Addition of Silver Electrophiles to an Electron-Rich Rhodium–Rhodium Bond. Synthesis and X-ray Crystal Structure of the $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}Ph_2PCH_2PPh_2)(\mu\text{-}AgOPF_2O)]$, a Triangular Rhodium–Silver Cluster with the Difluorophosphate Ion Coordinated to the Silver Atom

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$[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)]$ (1) [dppm = bis(diphenylphosphino)methane] reacts with AgX (X = BF_4^-, PF_6^-, ClO_4^-) to give $[Rh_2Ag(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)]X$ (**2a–c**); in solution the complexes **2a–c** are very unstable. During these experiments using, by accident, an old and humid sample of $AgPF_6$, the neutral compound $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}dppm)(\mu\text{-}AgOPF_2O)]$ (**3**) was obtained; the same compound is also obtained by reacting **1** with silver difluorophosphate. The compound **3** has been spectroscopically and structurally characterized. It crystallizes in the space group *Pnma*; the cell dimensions are $a = 14.471$ (1) Å, $b = 18.042$ (2) Å, $c = 12.772$ (1) Å, $V = 3334.5$ Å^3, and $Z = 4$. The structure has been refined to $R = 0.051$ and $R_w = 0.048$ for the 1281 reflections with $I \geq 3\sigma(I)$. In the triangular Rh_2Ag framework the two Rh–Ag distances [2.689 (2) Å] are equivalent, and the Rh–Rh bond [2.750 (3) Å] is lengthened by 0.067 Å on silver adduct formation. The rhodium atoms are bridged by the CO and the dppm ligands; each rhodium atoms is further coordinated to the η^5-cyclopentadienyl ligand. The structural features of the bridging dppm and CO groups remain essentially the same as in **1**. The cyclopentadienyl ligands are in cis position. The difluorophosphate ion is O bonded to silver atom [Ag–O(3) = 2.12 (2) Å] and shows the phosphorus atom tetrahedrally coordinated.

Introduction

Recently, we reported electrophilic attack of H^+ and $[Au(PPh_3)(solv)]^+$[1] and of the Lewis acid $HgCl_2$[2] at the electron-rich rhodium–rhodium bond of the complex $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)]$ (1)[3] [dppm = bis(diphenylphosphino)methane]. From these reactions the cationic hydride bridge complex $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}H)(\mu\text{-}CO)(\mu\text{-}dppm)]^+$ and the triangular clusters $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)(\mu\text{-}AuPPh_3)]^+$ and $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)(\mu\text{-}HgCl_2)]$ have been obtained. This report deals with the reactions of some electrophiles containing silver with complex 1.

Results and Discussion

The silver salts AgX (X = BF_4^-, PF_6^-, ClO_4^-) react with the rhodium complex 1 giving the mixed trinuclear clusters $[Rh_2Ag(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)]X$ (**2a–c**) as green solids. The compounds show the ν(CO) band at 1747 cm^{-1}, slightly shifted to higher wavenumbers compared to those of 1; the IR bands of the uncoordinated anions are found at 1060 cm^{-1} [ν(BF)] in **2a**, 835 cm^{-1} [ν(PF)] in **2b**, and 1050–1150 cm^{-1} [ν(ClO)] in **2c**. Their high instability in solution did not allow a full spectroscopic characterization.

During these experiments we used, by accident, an old and humid sample of $AgPF_6$ and obtained a different product. On adding a saturated benzene solution of the old $AgPF_6$ sample to a solution of complex 1 in the same solvent, the yellow-brown solution turned green. Working up as described in the Experimental Section gave the title compound as a dark green powder. This dissolved in dichloromethane and, after evaporation of the solvent, gave the product as red-brown crystals. The spectroscopic IR and ^{1}H NMR data for the green crude product and the red-brown crystals are coincident. A relevant aspect in the IR spectra was the lack of the bands assignable to PF_6^-. The complex has been characterized by X-ray diffraction, which showed it to be $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)(\mu\text{-}AgOPF_2O)]$ (**3**). Spectroscopic data for **3** are consistent with the determined structure. The IR spectrum shows the ν(CO) at 1728 cm^{-1} and bands associated with the coordinated difluorophosphate ion at 820 (m), 840 (m) [ν(PF)], 1300 (s), and 1125 (s) cm^{-1} [ν(PO)]. The ^{1}H NMR spectrum (CD_2Cl_2) shows the cyclopentadienyl proton resonance as doublet of doublets, δ 5.12, with $J_{H\text{-}P} = 0.8$ and $J_{H\text{-}Rh} = 0.5$ Hz. The ^{31}P NMR (CD_2Cl_2, H_3PO_4) exhibits for the phosphorus atoms of the dppm ligand a pattern typical of an AA′XX′ spin system centered at δ 49.51 ($^1J_{Rh\text{-}P} = 182.5$, $^2J_{Rh\text{-}P} = 12.5$, $^1J_{Rh\text{-}Rh} = 11.5$, $^1J_{P\text{-}C\text{-}P} = 80$ Hz). The phosphorus resonance of the coordinated difluorophosphate ion is complicated owing to the coupling to the F, ^{107}Ag, ^{109}Ag, and Rh atoms. Prompted by these results, we prepared compound **3** by reacting **1** with silver difluorophosphate in a benzene solution.

We ascertained, by ^{31}P NMR,[4] that the $PF_2O_2^-$ ion was present in the old sample of $AgPF_6$ and that it was not generated by solvolysis of the PF_6^- anion in $[Rh_2Ag(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)]PF_6$. This is rather surprising because the hexafluorophosphate ion is normally considered extremely stable.[5-8] Maitlis reported that in the complex $[\{Rh(\eta\text{-}C_5Me_2)\}_2(PO_2F_2)_3]PF_6$ the $PF_2O_2^-$ ion is generated by partial solvolysis of the PF_6^- in $[Rh(\eta\text{-}C_5Me_5)(Me_2SO)_3][PF_6]_2$.[9,10]

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[4] ^{31}P NMR (CD_2Cl_2, H_3PO_4) δ −14.39 [t, P, J(P–F) = 952.4 Hz].

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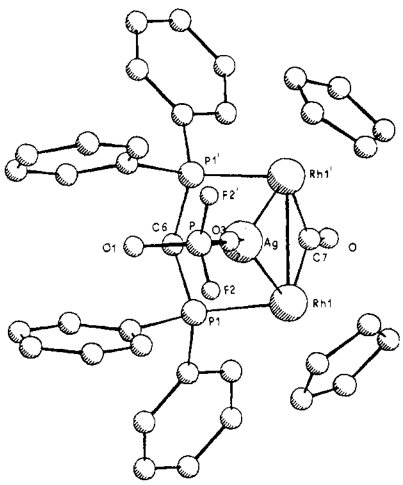

Figure 1. Molecular structure of $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)(\mu\text{-}AgOPF_2O)]$ (**3**).

Table I. Final Fractional Atomic Coordinates (×10⁴) for Non-Hydrogen Atoms with Estimated Standard Deviation in Parentheses

atom	*x/a*	*y/b*	*z/c*
Ag	1094 (1)	2500 (0)	6089 (1)
Rh(1)	1770 (1)	1738 (1)	4449 (1)
P	441 (5)	2500 (0)	8536 (5)
O(1)	−542 (10)	2500 (0)	8341 (15)
F(2)	613 (11)	1927 (9)	9253 (17)
O(3)	977 (14)	2500 (0)	7740 (15)
C(1)	3190 (14)	1241 (14)	4513 (21)
C(2)	2560 (18)	715 (12)	4207 (15)
C(3)	1929 (12)	580 (8)	4965 (18)
C(4)	2170 (13)	990 (10)	5811 (12)
C(5)	2918 (13)	1431 (9)	5545 (20)
P(1)	355 (2)	1668 (2)	3794 (3)
C(6)	46 (12)	2500 (0)	3056 (14)
C(7)	2087 (11)	2500 (0)	3417 (14)
O	2356 (10)	2500 (0)	2580 (12)
C(12)	−1514 (5)	1603 (4)	4305 (5)
C(13)	−2254 (5)	1526 (4)	4998 (5)
C(14)	−2090 (5)	1342 (4)	6042 (5)
C(15)	−1187 (5)	1233 (4)	6393 (5)
C(16)	−448 (15)	1310 (4)	5700 (5)
C(11)	−612 (5)	1495 (4)	4656 (5)
C(18)	−424 (5)	386 (5)	2852 (6)
C(19)	−433 (5)	−170 (5)	2094 (6)
C(110)	223 (5)	−167 (5)	1293 (6)
C(111)	886 (5)	393 (5)	1251 (6)
C(112)	895 (5)	949 (5)	2009 (6)
C(17)	239 (5)	946 (5)	2810 (6)

Description of the Structure of $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)(\mu\text{-}AgOPF_2O)]$. The molecular structure of **3** is shown in Figure 1. The positional coordinates and the interatomic distances and angles are given in Tables I and II, respectively. The molecule shows a crystallographic mirror plane passing through the methylenic carbon, the carbonyl group, the silver atom, the phosphorus and oxygen (O(1) and O(3)) atoms of the PO_2F_2 group, and the middle of the rhodium–rhodium bond. The basic trinuclear skeleton consists of an almost equilateral Rh_2Ag triangle with the Rh–Rh bond bridged by the dppm ligand and the carbon atom of the carbonyl group.

Table II. Bond Distances (Å) and Angles (deg) for $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)(\mu\text{-}AgOPF_2O)]$

Bond Distances

Rh(1)-Rh(1′)	2.750 (3)	C(7)-O	1.138 (23)
Rh(1)-P(1)	2.216 (3)	Ag-Rh(1)	2.689 (2)
Rh(1)-C(7)	1.959 (13)	Ag-O(3)	2.115 (19)
Rh(1)-C(1)	2.243 (21)	C(1)-C(2)	1.373 (33)
Rh(1)-C(2)	2.193 (23)	C(2)-C(3)	1.353 (30)
Rh(1)-C(3)	2.202 (16)	C(3)-C(4)	1.354 (26)
Rh(1)-C(4)	2.276 (17)	C(4)-C(5)	1.385 (26)
Rh(1)-C(5)	2.241 (22)	C(5)-C(1)	1.418 (36)
av Rh(1)-C	2.231 (19)	av C-C	1.376 (30)
P-F(2)	1.404 (19)	P(1)-C(6)	1.828 (11)
P-O(1)	1.445 (16)	P(1)-C(11)	1.808 (8)
P-O(3)	1.280 (21)	P(1)-C(17)	1.818 (9)

Bond Angles

Rh(1)-Ag-Rh(1′)	61.51 (5)	Rh(1)-C(7)-O	135.42 (6)
Rh(1)-Ag-O(3)	143.64 (4)	C(1)-C(5)-C(4)	108 (1)
P(1)-Rh(1)-Ag	89.3 (1)	C(5)-C(4)-C(3)	108 (1)
P(1)-Rh(1)-Rh(1′)	93.3 (1)	C(4)-C(3)-C(2)	107 (2)
P(1)-Rh(1)-C(7)	90.1 (1)	C(3)-C(2)-C(1)	111 (2)
Rh(1)-P(1)-C(6)	112.0 (2)	C(2)-C(1)-C(5)	104 (2)
Rh(1)-P(1)-C(11)	119.6 (3)	O(1)-P-F(2)	106.7 (7)
P(1′)-C(6)-P(1)	110.4 (2)	P-O(3)-Ag	147 (1)
Rh(1)-C(7)-Rh(1′)	89.14 (6)		

The Rh–Rh bond (2.750 (3) Å) is lengthened only by ≃0.067 Å on silver adduct formation [2.683 (1) Å in compound **1**]. The two equivalent Rh–Ag distances [2.689 (2) Å] are comparable to the Ag–Fe bond length in $[Fe_2Ag(CO)_6\{CHC(NHCH_3)C_6H_5\}P(C_6H_5)_2]^+$ [11] and are slightly larger than that observed in $[\{(\eta\text{-}C_5H_5)Rh(CO)(PPh_3)\}_2Ag]PF_6$ [12] [Rh–Ag = 2.651 (1) and 2.636 (1) Å] where the silver atom is linearly two coordinated. An examination of the bond distances of molecules **1** and **3** does not reveal any significant changes in Rh–C(CO) [1.953 (13) Å in **3** and 1.974 (9) Å in **1**] and Rh–P distances [2.216 (3) Å in **3** and 2.211 (2) Å in **1**]. The structural features of the bridging dppm and CO groups remain essentially the same as those in **1**, retaining the six-membered ring Rh(1)Rh(1′)C(7)P(1)C(6)P(1′) in the boat conformation. In the compound $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)(\mu\text{-}HgCl_2)]$ the six-membered ring assumes a chair conformation,[2] with the methylene carbon and the carbonyl carbon directed toward opposite sides. The Rh–C(CO)–Rh angle enlarges from 85.6 (4)° in **1** to 89.14 (6)° in **3** and the P–C–P angle from 107.8 (4)° in **1** to 110.4 (2)° in **3**; these angular increases appear to be a direct consequence of the lengthening of the Rh–Rh bond. The cyclopentadienyl groups are in a cis position with an interplanar angle of 92.8 (6)°; the averaged values for the Rh–C(C_5H_5) distance [2.231 (19) Å] are in agreement with those in the literature reports (2.19–2.27 Å).[3,13] The corresponding Rh–(C_5H_5) separation is 1.90 (2) Å. A final difference Fourier synthesis (R = 0.051) indicated the fluorine and oxygen atoms to be disordered; it is not possible to distinguish between the O and F atoms of the PO_2F_2 ligand. The formulation of the difluorophosphate as O-bonded to the silver atom arises from considerations on its nature. In the only reported structural determination of a transition-metal difluorophosphate complex, $[Rh_2(\eta\text{-}C_5Me_2)_2(PF_2O_2)_3]PF_6$, the PO_2F_2 ligands bridge two rhodium atoms.[9]

The phosphorus atom of the PF_2O_2 group in **3** is tetrahedrally coordinated. The silver atom is three coordinated and shows a short Ag–O(3) distance [2.12 (2) Å].

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Experimental Section

General Data. The compound $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-dppm})]$ was obtained as reported.[3] The silver difluorophosphate was prepared by adding $AgNO_3$ to a freshly prepared solution of ammonium difluorophosphate.[14] Other reagents were obtained from commercial sources. Solvents used were dried by standard procedures, and all manipulations were carried out under an atmosphere of oxygen-free nitrogen. IR spectra of solids were obtained on Nujol mulls with a Perkin-Elmer 783 grating infrared spectrophotometer. ^1H and ^{31}P NMR spectra were recorded on a Bruker spectrometer operating at 80 MHz, referenced respectively to internal tetramethylsilane and external 85% H_3PO_4; positive chemical shifts are downfield for both nuclei.

Preparation of $[Rh_2Ag(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}Ph_2PCH_2PPh_2)]BF_4$ (2a). A benzene solution of $AgBF_4$ (0.0181 g, 0.093 mmol) was rapidly added, at room temperature, to a solution (15 mL) of **1** (0.080 g, 0.106 mmol). Immediately afterward the color solution changed from yellow-brown to light green (a few seconds). Then the reaction was stopped, the solvent evaporated, and the residue washed with a mixture of 50:50 $C_6H_6\text{-}Et_2O$ (4 × 8 mL) in order to remove the starting complex. Compound **2a** was obtained as a light green powder (0.020 g, 0.021 mmol) in 20% yield. Anal. Calcd for $C_{36}H_{32}AgBF_4OP_2Rh_2$: C, 45.85; H, 3.42; F, 8.06. Found: C, 45.81; H, 3.22; F, 8.02.

Compounds $[Rh_2Ag(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}Ph_2PCH_2PPh_2)]PF_6$ (2b) and $[Rh_2Ag(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}Ph_2]PCH_2PPh_2)]ClO_4$ (2c) were prepared in a similar way and obtained as light green powders, with 15 and 20% yields, respectively. Anal. Calcd for $C_{36}H_{32}AgF_6OP_3Rh_2$ (**2b**): C, 43.18; H, 3.22; F, 11.38. Found: C, 43.13; H, 3.20; F, 11.32. Anal. Calcd for $C_{36}H_{32}AgClO_5P_2Rh_2$ (**2c**): C, 45.24; H, 3.38; Cl, 3.7. Found: C, 45.21; H, 3.36; Cl, 3.4.

Preparation of $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}Ph_2PCH_2PPh_2)(\mu\text{-}AgOPF_2O)]$ (3). Silver difluorophosphate (0.0142 g, 0.068 mmol) dissolved in benzene (ca. 15 mL) was added to a solution (20 mL) of **1** (0.060 g, 0.08 mmol) at room temperature. In a few seconds the color of the solution changed from yellow-brown to green. The volume was reduced to 5 mL, and 40 mL of diethyl ether then was added to give a dark green precipitate. The mother liquor was removed by syringe and the product washed with diethyl ether and dried in vacuo: yield 0.034 g (0.036 mmol), 45%. Anal. Calcd for $C_{36}H_{32}AgF_2O_3P_3Rh_2$: C, 45.17; H, 3.37; F, 3.97. Found: C, 45.70; H, 3.38; F, 3.93.

X-ray Data Collection and Structure Refinement. Suitable red-brown crystals of the complex were obtained by slow evaporation from a dichloromethane solution. A crystal of cubic habit of dimensions 0.07 × 0.07 × 0.07 mm was selected and mounted on a Siemens-Stoe automatic four-circle diffractometer. Accurate unit-cell dimensions and crystal orientation matrices together with their estimated standard errors were obtained from least-squares refinement of 2θ, ω, χ, and ψ values of 20 carefully centered high-angle reflections using graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). The crystals were found to be ortohorhombic (*Pnma*) with unit-cell dimensions $a = 14.471$ (1) Å, $b = 18.042$ (2) Å, $c = 12.772$ (1) Å, $V = 3334.5$ Å,[3] $F(000) = 1864$, $Z = 4$, and $D_{calcd} = 1.822$ g.cm^{-3}. Intensities were collected at room temperature in the range $3 \leq 2\theta \leq 50$. An ω/θ scan technique was used for each reflection with a scan speed of 0.03 s^{-1} and scan width of 1.2°. Three standard reflections were monitored periodically during the course of the data collection as a check of crystal stability, and these varied by less than 3%. In the reduction of the data, Lorentz and polarization factors were applied, but no absorption correction was made. Of 2918 independent reflections measured 1281 having $I \geq 3\sigma(I)$ were used in all calculations. The structure was solved by interpretation of the Patterson map, which clearly indicated the positions of the two independent metal atoms. The Fourier difference synthesis phased with the heavy-atom positions allowed the location of the non-hydrogen atoms. Full-matrix least-squares refinement of this model was carried out by minimizing the function $\sum w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factors. The weighting scheme used in the last refinement cycles was $w = 1.753/(\sigma^2(F_o) + 0.000417F_o^2)$ which showed reasonable consistency in a test of $w\Delta^2$ for data sectioned with respect to both F_o and $(\sin\theta)/\lambda$. Anisotropic temperature factors were introduced for all the non-hydrogen atoms except for those belonging to the phenyl rings. These were refined as rigid groups and restricted to their normal geometry (D_{6h} symmetry; C–C = 1.395 Å) by using the group refinement procedure. Each ring was assigned six variable positional parameters, and each ring carbon atom was assigned an individual isotropic thermal parameters. Hydrogen atom contributions were used as fixed atoms in calculated positions: $d(\text{C–H}) = 0.95$ Å and $B_{iso} = 6$ A^2.

This model reached convergency with values $R = [\sum|F_o| - |F_c|]/\sum(F_o) = 0.052$ and $R' = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.045$. A difference Fourier map calculated at this point showed ripples of ca. 0.7 e Å^{-3} close to the O(3) and F(2) atom positions of PO_2F_2 group. The anomalous dispersion terms for Rh, Ag, and P atoms were taken into account in the refinement. Atomic scattering factors for all non-hydrogen atoms were taken from ref 15 and for hydrogen atoms from ref 16. All the calculation were performed with SHELX 76 set of programs on the IBM 4341 computer of the "Centro di Calcolo, Universitã di Messina".

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Registry No. **1**, 88979-33-3; **2a**, 95464-83-8; **2b**, 95464-84-9; **2c**, 95464-85-0; **3**, 95464-86-1; $AgBF_4$, 14104-20-2; $AgPF_6$, 26042-63-7; $AgClO_4$, 7783-93-9; Rh, 7440-16-6; Ag, 7440-22-4; silver difluorophosphate, 95464-87-2.

Supplementary Material Available: A listing of structure factor amplitudes for the title compound (8 pages). Ordering information is given on any current masthead page.

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