(MULTAN78) and Fourier techniques and refined by full-matrix least squares. Hydrogen atoms were visible in a Fourier phased on the non-hydrogen parameters and were included in the final cycles. Non-hydrogen atoms were assigned anisotropic thermal parameters while hydrogens were allowed to vary isotropically. A ψ scan of a reflection located at ca. $\chi = 90°$ indicated a fluctuation of over 10%, so an absorption correction was applied.

A final difference Fourier was essentially featureless, with the largest peak being 0.50 e/A^3, other than one peak located at the Hf site which was 1.04 e/A^3.

$Th(OAr')_2(CH_2\text{-}py\text{-}6Me)_2$ (IIb). A suitable crystal was located and mounted in a 0.5-mm capillary surrounded by epoxy resin. Data collection and refinement were carried out by using the standard procedures of the Purdue Crystallographic facility.

Hydrogen atoms were located such that the hydrogen–carbon bond was 0.95 Å and the angles were correct. For methyl groups, one hydrogen was located in the Fourier map, its position was idealized, and the remaining hydrogen positions were calculated on the basis of it. Hydrogen temperature factors and positions were not refined.

The absorption in these crystals was very large. This was not helped by the fact that they were large plates. All ψ scan sets displayed positions where the diffracted beam disappeared. Attempts to base corrections on these ψ scans were not successful.

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Registry No. Ia, 110527-86-1; Ib, 110527-88-3; IIa, 110527-87-2; IIb, 110527-89-4; $LiCH_2\text{-}py\text{-}6\text{-}CH_3$, 34667-18-0; LiOAr', 55894-67-2; $HFCl_4$, 13499-05-3; $ThCl_4$, 10026-08-1; 2,6-dimethylpyridine, 108-48-5.

Supplementary Material Available: Tables of positional parameters, general temperature factors, bond distances, and bond angles (13 pages); listings of structure factor amplitudes (14 pages). Ordering information is given on any current masthead page.

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

Giuseppe Bruno, Sandra Lo Schiavo, Enrico Rotondo, Pasquale Piraino, and Felice Faraone*

Dipartimento di Chimica Inorganica e Struttura Molecolare, Università di Messina, Piazza S. Pugliatti,
98100 Messina, Italy

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The new Rh_2Cu mixed-metal clusters $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)(\mu\text{-}CuX)]$ (X = Cl, **2**; X = I, **3**; dppm = bis(diphenylphosphino)methane) have been prepared by reacting $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)]$ (**1**) with CuX and have been spectroscopically characterized. The structure of **3** has also been established by X-ray crystallography. The compound crystallizes in the orthorhombic space group *Pnma* with a = 14.002 (2) Å, b = 18.306 (2) Å, c = 13.025 (1) Å, V = 3338.5 Å^3, and Z = 4. The structure has been refined to R = 0.034 and R_w = 0.039 for the 1064 reflections with $I \geq 3\sigma(I)$. Complex **3** reacts with AgO_2CCF_3 to yield $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)(\mu\text{-}AgO_2CCF_3)]$ (**4**) which has been structurally characterized. Crystals of **4** are also orthorhombic of space group *Pnma* with a = 15.133 (2) Å, b = 18.176 (3) Å, c = 12.656 (1) Å, V = 3481.0 Å^3, and Z = 4. R = 0.034 and R_w = 0.034 for the 1993 reflections with $I \geq 3\sigma(I)$. In both complexes structurally characterized the three metal atoms define a triangular cluster [in **3** Rh(1)–Rh(1') = 2.746 (1), Rh(1)–Cu = 2.588 (2) Å; in **4** Rh(1)–Rh(1') = 2.776 (1), Rh(1)–Ag = 2.719 (1) Å] with the Rh–Rh bond bridged by the dppm and the CO ligands. The rhodium atoms are each symmetrically capped by one η-cyclopentadienyl ligand, and the interplanar angle between the cyclopentadienyl rings can be related to the bulk of the group 11 metal. In **3** the iodine atom is bonded to copper while in **4** the trifluoroacetate group is chelated to the silver atom. The structural features of **3** and **4** have been compared with those of the other compounds of this class already reported. The results show that the formation of stable Rh_2Ag and Rh_2Cu triangular clusters by addition of electrophiles containing the group 11 metals to **1** requires the use of silver or copper salts of coordinating anions.

Introduction

We recently reported the synthesis and the X-ray structural characterization of mixed-metal clusters in which a group 11 atom, Au or Ag, is part of a triangular cluster.[1-4] These species, $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)(\mu\text{-}AuPPh_3)]X$, $[Rh_2Ag(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)]X$ (X = BF_4, PF_6), and $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)(\mu\text{-}AgY)]$ (Y = O_2PF_2, O_2CCH_3, O_2CCF_3, S_2PEt_2), were obtained by addition of silver or gold electrophiles to the electron-rich rhodium–rhodium bond of $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)]$ (**1**) (dppm = bis(diphenylphosphino)methane).

In this paper we describe the synthesis of the analogous copper derivatives $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)(\mu\text{-}CuX)]$

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(**2**, X = Cl; **3**, X = I) and the X-ray crystal structures of **3** and $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-dppm})(\mu\text{-}AgO_2CCF_3)]$ (**4**).

Compound **4** was recently reported by us,[4] but the bonding mode of AgO_2CCF_3 was not fully characterized because of the uncertainty of the IR data which are on the borderline between bidentate and monodentate coordination.

We became interested in extending the above gold and silver series to copper especially as there are relatively few compounds known having bonds between copper and any transition element,[5] particularly rhodium.[6-8]

Results and Discussion

Preparation and Characterization of $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-dppm})(\mu\text{-}CuX)]$ (X = Cl, I). We have previously succeeded[2-4] in preparing triangular Rh_2Au and Rh_2Ag mixed-metal clusters by the reaction of electrophiles containing the group 11 metals, Au or Ag, with $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-dppm})]$ (**1**).

This synthetic route has been easily extended to prepare the analogous Rh_2Cu complexes, $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-dppm})(\mu\text{-}CuCl)]$ (**2**) and $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-dppm})(\mu\text{-}CuI)]$ (**3**), by using CuCl and CuI as electrophilic reagents. $[Cu(NCMe)_4]PF_6$, $[CuCl(PPh_3)]_4$, and $[Cu(PPh_3)]PF_6$ failed to react with **1**.

Complexes **2** and **3** are dark green crystalline solids which easily dissolve in chlorinated solvents and to a lesser extent in benzene and methanol. Their solutions are air-sensitive and the color changes from green to red (within 15 min for **2** and 14 h for **3**, in CH_2Cl_2) while the conductivity increases, reaching values consistent with the formation of a 1:1 electrolyte, and CO is released. All the attempts to isolate the formed ionic compound by addition of $NaBPh_4$ to a red methanolic solution of **2** or **3** failed to give a pure compound.

The new compounds **2** and **3** have been characterized by their spectroscopic data with **3** also defined by an X-ray diffraction study. The IR and NMR data for both complexes are consistent with the structure drawn in Figure 2 for **3**. The ν(CO) of the bridging carbonyls are at 1733 and 1722 cm^{-1} for **2** and **3**, respectively.

The ^1H NMR spectra of **2** and **3** are similar and show signals attributable to the phenyl groups (δ 7.5 (br)) and the cyclopentadienyl and methylene hydrogens. The methylene hydrogen resonances appear in both spectra as a triplet of triplets centered at δ 3.19 ($^2J_{PH}$ = 1.1, $^3J_{RhH}$ = 9 Hz), indicating that the fast motion of the CP_2Rh_2 ring renders the two protons equivalent on the NMR time scale.[9] The proton spectra of **2** and **3** present some differences in the cyclopentadienyl region; in fact while in the former only two rather wide signals at δ 5.28 and 5.29 can be detected, in the latter six different transitions centered at δ 5.28 can be resolved (Figure 1).

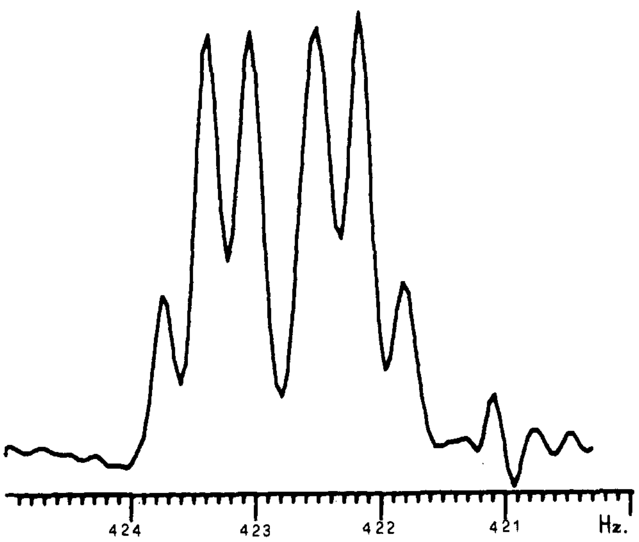

Figure 1. ^1H NMR spectrum, 80 MHz, of $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-dppm})(\mu\text{-}CuI)]$ (**3**) in the C_5H_5 region.

The analysis of the nuclear system AA′XX′YY′ (AA′ = ^{103}Rh, XX′ = ^{31}P, YY′ = ^1H), carried out with the X approximation principle,[10] indicates that 76 transitions, 12 of which of very low intensity, should be present in the cyclopentadienyl region. The shape of the experimental spectrum is strictly connected with the number of transitions that can be resolved in each case. Even under the most favorable conditions (complex **3**) in the experimental spectrum, there are not enough resolved transitions to provide sufficient information for an unequivocal assignment of the proton–^{103}Rh and proton–^{31}P coupling constants.

The $^{31}P\{^1H\}$ NMR of **2** and **3** are identical and clearly show the expected ten peaks of the X portion of an AA′XX′ system. The coupling constants are in the same range of those reported for the other related trinuclear clusters.[2-4]

Treatment of a dichloromethane solution of **3** with the stoichiometric amount of CF_3COOAg results in the replacement of the CuI moiety by the CF_3COOAg and the formation of $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-dppm})(\mu\text{-}AgO_2CCF_3)]$ (**4**). A product, which did not contain carbonyls, was also detected. A CuO_2CCF_3 derivative was not formed. The exchange reactions with the group 11 metals was successfully used in order to obtain heteronuclear clusters containing $M(PPh_3)$ (M = Cu, Ag, Au) fragments.[5o,p]

Complex **4** was previously isolated by us with higher yields by reaction of CF_3CO_2Ag with **1**.[3] On the analogy of that found by X-ray analysis in $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-dppm})(\mu\text{-}AgO_2CCH_3)]$, we suggested for **4** a structure in which the trifluoroacetate group is chelated to the silver atom.

We undertook the structural characterization of **4** also in the light of some literature reports indicating a different coordination mode of CF_3CO_2Ag in some metal clusters;

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Table I. Crystal and Refinement Data

	3	4
formula	$C_{36}H_{32}CuIOP_2Rh_2$	$C_{38}H_{32}AgF_3O_3P_2Rh_2$
fw	938.4	969.3
cryst system	orthorhombic	orthorhombic
space group	*Pnma*	*Pnma*
a, Å	14.002 (2)	15.133 (2)
b, Å	18.306 (2)	18.176 (3)
c, Å	13.025 (1)	12.656 (1)
V, Å^3	3338.5	3481.0
Z	4	4
d_{calcd}, g/cm^3	1.87	1.84
cryst size, mm	0.1 × 0.1 × 0.12	0.12 × 0.09 × 0.015
orientatn reflctn, no., range (2θ)	20, $15 < 2\theta < 28$	20, $16 < 2\theta < 26$
T, °C	21	23
abs coeff, cm^{-1}	23.5	16.2
radiation, Å	Mo Kα, $\lambda = 0.71069$	Mo Kα, $\lambda = 0.71069$
monochromator	graphite crystal	graphite crystal
scan type	$\omega-\theta$	$2\theta-\omega$
scan speed, s^{-1}	0.03	0.03
scan range, deg	1.2	1.2
reflctns measd	$+h,+k,+l$	$+h,+k,+l$
std reflctns	3 measd after every 140	3 measd after every 120
data limits	$3 < 2\theta < 50$	$3 < 2\theta < 52$
obsd data	1064 [$I \geq 3\sigma(I)$]	1993 [$I \geq 3\sigma(I)$]
no. of parameters refined	116	237
R	0.034	0.034
R_w	0.039	0.034
largest shift esd in final cycle	0.82	0.11
largest peak, e/Å^3	0.60	0.40

Table II. Final Fractional Atomic Coordinates (×10^4) for [$Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-dppm})(\mu\text{-CuI})$]

atom	x/a	y/b	z/c
Cu	1043 (2)	2500	6020 (1)
Rh(1)	1796 (1)	1750 (1)	4542 (1)
P(1)	338 (3)	1669 (1)	3857 (1)
I	568 (1)	2500	7846 (1)
O(1)	2436 (12)	2500	2681 (6)
C(6)	2125 (16)	2500	3508 (9)
C(7)	31 (20)	2500	3132 (7)
C(1)	2631 (15)	732 (5)	4318 (7)
C(2)	3276 (14)	1242 (7)	4628 (9)
C(3)	2992 (14)	1461 (7)	5634 (9)
C(4)	2206 (13)	1038 (6)	5926 (7)
C(5)	1954 (12)	599 (5)	5081 (8)
C(11)	236 (11)	957 (4)	2867 (5)
C(12)	945 (12)	935 (5)	2109 (6)
C(13)	935 (12)	389 (5)	1360 (7)
C(14)	213 (12)	−118 (5)	1371 (6)
C(15)	−448 (11)	−118 (5)	2121 (6)
C(16)	−452 (11)	430 (5)	2866 (6)
C(17)	−677 (13)	1499 (4)	4691 (6)
C(18)	−537 (12)	1264 (4)	5702 (6)
C(19)	−1356 (13)	1176 (5)	6337 (7)
C(20)	−2243 (14)	1323 (5)	6025 (7)
C(21)	−2389 (14)	1537 (5)	5037 (8)
C(22)	−1639 (13)	1612 (5)	4370 (8)

an example is the complex [$Ru_3(\mu\text{-}Ph_2PCH_2PPh_2)_2(CO)_8(\mu\text{-}AgO_2CCF_3)\cdot{}^1/_2CH_2Cl_2$].[11]

Compounds 2 and 3 reacts with PPh_3 giving 1 and [$Cu(PPh_3)X$] (X = Cl, I); the lack of reaction of 1 with [$Cu(PPh_3)X$] is in agreement with this result.

It is worthwhile mentioning that 1 reacts with [$Au(PPh_3)$]$^+$ giving the Rh_2Au cluster but it does not with [$Ag(PPh_3)$]$^+$ or [$Cu(PPh_3)$]$^+$. This is due to the differences in bonding modes of the group 11 metal $M(PPh_3)$ fragments, as pointed by Evans and Mingos.[12]

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

Bond Distances			
Rh(1)–Rh(1′)	2.746 (1)	C(6)–O(1)	1.161 (17)
Rh(1)–P(1)	3.655 (3)	Cu–Rh(1)	2.588 (2)
Rh(1)–C(6)	1.978 (10)	Cu–I	2.470 (2)
Rh(1)–C(1)	2.219 (14)	C(1)–C(2)	1.360 (22)
Rh(1)–C(2)	2.274 (19)	C(1)–C(5)	1.395 (21)
Rh(1)–C(3)	2.259 (17)	C(2)–C(3)	1.426 (18)
Rh(1)–C(4)	2.297 (11)	C(3)–C(4)	1.398 (23)
Rh(1)–C(5)	2.233 (9)	C(4)–C(5)	1.408 (15)
Rh(1)–C(av)	2.256 (14)	C–C(av)	1.397 (20)
Rh(1)–Cp*	1.918 (1)		
Bond Angles			
Rh(1)–Cu–Rh(1′)	64.06 (4)	P(1)–Rh(1)–Cu	87.70 (4)
Rh(1)–C(6)–Rh(1′)	87.9 (6)	C(6)–Rh(1)–P(1)	89.24 (4)
Rh(1)–C(6)–O(1)	135.95 (2)	P(1)–C(7)–P(1′)	111.4 (8)
C(6)–Rh(1)–Cu	103.48 (1)	Rh(1)–Cu–I	145.67 (1)

Table IV. Final Fractional Atomic Coordinates (×10^4) for [$Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-dppm})(\mu\text{-}AgO_2CCF_3)$]

atom	x/a	y/b	z/c
Ag	1012 (1)	2500	6137 (1)
Rh(1)	1727 (1)	1736 (1)	4500 (1)
P(1)	378 (1)	1666 (1)	3784 (1)
O(2)	816 (7)	1929 (5)	7938 (7)
C(8)	695 (9)	2500	8329 (10)
C(9)	375 (8)	2500	9461 (10)
F(1)	−436 (6)	2500	9574 (9)
F(2)	618 (7)	1960 (6)	9971 (6)
O(1)	2351 (5)	2500 (1)	2600 (6)
C(6)	2056 (7)	2500	3448 (7)
C(7)	94 (7)	2500	3044 (7)
C(1)	2487 (6)	694 (5)	4247 (7)
C(2)	3081 (5)	1215 (5)	4642 (8)
C(3)	2810 (6)	1421 (4)	5660 (7)
C(4)	2059 (6)	1014 (5)	5918 (7)
C(5)	1853 (5)	577 (4)	5051 (8)
C(11)	302 (5)	947 (3)	2776 (5)
C(12)	970 (5)	893 (4)	2038 (6)
C(13)	985 (6)	345 (4)	1291 (6)
C(14)	316 (6)	−159 (4)	1269 (6)
C(15)	−351 (6)	−117 (4)	1973 (7)
C(16)	−374 (5)	430 (4)	2731 (6)
C(17)	−577 (4)	1511 (3)	4635 (5)
C(18)	−464 (5)	1305 (4)	5681 (6)
C(19)	−1175 (6)	1211 (5)	6346 (6)
C(20)	−2015 (5)	1327 (5)	5984 (7)
C(21)	−2143 (5)	1518 (4)	4943 (7)
C(22)	−1430 (4)	1606 (4)	4269 (5)

Our results show that silver and copper salts of coordinating anions, such as AgO_2CCF_3, CuCl, and CuI, stabilize the Rh_2Ag and Rh_2Cu frameworks.

Description of the Structures of [$Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-dppm})(\mu\text{-CuI})$] (3) and [$Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-dppm})(\mu\text{-}AgO_2CCF_3)$] (4). Pertinent crystallographic data for 3 and 4 are listed in Table I. Tables II–V give the atomic positional parameters and selected bond distances. The molecular structures of 3 and 4, together with the atomic labeling, are shown in Figures 2 and 3, respectively. The overall geometries of complexes 3 and 4 are quite similar; the structure of compound 4 may be related to that of the previously described [$Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-dppm})(\mu\text{-}AgO_2CCH_3)$].[4]

Complexes 3 and 4 contain a triangular array of one group 11 atom, Cu or Ag, and two rhodium atoms bridged by the dppm and CO ligands. Each rhodium atom is bound to one η^5-cyclopentadienyl group; in 4 the trifluoroacetate group is chelated to the silver atom, while

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Table V. Bond Distances (Å) and Angles (deg) for $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)(\mu\text{-}AgO_2CCF_3)]$

Bond Distances			
Rh(1)-Rh(1′)	2.776 (1)	C(6)-O(1)	1.162 (12)
Rh(1)-P(1)	2.236 (1)	Ag-Rh(1)	2.719 (1)
Rh(1)-C(6)	1.986 (7)	Ag-O(2)	2.522 (9)
Rh(1)-C(1)	2.240 (9)	C(1)-C(2)	1.398 (13)
Rh(1)-C(2)	2.264 (8)	C(1)-C(5)	1.414 (13)
Rh(1)-C(3)	2.274 (9)	C(2)-C(3)	1.404 (13)
Rh(1)-C(4)	2.280 (9)	C(3)-C(4)	1.395 (12)
Rh(1)-C(5)	2.228 (8)	C(4)-C(5)	1.390 (13)
Rh(1)-C(av)	2.257 (9)	C-C(Av)	1.400 (13)
P(1)-C(7)	1.834 (5)	C(8)-O(2)	1.164 (11)
P(1)-C(11)	1.830 (6)	C(8)-C(9)	1.512 (18)
P(1)-C(17)	1.824 (6)	C(9)-F(1)	1.236 (15)
Rh(1)-Cp*	1.918 (9)	C(9)-F(2)	1.232 (13)

Bond Angles			
Rh(1)-Ag-Rh(1′)	61.4 (1)	P(1)-C(7)-P(1′)	110.4 (5)
Rh(1)-C(6)-Rh(1′)	88.7 (1)	O(2)-Ag-O(2′)	48.6 (6)
Rh(1)-C(6)-O(1)	135.6 (2)	O(2)-C(8)-O(2′)	126.0 (10)
C(6)-Rh(1)-Ag	104.7 (1)	O(2)-Ag-Rh(1)	121.7 (2)
P(1)-Rh(1)-Ag	88.5 (1)	O(2)-C(8)-C(9)	117.0 (4)
C(6)-Rh(1)-P(1)	89.7 (1)		

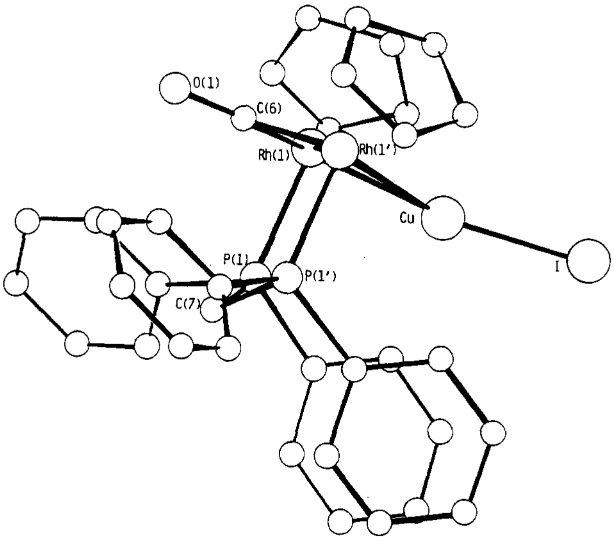

Figure 2. View of the molecule $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)(\mu\text{-}CuI)]$ (3).

in 3 the iodine atom is linked to copper. The six-membered ring Rh(1)P(1)C(7)P(1′)Rh(1′)C(6) assumes the boat conformation as in the precursor 1, the methylene carbon and the CO group being directed on the same side to minimize the repulsive contact between the phenyl groups. The molecules show a crystallographic mirror plane passing through the carbonyl group, the methylene carbon of the dppm ligand, and the copper or silver atom.

The rhodium-rhodium bond distances in 3 [2.746 (1) Å] and in 4 [2.776 (1) Å] are consistent with a single bond between these atoms. It should be noted that the Rh-Rh distance in 4 is longer than the values of 2.751 (1) and 2.750 (3) Å reported for $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)(\mu\text{-}AgO_2CCH_3)]$[4] and $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)(\mu\text{-}AgOPF_2O)]$,[2] respectively. The Rh-Ag bond length in 4 [2.719 (1) Å] is somewhat shorter than that found in the corresponding $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)(\mu\text{-}AgO_2CCH_3)]$ [2.730 (1) Å], but it is longer than the value 2.689 (2) Å observed in the difluorophosphate derivative.

A correlation between the Rh-Rh and Rh-Ag bond distances can be found for the complexes 4 and $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)(\mu\text{-}AgO_2CCH_3)]$ but not for the difluorophosphate derivative. Different from the acetate and trifluoroacetate groups, chelating the silver atoms in the corresponding Rh_2Ag derivatives, the difluorophosphate anion is monocoordinated in $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)(\mu\text{-}AgOPF_2O)]$. This suggests that the overall electronegativity of the group attached to the silver atom is not the only critical factor in determining the Rh-Rh distance but the coordination number around silver also has to be considered. The shortest Rh-Ag and the longest Rh-Rh bond distances observed in 4 with respect to $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)(\mu\text{-}AgO_2CCH_3)]$ are a consequence of the increased electrophilic character of the silver atom in the difluoroacetate derivative.

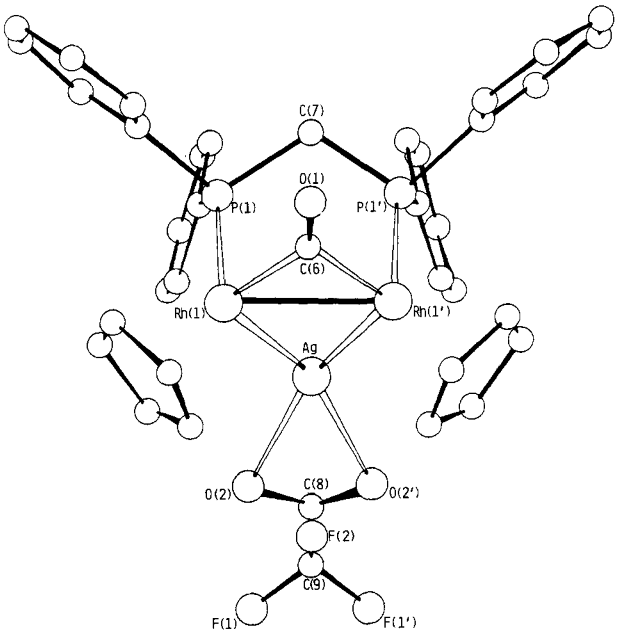

Figure 3. View of the molecule $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)(\mu\text{-}AgO_2CCF_3)]$ (4).

In this class of Rh_2Ag clusters the Rh-Ag distances are shorter than those found in the cation $[Rh_3Ag_3H(\text{tripod})_3]^{3+}$[13] [in the range 2.795 (4)-2.807 (4) and 2.884-2.933 (4) Å] and in the benzothiazole-2-thiolate derivative $[(C_8H_{12})_2Rh_2(\mu_3\text{-}C_7H_4NS_2)_2AgO_2ClO_2]$[14] [2.796 (3) Å].

The Rh-Rh [2.746 (1) Å] and Rh-Cu [2.588 (2) Å] bond lengths in 3 fit well into the trend observed in this class of triangular mixed-metal clusters (Table VI), being the shortest Rh-Rh and Rh-group 11 metal distances found.

The main differences in the Rh-Rh and Rh-X (X = H, Cu, Ag, Au, Hg) distances may be rationalized in terms of steric requirements of X; the longest Rh-Rh and Rh-X distances are reported for X = $HgCl_2$,[15] namely, for the electrophile which shows the greatest steric bulk. Moreover when this ligand is present, the conformation of the six-membered ring $Rh(1)P(1)C(CH_2)P(2)Rh(2)C(CO)$ changes from boat, as in 1, to chair.

The Rh-Cu distance of 2.588 (2) Å is slightly shorter than the value expected on the basis of the covalent radii of rhodium (1.39 Å) and copper (1.27 Å) in cluster compounds.[16] In the compound $[Cu_2Rh_6C(CO)_{15}(NCMe)_2]$, where a prism of rhodium atoms is capped on the triangular faces by two Cu(NCMe) linear fragments, the Rh-Cu mean distance is 2.660 (1) Å.[6] In this compound the copper atoms are formally four-coordinate, but the Rh-Cu-Rh

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Table VI. Selected Bond Distances (Å) and Angles (deg) in the Complexes $[Rh_2(\mu\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-dppm})(\mu\text{-}X)]$ and $[Rh_2(\mu\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-dppm})(\mu\text{-}X)]^+$

μ-X	Rh–X	Rh–Rh	Rh–P	Rh–C(CO)	Rh–X–Rh	Rh–C(CO)–Rh	P···P	P–C–P	Cp*–Cp*^{a}	ref
		2.683 (1)	2.205 (2)	1.970 (10)		85.6 (4)	2.983 (3)	107.8 (4)	82.1	1
			2.218 (2)							
μ-H^{b,d}	1.74	2.721 (2)	2.264 (4)	1.97 (2)		85.7 (9)	3.019 (6)	112.2 (8)	92.7	3
			2.241 (4)	2.03 (2)						
μ-CuI^{c,d}	2.588 (2)	2.746 (1)	2.233 (4)	1.978 (10)	64.06 (4)	87.9 (6)	3.042 (2)	111.4 (8)	91.8	*f*
μ-AgO$_2$PF$_2$^{c,d}	2.689 (2)	2.750 (3)	2.216 (3)	1.959 (13)	61.51 (5)	89.14 (6)	3.002 (6)	110.4 (2)	92.8	2
μ-AgO$_2$CCH$_3$^{c,d}	2.730 (1)	2.751 (1)	2.217 (2)	1.974 (9)	60.51 (2)	88.6 (5)	3.004 (6)	110.2 (5)	93.4	4
μ-AgO$_2$CCF$_3$^{c,d}	2.719 (1)	2.776 (1)	2.236 (1)	1.986 (7)	61.4 (1)	88.7 (1)	3.033 (2)	110.4 (5)	93.8	*f*
μ-AuPPh$_3$^{b,d}	2.718 (1)	2.760 (2)	2.247 (4)	1.966 (17)	60.9 (1)	89.0 (7)	3.116 (2)	115.1 (8)	94.4	3
	2.732 (1)		2.248 (4)	1.973 (16)						
μ-HgCl$_2$^{c,e}	2.692 (1)	2.853 (2)	2.260 (4)	2.00 (1)	63.3 (1)	91.0 (6)	3.028 (2)	110.3 (7)	101.3	15
	2.744 (1)		2.270 (4)							

^{a}Interplanar angle between the cyclopentadienyl rings. ^{b}Cationic complex. ^{c}Neutral complex. ^{d}Boat conformation of the Rh(1)–P(1)–C(CH$_2$)–P(2)–Rh(2)–C(CO) ring, as in the precursor 1. ^{e}Chair conformation of the ring. ^{f}Present work.

and Rh–Cu–N bond angles [62.6 (1)° and 143.1 (5)°, respectively] are similar to those found for the Rh–Cu–Rh and Rh–Cu–I angles [64.06 (1)° and 145.67 (1)°, respectively] in 3, where the Cu atom is three-coordinate. Thus the copper–rhodium interactions in 3 seem to have the same character as in $[Cu_2Rh_6C(CO)_{15}(NCMe)_2]$, even though the copper coordination in the two compounds is formally different. To our knowledge this is the only comparable study of a copper derivative bonded to rhodium atoms.

The Cu–I distance is 2.470 (2) Å, and the iodine atom is 0.0559 Å away from the plane Rh(1)Rh(1′)Cu; the Cu–I bond orientation is such that the iodine atom avoids the phenyl groups of the dppm ligand.

As for all the other compounds in this class, except the HgCl$_2$ derivative, the dppm ligand is oriented so that two of the phenyls are nearly parallel.

The Rh–C, Rh–P, and Rh–Cp* (Cp* = centroid of the cyclopentadienyl ring) and the Rh–C(CO)–Rh and P(1)–C–P(1′) angles fit well into the trend observed for the compounds of this series (Table VI). Owing to the negligible variations in the Rh–Rh bond distances (Table VI) the Rh–P distance and the P···P separation cannot be correlated to the Rh–Rh distance according to Schubert's method.[17] The geometry of the bridging carbonyl group (Rh–C(CO)–Rh = 87.9 (6)° and 88.7 (1)° in 3 and 4, respectively) is consistent with the existence of a metal–metal bond.[18] The cyclopentadienyl rings are in cis positions and located on the less hindered side of the molecule. With the exception of the μ-H derivative, in which the electronic effects are predominant, the interplanar angle between the cyclopentadienyl rings can be related to the dimension of the electrophile: in fact, the copper derivative shows the lowest angle (91.8°, Table VI).

In general, the addition of an electrophile containing the metal to 1 leads to an increase of the interplanar angle between the cyclopentadienyl rings, but it does not modify significantly the Cp*–Rh–Rh angle (134.6° and 135.5° in 3 and 4, respectively; 130.1° in 1).

Conclusions

The results show, unambiguously, that the synthesis of mixed triangular clusters Rh$_2$X (X = Cu, Ag, Au) can be carried out by electrophilic attack of a group 11 metal on an electron-rich rhodium–rhodium bond. The easy formation of the Rh$_2$X compounds indicates also that this route can be extended to synthesize M$_2$X triangular clusters involving other electron-rich transition metals.

It should be noted that while general synthetic routes were developed for the synthesis of mixed-metal clusters containing gold atoms, few systematic methods are available for the introduction of fragments containing the silver or copper atoms into a bi- or polynuclear framework.

It is worthwhile mentioning the role played by the anionic group coordinated to the silver or copper atoms in the stabilization of the Rh$_2$X (X = Cu, Ag) framework. The Rh$_2$X mixed-metal clusters only have been obtained by using CH_3CO_2Ag, CF_3CO_2Ag, $(C_2H_5)_2NCS_2Ag$, CuCl, or CuI as electrophiles, while no reaction has occurred with $[Ag(PPh_3)]PF_6$, $[Cu(PPh_3)]PF_6$, or $[Cu(NCMe)_4]PF_6$. This suggests that the anion determines the electrophilic character of the group 11 metal stabilizing the Rh$_2$X framework.

Experimental Section

Established methods were used to prepare the compounds $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-dppm})]$ (1),[1] $[Cu(NCMe)_4]PF_6$,[19] and $[Cu(PPh_3)Cl]$.[20] Other reagents were obtained from commercial sources. All reactions were carried out under nitrogen, but no special precautions to exclude air were taken during workup. General experimental conditions are similar to those described in other papers from this laboratory.

Preparation of $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-dppm})(\mu\text{-}CuCl)]$ (2). Solid CuCl (0.025 g, 0.25 mmol) was added to a solution of 1 (0.085 g, 0.113 mmol) in benzene (25 mL). The yellow-brown solution was allowed to stir at room temperature (30 min) during which time the solution turned dark green. After rapid filtration of the mixture to remove the excess CuCl, the resulting solution was reduced in volume to ca. 5 mL and 10 mL of diethyl ether was added to precipitate the product as a microcrystalline dark green solid: yield 0.082 g (0.097 mmol), 85.24%; IR (KBr, Nujol) ν(CO) 1733 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 5.28, 5.29 (C$_5$H$_5$), 3.19 (tt, PCH$_2$P, $^2J_{HP}$ = 1.1, $^3H_{HRh}$ = 9 Hz); ^{31}P{^{1}H} NMR (CDCl$_3$) δ 48.7 (AA′XX′ system, $^1J_{RhP}$ = 176.2, $^2J_{RhP}$ = 0.2, $^2J_{PP}$ = 81.6, $^1J_{RhRh}$ = 8.8 Hz). Anal. Calcd for $C_{36}H_{32}ClCuOP_2Rh_2$: C, 51.02, H, 3.80; Cl, 4.21. Found: C, 50.97; H, 3.70; Cl, 4.21.

Preparation of $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-dppm})(\mu\text{-}CuI)]$ (3). In a similar manner to the preparation of 2 above, compound 3 was synthesized in 92% yield by the reaction of a benzene solution of 1 (0.096 g, 0.128 mmol) with CuI (0.053 g, 0.28 mmol) and a reaction time of 150 min. The complex was isolated as dark green crystals upon crystallization from a dichloromethane–diethyl ether (1:2) solution: IR (KBr, Nujol) ν(CO) 1722 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 5.28 (C$_5$H$_5$), 3.19 (tt, PCH$_2$P, $^2J_{HP}$ = 1.1, $^3J_{HRh}$ = 9 Hz); ^{31}P{^{1}H} NMR (CDCl$_3$) δ 48.07 (AA′XX′ system, $^1J_{RhP}$ = 176.2, $^2J_{RhP}$ = 0.2, $^2J_{PP}$ = 81.6, $^1J_{RhRh}$ = 8.8 Hz). Anal. Calcd for $C_{36}H_{32}CuIOP_2Rh_2$: C, 46.09; H, 3.43; I, 13.51. Found: C, 46.13; H, 3.45; I, 13.47.

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Reaction of 3 with AgO_2CCF_3. A dichloromethane (20 mL) solution of $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)(\mu\text{-}CuI)]$ (**3**) (0.070 g, 0.074 mmol) was treated with a solution of AgO_2CCF_3 (0.017 g, 0.076 mmol) in the same solvent (10 mL). The mixture was allowed to stir for about 1 h, and the solvent was then removed under reduced pressure. The crude residue was extracted with benzene (20 mL). A dark green precipitate was obtained by adding diethyl ether (30 mL) to the benzene extract. From the mother liquor an unidentified solid was also isolated. The dark green precipitate was recrystallized from dichloromethane–hexane (1:3) to give $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)(\mu\text{-}AgO_2CCF_3)]$ (**4**), as confirmed by analytical and spectroscopic data;[4] yield 0.034 g (0.035 mmol), 48.5%. Anal. Calcd for $C_{38}H_{32}AgF_3O_3P_2Rh_2$: C, 47.09; H, 3.33; F, 5.88. Found: C, 47.12; H, 3.39; F, 5.82.

Attempted Reaction of 1 with $[Cu(NCMe)_4]PF_6$ or $[Cu(PPh_3)]PF_6$. Compound **1** failed to react with an excess of $[Cu(NCMe)_4]PF_6$ or $[Cu(PPh_3)Cl]$ in the presence of $TlPF_6$. The reactions were carried out by adding an excess of the copper complex (in the case of $[Cu(PPh_3)Cl]$, $TlPF_6$ was also added) to a benzene solution of **1** and stirring the reaction mixture. The starting materials were recovered unchanged after 24 h.

Reaction of 3 with PPh_3. The stoichiometric amount of PPh_3 was added to a dichloromethane solution of **3** (0.035 g, 0.037 mmol). The mixture was stirred for about 30 min at room temperature. The solvent was evaporated under reduced pressure and the residue extracted with diethyl ether (30 mL). From the resulting solution compound **1** was recovered while the solid residue was characterized as $[Cu(PPh_3)I]$, by comparison with an authentic sample. The reaction of **2** with PPh_3 proceeded in the same way.

X-ray Data Collection and Structure Refinement for 3 and 4. Data for **3** and **4** were collected on a Siemens-Stoe diffractometer using Mo Kα radiation with a graphite-crystal monochromator. Accurate unit-cell dimension and crystal orientation matrices together with their estimated standard deviations were obtained from least-squares refinement of 2θ, ω, χ, and ψ values of 20 carefully centered high-angle reflections. Three standard reflections were monitored periodically during the course of the data collection as a check of crystal stability and those varied by less than 3% for both compounds. Crystallographic data and other pertinent information are summarized in Table I. Lorentz and polarization corrections were applied to the intensity data; absorption correction was not applied. Both the structures were solved by interpretation of the Patterson maps which clearly indicated the position of the independent metal atoms. The Fourier difference synthesis phased with the heavy-atom position allowed the location of the non-hydrogen atoms in **3** and **4**. Full-matrix least-squares refinement of the models 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 were $w = 1.369/(\sigma^2(F_o) + 0.000\,72(F_o^2))$ for **3** and $w = 1.110/(\sigma^2(F_o) + 0.000\,96(F_o^2))$ for **4**, which showed reasonable consistency in a test of $\omega\Delta^2$ for data sectioned with respect to both F_o and $(\sin\theta)/\lambda$. Anisotropic temperture factors were introduced for all non-hydrogen atoms in compound **4** while in the compound **3** Rh, Cu, I, P, and O atoms were anisotropically refined. Hydrogen atom contributions were used as fixed atoms in calculated positions: $d(C\text{–}H) = 0.96$ Å. Both the models reached convergence with $R = [\sum|F_o| - |F_c|]/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/[\sum w|F_o|^2]^{1/2}$ having the values listed in Table I. The anomalous dispersion terms for Rh, Cu, Ag, P, and I atoms were taken into account in the refinement. Atomic scattering factors for all non-hydrogen atoms were taken from ref 21 and for hydrogen atoms from ref 22.

All the calculations were performed with the SHELX 76[23] set of programs on the IBM 4341 computer at the "Centro di Calcolo del'Universitâ di Messina".

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Registry No. **1**, 88979-33-3; **2**, 110682-60-5; **3**, 110682-61-6; **4**, 101835-32-9; **5**, 47107-74-4; Rh, 7440-16-6; Cu, 7440-50-8; Ag, 7440-22-4.

Supplementary Material Available: Tables of final fractional coordinates and anisotropic and isotropic thermal parameters for **3** and **4** (4 pages); listings of structure factor amplitudes (19 pages). Ordering information is given on any current masthead page.

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