Neutral and Anionic Binuclear Perhalogenophenyl Platinum–Silver Complexes with Pt→Ag Bonds Unsupported by Covalent Bridges. Molecular Structures of [(tht)(C_6Cl_5)(C_6F_5)$_2$PtAg(PPh_3)], [NBu_4][(C_6F_5)$_4$PtAg(tht)] and [NBu_4][*cis*-(C_6Cl_5)$_2$(C_6F_5)$_2$PtAg(tht)] (tht = tetrahydrothiophene) *

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Heterobinuclear complexes of general formula [L(C_6Cl_5)$_{3-x}$(C_6F_5)$_x$PtAg(PPh_3)] [x = 2–0; L = tht (tetrahydrothiophene), PPh_3 or pyridine (py)] **14–21** have been prepared by treating the anionic platinum derivatives [NBu_4][PtL(C_6F_5)$_x$(C_6Cl_5)$_{3-x}$] with [Ag($OClO_3$)(PPh_3)] (molar ratio 1:1) in dichloromethane. The anionic [NBu_4][(C_6F_5)$_4$PtAgL] (L = OEt_2, PPh_3 or tht) **22–24** and [NBu_4][*cis*-(C_6Cl_5)$_2$(C_6F_5)$_2$PtAg(tht)] **25** have been obtained from the corresponding [NBu_4]$_2$[Pt(C_6X_5)$_2$($C_6X'_5$)$_2$] and [Ag($OClO_3$)L] (molar ratio 1:1) in CH_2Cl_2–diethyl ether. The reaction between [NBu_4][Pd(C_6F_5)$_3$(tht)] and [Ag($OClO_3$)(PPh_3)] renders Ag(C_6F_5) and *cis*-[Pd(C_6F_5)$_2$(PPh_3)(tht)]. The salts [NBu_4]$_2$[Pt(C_6Cl_5)$_4$] and [NBu_4]$_2$[Pd(C_6F_5)$_4$] react with [Ag($OClO_3$)(tht)] yielding [NBu_4][Pt(C_6Cl_5)$_3$(tht)] and [NBu_4][Pd(C_6F_5)$_3$(tht)], respectively. The reactions between [NBu_4]$_2$[Pt(C_6F_5)$_4$] and [Ag($OClO_3$)(tht)] or [Ag($OClO_3$)(PPh_3)] (molar ratio 1:2) render in the first case complex **24** while in the second an unstable material which evolves to [(Ph_3P)(C_6F_5)$_3$PtAg(PPh_3)] **27** is obtained. The reaction between [NBu_4]$_2$[*trans*-$PtCl_2$(C_6X_5)$_2$] (X = F or Cl) and [Ag($OClO_3$)(tht)] or [Ag(tht)$_2$]ClO_4 have also been studied. The structures of [(tht)(C_6Cl_5)(C_6F_5)$_2$PtAg(PPh_3)] **14**, [NBu_4][(C_6F_5)$_4$PtAg(tht)] **24** and [NBu_4][*cis*-(C_6Cl_5)$_2$(C_6F_5)$_2$PtAg(tht)] **25** have been established by single-crystal X-ray diffraction studies. The complexes contain a strong Pt→Ag bond [2.650(2), **14**; 2.641(1), **24**; and 2.692(2) Å, **25**] unsupported by covalent bridges, and short contacts between the *o*-F or *o*-Cl atoms of the C_6X_5 (X = F or Cl) groups and the Ag atom are present. The relative strength of such contacts is discussed. Methods for the synthesis of mixed pentachloro-pentafluorophenyl starting complexes **1–13** have been investigated.

The synthesis of heteropolynuclear complexes containing Pt→Ag bonds is the subject of our current interest.[1,2] If the platinum centre is to act as a donor atom, anionic platinum complexes are the adequate precursors since the anionic nature should enhance their basic properties. Other Pt→Ag complexes prepared from neutral [$PtMe_2$(bipy)] (bipy = 2,2′-bipyridine) have been discussed recently, but lack of stability precluded their isolation.[3] We have however been able to isolate stable Pt→Ag complexes of different stoicheiometries using anionic platinum(II) complexes containing pentafluoro- or pentachlorophenyl ligands.[4]

An additional striking feature in our Pt→Ag complexes is the structural role played by the pentahalogenophenyl groups, which are usually orientated in such a way that one of the *o*-X substituents (X = F or Cl) makes a 'short contact' (*o*-X ··· Ag) with the silver atom. We think that these contacts imply donation of electron density from the halogen atom to the silver centre thereby contributing to both the structure and the stability of the cluster. It seems sensible to assume that the strength of such contacts depends on the overall balance of electron density around the silver atom, *i.e.* the interactions with all the ligands present and the nature (F or Cl) of the halide substituent in the C_6X_5 groups. So far, it has not been possible to evaluate the last factor because anionic platinum complexes of given stoichiometry but containing different aryl groups (C_6F_5 or C_6Cl_5) reacted with silver salts or silver complexes to give Pt→Ag complexes of very different structure.[5–7]

Therefore, we decided to explore the problem by another approach: the synthesis of anionic platinum complexes containing simultaneously both C_6F_5 and C_6Cl_5 groups in order to treat them with suitable silver compounds with the aim of preparing binuclear complexes containing Pt→Ag bonds. Structural studies of the resulting products should give us the necessary data to compare both types of *o*-X ··· Ag short contacts. Two types of anionic complexes have been chosen for such reactions: (*a*) monoanionic complexes of general formula $[Pt(C_6F_5)_x(C_6Cl_5)_{3-x}L]^-$ (x = 2, 1 or 0) and (*b*) dianionic complexes $[Pt(C_6X_5)_2(C_6X'_5)_2]^{2-}$ (X = F, X′ = Cl or X = X′ = F or Cl). It was to be expected that, in both cases, their reactions with silver salts or complexes would render heterometallic Pt→Ag complexes.

Since the structure of [(tht)(C_6F_5)$_3$PtAg(PPh_3)] (tht = tetrahydrothiophene) had already been reported by us[8] we have established now, by X-ray diffraction studies, the structures of [(tht)(C_6Cl_5)(C_6F_5)$_2$PtAg(PPh_3)], [NBu_4][*cis*-(C_6Cl_5)$_2$(C_6F_5)$_2$PtAg(tht)] and [NBu_4][(C_6F_5)$_4$PtAg(tht)]. The structural data reported enable (*a*) a meaningful comparison of the halogen effect on the strength of the *o*-X ··· Ag contacts in this class of complexes and (*b*) a check on the

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* Bis(pentachlorophenyl)-1κ$^2C^1$-pentafluorophenyl-1κC^1-tetrahydrothiophene-1κ*S*-triphenylphosphine-2κ*P*-platinumsilver (*Ag–Pt*), tetrabutylammonium tetrakis(pentafluorophenyl)-1κ$^4C^1$-tetrahydrothiophene-2κ*S*-platinumargentate (*Ag–Pt*) and tetrabutylammonium *cis*-bis(pentachlorophenyl)-1κ$^2C^1$-bis(pentafluorophenyl)-1κ$^2C^1$-tetrahydrothiophene-2κ*S*-platinumargentate (*Ag–Pt*).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

influence of the C_6X_5 groups on the structure of the reported complexes.[9]

No preparative methods for the synthesis of mixed (C_6F_5,C_6Cl_5) complexes have been reported so far. We have studied their synthesis and have found that they cannot be adequately prepared by arylating with $Li(C_6X_5)$ but are readily accessible using instead $Ag(C_6X_5)$ as an arylating agent.

Since in this work we have used for the first time $[Ag(tht)]^+$ and $[Ag(tht)_2]^+$ as the cationic counterpart to the anionic platinum complexes, we have also explored their reactions with other anionic platinum complexes $[NBu_4]_2[Pt(C_6Cl_5)_4]$ and $[NBu_4]_2$[*trans*-$PtCl_2(C_6X_5)_2$] (X = F or Cl) but no products containing Pt→Ag bonds could be isolated.

Results and Discussion

(*a*) *Synthesis of* $[NBu_4]$[*cis*-$M(C_6F_5)_x(C_6Cl_5)_{3-x}L$] (M = Pd *or* Pt) *and* $[NBu_4]_2[M(C_6F_5)_2(C_6Cl_5)_2]$ **1–13**.—The synthesis of perhalogenoaryl (C_6F_5 or C_6Cl_5) derivatives of palladium or platinum is usually achieved by treating suitable halogeno-complexes with organo-lithium or -magnesium reagents $Li(C_6X_5)$ or $MgBr(C_6X_5)$ the former being the more reactive.[4] As far as we know, for the group Ni, Pd and Pt only two mixed pentachloro-pentafluoro-phenyl derivatives have hitherto been reported: *trans*-$[Ni(C_6F_5)(C_6Cl_5)(PMePh_2)_2]$[10] (15% yield) and *trans*-$[Pd(C_6F_5)(C_6Cl_5)(PEt_3)_2]$[11] (53% yield); they were prepared by arylating the precursors $[NiCl(C_6F_5)L_2]$ or $[PdCl(C_6Cl_5)L_2]$ with the lithium reagents $Li(C_6Cl_5)$ or, respectively $Li(C_6F_5)$.

We have established that the arylation of substrata of the type $[NBu_4]$[*cis*-$PtCl(C_6F_5)_2L$] (L = PPh_3 or tht) with $Li(C_6Cl_5)$ (molar ratio 1:4 to 1:9) gives $[NBu_4]$[*cis*-$Pt(C_6Cl_5)(C_6F_5)_2L$] in <30% yields, whilst arylation of $[NBu_4]$[*cis*-$PtCl(C_6Cl_5)_2(PPh_3)$] with $Li(C_6F_5)$ (molar ratio 1:9) renders $[NBu_4]$[*cis*-$Pt(C_6F_5)(C_6Cl_5)_2(PPh_3)$] **8** 28% yield, but the arylation of $[NBu_4]$[*cis*-$MCl(C_6Cl_5)_2(tht)$] (M = Pd or Pt) with $Li(C_6F_5)$ renders $[NBu_4]_2$[*cis*-$Pt(C_6F_5)_2(C_6Cl_5)_2$] **12** (47% yield) or $[NBu_4]_2$[*trans*-$Pd(C_6F_5)_2(C_6Cl_5)_2$] **13** (25% yield) albeit in low yields, the neutral ligand tht also being displaced. Moreover, simultaneous isomerisation was observed for the palladium complex. However **12** and **13** can be prepared in better yields by reacting *cis*-$[Pt(C_6F_5)_2(thf)_2]$ (thf = tetrahydrofuran) or $[NBu_4]_2[\{Pd(\mu\text{-}Cl)(C_6F_5)_2\}_2]$ with $Li(C_6Cl_5)$ (75 and 73% yield respectively, see Experimental section). It should be noted that the arylation of $[NBu_4]_2[\{Pd(\mu\text{-}Cl)(C_6F_5)_2\}_2]$ also takes place with isomerisation.

For all these reasons, the synthesis of the mixed-ligand complexes $[NBu_4]$[*cis*-$M(C_6F_5)_x(C_6Cl_5)_{3-x}L$] (M = Pd or Pt, x = 2 or 1; L = neutral S, N or P donor ligands) has been achieved by using $Ag(C_6X_5)$ as arylating agent. The reactions have been carried out in CH_2Cl_2 [equations (1) and (2)] at room temperature and protected from the light. The arylations with $Ag(C_6Cl_5)$ [equation (1)] need 4 h for completion while when $Ag(C_6F_5)$ is used only 1 h is necessary. In all cases the AgCl, which precipitates slowly, was separated by filtration and from the resulting solution, after evaporating to dryness and treating the oily residues with isopropyl alcohol, the corresponding mixed-ligand complexes **1–8**, **10** and **11** were isolated. Experimental details and yields (>85% for **1–8**, 70–80% for **10** and **11**) are collected in Table 9.

$$[NBu_4][cis\text{-}MCl(C_6F_5)_2L] + Ag(C_6Cl_5) \longrightarrow AgCl\downarrow + [NBu_4][cis\text{-}M(C_6F_5)_2(C_6Cl_5)L] \quad (1)$$

M = Pt, L = tht, **1**; PPh_3, **2**; $PMePh_2$, **3**; or py **4**
M = Pd, L = PPh_3, **5**; or $PMePh_2$, **6**

$$[NBu_4][cis\text{-}MCl(C_6Cl_5)_2L] + Ag(C_6F_5) \longrightarrow AgCl\downarrow + [NBu_4][cis\text{-}M(C_6F_5)(C_6Cl_5)_2L] \quad (2)$$

M = Pt, L = tht, **7**; or PPh_3, **8**; M = Pd, L = tht, **10**; or PPh_3, **11**

As is to be expected, complexes containing tht can be used as starting materials for the synthesis of other $[NBu_4]$[*cis*-$M(C_6F_5)_x(C_6Cl_5)_{3-x}L$] (M = Pd or Pt; x = 1 or 2; L = neutral S, N or P donor ligands) complexes since the tht ligands can be displaced by other neutral ligands L. In fact we have also obtained $[NBu_4]$[*cis*-$Pt(C_6F_5)_2(C_6Cl_5)(py)$] **4** (py = pyridine), 66% yield, $[NBu_4]$[*cis*-$Pt(C_6F_5)(C_6Cl_5)_2(PMePh_2)$] **9**, 62% yield, by this procedure, although longer reaction times (8 h) and higher temperatures (refluxing toluene) are necessary to drive the reactions to completion and the complexes are obtained in lower yields than when prepared by the direct method [equations (1) or (2)]. Analytical and conductivity data are collected in Table 1.

(*b*) *Structure of Complexes* **1–13**.—The configuration of complexes **1–13** can be established from their IR spectra, since the absorptions assignable to the X-sensitive modes of either the C_6F_5 (≈800 cm^{-1}) or the C_6Cl_5 groups[12] (≈830 cm^{-1}) along with those due to the ν(M–C) modes of the M–C_6Cl_5 bonds (≈600 cm^{-1})[13] allow us to distinguish between *cis* or *trans* isomers. For complexes **1–11**, which are of the type $[NBu_4][M(C_6X_5)(C_6X'_5)_2L]$, only one absorption due to the C_6X_5 group can be expected [X-sensitive or ν(M–C) for X = Cl] whilst the number of absorptions due to the $C_6X'_5$ group depends on the configuration, since despite the fact that group theory predicts the same number of IR-active vibrations for the two isomers (*cis* isomer C_s, 2A′; *trans* isomer C_{2v}, $A_1 + B_1$), in practice two strong absorptions are observed in case of the *cis* isomer and one strong and another very weak (sometimes imperceptible) absorption appear for the *trans* isomer.[14,15] These absorptions are collected in Table 2. For complexes **7–12** containing two C_6Cl_5 groups the X-sensitive modes appear as an unresolved broad absorption but ν(M–C) gives two absorptions in all cases, thereby allowing the assignation of a *cis* configuration. As can be seen from Table 2 the synthesis of complexes **1–12** takes place with stereoretention, whereas for **13** the *trans* isomer is formed from the *cis* precursor.

(*c*) *Synthesis of* $[L(C_6Cl_5)_{3-x}(C_6F_5)_xPtAg(PPh_3)]$ **14–21**.—The reactions between $[NBu_4][Pt(C_6F_5)_x(C_6Cl_5)_{3-x}L]$ and $[Ag(OClO_3)(PPh_3)]$ (1:1 molar ratio, dichloromethane, 0 °C) render [equation (3)] neutral bimetallic complexes. After

$$[NBu_4][Pt(C_6F_5)_x(C_6Cl_5)_{3-x}L] + [Ag(OClO_3)(PPh_3)] \longrightarrow NBu_4ClO_4 + [L(C_6Cl_5)_{3-x}(C_6F_5)_xPtAg(PPh_3)] \quad (3)$$

x = 2, L = tht, **14**; PPh_3, **15**; or py, **16**
x = 1, L = tht, **17**; or PPh_3, **18**
x = 0, L = tht, **19**; PPh_3, **20**, or py, **21**

stirring for 30–60 min, the complexes **14–21** could be isolated (see Experimental section). Analytical, conductivity, molecular weight and melting point data are given in Table 1. Lack of solubility (**14**) or poor stability (**19–21**) in chloroform solution precluded determination of the molecular weight in several cases.

According to previous results,[8] it seems sensible to assume that complexes **14–21** are formed by a donor–acceptor interaction between the platinum centre of the anionic complex and the $[Ag(PPh_3)]^+$ cationic fragment, resulting in a Pt→Ag bond, an assumption which is confirmed, for complex **14**, whose crystal structure has been established (see below) by X-ray crystallography. Dichloromethane solutions of **14–21** are non-conducting but their acetone solutions (≈5 × 10^{-4} mol dm^{-3}) behave as 1:1 electrolytes, as a consequence of cleavage of the Pt→Ag bond by the donor solvent, forming $[Ag(PPh_3)(OCMe_2)_x]^+$ and $[Pt(C_6F_5)_x(C_6Cl_5)_{3-x}L]^-$ ions, a behaviour which has also been observed in other Pt→Ag complexes.[8]

Table 1 Analysis, molar conductivity and other data (calculated values in parentheses)

Complex	Analysis (%) C	H	N	Cl	$\Lambda_M{}^a$/Ohm^{-1} cm^2 mol^{-1} Me$_2$CO	CH$_2$Cl$_2$	*M*	M.p./°C
1 [NBu$_4$][*cis*-Pt(C$_6$F$_5$)$_2$(C$_6$Cl$_5$)(tht)]	40.90	4.15	1.15	15.60	95			174
	(41.15)	(3.95)	(1.25)	(16.00)				
2 [NBu$_4$][*cis*-Pt(C$_6$F$_5$)$_2$(C$_6$Cl$_5$)(PPh$_3$)]	48.90	4.25	1.05	14.10	91			198
	(48.65)	(4.60)	(1.10)	(13.80)				
3 [NBu$_4$][*cis*-Pt(C$_6$F$_5$)$_2$(C$_6$Cl$_5$)(PMePh$_2$)]	46.00	4.15	0.95	14.65	88			194
	(46.20)	(3.95)	(1.15)	(14.50)				
4 [NBu$_4$][*cis*-Pt(C$_6$F$_5$)$_2$(C$_6$Cl$_5$)(py)]	42.25	3.80	2.40	15.70	94			165
	(42.55)	(3.70)	(2.55)	(16.10)				
5 [NBu$_4$][*cis*-Pd(C$_6$F$_5$)$_2$(C$_6$Cl$_5$)(PPh$_3$)]	52.35	4.70	1.25	15.10	87			178
	(52.30)	(4.25)	(1.15)	(14.85)				
6 [NBu$_4$][*cis*-Pd(C$_6$F$_5$)$_2$(C$_6$Cl$_5$)(PMePh$_2$)]	49.95	4.60	1.25	16.05	90			160
	(49.85)	(4.25)	(1.25)	(15.65)				
7 [NBu$_4$][*cis*-Pt(C$_6$F$_5$)(C$_6$Cl$_5$)$_2$(tht)]	38.35	3.90	1.15	29.50	99			108
	(38.30)	(3.70)	(1.15)	(29.75)				
8 [NBu$_4$][*cis*-Pt(C$_6$F$_5$)(C$_6$Cl$_5$)$_2$(PPh$_3$)]	45.45	3.95	1.10	25.85	106			165
	(45.75)	(3.75)	(1.00)	(25.95)				
9 [NBu$_4$][*cis*-Pt(C$_6$F$_5$)(C$_6$Cl$_5$)$_2$(PMePh$_2$)]	43.55	3.80	0.95	27.20	100			140
	(43.30)	(3.70)	(1.05)	(27.20)				
10 [NBu$_4$][*cis*-Pd(C$_6$F$_5$)(C$_6$Cl$_5$)$_2$(tht)]	41.60	4.15	1.15	32.50	102			138
	(41.40)	(4.00)	(1.25)	(32.15)				
11 [NBu$_4$][*cis*-Pd(C$_6$F$_5$)(C$_6$Cl$_5$)$_2$(PPh$_3$)]	48.60	4.30	1.15	28.80	84			175 (decomp.)
	(48.90)	(4.00)	(1.10)	(27.75)				
12 [NBu$_4$]$_2$[*cis*-Pt(C$_6$F$_5$)$_2$(C$_6$Cl$_5$)$_2$]	44.35	4.45	1.70	23.75	206			168 (decomp.)
	(44.45)	(4.75)	(1.85)	(23.45)				
13 [NBu$_4$]$_2$[*trans*-Pd(C$_6$F$_5$)$_2$(C$_6$Cl$_5$)$_2$]	47.65	5.30	1.85	24.60	170			127
	(47.25)	(5.05)	(1.95)	(24.90)				
14 [(tht)(C$_6$Cl$_5$)(C$_6$F$_5$)$_2$PtAg(PPh$_3$)]	38.85	1.95	—	13.95	82	6	*b*	158 (decomp.)
	(38.85)	(1.85)		(14.35)				
15 [(Ph$_3$P)(C$_6$Cl$_5$)(C$_6$F$_5$)$_2$PtAg(PPh$_3$)]	45.75	2.50	—	12.30	96	4	1538	220 (decomp.)
	(45.95)	(2.15)		(12.55)			(1410.9)	
16 [(py)(C$_6$Cl$_5$)(C$_6$F$_5$)$_2$PtAg(PPh$_3$)]	39.80	1.90	0.90	14.00	94	5	1280	118 (decomp.)
	(40.10)	(1.65)	(1.15)	(14.45)			(1282.8)	
17 [(tht)(C$_6$Cl$_5$)$_2$(C$_6$F$_5$)PtAg(PPh$_3$)]	36.65	2.00		26.70	76	2	1325	95 (decomp.)
	(36.40)	(1.75)		(26.85)			(1309.1)	
18 [(Ph$_3$P)(C$_6$Cl$_5$)$_2$(C$_6$F$_5$)PtAg(PPh$_3$)]	43.20	2.25		23.50	93	8	1407	105 (decomp.)
	(43.45)	(2.00)		(23.75)			(1493.3)	
19 [(tht)(C$_6$Cl$_5$)$_3$PtAg(PPh$_3$)]	34.35	1.90		37.65	72	4	*c*	98 (decomp.)
	(34.30)	(1.65)		(37.95)				
20 [(Ph$_3$P)(C$_6$Cl$_5$)$_3$PtAg(PPh$_3$)]	41.10	2.55	—	33.45	39	5	*c*	96 (decomp.)
	(41.15)	(1.90)		(33.75)				
21 [(py)(C$_6$Cl$_5$)$_3$PtAg(PPh$_3$)]	34.95	1.95	0.80	37.85	75	4	*c*	121 (decomp.)
	(35.35)	(1.45)	(1.00)	(38.20)				
22 [NBu$_4$][(C$_6$F$_5$)$_4$PtAg(OEt$_2$)]	41.05	3.75	1.35	—	115			65
	(41.05)	(3.60)	(1.10)					
23 [NBu$_4$][(C$_6$F$_5$)$_4$PtAg(PPh$_3$)]	47.10	3.75	0.95	—	92			62
	(47.20)	(3.50)	(0.95)					
24 [NBu$_4$][(C$_6$F$_5$)$_4$PtAg(tht)]	40.80	3.55	1.15	—	96			105 (decomp.)
	(40.60)	(3.40)	(1.05)					
25 [NBu$_4$][(C$_6$Cl$_5$)$_2$(C$_6$F$_5$)$_2$PtAg(tht)]	36.35	3.00	1.15	23.80	112			—
	(36.05)	(3.00)	(0.95)	(24.15)				
26 [(C$_6$F$_5$)$_4$Pt{Ag(PPh$_3$)}$_2$]	44.65	2.20	—		—			—
	(44.95)	(1.85)						
27 [(Ph$_3$P)(C$_6$F$_5$)$_3$PtAg(PPh$_3$)]	48.55	2.95	—		—			
	(48.80)	(2.25)						
28 [NBu$_4$]$_x$[PtAg(μ-Cl)$_2$(C$_6$Cl$_5$)$_2$]$_x$	29.80	3.30	1.05		—			—
	(30.05)	(3.25)	(1.25)					
29 [Pd(C$_6$F$_5$)$_2$(tht)(PPh$_3$)]	51.60	2.90	—		—			—
	(52.00)	(3.15)						

[a] $\approx 5 \times 10^{-4}$ mol dm^{-3}. [b] Not soluble enough for molecular weight determination. [c] Decomposition of the solution precludes molecular weight determination.

In the absence of light, complexes **14–21** are stable at room temperature for several hours and at −20 °C for several weeks. They are, however, less stable than the tris(pentafluorophenyl) analogues [L(C$_6$F$_5$)$_3$PtAgL′], which can be prepared at room temperature and their CH$_2$Cl$_2$ solutions do not darken in 48 h, whilst the present complexes must be prepared at 0 °C and their CH$_2$Cl$_2$ solutions darken within a few hours. The stability decreases with increasing number of C$_6$Cl$_5$ groups.

(*d*) *Structure of* [(tht)(C$_6$Cl$_5$)(C$_6$F$_5$)$_2$PtAg(PPh$_3$)] **14**.—The structure of complex **14** has been determined by single-crystal X-ray diffraction (see Experimental section). Single crystals were grown at −30 °C by slow diffusion of hexane into a dichloromethane solution of **14**, which initially was separated from the hexane by a layer (0.5 cm^3) of 1,2-dichloroethane. Atomic coordinates and bond distances and angles are given in Tables 3 and 4, respectively. The structure is shown in Fig. 1

Table 2 Relevant IR absorptions (cm^{-1})

	C_6F_5	C_6Cl_5		
Complex	X-sensitive	X-sensitive	ν(M–C)	L
1	789s, 776s	830m	610s	
2	781s, 772s	831m	611s	1096s, 748s, 697vs, 535s, 509s, 492s
3	778s, 770s	832m	613s	1097s, 891s, 882s, 756s, 693s, 516s, 481s, 436s
4	796s, 777s	832m	610s	1604m, 758s, 691s
5	768s, 761s	825m	605s	1095s, 746vs, 696vs, 530vs, 509vs, 490s, 453m, 428m
6	766s, 756s	826m	609m (sh)	1096s, 891s, 826s, 740s, 700s, 693s, 512s, 477s, 430s
7	775m	827w	612m, 602m	—
8	771m	826m	609m, 602m	1095s, 746s, 694s, 532s, 510s, 490m, 426m
9	774s	833m, 827m	608m, 603m	1102s, 893s, 886s, 750s, 697s, 691s, 516s, 483m, 446s, 421m
10	765s	822s	608w, 595w	—
11	746m	825m	604w, 593w	1095s, 748s, 694s, 527s, 507s, 488m, 454w, 428w
12	774s, 766m	830m	604s, 600s	—
13	749s	817m	590m	—
14	796s, 780s	832m	610m	1097s, 742s, 693s, 522s, 500m, 491m
15	783s, 773s	832m	609m	1095s, 763s, 742vs, 702s, 692vs, 525vs, 508vs, 489s
16	799s, 779m	832m	611m	1604m, 1096s, 1028m, 1018m, 997m, 757s, 742s, 707s, 692vs, 642w, 517s, 500m, 491m
17	776s	828w	617m, 604w	1096s, 743s, 692s, 536s, 518s, 508s, 488s
18	773m	838w, 831w	618w, 600w	1097s, 741s, 710s, 691s, 519s, 500m, 490m
19	—	829m	618m, 612m, 601m	1097s, 744s, 694s, 512s, 503m, 489m
20	—	830m, 823m	630m, 620m, 608m	1096s, 747s, 684vs, 545m, 531s, 495s, 423s
21	—	825s	616m (sh), 594m	1601s, 1094s, 1066s, 1022m, 1012m, 994m, 740s, 707s, 690vs, 515s, 500m, 487m
22	766vs	—	—	—
23	766vs	—	—	740s, 704s, 690s, 518s, 501s, 495 (sh)
24	769vs	—	—	1273m, 894m
25	776s, 769s	832m, 824m	605m, 600m	1211m, 895 (sh)

Table 3 Fractional atomic coordinates (× 10^4) and their estimated standard deviations (e.s.d.s) for $[(tht)(C_6Cl_5)(C_6F_5)_2PtAg(PPh_3)]$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pt	688(1)	1318(1)	1842(1)	C(13)	2127(21)	3132(16)	3477(17)
Ag	−875(2)	1576(1)	2274(1)	C(14)	2826(20)	3396(16)	3216(16)
S	−139(5)	265(4)	1116(4)	C(15)	2878(18)	3079(15)	2508(15)
Cl(1)	226(5)	670(5)	3592(4)	C(16)	2228(18)	2507(14)	2131(14)
Cl(2)	1707(7)	−256(5)	4916(5)	C(17)	38(16)	2092(13)	921(13)
Cl(3)	3673(8)	−799(7)	4748(6)	C(18)	−455(20)	2730(16)	965(17)
Cl(4)	4130(7)	−422(6)	3232(6)	C(19)	−872(19)	3228(16)	289(16)
Cl(5)	2682(6)	550(5)	1880(5)	C(20)	−661(21)	3060(17)	−398(17)
F(1)	859(11)	2294(9)	3448(8)	C(21)	−148(20)	2446(16)	−492(16)
F(2)	2064(13)	3428(10)	4176(10)	C(22)	158(20)	1957(16)	180(16)
F(3)	3447(12)	3954(9)	3571(9)	P	−2373(6)	1848(5)	2494(5)
F(4)	3544(11)	3361(10)	2195(9)	C(23)	−3191(13)	2518(10)	1802(10)
F(5)	2315(11)	2241(8)	1447(8)	C(24)	−3891(13)	2944(10)	1998(10)
F(6)	−608(11)	2952(7)	1655(8)	C(25)	−4505(13)	3445(10)	1438(10)
F(7)	−1378(11)	3873(8)	348(9)	C(26)	−4420(13)	3520(10)	682(10)
F(8)	−1036(12)	3545(8)	−1078(8)	C(27)	−3719(13)	3093(10)	486(10)
F(9)	30(13)	2296(10)	−1188(8)	C(28)	−3105(13)	2592(10)	1046(10)
F(10)	693(13)	1302(10)	83(7)	C(29)	−2130(16)	2224(12)	3496(10)
C(1)	−567(20)	−388(15)	1715(16)	C(30)	−2657(16)	2041(12)	4000(10)
C(2)	−1687(27)	−464(21)	1336(22)	C(31)	−2409(16)	2379(12)	4755(10)
C(3)	−2083(34)	37(27)	715(28)	C(32)	−1634(16)	2900(12)	5005(10)
C(4)	−1382(19)	420(15)	378(15)	C(33)	−1107(16)	3083(12)	4501(10)
C(5)	1539(16)	588(12)	2774(13)	C(34)	−1355(16)	2744(12)	3747(10)
C(6)	1329(19)	386(14)	3472(15)	C(35)	−3155(20)	997(11)	2475(15)
C(7)	1946(19)	−5(15)	4085(15)	C(36)	−2683(20)	388(11)	2953(15)
C(8)	2856(21)	−278(16)	4011(17)	C(37)	−3181(20)	−297(11)	2892(15)
C(9)	3082(21)	−137(17)	3338(18)	C(38)	−4152(20)	−372(11)	2353(15)
C(10)	2397(19)	300(15)	2740(15)	C(39)	−4624(20)	236(11)	1874(15)
C(11)	1549(16)	2179(13)	2434(13)	C(40)	−4125(20)	921(11)	1935(15)
C(12)	1544(19)	2559(15)	3091(15)				

and, as expected, is very similar to that of $[(tht)(C_6F_5)_3Pt-Ag(PPh_3)]$ which has previously been described.[8] The Pt atom displays a distorted square-pyramidal environment, the apical position being occupied by the Ag atom in the $[Ag(PPh_3)]^+$ moiety whilst the basal plane is formed by the C_{ipso} atoms of two C_6F_5 (*cis*) and one C_6Cl_5 group and the S atom of the tht ligand. In the basal plane the angles between *cis* ligands around the platinum centre range from 86.3(9) to 95.2(6)°; the angles between *trans* ligands are identical within the experimental error [S–Pt–C(11) 172.8(7), C(5)–Pt–C(17) 172.1(8)°] and the dihedral angle between the planes Pt–C(5)–S and Pt–C(11)–C(17) is 9.2(8)°.[16] The Pt–C distances are very similar, the shortest being that corresponding to the pentafluorophenyl group *trans* to the tht ligand. However it should be mentioned that these Pt–C lengths are similar to other Pt–C distances found for terminal C_6F_5 [8,17] or C_6Cl_5 groups [2,9] and that not important differences have been found for Pt–C lengths corresponding to Pt–C_6F_5 [2.016(22), 2.090(22) Å] or Pt–C_6Cl_5 [2.120(21) Å] bonds. The platinum [(tht)(C_6Cl_5)(C_6F_5)$_2$Pt] and silver [Ag(PPh_3)] fragments are bonded by a donor–acceptor Pt→Ag bond, unsupported by other covalent bridging ligands, with a distance of 2.650(2) Å. The Pt→Ag bond deviates only 8.4(4)° from perpendicularity to the basal plane.[16]

The silver atom is also bonded to PPh_3, the Ag–P distance being 2.363(8) Å, in the range found for other Ag–P distances,[8] and the angle Pt–Ag–P is 173.0(2)°.

Table 4 Selected bond distances (Å) and angles (°) and their e.s.d.s for [(tht)(C_6Cl_5)(C_6F_5)$_2$PtAg(PPh_3)]

Ag–Pt	2.650(2)	S–Pt	2.345(7)
C(5)–Pt	2.120(21)	P–Ag	2.363(8)
C(11)–Pt	2.016(22)	Cl(1) ··· Ag	2.824(7)
C(17)–Pt	2.090(22)	F(1) ··· Ag	2.912(13)
		F(6) ··· Ag	2.763(14)
S–Pt–Ag	88.8(2)	C(5)–Pt–Ag	101.3(6)
C(5)–Pt–S	89.2(6)	C(11)–Pt–Ag	98.4(6)
C(11)–Pt–S	172.8(7)	C(11)–Pt–C(5)	88.6(9)
C(17)–Pt–Ag	85.4(6)	C(17)–Pt–S	95.2(6)
C(17)–Pt–C(5)	172.1(8)	C(17)–Pt–C(11)	86.3(9)
P–Ag–Pt	173.0(2)	Cl(1)–Ag–Pt	81.7(2)
P–Ag–Cl(1)	105.0(2)		

Finally, as usual in most heteronuclear Pt→Ag complexes,[1] the C_6X_5 groups attached to the platinum atoms are so positioned that one *ortho*-X substituent of each group makes a close contact with the silver atom and we think that these contacts imply donation of electron density to the silver atom. Since complex **14** is the first example of a Pt→Ag compound in which pentachloro- and pentafluoro-phenyl groups, and consequently *o*-F ··· Ag and *o*-Cl ··· Ag contacts, are present we have dedicated some attention to these contacts. The Ag ··· X distance may give information on the strength of the Ag–X contact, however in order to minimise the influence of the size of the halogen on the Ag ··· X distance we have expressed such distances as ρ [experimental distances/sum of covalent radii: 0.64 (F) + 1.34 (Ag) = 1.98 Å; 0.99 (Cl) + 1.34 (Ag) = 2.33 Å [18]]. Such values are collected in Table 5 for [(tht)(C_6F_5)$_3$PtAg(PPh_3)] and [(tht)(C_6Cl_5)(C_6F_5)$_2$PtAg(PPh_3)]. The ρ value for *o*-Cl ··· Ag (1.21) is distinctly smaller than the values for *o*-F ··· Ag contacts (ranging between 1.39 and 1.48) probably owing to the higher electronegativity of the F atom which makes it more reluctant to donate electron density to the silver centre. For comparison, Table 5 collects the main bond distances in both cases. The slightly longer Pt–Ag and Ag ··· F(1) distances in **14** may also be a consequence of the stronger *o*-Cl ··· Ag interaction.

(*e*) *IR Spectra of Complexes* [L(C_6Cl_5)$_{3-x}$(C_6F_5)$_x$PtAg(PPh_3)] **14–21**.—Table 2 collects relevant IR absorptions of complexes **14–21** that have been assigned to the C_6F_5, C_6Cl_5 groups or to the ligand L or PPh_3. No significant differences in the absorption due to the X-sensitive (C_6F_5 or C_6Cl_5) and ν(M–C) (C_6Cl_5) modes have been observed with respect to the starting materials.

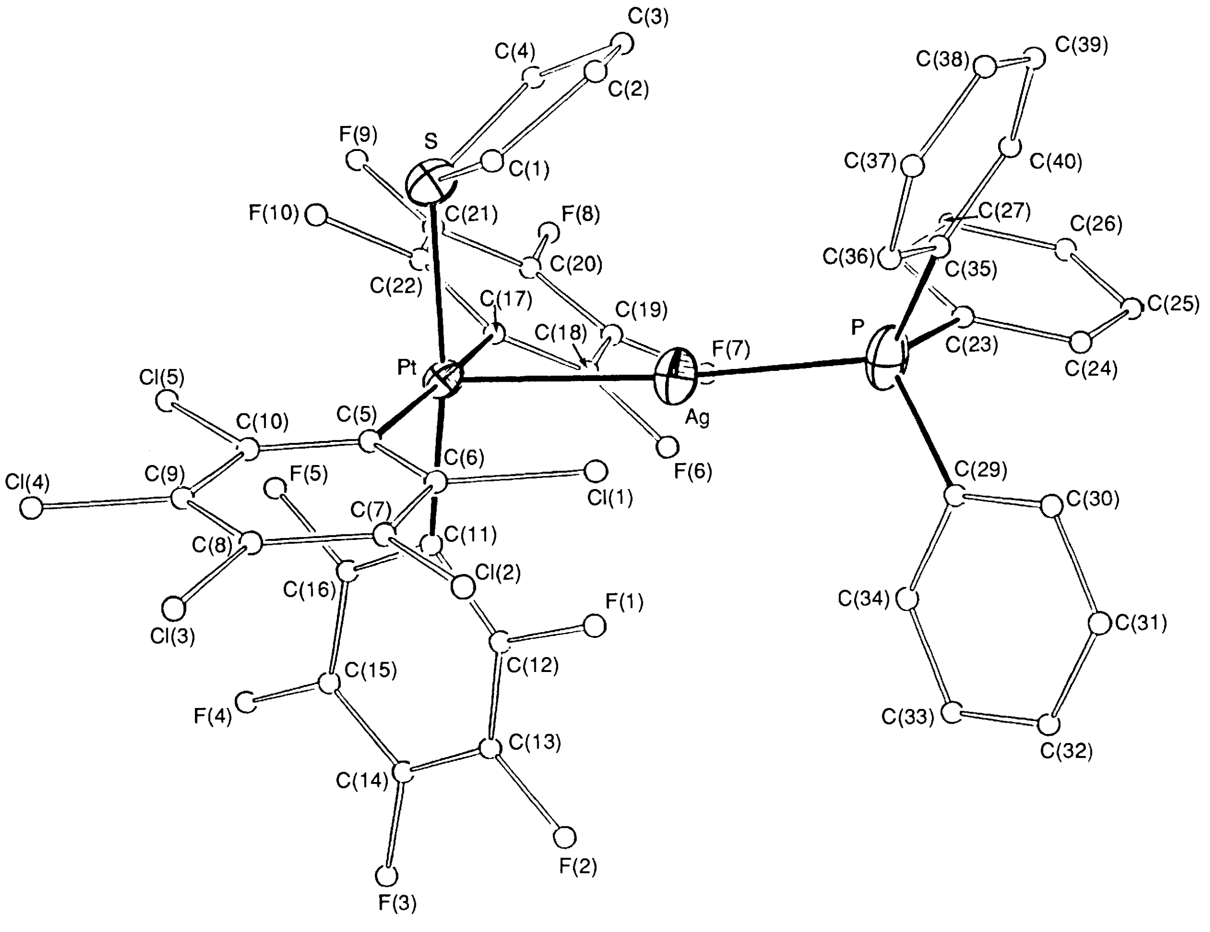

Fig. 1 ORTEP drawing of [(tht)(C_6Cl_5)(C_6F_5)$_2$PtAg(PPh_3)] **14**

Table 5 Comparison of distances (Å) for two similar platinum–silver compounds*

	$[(tht)(C_6Cl_5)(C_6F_5)_2PtAg(PPh_3)]$		$[(tht)(C_6F_5)_3PtAg(PPh_3)]$[8]
Pt–Ag	2.650(2)		2.637(1)
Pt–S	2.345(7)		2.328(3)
Pt–C(5)	2.120(21)		2.096(12)
Pt–C(11)	2.016(22)		2.002(11)
Pt–C(17)	2.090(22)		2.068(12)
Ag–P	2.363(8)		2.358(3)
Ag···F(1)	2.923(13) [1.48]		2.791(7) [1.41]
Ag···F(6)	2.758(14) [1.39]		2.763(8) [1.40]
Ag···Cl(1)	2.824(7) [1.21]	(Ag···F)	2.757(7) [1.39]

*ρ Values in square brackets.

(*f*) *Synthesis of* $[NBu_4][(C_6X_5)_2(C_6X'_5)_2PtAgL]$ ($X = X' = F$, $L = OEt_2$, **22**; PPh_3, **23**; *or* tht, **24**; $X = F$, $X' = Cl$, $L =$ tht, **25**).—Anionic complexes of general formula $[NBu_4][(C_6X_5)_2(C_6X'_5)_2PtAgL]$ ($X = X' = F$, $L = OEt_2$, PPh_3, or tht; $X = F$, $X' = Cl$, $L =$ tht) have been obtained by treating the appropriate $[NBu_4]_2[Pt(C_6X_5)_2(C_6X'_5)_2]$ precursors with $AgClO_4$ or $[Ag(OClO_3)L]$ in dichloromethane (molar ratio 1:1), diethyl ether being used for the elimination of the insoluble NBu_4ClO_4 [equation (4)].

$$[NBu_4]_2[Pt(C_6X_5)_2(C_6X'_5)_2] + \begin{matrix} AgClO_4 \\ \text{or} \\ [Ag(OClO_3)L] \end{matrix} \xrightarrow[(Et_2O)]{CH_2Cl_2} NBu_4ClO_4 + [NBu_4][(C_6X_5)_2(C_6X'_5)_2PtAgL] \quad (4)$$

$X = X' = F$, $L = OEt_2$, **22**; PPh_3, **23** or tht, **24**;
$X = F$, $X' = Cl$, $L =$ tht, **25**

Analytical and conductivity (in acetone solutions $\approx 5 \times 10^{-4}$ mol dm^{-3}) data for complexes **22**–**25** are collected in Table 1. The conductivity values point to 1:1 electrolytes indicating that the donor solvent is not able to cleave the Pt→Ag bond. This result is noteworthy since as we have described in (*c*) complexes of the type $[L(C_6Cl_5)_{3-x}(C_6F_5)_xPtAgL]$ [$x = 3$,[8] $x = 2$ (this paper)] are non-conducting in dichloromethane but they behave as 1:1 electrolytes in acetone solutions. More surprising is the fact that upon addition of tht, PPh_3 or py to acetone solutions of **24** (1:1 molar ratio) no change in conductivity takes place, *i.e.* these ligands do not cleave the Pt→Ag bond. Moreover, addition of PPh_3 to a dichloromethane solution of **24** (molar ratio 1:1) gives **23**, *i.e.* substitution of tht by PPh_3 is the only observed process.

In accordance with the above observations, the reaction between $[NBu_4]_2[Pt(C_6F_5)_4]$ and $[Ag(tht)_2]ClO_4$ also leads to complex **24** and the extra 1 mol tht in the silver compound is of no consequence, as expected.

Table 2 collects IR absorptions of structural interest for complex **22**–**25**.

The pentachlorophenyl derivative $[NBu_4]_2[Pt(C_6Cl_5)_4]$ behaves differently, since with $[Ag(OClO_3)(tht)]$ or $[Ag(tht)_2]ClO_4$ partial decomposition is observed (even at 0 °C) and only $[NBu_4][Pt(C_6Cl_5)_3(tht)]$ can be recovered, albeit in low yields.

(*g*) *Molecular Structures of* $[NBu_4][(C_6F_5)_4PtAg(tht)]$ **24** *and* $[NBu_4][(C_6Cl_5)_2(C_6F_5)_2PtAg(tht)]$ **25**.—Suitable crystals of complexes **24** and **25** for X-ray studies were obtained by slow diffusion at −30 °C of hexane into a dichloromethane solution of the respective complex. Fractional atomic coordinates are collected in Tables 6 and 7 respectively.

The structures of the anions in complexes **24** and **25** are depicted in Figs. 2 and 3 respectively. Selected bond distances and angles are given in Table 8. The structures are very similar, and show the platinum atom in a square-pyramidal environment in a basal plane formed by four C atoms (from four C_6F_5 groups, **24**, or two pairs of *cis*-C_6F_5 and *cis*-C_6Cl_5 groups, **25**) and the Ag(tht) fragment at the apex of the pyramid, with a donor–acceptor Pt→Ag bond, unsupported by any covalent bridge. The Pt–Ag distances [2.641(1), **24**; 2.692(2) Å, **25**] belong to the shortest ever found in complexes of this type[1,2] and therefore imply strong Pt→Ag bonds, which are roughly perpendicular to the basal plane,[16] with the platinum centre only 0.093 **24** or 0.045 Å **25** above the best least-square planes defined by the four C_{ipso} atoms of the C_6X_5 groups. The Pt–C distances are similar and in **25** there are no perceptible differences in Pt–C_6F_5 or Pt–C_6Cl_5 distances: Pt–C_6F_5 2.038(23), 2.105(20) Å or Pt–C_6Cl_5 2.123(22), 2.060(21) Å in keeping with Pt–C distances found for **14**.

The silver atom is also bonded to the S atom of the tht ligand, the Ag–S distance [2.401(6), **24**; 2.424(8) Å, **25**] being slightly shorter than other reported Ag–S distances for terminal tht ligands: 2.445(2) in $[Ag(tht)_2]BF_4$,[19] and 2.454(4) Å in $[Au(C_6F_5)_2\{\mu\text{-}Ag(tht)\}]_x$.[20]

As in complex **14**, short *o*-X··· Ag contacts are present and the corresponding ρ values are collected in Table 8, those for *o*-Cl··· Ag being smaller than those for *o*-F··· Ag, in keeping with ρ values found for **14**. The slightly longer Pt–Ag distance in **25** might be a consequence of the decreased acidity of the silver centre owing to the two stronger *o*-Cl··· Ag contacts.

Finally, it seems worthwhile to comment that the Pt→Ag distances [2.641(1), **24**; 2.692(2) Å, **25**] are similar to that found in $[(tht)(C_6F_5)_3PtAg(PPh_3)]$ [2.637(1) Å][8] or in $[(tht)(C_6Cl_5)(C_6F_5)_2PtAg(PPh_3)]$ **14** [2.650(2) Å] pointing to bonds of similar strengths in all cases, albeit those in **24** or **25** are more inert and not cleaved by neutral ligands.

(*h*) *Attempts to synthesise other Polynuclear* Pt→Ag *Complexes*.—Given the anionic character of complexes **22**–**25**, the platinum centres could have enough electron density to act as a Lewis base. For this reason we have studied the reactions between $[NBu_4]_2[Pt(C_6F_5)_4]$ and $[Ag(OClO_3)L]$ ($L = PPh_3$ or tht) in a 1:2 molar ratio.

The (1:2) reactions at room temperature in dichloromethane solution render (after evaporation to dryness and extraction with diethyl ether to separate the insoluble NBu_4ClO_4) a solution which was evaporated to dryness leaving a white solid of poor stability, even at low temperature (0 °C). The analytical data (C, H and N) are in accordance with those expected for $[(C_6F_5)_4Pt\{Ag(PPh_3)\}_2]$ **26** but the lack of stability precludes other structural studies. At room temperature the white solid changes to an orange one and by washing it with Et_2O a dark orange residue and a colourless solution are obtained. By evaporating to dryness the solution, $[(PPh_3)(C_6F_5)_3PtAg(PPh_3)]$[8] **27** can be isolated.

The 1:2 reaction between $[NBu_4]_2[Pt(C_6F_5)_4]$ and $[Ag(OClO_3)(tht)]$ under similar conditions gives only the bimetallic complex **24**.

The 1:2 reaction between $[NBu_4]_2[Pt(C_6Cl_5)_4]$ and $[Ag(OClO_3)(PPh_3)]$ renders $Ag(C_6Cl_5)$ and a mixture of neutral and anionic platinum derivatives. Since the 1:1 reaction [see section (*f*)] did not give any bimetallic complex the above mixture was not investigated further.

(*i*) *Reactions of* $[NBu_4]_2[$*trans*-$PtCl_2(C_6X_5)_2]$ ($X = F$ *or* Cl) *with* $[Ag(OClO_3)(tht)]$ *or* $[Ag(tht)_2]ClO_4$.—The study of the reactivity of the dianionic substrata $[NBu_4]_2[$*trans*-$PtCl_2(C_6X_5)_2]$ ($X = F$ or Cl) towards $AgClO_4$ or $[Ag(OClO_3)L]$ has been the subject of previous papers and the results can be summarised as follows. (*a*) The reactions with $AgClO_4$ result in the formation of tetranuclear $[NBu_4]_2[Pt_2Ag_2Cl_4(C_6F_5)_4]$[5] for $X = F$ or the polynuclear $[NBu_4]_x[PtAg(\mu\text{-}Cl)_2(C_6Cl_5)_2]_x$[6] for $X = Cl$, the former containing Pt→Ag and Ag–Ag bonds

Table 6 Fractional atomic coordinates (× 10^4) and their e.s.d.s for $[NBu_4][(C_6F_5)_4PtAg(tht)]$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pt	2 963(1)	2 340(1)	2 398(1)	C(20)	3 580(18)	4 001(16)	1 408(10)
Ag	5 491(1)	3 328(1)	2 374(1)	C(21)	3 347(25)	4 368(18)	877(12)
C(1)	2 586(15)	569(14)	1 805(7)	C(22)	2 183(28)	3 659(24)	478(12)
C(2)	3 323(14)	243(15)	1 401(8)	C(23)	1 229(23)	2 622(21)	622(11)
C(3)	2 916(18)	−1 010(18)	956(8)	C(24)	1 522(19)	2 276(17)	1 153(10)
C(4)	1 709(20)	−1 966(16)	967(8)	F(20)	4 790(10)	4 744(9)	1 787(5)
C(5)	957(16)	−1 649(16)	1 366(7)	F(21)	4 321(14)	5 405(10)	745(5)
C(6)	1 399(13)	−469(14)	1 757(8)	F(22)	1 955(16)	4 053(13)	−55(7)
F(2)	4 550(9)	1 129(9)	1 337(5)	F(23)	105(13)	1 943(13)	220(6)
F(3)	3 747(11)	−1 244(11)	584(5)	F(24)	524(9)	1 248(10)	1 258(5)
F(4)	1 328(11)	−3 138(9)	570(5)	S(1)	7 691(6)	4 355(6)	2 168(3)
F(5)	−243(10)	−2 611(9)	1 377(5)	C(25)	8 092(28)	2 933(28)	1 865(16)
F(6)	554(8)	−250(8)	2 143(5)	C(26)	8 180(32)	2 967(33)	1 175(19)
C(7)	3 139(15)	1 715(13)	3 193(8)	C(27)	7 841(40)	3 708(42)	949(21)
C(8)	4 082(16)	1 385(15)	3 375(7)	C(28)	7 493(33)	4 452(35)	1 306(20)
C(9)	4 133(16)	933(15)	3 890(10)	N	6 999(10)	−1 021(10)	2 630(6)
C(10)	3 228(18)	775(15)	4 322(8)	C(29)	5 633(14)	−1 162(14)	2 677(8)
C(11)	2 255(15)	1 097(14)	4 182(9)	C(30)	4 524(15)	−2 447(15)	2 292(8)
C(12)	2 236(15)	1 551(13)	3 642(8)	C(31)	3 241(16)	−2 412(16)	2 428(9)
F(8)	5 037(8)	1 485(9)	2 985(5)	C(32)	2 094(18)	−3 669(18)	2 034(9)
F(9)	5 087(11)	626(11)	4 028(5)	C(33)	8 035(14)	396(14)	2 939(8)
F(10)	3 264(11)	324(9)	4 852(5)	C(34)	8 146(14)	833(15)	3 700(8)
F(11)	1 352(10)	942(9)	4 596(5)	C(35)	8 795(17)	2 328(17)	3 898(9)
F(12)	1 257(8)	1 798(9)	3 554(5)	C(36)	9 143(21)	2 854(21)	4 659(11)
C(13)	3 091(16)	3 996(14)	2 995(8)	C(37)	7 175(14)	−1 919(14)	3 010(8)
C(14)	4 153(19)	5 087(18)	3 348(8)	C(38)	8 562(15)	−1 787(15)	3 050(8)
C(15)	4 140(28)	6 192(19)	3 739(10)	C(39)	8 648(17)	−2 479(17)	3 571(9)
C(16)	2 994(31)	6 188(22)	3 807(12)	C(40)	10 004(19)	−2 465(19)	3 574(10)
C(17)	1 943(23)	5 157(21)	3 475(11)	C(41)	7 181(14)	−1 491(14)	1 913(8)
C(18)	1 943(19)	4 081(17)	3 040(9)	C(42)	6 958(15)	−808(15)	1 433(8)
F(14)	5 365(9)	5 200(9)	3 323(5)	C(43)	7 104(17)	−1 516(17)	726(9)
F(15)	5 270(13)	7 238(11)	4 084(6)	C(44)	6 922(20)	−833(20)	230(11)
F(16)	2 983(15)	7 242(11)	4 191(6)	C(45)	2 858(27)	5 546(27)	5 629(14)
F(17)	740(14)	5 141(12)	3 506(7)	C(46)	3 303(22)	4 660(21)	5 183(11)
F(18)	819(11)	3 153(11)	2 704(6)	C(47)	4 769(18)	5 392(17)	5 195(9)
C(19)	2 673(17)	2 927(14)	1 576(7)				

whilst the latter contains no M–M bonds. (*b*) The reaction with $[Ag(OClO_3)L]$ (L = PPh_3 or $PMePh_2$) at room temperature (X = F) results in the precipitation of AgCl and formation of a mixture of $[NBu_4][PtCl(C_6F_5)_2L]$ and $[Pt(C_6F_5)_2L_2]$, whilst for X = Cl, binuclear $[NBu_4][PtAgCl_2(C_6Cl_5)_2L]$ (L = PEt_3 or PPh_3) or trinuclear $[Pt(C_6Cl_5)_2\{(\mu\text{-}Cl)AgL\}_2]$ (L = $PMePh_2$, PPh_3 or PEt_3) complexes are obtained depending on the phosphine and on the molar ratio.[9] We have now studied the 1:1 reactions between $[NBu_4]_2[\textit{trans}\text{-}PtCl_2(C_6X_5)_2]$ (X = F or Cl) and $[Ag(OClO_3)(tht)]$ or $[Ag(tht)_2]ClO_4$ in CH_2Cl_2 solution, and for X = F the room-temperature reaction leads to precipitation of AgCl and no cluster is formed. From the mother-liquor NBu_4ClO_4 and some unreacted $[NBu_4]_2[\textit{trans}\text{-}PtCl_2(C_6F_5)_2]$ can be separated as insoluble residues after evaporating to dryness and extracting with OEt_2. The diethyl ether solution renders a mixture of platinum complexes which has not been investigated further. Similar results are obtained with $[Ag(tht)_2]ClO_4$.

The 1:1 reaction between $[NBu_4]_2[\textit{trans}\text{-}PtCl_2(C_6Cl_5)_2]$ and $[Ag(OClO_3)(tht)]$ or $[Ag(tht)_2]ClO_4$ renders the same polynuclear complex $[NBu_4][PtAg(\mu\text{-}Cl)_2(C_6Cl_5)_2]_x$ **28** which has previously been reported.[6]

(*j*) *Attempts to synthesise Complexes containing* Pd–Ag *Bonds*.—Since no similar complexes containing Pd–Ag bonds have been reported, we have carried out the following reactions in order to evaluate the possibility of synthesising such complexes.

(*i*) The reaction (1:1) between $[NBu_4]_2[Pd(C_6F_5)_4]$ and $[Ag(OClO_3)(tht)]$ in CH_2Cl_2 does not render the expected Pd–Ag compound and from the mother-liquors, after the elimination of NBu_4ClO_4, $[NBu_4][Pd(C_6F_5)_3(tht)]$ **30** (identified by IR and ^{19}F NMR spectroscopy)[21] has been obtained, albeit in low yield.

(*ii*) The reaction between $[NBu_4][Pd(C_6F_5)_3(tht)]$ and $[Ag(OClO_3)(PPh_3)]$ in CH_2Cl_2 at 0 °C for 10 min yields *cis*-$[Pd(C_6F_5)_2(tht)(PPh_3)]$ **29**.

The formation of **29** and **30** indicates that the Pd–Ag compounds, if formed, decompose very rapidly with rearrangement of the ligands, the palladium centre acting as an arylating agent. To date, we have not succeeded in attempts to prepare complexes containing Pd–Ag bonds. The higher ability of the palladium anionic complexes to transfer C_6X_5 groups to other metallic centres[21] and the lower tendency of palladium, relative to platinum, to form metal–metal bonds,[22] could be the cause of the different behaviour of the palladium substrata with respect to platinum in these reactions.

Experimental

The C, H and N analyses were carried out on a Perkin-Elmer 240 microanalyser. Conductivities were measured in approximately 5×10^{-4} mol dm^{-3} acetone solutions with a Philips PW 9501/01 conductimeter. The IR spectra were recorded (4000–200 cm^{-1}) on a Perkin-Elmer 599 spectrophotometer using Nujol mulls between polyethylene sheets. Literature methods were used for the preparation of the following starting materials: $Ag(C_6F_5)$,[23] $Ag(C_6Cl_5)$,[24] $[NBu_4][MCl(C_6F_5)_2L]$ (M = Pt or Pd),[14] $[NBu_4][MCl(C_6Cl_5)_2L]$ (M = Pt or Pd),[25] $[NBu_4][Pd(C_6F_5)_3(tht)]$,[21] $[NBu_4]_2[M(C_6F_5)_4]$ (M = Pt or Pd),[21] $[NBu_4]_2[Pt(C_6Cl_5)_4]$,[25] $[NBu_4]_2[\textit{trans}\text{-}MCl_2(C_6F_5)_2]$ (M = Pt or Pd)[21] and $[Ag(OClO_3)(PPh_3)]$.[8] All the reactions were carried out with exclusion of light.

Table 7 Fractional atomic coordinates (× 10^4) and their e.s.d.s for $[NBu_4][(C_6Cl_5)_2(C_6F_5)_2PtAg(tht)]$

Atom	*x*	*y*	*z*
Pt	−1 272(1)	7 608(1)	7 489(1)
Ag	1 076(2)	7 967(2)	7 302(1)
C(1)	−1 222(17)	8 652(17)	6 691(10)
C(2)	−202(17)	9 664(18)	6 559(10)
C(3)	−285(19)	10 365(19)	6 039(12)
C(4)	−1 323(21)	9 990(20)	5 621(12)
C(5)	−2 370(19)	8 956(20)	5 732(12)
C(6)	−2 335(18)	8 308(18)	6 257(11)
Cl(2)	1 186(5)	10 207(5)	7 021(3)
Cl(3)	1 045(6)	11 620(5)	5 874(3)
Cl(4)	−1 391(7)	10 853(7)	4 997(4)
Cl(5)	−3 716(6)	8 486(7)	5 213(3)
Cl(6)	−3 691(5)	7 082(6)	6 389(3)
C(7)	−861(18)	9 086(18)	8 179(11)
C(8)	220(19)	9 630(19)	8 633(11)
C(9)	449(21)	10 626(21)	9 147(12)
C(10)	−395(21)	11 081(21)	9 160(12)
C(11)	−1 527(21)	10 496(21)	8 794(12)
C(12)	−1 692(19)	9 549(19)	8 292(11)
Cl(8)	1 378(5)	9 130(6)	8 619(3)
Cl(9)	1 801(6)	11 245(6)	9 669(3)
Cl(10)	−163(8)	12 248(7)	9 774(4)
Cl(11)	−2 610(8)	11 040(7)	8 875(4)
Cl(12)	−3 078(5)	8 922(6)	7 801(3)
C(13)	−1 359(18)	6 640(18)	8 277(10)
C(14)	−701(18)	6 048(18)	8 436(11)
C(15)	−832(22)	5 281(22)	8 959(13)
C(16)	−1 797(19)	5 100(20)	9 374(12)
C(17)	−2 508(19)	5 666(19)	9 256(11)
C(18)	−2 329(20)	6 424(20)	8 756(12)
F(14)	267(10)	6 113(10)	8 042(6)
F(15)	−100(13)	4 740(13)	9 053(7)
F(16)	−1 963(13)	4 383(13)	9 889(7)
F(17)	−3 438(12)	5 536(12)	9 676(7)
F(18)	−3 130(11)	6 902(11)	8 676(6)
C(19)	−1 808(18)	6 021(18)	6 828(11)
C(20)	−1 215(21)	5 836(21)	6 292(12)
C(21)	−1 639(23)	4 747(23)	5 881(14)
C(22)	−2 779(22)	3 822(22)	6 004(13)
C(23)	−3 386(19)	3 918(19)	6 505(11)
C(24)	−2 917(18)	5 029(18)	6 897(11)
F(20)	−150(12)	6 766(12)	6 094(7)
F(21)	−977(15)	4 662(18)	5 364(8)
F(22)	−3 176(15)	2 717(13)	5 594(8)
F(23)	−4 478(12)	3 005(11)	6 624(7)
F(24)	−3 632(11)	5 077(10)	7 406(6)
S	3 006(6)	7 923(6)	7 012(4)
C(25)	4 180(26)	9 490(26)	7 259(15)
C(26)	4 801(34)	9 900(33)	6 596(20)
C(27)	3 932(35)	9 355(34)	6 062(20)
C(28)	3 130(26)	7 995(27)	6 108(15)
N	2 818(15)	4 368(16)	7 865(9)
C(29)	3 716(20)	5 720(21)	8 100(12)
C(30)	3 518(23)	6 142(24)	8 830(13)
C(31)	4 287(31)	7 529(31)	8 962(18)
C(32)	4 020(42)	8 161(43)	9 465(25)
C(33)	1 484(21)	4 288(21)	7 780(12)
C(34)	498(21)	3 063(20)	7 500(12)
C(35)	−740(26)	3 143(26)	7 380(15)
C(36)	−1 797(25)	1 998(25)	7 036(15)
C(37)	2 844(21)	3 506(21)	8 396(12)
C(38)	4 102(22)	3 596(22)	8 567(13)
C(39)	4 180(26)	2 460(25)	8 250(15)
C(40)	5 425(28)	2 475(27)	8 454(16)
C(41)	3 241(18)	4 012(18)	7 191(11)
C(42)	3 087(20)	4 695(20)	6 634(12)
C(43)	3 661(23)	4 287(23)	5 996(14)
C(44)	3 373(27)	4 708(27)	5 365(16)

Table 8 Selected bond distances (Å) and angles (°) in the complexes **24** and **25**

$[NBu_4][(C_6F_5)_4PtAg(tht)]$ **24**		$[NBu_4][cis\text{-}(C_6Cl_5)_2\text{-}(C_6F_5)_2PtAg(tht)]$ **25**	
Ag–Pt	2.641(1)		2.692(2)
Pt–C(1)	2.054(16)		2.123(22)
Pt–C(7)	2.035(18)		2.060(21)
Pt–C(13)	2.040(17)		2.038(23)
Pt–C(19)	2.092(18)		2.105(20)
Ag–S	2.401(6)		2.424(8)
Ag ··· F(2)	2.738(9) [1.38]*	Ag ··· Cl(2)	2.827(7) [1.21]
Ag ··· F(8)	2.712(12) [1.37]	Ag ··· Cl(8)	2.827(6) [1.21]
Ag ··· F(14)	2.704(10) [1.37]	Ag ··· F(14)	2.671(12) [1.34]
Ag ··· F(20)	2.722(14) [1.37]	Ag ··· F(20)	2.778(12) [1.37]
C(1)–Pt–Ag	93.0(4)	C(1)–Pt–Ag	90.1(6)
C(7)–Pt–Ag	91.5(5)	C(7)–Pt–Ag	98.2(6)
C(13)–Pt–Ag	94.3(5)	C(13)–Pt–Ag	91.7(6)
C(19)–Pt–Ag	91.5(5)	C(19)–Pt–Ag	85.2(6)
C(1)–Pt–C(7)	87.1(6)	C(1)–Pt–C(7)	90.1(8)
C(7)–Pt–C(13)	92.3(7)	C(7)–Pt–C(13)	88.0(9)
C(13)–Pt–C(19)	88.0(7)	C(13)–Pt–C(19)	89.0(8)
C(19)–Pt–C(1)	92.3(6)	C(19)–Pt–C(1)	92.7(8)
Pt–Ag–S	168.6(2)	Pt–Ag–S	169.3(2)

* ρ Values in square brackets.

$[Ag(tht)_2]ClO_4$.—The salt $AgClO_4$ (1 g) was dissolved in tht (5 cm^3) and then stirred at room temperature for 1 h. The solution was evaporated to dryness and the white residue was washed with hexane (15 cm^3). The resulting white solid was dissolved in CH_2Cl_2 (5 cm^3) and hexane (30 cm^3) was added. Partial evaporation rendered a white solid which was filtered off. In order to eliminate the excess of tht, the white solid was treated in the same way twice, yielding $[Ag(tht)_2]ClO_4$ (80% yield) [Found (Calc.): C, 24.65 (25.05); H, 4.25 (4.20%)]; Λ_M = 138 ohm^{-1} cm^2 mol^{-1}.

$[Ag(OClO_3)(tht)]$.—A mixture of $AgClO_4$ (0.2 g, 0.965 mmol), tht (85 μl, 0.965 mmol), and OEt_2 (4 cm^3) was stirred at room temperature for 15 min. The resulting white solid was filtered off and washed with hexane (25 cm^3). Yield 85% [Found (Calc.): C, 16.30 (16.25); H, 2.70 (2.75%)]; Λ_M = 132 ohm^{-1} cm^2 mol^{-1}.

$[NBu_4][Pt(C_6F_5)_2(C_6Cl_5)L]$ (L = tht, **1**; PPh_3, **2**; $PMePh_2$, **3**; *or* py, **4**).—A typical preparation (L = tht) was as follows. To a CH_2Cl_2 (20 cm^3) solution of $[NBu_4][cis\text{-}PtCl(C_6F_5)_2(tht)]$ (0.16 g, 0.17 mmol) was added $Ag(C_6Cl_5)$ (0.0638 g, 0.178 mmol) and the mixture was stirred at room temperature for 4 h. The AgCl was filtered off, the resulting solution was evaporated to dryness and the residue was treated with isopropyl alcohol, giving white solid **1** which was washed with hexane, 86% yield. Complexes **2**–**4** were obtained similarly by using the corresponding starting materials; **4** was recrystallised from methanol–hexane. Table 9 collects pertinent preparative information.

Complex **4** was also prepared as follows. To a solution of $[NBu_4][cis\text{-}Pt(C_6F_5)_2(C_6Cl_5)(tht)]$ (0.15 g, 0.135 mmol) in CH_2Cl_2–toluene (1 : 6, *ca.* 30 cm^3) was added pyridine (10.98 μl, 0.135 mmol). The solution was refluxed for 8 h and then evaporated to dryness. The residue was washed with hexane (3 × 5 cm^3) and treated with isopropyl alcohol, giving a white solid **4** (66% yield).

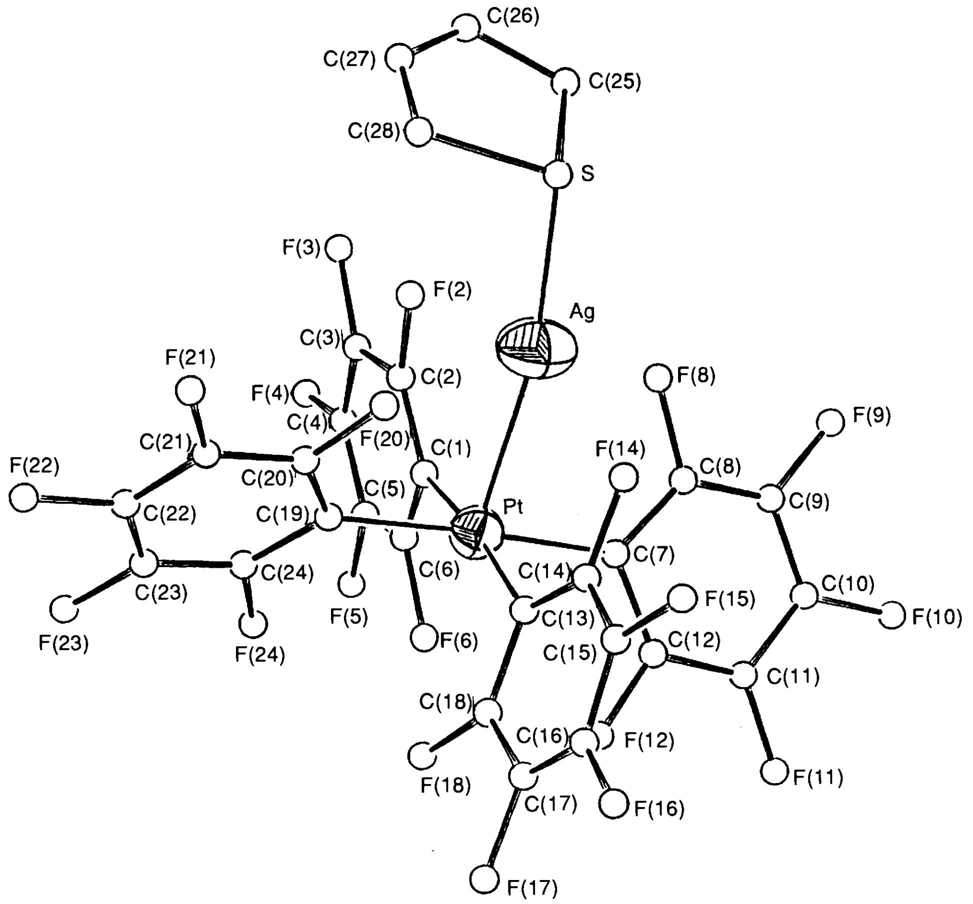

Fig. 2 ORTEP drawing of $[(C_6F_5)_4PtAg(tht)]^-$ **24**

Table 9 Some experimental details for the synthesis of complexes **2**–**11**

Complex	Amount (g, mmol) $[NBu_4][MCl(C_6X_5)_2L]$	$Ag(C_6X'_5)$	Yield (%)
2	0.17, 0.159[a]	0.0567, 0.159[b]	92
3	0.20, 0.198[a]	0.0706, 0.198[b]	88
4	0.15, 0.167[a]	0.0598, 0.167[b]	86
5	0.207, 0.211[c]	0.0753, 0.211[b]	92
6	0.163, 0.177[c]	0.063, 0.177[b]	91
8	0.3, 0.243[d]	0.0668, 0.243[e]	96
10	0.15, 0.154[f]	0.0425, 0.154[e]	78
11	0.10, 0.087[f]	0.0240, 0.087[e]	72

[a] M = Pt, X = F or Cl. [b] X′ = Cl. [c] M = Pd, X = F. [d] M = Pt, X = Cl. [e] X′ = F. [f] M = Pd, X = Cl.

$[NBu_4][Pd(C_6F_5)_2(C_6Cl_5)L]$ (L = PPh_3, **5**; *or* $PMePh_2$, **6**).—Complexes **5** and **6** were prepared as for **1**–**4**. Some preparative information is collected in Table 9.

$[NBu_4][M(C_6F_5)(C_6Cl_5)_2L]$ (M = Pt, L = tht, **7**; PPh_3, **8**; *or* $PMePh_2$, **9**; M = Pd, L = tht, **10**; *or* PPh_3, **11**).—*Complex* **7**. To a CH_2Cl_2 solution (20 cm^3) of $[NBu_4][PtCl(C_6Cl_5)_2(tht)]$ (0.2 g, 0.289 mmol) was added $Ag(C_6F_5)$ (0.0517 g, 0.289 mmol) and the mixture was stirred at room temperature for 1 h. The AgCl formed was filtered off and the resulting solution was evaporated to dryness. The white residue was treated with isopropyl alcohol (10 cm^3) and washed with hexane; 80% yield. Complexes **8**, **10** and **11** were prepared similarly. For complexes **10** and **11**, after evaporating the solution to dryness, the resulting solids were treated with hexane instead of isopropyl alcohol. Table 9 collects pertinent preparative information.

Complex **9** was prepared as follows. To a solution of $[NBu_4][Pt(C_6F_5)(C_6Cl_5)_2(tht)]$ (0.13 g, 0.109 mmol) in toluene (25 cm^3) was added $PMePh_2$ (21.84 μl, 0.109 mmol) and the mixture was refluxed for 8 h. The solution was evaporated to dryness and the residue washed with hexane (3 × 5 cm^3). The resulting solid was treated with isopropyl alcohol giving a white solid **9** in 62% yield.

$[NBu_4]_2[$*cis*-$Pt(C_6F_5)_2(C_6Cl_5)_2]$ **12**.—(*a*) To a solution of $Li(C_6F_5)$ (4.246 mmol) in diethyl ether (60 cm^3) at −78 °C was added $[NBu_4][$*cis*-$PtCl(C_6Cl_5)_2(tht)]$ (0.45 g, 0.4246 mmol) and the mixture was stirred for 14 h at room temperature. The solid obtained after filtration was dissolved in CH_2Cl_2 (20 cm^3) and the solution evaporated to dryness. The residue was treated with isopropyl alcohol (5 cm^3) yielding a white solid **12** in 47% yield. The addition of NBu_4Br to the mother-liquors did not allow the isolation of more product.

(*b*) To a Et_2O (40 cm^3) solution of $Li(C_6Cl_5)$ (7.42 mmol), at −78 °C was added *cis*-$[Pt(C_6F_5)_2(thf)_2]$ (1 g, 1.47 mmol). The mixture was stirred at −78 °C for 15 min and then allowed slowly to reach room temperature while stirring for 10 h. The resulting suspension was evaporated to dryness, the residue was treated with CH_2Cl_2 (30 cm^3) and the solution obtained was evaporated to dryness. The residue was dissolved in Pr^iOH (15 cm^3) and NBu_4Br (0.9 g) was added so that a white solid, which was washed with Pr^iOH (5 cm^3), precipitated. Yield 75%.

$[NBu_4]_2[$*trans*-$Pd(C_6F_5)_2(C_6Cl_5)_2]$ **13**.—(*a*) The procedure was as described for complex **12**; $Li(C_6F_5)$ (4.94 mmol), $[NBu_4]_2[$*cis*-$PdCl(C_6Cl_5)_2(tht)]$ (0.6 g, 0.417 mmol), diethyl ether (40 cm^3). Yield 25%.

(*b*) To a solution of $Li(C_6Cl_5)$ (3.34 mmol) in Et_2O (40 cm^3) at −78 °C and under a nitrogen atmosphere was added $[NBu_4]_2[\{Pd(\mu\text{-}Cl)(C_6F_5)_2\}_2]$ (0.6 g, 0.417 mmol) and NBu_4Br

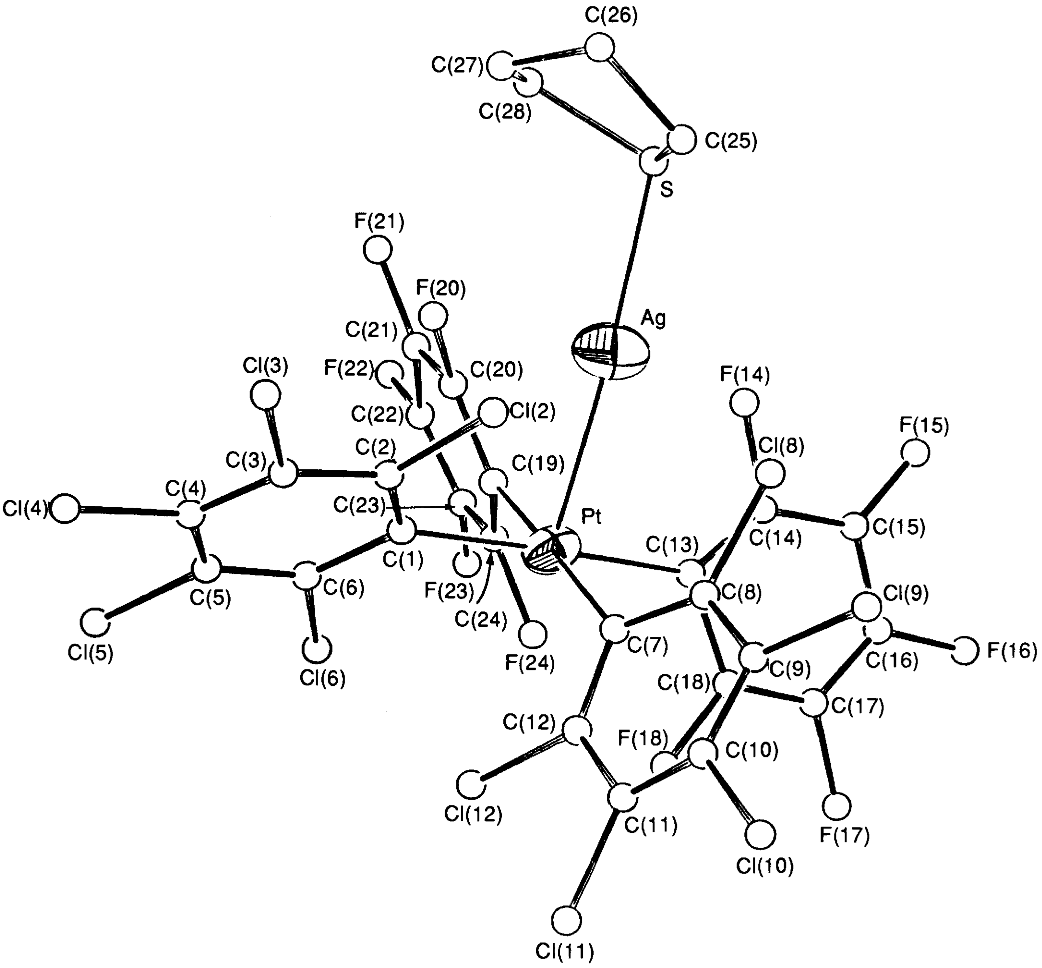

Fig. 3 ORTEP drawing of $[(C_6Cl_5)_2(C_6F_5)_2PtAg(tht)]^-$ **25**

Table 10 Some experimental details for the synthesis of complexes **14**–**21**

		Amount (g, mmol)		
L	Complex	$[NBu_4][Pt(C_6F_5)_2$-$(C_6Cl_5)L]$	$[Ag(OClO_3)$-$(PPh_3)]$	Yield (%)
tht	**14**	0.18, 0.162	0.076, 0.162	78
PPh_3	**15**	0.11, 0.086	0.040, 0.086	73
py	**16**	0.2, 0.182	0.085, 0.182	72
		$[NBu_4][Pt(C_6F_5)$-$(C_6Cl_5)_2L]$		
tht	**17**	0.14, 0.117	0.0551, 0.117	76
PPh_3	**18**	0.15, 0.11	0.0515, 0.11	77
		$[NBu_4][Pt$ $(C_6Cl_5)_3L]$		
tht	**19**	0.1, 0.079	0.037, 0.079	68
PPh_3	**20**	0.1, 0.069	0.033, 0.069	70
py	**21**	0.2, 0.0158	0.073, 0.158	75

(0.269 g, 0.835 mmol). The mixture was stirred for 8 h at room temperature. After evaporating to dryness, the residue was extracted with acetone and the solution again evaporated to dryness. By addition of isopropyl alcohol (25 cm^3) a white solid **13** (73% yield) was recovered.

$[L(C_6Cl_5)(C_6F_5)_2PtAg(PPh_3)]$ (L = tht, **14**; PPh_3, **15**; *or* py, **16**).—To a solution of $[NBu_4]_2[Pt(C_6F_5)_2(C_6Cl_5)L]$ in CH_2Cl_2 (25 cm^3) was added $[Ag(OClO_3)(PPh_3)]$ (molar ratio 1:1) and the mixture was stirred at 0 °C for 30 min. The solution was evaporated to dryness and the residue extracted (L = PPh_3 or py) with diethyl ether. The insoluble NBu_4ClO_4 was filtered off and after evaporating the solution to dryness the residue was treated with hexane. For L = tht the final product **14** was not soluble in diethyl ether so that the elimination of NBu_4ClO_4 was carried out by washing the residue with isopropyl alcohol (3 × 2 cm^3) in which **14** is insoluble but NBu_4ClO_4 is soluble. Details of the respective preparations are collected in Table 10. Complexes **17**–**21** were obtained similarly.

$[NBu_4][(C_6F_5)_4PtAgL]$.—L = OEt_2, **22**. To a solution of $AgClO_4$ (0.046 g, 0.223 mmol) in CH_2Cl_2 (20 cm^3) was added $[NBu_4]_2[Pt(C_6F_5)_4]$ (0.3 g, 0.223 mmol). The resulting solution was stirred at room temperature for 5 min and then evaporated to dryness. By adding diethyl ether a residue of NBu_4ClO_4 (separated by filtration) and a yellow solution were obtained. The solution was evaporated to dryness and the oily residue was washed with hexane and then dried under vacuum yielding complex **22** (0.171 g, 50% yield).

L = PPh_3, **23**. Under similar conditions $[NBu_4]_2[Pt(C_6F_5)_4]$ (0.15 g, 0.111 mmol), $[Ag(OClO_3)(PPh_3)]$ (0.0522 g, 0.111 mmol) and CH_2Cl_2 (20 cm^3) rendered **23** (0.130 g, 68% yield).

L = tht, **24**. (*a*) To a suspension of $[Ag(OClO_3)(tht)]$ (0.033 g, 0.111 mmol) in CH_2Cl_2 (25 cm^3) was added $[NBu_4]_2[Pt(C_6F_5)_4]$ (0.15 g, 0.111 mmol). The mixture was stirred at room temperature for 5 min and then evaporated to dryness. The white residue was treated with Et_2O (40 cm^3) and the insoluble NBu_4ClO_4 was removed by filtration. The solution was evaporated to dryness and the resulting white solid was washed with hexane yielding **24** (0.1371 g, 80% yield).

(*b*) When the reaction was carried out in a 2:1 molar ratio complex **24** was also obtained: $[Ag(OClO_3)(tht)]$ (0.065 g, 0.222 mmol), $[NBu_4]_2[Pt(C_6F_5)_4]$ (0.15 g, 0.111 mmol) and CH_2Cl_2 (15 cm^3). Yield 87%.

(*c*) Under the same conditions the reaction between $[NBu_4]_2[Pt(C_6F_5)_4]$ (0.150 g, 0.111 mmol) and $[Ag(tht)_2]ClO_4$ (0.043 g, 0.111 mmol) (molar ratio 1:1) rendered complex **24** in 79% yield.

$[NBu_4][(C_6Cl_5)_2(C_6F_5)_2PtAg(tht)]$ **25**.—The salt $[NBu_4]_2$-[*cis*-$Pt(C_6F_5)_2(C_6Cl_5)_2$] (0.2 g, 0.132 mmol), $[Ag(OClO_3)(tht)]$ (0.039 g, 0.132 mmol) and CH_2Cl_2 (20 cm^3) were stirred at 0 °C for 1 h and then evaporated to dryness. The residue was treated with Et_2O (30 cm^3) and, after filtering off the insoluble residue containing NBu_4ClO_4 and **25**, it was washed with Pr^iOH (3 × 5 cm^3), yielding a white solid, **25**. From the ethereal solution, **25** could also be obtained. Yield 76%.

Reaction between $[NBu_4]_2[Pt(C_6F_5)_4]$ *and* $[Ag(OClO_3)(PPh_3)]$ (*molar ratio* 1:2).—To a dichloromethane solution (20 cm^3) of $[NBu_4]_2[Pt(C_6F_5)_4]$ (0.3 g, 0.222 mmol) was added $[Ag(OClO_3)(PPh_3)]$ (0.209 g, 0.445 mmol) and the mixture was stirred at room temperature for 1 h. The resulting solution was evaporated to dryness and the residue was treated with Et_2O. The ether solution, after filtering off the insoluble NBu_4ClO_4, was evaporated to dryness yielding a very unstable white solid the analysis of which was in accordance with $[(C_6F_5)_4Pt\{Ag(PPh_3)\}_2]$ **26**. At room temperature the white solid turns orange in a few minutes. Treatment of this orange solid with Et_2O (10 cm^3) renders an insoluble dark orange solid and a colourless solution. After evaporation to dryness a white solid **27** was obtained.[8]

Reaction between $[NBu_4]_2$[*trans*-$PtCl_2(C_6Cl_5)_2$] *and* $[Ag(OClO_3)(tht)]$.—To a suspension of $[Ag(OClO_3)(tht)]$ (0.0355 g, 0.120 mmol) in CH_2Cl_2 (30 cm^3) was added $[NBu_4]_2$[*trans*-$PtCl_2(C_6Cl_5)_2$] (0.16 g, 0.120 mmol) and after stirring for 5 min at room temperature the resulting yellow solution was evaporated to dryness. The yellowish solid was treated with Pr^iOH (3 × 10 cm^3) in order to eliminate NBu_4ClO_4. The resulting pale yellow solid was identified as $[NBu_4]_x[PtAg(\mu\text{-}Cl)_2(C_6Cl_5)_2]_x$ **28**. Yield 79%.

The reaction between $[NBu_4]_2$[*trans*-$PtCl_2(C_6Cl_5)_2$] (0.15 g, 0.111 mmol), $[Ag(tht)_2]ClO_4$ (0.056 g, 0.111 mmol) and CH_2Cl_2 (30 cm^3) under similar conditions rendered the same polynuclear compound **28** (0.0792 g, 64% yield).

Reaction between $[NBu_4][Pd(C_6F_5)_3(tht)]$ *and* $[Ag(OClO_3)(PPh_3)]$.—To a CH_2Cl_2 (30 cm^3) solution of $[NBu_4][Pd(C_6F_5)_3(tht)]$ (0.2 g, 0.21 mmol) at 0 °C was added $[Ag(OClO_3)(PPh_3)]$ (0.1 g, 0.21 mmol) and the mixture was stirred at this temperature for 10 min. The resulting solution was evaporated to dryness and the residue was treated with diethyl ether (15 cm^3) at 0 °C. From the ether solution, *cis*-$[Pd(C_6F_5)_2(tht)(PPh_3)]$ **29** precipitated in a few seconds in 46% yield.

Reaction between $[NBu_4]_2[Pd(C_6F_5)_4]$ *and* $[Ag(tht)_2]ClO_4$.—Over a solution of $[Ag(tht)_2]ClO_4$ (0.046 g, 0.119 mmol) in CH_2Cl_2 was added $[NBu_4]_2[Pd(C_6F_5)_4]$ (0.15 g, 0.119 mmol) and the solvent was quickly removed under vacuum. The residue was treated with OEt_2 and the solid mixture of NBu_4ClO_4 and $Ag(C_6F_5)$ was filtered off. The remaining solution was evaporated to dryness and the resulting solid $[NBu_4][Pd(C_6F_5)_3(tht)]$ was washed with hexane and filtered off.

Structure Determination of Complexes $[(tht)(C_6Cl_5)(C_6F_5)_2PtAg(PPh_3)]$ **14**, $[NBu_4][(C_6F_5)_4PtAg(tht)]\cdot 0.5C_6H_{14}$ **24** *and* $[NBu_4]$[*cis*-$(C_6Cl_5)_2(C_6F_5)_2PtAg(tht)$] **25**.—*Crystal data.* **14**, $C_{40}H_{23}AgCl_5F_{10}PPtS$, M = 1236.24, monoclinic, space group $P2_1/n$ (non-standard setting of no. 14), a = 14.350(3), b = 17.750(5), c = 17.733(4) Å, β = 110.35(2)°, U = 4235.03 $Å^3$, $F(000)$ = 2376, μ(Mo-Kα) = 40.47 cm^{-1}, Z = 4, D_c = 1.938 g cm^{-3}. Very thin plate of 0.035 × 0.26 × 0.23 mm.

24, $C_{44}H_{44}AgF_{20}NPtS\cdot 0.5C_6H_{14}$, M = 1344.86, triclinic, space group $P\bar{1}$ (no. 2), a = 11.670(8), b = 12.235(5), c = 20.92(10) Å, α = 103.87(3), β = 91.64(4), γ = 116.95(2)°, U = 2547.8 $Å^3$, $F(000)$ = 1322, μ(Mo-Kα) = 31.21 cm^{-1}, Z = 2, D_c = 1.758 g cm^{-3}. Crystal size 0.08 × 0.17 × 0.25 mm.

25, $C_{44}H_{44}AgCl_{10}F_{10}NPtS$, M = 1465.7, triclinic, space group $P\bar{1}$ (no 2), a = 11.976(2), b = 12.398(3), c = 19.996(4) Å, α = 94.812(11), β = 91.950(10), γ = 116.016(10)°, U = 2650.47 $Å^3$, $F(000)$ = 1432, μ(Mo-Kα) = 34.48 cm^{-1}, Z = 2, D_c = 1.842 g, cm^{-3}. Crystal size 0.12 × 0.12 × 0.08 mm.

Data collection and processing. Siemens/Stoe AED2 four-circle diffractometer, graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å). Scan method ω–2θ. Room temperature. Data corrected for Lorentz and polarisation effects. Three check reflections were measured every 45 min. Complex **14** only showed 4% loss of intensity during the data collection, however **24** showed 33% decay and **25** 25% decay. Interpolative decay corrections were applied.

Complex **14**. Scan range $4 \leqslant 2\theta \leqslant 50°$. Index range $+h$, $+k$, $\pm l$, profile-fitted intensities,[26] total number of reflections 8036, unique reflections 6248, 2766 with $F_o \geqslant 5\sigma(F_o)$ used for all calculations. Absorption corrections (ψ-scan method, 11 reflections). Transmission factors 0.6913–0.3546.

Complex **24**. Scan range $4 \leqslant 2\theta \leqslant 50°$. Index range $+h$, $\pm k$, $\pm l$, total number of reflections 9454, unique reflections 7666, 3591 with $F_o \geqslant 5\sigma(F_o)$ used for all calculations. Absorption correction.[27] Transmission factors 1.256–0.596.

Complex **25**. Scan range $4 \leqslant 2\theta \leqslant 47°$. Index range $+h$, $\pm k$, $\pm l$, profile-fitted intensities.[26] Total number of reflections 8214, unique reflections 6748, 2624 with $F_o \geqslant 6\sigma(F_o)$ used for all calculations. Absorption correction.[27] Transmission factors 0.844–0.501.

Structure analysis and refinement. Heavy-atom method, Program system SHELX 76.[28]

Complex **14**. Refinement on F to R = 0.063 and R' = 0.060. All atoms excluding the carbon atoms were treated with anisotropic displacement parameters. The C_6 rings of the PPh_3 group were idealised as regular, planar hexagons (C–C 1.395 Å); 296 parameters. Weighting scheme $w^{-1} = \sigma^2(F_o) + 0.001\,194F^2$. Shift/error 0.00; four peaks higher than 1 e $Å^{-3}$ in final Fourier difference map, all close to the heavy atoms and with no chemical significance.

Complex **24**. Refinement on F to R = 0.049 and R' = 0.049. All atoms of the anionic part of the compound excluding the four carbon atoms of the tht group were treated as anisotropic, the remaining atoms as isotropic; 520 parameters. Weighting scheme $w^{-1} = \sigma^2(F_o) + 0.001\,72F^2$. Maximum shift/error 0.009; highest peak in difference map 0.92 e $Å^{-3}$.

Complex **25**. Refinement on F to R = 0.051 and R' = 0.052. All atoms excluding carbon were treated as anisotropic; 393 parameters. Weighting scheme $w^{-1} = \sigma^2(F_o) + 0.002\,46F^2$. Maximum shift/error 0.009; highest peak in difference map 0.84 e $Å^{-3}$.

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

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References

1 R. Usón, J. Forniés and M. Tomás, *J. Organomet. Chem.*, 1988, **358**, 525 and refs. therein.

2 R. Usón, J. Forniés, M. Tomás and J. M. Casas, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 748.

3 G. J. Arsenault, C. M. Anderson and R. J. Puddephatt, *Organometallics*, 1988, **7**, 2094.

4 R. Usón and J. Forniés, *Adv. Organomet. Chem.*, 1988, **28**, 219 and refs. therein.

5 R. Usón, J. Forniés, B. Menjón, F. A. Cotton, L. R. Falvello and M. Tomás, *Inorg. Chem.*, 1985, **24**, 4651.

6 R. Usón, J. Forniés, M. Tomás, J. M. Casas, F. A. Cotton and L. R. Falvello, *Inorg. Chem.*, 1986, **25**, 4519.

7 R. Usón, J. Forniés, M. Tomás, J. M. Casas, F. A. Cotton and L. R. Falvello, *Inorg. Chem.*, 1987, **26**, 3482.

8 F. A. Cotton, L. R. Falvello, R. Usón, J. Forniés, M. Tomás, J. M. Casas and I. Ara, *Inorg. Chem.*, 1987, **26**, 1366.

9 R. Usón, J. Forniés, M. Tomás, I. Ara and J. M. Casas, *Inorg. Chem.*, 1989, **28**, 2388.

10 M. D. Rausch and F. E. Tibbets, *Inorg. Chem.*, 1970, **9**, 512.

11 R. Usón, J. Forniés and F. Martínez, *J. Organomet. Chem.*, 1977, **132**, 429.

12 E. Maslowsky, jun., *Vibrational Spectra of Organometallic Compounds*, Wiley, New York, 1977, p. 437.

13 J. Casabó, J. M. Coronas and J. Sales, *Inorg. Chim. Acta*, 1974, **11**, 5.

14 R. Usón, J. Forniés, P. Espinet, F. Martinez and M. Tomás, *J. Chem. Soc., Dalton Trans.*, 1981, 463.

15 R. Usón, J. Forniés, M. Tomás and B. Menjón, *Organometallics*, 1986, **5**, 1581.

16 M. Nardelli, *Comput. Chem.*, 1983, **7**, 95.

17 R. Usón, J. Forniés, M. Tomás, J. M. Casas, F. A. Cotton, L. R. Falvello and R. Llusar, *Organometallics*, 1988, **7**, 2279.

18 L. Pauling, *The Nature of the Chemical Bond*, 3rd edn., Cornell University Press, Ithaca, NY, 1960, p. 403.

19 B. Norén and Å. Oskarsson, *Acta Chem. Scand., Ser. A*, 1984, **38**, 479.

20 R. Usón, A. Laguna, M. Laguna, B. R. Manzano, P. G. Jones and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1984, 285.

21 R. Usón, J. Forniés, F. Martínez and M. Tomás, *J. Chem. Soc., Dalton Trans.*, 1980, 888.

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

23 R. Usón and A. Laguna, *Organometallic Synthesis*, eds. R. B. King and J. J. Eisch, Elsevier, New York, 1986, vol. 3, p. 331.

24 R. Usón, A. Laguna and A. Abad, *J. Organomet. Chem.*, 1983, **246**, 341.

25 R. Usón, J. Forniés, F. Martínez, M. Tomás and I. Reoyo, *Organometallics*, 1983, **2**, 1386.

26 W. Clegg, *Acta Crystallogr., Sect. A*, 1981, **37**, 22.

27 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.

28 G. M. Sheldrick, SHELX 76, Program for Crystal Structure Determination, University of Cambridge, Cambridge, 1976.

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