | 6. | M=M'= Pd |
| 3. | M= Pt, M'= Pd | 7. | M= Pt, M'= Pd |
| 4. | M= Pd, M'= Pt | 8. | M= Pd, M'= Pt |

n= 1　(solution)

n= 2　(complex 3, solid state)

X-ray crystallography (Fig. 7). The platinum atom is in the centre of an approximately square planar environment with normal Pt-C(1) and Pt-C(2) distances, whilst the midpoints of the two C≡C bonds are 0.11 above and respectively below the plane C(1)-Pt-C(2). The structure of the $C_2Ph$ ligands is only little modified upon coordination: the C≡C distance is 1.190(8)Å (1.19 in the free $C_2Ph_2$) and the angle C≡C-C is only 14.8(6)° apart from linearity. Since this is the only Pt(II) complex containing two dfa groups a meaningful comparison is not possible. However, the Pt(0) derivatives $|Pt(PPh_3)_2(dfa)|$ and $|Pt(dfa)_2|$ show C≡C distances of 1.32(a) and 1.28(6) Å and the C≡C-C angles are 40° and, respectively 27°, these sets of parameters being indicative of stronger interaction in both cases.
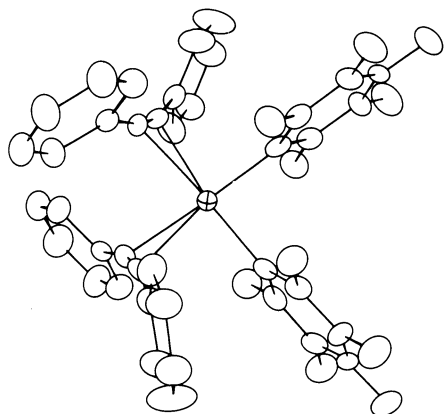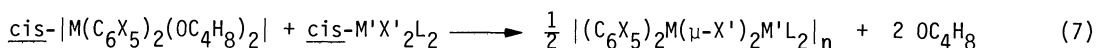


Fig. 7.　The structure of cis-$|PtR_2(dfa)_2|$

(iv)  Since the described substitution reactions are stereospecific, and no ligand
       rearrangement takes place, it was tempting to undertake the syntheses of the hitherto
       unknown binuclear gem-derivatives, according to eqn. 7

$$\underline{cis}\text{-}|M(C_6X_5)_2(OC_4H_8)_2| + \underline{cis}\text{-}M'X'_2L_2 \longrightarrow \tfrac{1}{2}|(C_6X_5)_2M(\mu\text{-}X')_2M'L_2|_n + 2\ OC_4H_8 \qquad (7)$$

using a chelating ligand 1,5-cyclooctadiene (COD) instead of the two neutral ones L to
hinder any possible rearrangement of L.  The following complexes have been isolated (X'= Cl,
Br or I):

| $C_6X_5=$ | $C_6F_5$ | | Color | | $C_6F_5$ | | Color |
|---|---|---|---|---|---|---|---|
| | M | M' | solid/$CH_2Cl_2$ sol. | | M | M' | solid/$CH_2Cl_2$ sol. |
| 1. | Pt | Pt | yellow/yellow | 5. | Pt | Pt | orange/orange* |
| 2. | Pd | Pd | orange/red* | 6. | Pd | Pd | orange/red |
| 3. | Pt | Pd | salmon/green | 7. | Pt | Pd | garnet/green* |
| 4. | Pd | Pt | brown/yellow | 8. | Pd | Pt | yellow/orange |

The low solubility of complexes 2, 5 and 7 precludes determination of their molecular
weights (osmometric, in $CHCl_3$ solution).  The other five complexes show Mol. weights in
agreement with n= 1 in the above formula; they are also binuclear derivatives.  The striking
changes of colour observed in complexes 3 and 7 could be indicative of a structural change.
Therefore, the structure of complex 3, which is binuclear in $CHCl_3$ solution, was solved by
single crystal X-ray crystallography. (ref. 10).  The result is shown in Fig. 8.
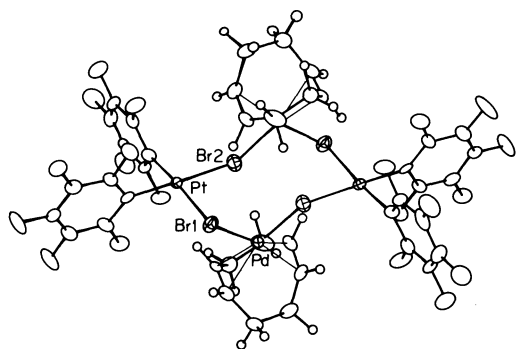


Fig. 8.  The structure of $|(C_6F_5)_2Pt(\mu\text{-}Br)_2Pd(COD)|_2$

The entire molecule is centro symmetric and the
central $Pt_2Pd_2X_4$ (X= Br) unit is an eight-membered
puckered ring, where metal and halogen atoms
alternate.  (Fig. 9). The structure is unprece-
dented in Pd or Pt chemistry and we feel that
an extrapolation requires the prior determination
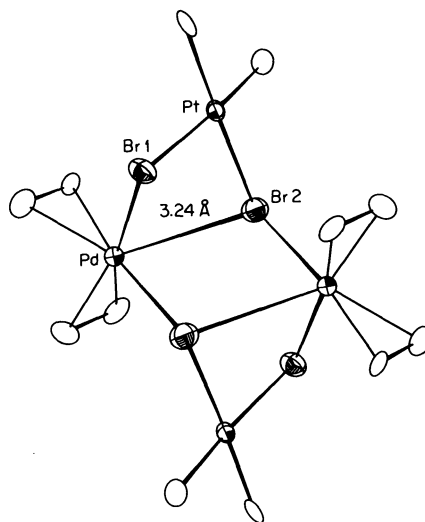of other structures in the series.



Fig. 9.  Simplified drawing of the
central unit in Fig. 8.

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