terminal η^1- or η^2-CH_2PMePh ligands or to dinuclear species with bridging $-PMe(Ph)CH_2-$groups and a six-membered (alternating Ta, C, P) ring. Oxidative addition to Ta(V) is likely for all metalated species. The ^1H spectra show a broad multiplet at 6.80 ppm, which appears as a triplet in the $^1H\{^{31}P\}$ spectra ($J_{H-H} = 16$ Hz) (Figure 2) and is attributed to the hydrido ligands (from -3 to $+10$ ppm[7,31] are reported for terminal Ta–H). Attempts to trap hydrobromic acid (which could be eliminated in the C–H activation process) failed. No further coordination by addition of phenyldimethylphosphine was observed. This, as well as the absence of ionic species,[7] supports coordinatively saturated molecular tantalum(V) species (Scheme I).

The C–H bond activation in the tantalum complex showed no evidence of fast (NMR time scale) reversal up to temperatures as high as 80 °C.

Reactions between $TaBr_3(PhPMe_2)_2$ and H_2, C_1 molecules, alkenes, and alkynes are in progress.

Acknowledgment. The authors thank A. Mari, G. Commenges (Laboratoire de Chimie de Coordination, Toulouse, France) and M. Bourdonneau (Laboratoire d'Applications Bruker-Wissembourg) for measuring the magnetic susceptibility (solid state) and $^1H\{^{31}P\}$ and ^{13}C spectra, respectively. We are also indebted to Professor D. Grandjean for the use of the Enraf-Nonius CAD-4 automatic diffractometer and the PDP 11/60 computer at the University of Rennes I.

Registry No. $TaBr_3(PhPMe_2)_2$, 99211-55-9; $TaBr_3(PhPMe_2)$, 99128-45-7; $[(PhPMe_2)Br_3HTa(\eta^2\text{-}CH_2PMePh)]_n$, 99128-46-8; PMe_2Ph, 672-66-2; $TaBr_5$, 13842-76-7.

Supplementary Material Available: Tables IV and V, containing anisotropic thermal parameters (β's) and least-square planes, and listings of observed and calculated structure factors and nonessential bond lengths and angles for $TaBr_3(PhPMe_2)_2$ (15 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Inorganic Chemistry, University of Zaragoza, 50009 Zaragoza, Spain,
and Department of Chemistry and Laboratory for Molecular Structure and Bonding,
Texas A&M University, College Station, Texas 77843

Synthesis, X-ray Structure, and Chemical Reactivity of the Tetranuclear Cluster $(NBu_4)_2[Pt_2Ag_2Cl_4(C_6F_5)_4]$. X-ray Structure of the Binuclear Compound $(NBu_4)[PtAgCl_2(C_6F_5)_2PPh_3]$

R. Usón,*[1a] J. Forniés,[1a] B. Menjón,[1a] F. A. Cotton,*[1b] L. R. Falvello,[1b] and M. Tomás[1b]

Received March 4, 1985

The preparation of a mixed-metal atom cluster compound, $(NBu_4)_2[Pt_2Ag_2Cl_4(C_6F_5)_4]$ (**1**), containing Pt–Ag and Ag–Ag bonds is described. The molecular structure of this compound has been determined by a single-crystal X-ray diffraction study. The crystals are found to be triclinic, space group $P\bar{1}$, with $a = 12.438$ (9) Å, $b = 13.160$ (7) Å, $c = 11.128$ (7) Å, $\alpha = 103.53$ (5)°, $\beta = 101.27$ (6)°, $\gamma = 74.75$ (5)°, and $Z = 1$. The structure was refined to $R = 0.079$ and $R_w = 0.096$ with use of 1615 unique reflections with $F^2 \geqslant 3\sigma(F^2)$. The anion resides on a center of symmetry and shows interesting distances: Pt–Ag′ = 2.772 (3) Å, Pt–Ag = 3.063 (3) Å, Ag–Ag′ = 2.994 (6) Å, F···Ag = 2.60 (1) Å, and F···Ag = 2.69 (1) Å. The chemical reactivity of this unusual cluster toward different kinds of neutral ligands has been studied. The reaction of **1** with PPh_3 gives a new anionic organometallic compound, $(NBu_4)[PtAgCl_2(C_6F_5)_2PPh_3]$ (**2**), that crystallizes in space group $P\bar{1}$ with $a = 12.710$ (3) Å, $b = 18.865$ (5) Å, $c = 12.129$ (5) Å, $\alpha = 103.10$ (3)°, $\beta = 114.44$ (2)°, $\gamma = 77.07$ (2)°, and $Z = 2$. The structure was refined to $R = 0.066$ and $R_w = 0.076$ using 3291 unique reflections with $F^2 \geqslant 2\sigma(F^2)$. Compound **2** retains the Pt–Ag bond (Pt–Ag = 2.796 (2) Å) of the starting cluster, but there are no weak contacts between F and Ag, probably as a consequence of the coordination of the PPh_3 to the Ag. $(NBu_4)_2[Pt_2Ag_2Cl_4(C_6F_5)_4]$ reacts with L = $AsPh_3$ or $SbPh_3$ with precipitation of silver chloride and formation of $[trans\text{-}Pt(C_6F_5)_2L_2]$ and $(NBu_4)_2[trans\text{-}PtCl_2(C_6F_5)_2]$ and with CO to give AgCl and the new anionic carbonyl $(NBu_4)[trans\text{-}PtCl(C_6F_5)_2(CO)]$, which is air- and temperature-stable (ν(CO) at 2084 cm^{-1}).

Introduction

Silver salts, AgA, of weakly coordinating anions (A = BF_4, PF_6, NO_3, $^1/_2$ SO_4 or ClO_4) have frequently been used as halide abstractors from halo complexes of transition metals, since the insolubility of silver halides leads to precipitation of AgX and to the replacement of X by the less nucleophilic anion A. The anion A can, in turn, be easily displaced by other ligands, neutral or anionic, thus making this method a very powerful one for the synthesis of a variety of cationic or neutral complexes.[2,3]

In a number of recently reported cases, the interaction of a silver salt with an anionic or neutral complex has led to polynuclear complexes containing metal–silver bonds.[4–8] In most of the reported processes the precursor has been a halide-free complex, but in one case an iodine-containing complex $\{[WI(CO)_3(\eta^5\text{-}C_5H_5)]_4Ag\}BF_4$, with Ag–I bonds and without any W–Ag bond has been described.[9] Here we wish to report an example of the halide-containing precursor[10] $(NBu_4)_2[trans\text{-}PtCl_2(C_6F_5)_2]$ that can react with $AgNO_3$ or $AgClO_4$ without AgCl precipitation to give the new type of anionic Pt–Ag cluster $(NBu_4)_2[trans\text{-}Pt_2Ag_2Cl_4(C_6F_5)_4]$ (**1**), with platinum–silver as well as silver–silver bonds.

Reaction of **1** with $AsPh_3$ or $SbPh_3$ causes AgCl precipitation and formation of a mixture of $[trans\text{-}Pt(C_6F_5)_2L_2]$ and $(NBu_4)_2[trans\text{-}PtCl_2(C_6F_5)_2]$, whereas with PPh_3 the intermediate $(NBu_4)[PtAgCl_2(C_6F_5)_2PPh_3]$ (**2**) can be isolated. On the other hand, complex **1** reacts with CO at normal pressure to give the

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Table I. Analytical and Conductivity Data

	% C	% H	% N	Λ_M, Ω^{-1} cm^2 mol^{-1}
$(NBu_4)_2[Pt_2Ag_2Cl_4(C_6F_5)_4]$ (**1**)	35.20 (35.38)	3.73 (3.79)	1.48 (1.47)	218
$(NBu_4)[PtAgCl_2(C_6F_5)_2PPh_3]$ (**2**)	45.97 (45.56)	4.19 (4.20)	1.36 (1.15)	90
(NBu_4)[*trans*-$PtCl(C_6F_5)_2(CO)$] (**3**)	42.12 (41.71)	4.24 (4.31)	1.62 (1.67)	90

Table II. Relevant IR Data (cm^{-1})

	ν(CO)	C_6F_5 vib	ν(C–Pt)	ν(M–Cl)
$(NBu_4)_2$[*trans*-$Pt(C_6F_5)_2Cl_2$]		1484 (vs), 1048 (s), 1036 (s), 946 (vs)	763 (s)	320 (s)
$(NBu_4)_2[Pt_2Ag_2Cl_4(C_6F_5)_4]$ (**1**)		1499 (vs), 1052 (s), 1042 (s), 952 (vs)	771 (s)	320 (m)
$(NBu_4)_2[PtAgCl_2(C_6F_5)_2(PPh_3)]$ (**2**)^a		1496 (vs), 1054 (s), 1044 (s), 954 (vs), 947 (sh)	768 (s)	342 (m), 298 (m)
(NBu_4)[*trans*-$Pt(C_6F_5)_2Cl(CO)$] (**3**)	2084 (vs)	1504 (vs), 1061 (s), 962 (vs)	790 (sh), 779 (s)	330 (m)

^{a}PPh_3 absorptions: 768 (s), 754 (s), 747 (s), 741 (s), 707 (s), 696 (sh), 690 (s), 526 (s), 511 (s), 492 (s) cm^{-1}.

air- and moisture-stable (at room temperature) novel anionic carbonyl (NBu_4)[*trans*-$PtCl(C_6F_5)_2(CO)$] (**3**), which displays a ν(CO) band at 2084 cm^{-1}. The crystal structures of complexes **1** and **2** have been determined. Some of these results have been the subject of a preliminary communication.[11]

Results and Discussion

(a) Synthesis. The 1:1 reaction between $AgNO_3$ or $AgClO_4$ and $(NBu_4)_2$[*trans*-$PtCl_2(C_6F_5)_2$] in methanol solution takes place with the immediate precipitation not of AgCl but of a pale yellow solid, complex **1**, in 90% yield as shown in eq 1.

$$2(NBu_4)_2[\textit{trans}\text{-}PtCl_2(C_6F_5)_2] + 2AgA \xrightarrow{MeOH} 2(NBu_4)A + (NBu_4)_2[Pt_2Ag_2Cl_4(C_6F_5)_4] \quad (1)$$

$$A = NO_3, ClO_4$$

In acetone (in which complex **1** is soluble) a lower yield (ca. 60%) is obtained, since the complex partially decomposes, precipitating AgCl, during workup. A darkening of the crystals to pale brown can be noticed within 1 month, while in acetone solution the complex decomposes, even at −25 °C, in a few hours.

We have studied the reactivity of complex **1** with ligands of group 15[41] and with CO. Thus, a dichloromethane suspension of complex **1** reacts instantaneously (even at 0 °C) with $AsPh_3$ or $SbPh_3$ with precipitation of AgCl and formation of [*trans*-$Pt(C_6F_5)_2L_2$] and $(NBu_4)_2$[*trans*-$PtCl_2(C_6F_5)_2$]. In neither case were we able to detect the formation of any intermediate. In contrast, the reaction of complex **1** with PPh_3, in CH_2Cl_2 at room temperature, in 1:1 mole ratio, causes the suspended solid to go into solution. If this solution is allowed to stand, AgCl is precipitated and the same decomposition products as above are collected. However, very rapid workup of the solution, i.e., centrifugation of a very slight turbidity (due to AgCl) and vacuum evaporation to dryness, followed by addition of 2-PrOH and washing with MeOH all within ca. 10 min, leads to the pale yellow solid complex **2**. This is formed in about 63% yield according to eq 2.

$$(NBu_4)_2[Pt_2Ag_2Cl_4(C_6F_5)_4] + 2PPh_3 \rightarrow 2(NBu_4)[PtAgCl_2(C_6F_5)_2PPh_3] \quad (2)$$

On the other hand, a dichloromethane suspension of complex **1** absorbs CO at room temperature and normal pressure, with simultaneous precipitation of AgCl. After AgCl is removed by filtration, (NBu_4)[*trans*-$PtCl(C_6F_5)_2(CO)$] (**3**) is obtained from the solution in 71% yield. Further bubbling of CO through the CH_2Cl_2 solution of **3** is ineffectual, in sharp contrast with the reaction of **1** with $AsPh_3$ and $SbPh_3$ where the intermediate $[PtCl(C_6F_5)_2L]^-$ cannot be intercepted or even observed, and only the neutral $[Pt(C_6F_5)_2L_2]$ products are obtained.

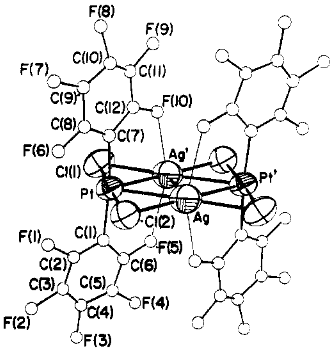

Figure 1. ORTEP drawing of the dianion $[Pt_2Ag_2Cl_4(C_6F_5)_4]^{2-}$ of **1**, showing the atom-labeling scheme. The complex is on a crystallographic inversion center. Carbon and fluorine atoms are shown as small circles, for clarity. Pt, Ag, and Cl atoms are represented by their 50% probability ellipsoids.

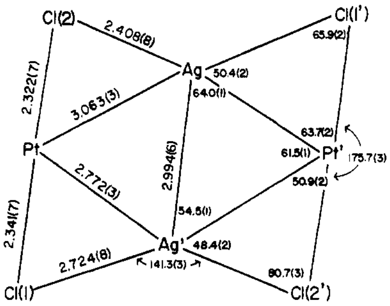

Figure 2. Scale drawing of the $Pt_2Ag_2Cl_4$ plane in compound **1**, annotated with bond distances and angles.

Analytical and some other data for complexes **1**–**3** are collected in Table I. Conductivity values are in the expected ranges in each case.[12] Some relevant IR data are given in Table II.

(b) Structures. The structures of complexes **1** and **2** have been solved by single-crystal X-ray crystallography. General crystallographic information is presented in Table III for both compounds. For complex **1**, $(NBu_4)_2[Pt_2Ag_2Cl_4(C_6F_5)_4]$, positional parameters and selected bond distances and angles are given in Tables IV and V, respectively.

The anionic tetranuclear cluster contains two platinum and two silver atoms and is located around a center of symmetry. The entire anionic structure, shown in Figure 1, is built around an essentially planar $Ag_2Pt_2Cl_4$ unit (important bond lengths and angles are shown in Figure 2) with one pentafluorophenyl ring per platinum atom above and another below this almost planar unit. The silver atoms are located 0.16 Å above and below the plane formed by the four chlorine and the two platinum atoms. Each platinum atom is bonded to two chlorine and two pentafluorophenyl rings in trans positions. Thus, there are "$PtCl_2(C_6F_5)_2$" units as in the starting mononuclear compound, in which

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Table III. Crystal Data for $(NBu_4)_2[Pt_2Ag_2Cl_4(C_6F_5)_4]$ (**1**) and $(NBu_4)[(C_6F_5)_2ClPt(\mu\text{-}Cl)AgPPh_3]\cdot 0.1CH_2Cl_2$ (**2**)

	1	**2**
formula	$Pt_2Ag_2Cl_4F_{20}N_2C_{56}H_{72}$	$PtAgCl_2PF_{10}NC_{46}H_{51}\cdot 0.1CH_2Cl_2$
fw	1900.9	1221.2
space group	$P\bar{1}$	$P\bar{1}$
a, Å	12.438 (9)	12.710 (3)
b, Å	13.160 (7)	18.865 (5)
c, Å	11.128 (7)	12.129 (5)
α, deg	103.53 (5)	103.10 (3)
β, deg	101.27 (6)	114.44 (2)
γ, deg	74.75 (5)	77.07 (2)
V, Å^3	1691 (2)	2551 (1)
Z	1	2
d_{calcd}, g/cm^3	1.87	1.59
cryst size, mm	0.25 × 0.20 × 0.09	0.57 × 0.42 × 0.20
μ(Mo Kα), cm^{-1}	51.5	34.7
data collecn instrument	Syntex P$\bar{1}$	Syntex P$\bar{1}$
radiation (monochromated in incident beam)	Mo Kα (λ_α = 0.71073 Å)	Mo Kα
orientation reflecns: no., range (2θ)	15, $21 < 2\theta < 30°$	13, $27 < 2\theta < 31°$
scan method	ω–2θ	ω–2θ
data collecn range, 2θ, deg	4.0–47.0	4.0–45.0
no. of unique data, total	2621	4194
no. of data in refinement	1615 ($F_o^2 \geq 3\sigma(F_o^2)$	3291 ($F_o^2 \geq 2\sigma(F_o^2)$)
no. of parameters refined	293	544
transmission factors: max, min	obsd 1.00, 0.62; calcd 0.63, 0.18	obsd 1.00, 0.80; calcd 0.50, 0.08
R^a	0.0786	0.0657
$R_w{}^b$	0.0957	0.0760
quality-of-fit indicator^c	2.030	1.399
largest shift/esd, final cycle	0.36	0.08
largest peak, e/Å^3	1.84	2.25

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality of fit $= [\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{parameters})]^{1/2}$.

Table IV. Atomic Positional Parameters and Equivalent Isotropic Displacement Parameters (Å^2) and Their Estimated Standard Deviations for $(NBu_4)_2[Pt_2Ag_2Cl_4(C_6F_5)_4]$ (**1**)[a]

atom	x	y	z	B
Pt	0.3463 (1)	0.5217 (1)	0.8185 (2)	7.52 (4)
Ag	0.4247 (3)	0.5320 (2)	1.0988 (3)	10.6 (1)
Cl(1)	0.4657 (8)	0.4924 (7)	0.6691 (8)	9.4 (3)
Cl(2)	0.2400 (8)	0.5484 (7)	0.9777 (8)	8.8 (3)
F(1)	0.144 (2)	0.424 (1)	0.680 (2)	9.4 (5)*
F(2)	0.107 (2)	0.229 (2)	0.594 (2)	12.8 (7)*
F(3)	0.271 (2)	0.058 (2)	0.636 (2)	14.1 (8)*
F(4)	0.477 (2)	0.086 (2)	0.760 (2)	11.8 (6)*
F(5)	0.517 (2)	0.277 (1)	0.836 (2)	9.8 (5)*
F(6)	0.148 (2)	0.717 (2)	0.786 (2)	11.6 (6)*
F(7)	0.131 (2)	0.924 (2)	0.823 (2)	15.7 (9)*
F(8)	0.301 (2)	1.013 (2)	0.907 (2)	13.6 (7)*
F(9)	0.508 (2)	0.888 (2)	0.957 (2)	11.6 (6)*
F(10)	0.535 (1)	0.675 (1)	0.920 (1)	7.9 (4)*
N	0.219 (2)	0.288 (2)	0.261 (3)	10 (1)
C(1)	0.331 (3)	0.364 (3)	0.773 (3)	9 (1)
C(2)	0.231 (3)	0.351 (2)	0.713 (3)	9 (1)
C(3)	0.201 (3)	0.258 (3)	0.668 (4)	13 (2)
C(4)	0.273 (3)	0.171 (3)	0.678 (4)	11 (1)
C(5)	0.387 (3)	0.167 (2)	0.735 (3)	9 (1)
C(6)	0.410 (3)	0.269 (2)	0.788 (3)	10 (1)
C(7)	0.344 (3)	0.681 (3)	0.849 (3)	10 (1)*
C(8)	0.241 (3)	0.753 (3)	0.834 (4)	11 (1)
C(9)	0.237 (3)	0.867 (3)	0.854 (3)	12 (1)
C(10)	0.339 (3)	0.896 (2)	0.896 (4)	13 (1)
C(11)	0.426 (3)	0.836 (4)	0.906 (4)	12 (2)
C(12)	0.441 (3)	0.726 (2)	0.891 (3)	8 (1)
C(13)	0.353 (3)	0.260 (3)	0.289 (3)	9 (1)
C(14)	0.409 (3)	0.235 (3)	0.420 (3)	9 (1)
C(15)	0.536 (3)	0.202 (3)	0.419 (3)	10 (1)*
C(16)	0.591 (4)	0.164 (4)	0.538 (4)	14 (2)*
C(17)	0.174 (3)	0.203 (2)	0.295 (3)	10 (1)
C(18)	0.214 (4)	0.095 (3)	0.212 (4)	12 (1)
C(19)	0.169 (4)	0.011 (3)	0.262 (4)	13 (1)*
C(20)	0.202 (5)	−0.102 (4)	0.181 (5)	16 (2)*
C(21)	0.180 (3)	0.397 (3)	0.361 (3)	9 (1)
C(22)	0.215 (4)	0.495 (3)	0.344 (4)	12 (2)
C(23)	0.160 (4)	0.577 (3)	0.442 (4)	13 (1)*
C(24)	0.191 (5)	0.677 (4)	0.448 (5)	17 (2)*
C(25)	0.194 (3)	0.301 (3)	0.130 (3)	9 (1)
C(26)	0.072 (3)	0.346 (3)	0.092 (4)	14 (1)
C(27)	0.051 (4)	0.326 (3)	−0.060 (4)	12 (1)*
C(28)	0.053 (5)	0.224 (4)	−0.119 (4)	15 (2)*

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

Table V. Selected Bond Distances (Å) and Bond Angles (deg) in $(NBu_4)_2[Pt_2Ag_2Cl_4(C_6F_5)_4]$ (1)

	Bond Distances		
Pt–Ag	3.063 (3)	Ag–Ag′	2.994 (6)
Pt–Ag′	2.772 (3)	Ag–Cl(1′)	2.724 (8)
Pt–Cl(1)	2.341 (7)	Ag–Cl(2)	2.408 (8)
Pt–Cl(2)	2.322 (7)	Ag···F(10′)	2.60 (1)
Pt–C(1)	2.07 (3)	Ag···F(5′)	2.69 (1)
Pt–C(7)	2.04 (3)		
	Bond Angles		
Ag–Pt–Ag′	61.5 (1)	C(1)–Pt–C(7)	173 (2)
Ag–Pt–Cl(1)	124.8 (2)	Pt–Ag–Pt′	118.5 (1)
–Cl(2)	50.9 (2)	Pt–Ag–Ag′	54.45 (8)
–C(1)	97.5 (9)	Pt–Ag–Cl(1′)	167.3 (2)
–C(7)	87.6 (9)	Pt–Ag–Cl(2)	48.4 (2)
Ag′–Pt–Cl(1)	63.7 (2)	Pt–Ag′–Ag	64.04 (9)
Ag′–Pt–Cl(2)	111.9 (2)	Pt–Ag′–Cl(1)	50.4 (2)
Ag′–Pt–C(1)	94 (1)	Pt–Ag′–Cl(2′)	165.1 (2)
Ag′–Pt–C(7)	93 (1)	Ag–Ag′–Cl(1)	114.1 (2)
Cl(1)–Pt–Cl(2)	175.7 (3)	Ag–Ag′–Cl(2′)	102.5 (2)
Cl(1)–Pt–C(1)	92.4 (9)	Cl(1)–Ag′–Cl(2′)	141.3 (2)
Cl(1)–Pt–C(7)	88 (1)	Pt–Cl(1)–Ag′	65.9 (2)
Cl(2)–Pt–C(1)	88.0 (8)	Pt–Cl(2)–Ag	80.7 (3)
Cl(2)–Pt–C(7)	92 (1)	F(5′)···Ag···F(10′)	153.5 (6)

two carbon and the two chlorine atoms form a slightly distorted-square-planar environment around the platinum atom. The corresponding angles between trans atoms are Cl(1)–Pt–Cl(2) = 175.7 (3)° and C(1)–Pt–C(7) = 173 (2)°, and the angles Cl–Pt–C are in the range of 92.4–88.0° (see Table V).

The two "$PtCl_2(C_6F_5)_2$" units then embrace a central Ag_2 unit in which the Ag–Ag distance is 2.994 (6) Å. These silver atoms show different kinds of contacts with the $PtCl_2(C_6F_5)_2$ units. As can be seen from Figure 2, each silver atom has a close contact with one platinum atom at 2.772 (3) Å and another longer contact with the other platinum atom at 3.063 (3) Å as well as a short Ag–Cl distance (2.408 (8) Å) and a longer one (2.724 (8) Å). Finally, the pentafluorophenyl groups are oriented in such a way (see Figure 1) that one of the ortho fluorine atoms of each group is located at about 2.6 Å from a silver atom (F(5′)–Ag = 2.69 (1) Å and F(10′)–Ag = 2.60 (1) Å, respectively). Fluorine atoms in contact with a given silver atom belong to the two C_6F_5 rings bonded to the same platinum center and are therefore above and below the cluster plane containing the four metal atoms. The angle F(5′)–Ag–F(10′) is 153.5 (6)°.

The short Pt–Ag′ distance (2.772 (3) Å) surely represents a platinum–silver bond, perhaps one of considerable strength. Until recently, there were very few reported examples of Pt–Ag bonds,[13-18] and in every case there were bridging ligands between

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Table VI. Atomic Positional Parameters and Equivalent Isotropic Displacement Parameters (Å^2) and Their Estimated Standard Deviations for $(NBu_4)[(C_6F_5)_2ClPt(\mu\text{-}Cl)AgPPh_3]\cdot 0.1CH_2Cl_2$ (**2**)[a]

atom	*x*	*y*	*z*	*B*	atom	*x*	*y*	*z*	*B*
Pt	0.20072 (7)	0.30112 (5)	0.15525 (8)	4.17 (2)	C(17)	0.099 (2)	0.085 (2)	−0.458 (3)	12 (1)
Ag	0.2199 (2)	0.1503 (1)	0.0673 (2)	6.43 (6)	C(18)	0.121 (2)	0.055 (2)	−0.356 (2)	8.2 (8)
Cl(1)	0.3090 (5)	0.2114 (3)	0.2808 (5)	5.7 (2)	C(19)	0.050 (2)	0.017 (1)	−0.153 (2)	5.5 (6)
Cl(2)	0.0963 (5)	0.3873 (3)	0.0278 (5)	6.3 (2)	C(20)	−0.053 (2)	0.067 (1)	−0.161 (3)	9.0 (9)
P	0.1801 (5)	0.0608 (3)	−0.1088 (6)	6.3 (2)	C(21)	−0.153 (2)	0.037 (2)	−0.194 (3)	10 (1)
F(1)	0.3277 (9)	0.2804 (7)	−0.040 (1)	7.3 (4)	C(22)	−0.152 (2)	−0.044 (1)	−0.225 (2)	7.0 (7)
F(2)	0.517 (1)	0.3285 (9)	−0.020 (1)	9.0 (4)	C(23)	−0.051 (2)	−0.090 (1)	−0.216 (2)	7.4 (8)
F(3)	0.646 (1)	0.4067 (7)	0.193 (1)	10.0 (4)	C(24)	0.057 (2)	−0.059 (1)	−0.176 (2)	7.2 (8)
F(4)	0.579 (1)	0.4352 (7)	0.384 (1)	8.2 (4)	C(25)	0.303 (2)	−0.014 (1)	−0.096 (2)	7.4 (8)
F(5)	0.3961 (9)	0.3847 (7)	0.370 (1)	6.7 (4)	C(26)	0.336 (2)	−0.054 (2)	−0.003 (3)	11 (1)
F(6)	−0.0316 (9)	0.2376 (6)	−0.0595 (9)	5.6 (3)	C(27)	0.438 (3)	−0.113 (2)	0.011 (3)	13 (1)
F(7)	−0.227 (1)	0.2151 (7)	−0.055 (1)	9.0 (5)	C(28)	0.490 (3)	−0.123 (2)	−0.072 (4)	14 (1)
F(8)	−0.263 (1)	0.2457 (8)	0.157 (1)	11.4 (5)	C(29)	0.459 (2)	−0.084 (2)	−0.161 (3)	12 (1)
F(9)	−0.095 (1)	0.2996 (8)	0.366 (1)	9.6 (4)	C(30)	0.360 (2)	−0.025 (2)	−0.179 (3)	11 (1)
F(10)	0.104 (1)	0.3223 (7)	0.366 (1)	7.9 (4)	C(31)	0.243 (2)	0.559 (1)	0.320 (2)	5.3 (6)
N	0.274 (1)	0.6160 (9)	0.272 (1)	5.5 (5)	C(32)	0.112 (2)	0.562 (1)	0.284 (2)	7.0 (7)
C(1)	0.352 (1)	0.331 (1)	0.168 (2)	4.7 (6)	C(33)	0.093 (2)	0.501 (1)	0.343 (2)	8.4 (8)
C(2)	0.387 (2)	0.316 (1)	0.070 (2)	5.3 (6)	C(34)	0.131 (2)	0.518 (2)	0.475 (2)	12 (1)
C(3)	0.492 (2)	0.344 (1)	0.080 (2)	5.6 (6)	C(35)	0.224 (2)	0.607 (1)	0.132 (2)	5.7 (7)
C(4)	0.553 (2)	0.381 (1)	0.183 (2)	6.3 (7)	C(36)	0.272 (2)	0.534 (1)	0.071 (2)	6.2 (7)
C(5)	0.519 (2)	0.394 (1)	0.278 (2)	5.4 (6)	C(37)	0.207 (2)	0.533 (1)	−0.068 (2)	6.5 (7)
C(6)	0.420 (1)	0.367 (1)	0.268 (2)	4.5 (5)	C(38)	0.246 (2)	0.464 (1)	−0.142 (2)	7.0 (8)
C(7)	0.046 (1)	0.278 (1)	0.154 (2)	4.8 (6)	C(39)	0.407 (2)	0.605 (1)	0.331 (2)	5.9 (6)
C(8)	−0.042 (1)	0.255 (1)	0.053 (2)	4.3 (6)	C(40)	0.461 (2)	0.661 (1)	0.292 (2)	8.4 (9)
C(9)	−0.145 (2)	0.242 (1)	0.053 (2)	5.7 (7)	C(41)	0.600 (2)	0.635 (2)	0.358 (2)	11.3 (9)
C(10)	−0.162 (2)	0.254 (1)	0.153 (2)	5.5 (5)*	C(42)	0.660 (2)	0.691 (2)	0.347 (3)	12 (1)
C(11)	−0.080 (2)	0.285 (1)	0.261 (2)	6.3 (6)	C(43)	0.226 (2)	0.694 (1)	0.317 (2)	7.0 (8)
C(12)	0.018 (2)	0.294 (1)	0.258 (2)	6.0 (6)	C(44)	0.266 (2)	0.714 (1)	0.458 (2)	8.2 (9)
C(13)	0.151 (2)	0.099 (1)	−0.243 (2)	6.3 (7)	C(45)	0.214 (3)	0.792 (2)	0.495 (3)	15 (1)*
C(14)	0.156 (2)	0.175 (1)	−0.222 (2)	9.5 (9)	C(46)	0.247 (6)	0.844 (4)	0.485 (6)	28 (3)*
C(15)	0.138 (2)	0.210 (2)	−0.321 (3)	12 (1)	C(47)	0.48 (4)	0.98 (3)	0.54 (4)	20[b]
C(16)	0.112 (2)	0.163 (2)	−0.443 (2)	14 (1)	Cl(3)	0.515 (6)	0.933 (4)	0.398 (6)	21 (2)*

[a] Atoms marked with an asterisk were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as in Table IV. [b] The displacement parameter of atom C(47) was not included in the last cycle in which this atom was refined.

Table VII. Selected Bond Distances (Å) and Bond Angles (deg) in $(NBu_4)[PtAgCl_2(C_6F_5)_2PPh_3]$ (**2**)

	Bond Distances		
Pt-Ag	2.796 (2)	Pt-C(7)	2.10 (2)
Pt-Cl(1)	2.339 (5)	Ag-Cl(1)	2.473 (5)
Pt-Cl(2)	2.296 (5)	Ag-P	2.350 (6)
Pt-C(1)	2.05 (2)		
	Bond Angles		
Ag-Pt-Cl(1)	56.8 (1)	Cl(2)-Pt-C(1)	88.7 (6)
-Cl(2)	122.0 (2)	-C(7)	90.8 (5)
-C(1)	104.2 (5)	C(1)-Pt-C(7)	175 (1)
-C(7)	80.1 (6)	Pt-Ag-Cl(1)	52.3 (1)
Cl(1)-Pt-Cl(2)	178.4 (2)	Pt-Ag-P	145.2 (2)
-C(1)	90.7 (6)	Cl(1)-Ag-P	161.6 (2)
-C(7)	90.0 (5)	Pt-Cl(1)-Ag	71.0 (1)

platinum and silver that might be responsible for the observed distances (in the range of 2.787–3.146 Å). However, we have recently described[19] the compound $(NBu_4)[Pt_2Ag(C_6F_5)_6OEt_2]\cdot OEt_2$, which contains two platinum-silver bonds, with distances 2.827 (2) and 2.815 (2) Å, unsupported by any covalent bridge. In complex **1**, $(NBu_4)_2[Pt_2Ag_2Cl_4(C_6F_5)_4]$, although Cl(1) is acting as a bridging ligand between the Pt and Ag′ atoms, the Cl(1)–Ag′ distance is rather long and, moreover, the angle Pt–Cl(1)–Ag′ is only 65.9 (2)°. It is thus difficult to believe that Cl(1) is forcing the close approach of the Pt and Ag′ atoms. On the contrary, the distances and angles[20] imply the existence of a direct Pt–Ag′ bond. The presence of another Pt–Ag bond between atoms located at a distance of 3.063 (3) Å (see Figure 2)—or the strength of such a bond—is more questionable. In this case we note that the Cl(2) atom, which is acting as a bridge between the metal atoms, appears to be strongly bonded to both, with Pt–Cl(2) and Cl(2)–Ag distances of 2.322 (7) and 2.408 (8) Å, respectively, and the angle Pt–Cl(2)–Ag of 80.7 (3)° is larger than the previous one. It is possible that the two metal atoms are in this case only weakly if at all bonded to each other.[20]

The Ag–Ag distance is near the high end of the range spanned by previous cases in which Ag–Ag bonding has been presumed to occur; most of the distances reported in the literature[21-32] range from 2.740 (2) to 3.085 (2) Å. Nevertheless, the longer distances seem to be compatible with Ag–Ag bonds. For example, in silver(I) imidazole perchlorate,[27] there is a planar $(Ag^+)_6$ cluster,

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in which there are two different Ag–Ag distances of 3.051 (1) and 3.493 (1) Å, and the absence of any bridging group between silver atoms was considered by the authors as a proof of the presence of Ag–Ag bonds even for the longer distance. As further points of reference we note that the Ag–Ag distance in metallic silver[33] is 2.889 (6) Å and the sum of Pauling R_1 radii[34] is 2.68 Å for an Ag–Ag bond.

Another remarkable feature of this structure is the close approach of the two ortho fluorine atoms to each silver atom (2.60 (1) and 2.69 (1) Å). The expected length for a Ag–F bond[34] would be 1.98 Å, so that here the interaction does not approach true bond formation. However, some cationic silver compounds where the counterion is a fluorinated anion (PF_6^- or AsF_6^-) show Ag–F contacts with similar or longer distances. For example, in $[Ag(2,4,6\text{-}tert\text{-}Bu_3C_6H_2NC)_2]PF_6$[35] the Ag–F distance is 2.668 (4) Å and it is 2.844 (8) Å in $[Ag(S_3N_2O)_2]AsF_6$.[36] In the present case it seems that these Ag···F interactions might contribute to the stability of the cluster, since rotation around the Pt–C bond could easily lead to an apparent overall lessening of nominally nonbonding contacts. This situation is also present in $(NBu_4)[Pt_2Ag(C_6F_5)_6OEt_2]\cdot OEt_2$ and $[Pt(C_6F_5)_3(SC_4H_8)AgPPh_3]$, recently reported by us,[19] but as far as we know, no other cases have been observed.

For complex **2**, Table VI gives positional parameters and Table VII gives bond distances and angles. The structure of the anion, $[PtAgCl_2(C_6F_5)_2PPh_3]^-$, is shown in Figure 3. It consists of an almost square-planar $[trans\text{-}PtCl_2(C_6F_5)_2]^{2-}$ unit linked to the cationic part $[Ag(PPh_3)]^+$ both by a platinum–silver bond and by a chlorine bridge.

Within the square-planar unit, all the bond lengths are normal: Pt–C(1) = 2.05 (2) Å, Pt–C(7) = 2.10 (2) Å, Pt–Cl(1) = 2.339 (5) Å, and Pt–Cl(2) = 2.296 (5) Å. In addition, the Pt atom is in contact with the silver atom, forming a bond of considerable strength, with a Pt–Ag distance of 2.796 (2) Å. The Pt atom is thus pentacoordinated, and since the Pt–Ag bond is not perpendicular to the plane formed by C(1), C(7), Cl(1), and Cl(2), the geometry is a very distorted-square-pyramidal one, with angles Ag–Pt–Cl(1), Ag–Pt–Cl(2), Ag–Pt–C(1), and Ag–Pt–C(7) of, respectively, 56.8 (1), 122.0 (2), 104.2 (5), and 80.1 (6)°. The silver atom is three-coordinate with bond distances Ag–P = 2.350 (6) Å, Ag–Cl(1) = 2.473 (5) Å, and Ag–Pt = 2.796 (2) Å. Bond angles around the Ag atom are Cl(1)–Ag–P = 161.6 (2)°, Pt–Ag–P = 145.2 (2)°, and Pt–Ag–Cl(1) = 52.3 (1)°.

On comparison of the two structures it is seen that even though complex **2** results chemically from the splitting of the tetranuclear complex **1** by the PPh_3 ligands, the structure of complex **2** is not simply that of half of the anion in compound **1**. In complex **1** the longer Pt–Ag distance is bridged by the Cl(2) atom, which forms a short bond to the Ag atom, while the shorter Pt–Ag distance bridged by Cl(1) has a long Cl–Ag distance. Complex **2** shows at the same time short Pt–Ag and Ag–Cl distances, indicating that the split of the tetranuclear compound is accompanied by changes in the strengths of the platinum–silver or silver–chloride bonds.

It is also remarkable that in complex **2** no distances less than 3.1 Å are observed between any of the ortho fluorine atoms of the C_6F_5 group and the silver atom. This dissimilarity to the structure of complex **1** might be due to the fact that the coordination of the PPh_3 ligand to the silver atom increases the electron density around the metal atom, making it less acidic. It is also possible that the steric requirements of the triphenylphosphine oppose the formation of F···Ag interactions.

(c) IR Spectra. Significant absorption frequencies for complexes **1**–**3** are listed in Table II. In addition to the bands internal to the C_6F_5 groups, there are C–Pt stretching modes (the so-called X-sensitive modes) of the C_6F_5–X group,[37] which are found as single absorptions in complexes **1** and **2**. In the mononuclear precursor, a single strong band is found at 765 cm^{-1}.

In the ν(Pt–Cl) region, complex **1** shows a broad absorption at 320 cm^{-1}, which may be compared to the occurrence of a sharp band at 320 cm^{-1} in the monomeric precursor. The breadth is presumably due to the existence of several M–Cl bonds of different strengths. Complex **2** shows two bands, at 342 (m) and 298 (m) cm^{-1}, in the ν(Pt–Cl) region, in accord with presence of both terminal and bridging Cl ligands.

The IR spectrum of complex **3** shows bands due to the C_6F_5 group,[37] along with a very strong absorption at 2084 cm^{-1}, due to ν(CO) and a band at 330 (m) cm^{-1}, which can be assigned to the ν(Pt–Cl) vibration. A shoulder (790 cm^{-1}) on the strong band at 779 cm^{-1} is present both in the solid-state IR spectrum and in a spectrum taken from a benzene solution of complex **3**. These two bands, which we assign to X-sensitive modes of the C_6F_5 group,[37] do not distinguish between cis and trans isomers, since both are expected to give two IR-active X-sensitive modes in this region (cis, point group C_s, two A′ modes; trans, point group C_{2v}, $A_1 + B_2$). However, since we usually have not observed any isomerization by the splitting of binuclear bridged complexes with neutral ligands, it seems sensible tentatively to assume that a trans configuration persists in complex **3**.

Experimental Section

Elemental analyses for C, H, and N were made with a Perkin-Elmer 240 C microanalyzer; conductivities were measured in approximately 5×10^{-4} M acetone solutions with a Philips PW 9501/01 conductimeter. IR spectra (4000–200 cm^{-1}) were recorded on a Perkin-Elmer 599 spectrometer using Nujol mulls between polyethylene sheets. All the reactions were carried out under exclusion of light. $(NBu_4)_2[trans\text{-}PtCl_2(C_6F_5)_2]$ was prepared as described elsewhere.[10]

Preparation of $(NBu_4)_2[Pt_2Ag_2Cl_4(C_6F_5)_4]$ (1). Method a. To a solution of 0.90 g (0.83 mmol) of $(NBu_4)_2[trans\text{-}PtCl_2(C_6F_5)_2]$ in 20 mL of MeOH was added 0.141 g (0.83 mmol) of $AgNO_3$ or 0.172 g (0.83 mmol) of $AgClO_4$. A pale yellow precipitate (complex **1**) was immediately formed. The solid was filtered off and washed with MeOH (90% yield).

Method b. A 1.164-g (1.074-mmol) quantity of $(NBu_4)_2[trans\text{-}PtCl_2(C_6F_5)_2]$ in 25 mL of acetone was treated with 0.222 g (1.074 mmol) of $AgClO_4$ for 2 h. A white solid was filtered off, and the pale yellow solution was evaporated to dryness and the residue washed with 2-PrOH. Complex **1** was obtained in 68% yield.

Preparation of $(NBu_4)[PtAgCl_2(C_6F_5)_2PPh_3]$ (2). To a suspension of 0.5 g (0.26 mmol) of complex **1** in 40 mL of CH_2Cl_2 was added 0.138 g (0.52 mmol) of PPh_3 at room temperature. Complex **1** dissolved immediately, leaving a very slight turbidity, due to AgCl. The mixture was centrifuged to separate the very small amount of AgCl. The yellow solution was immediately evaporated to dryness, and the residue was treated with 10 mL of 2-PrOH and washed with 5 mL of cold MeOH (yield 63%).

Similar reactions were attempted with $AsPh_3$ or $SbPh_3$, but they did not lead to binuclear Pt–Ag compounds. Instead, large amounts of AgCl precipitated and a mixture of $[trans\text{-}Pt(C_6F_5)_2L_2]$ and $(NBu_4)_2[PtCl_2(C_6F_5)_2]$ was obtained. The mixture of neutral and anionic compounds could be separated because of the insolubility of the former in MeOH. $[Pt(C_6F_5)_2(AsPh_3)_2]$, $[Pt(C_6F_5)_2(SbPh_3)_2]$, and $(NBu_4)_2[PtCl_2(C_6F_5)_2]$ were identified (IR spectra and analysis).

Preparation of $(NBu_4)[trans\text{-}PtCl(C_6F_5)_2(CO)]$ (3). Carbon monoxide was bubbled through a solution of 0.2 g (0.105 mmol) of complex **1** in 50 mL of CH_2Cl_2 at room temperature for 30 min. A white solid (AgCl) precipitated. The colorless solution obtained after separating the AgCl by centrifugation was concentrated to ca. 5 mL. Colorless needles of complex **3** (71% yield) were obtained by diffusion of 30 mL of *n*-hexane at −30 °C into the CH_2Cl_2 solution of the complex.

Preparation of Crystals for X-ray Structure Determination. Crystals of complex **1**, $(NBu_4)_2[Pt_2Ag_2Cl_4(C_6F_5)_4]$, were obtained by slow diffusion (ca. 3 weeks) of 2-PrOH into an acetone solution of the complex at −25 °C. Partial decomposition took place, and some AgCl was also identified.

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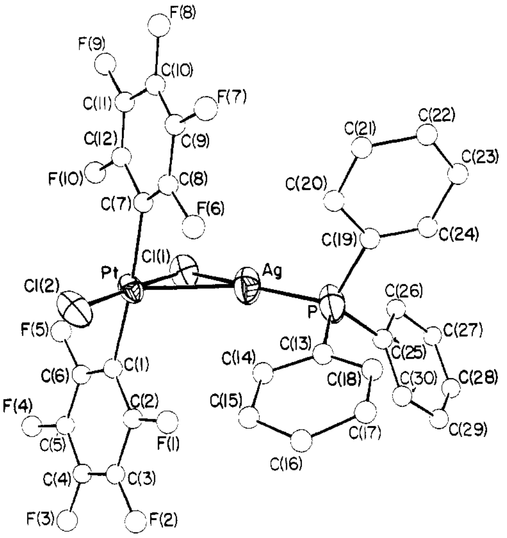

Figure 3. ORTEP drawing of the complex anion $[PtAgCl_2(C_6F_5)_2PPh_3]$, showing the atom-labeling scheme. Carbon and fluorine atoms are shown as small circles, for clarity. Pt, Ag, Cl, and P atoms are represented by their 40% probability ellipsoids.

Crystals of complex **2**, $(NBu_4)[PtAgCl_2(C_6F_5)_2PPh_3]$, were obtained by slow diffusion (ca. 3 weeks) of *n*-hexane into a solution of the complex in CH_2Cl_2 at −20 °C. Some AgCl was again formed.

X-ray Structure Analyses. Crystal data were taken by routine procedures,[38] from a crystal of compound **1** sealed in a glass capillary tube, and from a crystal of compound **2** mounted at the end of a glass fiber and covered with a thin layer of epoxy. Crystal data, data collection parameters, and residuals from the refinements of both structures are given in Table III. During intensity data collection for each structure, three standard reflections were measured after each 97 data scans. These lost an average of 45% of their initial intensities over the total X-ray beam time of 157 h for **1**; for **2** the average decay was 42% over 81 h of beam time.

Data reduction[39] for each compound included an interpolative decay correction as well as an empirical absorption correction[40] based on azimuthal scans of six reflections for **1** and five reflections for **2**.

The structure of compound **1** was solved by direct methods and developed and refined in a series of alternating difference Fourier maps and least-squares analyses. The least-squares calculations converged with the residuals given in Table III, with a data-to-parameter ratio of 5.5. The least-squares variance was slightly larger than normal, as reflected by a quality-of-fit indicator of 2.03; see Table III. This is in line with our observation of a gradual but systematic increase in the quantity $w(|F_o| - |F_c|)^2$ as a function of data-collection order, which is in turn consistent with the observed decay of the crystal. The effect was not serious enough to warrant systematic omission of data from the refinement. A difference map following convergence had four peaks above 1 e/Å^3, all located in the area of the central metal cluster. This effect is common in crystals containing strongly scattering and strongly absorbing elements.

For compound **2** the positions of the Pt and Ag atoms were derived from a Patterson map, and the structure was developed in a series of difference maps and least-squares refinements. Near the end of the structure development, a difference map showed a molecule of CH_2Cl_2 disordered near a crystallographic inversion center. The multiplicities and displacement parameters of the C and Cl atoms of this moiety were refined alternately (in least-squares analyses including the entire structure), yielding a model with a multiplicity of 0.1 for the CH_2Cl_2 molecule. The final least-squares calculation, in which the CH_2Cl_2 molecule was not refined, converged with residuals as given in Table III. The data-to-parameter ratio was 6.0. A difference map following the refinement had several peaks, the largest of which had a density of 2.25 e/Å^3, in the vicinity of the Pt and Ag atoms, and two peaks of density 1 e/Å^3 which were ghosts of the atoms of the dichloromethane molecule. Several models had been refined for the CH_2Cl_2 moiety, and despite the presence of these small residual Fourier peaks, it was quite clear that the model used was the only acceptable one.

Acknowledgment. This work was supported by the U.S. National Science Foundation and by the CAYCIT in Spain.

Registry No. **1**, 98839-46-4; **2**, 98839-48-6; **2**·xCH$_2$Cl$_2$, 98839-49-7; **3**, 98839-51-1; $(Bu_4N)_2$[*trans*-$PtCl_2(C_6F_5)_2$], 74436-22-9; [*trans*-$Pt(C_6F_5)_2(PPh_3)_2$], 14832-07-6; [*trans*-$Pt(C_6F_5)_2(AsPh_3)_2$], 60873-45-2; [*trans*-$Pt(C_6F_5)_2(SbPh_3)_2$], 98919-99-4; $AgNO_3$, 7761-88-8; $AgClO_4$, 7783-93-9; $AsPh_3$, 603-32-7; $SbPh_3$, 603-36-1; Ag, 7440-22-4; Pt, 7440-06-4; F_2, 7782-41-4.

Supplementary Material Available: Full listings of bond distances and angles, anisotropic displacement parameters, and observed and calculated structure factors for **1** and **2** (37 pages). Ordering information is given on any current masthead page.

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(38) Cotton, F. A.; Frenz, B. A.; Deganello, G.; Shaver, A. *J. Organomet. Chem.* **1973**, *50*, 227.

(39) Calculations were done on a VAX-11/780 (VMS V3.6) computer with software from the package VAXSDP and with SHELX76 and on a PDP-11/60 (RSX-11M V4.1) with PDP-11 simulated VAXSDP.

(40) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 351.

(41) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)