Electrophilic Attack of H^+ and $[Au(PPh_3)]^+$ on an Electron-Rich Rhodium–Rhodium Bond. Synthesis and Structural Characterization of $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}H)(\mu\text{-}Ph_2PCH_2PPh_2)]^+$ and $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}AuPPh_3)(\mu\text{-}Ph_2PCH_2PPh_2)]^+$

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The synthesis of compounds $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}H)(\mu\text{-}dppm)]X$ (**2a**, X = BF_4; **2b**, X = PF_6) and $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}AuPPh_3)(\mu\text{-}dppm)]X$ (**3a**, X = BF_4; **3b**, X = PF_6) (dppm = $Ph_2PCH_2PPh_2$), via the addition of H^+ and $[AuPPh_3]^+$ to the electron-rich metal–metal bond of the complex $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)]$ (**1**), is described. Crystals of **2a** are orthorhombic of space group *Pbca* with a = 11.399 (1) Å, b = 17.991 (2) Å, c = 32.819 (4) Å, and Z = 8. The structure was solved and refined to R and R_w values of 0.061 and 0.064 for the 2046 reflections with $I \geq 3\sigma(I)$. The hydride ligand bridges the Rh–Rh bond [2.721 (2) Å] with Rh(1)–H and Rh(2)–H distances [1.62 (14) and 1.71 (14) Å, respectively] which do not differ significantly. The metals are also bridged by the dppm and CO ligands. Complex **3a** crystallizes in the space group $P2_12_12_1$ with a = 26.589 (3) Å, b = 16.080 (2) Å, c = 11.710 (1) Å, and Z = 4. The structure has been refined to R = 0.037 and R_w = 0.042 for the 3066 reflections with $I \geq 3\sigma(I)$. The basic trinuclear skeleton consists of an almost equilateral triangle formed by the two rhodium atoms and the gold atom [Rh(1)–Rh(2) = 2.760 (2) Å, Rh(1)–Au = 2.718 (1) Å, and Rh(2)–Au = 2.732 (1) Å] with the Rh–Rh bond bridged by the dppm and the carbonyl ligands. The structural features of the bridging dppm and CO groups in **2a** and **3a** remain essentially the same as in **1**; the two cyclopentadienyl ligands are in the cis position with an interplanar angle of 92.7° in **2a** and 93.9° in **3a**. The structural modification of **1** caused by the presence of the bridging hydride and $AuPPh_3$ groups is discussed. Spectroscopic IR and ^1H and ^{31}P NMR data for the new compounds are presented.

Introduction

Attention has been recently centered[1] on the isolobal relationship between the bridging hydride and the bridging $AuPR_3$ ligands. The synthesis and the structural characterization of hydride cluster complexes and the corresponding $AuPr_3$ derivatives gave some insight into this field and pointed out that the above isolobal relationship must be applied with care.[2-6]

Recently, we reported[7] the synthesis and the molecular structure of the complex $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)]$ (**1**) [dppm = bis(diphenylphosphino)methane]. This species contains an electron-rich rhodium–rhodium bond as pointed out by the reaction with $HgCl_2$[8] and electrophilic agents containing silver atoms.[9] Herein we report the synthesis of the cationic complexes $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)(\mu\text{-}H)]X$ (**2a**, X = BF_4; **2b**, X = PF_6) and $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)(\mu\text{-}AuPPh_3)]X$ (**3a**, X = BF_4; **3b**, X = PF_6) obtained by treating complex **1** with noncoordinating acids or $[AuPPh_3(solv)]X$. We also report the crystal structure of **2a** and **3a** in order to compare the structural modifications of **1** caused by the presence of bridging μ-H and μ-$AuPPh_3$ ligands.

Results

Synthesis and Spectroscopic Characterization of $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)(\mu\text{-}H)]X$ (2) and $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)(\mu\text{-}AuPPh_3)]X$ (3) (X = BF_4, PF_6). The addition of the protic acids HBF_4 and HPF_6 to a benzene solution of the complex $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)]$ (**1**) leads to protonation of the Rh–Rh bond with formation of the cationic μ-hydride complexes $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)(\mu\text{-}H)]X$ (**2a**, X = BF_4; **2b**, X = PF_6). These are brown crystalline solids which are stable for long periods also in solution. In these reactions complex **1** is simply protonated since the anion of the acid is not involved in coordination to the metal by oxidative addition.[10] The ν(CO) band at 1770 cm^{-1} is shifted by ca. 40 cm^{-1} to a higher frequency than in the precursor. The

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(10) Recently it was shown that $[Rh_2Cl_2(dppm)_2(\mu\text{-}CO)]$ reacts with the protic acids HA (A = Cl, BF_4, $SO_3C_6H_4CH_3$) by protonation of the Rh–Rh bond and coordination of the anion to one rhodium atom to give $[Rh_2Cl_2(\mu\text{-}H)(\mu\text{-}CO)(dppm)_2A]$. Sutherland, B. R.; Cowie, M. *Inorg. Chem.* **1984**, *23*, 1290.

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NMR spectra of **2a,b** show the cyclopentadienyl proton resonance at δ 5.42 (CD_2Cl_2) as a doublet of doublets (J_{P-H} = 0.7 and J_{H-Rh} = 0.5 Hz) and the μ-hydride resonance as multiplet centered at δ −12.76. This clearly supports a symmetrical structure for complexes **2a,b** with coupling of C_5H_5 and μ-H protons with the phosphorus and the rhodium atoms. The values of the coupling constants are in the range normally found for cyclopentadienyl(phosphine)rhodium(I) complexes.[7,11-13] The methylene hydrogen resonance of the dppm ligand appears the same as usually observed when this ligand is bridge bonded and no motion of the CP_2M_2 ring can render the two protons equivalent.[14] It consists of two superimposed multiplets centered at δ 2.47 and 2.34. The $^{31}P\{^1H\}$ NMR spectra are consistent with the proposed structure and display a symmetrical pattern, typical of an AA′XX spin system, centered at δ 52.13 (in CD_2Cl_2, relative to H_3PO_4; $^1J_{Rh-P}$ = 1.66, $^2J_{Rh-P}$ = 9.5, $^1J_{Rh-Rh}$ = 10, $^1J_{P-C-P}$ = 72 Hz).[15]

The reaction of $[AuPPh_3]X$ (X = BF_4, PF_6) with the rhodium complex **1** results in the simple addition of the $[AuPPh_3]^+$ ion to the binuclear framework with formation of the cationic complex $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-dppm})(\mu\text{-}AuPPh_3)]X$ (**3a**, X = BF_4; **3b**, X = PF_6). Compounds **3a,b** form green crystals, air stable as a solid and in solution. Spectroscopic data for these compounds support a Rh_2Au triangular cluster structure, with the $AuPPh_3$ group bridged to the rhodium–rhodium bond of **1**. The IR spectra show the ν(CO) band at 1750 cm^{-1}. The ^1H NMR spectra each exhibit a triplet at δ 5.35 (CD_2Cl_2)(J_{P-H} = J_{Rh-H} = 0.5 Hz) for the cyclopentadienyl protons and clearly support a symmetrical structure for the compounds.

The values of J_{Rh-H} are in the range expected for cyclopentadienylrhodium complexes,[7,11-13] while the J_{P-H} values, which are the same as those in **1**, are among the lowest reported for this class of compounds. Since the J_{P-H} value in the cyclopentadienyl(phosphine)rhodium complexes is dramatically affected by the formal oxidation state of the rhodium atom,[16] it can be assumed that the addition of $[AuPPh_3]^+$ occurs without any significative variation in the formal oxidation number of the two metal centers. The methylene protons of the dppm ligand resonate as a triplet of doublets centered at δ 2.89 (J_{P-H} = 10.5 and J_{H-Rh} = 1 Hz); this situation could be due to a rapid conformational change in the CP_2Rh_2 ring[14] rather than to a real equivalence of the PCH_2P protons. The $^{31}P\{^1H\}$ NMR spectra of complexes **3a,b** are like those of complexes **2a,b**. They exhibit for the phosphorus atoms of the dppm ligand a pattern typical of an AA′XX′ spin system centered at δ 51.56 (CD_2Cl_2, H_3PO_4; $^1J_{Rh-P}$ = 177, $^2J_{Rh-P}$ = 11, $^1J_{Rh-Rh}$ = 9.5, $^1J_{P-C-P}$ = 77 Hz). The phosphorus atom of the PPh_3 bound to the gold atom is observed as a triplet at δ 47.51 (J_{Rh-P} = 8 Hz); the lack of coupling between this phosphorus atom and those of the dppm ligand implies that these ligands are bound to different metals.

Table I. Crystal and Refinement Data

	2a	3a
formula	$C_{36}H_{33}BF_4OP_2Rh_2$	$C_{54}H_{47}AuBF_4OP_3Rh_2$
fw	836.22	1352.63
cryst system	orthorhombic	orthorhombic
space group	*Pbca*	$P2_12_12_1$
a, Å	11.399 (1)	26.589 (3)
b, Å	17.991 (2)	16.080 (2)
c, Å	32.819 (4)	11.710 (1)
V, $Å^3$	6730.5	5006.5
Z	8	4
d_{calcd}, g/cm^3	1.65	1.72
cryst size, mm	0.1 × 0.07 × 0.15	0.17 × 0.15 × 0.11
orientatn reflctns, no., range (2θ)	20, $18 < 2\theta < 30$	20, $22 < 2\theta < 32$
T, °C	20	22
abs coeff, cm^{-1}	11.08	36.1
radiation, Å	Mo Kα, λ = 0.710 69	Mo Kα, λ = 0.710 69
monochromator	graphite crystal	graphite crystal
scan type	$2\theta-\omega$	$2\theta-\omega$
scan speed, s^{-1}	0.03	0.03
scan range, deg	1.2	1.2
reflectns measd	$+h,+k,+l$	$+h,+k,+l$
std reflectns	3 measd after every 120	3 measd after every 120
data limits	$3 < 2\theta < 50$	$3 \leq 2\theta \leq 50$
obsd data	2046 [$I \geq 3\sigma(I)$]	3066 [$I \geq 3\sigma(I)$]
no. of parameters refined	226	304
R	0.061	0.037
R_w	0.064	0.042
largest shift/ESD in final cycle	0.22	0.18
largest peak, e/A^3	0.72	0.33

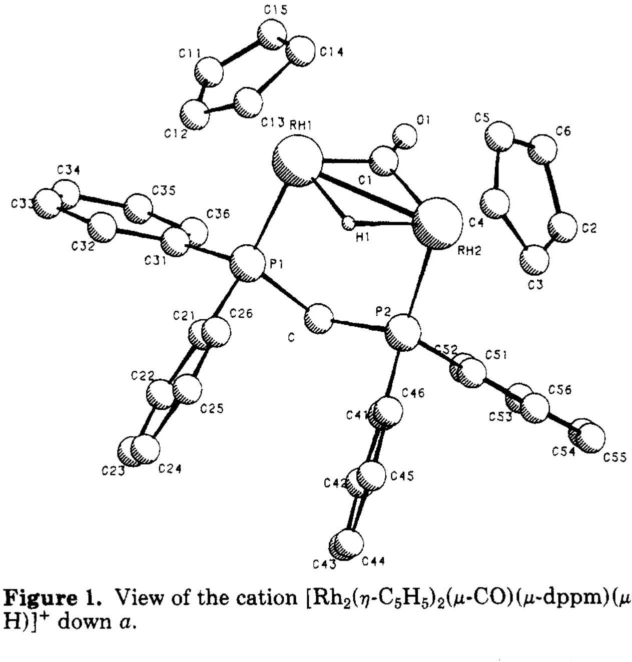

Figure 1. View of the cation $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-dppm})(\mu\text{-}H)]^+$ down *a*.

Crystal and Molecular Structure of 2a. The experimental details, including the crystal parameters, of the X-ray diffraction study of **2a** are reported in Table I. The crystal structure of **2a** consists of discrete molecules, drawn in Figure 1 along with the atom numbering scheme. Fractional atomic coordinates are listed in Table II; relevant bond distances and angles are listed in Table III. The cation consists of two rhodium atoms bridged by a carbonyl group and the hydride and dppm ligands; the terminal cyclopentadienyl ligand completes the coordi-

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Table II. Final Fractional Atomic Coordinates (×10⁴) for $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)(\mu\text{-}H)]BF_4$

atom	x/a	y/b	z/c
H	1697 (129)	2857 (77)	1635 (44)
Rh(1)	977 (1)	2352 (1)	1957 (1)
Rh(2)	1136 (1)	3741 (1)	1634 (1)
P(1)	88 (4)	1871 (2)	1409 (1)
P(2)	186 (4)	3419 (3)	1054 (1)
C	−691 (14)	2581 (9)	1124 (5)
C(1)	−115 (18)	3200 (10)	1960 (6)
O(1)	−1005 (13)	3404 (7)	2095 (4)
C(2)	1239 (14)	4979 (7)	1619 (7)
C(3)	2265 (14)	4701 (7)	1448 (7)
C(4)	2858 (14)	4305 (7)	1748 (7)
C(5)	2199 (14)	4339 (7)	2104 (7)
C(6)	1198 (14)	4755 (7)	2024 (7)
C(11)	720 (15)	1446 (10)	2414 (6)
C(12)	1728 (15)	1291 (10)	2192 (6)
C(13)	2535 (15)	1854 (10)	2266 (6)
C(14)	2026 (15)	2357 (10)	2535 (6)
C(15)	904 (15)	2105 (10)	2626 (6)
C(21)	1040 (9)	1442 (7)	1033 (4)
C(22)	561 (9)	1040 (7)	710 (4)
C(23)	1288 (9)	764 (7)	404 (4)
C(24)	2494 (9)	891 (7)	420 (4)
C(25)	2974 (9)	1294 (7)	742 (4)
C(26)	2247 (9)	1569 (7)	1049 (4)
C(31)	−998 (8)	1153 (6)	1521 (4)
C(32)	−606 (8)	430 (6)	1592 (4)
C(33)	−1397 (8)	−118 (6)	1714 (4)
C(34)	−2580 (8)	58 (6)	1766 (4)
C(35)	−2972 (8)	781 (6)	1695 (4)
C(36)	−2181 (8)	1328 (6)	1572 (4)
C(41)	1070 (9)	3228 (7)	615 (4)
C(42)	529 (9)	3016 (7)	252 (4)
C(43)	1206 (9)	2859 (7)	−91 (4)
C(44)	2426 (9)	2915 (7)	−71 (4)
C(45)	2967 (9)	3126 (7)	292 (4)
C(46)	2290 (9)	3283 (7)	635 (4)
C(51)	−829 (10)	4102 (6)	844 (3)
C(52)	−2045 (10)	4027 (6)	871 (3)
C(53)	−2774 (10)	4580 (6)	713 (3)
C(54)	−2287 (10)	5207 (6)	529 (3)
C(55)	−1071 (10)	5282 (6)	503 (3)
C(56)	−342 (10)	4729 (6)	660 (3)
B	5354 (13)	2773 (8)	1262 (5)
F(1)	6325 (13)	2985 (8)	1479 (5)
F(2)	4899 (13)	3377 (8)	1063 (5)
F(3)	5664 (13)	2241 (8)	984 (5)
F(4)	4530 (13)	2489 (8)	1523 (5)

Table III. Bond Distances (Å) and Angles (deg) for $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)(\mu\text{-}H)]BF_4$[a]

Bond Distances			
Rh(1)–Rh(2)	2.721 (2)	C(1)–O(1)	1.167 (25)
Rh(1)–H	1.62 (14)	Rh(2)–H	1.71 (14)
Rh(1)–C(1)	1.969 (19)	Rh(2)–C(1)	2.031 (20)
Rh(1)–P(1)	2.241 (4)	Rh(2)–P(2)	2.264 (4)
Rh(1)–C(11)	2.234 (19)	Rh(2)–C(2)	2.231 (13)
Rh(1)–C(12)	2.229 (18)	Rh(2)–C(3)	2.238 (15)
Rh(1)–C(13)	2.233 (18)	Rh(2)–C(4)	2.242 (16)
Rh(1)–C(14)	2.240 (19)	Rh(2)–C(5)	2.237 (19)
Rh(1)–C(15)	2.241 (20)	Rh(2)–C(6)	2.230 (17)
Rh(1)–C(av)	2.23 (2)	Rh(2)–C(av)	2.23 (2)
P(1)–C	1.814 (17)	P(2)–C	1.823 (17)
P(1)–C(21)	1.815 (13)	P(2)–C(41)	1.791 (13)
P(1)–C(31)	1.827 (11)	P(2)–C(51)	1.824 (12)
Rh(1)–Cp^*_A	1.90 (2)	Rh(2)–Cp^*_B	1.90 (2)
B–F(1)	1.370 (22)	B–F(3)	1.370 (22)
B–F(2)	1.370 (21)	B–F(4)	1.370 (22)
Bond Angles			
Rh(1)–C(1)–Rh(2)	85.7 (9)	P(1)–C–P(2)	112.2 (9)
Rh(1)–Rh(2)–C(1)	46.2 (5)	Rh(2)–Rh(1)–C(1)	48.1 (5)
P(1)–Rh(1)–Rh(2)	94.1 (1)	P(2)–Rh(2)–Rh(1)	93.5 (1)
P(1)–Rh(1)–C(1)	91.0 (6)	P(2)–Rh(2)–C(1)	89.1 (6)
Rh(1)–C(1)–O	143.0 (1)	Rh(2)–C(1)–O	131.0 (1)
C–P(1)–C(31)	105.7 (6)	C–P(2)–C(51)	104.9 (7)
C–P(1)–C(21)	104.0 (7)	C–P(2)–C(41)	104.5 (7)
Rh(1)–P(1)–C(31)	114.7 (4)	Rh(2)–P(2)–C(51)	116.7 (4)
Rh(1)–P(1)–C(21)	116.1 (4)	Rh(2)–P(2)–C(41)	117.1 (4)
C–P(1)–Rh(1)	111.3 (5)	C–P(2)–Rh(2)	111.6 (6)
C(31)–P(1)–C(21)	104.0 (5)	C(51)–P(2)–C(41)	100.5 (5)
Rh(1)–Rh(2)–Cp^*_B	133.6 (6)	Rh(2)–Rh(1)–Cp^*_A	138.7 (5)

[a] Cp* = centroids of the cyclopentadienyl rings.

nation sphere of each rhodium atom. The molecule approximates idealized C_s symmetry, with a mirror plane passing through the carbonyl group, the methylene carbon, and the hydride ligand; this is destroyed by the nonsymmetrical orientation of the cyclopentadienyl ligands and the phenyl groups.

The Rh–Rh bond distance of 2.721 (2) Å is lengthened only by 0.038 Å with respect to **1**, as a consequence of the protonation of the rhodium–rhodium bond. The bridging hydride ligand in this structure is well-behaved crystallographically, and the resulting Rh–H distances are essentially as expected and do not differ significantly each other. The Rh(1)–C(1) and Rh(2)–C(1) bond distances of 1.969 (19) and 2.031 (20) Å, respectively, and the Rh(1)–C(1)–Rh(2) angle of 85.7 (9)° are comparable with the values found for **1** and other related rhodium complexes.[17-19] Within the Rh–dppm framework the parameters are essentially as those observed in other similar dppm-bridged complexes. The two independent Rh–P distances [2.241 (4) and 2.264 (4) Å] are slightly different; however, no chemical significance is attached to this difference which is probably a consequence of packing effects. Both the Rh–P distances are significantly lengthened with respect to the precursor **1** [2.205 (2) and 2.218 (2) Å]. The strain of the dppm ligand is greater in **2a** than in **1** as evidenced by the value of 122.2 (9)° for the P(1)–C–P(2) angle [107.8(4)° in **1**]. The two cyclopentadienyl ligands are in the cis position with an interplanar angle of 92.7°; they are located on the less hindered side of the molecule. As expected,[19,20] the averaged values of Rh(1)–C(C_5H_5) distances are both 2.23 (2) Å; the corresponding Rh–Cp* (Cp* = centroids of the cyclopentadienyl rings) separations for both the rhodium atoms are 1.90 (2) Å.

Crystal and Molecular Structure of 3a. The crystal parameters of **3a**, are reported in Table I. A view of the structure of cation **3a**, including the numbering scheme, is presented in Figure 2. Fractional atomic coordinates and relevant bond distances and angles in the cation are listed in Tables IV and V, respectively.

The basic trinuclear skeleton of **3a** consists of an almost equilateral triangle of two rhodium atoms and a gold atom with the Rh–Rh bond bridged by the dppm and carbonyl ligands and with the PPh_3 ligand bonded to the gold atom. The Rh–Rh distance of 2.760 (2) Å falls within the range previously reported for similar Rh–Rh bonded species and is lengthened by ≃0.077 Å with respect to **1**. The two Au–Rh distances [2.718 (1) and 2.732 (1) Å] as well as the angles Rh(2)–Rh(1)–Au, Rh(1)–Rh(2)–Au, and Rh(2)–Au–Rh(1) [respectively 59.8 (1), 59.3 (1), and 60.9 (1)°] are not significantly different. The structural features of the bridging dppm and CO groups remain essentially the same

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Table IV. Final Fractional Atomic Coordinates (×10⁴) for $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-dppm})(\mu\text{-}AuPPh_3)]BF_4$

atom	x/a	y/b	z/c
Au	1254 (1)	2665 (1)	1767 (1)
Rh(1)	1133 (1)	2048 (1)	3910 (1)
Rh(2)	313 (1)	2623 (1)	2699 (1)
P(1)	1134 (2)	789 (2)	3077 (3)
C(11)	401 (6)	1902 (9)	4048 (15)
O(1)	130 (4)	1676 (7)	4763 (10)
C(1)	95 (8)	3760 (11)	3616 (11)
C(2)	376 (8)	4048 (9)	2600 (19)
C(3)	116 (7)	3798 (9)	1665 (16)
C(4)	-307 (7)	3360 (9)	2030 (18)
C(5)	-330 (7)	3399 (10)	3223 (20)
C(6)	1851 (9)	2075 (17)	4917 (25)
C(7)	1845 (11)	2806 (18)	4313 (16)
C(8)	1444 (14)	3223 (12)	4714 (25)
C(9)	1223 (9)	2734 (20)	5584 (23)
C(10)	1465 (10)	2035 (18)	5680 (19)
C(12)	517 (7)	567 (9)	2406 (15)
P(2)	225 (2)	1452 (2)	1668 (3)
P(3)	1672 (2)	3306 (2)	319 (3)
C(112)	1590 (4)	-44 (6)	1204 (9)
C(113)	1998 (4)	-231 (6)	501 (9)
C(114)	2456 (4)	177 (6)	658 (9)
C(115)	2506 (4)	771 (6)	1518 (9)
C(116)	2097 (4)	958 (6)	2221 (9)
C(111)	1640 (4)	550 (6)	2064 (9)
C(122)	1490 (4)	-766 (7)	3916 (8)
C(123)	1491 (4)	-1430 (7)	4682 (8)
C(124)	1161 (4)	-1431 (7)	5609 (8)
C(125)	831 (4)	-768 (7)	5769 (8)
C(126)	829 (4)	-104 (7)	5003 (8)
C(121)	1159 (4)	-103 (7)	4076 (8)
C(212)	583 (5)	695 (6)	-332 (10)
C(213)	646 (5)	650 (6)	-1513 (10)
C(214)	525 (5)	1333 (6)	-2195 (10)
C(215)	343 (5)	2061 (6)	-1697 (10)
C(216)	281 (5)	2106 (6)	-515 (10)
C(211)	400 (5)	1423 (6)	167 (10)
C(222)	-653 (5)	811 (8)	606 (8)
C(223)	-1159 (5)	584 (8)	595 (8)
C(224)	-1452 (5)	685 (8)	1574 (8)
C(225)	-1238 (5)	1012 (8)	2565 (8)
C(226)	-732 (5)	1239 (8)	2576 (8)
C(221)	-439 (5)	1138 (8)	1597 (8)
C(312)	1835 (4)	1839 (7)	-843 (10)
C(313)	2050 (4)	1350 (7)	-1698 (10)
C(314)	2405 (4)	1694 (7)	-2437 (10)
C(315)	2546 (4)	2526 (7)	-2320 (10)
C(316)	2330 (4)	3014 (7)	-1465 (10)
C(311)	1975 (4)	2670 (7)	-727 (10)
C(322)	1115 (5)	3764 (6)	-1643 (9)
C(323)	785 (5)	4278 (6)	-2244 (9)
C(324)	588 (5)	4987 (6)	-1724 (9)
C(325)	721 (5)	5183 (6)	-604 (9)
C(326)	1051 (5)	4669 (6)	-3 (9)
C(321)	1248 (5)	3960 (6)	-522 (9)
C(332)	2210 (5)	4819 (7)	451 (10)
C(333)	2593 (5)	5323 (7)	878 (10)
C(334)	2924 (5)	5013 (7)	1700 (10)
C(335)	2871 (5)	4200 (7)	2095 (10)
C(336)	2487 (5)	3696 (7)	1668 (10)
C(331)	2157 (5)	4005 (7)	846 (10)
B	3490 (4)	2263 (8)	4104 (8)
F(1)	3746 (10)	2915 (19)	3458 (38)
F(2)	3048 (7)	2061 (13)	3606 (21)
F(3)	3830 (12)	1585 (24)	4260 (41)
F(4)	3369 (20)	2692 (39)	5079 (35)

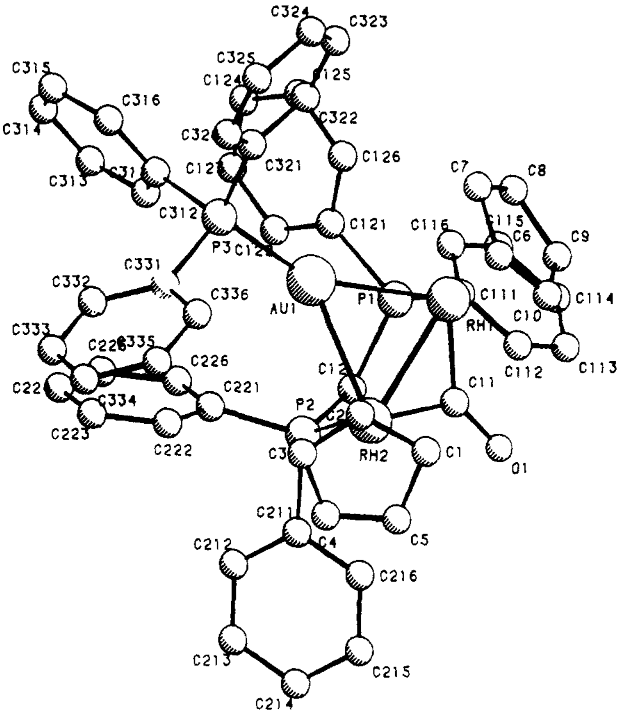

Figure 2. View of the cation $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-dppm})(\mu\text{-}AuPPh_3)]^+$ down b.

Table V. Bond Distances (Å) and Angles (deg) for $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-dppm})(\mu\text{-}AuPPh_3)]BF_4$[a]

	Bond Distances		
Rh(1)–Rh(2)	2.760 (2)	C(11)–O(1)	1.163 (18)
Rh(1)–Au	2.718 (1)	Rh(2)–Au	2.732 (1)
Rh(1)–C(11)	1.966 (17)	Rh(2)–C(11)	1.973 (16)
Rh(1)–P(1)	2.247 (4)	Rh(2)–P(2)	2.248 (4)
Rh(1)–C(6)	2.245 (17)	Rh(2)–C(1)	2.199 (16)
Rh(1)–C(7)	2.300 (20)	Rh(2)–C(2)	2.302 (15)
Rh(1)–C(8)	2.267 (18)	Rh(2)–C(3)	2.305 (16)
Rh(1)–C(9)	2.262 (21)	Rh(2)–C(4)	2.176 (16)
Rh(1)–C(10)	2.254 (22)	Rh(2)–C(5)	2.204 (17)
Rh(1)–C(av)	2.265 (20)	Rh(2)–C(av)	2.237 (16)
P(1)–C(12)	1.854 (19)	P(2)–C(12)	1.838 (17)
P(1)–C(111)	1.833 (11)	P(2)–C(211)	1.819 (12)
P(1)–C(121)	1.852 (11)	P(2)–C(221)	1.838 (13)
Rh(1)–Cp*$_A$	1.949	Rh(2)–Cp*$_B$	1.897
Au–P(3)	2.273 (4)	P(3)–C(321)	1.829 (12)
P(3)–C(311)	1.787 (12)	P(3)–C(331)	1.820 (13)
	Bond Angles		
Rh(1)–C(11)–Rh(2)	89.0 (7)	Au–P(3)–C(331)	111.9 (4)
Rh(1)–Au–Rh(2)	60.9 (1)	Au–P(3)–C(321)	111.2 (4)
P(1)–C(12)–P(2)	115.1 (2)	Au–P(3)–C(311)	118.2 (4)
Rh(1)–Au–P(3)	155.8 (1)	Rh(2)–Au–P(3)	139.2 (1)
Rh(1)–Rh(2)–C(11)	45.4 (5)	Rh(2)–Rh(1)–C(11)	45.6 (5)
Rh(1)–Rh(2)–Au	59.3 (1)	Rh(2)–Rh(1)–Au	59.8 (1)
P(1)–Rh(1)–Au	85.9 (1)	P(2)–Rh(2)–Au	84.4 (1)
P(1)–Rh(1)–Rh(2)	94.6 (1)	P(2)–Rh(2)–Rh(1)	94.5 (1)
P(1)–Rh(1)–C(11)	86.0 (5)	P(2)–Rh(2)–C(11)	87.2 (5)
Rh(1)–C(11)–O(1)	135.2 (14)	Rh(2)–C(11)–O(1)	133.3 (13)
C(12)–P(1)–C(111)	109.5 (6)	C(12)–P(2)–C(211)	109.0 (6)
C(12)–P(1)–C(121)	98.6 (6)	C(12)–P(2)–C(221)	102.4 (7)
Rh(1)–P(1)–C(111)	118.1 (3)	Rh(2)–P(2)–C(211)	120.9 (4)
Rh(1)–P(1)–C(121)	115.0 (4)	Rh(2)–P(2)–C(221)	110.7 (4)
C(12)–P(1)–Rh(1)	110.9 (5)	C(12)–P(2)–Rh(2)	110.6 (5)
C(111)–P(1)–C(121)	102.7 (5)	C(211)–P(2)–C(221)	101.3 (5)
Rh(1)–Rh(2)–Cp*$_B$	132.7	Rh(2)–Rh(1)–Cp*$_A$	132.1

[a] Cp* = centroids of the cyclopentadienyl rings.

as those in **1** and **2a**. The only significant differences are the increase in the angle subtended at the bridging carbon atom [Rh(1)–C(11)–Rh(2) = 89.0 (7)° and 85.6 (4)° in **1**], shorter Rh–C distances [Rh(1)–C(11) = 1.966 (17) Å and Rh(2)–C(11) = 1.973 (16) Å 1.978 (9) and 1.971 (9) Å, respectively, in **1**], and an increase in the P(1)–C(12)–P(2) angle [115.1 (2)° and 107.8 (4)° in **1**]. It is worthwhile to mention that the value of 115.1 (8)° for the P–C–P angle is among the highest up until now reported for binuclear rhodium complexes with a Rh–Rh bond and dppm as a bridging ligand. In fact this angle ranges from 108 to 112° when a Rh–Rh bond is present while it increases up to 116° (for instance 116.8° in *trans*-$[Rh_2Cl_2(CO)_2(dppm)_2]$[21]) when the metal–metal bond is not present.

The mode of bonding of the $AuPPh_3$ group to the Rh–Rh bond can be considered as a three-center-delocalized bond involving the two rhodium atoms and the Au atom. The P(3) atom lies 0.454 Å out of the Rh(1)Rh(2)Au plane; the Rh(1)–Au–P(3) and Rh(2)–Au–P(3) angles are significantly different [155.8 (1) and 139.2 (1)°, respectively]. Since chemically there is no a priori reason to expect a difference in these angles and a separation of the P(3) atom from the metal skeleton plane, the observed values more likely are a consequence of steric and packing effects. The bond parameters within the $AuPPh_3$ ligand are similar to those found in similar complexes.[4,5,22]

The two cyclopentadienyl ligands are in the cis position with an interplanar angle of 93.9°; the averaged values for Rh(1)–C(C_5H_5) and Rh(2)–C(C_5H_5) are 2.265 (20) and 2.237 (16) Å, respectively. These values are in agreement with the literature reports.[20] The corresponding Rh–Cp* (Cp* = centroids of the cyclopentadienyl rings) separations for Rh(1) and Rh(2) are repsectively 1.949 and 1.897 Å.

Discussion

The main goal of the crystallographic study of complexes **2a** and **3a** was to evaluate the structural modifications of 1 caused by the presence of the bridging hydride and $AuPPh_3$ groups as well as to compare complexes **2a** and **3a** with the analogous compounds [$Rh_2(\eta$-$C_5H_5)_2(\mu$-CO)(μ-dppm)(μ-$HgCl_2$)][8] and [$Rh_2(\eta$-$C_5H_5)_2(\mu$-CO)(μ-dppm)(μ-$AgOPF_2O$)].[9]

The rhodium–rhodium distances are lengthened with respect to 1 as a consequence of the interaction of the electrophilic agent with the Rh–Rh bond. In the protonation product **2a** this distance is significantly shorter than those in corresponding compounds containing $AuPPh_3$, $AgOPF_2O$, or $HgCl_2$. A concern of the cationic compounds **2a** and **3a** is evident in that the steric bulk of the gold–phosphine ligand influences considerably the length of the rhodium–rhodium bond.

Along the series of the complexes studied it is not possible to find any correlation among the Rh–Rh and Rh–P bond distances and the P···P separation. The lengthening of the Rh–P distances with respect to the precursor 1 could be mainly a consequence of a reduced interaction between the rhodium and phosphorus atoms. The Rh–P distances are significantly shorter than those in the A-frame complexes of rhodium[17,21,23] because in the latter compounds the phosphorus atoms are almost mutually trans. In all the above complexes the Rh–Rh distance is significantly shorter than the P···P intraligand separation [3.019 (6) Å for **2a** and 3.116 (4) Å for **3a**] as usually observed for analogous systems where a metal–metal bond is present.[17,23] The rhodium and phosphorus atoms are not strictly planar; the Rh–P vectors on each metal are almost eclipsed when viewed down the Rh–Rh axis, as it is shown by the values of the P(1)–Rh(1)–Rh(2)–P(2) torsion angles which are respectively 2.2 (2) and 1.78 (1)° for **2a** and **3a**; the complexes **1**, [$Rh_2(\eta$-$C_5H_5)_2$(μ-CO)(μ-dppm)(μ-$HgCl_2$)], and [Rh_2 (η-$C_5H_5)_2(\mu$-CO)(μ-dppm)(μ-$AgOPF_2O$)] exhibit similar values. A slight twisting about the metal–metal axis has been observed also in other complexes containing the bridging dppm ligand.[23,24] Although the Rh–P–P–Rh plane is not exactly planar, the distance of the methylene carbon atom from this best least-squares plane (0.833 Å in 1 and 0.663 and 0.610 Å, respectively, in **2a** and **3a**) is a useful indication of the fold about the intraligand P–P axis.

In the complexes containing the bridging dppm ligand, the methylene group is bent toward the larger ligand or the more sterically hindered position so as to minimize repulsive contacts between the more bulky phenyl groups. This occurs in complexes **1**, **2a**, **3a**, and [$Rh_2(\eta$-$C_5H_5)_2(\mu$-CO)(μ-dppm)(μ-$AgOPF_2O$)], folding the P(1)–C–P(2) and Rh(1)–CO–Rh(2) fragments on the same side, and, because of the steric bulk of the $HgCl_2$ ligand, in the complex [$Rh_2(\eta$-$C_5H_5)_2(\mu$-CO)(μ-dppm)(μ-$HgCl_2$)], folding the methylene fragment toward the open site, namely, away from the bridging carbonyl ligand.[25]

In conclusion, a close structural analogy between the bridging hydride and the bridging gold–phosphine ligands has been found in complexes **2a** and **3a**. The main structural differences may be rationalized in terms of greater steric bulk of the gold–phosphine group compared with that of the hydride ligand. The comparison among the structures of complexes **2a**, **3a** [$Rh_2(\eta$-$C_5H_5)_2(\mu$-CO)(μ-dppm)(μ-$AgOPF_2O$)], and [$Rh_2(\eta$-$C_5H_5)_2(\mu$-CO)(μ-dppm)(μ-$HgCl_2$)] points out the role played by the steric requirements of the electrophile in determining structural differences; the $HgCl_2$ ligand, which shows the greatest steric bulk, leads to the greatest alterations in the structure of 1 . Thus only in the $HgCl_2$ adduct does the six-membered Rh(1)–C–Rh(2)–P(2)–C–P(1) ring change its conformation from boat to chair.

The reactivity of 1 is, for some aspects, comparable with that of the "A-frame"[26] compounds, although these are structurally different.

Experimental Section

The compounds [$Rh_2(\eta$-$C_5H_5)_2(\mu$-CO)(μ-dppm)] (1) and [$AuPPh_3Cl$] were obtained as reported.[7,27] Other reagents were obtained from commercial sources. Solvents used were dried by standard procedures. 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. Conductivity measurements were made with a Radiometer CDM 3 conductivity meter.

Preparation of [$Rh_2(\eta$-$C_5H_5)_2(\mu$-CO)(μ-H)(μ-$Ph_2PCH_2PPh_2$)]BF_4 (2a). A solution of tetrafluoroboric acid–diethyl ether was added, drop by drop, to a stirred solution (15 mL) of 1 (0.075 g, 0.1 mmol) until the solution became colorless. During this time (a few seconds) a brown powder was formed. Stirring was continued for 5 min to ensure complete reaction, and the precipitate was allowed to settle. The mother liquor was removed by syringe and the solid product washed with benzene and dried. The crude product was subsequently recrystallized from dichloromethane–hexane (1:3) to give **2a** as a brown microcrystalline solid (0.071 g, 0.085 mmol) in an 85% yield. Anal. Calcd for $C_{36}H_{33}BF_4OP_2Rh_2$: C, 51.71; H, 3.97; F, 9.08. Found: C, 51.67; H, 3.94; F, 9.04.

[$Rh_2(\eta$-$C_5H_5)_2(\mu$-CO)(μ-H)(μ-$Ph_2PCH_2PPh_2$)]PF_6 (2b) was prepared in a similar way and obtained as a brown powder, with

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an 80% yield. It can be also obtained by adding a methanol solution of NH_4PF_6 to **2a** in the same solvent. The solid obtained was subsequently recrystallized from dichloromethane–hexane. Anal. Calcd for $C_{36}H_{33}F_6OP_3Rh_2$: C, 48.34; H, 3.71; F, 12.74. Found: C, 48.30; H, 3.69; F, 12.70.

Preparation of $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}AuPPh_3)(\mu\text{-}Ph_2PCH_2PPh_2)]BF_4$ (3a). Solid $AgBF_4$ (0.026 g, 0.134 mmol) was added to a stirred solution of $AuPPh_3Cl$ (0.066 g, 0.134 mmol) in benzene (20 mL). Stirring was continued for ca. 10 min to ensure complete reaction, and the silver chloride precipitate was filtered off. The filtrate was added to a stirred solution of 1 (0.100 g, 0.134 mmol) in benzene (15 mL). Within a few seconds a green precipitate was formed. Stirring was continued for 5 min to ensure complete reaction, and the mother liquor was pumped to small volume and successively removed by syringe. The solid product was washed with diethyl ether and dried in vacuo. It was subsequently recrystallized from dichloromethane–hexane (1:3) to give **3a** as green crystals (0.165 g, 0.127 mmol) in a 95% yield. Anal. Calcd for $C_{54}H_{47}AuBF_4OP_3Rh_2$: C, 50.10; H, 3.66; F, 5.87. Found: C, 50.14; H, 3.68; F, 5.85.

$[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}AuPPh_3)(\mu\text{-}Ph_2PCH_2PPh_2)]PF_6$ (3b) was prepared in a similar way, using $AgPF_6$, and obtained as green crystals, with a 90% yield. Anal. Calcd for $C_{54}H_{47}AuF_6OP_4Rh_2$: C, 47.95; H, 3.5; F, 8.42. Found: C, 47.93; H, 3.4; F, 8.40.

X-ray Data Collection and Structure Refinement for 2a and 3a. Data for **2a** and **3a** were collected on a Siemens-Stoe diffractometer using Mo Kα radiation with graphite-crystal monochromator. Accurate unit-cell dimension and crystal orientation matrices together with their esd's 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 informations are summarized in Table I. Lorentz and polarization corrections were applied to the intensity data; an absorption correction was applied only for the compound **3a** using an empirical method based on ψ scans (ψ = 0–350° every 10°) for χ values near 90°. Five sets of ψ scan curves were used with maximum, minimum, and average relative transmission values of 1.00, 0.80, and 0.90, respectively; the absorption correction for **2a** was not applied because of the small linear absorption coefficient. 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 positions allowed the location of the nonhydrogen atoms in **2a** and **3a**. 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 schemes used in the last refinement cycles were $w = 2.376/(\sigma^2 F_o + 0.000977 F_o^2)$ for **2a** and $w = 0.717/(\sigma^2 F_o + 0.007 F_o^2)$ for **3a**, 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 non-hydrogen atoms except for those belonging to the phenyl rings in **3a** and the phenyl and cyclopentadienyl rings in **2a**. These were refined as rigid groups and restricted to their normal geometry by using the group refinement procedure. Each ring carbon atom was assigned an isotropic thermal parameter. Hydrogen atom contributions were used as fixed atoms in calculated positions: d(C–H) = 0.96 Å. The hydride ligand in **2a** was located and was refined isotropically. 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[28] for the Rh, Au, and P atoms were taken into account in the refinement. Atomic scattering factors for all non-hydrogen atoms were taken from ref 29 and for hydrogen atoms from ref 30. Reversing the sign of the imaginary anomalous-scattering component for **3a**, which has the non-centrosymmetric space $P2_12_12_1$, increased R from 0.037 to 0.076. The difference is highly significant, and therefore the model has the correct absolute configuration.

All the calculations were performed with SHELX 76[31] set of programs on the IBM 4341 compouter at the "Centro di Calcolo dell Università di Messina".

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Registry No. 1, 88979-33-3; **2a**, 98330-45-1; **2b**, 98330-46-2; **3a**, 98330-48-4; **3b**, 98330-49-5; $AuPPh_3Cl$, 14243-64-2; $[AuPPh_3]BF_4$, 67215-70-7; $[AuPPh_3]PF_6$, 83214-85-1; Rh, 7440-16-6.

Supplementary Material Available: Listings of thermal parameters, selected least-squares planes, final fractional atomic coordinates for hydrogen atoms, and structure factors for compounds **2a** and **3a** (57 pages). Ordering information is given on any current masthead page.

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