perturbation (i.e., large positive α_E values) the π-bond orders calculated for either symmetric or antisymmetric interactions will merge; the model collapses to an open-chain NSNSNSN fragment. (2) For electronegative values of α_E the omission of antisymmetric interactions becomes more serious; their inclusion will tend to offset the trend observed for the symmetric perturbation. The lack of agreement between the lengths of the S_a–N_b and N_b–S_b bonds in $(\eta^5\text{-}C_5H_5)_2TiS_3N_4$ and the bond orders predicted from the above "symmetric-only" calculations are manifestations of this deficiency.

The above comments notwithstanding, the molecular orbital issues developed here provide an appealing framework for understanding the structural dichotomy between $(\eta^5\text{-}C_5H_5)_2TiS_3N_4$ and $SO_2S_3N_4$. The fundamental importance of the metal d orbitals in $(\eta^5\text{-}C_5H_5)_2TiS_3N_4$ in influencing the structural features of the NSNSNSN fragment are readily apparent. By contrast the structure of $SO_2S_3N_4$ suggests only limited involvement of sulfur d orbitals (on the sulfone moiety) with the delocalized π-system of the NSNSNSN chain. The implications of these conclusions on the interpretation of the electronic spectra of these derivatives is currently being investigated.

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Supplementary Material Available: Tables of anisotropic thermal parameters for 3 and 4 and structure factor tables for each structure (53 pages). Ordering information is given on any current masthead page.

Synthesis of Triangular Rhodium–Silver Clusters by the Addition of Silver Electrophiles to an Electron-Rich Rhodium–Rhodium Bond. X-ray Crystal Structure of $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}Ph_2PCH_2PPh_2)(\mu\text{-}AgO_2CCH_3)]$

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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 silver acetate, trifluoroacetate, and diethyldithiocarbamate, AgY, to give the triangular mixed clusters $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)(\mu\text{-}AgY)]$ (2, Y = CH_3CO_2; 3, Y = CF_3CO_2; 4, Y = $(C_2H_5)_2NCS_2$); the reactions occur by electrophilic attack of the silver salts on the electron-rich rhodium–rhodium bond of 1. Compounds 2–4 have been spectroscopically characterized; compound 2 has been also characterized by X-ray analysis. Crystals of 2 are orthorombic of space group *Pnma* with $a = 14.426$ (1) Å, $b = 18.134$ (2) Å, $c = 12.614$ (1) Å, and $Z = 4$. The structure was solved and refined to R and R_w values of 0.035 and 0.034 for the 1629 reflections with $I \geq 3\sigma(I)$. In the triangular Rh_2Ag framework the two equivalent Rh–Ag distances are 2.730 (1) Å, and the Rh(1)–Rh(1′) bond distance is 2.751 (1) Å. The rhodium atoms are bridged by CO and dppm ligands and are symmetrically capped by η-cyclopentadienyl ligands. The cyclopentadienyl ligands are in cis position with an interplanar angle of 93.4 (3)° and are located in the less hindered side of the molecule. The acetate group is chelated to the silver atom [Ag–O(2) = 2.432 (7) Å; O(2)–Ag–O(2′) and O(2)–C(8)–O(2′) angles are respectively 51.0 (3)° and 123.7 (13)°]. The Ag, Rh(1), Rh(1′), O(2), and O(2′) atoms form a distorted square-planar pyramid with the silver atom in the apical position. The structural modification of 1 caused by the presence of the bridged AgO_2CCH_3 is discussed. Compound 1 reacts with silver malonate to give $[\{Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)\}_2\{\mu\text{-}Ag_2(CO_2)_2CH_2\}]$ (5) in which two triangular Rh_2Ag skeletons are joined by the bridged malonate group.

Introduction

In recent studies several mixed-metal clusters in which a group 11 element, Cu, Ag, or Au, is part of a cluster polyhedron have been reported; while general synthetic routes were developed for the synthesis of mixed-metal clusters containing gold atoms,[1] few systematic methods are available for the introduction of fragments containing silver or copper atoms into a bi- or polynuclear framework.[2] The interest in these studies arises from the isolobal relationship between the proton and the group 11 cations (especially Au(I) as $Au(PPh_3)$[2]] so that the latter react with anionic metal complexes or polynuclear clusters as the H^+ species does. (However, there are exceptions to this correlation, so caution must be exercised in its use.)

Among the mixed-metal complexes containing silver, some show a linear arrangement of metal atoms, as, for example, in $[\{(\eta\text{-}C_5H_5)Rh(CO)PPh_3\}_2Ag]PF_6$,[2a,b] while most of them are closed clusters in which the electrophile Ag^+ or $[AgPPh_3]^+$ bridges two metal atoms[2c,f,h,n] or caps a triangular face of a metal cluster.[2e]

We recently reported the synthesis of the trinuclear mixed-metal clusters $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)(\mu\text{-}HgCl_2)]$,[3] $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)(\mu\text{-}AuPPh_3)]X$ (X = BF_4, PF_6),[4] and $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)(\mu\text{-}AgOPF_2O)]$[5] by addition of an electrophile containing the metal to the electron-rich rhodium–rhodium bond of $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)]$[6] (1) [dppm = bis(diphenylphosphino)methane]. During these studies we found that in contrast to the $[Rh_2Ag(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)]X$[5] (X = BF_4, PF_6) complexes, the difluorophosphate derivative is very stable. Thus, the presence

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Table I. IR and NMR Data of the Complexes

	IR[a]		^{1}H NMR[b]		^{31}P{^{1}H} NMR[c]
complex	ν(CO)	other bands	$\delta(C_5H_5)$	other signals	$\delta(^{31}P)$[d]
2	1728 vs	1565 s (ν_{asym}(CO))	5.33 (t, $J_{PH} = J_{RhH} = 0.55$ Hz)	3.13 (t, PCH_2P, $J_{PH} = 10$ Hz), 2.24 (s, CH_3)	49.68 ($^1J_{PRh} = 188.5$ Hz, $^2J_{PP} = 81.5$ Hz, $^2J_{PRh} = 12.5$ Hz, $^1J_{RhRh} = 8.5$ Hz)
3	1728 vs	1670 vs (ν_{asym}(CO))	5.35 (t, $J_{PH} = J_{RhH} = 0.55$ Hz)	2.93 (m, PCH_2P)	49.54 ($^1J_{PRh} = 187.5$ Hz, $^2J_{PP} = 80.2$ Hz, $^2J_{PRh} = 12.5$ Hz, $^1J_{RhRh} = 9$ Hz)
4	1765 vs	1470 vs (ν(CN))	5.36 (t, $J_{PH} = J_{Rh} = 0.6$ Hz)	3.21 (t, PCH_2P, $J_{PH} = 10$ Hz), 4.15 (q, CH_2, $J_{HH} = 9$ Hz), 1.42 (t, CH_3, $J_{HH} = 9$ Hz)	50.0 ($^1J_{PRh} = 193$ Hz, $^2J_{PP} = 82$ Hz, $^2J_{PRh} = 13$ Hz, $^1J_{RhRh} = 9$ Hz)
5	1755 vs, 1732 vs	1555 vs (ν_{asym}(CO)), 1568 sh	5.34 (t, $J_{PH} = J_{RhH} = 0.6$ Hz)	3.12 (t, PCH_2P, $J_{PH} = 10$ Hz), 3.15 (t, PCH_2P, $J_{PH} = 10$ Hz), 3.70 (s, CH_2)	49.65 ($^1J_{PRh} = 190$ Hz, $^2J_{PP} = 81$ Hz, $^2J_{PP} = 13$ Hz, $^1J_{RhRh} = 8$ Hz)

[a] cm^{-1}, Nujol mull (KBr). [b] ppm from Me_4Si, in CD_2Cl_2. [c] ppm from 85% H_3PO_4, in CD_2Cl_2. [d] AA′XX′ system.

of an anionic group coordinated to the silver atom, modifying its electrophilic character, appears to stabilize the Rh_2Ag framework. In an effort to evaluate these considerations, we synthesized trinuclear rhodium–silver clusters by using as electrophiles silver salts containing as counterions, the acetate, trifluoroacetate, diethyldithiocarbamate, and malonate anions. We also report the X-ray structural characterization of the acetate derivative $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-dppm})(\mu\text{-}AgO_2CCH_3)]$.

Results and Discussion

Synthesis, Characterization, and Properties of Rhodium–Silver Mixed-Metal Clusters. The addition of silver acetate, trifluoroacetate, or diethyldithiocarbamate to the complex $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-dppm})]$ (**1**) in benzene solution leads readily to the trinuclear mixed-metal clusters $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-dppm})(\mu\text{-}AgY)]$ (**2**, Y = CH_3CO_2; **3**, Y = CF_3CO_2; **4**, Y = $(C_2H_5)_2NCS_2$) in high yields. These are air-stable, dark green crystalline solids, which dissolve easily in dichloromethane and to a lesser extent in benzene and are insoluble in diethyl ether and petroleum ether. Their solutions are stable for about 1 day; this is different from the analogous compounds $[Rh_2Ag(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-dppm})]X$ (X = BF_4, PF_6)[5] which decompose immediately in solution, in all the solvents. The conductivities of **2**–**4** indicate that these complexes are nonionic. The general structure of the complexes was deduced by elemental analysis (Experimental Section) and IR and ^{1}H and ^{31}P{^{1}H} NMR spectroscopy (Table I); the precise nature of compound **2** was also established by X-ray crystallography. The IR spectra of **2** and **3** show ν(CO) of the bridging carbonyls at frequencies comparable to that of the starting complex, whereas in the diethyldithiocarbamate derivative **4** ν(CO) is shifted to higher frequencies. The chelating nature of the acetate group in **2** is clearly shown by the IR spectrum which exhibits a broad band at 1565 cm^{-1}, typical of a bidentate chelating acetate.[7] We suggest that a similar coordination mode for the trifluoroacetate and diethyldithiocarbamate groups is operative in complexes **3** and **4** although ν(CO) and ν(CN), which are indicative of the coordination mode of these ligands, fall at values which are on the borderline between bidentate and monodentate coordination.[8,9] The ^{1}H and ^{31}P{^{1}H} NMR spectra of complexes **2**–**4** are very similar and support a Rh_2Ag triangular cluster structure with the AgY group bridging the rhodium–rhodium bond of **1**. The cyclopentadienyl proton resonances appear as a triplet and support a symmetrical structure for the complexes. The

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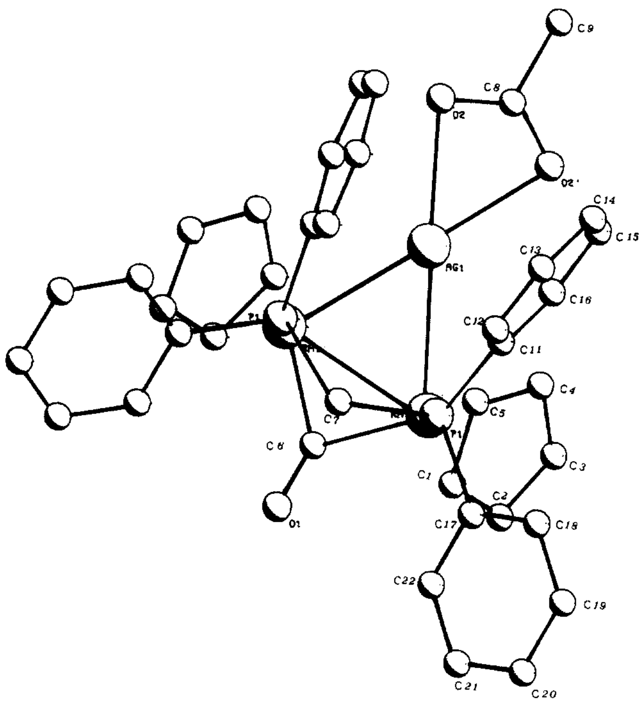


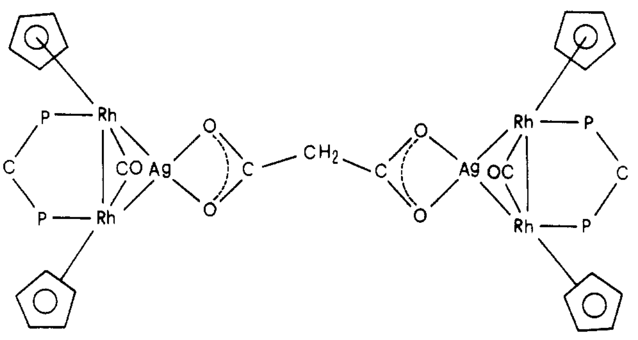
Figure 1. View of the molecular structure of $[\mathrm{Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)(\mu\text{-}AgO_2CCH_3)}]$ showing the numbering scheme.

magnitude of the coupling constants ($J_{\mathrm{Rh-H}} = J_{\mathrm{P-H}} \simeq 0.55$ Hz) is the same as in 1 and indicates that the addition of the silver electrophile occurs without significant variation in the formal oxidation number of the two rhodium atoms. The methylene hydrogen resonance of the PCH_2P moiety appears the same as is usually observed when a rapid conformational change in the CP_2Rh_2 ring renders the two protons equivalent.[10]

The $^{31}P\{^1H\}$ NMR spectra exhibit a pattern typical of an AA′XX′ spin system and clearly support a symmetrical structure for complexes 2–4. The values of the chemical shift and the coupling constants fall in the range quoted for other related trinuclear mixed-metal clusters.[4,5]

Reaction of 1 with Silver Malonate. The formation of 2–4 by addition of silver electrophiles containing coordinating anions to the electron-rich rhodium–rhodium bond of 1 prompted us to extend this route to prepare compounds in which two triangular rhodium–silver skeletons are joined by a bridging group. This could be achieved by using as an electrophile the silver salt of a coordinating dianion (containing two electrophilic metal centers). Accordingly, we have treated compound 1 with silver malonate, following the procedure used for 2. The reaction product 5 is a green microcrystalline solid, soluble in dichloromethane and acetone and stable for long periods as the solid but only moderately stable on exposure to air in solution; it is nonconducting in dichloromethane solution. The many attempts to isolate crystals of complex 5 of X-ray quality failed. However, elemental analyses and spectroscopic data are consistent with the structure shown ($PCP = Ph_2PCH_2PPh_2$).

Furthermore, the molecular weight in CH_2Cl_2 solution was 1780 (calc. 1814.6) which clearly indicates that *5* contains two Rh_2Ag skeletons. The IR, ^1H and $^{31}P\{^1H\}$ NMR spectra are very similar to those of *2*. The IR spectrum shows bands at 1555 and 1568 cm^{-1} due to $\nu_{\mathrm{asym}}(CO)$ of the carboxylate group; this suggests either that both the silver atoms are bonded to the rhodium atoms or that the carboxylate groups are chelated to the silver atoms. In the ^1H NMR spectrum the cyclopentadienyl proton resonance is detected at δ 5.34 (CD_2Cl_2) as a triplet ($J_{PH} = J_{RhH} \cong 0.6$ Hz). The coupling constant values are as expected for this class of compounds.[3-6,11] The methylene hydrogen resonance of the malonate group appears as a singlet at δ 3.70; as expected, the approximate ratio of methylene protons to cyclopentadienyl and phenyl protons is 1:10:20. Unlike 2–4, the methylene proton resonance of the dppm ligand consists of two superimposed multiplets, as usually observed when this ligand is bridge-bonded and no motion of the CP_2M_2 ring renders the two protons equivalent.[10]



The $^{31}P\{^1H\}$ NMR spectrum is like those of complexes 2–4; it exhibits for the phosphorus atoms of the dppm ligands an AA′XX′ spin system centered at δ 49.65 (Table I).

Crystal and Molecular Structure of 2. In order to accurately determine the molecular structure of one member of the series, a single-crystal X-ray diffraction study of 2 was undertaken. The molecular structure is shown in Figure 1, which also indicates the labeling of the atoms. The experimental details, including the crystal parameters, are reported in Table II. Fractional atomic coordinates for non-hydrogen atoms are listed in Table III; relevant bond distances and angles are given in Table IV.

The molecule shows a crystallographic mirror plane passing through the carbonyl group, the methylene carbon of the dppm, the silver atom, and the carbon atoms of the acetate ligand. The overall structure of 2 may be described as a triangular arrangement of the three metal atoms Ag, Rh(1), and Rh(1′) with the rhodium atoms bridged by the carbonyl and the dppm ligands; each Rh(1) and Rh(1′) corner is symmetrically capped by a cyclopentadienyl ring. The methylene carbon of the dppm and CO groups are directed on the same side so that the six-membered ring Rh(1)P(1)C(7)P(1′)Rh(1′)C(6) assumes the boat conformation, as in 1, to minimize repulsive contacts between the most bulky phenyl groups. The acetate group is chelated to the silver atom.

The structural features of the bridging dppm and CO groups remain essentially the same as in the precursor 1. The only significant differences are the lengthening of the rhodium–rhodium bond [2.683 (1) Å in 1], the increase in the angle subtended at the bridging carbon atom [85.6 (4)° in 1], a shorter distance Rh–C [1.978 (9) and 1.971 (9) Å, in 1], and an increase in the P(1)–C(7)–P(1′) angle [107.8 (4)° in 1]. The lengthening of the Rh–Rh distance caused by the interaction of the silver acetate with 1 is slightly smaller than that due to the electrophiles $[AuPPh_3]^+$ and $HgCl_2$; this may be a direct consequence of the dimensions of the electrophilic atom.

The internal structures of 2 and $[\mathrm{Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}}$

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Table II. Crystal and Refinement Data for $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-dppm})(\mu\text{-}AgO_2CCH_3)]$

formula	$C_{38}H_{35}AgO_3P_2Rh_2$
fw	915.32
cryst system	orthorombic
space group	*Pnma*
a, Å	14.426 (1)
b, Å	18.134 (2)
c, Å	12.614 (1)
V, Å^3	3299.8 (5)
Z	4
d_{calcd}, g/cm^3	1.84
cryst size, mm	0.12 × 0.08 × 0.08
orientatn reflctns	
no., range (2θ)	20, $15 < 2\theta < 30$
T, °C	22
abs coeff, cm^{-1}	16.8
radiation	Mo Kα, λ = 0.71069
monochromator	graphite crystal
scan type	$2\theta-\omega$
scan speed	0.03 s^{-1}
scan range	1.2°
reflctns measd	$+h,+k,+l$
std. reflctns	3 measd after every 120
data limits	$3 < 2\theta \leq 50$
total no. of reflectns collected	3220
collected obsd data	1629 [$I \geq 3\sigma(I)$]
no. of parameters refined	145
$R_b{}^a$	0.035
$R_w{}^b$	0.034
largest shift/esd final cycle	0.08
largest peak, e/Å^3	0.54

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

Table III. Final Fractinal Atomic Coordinates (×10^4) for Non-Hydrogen Atoms with Estimated Standard Deviation in Parentheses

atom	*x/a*	*y/b*	*z/c*
Ag	1109 (1)	2500	6182 (1)
Rh(1)	1781 (1)	1741 (1)	4477 (1)
P(1)	361 (1)	1672 (1)	3811 (1)
C(6)	2073 (8)	2500	3410 (9)
O(1)	2373 (6)	2500	2554 (6)
C(7)	31 (8)	2500	3072 (8)
O(2)	806 (5)	3077 (4)	7887 (5)
C(8)	680 (8)	2500	8307 (10)
C(9)	364 (13)	2500	9468 (12)
C(1)	3207 (6)	1239 (5)	4561 (8)
C(2)	2583 (8)	720 (5)	4200 (6)
C(3)	1928 (7)	579 (4)	5008 (8)
C(4)	2164 (7)	1001 (5)	5878 (7)
C(5)	2938 (6)	1432 (5)	5597 (7)
C(11)	−616 (3)	1508 (2)	4676 (3)
C(12)	−1522 (3)	1603 (2)	4314 (3)
C(13)	−2265 (3)	1522 (2)	5011 (3)
C(14)	−2103 (3)	1345 (2)	6071 (3)
C(15)	−1197 (3)	1250 (2)	6434 (3)
C(16)	−454 (3)	1331 (2)	5736 (3)
C(17)	257 (3)	953 (3)	2820 (3)
C(18)	−419 (3)	403 (3)	2853 (3)
C(19)	−424 (3)	−153 (3)	2090 (3)
C(20)	247 (3)	−160 (3)	1293 (3)
C(21)	922 (3)	390 (3)	1260 (3)
C(22)	928 (3)	946 (3)	2023 (3)

Table IV. Bond Distances (Å) and Angles (deg) for $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-dppm})(\mu\text{-}AgO_2CCH_3)]$

Bond Distances			
Rh(1)–Rh(1′)	2.751 (1)	C(6)–O(1)	1.163 (11)
Rh(1)–P(1)	2.217 (2)	Ag–Rh(1)	2.730 (1)
Rh(1)–C(6)	1.970 (8)	Ag–O(2)	2.432 (7)
Rh(1)–C(1)	2.253 (8)	C(1)–C(2)	1.380 (12)
Rh(1)–C(2)	2.212 (7)	C(1)–C(5)	1.407 (11)
Rh(1)–C(3)	2.221 (7)	C(2)–C(3)	1.412 (12)
Rh(1)–C(4)	2.288 (7)	C(3)–C(4)	1.380 (11)
Rh(1)–C(5)	2.257 (7)	C(4)–C(5)	1.409 (11)
av Rh(1)–C	2.246 (7)	C–C(av)	1.398 (11)
P(1)–C(7)	1.831 (6)	C(8)–O(2)	1.186 (8)
P(1)–C(11)	1.808 (5)	C(8)–C(9)	1.534 (18)
P(1)–C(17)	1.812 (5)		
Rh(1)–Cp*	1.906 (9)		

Bond Angles			
Rh(1)–Ag–Rh(1′)	60.5 (2)	P(1)–C(7)–P(1′)	110.2 (5)
Rh(1)–C(6)–Rh(1′)	88.6 (5)	O(2)–Ag–O(2′)	51.0 (3)
Rh(1)–C(6)–O(1)	135.5 (2)	O(2)–C(8)–O(2′)	123.7 (13)
C(6)–Rh(1)–Ag	105.2 (2)	O(2)–Ag–Rh(1)	167.7 (2)
P(1)–Rh(1)–Ag	90.0 (1)	O(2)–C(8)–C(9)	118.1 (7)
C(6)–Rh(1)–P(1)	88.8 (3)		

CO)(μ-dppm)(μ-$AgOPF_2O$)][5] are nearly identical. They only differ for the coordination of the anionic ligand bound to the silver atom. The Rh–Rh bond distance of 2.751 (1) Å is comparable to that found in $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-dppm})(\mu\text{-}AgOPF_2O)]$ [2.750 (3) Å]. The Rh–Ag distance of 2.730 (1) Å is significatively longer than the 2.689 (2) Å distance found for $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-dppm})(\mu\text{-}AgOPF_2O)]$; this is a direct consequence of the different coordination around the silver atom. Few other rhodium–silver bond lengths are available for comparison. The values of 2.651 (1) and 2.636 (1) Å for the complex $[\{Rh(\eta\text{-}C_5H_5)(CO)(PPh_3)\}_2Ag]PF_6$ which has a nearly linear trimetal sequence, Rh–Ag–Rh,[2a,b] may be cited.

The Rh–C(C_5H_5) distances range from 2.212 (8) to 2.288 (7) Å; these values are in agreement with literature reports.[3-6,12] The corresponding Rh–Cp* (Cp* = centroid of the cyclopentadienyl ring) separations are 1.906 (9) Å. The cyclopentadienyl rings are located on the less hindered side of the molecule; the interplanar angle between the cyclopentadienyl rings is 93.4 (3)° (the corresponding angle in 1 is 82.1°). The electrophilic attack that the Rh–Rh bond of 1 does not modify the Cp*–Rh–Rh angle but leads to an increase of the interplanar angle between the cyclopentadienyl rings which can be related to the steric bulk of the electrophile. Thus, $HgCl_2$, which is the bulkiest of the electrophiles used, leads to the largest value of the interplanar cyclopentadienyl ring angle (100.7°) in the corresponding adduct.[3]

The acetate group chelated to the silver atom shows values of the O(2)–Ag–O(2′) and O(2)–C(8)–O(2′) angles of 51.0 (3)° and 123.7 (13)°, respectively. The Ag, Rh(1), Rh(1′), O (2), and O(2′) atoms form a distorted square-planar pyramid with the silver atom in the apical position at 0.2534 (2) Å from the plane Rh(1)Rh(1′)O(2)O(2′). The Ag–O(2) distance of 2.432 (7) Å is longer thant that of 2.115 (19) Å found for $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-dppm})(\mu\text{-}AgOPF_2O)]$ in which the difluorophosphate anion is monocoordinated to silver atom. The different coordination of the difluorophosphate and acetate groups to the silver can be rationalized in terms of the O–P–O angle which is significantly smaller than the O(2)–C(8)–O(2′) angle owing to the tetrahedral coordination of the phosphorus atom in the difluorophosphate complex. As the carbon atoms in the acetate, trifluoroacetate, diethyldithiocarbamate, and malonate groups are sp^2 hybridized, it is likely, in the light of the X-ray structure of 2, that also in complexes 3–5 chelation of the anionic ligand to silver occurs.

Experimental Section

The compound $[R_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-dppm})]$ (1) was obtained as reported.[6] Other reagents were obtained from commercial sources. The solvents used were dried by standard procedures. All manipulations were carried out under an atmosphere of ox-

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(12) (a) Mills, M. S.; Paulus, E. F. *J. Organomet. Chem.* **1967**, *10*, 331. (b) Herrmann, W. A.; Bauer, C.; Kriechbaum, G.; Kunkely, H.; Ziegler, M. L.; Speth, D.; Guggolz, E. *Chem. Ber.* **1982**, *115*, 878. (c) Herrmann, W. A.; Goddard, C. K. R.; Bernal, I. *J. Organomet. Chem.* **1977**, *140*, 73.

ygen-free nitrogen. IR spectra of solids were obtained on Nujol mulls with a Perkin-Elmer 783 grating infrared spectrophotometer. ^{1}H 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. Conductivity measurements were made with a Radiometer CDM 3 conductivity meter. Molecular weights were determined with a Knauer vapor pressure osmometer. Elemental analyses were performed by Bernhardt Mikroanalytishes Laboratorium, Elbach, Germany, and by the Microanalytical Laboratory of the Organic Chemistry Institute of Milan.

Preparation of $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)(\mu\text{-}AgO_2CCH_3)]$ (2). Solid silver acetate (0.0186 g, 0.120 mmol) was added to a stirred benzene solution (20 mL) of 1 (0.060 g, 0.080 mmol); the mixture was stirred for about 20 min. During this time the solution color changed from yellow-brown to dark-green. The solution was filtered rapidly to remove the excess of silver acetate; then when diethylether was added, a dark green solid was obtained. The compound was recrystallized from dichloromethane–hexane (1:3); yield 0.062 g (0.068 mmol), 85%. Anal. Calcd for $C_{38}H_{35}AgO_3P_2Rh_2$: C, 49.86; H, 3.85. Found: C, 49.91; H, 3.87.

Preparation of $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)(\mu\text{-}AgO_2CCF_3)]$ (3). To a stirred benzene solution (15 mL) of 1 (0.075 g, 0.100 mmol) was added a solution (20 mL) of silver trifluoroacetate (0.021 g, 0.100 mmol) in the same solvent. The color of the solution turned rapidly green. Stirring was continued for ca. 10 min to ensure complete reaction. When 50 mL of diethyl ether was added, the product was obtained as a green microcrystalline solid. The mother liquor was removed by syringe, and the solid product was recrystallized from dichloromethane–hexane (1:3) to give 3 as green crystals (0.086 g, 0.09 mmol) in 90% yeilds. Anal. Calcd for $C_{38}H_{32}AgF_3O_3P_2Rh_2$: C, 47.09; H, 3.33; F, 5.88. Found: C, 46.91; H, 3.36; F, 6.00.

Preparation of $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)(\mu\text{-}AgS_2CNEt_2)]$ (4). A solution (20 mL) of silver diethyldithiocarbamate (0.0235, 0.094 mmol) in benzene was added to a stirred solution (15 mL) of 1 (0.070 g, 0.094 mmol). The solution color immediately changed from yellow-brown to green. After about 10 min the solution was evaporated to 10 mL; when hexane (30 mL) was added, a green solid was obtained. The mother liquor was removed by syringe, and the residue was washed with diethyl ether and dried in vacuo. It was subsequently recrystallized from dichloromethane–diethyl ether (1:4) to give 4 as a green microcrystalline solid (0.075 g, 0.075 mmol) in 80% yield. Anal. Calcd for $C_{41}H_{42}AgOP_2Rh_2S_2$: C, 49.72; H, 4.27; S, 6.47. Found: C, 49.80; H, 4.28; S, 6.50.

Preparation of $[\{Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)\}_2\{\mu\text{-}(AgO_2C)_2CH_2\}]$ (5). An excess of silver malonate (0.032 g, 0.100 mmol) was added to a stirred solution of 1 in benzene (30 mL). Stirring was continued for ca. 20 min, and the excess silver malonate was filtered, and the volume of the solution was reduced to 10 mL. Diethyl ether (20 mL) then was added. On standing, compound 5 precipitated a green microcrystalline solid (0.073 g, 0.041 mmol) in 60% yield. Anal. Calcd for $C_{75}H_{66}Ag_2O_6P_4Rh_4$: C, 49.64; H, 3.67. Found: C, 49.70; H, 3.69.

X-ray Data Collection and Structure Refinement. Suitable dark green crystals of the complex were obtained by slow evaporation from a dichloromethane–hexane solution. Diffraction data were collected on a Siemens-Stoe four-circle diffractometer using graphite-monochromated Mo Kα (λ = 0.71069 Å) radiation. Accurate unit-cell dimensions and crystal orientation matrices were obtained from least-squares refiniment of 2θ, χ, and ϕ values of 20 strong reflections in the range $15° < 2\theta < 34°$. Crystallographic data and other pertinent information are summarized in Table II. 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 2.5%. In the reduction of the data, Lorentz and polarization factors were applied, but no absorption correction was made. Of 3220 measured, 1629 independent reflections having $I > 3\sigma(I)$ 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 phase with the heavy-atom positions allowed the location of the nonhydrogen atoms. Full-matrix least-squares refinement of this model was carried out by minimizing the function $\sum w(|Fo| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factors. The weighting scheme used in the last refinement cycle was $w = 1.3101/(\sigma^2(F_o) + 0.000262F_o^2)$.

Anisotropic temperature factors were introduced for all nonhydrogen atoms except 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 an individual isotropic thermal parameter. Hydrogen atoms were included in the scattering model in calculated idealized positions (d(C–H) = 0.96 Å) with a common thermal parameter $(B_{iso} = 6\ \text{Å})^2$.

The anomalous dispersion terms for Rh, Ag, and P atoms[13] were taken into account in the refinement. Atomic scattering factors for all non-hydrogen atoms were taken from ref 14 and for hydrogen atoms from ref 15.

All the calculations were performed with the SHELX 76[16] and PARST[17] set of programs on the IBM 4341 computer at the "Centro di Calcolo, Università di Messina".

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Registry No. 1, 88979-33-3; 2, 101835-31-8; 3, 101835-32-9; 4, 101835-33-0; 5, 101835-34-1; Rh, 7440-16-6; Ag, 7440-22-4; silver acetate, 563-63-3; silver trifluoroacetate, 2966-50-9; silver diethyldithiocarbamate, 1470-61-7; silver malonate, 75225-48-8.

Supplementary Material Available: Tables of observed and calculated structure factors, final fractional coordinates for hydrogen atoms, and anisotropic and isotropic thermal parameters for 2 (12 pages). Ordering information is given on any current masthead page.

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