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Synthesis, X-ray Structure, and Reactivity of $(NBu_4)_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]\cdot H_2O$ and $(NBu_4)[Pt_2Ag(\mu\text{-}C_6F_5)_2(C_6F_5)_4O(C_2H_5)_2]$. The First Complexes Containing Bridging Pentafluorophenyl Groups

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By reacting $(NBu_4)_2[Pt(C_6F_5)_3Cl]$ with $AgClO_4$ (molar ratio 1:1) in CH_2Cl_2/diethyl ether, the binuclear complex $(NBu_4)_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$ (1) is obtained. $(NBu_4)[Pt_2Ag(\mu\text{-}C_6F_5)_2(C_6F_5)_4]\cdot O(C_2H_5)_2$ (2) can be prepared by reacting 1 with $AgClO_4$ (molar ratio 1:1) or by treating $(NBu_4)_2[Pt(C_6F_5)_3Cl]$ with $AgClO_4$ (molar ratio 1:2) in CH_2Cl_2/diethyl ether. Complex 2 reacts with neutral monodentate ligands (L) yielding $(NBu_4)[Pt_2Ag(\mu\text{-}C_6F_5)_2(C_6F_5)_4L]$ (L = PPh_3, 3; L = CNCy, 4). The structures of the binuclear platinum complex 1 and the trinuclear Pt_2Ag complex 2 have been solved by single-crystal X-ray diffraction. Complex 1 contains the platinum atoms bridged by pentafluorophenyl groups (Pt–Pt distance = 2.714 (1) Å). Complex 2 contains two Pt–Ag bonds unsupported by other covalent bridges (Pt–Ag distances = 2.815 (2) and 2.804 (2) Å. The platinum atoms (Pt–Pt distance = 2.687 (1) Å) are bridged by two pentafluorophenyl groups and one silver atom. The bridging pentafluorophenyl groups are oriented in such a way that the silver atom makes short contacts with ortho fluorine atoms of these groups (Ag···F(5) = 2.653 (10) Å, Ag···F(10) = 2.670 (10) Å). These complexes are the only cases in which C_6F_5 groups have been proved to act as bridging ligands.

Introduction

We have recently described the synthesis of polynuclear Pt–Ag complexes containing Pt–Ag bonds,[1-5] most of them unsupported by covalent bridges.[2,4,5] These complexes are obtained by reacting anionic perhalophenylplatinum(II) complexes and suitable silver salts ($AgClO_4$, $AgNO_3$) or complexes ($R_3PAgOClO_3$).

In this paper we report the study of the reaction between $(NBu_4)_2[Pt(C_6F_5)_3Cl]$, a mononuclear halide-containing platinum complex, and $AgClO_4$ in CH_2Cl_2, in different molar ratios. The binuclear derivative $(NBu_4)_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$ is obtained for a molar ratio of 1:1; and the trinuclear $(NBu_4)[Pt_2Ag(\mu\text{-}C_6F_5)_2(C_6F_5)_4\cdot O(C_2H_5)_2]$ can be isolated for a molar ratio of 1:2. The trinuclear complex **2** can also be obtained by reacting **1** with $AgClO_4$. The structures of **1** and **2** have been established by single-crystal X-ray diffraction studies. Some of these results have been the subject of a preliminary communication.[2]

Results and Discussion

(a) Synthesis of $(NBu_4)_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$. When $AgClO_4$ is added to a colorless solution of $(NBu_4)_2[Pt(C_6F_5)_3Cl]$ in dichloromethane, AgCl precipitates; and after 2 h of stirring at room temperature, a yellow solution is obtained. When this solution is evaporated to dryness, a yellow solid containing $(NBu_4)_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$ (1; 76% yield) and NBu_4ClO_4 is obtained (eq 1). Both can be separated by treatment with diethyl ether, in which complex 1 is soluble. Analytical and conductivity data for 1 are given in Table I.

$$2(NBu_4)_2[Pt(C_6F_5)_3Cl] + 2AgClO_4 \rightarrow 2AgCl + 2NBu_4ClO_4 + (NBu_4)_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4] \quad (1)$$

When dichloromethane solutions of 1 are treated with L (L = PPh_3, CO), $(NBu_4)[Pt(C_6F_5)_3L]$ can be isolated[7,8] (eq 2). The yellow acetone or THF solutions of complex 1 slowly turn colorless (~3 h), probably because of the breaking of the binuclear complex by the donor solvent (eq 2); however, if these colorless solutions are evaporated to dryness, the yellow complex 1 can be recovered. No change in the color of the solutions of complex 1 is observed in nondonor solvents (CH_2Cl_2, $CHCl_3$).

$$(NBu_4)_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4] + 2L \rightarrow 2(NBu_4)[Pt(C_6F_5)_3L] \quad (2)$$

(b) Structure of $(NBu_4)_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]\cdot H_2O$ (1). The structure of complex 1 has been determined by single-crystal X-ray diffraction. General crystallographic information is collected in Table II. Positional and equivalent isotropic displacement parameters are listed in Table III. Selected bond distances and angles are given in Table IV. The structure of the complex anion in 1 is shown in Figure 1. It is a binuclear platinum complex with a pair of pentafluorophenyl groups bridging the metal centers. Each platinum atom has two cis C_6F_5 groups in terminal positions, so that the platinum atoms are in

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Table I. Analytical and Conductivity Data for Compounds 1–4[a]

	C	H	N	Λ_M,[b] Ω^{-1} cm^2 mol^{-1}
$(NBu_4)_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$ (1)	43.65 (43.50)	4.25 (3.85)	1.50 (1.50)	203
$(NBu_4)[Pt_2Ag(\mu\text{-}C_6F_5)_2(C_6F_5)_4{\cdot}O(C_2H_5)_2]$ (2)	37.0 (37.0)	2.50 (2.55)	0.70 (0.80)	115
$(NBu_4)[Pt_2Ag(\mu\text{-}C_6F_5)_2(C_6F_5)_4PPh_3]$ (3)	42.40 (41.98)	2.80 (2.55)	0.80 (0.70)	109
$(NBu_4)[Pt_2Ag(\mu\text{-}C_6F_5)_2(C_6F_5)_4CNCy]$ (4)	37.50 (36.80)	2.45 (2.45)	1.45 (1.45)	111

[a] Calculated values are given in parentheses. [b] Acetone.

Table II. Crystallographic Data for $(NBu_4)_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]\bullet H_2O$ (1) and $(NBu_4)[Pt_2Ag(\mu\text{-}C_6F_5)_2(C_6F_5)_4\bullet O(C_2H_5)_2]\bullet {}^1/_2n\text{-}C_6H_{14}$ (2)

	1	2
formula	$Pt_2F_{30}ON_2C_{68}H_{74}$	$Pt_2AgF_{30}ONC_{59}H_{53}$
fw	1895.47	1860.07
space group	$C2/c$	$P2_1/c$
systematic absences	hkl, $h + k \neq 2n$; $h0l$, $l \neq 2n$	$0k0$, $k \neq 2n$; $h0l$, $l \neq 2n$
a, Å	29.281 (6)	11.278 (6)
b, Å	12.629 (3)	25.643 (8)
c, Å	21.248 (3)	22.359 (7)
β, deg	113.74 (1)	94.92 (3)
V, Å^3	7193 (5)	6443 (8)
Z	4	4
d_{calcd}, g/cm^3	1.750	1.917
cryst size, mm	0.43 × 0.38 × 0.30	0.29 × 0.12 × 0.08
μ(Mo Kα), cm^{-1}	42.2	49.9
data collectn instrument	Nicolet P3/F	Enraf-Nonius CAD-4F
radiatn (monochromated in incident beam)	Mo Kα (λ_α = 0.71073 Å)	
orientatn reflectns, no., range (2θ)	25; 21–28	20; 25–40
temp, °C	20 ± 2	23 ± 3
scan method	ω-scans	ω-scans
data collectn range, 2θ, deg	4–50	4–47
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	5056, 3671	6484, 4061
no. of parameters refined	465	779
trans factors, max, min	obsd 1.00, 0.88	obsd 1.00, 0.82
R[a]	0.0463	0.0437
R_w[b]	0.0599	0.0510
quality-of-fit indicator[c]	1.07	1.065
largest shift/esd, final cycle	0.01	0.19
largest peak, e/Å^3	0.92	0.87

[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 $= [\sum w(|F_o| - |F_c|)^2/(N_{obsd} - N_{parameters})]^{1/2}$.

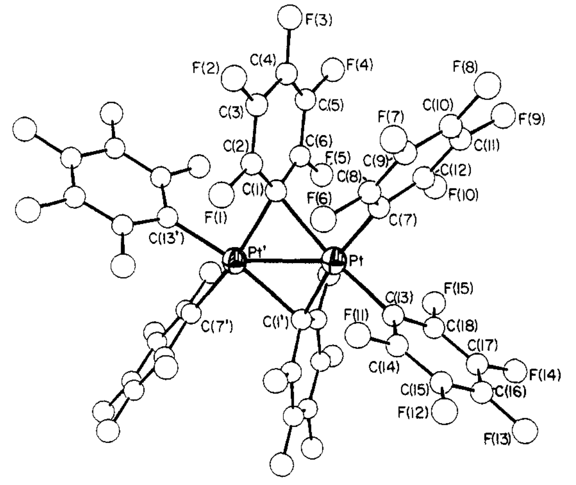

Figure 1. ORTEP drawing of the yellow anion $[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]^{2-}$.

Table III. Positional and Equivalent Isotropic Displacement Parameters and Their Estimated Standard Deviations for $(NBu_4)_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]\bullet H_2O$ (1)[a]

atom	x	y	z	B (Å^2)
Pt	0.45058 (1)	0.39940 (4)	0.20871 (2)	3.266 (8)
C(1)	0.4885 (4)	0.3725 (9)	0.3226 (5)	3.5 (2)
C(2)	0.4802 (4)	0.453 (1)	0.3638 (6)	4.4 (3)
C(3)	0.4599 (4)	0.434 (1)	0.4112 (6)	4.6 (3)
C(4)	0.4478 (4)	0.332 (1)	0.4206 (6)	5.8 (4)
C(5)	0.4580 (5)	0.251 (1)	0.3855 (6)	5.2 (3)
C(6)	0.4775 (4)	0.2746 (9)	0.3377 (5)	4.1 (3)
C(7)	0.3868 (4)	0.408 (1)	0.2228 (5)	4.0 (3)
C(8)	0.3691 (4)	0.500 (1)	0.2431 (5)	4.2 (3)
C(9)	0.3242 (4)	0.507 (1)	0.2497 (6)	6.3 (4)
C(10)	0.2952 (5)	0.422 (2)	0.2376 (7)	7.9 (5)
C(11)	0.3095 (5)	0.328 (1)	0.2191 (7)	7.1 (4)
C(12)	0.3553 (4)	0.324 (1)	0.2130 (6)	5.0 (3)
C(13)	0.4066 (4)	0.423 (1)	0.1090 (5)	3.8 (3)
C(14)	0.3891 (4)	0.522 (1)	0.0828 (5)	4.6 (3)
C(15)	0.3573 (4)	0.540 (1)	0.0168 (6)	5.6 (3)
C(16)	0.3423 (5)	0.460 (2)	−0.0291 (6)	6.6 (4)
C(17)	0.3594 (5)	0.360 (1)	−0.0073 (6)	6.4 (4)
C(18)	0.3911 (4)	0.344 (1)	0.0608 (6)	4.8 (3)
F(1)	0.4913 (3)	0.5547 (6)	0.3569 (4)	5.7 (2)
F(2)	0.4513 (3)	0.5124 (7)	0.4470 (4)	7.3 (2)
F(3)	0.4301 (3)	0.3111 (9)	0.4682 (4)	9.5 (3)
F(4)	0.4453 (3)	0.1500 (7)	0.3943 (5)	8.8 (3)
F(5)	0.4844 (3)	0.1885 (6)	0.3031 (4)	6.0 (2)
F(6)	0.3969 (3)	0.5889 (6)	0.2552 (4)	6.1 (2)
F(7)	0.3102 (3)	0.5972 (8)	0.2681 (4)	8.9 (2)
F(8)	0.2514 (3)	0.430 (1)	0.2441 (5)	11.2 (3)
F(9)	0.2812 (3)	0.2405 (9)	0.2050 (5)	10.6 (3)
F(10)	0.3684 (3)	0.2280 (6)	0.1946 (4)	7.6 (2)
F(11)	0.4006 (3)	0.6055 (7)	0.1260 (4)	6.7 (2)
F(12)	0.3397 (3)	0.6409 (8)	−0.0031 (5)	9.1 (3)
F(13)	0.3116 (3)	0.479 (1)	−0.0947 (4)	10.5 (3)
F(14)	0.3436 (3)	0.277 (1)	−0.0508 (4)	9.6 (3)
F(15)	0.4056 (3)	0.2422 (6)	0.0795 (4)	6.7 (2)
N	0.1514 (3)	0.3994 (8)	0.3361 (4)	4.2 (2)
C(19)	0.1807 (5)	0.295 (1)	0.3611 (7)	5.3 (3)
C(20)	0.2287 (5)	0.287 (1)	0.3487 (7)	5.3 (3)
C(21)	0.2572 (5)	0.190 (1)	0.3881 (7)	5.5 (4)
C(22)	0.3042 (5)	0.169 (1)	0.3742 (8)	7.1 (4)
C(23)	0.1366 (4)	0.4208 (9)	0.2596 (5)	4.5 (3)
C(24)	0.1054 (4)	0.332 (1)	0.2110 (6)	4.8 (3)
C(25)	0.0942 (5)	0.364 (1)	0.1376 (7)	5.8 (4)
C(26)	0.0610 (6)	0.279 (1)	0.0860 (7)	7.5 (5)
C(27)	0.1827 (5)	0.495 (1)	0.3710 (6)	4.9 (3)
C(28)	0.2040 (5)	0.490 (1)	0.4523 (6)	5.8 (4)
C(29)	0.2237 (6)	0.605 (1)	0.4763 (7)	6.3 (4)
C(30)	0.2502 (6)	0.604 (1)	0.5540 (8)	7.0 (4)
C(31)	0.1051 (4)	0.3826 (9)	0.3525 (6)	4.8 (3)
C(32)	0.0695 (5)	0.480 (1)	0.3369 (7)	6.3 (4)
C(33)	0.0315 (5)	0.459 (1)	0.3701 (8)	7.0 (4)
C(34)	0.0554 (6)	0.471 (2)	0.4481 (7)	8.5 (5)
O(1)	0.000	0.214 (1)	0.250	7.6 (4)

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

distorted square-planar environments. The four Pt–C terminal bond distances are the same (Pt–C(7) and Pt–C(13) = 2.010 (11) Å) and are in the range commonly found for other pentafluorophenyl Pt(II) complexes.[5,9,10]

The Pt–C bridging distances are longer than the Pt–C terminal ones (Pt–C(1) = 2.246 (11) Å and Pt–C(1′) = 2.166

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Table IV. Selected Bond Distances and Angles for $(NBu_4)_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]\cdot H_2O$ (1)

Bond Distances (Å)

Pt-Pt'	2.714 (1)	Pt-C(7)	2.010 (11)
Pt-C(1)	2.246 (11)	Pt-C(13)	2.010 (11)
Pt-C(1')	2.166 (11)	O(1)···F(1)	3.117 (13)

Bond Angles (deg)

Pt'-Pt-C(1)	50.7 (3)	C(1)-Pt-C(13)	171.0 (4)
Pt'-Pt-C(1')	53.4 (3)	C(1')-Pt-C(7)	169.6 (4)
Pt'-Pt-C(7)	135.8 (3)	C(1')-Pt-C(13)	87.5 (4)
Pt'-Pt-C(13)	138.2 (3)	C(7)-Pt-C(13)	84.8 (5)
C(1)-Pt-C(1')	101.3 (4)	Pt-C(1)-Pt'	75.9 (4)
C(1)-Pt-C(7)	86.2 (4)		

(11) Å), in keeping with a trend observed in Al_2Ph_6, a binuclear complex containing both bridging and terminal phenyl groups, in which the Al–C(terminal) bonds are shorter than the bridging ones.[11] The bond angles around each Pt center are in the range 84.8–101.3°; the least acute angle is subtended by the two bridging carbon atoms. The Pt–C(1)–Pt' angle has a value of 75.9 (4)°. The entire $Pt_2(\mu\text{-}C)_2C_4$ unit is bent so that the dihedral angle formed by the Pt–C(1)–C(1') and Pt'–C(1)–C(1') planes has a value of 151.9°. (The complex lies across a crystallographic 2-fold axis with the Pt–Pt' bond perpendicular to the symmetry element.) The bridging C_6F_5 groups are oriented in such a way that the line perpendicular to the C_6 ring and the line between the platinum centers form an angle of 11.25°. The distance between the two platinum atoms is 2.714 (1) Å, shorter than the Pt–Pt distance in metallic platinum[12] and also shorter than distances found for other binuclear platinum(II) complexes.[13-15] The presence of a Pt–Pt bond, the steric requirements of the C_6F_5 bridging ligands, or both, can be responsible for this short Pt–Pt distance.

There is also, in this crystal, a molecule of water (probably due to the use of hydrous solvents for growing suitable crystals for X-ray studies); the oxygen atom is located at 3.117 (13) Å from the F(1) and F(1') atoms. This location may indicate very weak contacts between F(1)/F(1') and the hydrogen atoms.[16]

The presence of C_6F_5 groups acting as bridging ligands is noteworthy. As far as we know, the complexes described in this paper are the only ones in which C_6F_5 groups have been proved to act as bridging ligands.

(c) Synthesis of $(NBu_4)[Pt_2Ag(\mu\text{-}C_6F_5)_2(C_6F_5)_4\cdot O(C_2H_5)_2]$ (2). The reaction between $(NBu_4)_2[Pt(C_6F_5)_3Cl]$ and an excess of $AgClO_4$ (molar ratio 1:2) in CH_2Cl_2 at room temperature for 2 h leads to precipitation of AgCl. From the yellow supernatant, after treatment with diethyl ether, $(NBu_4)[Pt_2Ag(\mu\text{-}C_6F_5)_2(C_6F_5)_4\cdot O(C_2H_5)_2]$ (2; 72% yield) (eq 3) can be isolated. Although eq 3 suggests a

$$2(NBu_4)_2[Pt(C_6F_5)_3Cl] + 3\ AgClO_4 \xrightarrow{CH_2Cl_2/O(C_2H_5)_2} 2AgCl + 2(NBu_4)ClO_4 + (NBu_4)[Pt_2Ag(\mu\text{-}C_6F_5)_2(C_6F_5)_4\cdot O(C_2H_5)_2] \quad (3)$$

molar ratio of 1:1.5 for the Pt compound and $AgClO_4$, we obtain better yields with an excess of $AgClO_4$. NBu_4ClO_4 is also formed, and the separation is carried out by using diethyl ether, in which complex 2 is soluble but NBu_4ClO_4 insoluble.

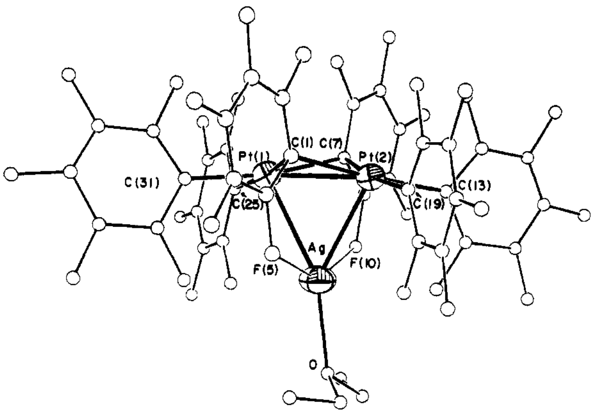

Figure 2. ORTEP drawing of the anion $[Pt_2Ag(C_6F_5)_6OEt_2]^-$.

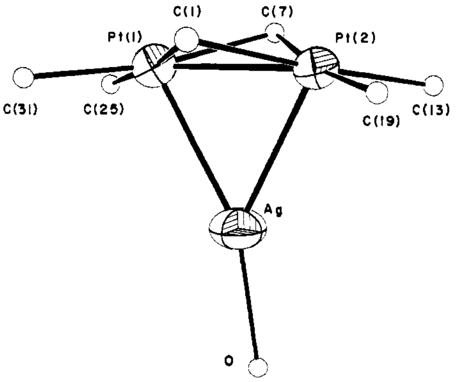

Figure 3. Core of the anion $[Pt_2Ag(C_6F_5)_6OEt_2]^-$.

It seems sensible to assume that the binuclear platinum derivative is formed initially and that it further reacts with $AgClO_4$ to yield the trinuclear Pt_2Ag complex 2. In fact $(NBu_4)_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$ reacts with $AgClO_4$ (molar ratio 1:1) in $CH_2Cl_2/O(C_2H_5)_2$, yielding (76%) $(NBu_4)[Pt_2Ag(\mu\text{-}C_6F_5)_2(C_6F_5)_4\cdot O(C_2H_5)_2]$ (2) (eq 4). The structure

$$(NBu_4)_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4] + AgClO_4 \xrightarrow{CH_2Cl_2/O(C_2H_5)_2O} (NBu_4)ClO_4 + (NBu_4)[Pt_2Ag(\mu\text{-}C_6F_5)_2(C_6F_5)_4\cdot O(C_2H_5)_2] \quad (4)$$

of complex 2 (described below) reveals the presence of two Pt–Ag bonds, so that the binuclear platinum complex 1 is acting in 2 as a bidentate ligand bonded to the silver atom through the platinum atoms.

Analytical and conductivity data for complex 2 are collected in Table I.

Acetone solutions of complex 2 show the expected conductivity for a 1:1 electrolyte, showing that the donor solvent is not able to break the Pt–Ag bonds. A similar behavior is observed for the complex $(NBu_4)[Pt_2Ag(\mu\text{-}Cl)_2(C_6F_5)_4\cdot O(C_2H_5)_4]$.[5] In contrast, acetone solutions of $(C_6F_5)_3LPtAgL'$[4] show conductivity values for 1:1 electrolytes due to the breaking of the Pt–Ag bonds in the binuclear complexes, although the Pt–Ag distance in $(C_6F_5)_3(tht)PtAgPPh_3$ (tht = tetrahydrothiophene) is shorter than that found in the trinuclear complexes $(NBu_4)[Pt_2Ag(\mu\text{-}X)_2(C_6F_5)_4\cdot O(C_2H_5)_2]$ (X = Cl, C_6F_5).

(d) Structure of $(NBu_4)[Pt_2Ag(\mu\text{-}C_6F_5)_2(C_6F_5)_4\cdot O(C_2H_5)_2]$ (2). The structure of complex 2 has been determined by single-crystal X-ray diffraction. General crystallographic information is collected in Table II. Positional parameters are listed in Table V. Selected bond

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Table V. Positional and Equivalent Isotropic Displacement Parameters and Their Estimated Standard Deviations for $(NBu_4)[Pt_2Ag(\mu\text{-}C_6F_5)_2(C_6F_5)_4 \bullet O(C_2H_5)_2] \bullet {}^1/_2 n\text{-}C_6H_{14}$ (2)[a]

atom	x	y	z	B (Å^2)	atom	x	y	z	B (Å^2)
Pt(1)	0.91685 (6)	0.22375 (3)	0.99552 (3)	3.83 (2)	C(25)	1.059 (2)	0.1738 (8)	1.0108 (9)	5.5 (6)
Pt(2)	0.87192 (6)	0.32599 (3)	1.00701 (3)	3.70 (2)	C(26)	1.130 (2)	0.1618 (7)	0.967 (1)	5.2 (6)
Ag	0.8997 (1)	0.26484 (6)	1.11123 (6)	5.41 (4)	C(27)	1.226 (2)	0.131 (1)	0.980 (1)	8.8 (9)
C(1)	0.741 (1)	0.2667 (7)	0.9738 (7)	3.8 (5)	C(28)	1.247 (2)	0.110 (1)	1.040 (2)	10 (1)
C(2)	0.699 (2)	0.2675 (6)	0.9145 (8)	3.8 (5)	C(29)	1.180 (2)	0.122 (1)	1.079 (2)	9 (1)
C(3)	0.586 (2)	0.2541 (8)	0.8919 (8)	5.3 (6)	C(30)	1.091 (2)	0.1534 (8)	1.069 (1)	5.4 (6)
C(4)	0.507 (2)	0.2376 (9)	0.927 (1)	6.5 (7)	F(21)	1.107 (1)	0.1807 (5)	0.9125 (6)	8.3 (4)
C(5)	0.539 (2)	0.2364 (7)	0.987 (1)	5.4 (6)	F(22)	1.294 (1)	0.1208 (7)	0.9343 (8)	14.1 (7)
C(6)	0.653 (2)	0.2499 (7)	1.0082 (7)	4.0 (5)	F(23)	1.345 (1)	0.0797 (6)	1.0465 (8)	13.3 (6)
F(1)	0.7750 (9)	0.2832 (4)	0.8743 (4)	5.8 (3)	F(24)	1.210 (1)	0.1018 (6)	1.1346 (7)	11.5 (5)
F(2)	0.557 (1)	0.2587 (6)	0.8336 (5)	9.3 (4)	F(25)	1.026 (1)	0.1659 (5)	1.1139 (5)	8.2 (4)
F(3)	0.397 (1)	0.2266 (6)	0.9076 (6)	9.9 (5)	C(31)	0.814 (1)	0.1578 (6)	0.9885 (8)	3.8 (4)
F(4)	0.462 (1)	0.2233 (5)	1.0260 (6)	8.3 (4)	C(32)	0.785 (2)	0.1370 (8)	0.9342 (9)	5.3 (6)
F(5)	0.6753 (9)	0.2490 (4)	1.0693 (4)	6.2 (3)	C(33)	0.717 (2)	0.096 (1)	0.921 (1)	7.9 (8)
C(7)	1.045 (2)	0.2870 (8)	0.9878 (8)	5.5 (6)	C(34)	0.663 (2)	0.073 (1)	0.966 (1)	8.5 (9)
C(8)	1.073 (2)	0.2984 (7)	0.9302 (8)	4.1 (5)	C(35)	0.691 (2)	0.0897 (9)	1.024 (1)	8.7 (9)
C(9)	1.182 (2)	0.3164 (8)	0.9190 (8)	5.2 (6)	C(36)	0.763 (2)	0.1338 (8)	1.036 (1)	5.4 (6)
C(10)	1.268 (2)	0.3257 (9)	0.964 (1)	6.7 (7)	F(26)	0.833 (1)	0.1565 (5)	0.8878 (5)	8.6 (4)
C(11)	1.240 (2)	0.3134 (8)	1.022 (1)	6.0 (7)	F(27)	0.693 (1)	0.0760 (6)	0.8676 (7)	11.7 (5)
C(12)	1.138 (2)	0.2952 (7)	1.0332 (8)	3.8 (5)	F(28)	0.594 (1)	0.0288 (5)	0.9620 (8)	12.7 (6)
F(6)	0.9966 (9)	0.2930 (4)	0.8840 (4)	6.0 (3)	F(29)	0.645 (1)	0.0679 (5)	1.0749 (7)	11.3 (5)
F(7)	1.207 (1)	0.3283 (5)	0.8624 (5)	9.1 (4)	F(30)	0.784 (1)	0.1515 (5)	1.0934 (5)	8.2 (4)
F(8)	1.376 (1)	0.3437 (6)	0.9531 (6)	10.0 (5)	N	0.461 (1)	0.5489 (7)	0.2587 (7)	6.5 (5)
F(9)	1.331 (1)	0.3206 (5)	1.0668 (6)	8.7 (4)	C(37)	0.554 (2)	0.5401 (9)	0.2118 (9)	7.3 (7)
F(10)	1.1252 (9)	0.2840 (4)	1.0905 (5)	6.3 (3)	C(38)	0.672 (3)	0.518 (1)	0.237 (1)	11 (1)
C(13)	0.977 (1)	0.3867 (7)	1.0327 (8)	4.4 (5)	C(39)	0.749 (2)	0.515 (1)	0.182 (2)	13 (1)
C(14)	1.012 (2)	0.3980 (8)	1.091 (1)	5.5 (6)	C(40)	0.857 (4)	0.485 (2)	0.200 (2)	21 (2)
C(15)	1.099 (2)	0.440 (1)	1.107 (1)	6.6 (7)	C(41)	0.443 (2)	0.4998 (9)	0.2971 (9)	6.2 (6)
C(16)	1.145 (2)	0.468 (1)	1.063 (1)	6.6 (7)	C(42)	0.397 (2)	0.457 (1)	0.256 (1)	9.0 (8)
C(17)	1.111 (2)	0.4586 (7)	1.008 (1)	5.1 (6)	C(43)	0.386 (3)	0.408 (1)	0.298 (2)	14 (1)
C(18)	1.025 (2)	0.4208 (8)	0.9900 (9)	5.1 (6)	C(44)	0.355 (5)	0.355 (2)	0.273 (2)	22 (2)
F(11)	0.978 (1)	0.3696 (5)	1.1371 (5)	7.1 (3)	C(45)	0.347 (2)	0.5654 (9)	0.2193 (8)	6.7 (6)
F(12)	1.132 (1)	0.4467 (5)	1.1648 (6)	9.1 (4)	C(46)	0.244 (2)	0.579 (1)	0.255 (1)	8.8 (8)
F(13)	1.223 (1)	0.5041 (5)	1.0821 (7)	9.3 (4)	C(47)	0.132 (2)	0.595 (1)	0.215 (1)	9.0 (8)
F(14)	1.150 (1)	0.4866 (5)	0.9617 (6)	8.3 (4)	C(48)	0.033 (2)	0.613 (1)	0.252 (1)	10.1 (9)
F(15)	0.9938 (9)	0.4119 (4)	0.9326 (5)	6.8 (3)	C(49)	0.504 (2)	0.591 (1)	0.3036 (9)	8.1 (7)
C(19)	0.730 (1)	0.3701 (7)	1.0194 (9)	4.6 (5)	C(50)	0.535 (2)	0.643 (1)	0.278 (1)	9.3 (9)
C(20)	0.665 (2)	0.3924 (7)	0.9710 (9)	4.7 (6)	C(51)	0.547 (3)	0.679 (1)	0.332 (2)	14 (1)
C(21)	0.569 (2)	0.4201 (9)	0.973 (1)	6.4 (7)	C(52)	0.592 (4)	0.729 (2)	0.315 (1)	16 (2)
C(22)	0.521 (2)	0.4256 (9)	1.024 (2)	7.2 (8)	O	0.9239	0.2633	1.2125	12*
C(23)	0.581 (2)	0.4055 (8)	1.076 (1)	5.5 (6)	C(53)	1.0339	0.2865	1.2495	17*
C(24)	0.681 (2)	0.3783 (8)	1.0709 (9)	5.5 (6)	C(54)	1.1343	0.2549	1.2372	27*
F(16)	0.7032 (9)	0.3878 (4)	0.9151 (4)	5.9 (3)	C(55)	0.8114	0.2844	1.2393	24*
F(17)	0.506 (1)	0.4410 (5)	0.9244 (7)	9.6 (4)	C(56)	0.7152	0.2500	1.2195	18*
F(18)	0.418 (1)	0.4513 (6)	1.0320 (7)	10.1 (5)	C(100)	0.0129	0.4812	0.4775	21*
F(19)	0.537 (1)	0.4092 (5)	1.1298 (6)	9.5 (4)	C(101)	0.0260	0.5044	0.4199	21*
F(20)	0.735 (1)	0.3582 (5)	1.1227 (5)	7.5 (4)	C(102)	0.0527	0.4703	0.3747	21*

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

Table VI. Selected Bond Distances and Bond Angles and Their Estimated Standard Deviations for $(NBu_4)[Pt_2Ag(\mu\text{-}C_6F_5)_2(C_6F_5)_4 \bullet O(C_2H_5)_2] \bullet {}^1/_2 n\text{-}C_6H_{14}$ (2)[a]

		Bond Distances (Å)			
Pt(1)–Pt(2)	2.687 (1)	Pt(1)–C(31)	2.05 (2)	Pt(2)–C(19)	2.00 (2)
Pt(1)–Ag	2.815 (2)	Pt(2)–Ag	2.804 (2)	Ag–O	2.259 (1)
Pt(1)–C(1)	2.28 (2)	Pt(2)–C(1)	2.20 (2)	Ag···F(5)	2.653 (10)
Pt(1)–C(7)	2.19 (2)	Pt(2)–C(7)	2.27 (2)	Ag···F(10)	2.670 (10)
Pt(1)–C(25)	2.06 (2)	Pt(2)–C(13)	2.01 (2)		
		Bond Angles (deg)			
Pt(2)–Pt(1)–Ag	61.22 (4)	C(7)–Pt(1)–C(25)	87.9 (7)	C(1)–Pt(2)–C(7)	101.2 (6)
Pt(2)–Pt(1)–C(1)	51.8 (4)	C(7)–Pt(1)–C(31)	168.0 (7)	C(1)–Pt(2)–C(13)	172.9 (6)
Pt(2)–Pt(1)–C(7)	54.3 (5)	C(25)–Pt(1)–C(31)	85.7 (7)	C(1)–Pt(2)–C(19)	85.2 (7)
Pt(2)–Pt(1)–C(25)	137.9 (5)	Pt(1)–Pt(2)–Ag	61.65 (4)	C(7)–Pt(2)–C(13)	84.2 (7)
Pt(2)–Pt(1)–C(31)	134.7 (5)	Pt(1)–Pt(2)–C(1)	54.5 (4)	C(7)–Pt(2)–C(19)	171.5 (7)
Ag–Pt(1)–C(1)	83.6 (4)	Pt(1)–Pt(2)–C(7)	51.6 (5)	C(13)–Pt(2)–C(19)	89.0 (7)
Ag–Pt(1)–C(7)	83.9 (5)	Pt(1)–Pt(2)–C(13)	132.2 (5)	Pt(1)–Ag–Pt(2)	57.13 (3)
Ag–Pt(1)–C(25)	101.2 (6)	Pt(1)–Pt(2)–C(19)	136.4 (5)	Pt(1)–Ag–O	154.63 (7)
Ag–Pt(1)–C(31)	107.3 (5)	Ag–Pt(2)–C(1)	85.3 (4)	Pt(2)–Ag–O	146.92 (7)
C(1)–Pt(1)–C(7)	101.1 (6)	Ag–Pt(2)–C(7)	82.8 (5)	Pt(1)–C(1)–Pt(2)	73.7 (5)
C(1)–Pt(1)–C(25)	170.2 (7)	Ag–Pt(2)–C(13)	100.0 (5)	Pt(1)–C(7)–Pt(2)	74.0 (6)
C(1)–Pt(1)–C(31)	84.7 (6)	Ag–Pt(2)–C(19)	103.5 (5)		

distances and angles are given in Table VI. The structure of the complex anion in **2** is shown in Figure 2. Figure 3 presents the core of the cluster, which is formed by two platinum and one silver atom; the platinum atoms are bridged by two C_6F_5 groups. Each platinum center also has two terminal cis C_6F_5 groups; thus, each has a distorted square-pyramidal coordination formed by four carbon atoms and one silver atom. The two square pyramids share a pyramidal face, which is bounded by the two carbon bridges and the silver atom. The angles C–Pt–C corresponding to mutually cis C_6F_5 groups are around 90°, the largest being formed by bridging carbon atoms: C(1)–Pt(1)–C(7), 101.1 (6)°, C(1)–Pt(2)–C(7), 101.2 (6)°. The angles Ag–Pt–C are in the range 82.5 (5)–107.3 (5)°. The Pt–C terminal distances are equal within experimental error (2.00 (2)–2.06 (2) Å) and shorter by approximately 0.2 Å than the Pt–C bridging distances (Pt(1)–C(1), 2.28 (2); Pt(1)–C(7), 2.19 (2); Pt(2)–C(1), 2.20 (2); Pt(2)–C(7), 2.27 (2) Å); they are in the same range as distances found in $(NBu_4)_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$ (1).

The distances Pt(1)–Ag and Pt(2)–Ag are 2.815 (2) and 2.804 (2) Å, respectively. These short Pt–Ag distances and the absence of covalent bridges on the Pt–Ag edges imply the presence of significant Pt–Ag bonding. The distance between the platinum atoms is 2.687 (1) Å, somewhat shorter than the distance found in 1.

The silver atom in 2 is bonded not only to the platinum atoms but also to one diethyl ether molecule. The Ag–O distance is 2.259 (1) Å. Moreover, the C_6F_5 bridging groups are oriented in such a way (see Figure 2) that one of the ortho fluorine atoms of each C_6F_5 bridging group is located about 2.6 Å from the silver atom (Ag···F(5), 2.653 (10) Å; Ag···F(10) 2.670 (10) Å); these contacts have also been observed in other platinum–silver pentafluorophenyl derivatives, and they probably contribute to the stability of the cluster. The angles formed by the perpendiculars to the C_6F_5 bridging rings and the line between the two platinum atoms are 6.3 and 8.5°.

Complex 2 seems to be formed because of the nucleophilicity of the platinum atoms in $(NBu_4)_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$ and the electrophilicity of the silver atom in $AgClO_4$. Minor changes in the structure of $[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]^{2-}$ fragment have been observed as consequences of the reaction with Ag^+. The dihedral angle formed by the planes Pt(1)–C(1)–C(7) and Pt(2)–C(1)–C(7) is 142.2°. Complex 2 is similar to $(NBu_4)[Pt_2Ag(\mu\text{-}Cl)_2(C_6F_5)_4\cdot O(C_2H_5)_2]$,[5] although the Pt–Ag distances in the former (2.815 (2) and 2.804 (2) Å) are longer than the Pt–Ag distances in the chloro compound (2.781 (1) and 2.759 (1) Å).

(e) Reactivity of $(NBu_4)[Pt_2Ag(\mu\text{-}C_6F_5)_2(C_6F_5)_4\cdot O(C_2H_5)_2]$. (i) With Neutral Ligands L. Complex 2 reacts with an equimolar amount of L (PPh_3, CNCy) in CH_2Cl_2 at room temperature to give $(NBu_4)[Pt_2Ag(\mu\text{-}C_6F_5)_2(C_6F_5)_4L]$ (3, 4) (eq 5).

$$(NBu_4)[Pt_2Ag(\mu\text{-}C_6F_5)_2(C_6F_5)_4\cdot O(C_2H_5)_2] + L \rightarrow (NBu_4)[Pt_2Ag(\mu\text{-}C_6F_5)_2(C_6F_5)_4L] + O(C_2H_5)_2 \quad (5)$$

$$L = PPh_3,\ CNCy$$

^{19}F NMR data (discussed below) indicate that complexes 3 and 4 still have two C_6F_5 bridging groups so that ligand L produces the displacment of the diethyl ether coordinated to the silver atom, but not the breaking of the "$Pt_2(\mu\text{-}C_6F_5)_2$" system.

Analytical and conductivity data for complexes 3 and 4 are collected in Table I.

Complex 3, $(NBu_4)[Pt_2Ag(\mu\text{-}C_6F_5)_2(C_6F_5)_4\cdot PPh_3]$, can be obtained by reacting $(NBu_4)_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$ (1), in CH_2Cl_2 with $O_3ClOAgPPh_3$ at −30 °C (69% yield). However, if the reaction is carried out at room temperature, a mixture of complexes, which we have not been able to separate, is obtained.

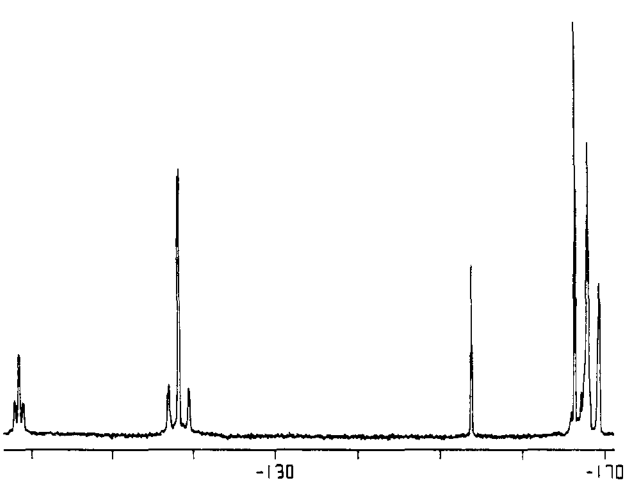

Figure 4. The ^{19}F NMR spectrum of $(NBu_4)_2[Pt_2(C_6F_5)_6]$ (1). The horizontal axis is labeled in ppm.

(ii) Reaction with NBu_4Br. The treatment of $(NBu_4)[Pt_2Ag(\mu\text{-}C_6F_5)_2(C_6F_5)_4\cdot O(C_2H_5)_2]$ with NBu_4Br (molar ratio 1:1) in CH_2Cl_2 results in the precipitation of AgBr, and from the resulting yellow solution, complex 1 (73% yield) can be isolated (eq 6).

$$(NBu_4)[Pt_2Ag(\mu\text{-}C_6F_5)_2(C_6F_5)_4\cdot O(C_2H_5)_2] + NBu_4Br \rightarrow AgBr + O(C_2H_5)_2 + (NBu_4)_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4] \quad (6)$$

(f) ^{19}F NMR Spectra. The ^{19}F NMR spectrum of complex 1 (see Figure 4) shows six multiplet signals. Three of them correspond to the terminal C_6F_5 groups and the other three to the bridging ones. In both cases (bridging and terminal groups) the two ortho fluorine atoms are isochronous, as are the two meta fluorines. Terminal C_6F_5 groups show one signal at −167.6 ppm due to the meta fluorines. The triplet at −166.1 ppm is due to the para fluorine atoms; ortho fluorines appear as a doublet at −116.8 ppm. The signal due to ortho fluorine also shows platinum satellites ($^3J(Pt\text{-}F_o)$ = 492.2 Hz; 1:4:1). Signals due to ortho and para fluorines of the bridging C_6F_5 appear at lower field than those due to the terminal C_6F_5 groups. Meta fluorines of the bridging C_6F_5 appear at −169 ppm; para fluorines show a triplet at −153.6 ppm. One signal, a doublet at −98.3 ppm with platinum satellites ($^3J(Pt\text{-}F_o)$ = 211.2 Hz) is due to ortho-fluorines. This signal (including the platinum satellites 1:2:1) is due to the presence of the isotopomers: (a) $Pt(\mu\text{-}C_6F_5)_2Pt$ (43.82%) and (b) $^{195}Pt(\mu\text{-}C_6F_5)_2Pt$ (44.74%); no platinum satellites due to the less abundant isotopomer (c) $^{195}Pt(\mu\text{-}C_6F_5)_2{}^{195}Pt$ (11.42%) are observed in the spectrum.

^{19}F NMR spectra of complexes 2, 3, and 4 are very similar. Table VII collects resonances of different fluorine atoms of bridging and terminal C_6F_5 groups and the coupling constants observed. In these cases ortho fluorines and meta fluorines of terminal C_6F_5 groups show two different signals; also, two signals are observed for ortho and meta fluorines of the bridging C_6F_5 groups, thus indicating that the coordination of the moiety "$[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$" to the $[AgL]^+$ fragment makes the ortho and meta fluorines inequivalent, probably because the rotation of C_6F_5 groups is precluded in these cases. As with complex 1, complexes 2, 3, and 4 show the resonances due to the ortho and para fluorines of the bridging C_6F_5 groups at lower fields than those of the ortho and para fluorines of the terminal C_6F_5 groups.

IR Spectra. Tables VIII and IX list significant IR absorption frequencies for complexes 1–4. All of the complexes show internal absorptions due to the C_6F_5 groups,[17] which are collected in Table VIII. Two sets of

Table VII. Fluorine-19 NMR Spectra[a]

complex	terminal C_6F_5 groups				bridging C_6F_5 groups			
	δ_{F_o}	δ_{F_m}	δ_{F_p}	$^3J_{Pt-F_o}$	δ_{F_o}	δ_{F_m}	δ_{F_p}	$^3J_{Pt-F_o}$
$(NBu_4)_2[Pt_2(\mu-C_6F_5)_2(C_6F_5)_4]$ (1)	−118	−167.6	−166.1	492.2	−98.3	−169	−153.6	211.2
$(NBu_4)[Pt_2Ag(\mu-C_6F_5)_2(C_6F_5)_4\cdot O(C_2H_5)_2]$ (2)	−117.4	−164.1	−162.2	670.3	−99.7	−164.1	−148.6	314.6
	−120.2	−165.2[b]		389.2	−101.5	−165.2[b]		
		−165.3				−165.3		
$(NBu_4)[Pt_2Ag(\mu-C_6F_5)_2(C_6F_5)_4PPh_3]$ (3)	−113.9	−164.6	−163	550	−97.1	−164.6	−150	
	−120.2	−165.3[b]		387.4	−101.1	−165.3[b]		
		−166.1				−166.1		
$(NBu_4)[Pt_2Ag(\mu-C_6F_{52}(C_6F_5)_4CNCy]$ (4)	−115.7	−164.4	−162.7	594.2	−97.3	−164.4	−149.4	
	−120.2	−165.2[b]		388.6	−101.6	−165.2[b]		
		−165.8				−165.8		

[a] δ referred $CFCl_3$; *J* in Hz, solvent $CDCl_3$. [b] Signals due to metafluorines of the bridging and terminal groups appear very close and make assignment difficult.

Table VIII. Relevant IR Absorptions Assigned to the C_6F_5 Groups (cm^{-1})

	X-sensitive		others	950 cm^{-1} region
$(NBu_4)_2[Pt_2(\mu-C_6F_5)_2(C_6F_5)_4]$ (1)	799 (vs)	750 (m)	1626 (m), 1600 (m), 1498 (vs), 1327 (s), 1242 (s), 1120 (vs), 1056 (vs)	961 (vs) (h)
	787 (vs)	742 (m)		
$(NBu_4)[Pt_2Ag(\mu-C_6F_5)_6(C_6F_5)_4\cdot O(C_2H_5)_2]$ (2)	801 (vs)	750 (m)	1625 (m), 1601 (m), 1498 (vs), 1323 (s), 1253 (s), 1124 (m), 1062 (vs)	964 (vs), 953 (vs)
	792 (vs)			
$(NBu_4)[Pt_2Ag(\mu-C_6F_5)_2(C_6F_5)_4PPh_3]$ (3)	800 (vs)	(749)[a]	1622 (s), 1598 (m), 1498 (vs), 1322 (s), 1250 (s), 1120 (m), 1057 (vs)	963 (vs) (h)
	790 (vs)			
$(NBu_4)[Pt_2Ag(\mu-C_6F_5)_2(C_6F_5)_4CN-Cy]$ (4)	801 (vs)	750 (m)	1624 (s), 1600 (m), 1498 (vs), 1322 (s), 1250 (s), 1124 (m), 1056 (vs)	962 (vs) (h)
	791 (vs)			

[a] Absorptions due to the other ligands precludes assignation.

Table IX. Absorptions Due to Ligands L (cm^{-1})

$(NBu_4)_2[Pt_2(\mu-C_6F_5)_2(C_6F_5)_4]\cdot H_2O$ (1)	
H_2O	3654 (w), 3590 (m)
$(NBu_4)_2[Pt_2Ag(\mu-C_6F_5)_2(C_6F_5)_4PPh_3]$ (3)	
PPh_3	1092 (vs), 748 (vs), 742 (vs), 706 (s), 696 (vs), 516 (vs), 500 (m), 490 (m)
$(NBu_4)_2[Pt_2Ag(\mu-C_6F_5)_2(C_6F_5)_4CNCy]$ (4)	
CN-Cy	2200 (vs)

absorptions at ~800 and ~750 cm^{-1} are assigned to the X-sensitive modes of the C_6F_5 groups. Those at lower wavenumbers must be due to the bridging C_6F_5 groups. Internal absorptions due to the ligand L are collected in Table IX.

Experimental Section

Infrared spectra, C, H, and N analyses, and conductance measurements were performed as described elsewhere.[1b] $(NBu_4)_2[Pt(C_6F_5)_3Cl]$ was prepared as described elsewhere.[7] All the reactions were carried out under exclusion of light.

Reaction between $(NBu_4)_2[Pt(C_6F_5)_3Cl]$ and $AgClO_4$ in CH_2Cl_2 (Molar Ratio 1:1). To a solution of 0.2000 g (0.1644 mmol) of $(NBu_4)_2[Pt(C_6F_5)_3Cl]$ in 15 mL of CH_2Cl_2 was added 0.0341 g (0.164 mmol) of $AgClO_4$; the mixture was stirred at room temperature for 2 h. After the AgCl formed was filtered off, the resulting yellow solution was evaporated to dryness and the oily residue obtained was treated with 40 mL of $O(C_2H_5)_2$ to separate the insoluble NBu_4ClO_4. The ether solution was evaporated to dryness giving a yellow solid, 1, in 76% yield.

Preparation of $(NBu_4)[Pt_2Ag(\mu-C_6F_5)_2(C_6F_5)_4\cdot O(C_2H_5)_2]$ (2). (a) To a solution of 0.31 g (0.25 mmol) of $(NBu_4)_2[Pt(C_6F_5)_3Cl]$ in 20 mL of CH_2Cl_2 was added $AgClO_4$ (0.1056 g, 0.5096 mmol, molar ratio 1:2). The mixture was stirred at room temperature for 2 h. After the AgCl formed and the excess of $AgClO_4$ were filtered off, the resulting yellow solution was evaporated to dryness and the oily residue was washed with 3 × 20 mL of $O(C_2H_5)_2$ to separate the NBu_4ClO_4. The yellow solution was partially evaporated (~10 mL), and by addition of 15 mL of n-hexane, a yellow solid, 2, was obtained (yield 72%).

(b) To a solution of 0.14 g (0.074 mmol) of $(NBu_4)_2[Pt_2(\mu-C_6F_5)_2(C_6F_5)_4]$ (1) in CH_2Cl_2 (10 mL) was added 0.0154 g (0.0745 mmol) of $AgClO_4$ (molar ratio 1:1); and the mixture was stirred at room temperature for 1 h. The solution was evaporated to dryness, and the resulting oily residue was treated with 2 × 15 mL of $O(C_2H_5)_2$ to separate the insoluble NBu_4ClO_4. The ether solution was evaporated to dryness giving a yellow solid, 2 (yield 76%).

Reactions of $(NBu_4)[Pt_2Ag(\mu-C_6F_5)_2(C_6F_5)_4\cdot O(C_5H_5)_2]$ with L (L = PPh_3, 3; L = CNCy, 4). $(NBu_4)[Pt_2Ag(\mu-C_6F_5)_2(C_6F_5)_4PPh_3]$ (3). To a solution of 0.10 g (0.055 mmol) of $(NBu_4)[Pt_2Ag(\mu-C_6F_5)_2(C_6F_5)_4\cdot O(C_2H_5)_2]$ (2) in 25 mL of CH_2Cl_2 was added 0.0144 g (0.055 mmol) of PPh_3; and the mixture was stirred at room temperature for 2 h. The solution was evaporated to dryness, and the yellow solid 3 was washed with *n*-hexane (yield 85%).

$(NBu_4)[Pt_2Ag(\mu-C_6F_5)_2(C_6F_5)_4CNCy]$ (4) was prepared in a similar way: 0.15 g (0.83 mmol) of $(NBu_4)[Pt_2Ag(\mu-C_6F_5)_2(C_6F_5)_4\cdot O(C_2H_5)_2]$ (2), 9.94 mL (0.086 mmol) of CNCy, 30 min of stirring; yield 79%.

Reaction of $(NBu_4)_2[Pt_2(\mu-C_6F_5)_2(C_6F_5)_4]$ with L (L = PPh_3, 5; L = CO, 6). (i) L = PPh_3. To a yellow solution of 0.19 g (0.053 mmol) of $(NBu_4)_2[Pt_2(\mu-C_6F_5)_2(C_6F_5)_4]$ in 20 mL of CH_2Cl_2 was added PPh_3 (0.0278 g, 0.106 mmol); and the mixture was stirred for 3 h. The resulting colorless solution was evaporated to dryness, and the residue was washed with 15 mL of $O(C_2H_5)_2$, giving $(NBu_4)[Pt(C_6F_5)_3PPh_3]$ in 88% yield.

(ii) L = CO. $(NBu_4)[Pt(C_6F_5)_3CO]$ (6) was obtained by bubbling CO through a CH_2Cl_2 solution of $(NBu_4)_2[Pt_2(\mu-C_6F_5)_2(C_6F_5)_4]$ (yield 74%).

Reaction of $(NBu_4)[Pt_2Ag(\mu-C_6F_5)_2(C_6F_5)_4\cdot O(C_2H_5)_2]$ with NBu_4Br. To a solution of $(NBu_4)[Pt_2Ag(\mu-C_6F_5)_2(C_6F_5)_4\cdot O(C_2H_5)_2]$ (2; 0.2 g, 0.1 mmol) in 15 mL of CH_2Cl_2 was added 0.0355 g (0.11 mmol) of $[NBu_4]Br$; the mixture was stirred at room

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temperature for 30 min. The AgBr formed was filtered off; the yellow solution was evaporated to dryness; and the residue was washed with 10 mL of *n*-hexane. Complex 1, in 73% yield, was obtained.

Reaction of $(NBu_4)_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$ with $O_3ClOAgPPh_3$. To a solution of 0.100 g (0.0532 mmol) of $(NBu_4)[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$ (1) in 15 mL of CH_2Cl_2 at −30 °C was added 0.025 g (0.053 mmol) of $O_3ClOAgPPh_3$; the mixture was stirred for 30 min at this temperature. The solution was pumped to dryness (−30 °C), and the residue was treated with 20 mL of $O(C_2H_5)_2$ (−30 °C). After separation of the insoluble NBu_4ClO_4, the solution was evaporated to dryness, and 10 mL of *n*-hexane was added. Complex 3 (69% yield) was obtained.

Preparation of Crystals for X-ray Structure Determination. Crystals of $(NBu_4)_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$ (1) and of $(NBu_4)[Pt_2Ag(\mu\text{-}C_6F_5)_2(C_6F_5)_4\cdot O(C_2H_5)_2]$ (2) were obtained by slow diffusion at −30 °C of *n*-hexane into dichloromethane solutions of the corresponding complexes.

Crystal Structure Analyses. Routine procedures were used for the collection of X-ray diffraction dat[18] from crystals of $(NBu_4)_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]\cdot H_2O$ (1) and $(NBu_4)[Pt_2Ag(\mu\text{-}C_6F_5)_2(C_6F_5)_4\cdot O(C_2H_5)_2$ (2). A crystal of 1 was mounted on a glass fiber and covered with epoxy; the specimen of compound 2 was sealed inside a capillary tube. The lattice dimensions and Laue group of each crystal were verified by normal-beam oscillation photography; these and other important crystal and experimental parameters are given in Table II.

Absorption corrections were applied to both data sets, based in each case on azimuthal scans of several reflections.[19] In addition, the data for compound 2 were corrected for decay, since the intensities of three monitor reflections dropped by an average of 24.5% during the course of 200 h of X-ray exposure.

The structure of 1 was solved by direct methods and developed and refined routinely.[20] No hydrogen atoms were included in the model. All non-hydrogen atoms were refined with anisotropic displacement parameters. In the final, convergent refinement, 465 parameters were fitted to 3671 data, for a data-to-parameter ratio of 7.9. The least-squares residuals are summarized in Table II.

The heavy atoms in the structure of 2 were located by direct methods, and the structure was developed and refined in a sequence of difference Fourier maps and least-squares calculations. During the late stages of refinement, the two terminal carbon atoms of the diethyl ether moiety ligated to silver showed signs of indeterminacy under normal least-squares analysis. Loose geometrical restraints were used for the C_α–C_β distances, in order to impose chemical sense on the dimensions of this group. In addition, a free *n*-hexane molecule was located on a crystallographic inversion center. Three unique atomic sites were identified which, along with their three symmetry congeners, formed a chain pattern which we modeled as one molecule of $n\text{-}C_6H_{14}$. The whole set of three unique sites was given an overall isotropic displacement parameter. The parameters of this group, like those of the carbon atoms of the ligated diethyl ether, were not allowed to vary in the final, unconditional structure-factor least-squares refinement.

In the final refinement, 779 variable parameters were fitted to 4061 data, for a data-to-parameter ratio of 5.2. The refinement converged with residuals given in Table II. There was no significant correlation in the least-squares analysis; and listings of residuals as functions of $(\sin\theta)/\lambda$, $|F_o|$, and indices revealed no systematic trends in the error function.

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Registry No. 1, 116349-58-7; $1\cdot H_2O$, 116323-87-6; 2, 95674-06-9; $2\cdot O(C_2H_5)_2\cdot {}^1/_2 n\text{-}C_6H_{14}$, 116323-90-1; 3, 116349-60-1; 4, 116323-82-1; 5, 66302-90-7; 6, 116323-84-3; $(NBu_4)_2[Pt(C_6F_5)_3Cl]$, 90621-02-6; Ag, 7440-22-4; Pt, 7440-06-4.

Supplementary Material Available: Complete lists of bond distances, bond angles, and anisotropic displacement parameters for the crystal structures of compounds 1 and 2 (14 pages); structure factor tables for 1 and 2 (40 pages). Ordering information can be found on any current masthead page.

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Preparation of Phenylplatinum–Zirconium Complexes with $Ph_2PC_5H_4$ or $PhP(C_5H_4)_2$ Bridging Ligands and Their Reactions with Carbon Monoxide

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Reaction of $[PtPh_2(cod)]$ or $[PtClPh(cod)]$ with $(Ph_2PC_5H_4)_2ZrCl_2$ yields the $Ph_2PC_5H_4$-bridged species $[PtXPh(Ph_2PC_5H_4)_2ZrCl_2]$ (X = Ph, Cl). Treatment of $[PtPh_2(cod)]$ or $[PtClPh(cod)]$ with 2 equiv of $PhP(C_5H_4)_2ZrCl_2$, prepared by reaction of $[ZrCl_4(THF)_2]$ with $(TlC_5H_4)_2PPh$, yields *cis*-$[PtPh_2\{PhP(C_5H_4)_2ZrCl_2\}_2]$ or *trans*-$[PtClPh\{PhP(C_5H_4)_2ZrCl_2\}_2]$. Each of the mixed-metal complexes has been isolated as an air-sensitive solid and characterized by elemental analysis and NMR spectroscopy. $[PtPh_2(Ph_2PC_5H_4)_2ZrCl_2]$ does not react with carbon monoxide, and *cis*-$[PtPh_2\{PhP(C_5H_4)_2ZrCl_2\}_2]$ undergoes a slow displacement of phosphine by CO, whereas the two chlorophenylplatinum complexes undergo smooth carbonylation to the corresponding benzoylplatinum species.

Introduction

Mixed-metal complexes in which the two metal centers are held in close proximity to one another have received considerable attention recently. Complexes suitable for the activation of small, polar molecules, such as carbon monoxide, should contain two widely different metals, yet few species containing a d^0 metal and a d^8 or d^{10} metal have been prepared. For those that have been formed, most have involved synthesis of an organometallic complex with one or two pendant phosphine groups, followed by coordination of these groups to a suitable late-transition-metal complex.[1-3] In addition, $[Cp_2Zr(PPh_2)_2]$ has been em-

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