arrangements of the four metal atoms with quadruply bridging phosphinidene ligands on the opposite sides of the cluster, but with only one bridging carbonyl ligand. In both of these compounds the carbonyl-bridged metal–metal bond is significantly shorter than the other three metal–metal bonds. Vahrenkamp has proposed that this shortening could be due to the existence of a localized multiple bond, but more recently has acknowledged that this could also be due to the influence of the bridging carbonyl ligand. The structure of **7** seems to support the latter explanation, since compound **7** contains two carbonyl-bridged metal–metal bonds and both of these metal–metal bonds are significantly shorter than the others. It should be mentioned that even though the clusters **7**–**9** are unsaturated according to the EAN rule, they do obey the polyhedral skeletal electron pair theory and the latter does not predict localized unsaturation.[23] Nevertheless, the high reactivity of **7** may be due to its unsaturation. Vahrenkamp has shown that the iron clusters undergo facile ligand substitution via a ligand addition/elimination sequence.[24] A simple mechanism could be operative for compounds **7** and **8**, but we have not been able to isolate any ligand adducts of these.

The formation and structure of compound **7** contrasts significantly with that of known osmium chemistry.[5] For example, the reaction of $Os_3(CO)_9(\mu_3\text{-}S)_2$ with $Os(CO)_5$ yields the cluster $Os_4(CO)_{13}(\mu_3\text{-}S)_2$.[6a] This loses CO to form $Os_4(CO)_{12}(\mu_3\text{-}S)_2$, which contains a butterfly tetrahedral cluster of osmium atoms. We have recently described a remarkable transformation of a butterfly cluster into a square,[25] but to date, the compound $Os_4(CO)_{11}(\mu_4\text{-}S)_2$ has not been prepared.

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Supplementary Material Available: Tables of anisotropic thermal parameters (*U* values) and hydrogen atom parameters (2 pages); tables of calculated and observed structure factors (26 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding,
Texas A&M University, College Station, Texas 77843, and Departamento de Quimica Inorganica,
Instituto de Ciencias de Materiales de Aragon, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain

Synthesis, Structure, and Reactivity of $(NBu_4)_x[Pt(C_6Cl_5)_2(\mu\text{-}Cl)_2Ag]_x$, a Novel Chain Polymeric Pt–Ag Compound. Structure of $(NBu_4)[PtAgCl_2(C_6Cl_5)_2(PPh_3)]$ and $[Pt(C_6Cl_5)_2(\mu\text{-}Cl)_2Ag_2(PPh_2Me)_2]$

Rafael Usón,* Juan Forniés, Milagros Tomás, José M. Casas, F. Albert Cotton,* and Larry R. Falvello

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Reaction of $(NBu_4)_2[\textit{trans}\text{-}PtCl_2(C_6Cl_5)_2]$ with $AgNO_3$ or $AgClO_4$ yields the novel polymeric $(NBu_4)_x[Pt(C_6Cl_5)_2(\mu\text{-}Cl)_2Ag]_x$ (I), which reacts with neutral ligands L to give either anionic binuclear complexes of the type $(NBu_4)[PtAgCl_2(C_6Cl_5)_2L]$, L = PPh_3 (II), PEt_3 (III), $AsPh_3$ (IV), $SbPh_3$ (V), or neutral trinuclear ones of the type $[PtAg_2Cl_2(C_6Cl_5)_2L_2]$, L = $PMePh_2$ (VI), $PEtPh_2$ (VII), PMe_2Ph (VIII). The structures of the parent compound I and one example of each of the last two types, II and VI, have been solved by single-crystal X-ray diffraction. A direct Pt–Ag bond is present in complex II but not in I or VI. Ag···Cl contacts with *o*-chlorine atoms of the C_6Cl_5 group present in complexes I and II appear to contribute to the stability of these compounds. Compound I gives monoclinic crystals, space group $C2/c$, with a = 19.300 (3) Å, b = 26.523 (4) Å, c = 8.450 (2) Å, β = 103.53 (2)°, V = 4205 (2) Å^3, and Z = 4. The crystal structure was refined to final residuals of R = 0.0610 and R_w= 0.0651. Compound II crystallizes in the monoclinic system, space group $P2_1/n$, with a = 20.076 (6) Å, b = 28.507 (5) Å, c = 9.479 (3) Å, β = 97.17 (3)°, V = 5382 (5) Å^3, and Z = 4. The structure was refined to residuals of R = 0.0433 and R_w = 0.0547. Crystals of compound VI are triclinic, space group $P\bar{1}$, with a = 10.821 (3) Å, b = 12.462 (3) Å, c = 9.268 (2) Å, α = 109.23 (2)°, β = 99.87 (2)°, γ = 70.85 (2)°, V = 1111.9 (4) Å^3, and Z = 1. The structure was refined to residuals of R = 0.0279 and R_w = 0.0423.

Introduction

Several mixed heteronuclear complexes containing silver atoms and other transition metals are known.[1–12] A few complexes containing Pt and Ag had been structurally characterized prior to 1980, and some of them showed short Pt–Ag distances. However, the existence of metal–metal bonding is not certain because the presence of bridging ligands might be responsible for the close approach of the metal atoms.[8,13–17]

Recently we have described the syntheses and structures of some clusters containing Pt–Ag bonds,[18–20] all of which were prepared by using pentafluorophenyl anionic platinum complexes, which can act as Lewis bases. One of them, $(NBu_4)_2[Pt_2Ag_2Cl_4(C_6F_5)_4]$,[18,19] was obtained by reacting $(NBu_4)_2[\textit{trans}\text{-}PtCl_2(C_6F_5)_2]$ with $AgClO_4$ and displays the following features: quite strong Pt–Ag bonds, perhaps weak Ag–Ag bonds, and Ag···F interactions that help in the stabilization of this unusual anion. The reaction of that compound with PPh_3 gave rise to

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* To whom correspondence should be addressed: R.U., Universidad de Zaragoza-CSIC; F.A.C., Texas A&M University.

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Table I. Analytical and Conductivity Data

complex	anal., %^{a} C	H	N	Λ_M, $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$ ^{b}
$(NBu_4)_x[Pt(C_6Cl_5)_2(\mu\text{-}Cl)_2Ag]_x$ (I)	29.80 (30.13)	3.02 (3.22)	1.12 (1.25)	*c*
$(NBu_4)[PtAgCl_2(C_6Cl_5)_2PPh_3]$ (II)	40.34 (40.07)	3.59 (3.70)	1.09 (1.01)	83.62
$(NBu_4)[PtAgCl_2(C_6Cl_5)_2PEt_3]$ (III)	32.88 (33.09)	4.17 (4.13)	1.10 (1.13)	80.86
$(NBu_4)[PtAgCl_2(C_6Cl_5)_2AsPh_3]$ (IV)	38.65 (38.84)	3.62 (3.58)	0.91 (0.98)	80.42
$(NBu_4)[PtAgCl_2(C_6Cl_5)_2SbPh_3]$ (V)	38.11 (37.60)	3.67 (3.47)	1.21 (0.95)	73.92
$[Pt(C_6Cl_5)_2Cl_2Ag_2(PMePh_2)_2]$ (VI)	32.79 (33.03)	1.96 (1.88)		*c*
$[Pt(C_6Cl_5)_2Cl_2Ag_2(PEtPh_2)_2]$ (VII)	34.07 (34.17)	2.12 (2.34)		*c*
$[Pt(C_6Cl_5)_2Cl_2Ag_2(PMe_2Ph)_2]$ (VIII)	27.11 (26.74)	1.69 (1.75)		*c*

^{a}Calculated values are given in parentheses. ^{b}In acetone. ^{c}Could not be determined owing to its low solubility.

$(NBu_4)[PtAgCl_2(C_6F_5)_2PPh_3]$, a compound having a Pt–Ag bond but lacking the Ag···F contacts.

In order to obtain some more information about the influence of the phenyl substituents, we have studied the reaction of the analogous pentachlorophenyl derivative $(NBu_4)_2[$*trans*-$PtCl_2(C_6Cl_5)_2]$ with $AgClO_4$ or $AgNO_3$, and we find that it gives the polymeric $(NBu_4)_x[Pt(C_6Cl_5)_2(\mu\text{-}Cl)_2Ag]_x$. From this compound, anionic binuclear $(NBu_4)[PtAgCl_2(C_6Cl_5)_2L]$, L = PPh_3 (II), PEt_3 (III), $AsPh_3$ (IV), $SbPh_3$ (V), and neutral trinuclear $[PtAg_2Cl_2(C_6Cl_5)_2L_2]$, L = $PMePh_2$ (VI), $PEtPh_2$ (VII), PMe_2Ph (VIII), complexes have been obtained. The structures of I, II, and VI have been established by single-crystal X-ray diffraction studies.

Experimental Section

The C, H, and N analyses and conductance measurements were performed as described elsewhere.[19] All the reactions were carried out under exclusion of light. $(NBu_4)_2[$*trans*-$PtCl_2(C_6Cl_5)_2]$ was prepared as described elsewhere.[21]

Preparation of $(NBu_4)_x[Pt(C_6Cl_5)_2(\mu\text{-}Cl)_2Ag]_x$ (I). $AgNO_3$ (0.0815 g, 0.48 mmol) was added to a solution of 0.6 g (0.48 mmol) of $(NBu_4)_2[$*trans*-$PtCl_2(C_6Cl_5)_2$ in 50 mL of methanol and 8 mL of acetone. A pale yellow precipitate of compound I was immediately formed. This suspension was stirred for 15 min, and then the volume was reduced by evaporation to ~30 mL. The pale yellow solid that precipitated was filtered and washed with methanol (88% yield).

Substituting $AgClO_4$ for $AgNO_3$ in the above procedure gives complex I in 87% yield.

Preparation of $(NBu_4)[PtAgCl_2(C_6Cl_5)_2L]$, L = PPh_3 (II), PEt_3 (III), $AsPh_3$ (IV), $SbPh_3$ (V). All these compounds were prepared by stirring a suspension of complex I in 40 mL of dichloromethane for 45 min at 0 °C with the respective ligand in a 1:1 ratio: complex II, 0.2 g (0.179 mmol) of I and 0.047 g (0.179 mmol) of PPh_3; complex III, 0.2 g (0.179 mmol) of I and 21.6 μL (0.179 mmol) of PEt_3; complex IV, 0.2 g (0.179 mmol) of I and 0.0548 g (0.179 mmol) of $AsPh_3$; complex V, 0.12 g (0.107 mmol) of I and 0.0379 g (0.1076 mmol) of $SbPh_3$.

After 45 min an almost transparent solution was obtained in each case. After filtration, the solutions were evaporated to dryness and the resulting oily residues were stirred with 15 mL of methanol at 0 °C for 30 min. Pale yellow solids were obtained. Yields: II, 69%; III, 55%, IV, 68%; V, 70%.

Preparation of $[PtAg_2Cl_2(C_6Cl_5)_2L_2]$, L = $PMePh_2$ (VI), $PEtPh_2$ (VII), PMe_2Ph (VIII). Stirring of dichloromethane suspensions of complex I with the corresponding ligands in a 1:1 ratio at 0 °C leads to almost transparent solutions: complex VI, 0.2 g (0.179 mmol) of I with 34.4 μL (0.179 mmol) of $PMePh_2$ and 30 min of stirring; complex VII, 0.2 g (0.179 mmol) of I with 38.4 μL (0.179 mmol) and $PEtPh_2$ and 30 min of stirring; complex VIII, 0.15 g (0.134 mmol) of I with 18.6 μL (0.134 mmol) of PMe_2Ph and 1 h of stirring.

In each case, the solution was then filtered, the residue was evaporated to dryness, and ~15 mL of methanol was added. After a few minutes pale yellow solids were obtained. Yields, according to eq 3: VI, 56%; VII, 54%; VIII, 47%.

Evaporation to dryness of the methanolic extract afforded $(NBu_4)_2[$*trans*-$PtCl_2(C_6Cl_5)_2]$ in 45–50% yield (according to eq 3).

Preparation of Crystals for X-ray Studies. Crystals of compound I, $(NBu_4)_x[Pt(C_6Cl_5)_2(\mu\text{-}Cl)_2Ag]_x$ were obtained by slow diffusion (ca. 3 weeks at −30 °C) of an acetone solution of $AgClO_4$ into a dichloromethane solution of $(NBu_4)_2[$*trans*-$PtCl_2(C_6Cl_5)_2]$ (molar ratio 1:1) separated from each other by an inert layer of 1,2-dichloroethane.

Crystals of complexes II, $(NBu_4)[PtAgCl_2(C_6Cl_5)_2PPh_3]$, and VI, $[PtAg_2Cl_2(C_6Cl_5)_2(PMePh_2)_2]$, were obtained by slow diffusion (ca. 1 week) of *n*-hexane into a solution of the complex in CH_2Cl_2 at −30 °C.

X-ray Structure Analyses. The methods used in analyzing the crystal structures of compounds I, II, and VI were the same, in general, as those described in ref 19. Important crystal data and data collection parameters for all three compounds are summarized in Table II.

Lattice dimensions and types were determined by routine procedures for all three compounds and were verified by oscillation photography. Crystals of I and II were found to be monoclinic (Laue class $2/m$), while VI was triclinic (Laue class $\bar{1}$).

During intensity-data collection for each sample, monitor reflections were measured at regular intervals. For I, these lost an average of 42% of their initial intensities during 51 h of beam time, and for II, the average loss was 18% over 107 h of beam time. For VI, the check reflections did not vary appreciably in intensity over 40 h of X-ray beam time.

Data reduction included absorption corrections (by the ψ-scan method) for all three data sets. For I and II, additionally, interpolative decay corrections were applied.

The positions of the unique Pt and Ag atoms were located by direct methods for compound I and were derived from Patterson maps for II and VI. All three structures were developed and refined in series of alternating difference Fourier maps and least-squares refinements. The refinements of II and VI were routine, with final cycles involving data-to-parameter ratios of 9.0 and 11.9, respectively. In the late stages of the refinement of I, however, the tetra-*n*-butylammonium cation was not refining stably; so in the final refinement the bond distances and angles of this group were loosely restrained. The final, convergent refinement used 1487 unique reflection data with $F_o^2 > 3\sigma(F_o^2)$ as well as 18 distance restraints, for a total of 1505 observations (data-to-parameter ratio 9.6). Final difference maps did not show any chemically significant peaks in any of the three structures. Final residuals for the three structures are summarized in Table II.

Results and Discussion

Synthesis of $(NBu_4)_x[Pt(C_6Cl_5)_2(\mu\text{-}Cl)_2Ag]_x$ (I). When $AgNO_3$ or $AgClO_4$ is added to a solution of $(NBu_4)_2[$*trans*-$PtCl_2(C_6Cl_5)_2]$[21]

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Table II. Crystal Data for $(NBu_4)_x[Pt(C_6Cl_5)_2(\mu\text{-}Cl)_2Ag]_x$ (I), $(NBu_4)[PtAgCl_2(C_6Cl_5)_2PPh_3]$ (II), and $[PtAg_2Cl_2(C_6Cl_5)_2(PMePh_2)_2]$ (VI)

	I	II	VI
formula	$PtAgCl_{12}NC_{28}H_{36}$	$PtAgCl_{12}PNC_{46}H_{51}$	$PtAg_2Cl_{12}P_2C_{38}H_{26}$
fw	1115.0	1377.3	1380.8
space group	$C2/c$	$P2_1/n$	$P\bar{1}$
systematic absences	(hkl): $h + k \neq 2n$ ($h0l$): $l(h) \neq 2n$	($0k0$): $k \neq 2n$ ($h0l$): $h + l \neq 2n$	none
a, Å	19.300 (3)	20.076 (6)	10.821 (3)
b, Å	26.523 (4)	28.507 (5)	12.462 (3)
c, Å	8.450 (2)	9.479 (3)	9.268 (2)
α, deg	90	90	109.23 (2)
β, deg	103.53 (2)	97.17 (3)	99.87 (2)
γ, deg	90	90	70.85 (2)
V, Å^3	4205 (2)	5382 (5)	1111.9 (4)
Z	4	4	1
d_{calcd}, g/cm^3	1.76	1.70	2.06
cryst size, mm	0.37 × 0.28 × 0.24	0.36 × 0.18 × 0.13	0.7 × 0.2 × 0.2
μ(Mo Kα), cm^{-1}	47.3	37.4	49.7
data collecn instrument	Enraf-Nonius CAD-4F	CAD-4F	Syntex P$\bar{1}$
radiation (monochromated in incident beam)	Mo Kα (λ_α = 0.71073 Å)	d	d
orientation reflecns: no.; range (2θ), deg	25; 20–30	19; 20–28	15; 23–32
temp, °C	26 ± 1	21 ± 1	4 ± 2
scan method	ω scans	ω–2θ scans	ω–2θ scans
data collecn range, 2θ, deg	4.0–45.0	4.0–47.0	4.0–47.0
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	2116 1487	6291 5020	2988 2979
no. of observns in refinement	1505 (see text)	5020	2979
no. of parameters refined	156	559	250
transmission factors: max, min	1.00, 0.78	1.00, 0.85	1.00, 0.51
R^a	0.0610	0.0433	0.0279
$R_w{}^b$	0.0651	0.0547	0.0423
quality-of-fit indicator^c	1.378	1.331	1.054
largest shift/esd, final cycle	0.10	0.01	0.01
largest peak, e/Å^3	0.74	1.14	1.06

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$ for II and VI. $R_w = [\sum(||F_o| - |F_c||)w^{1/2}]/[\sum|F_o|w^{1/2}]$; $w = [\sigma^2(|F_o|) + 0.002F_o{}^2]^{-1}$ for I. [c] Quality of fit $= [\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{parameters})]^{1/2}$. [d] As for compound I.

Table III. Positional and Equivalent Isotropic Displacement Parameters (Å^2) and Their Estimated Standard Deviations for $(NBu_4)_x[Pt(C_6Cl_5)_2(\mu\text{-}Cl)_2Ag]_x$ (I)^a

atom	x	y	z	B
Pt	0.000	0.09076 (3)	0.250	7.71 (4)
Ag	0.000	0.000	0.000	17.5 (2)
Cl(1)	−0.0011 (3)	0.0931 (2)	−0.0255 (6)	9.3 (2)
C(1)	0.111 (1)	0.0936 (8)	0.308 (2)	9.0 (6)
C(2)	0.156 (1)	0.0500 (7)	0.320 (2)	10.1 (8)
C(3)	0.231 (1)	0.050 (1)	0.342 (3)	13 (1)
C(4)	0.260 (1)	0.098 (2)	0.354 (3)	14 (1)
C(5)	0.214 (2)	0.143 (1)	0.344 (3)	12 (1)
C(6)	0.144 (1)	0.1376 (8)	0.317 (2)	8.5 (7)
Cl(2)	0.1166 (3)	−0.0091 (2)	0.305 (1)	14.6 (3)
Cl(3)	0.2786 (4)	−0.0015 (3)	0.358 (1)	20.2 (5)
Cl(4)	0.3515 (5)	0.1018 (4)	0.381 (2)	20.3 (5)
Cl(5)	0.2608 (5)	0.1996 (3)	0.367 (1)	17.2 (4)
Cl(6)	0.0987 (4)	0.1931 (2)	0.3052 (8)	11.8 (2)
N	0.500	0.2463 (8)	0.250	12 (1)
C(7)	0.561 (1)	0.272 (1)	0.203 (2)	18 (1)*
C(8)	0.604 (2)	0.302 (2)	0.344 (3)	24 (1)*
C(9)	0.665 (2)	0.326 (2)	0.295 (5)	29 (2)*
C(10)	0.701 (2)	0.362 (2)	0.424 (6)	30 (2)*
C(11)	0.518 (1)	0.215 (1)	0.404 (2)	20 (1)*
C(12)	0.584 (2)	0.184 (1)	0.408 (4)	24 (1)*
C(13)	0.592 (2)	0.146 (1)	0.541 (4)	29 (2)*
C(14)	0.585 (3)	0.171 (2)	0.695 (4)	30 (2)*

[a] Values marked with an asterisk are for atoms refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

in methanol–acetone, a pale yellow solid, compound I, precipitates from the solution (eq 1) in ~85% yield.

$$x(NBu_4)_2[trans\text{-}PtCl_2(C_6Cl_5)_2] + xAgX \xrightarrow{\text{MeOH–acetone}} xNBu_4X + (NBu_4)_x[Pt(C_6Cl_5)_2(\mu\text{-}Cl)_2Ag]_x \quad (1)$$

$$X = NO_3, ClO_4$$

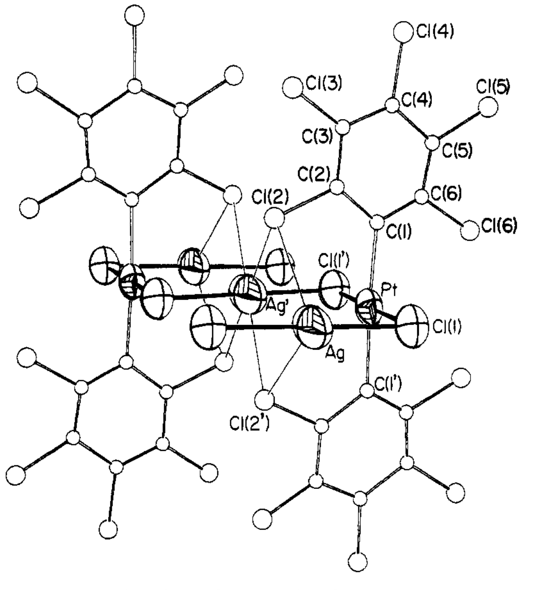

Figure 1. ORTEP drawing of one unit of the polymeric anion $[Pt(C_6Cl_5)_2(\mu\text{-}Cl)_2Ag]_x{}^{x+}$. Atoms of the C_6Cl_5 ligands are shown as small circles, for clarity. The atoms of the backbone are represented by their 35% probability ellipsoids.

Complex I (analytical data are given in Table I) is very slightly soluble in acetone and dichloromethane but insoluble in other common solvents. This lack of solubility precludes the successful use of routine crystallization methods, but by very slow diffusion at −25 °C of an acetone solution of $AgClO_4$ into a dichloromethane solution of $(NBu_4)_2[trans\text{-}PtCl_2(C_6Cl_5)_2]$ (molar ratio 1:1), both separated by an inert layer of 1,1-dichloroethane, needles of suitable size for X-ray diffraction studies could be obtained.

Structure of $(NBu_4)_x[Pt(C_6Cl_5)_2(\mu\text{-}Cl)_2Ag]_x$. Table III lists atomic coordinates, and selected distances and angles are given in Table IV.

Table IV. Selected Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for $(NBu_4)_x[Pt(C_6Cl_5)_2(\mu\text{-}Cl)_2Ag]_x$ (I)[a]

		Distances			
Pt···Ag	3.203 (1)	Ag–Cl(1)	2.477 (5)	Ag···Cl(2)	3.010 (8)
Pt–Cl(1)	2.324 (5)	C(1)–C(2)	1.44 (3)	Ag···Cl(2′)	3.092 (8)
Pt–C(1)	2.08 (2)	C(1)–C(6)	1.32 (2)		
		Angles			
Cl(1)–Pt–Cl(1′)	177.0 (2)	C(1)–Pt–C(1′)	175.8 (8)	Pt–C(1)–C(2)	124 (2)
Cl(1)–Pt–C(1)	90.1 (5)	Cl(1)–Ag–Cl(1′)	180.00	Pt–C(1)–C(6)	120 (2)
Cl(1)–Pt–C(1′)	89.8 (5)	Pt–Cl(1)–Ag	83.6 (2)	C(2)–C(1)–C(6)	115 (2)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Complex I consists of a bandlike polymeric anion and NBu_4^+ cations. A single repeat of the polymeric anion $[Cl(C_6Cl_5)_2PtClAg]_n^{n+}$ is shown in Figure 1. The $(\text{–Cl–Ag–Cl–Pt–})_n$ backbone of the polymer is planar and lies on the crystallographic *yz* plane with its propagation direction along the *z* axis. Silver atoms sit on crystallographic inversion centers at (0, 0, 0) and (0, 0, 0.5), while the platinum atoms are on twofold axes at (0, *y*, 0.25) and (0, –*y*, 0.75), with *y* = 0.09076 (3).

The structure can be described with primary reference to the $[trans\text{-}PtCl_2(C_6Cl_5)_2]^{2-}$ fragments (Figure 1). These lie on a pair of parallel planes (the planes are separated by 4.8 Å) perpendicular to the crystallographic *y* axis. The platinum centers on opposite planes are displaced with respect to each other by a translation of half of a lattice repeat along the *z* axis.

Each Cl atom linked to a platinum atom is also bridged to the Cl atom on the opposite plane by a silver atom that lies halfway between these planes. Thus, the shape of the whole backbone is crenelated, with each platinum atom coordinated by a square-planar trans arrangement of two chlorine atoms and two carbon atoms (of two C_6Cl_5 groups). The trans bond angles are near 180° [Cl(1)–Pt–Cl(1′) = 177.0 (2)°, C(1)–Pt–C(1′) = 175.8(8)°] and the *cis*-(Cl–Pt–C) angles are within 0.2° of 90.0° (see Table IV).

Furthermore, the C_6Cl_5 rings are nearly perpendicular to the coordination plane of platinum (angle between the C_6Cl_5 rings and the $PtCl_2C_2$ plane 89.1°); this orientation of the C_6Cl_5 rings enables nonbonded contacts between each silver atom in the polymeric chain and four *o*-chlorine atoms (generated by symmetry from Cl(2)). The distances are as follows (Å): Ag···Cl(2), 3.010 (8); Ag···Cl(2′), 3.092 (8). Each *o*-chlorine atom (from four different C_6Cl_5 rings, belonging to the two platinum centers nearest to each silver ion) displays two Cl···Ag contacts and is therefore connected to three centers, C(2), Ag, and Ag′. Considering these contacts as well as the two Ag–Cl bonds, the silver atoms are in the center of a rhombically distorted octahedron. On the other hand, the long Pt–Ag distance, 3.203 (1) Å, and the Pt–Cl–Ag angle, 83.6 (2)°, point to the absence of any significant Pt–Ag interaction.

Since steric factors would not prevent the C_6Cl_5 groups from adopting other orientations, we conclude that the Ag···Cl contacts contribute to the stability of this heterometallic compound. The role of the *o*-chlorine atoms in complex I is reminiscent of that played by *o*-fluorine atoms of C_6F_5 groups in previously reported compounds, e.g., $(NBu_4)_2[Pt_2Ag_2Cl_4(C_6F_5)_4]$.[18,19] If we compare the structures of this pentafluorophenyl compound and complex I, we can also find some interesting differences, the main one being that the polymer does not present any Pt–Ag bond. The fact that the Ag atom in complex I receives electron density from six chlorine atoms (two strong Ag–Cl bonds, four Ag···Cl contacts) makes the Pt→Ag bonding unnecessary as well as—with the adopted structure—sterically infeasible. In a complex of similar structure, with C_6F_5 groups substituted for C_6Cl_5, the smaller size of the fluorine atoms would not permit satisfactory F···Ag contact distances simultaneously to two Ag centers. Therefore, the orientation of each C_6F_5 ring would change in order to bring one *o*-fluorine atom into contact with at least one of the silver atoms. Indeed, this is the situation that we found in the $[Pt_2Ag_2Cl_4(C_6F_5)_4]^{2-}$ anion, and since the silver atoms there receive electron density only from two chlorine and two fluorine atoms, additional electron density is withdrawn from the anionic platinum center; Pt→Ag bonds are also present.

Thus, the size of the C_6Cl_5 groups as well as the electronic characteristics of the *o*-chlorine atoms prevent, or at least render unnecessary, the formation of Pt–Ag bonds in the present case.

Reactivity of the Polymeric Compound $(NBu_4)_x[Pt(C_6Cl_5)_2(\mu\text{-}Cl)_2Ag]_x$ (I). Complex I is quite stable in acetone and dichloromethane presumably because of its very low solubility. Bubbling of CO through a suspension of I in dichloromethane at atmospheric pressure and room temperature does not cause any change, and the starting material can be recovered. However, complex I reacts with group 15 ligands; depending on the ligand, two different kinds of compounds, the binuclear $(NBu_4)[PtAgCl_2(C_6Cl_5)_2L]$ (L = PPh_3, PEt_3, $AsPh_3$, $SbPh_3$) or the trinuclear $[PtAg_2Cl_2(C_6Cl_5)_2L_2]$ (L = PPh_2Me, PPh_2Et, $PPhMe_2$), can be obtained.

(a) Synthesis of $(NBu_4)[PtAgCl_2(C_6Cl_5)_2L]$ Complexes. A dichloromethane suspension of complex I reacts instantaneously with L = PPh_3, PEt_3, $AsPh_3$, and $SbPh_3$ at 0 °C in 1:1 molar ratio to give (in approximately 70% yield) the heterometallic Pt–Ag complexes, according to eq 2.

$$(NBu_4)_x[Pt(C_6Cl_5)_2(\mu\text{-}Cl)_2Ag]_x + xL \rightarrow x\{(NBu_4)[PtAgCl_2(C_6Cl_5)_2L]\} \quad (2)$$

$$L = PPh_3\ (II),\ PEt_3\ (III),\ AsPh_3\ (IV),\ SbPh_3\ (V)$$

Complexes II–V are similar to the C_6F_5 derivative $(NBu_4)[PtAgCl_2(C_6F_5)_2(PPh_3)]$, which was prepared[19] by addition of PPh_3 to solutions of $(NBu_4)_2[Pt_2Ag_2Cl_4(C_6F_5)_4]$. Solutions of the latter are unstable and must be handled quickly in order to avoid the precipitation of AgCl. Moreover, the $AsPh_3$ or $SbPh_3$ derivatives of the pentafluoro compound could not be isolated because of AgCl precipitation.

Complexes II–V, containing C_6Cl_5 instead C_6F_5, are much more stable; after 24 h of stirring at room temperature of a dichloromethane solution of complex II, 20% of the original solute can be recovered.

Analytical and some other data for complexes II–V are collected in Table I. Conductivities are in agreement with the expected values for 1:1 electrolytes.[22]

Structure of $(NBu_4)[PtAgCl_2(C_6Cl_5)_2(PPh_3)]$ (II). Atomic coordinates for the structure of II are given in Table V, and the principal interatomic distances and angles are listed in Table VI. A view of the $[PtAgCl_2(C_6Cl_5)_2(PPh_3)]^-$ anion is shown in Figure 2.

The anionic part of complex II is formed by the two moieties "$Pt(C_6Cl_5)_2Cl_2$" and "$Ag(PPh_3)$", bonded by a strong Pt–Ag bond (2.782 (1) Å); additionally one of the chlorine atoms of the first moiety weakly bridges the Ag atom (Cl–Ag distance 2.667 (3) Å). The Pt–Cl–Ag angle is very acute, 67.24 (6)°, as a consequence of the short Pt–Ag distance. The two chlorine atoms and the two C_6Cl_5 groups around the platinum atom are in trans positions, as in the starting material. The Pt–C(1) and Pt–C(7) distances are 2.064 (8) and 2.065 (9) Å, respectively; the Pt–Cl distances are slightly different as might be expected since one Cl atom is terminal (Pt–Cl =2.295 (2) Å) and the other bridges the two metals ($Pt\text{–}Cl_{br}$ = 2.331 (2) Å). Angles around the Pt atom are the usual for this Pt(II) stereochemistry (Table VI). The silver

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(22) Geary, W. J. *Coord. Chem. Rev.* **1971**, 7, 81.

Table V. Positional and Equivalent Isotropic Displacement Parameters (Å^2) and Their Estimated Standard Deviations for $(NBu_4)[PtAgCl_2(C_6Cl_5)_2PPh_3]$ (II)[a]

atom	*x*	*y*	*z*	*B*	atom	*x*	*y*	*z*	*B*
Pt	0.22647 (2)	0.19117 (1)	0.48490 (4)	3.460 (7)	C(16)	0.6001 (6)	0.1382 (5)	0.815 (2)	7.5 (4)
Ag	0.30714 (4)	0.13870 (3)	0.6864 (1)	5.60 (2)	C(17)	0.5837 (6)	0.1124 (5)	0.932 (1)	7.0 (4)
Cl(1)	0.3400 (1)	0.18426 (9)	0.4593 (3)	4.53 (6)	C(18)	0.5175 (6)	0.0944 (5)	0.931 (1)	6.2 (3)
Cl(2)	0.1150 (1)	0.2024 (1)	0.5067 (4)	6.05 (8)	C(19)	0.3742 (5)	0.0641 (4)	0.981 (1)	4.5 (2)
Cl(3)	0.1747 (2)	0.0924 (1)	0.6420 (3)	5.63 (7)	C(20)	0.3716 (6)	0.1001 (4)	1.081 (1)	5.6 (3)
Cl(4)	0.1432 (2)	−0.0022 (1)	0.4940 (4)	7.76 (9)	C(21)	0.3668 (6)	0.0883 (5)	1.223 (1)	6.8 (3)
Cl(5)	0.1599 (2)	−0.0147 (1)	0.1750 (4)	8.2 (1)	C(22)	0.3628 (7)	0.0432 (5)	1.263 (1)	7.2 (4)
Cl(6)	0.1900 (2)	0.0721 (1)	−0.0044 (3)	7.28 (9)	C(23)	0.3629 (7)	0.0064 (5)	1.162 (1)	7.4 (4)
Cl(7)	0.2196 (2)	0.1684 (1)	0.1426 (3)	5.69 (7)	C(24)	0.3696 (6)	0.0177 (4)	1.018 (1)	5.7 (3)
Cl(8)	0.2448 (2)	0.2179 (1)	0.8345 (3)	6.28 (8)	C(25)	0.3848 (5)	0.0277 (4)	0.701 (1)	4.8 (3)
Cl(9)	0.2636 (2)	0.3187 (2)	0.9583 (4)	9.3 (1)	C(26)	0.3239 (6)	0.0105 (4)	0.634 (1)	5.9 (3)
Cl(10)	0.2814 (2)	0.4027 (1)	0.7585 (5)	10.6 (1)	C(27)	0.3231 (7)	−0.0323 (5)	0.557 (1)	6.8 (3)
Cl(11)	0.2766 (2)	0.3870 (1)	0.4353 (5)	7.8 (1)	C(28)	0.3824 (7)	−0.0558 (5)	0.541 (1)	7.0 (4)
Cl(12)	0.2533 (2)	0.2875 (1)	0.3088 (3)	6.24 (8)	C(29)	0.4415 (7)	−0.0376 (5)	0.606 (2)	9.0 (4)
P	0.3839 (1)	0.0819 (1)	0.7998 (3)	4.34 (6)	C(30)	0.4449 (6)	0.0028 (4)	0.685 (1)	6.5 (3)
N	0.4896 (4)	0.3169 (3)	0.499 (1)	5.1 (2)	C(31)	0.4456 (6)	0.3311 (4)	0.363 (1)	5.4 (3)
C(1)	0.2027 (4)	0.1272 (3)	0.390 (1)	3.6 (2)	C(32)	0.4857 (7)	0.3578 (5)	0.260 (1)	7.2 (4)
C(2)	0.1830 (5)	0.0880 (4)	0.460 (1)	4.4 (2)	C(33)	0.4329 (8)	0.3708 (5)	0.130 (2)	8.9 (4)
C(3)	0.1686 (5)	0.0447 (4)	0.398 (1)	4.9 (3)	C(34)	0.4684 (9)	0.3931 (6)	0.014 (2)	10.4 (5)
C(4)	0.1745 (5)	0.0392 (4)	0.256 (1)	5.1 (3)	C(35)	0.5229 (6)	0.3592 (4)	0.582 (1)	6.2 (3)
C(5)	0.1902 (5)	0.0778 (4)	0.178 (1)	5.0 (3)	C(36)	0.4716 (7)	0.3981 (5)	0.606 (2)	7.5 (4)
C(6)	0.2037 (5)	0.1205 (4)	0.243 (1)	3.9 (2)	C(37)	0.5077 (7)	0.4398 (5)	0.672 (2)	8.2 (4)
C(7)	0.2468 (5)	0.2566 (3)	0.573 (1)	4.0 (2)	C(38)	0.4615 (8)	0.4799 (5)	0.697 (2)	9.4 (5)
C(8)	0.2498 (5)	0.2654 (4)	0.719 (1)	4.8 (3)	C(39)	0.4418 (5)	0.2909 (4)	0.592 (1)	5.1 (3)
C(9)	0.2601 (6)	0.3097 (4)	0.777 (1)	6.2 (3)	C(40)	0.4766 (5)	0.2723 (5)	0.732 (1)	5.7 (3)
C(10)	0.2668 (5)	0.3469 (4)	0.692 (1)	6.4 (3)	C(41)	0.4227 (7)	0.2528 (5)	0.816 (1)	6.9 (3)
C(11)	0.2652 (5)	0.3403 (4)	0.544 (1)	5.2 (3)	C(42)	0.4513 (7)	0.2323 (5)	0.957 (1)	7.5 (4)
C(12)	0.2557 (5)	0.2951 (3)	0.493 (1)	4.3 (2)	C(43)	0.5475 (5)	0.2846 (4)	0.465 (1)	5.4 (3)
C(13)	0.4701 (5)	0.1034 (4)	0.812 (1)	4.5 (2)	C(44)	0.5220 (6)	0.2408 (4)	0.385 (1)	6.6 (3)
C(14)	0.4866 (6)	0.1294 (4)	0.697 (1)	5.8 (3)	C(45)	0.5855 (7)	0.2127 (5)	0.354 (2)	8.3 (4)
C(15)	0.5521 (6)	0.1463 (4)	0.695 (2)	7.0 (3)	C(46)	0.564 (1)	0.1677 (6)	0.275 (2)	11.4 (5)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table VI. Selected Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for $(NBu_4)[PtAgCl_2(C_6Cl_5)_2PPh_3]$ (II)[a]

		Distances			
Pt–Ag	2.782 (1)	Ag–P	2.395 (2)	C(7)–C(8)	1.395 (13)
Pt–Cl(1)	2.331 (2)	P–C(13)	1.825 (9)	C(7)–C(12)	1.362 (12)
Pt–Cl(2)	2.295 (2)	P–C(19)	1.821 (10)	Ag···Cl(3)	2.951 (3)
Pt–C(1)	2.064 (8)	P–C(25)	1.810 (10)	Ag···Cl(8)	3.012 (3)
Pt–C(7)	2.065 (9)	C(1)–C(2)	1.384 (12)		
Ag–Cl(1)	2.667 (3)	C(1)–C(6)	1.408 (12)		
		Angles			
Ag–Pt–Cl(1)	62.16 (6)	C(1)–Pt–C(7)	177.3 (3)	C(13)–P–C(25)	104.4 (5)
Ag–Pt–Cl(2)	120.24 (8)	Pt–Ag–Cl(1)	50.60 (5)	C(19)–P–C(25)	105.0 (5)
Ag–Pt–C(1)	84.7 (2)	Pt–Ag–P	163.42 (8)	Pt–C(1)–C(2)	124.6 (7)
Ag–Pt–C(7)	97.9 (3)	Cl(1)–Ag–P	118.74 (9)	Pt–C(1)–C(6)	121.4 (7)
Cl(1)–Pt–Cl(2)	176.7 (1)	Pt–Cl(1)–Ag	67.24 (6)	C(2)–C(1)–C(6)	114.0 (8)
Cl(1)–Pt–C(1)	93.2 (2)	Ag–P–C(13)	110.7 (3)	Pt–C(7)–C(8)	123.1 (7)
Cl(1)–Pt–C(7)	88.4 (2)	Ag–P–C(19)	118.2 (3)	Pt–C(7)–C(12)	122.3 (7)
Cl(2)–Pt–C(1)	89.3 (2)	Ag–P–C(25)	113.0 (3)	C(8)–C(7)–C(12)	114.6 (9)
Cl(2)–Pt–C(7)	89.0 (3)	C(13)–P–C(19)	104.2 (5)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

atom is also bonded to the P atom in PPh_3 (Ag–P = 2.395 (2) Å). The bond angle Pt–Ag–P is 163.42 (8)°, not far from linearity. Other angles around the Ag atom are Pt–Ag–Cl = 50.60 (5)° and Cl–Ag–P = 118.74 (9)°. Moreover, the Ag atom has two contacts, Ag···Cl(3) = 2.951 (3) Å and Ag···Cl(8) = 3.012 (3) Å with two *o*-chlorine atoms of the C_6Cl_5 groups located above and below the Pt–Cl(1)–Ag plane. Thus, the Ag atom is inside a rather distorted trigonal bipyramid with Pt, P, and Cl(1) in the equatorial plane and Cl(3) and Cl(8) in the axial positions. The stronger bonds are Pt–Ag and Ag–P, which are nearly collinear as mentioned above.

A comparison of distances and angles with those previously found in the similar pentafluorophenyl derivative[19] shows only small differences around the platinum center, but they are significant around the silver atom (Table VII). The Pt–Ag distance is shorter in the C_6Cl_5 derivative, but the Ag–P and especially the Ag–Cl distances are shorter in the C_6F_5 complex, and the Pt–Ag–P angle is more open (163.42 (8)°) in the C_6Cl_5 than in the C_6F_5 complex (145.2 (2)°). Perhaps the two Cl···Ag contacts, which do not have any F···Ag counterpart, are related to the longer Ag–Cl(1) and Ag–P distances as well as to the opening of the Pt–Ag–PPh_3 angle in the C_6Cl_5 complex. If some electron density is obtained from the *o*-chlorine–Ag contacts, then the bonds to Cl(1) and P are weakened. The weaker interaction between Cl(1) and silver in the C_6Cl_5 derivatives may be related to the higher stability of these complexes toward decomposition under AgCl precipitation.

(b) Synthesis of $[PtAg_2Cl_2(C_6Cl_5)_2L_2]$. Stirring at 0 °C of a dichloromethane suspension of complex I to which PPh_2Me, PPh_2Et, or $PPhMe_2$ (in molar ratio Pt:P = 1:1) was added leads to a mixture of neutral $[Pt(C_6Cl_5)_2(\mu\text{-}Cl)_2Ag_2L_2]$ and anionic $(NBu_4)_2[\textit{trans}\text{-}PtCl_2(C_6Cl_5)_2]$ complexes (eq 3), which can be

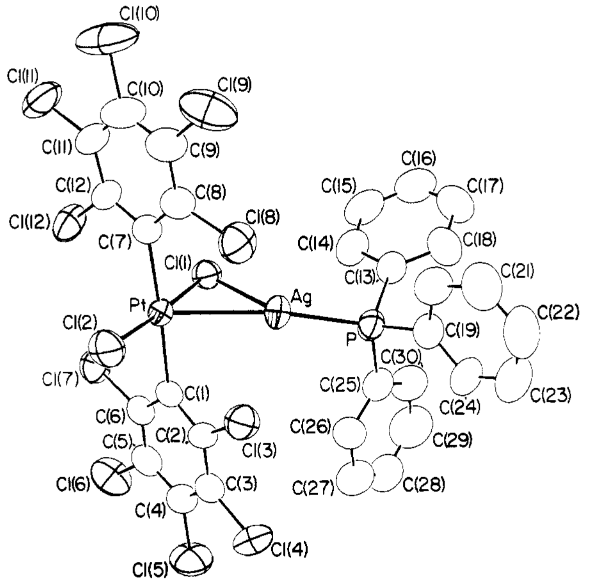


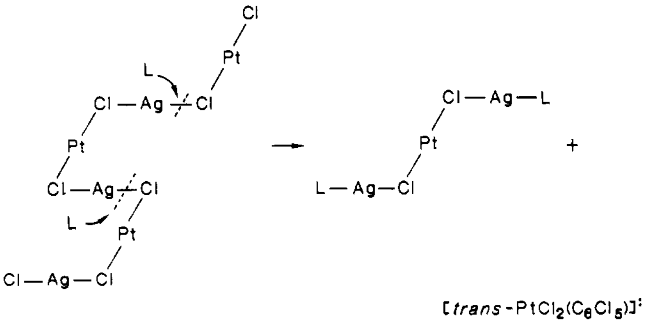
Figure 2. ORTEP drawing of the anion $[PtAgCl_2(C_6Cl_5)_2PPh_3]^-$ showing the structure and atom-labeling scheme. All atoms are represented by their 50% probability ellipsoids. Atom C(20) is not labeled, but the scheme is clear.

Table VII. Comparison of Bond Distances and Angles at the Metal Centers in $[PtAgCl_2(C_6Cl_5)_2PPh_3]^-$ and $[PtAgCl_2(C_6F_5)_2PPh_3]^{-}$ [19,a]

	$[PtAgCl_2(C_6F_5)_2PPh_3]^-$	$[PtAgCl_2(C_6Cl_5)_2PPh_3]^-$
	Bond Distances (Å)	
Pt–Ag	2.796 (2)	2.782 (1)
Ag–Cl	2.473 (5)	2.667 (3)
Ag–P	2.350 (6)	2.395 (2)
	Contact Distances (Å)	
Ag···Cl(3)		2.951 (3)
Ag···Cl(8)		3.012 (3)
	Angles deg)	
Pt–Ag–P	145.2 (2)	163.42 (8)
Pt–Ag–Cl	52.3 (1)	50.60 (5)
Cl–Ag–P	161.6 (2)	118.74 (9)

[a] Estimated standard deviations in units of the least significant digits are given in parentheses.

Scheme I



separated because the neutral complexes are insoluble in methanol. Analytical data for complexes VI–VIII are collected in Table I.

$$(NBu_4)_x[Pt(C_6Cl_5)_2(\mu\text{-}Cl)_2Ag]_x + xL \rightarrow (x/2)(NBu_4)_2[trans\text{-}PtCl_2(C_6Cl_5)_2] + (x/2)[PtAg_2Cl_2(C_6Cl_5)_2L_2] \quad (3)$$

$L = PPh_2Me$ (VI), PPh_2Et (VII), $PPhMe_2$ (VIII)

The formation of both complexes is a consequence of the splitting of the bridging system by the phosphines in such a way (see Scheme I) that two silver atoms remain bonded to the same "$PtCl_2(C_6Cl_5)_2$" unit. This gives rise to $[PtAg_2Cl_2(C_6Cl_5)_2L_2]$, in which the platinum atom is bonded to two AgL^+ moieties through bridging chloride. It is probably due to steric factors that there is a rotation around one of the Pt–Cl bonds which leads to the final structure with AgL^+ moieties located at opposite sides of the plane "$PtCl_2(C_6Cl_5)_2$". As a consequence of this way of breaking the bridging system, $(NBu_4)_2[trans\text{-}PtCl_2(C_6Cl_5)_2]$ is also obtained as a product.

Table VIII. Atomic Positional Parameters and Equivalent Isotropic Displacement Parameters (Å^2) and Their Estimated Standard Deviations for $[PtAg_2Cl_2(C_6Cl_5)_2(PMePh_2)_2]$ (VI)[a]

atom	x	y	z	B_{eqv}
Pt(1)	0.000	0.000	0.000	2.636 (5)
Ag	0.25319 (5)	–0.14474 (4)	0.15024 (6)	5.30 (1)
Cl(1)	0.2150 (1)	–0.0714 (1)	–0.0696 (2)	4.01 (3)
Cl(2)	0.0416 (1)	0.0563 (1)	0.3778 (1)	4.24 (3)
Cl(3)	0.1282 (2)	0.2699 (1)	0.6072 (2)	4.98 (4)
Cl(4)	0.1704 (2)	0.4607 (1)	0.4897 (2)	4.60 (3)
Cl(5)	0.1079 (2)	0.4468 (1)	0.1449 (2)	6.26 (4)
Cl(6)	0.0233 (2)	0.2346 (1)	–0.0849 (2)	4.83 (3)
P	0.3509 (1)	–0.2478 (1)	0.3344 (2)	3.98 (3)
C(1)	0.0416 (4)	0.1480 (4)	0.1524 (5)	2.8 (1)
C(2)	0.0620 (5)	0.1640 (4)	0.3091 (5)	3.1 (1)
C(3)	0.1003 (5)	0.2586 (4)	0.4154 (5)	3.3 (1)
C(4)	0.1168 (5)	0.3456 (4)	0.3636 (6)	3.4 (1)
C(5)	0.0918 (5)	0.3371 (4)	0.2071 (6)	3.4 (1)
C(6)	0.0550 (5)	0.2403 (4)	0.1073 (5)	3.2 (1)
C(7)	0.4811 (6)	–0.3831 (5)	0.2624 (6)	4.2 (1)
C(8)	0.4876 (7)	–0.4909 (5)	0.2833 (8)	5.6 (2)
C(9)	0.5930 (8)	–0.5936 (7)	0.2251 (9)	6.7 (2)
C(10)	0.6866 (8)	–0.5868 (7)	0.1524 (8)	6.6 (2)
C(11)	0.6814 (8)	–0.4831 (8)	0.1305 (9)	7.1 (2)
C(12)	0.5763 (7)	–0.3773 (7)	0.1825 (8)	5.9 (2)
C(13)	0.4221 (5)	–0.1625 (5)	0.5115 (6)	4.1 (1)
C(14)	0.5257 (8)	–0.2162 (8)	0.5915 (9)	7.9 (3)
C(15)	0.5717 (8)	–0.145 (1)	0.736 (1)	9.2 (3)
C(16)	0.5115 (7)	–0.0277 (7)	0.7872 (8)	6.6 (2)
C(17)	0.406 (1)	0.0241 (7)	0.707 (1)	9.9 (3)
C(18)	0.366 (1)	–0.0440 (7)	0.564 (1)	9.1 (3)
C(19)	0.2341 (6)	–0.2925 (6)	0.4063 (8)	5.6 (2)

[a] The displacement parameters for anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

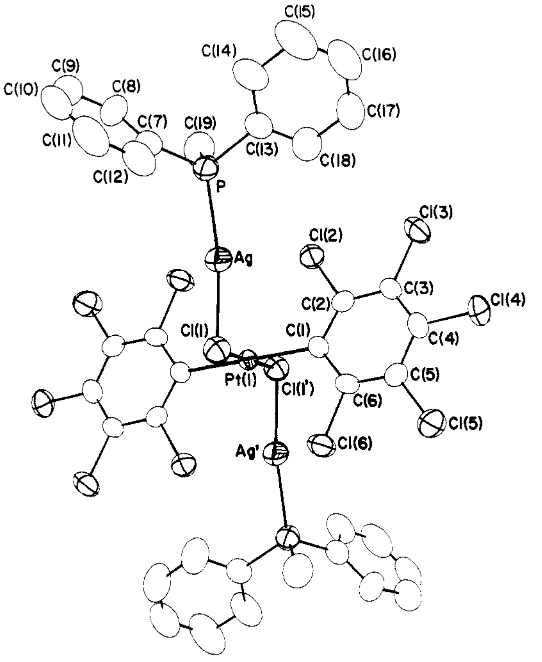


Figure 3. ORTEP drawing of $[PtAg_2Cl_2(C_6Cl_5)_2(PPh_2Me)_2]$. All atoms are represented by their 50% probability ellipsoids.

Table IX. Selected Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for $[PtAg_2Cl_2(C_6Cl_5)_2(PMePh_2)_2]$ (VI)[a]

		Distances			
Pt(1)–Cl(1)	2.323 (1)	Ag–P	2.370 (2)	P–C(19)	1.829 (9)
Pt(1)–C(1)	2.052 (4)	P–C(7)	1.815 (5)	C(1)–C(2)	1.388 (7)
Ag–Cl(1)	2.418 (2)	P–C(13)	1.836 (5)	C(1)–C(6)	1.403 (8)
		Angles			
Cl(1)–Pt(1)–Cl(1′)	180.0	Pt(1)–Cl(1)–Ag	82.63 (5)	C(7)–P–C(19)	105.8 (3)
Cl(1)–Pt(1)–C(1)	89.2 (1)	Ag–P–C(7)	113.4 (2)	C(13)–P–C(19)	102.3 (3)
Cl(1)–Pt(1)–C(1′)	90.8 (1)	Ag–P–C(13)	115.5 (2)	Pt(1)–C(1)–C(2)	122.8 (4)
C(1)–Pt(1)–C(1′)	180.0	Ag–P–C(19)	113.1 (2)	Pt(1)–C(1)–C(6)	123.1 (3)
Cl(1)–Ag–P	163.09 (5)	C(7)–P–C(13)	105.7 (2)	C(2)–C(1)–C(6)	114.1 (4)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table X. Some Relevant IR Absorptions (cm^{-1})

	C_6Cl_5 groups		
complex	X sensitive	ν(M–C)	ν(Pt–Cl)
$(NBu_4)_x[Pt(C_6Cl_5)_2(\mu\text{-}Cl)_2Ag]_x$ (I)	825 (s)	598 (m)	310 (m)
$(NBu_4)[PtAgCl_2(C_6Cl_5)_2PPh_3]$ (II)	825 (s)	600 (m)	330 (m), 298 (w)
$(NBu_4)[PtAgCl_2(C_6Cl_5)_2PEt_3]$ (III)	825 (m)	600 (m)	325 (m), 300 (s)
$(NBu_4)[PtAgCl_2(C_6Cl_5)_2AsPh_3]$ (IV)	825 (s)	600 (m)	329 (s), 300 (w)
$(NBu_4)[PtAgCl_2(C_6Cl_5)_2SbPh_3]$ (V)	827 (s)	600 (m)	331 (m), 299 (w)
$[Pt(C_6Cl_5)_2Cl_2Ag_2(PMePh_2)_2]$ (VI)	825 (s)	602 (m)	310 (m)
$[Pt(C_6Cl_5)_2Cl_2Ag_2(PEtPh_2)_2]$ (VII)	829 (s)	603 (m)	310 (m)
$[Pt(C_6Cl_5)_2Cl_2Ag_2(PMe_2Ph)_2]$ (VIII)	829 (s)	601 (s)	313 (m)

Structure of $[PtAg_2Cl_2(C_6Cl_5)_2(PPh_2Me)_2]$ (VI). Table VIII lists atomic coordinates for compound VI, and bond distances and angles are given in Table IX. The molecule contains one platinum and two silver atoms and has crystallographic inversion symmetry. The entire structure is shown in Figure 3. The Pt atom displays a square-planar environment with two chlorine atoms and two C_6Cl_5 groups in exactly trans positions with angles of 180° as a result of the center of symmetry at the platinum atom. The angle Cl(1)–Pt–C(1) is 90.8 (1)°. The distance Pt–C(1) is 2.052 (4) Å. Both chlorine atoms bonded to platinum act as monobridges between the Pt and the silver atoms. The Pt–Cl distance is 2.323 (1) Å, similar to that found in I (Pt–Cl(1) = 2.324 (5) Å) and II (Pt–Cl(1) = 2.331 (2) Å). These Pt–Cl distances where the Cl atoms are acting as bridging ligands between the metal atoms seem to be insensitive to the strengths of both the Pt–Ag and Ag–Cl bonds. In complex VI the Ag–Cl distance (2.418 (2) Å) is smaller than the analogous distances in the PPh_3 complexes which contain either C_6Cl_5 (II) or C_6F_5.[19]

The platinum and silver atoms are separated by 3.131 (1) Å, and the angle Pt–Cl–Ag is 82.63 (5)°. As in complex I (Pt–Ag = 3.203 (1) Å, Pt–Cl–Ag = 83.6 (2)°, there is no reason to postulate Pt–Ag bonds.

Finally, the silver atom is also bound to a phosphorus atom. The Ag–P distance, 2.370 (2) Å, seems to indicate a bond of considerable strength. The absence in complex VI of any other kind of interactions (Pt···Ag bond or Cl···Ag contacts) makes necessary the existence of strong Cl–Ag and Ag–P bonds.

Complex VI decomposes in solution faster than complexes I and II, in agreement with the existence of a strong Ag–Cl bond. However, despite this shorter Ag–Cl distance, complex VI is more stable than $(NBu_4)[Pt(C_6F_5)_2Cl_2AgPPh_3]$; this means that other factors (perhaps the presence or absence of one Pt–Ag bond) should be taken into account.

IR Spectra. All the complexes show absorptions characteristic for the C_6Cl_5 group.[23,24] Table X shows some selected absorptions of structural interest. The presence in all cases of only one absorption at ~850 cm^{-1}, assigned to the X-sensitive mode of the C_6Cl_5 group, and also only one absorption due to ν(M–C) is in agreement with the fact that both C_6Cl_5 groups are in trans positions. Table X also lists the absorptions due to ν(M–Cl). Complexes II–V show two bands due to the presence of both terminal and bridging chlorine atoms.

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Supplementary Material Available: Full lists of bond distances and angles and anisotropic displacement parameters for each of the three structures (13 pages); listings of observed and calculated structure factors for the three structures (51 pages). Ordering information is given on any current masthead page.

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