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X-ray structural analyses of copper(I) and silver(I) adducts of the Rh(III) trihydride [(triphos)RhH_3], with triphos = $CH_3C(CH_2PPh_2)_3$

F. Bachechi*

Istituto di Strutturistica Chimica 'G. Giacomello', C.N.R., Area della Ricerca di Roma, C.P. 10, 0000016 Monterotondo St. (Rome) (Italy)

C. Bianchini and A. Meli

Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione, C.N.R., via J. Nardi 39, 50132 Florence (Italy)

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Abstract

The two polyhydride complexes [(triphos)HRh(μ-H)$_2$Cu(μ-H)$_2$RhH(triphos)]$^+$ (**1**) and [(triphos)HRh(μ-H)$_2$Ag(μ-H)$_2$RhH(triphos)]$^+$ (**2**), where triphos is the tripod-like ligand $CH_3C(CH_2PPh_2)_3$, have been synthesized and characterized by X-ray analysis. They are isomorphous and crystallize in the tetragonal space group *P4/n* with $Z=4$ ($a=20.508(8)$, $c=21.021(8)$ Å and $V=8840.3$ Å^3 for **1** and $a=20.670(7)$, $c=20.501(9)$ Å and $V=8759.7$ Å^3 for **2**). Their structures consist of nearly linear clusters with the arrays, Rh–Cu–Rh in **1** and Rh–Ag–Rh in **2**, lying at angles of 170 and 168°, respectively. The hydride ligands were not located by the X-ray analyses. Taking into account IR data and the arrangement of the heavy atoms the most likely positions for the bridging and terminal hydrides were obtained by methods of potential energy.

Introduction

The synthesis and characterization of mixed-metal polyhydrido complexes is of both fundamental and practical interest. From the fundamental perspectives, heteropolynuclear polyhydrides, particularly those containing both terminal and bridging hydride ligands, are amenable compounds to study for their unusual structural, magnetic, electrochemical and spectroscopic properties [1]. Practical motivations arise from the fact that several polynuclear polyhydrides are involved in catalytic transformations, which often provide results different from those observed for comparable mononuclear moieties [1a, 2]. Indeed, the close proximity of two or more metals connected by hydride ligands may cause phenomena of synergism, particularly in cases of concerted reactions progressing successively upon each of the metal centers.

A common strategy for the synthesis of mixed-metal polyhydrido complexes involves the reaction of stable mononuclear transition metal polyhydrides with Lewis acid fragments. Through this strategy, a number of polynuclear polyhydrido complexes have been prepared in the last five years by Venanzi and co-workers [3], Caulton and co-workers [1k, 2g, 4], Bianchini *et al.* [1h–j] and Chaudret and co-workers [1o].

In the course of studies carried out in collaboration with Venanzi's group in Zurich, several Lewis acid adducts of the mononuclear rhodium and iridium trihydrides [(triphos)RhH_3] [5] and [(triphos)IrH_3] [6] have been isolated, including the hexahydrides [(triphos)HRh(μ-H)$_2$Cu(μ-H)$_2$RhH(triphos)] [SO_3CF_3] (**1**) [7a] and [(triphos)HRh(μ-H)$_2$Ag(μ-H)$_2$RhH(triphos)] [SO_3CF_3] (**2**) [7], where triphos is the tripod-like ligand $CH_3C(CH_2PPh_2)_3$. Both compounds are highy fluxional in solution on the NMR time scale, the slow exchange limit being unaccessible in the temperature window of most organic solvents (single resonances are observed for either the six hydrogens or phosphorus) [7]. However, the presence of two types of hydride ligands in **1** and **2** is strongly suggested by the IR spectra of solid samples which contain ν(M–H) bands in both the terminal and the bridging hydride region [7]. In order to clarify the structures of **1** and **2** X-ray analyses have been undertaken and the results are herein reported. Unfortunately, neither the terminal nor the briging hydrides were located. Nevertheless, valuable information on their position has been obtained by the energy minimization program HYDEX [8].

An understanding of the structural properties of **1** is not of merely academic interest as the mononuclear trihydride [(triphos)RhH_3] exhibits good catalytic ac-

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*Author to whom correspondence should be addressed.

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tivity in homogeneous hydroformylation, isomerization and hydrogenation reactions of unsaturated substrates [9].

Experimental

Synthesis and characterization of the complexes

Complex 1

To a suspension of $CuCF_3SO_3 \cdot (C_6H_6)_{0.5}$ (18 mg, 0.07 mmol) in 5 ml of CH_2CL_2 under nitrogen were added with stirring two equivalents of [(triphos)RhH_3] (105 mg). The resulting mixture was stirred at room temperature for 1 h to give a pale yellow solution. After addition of ethanol (5 ml) and evaporation to half volume under reduced pressure, 2 ml of diethyl ether were added. Off-white crystals of **1** were obtained in 72% yield on long standing at −20 °C, which were filtered-off under nitrogen, washed with diethyl ether and n-pentane, and dried under vacuum.

Anal. Calc. for $C_{83}H_{84}O_3F_3P_6SRh_2Cu$: C, 59.56; H, 5.06. Found: C, 58.90; H, 5.11%.

$^{31}P\{^1H\}$ NMR (101.21 MHz, CD_2Cl_2, 20 °C): A_3X spin system, δP_A 25.52 ppm, $^1J(P_ARh) = 98.2$ Hz. The spectrum is temperature independent down to −80 °C.

^1H NMR (250.13 MHz, CD_2Cl_2, 20 °C): second-order multiplet in the hydride region at −7.7 ppm (6H), $^1J(HRh) = 17.6$ Hz, $|^2J(HP) + 2^2J(H'P)| = 122.$Hz. The spectrum is temperature independent down to −80 °C.

IR (Rbl): 1907 cm^{-1} $\nu(Rh\text{–}H_{terminal})$; 1757 cm^{-1}, br, $\nu(Rh\text{–}\mu\text{-}H\text{–}Cu)$.

The crystals of **1** used for the X-ray structure determination were recrystallized with an $MeOH\text{–}CH_2Cl_2$ mixture through the slow diffusion technique.

Complex 2

To a cold (−78 °C), suspension of $AgCF_3SO_3$ (64 mg, 0.25 mmol) in 20 ml of tetrahydrofuran degassed with N_2 were added two equivalents of [(triphos)RhH_3] (365 mg, 0.5 mmol). This reaction mixture was allowed to reach room temperature. As a result a pale yellow solution was obtained, which was stirred for 30 min. Ethanol (20 ml) was then added and the resulting mixture maintained at −10 °C for 12 h. Almost colorless crystals of **2** were collected in 69% yield.

Anal. Calc. for $C_{83}H_{84}O_3F_3P_6SRh_2Ag$: C, 58.02; H, 4.93. Found: C, 57.87; H, 4.90%.

$^{31}P\{^1H\}$ NMR (101.21 MHz, CD_2Cl_2, 20 °C): A_3XY spin system, δP_A 25.5 ppm, $^1J(P_ARh) = 100$ Hz, $^1J(P_AAg) = 15$ Hz. The spectrum is temperature independent down to −80 °C.

^1H NMR (250.13 MHz, CD_2Cl_2, 20 °C): multiplet in the hydride region at −7.60 ppm (6H), $^1J(HRh) = 13$ Hz, $|^2J(HP) + 2^2J(H'P)| = 119$ Hz, $^1J(HAg) = 58$ Hz. The spectrum is temperature independent down to −80 °C.

IR (Rbl): 1900 cm^{-1} $\nu(R\text{–}H_{terminal})$; 1750 cm^{-1}, br, $\nu(Rh\text{–}\mu\text{-}H\text{–}Ag)$.

The crystals of **2** used for the X-ray structure determination were recrystallized with an $MeOH\text{–}CH_2Cl_2$ mixture through the slow diffusion technique.

X-ray structure determination

X-ray analyses were carried out on crystals of **1** and **2** sealed in glass capillaries with their mother liquid ($MeOH/CH_2Cl_2$). Systematic absences ($h\,k\,0, h+k=2n$) uniquely defined the space group P4/*n* (No. 85) for the two compounds, which were shown to be isomorphous. Unit-cell dimensions were determined by a least-squares refinement of the setting angles of 15 high angle reflections ($20 \geqslant 2\theta \geqslant 26°$) carefully centered. The intensities were collected on a Nicolet R3 computer controlled diffractometer using graphite-monochromated Mo Kα radiation in ω-scan mode at variable scan rate. Three standards were measured every 100 reflections. The intensities of the standard reflections were found to decrease gradually during the course of the data collection, reaching at the end of the run the maximum decay of 12% for **1** and 6% for **2**. Linear correction factors to account for the loss of intensities were therefore applied to the reflections. All the reflections were processed to yield values of I and $\sigma(I)$ [10]; in the estimation of $\sigma(I)$ the uncertainty factor p (0.0035 for **1** and 0.058 for **2**) was calculated from the variance of the standard reflections [11]. Corrections for Lorentz and polarization effects were applied. An empirical absorption correction [12] was applied using scan data of reflections at high χ angles (86.6 ° for **1** and 92.3° for **2**). The minimum normalized transmission factors were in the range 0.50–0.55 for **1** and 0.70–0.75 for **2**. Only the independent reflections which met the conditions $I \geqslant 3\sigma(I)$ were used in the subsequent calculations. Table 1 summarizes the crystallographic data. The structures were solved by the heavy atom method and the atoms of the cationic complexes could be located by Fourier maps. In both structures the central atom of the complex cation (Cu in **1** and Ag in **2**) lies in a special position so that only half molecule is contained in the asymmetric unit. The asymmetric unit should also contain half molecule of the $[CF_3SO_3]^-$ anion lying in one of the four possible special positions of the space group, which possess a two-fold axis and an inversion center. The $[CF_3SO_3]^-$ anion does not contain any symmetry element compatible with the space group, but in appropriate conformations around the C–S bond (staggered or eclipsed), it could assume pseudo-symmetries of either the C_i or C_2 type. Therefore, with a complicated model of disorder, it could lie in one or more special positions. It could also lie in a general position with 0.5 occupancy for all the atoms. During the first stages of the solution of the structures

TABLE 1. Crystallographic data

Formula	$C_{83}H_{84}O_3F_3P_6SRh_2Cu$	$C_{83}H_{84}O_3F_3P_6SRh_2Ag$
Molecular weight	1673.8	1718.1
a (Å)	20.508(8)	20.670(7)
c (Å)	21.021(8)	20.501(9)
V (Å^3)	8840.3	8759.7
Z	4	4
Crystal system	tetragonal	tetragonal
Space group	$P4/n$	$P4/n$
Density (g cm^{-3}) calc.	1.258	1.303
Cryst dimensions (mm)	0.20×0.35×0.40	0.30×0.45×0.60
Radiation	graphite-monochromatized Mo Kα, $\lambda = 0.71069$	
Absorption coefficient (cm^{-1})	7.78	7.64
Scan range (°)	0.80	0.80
Scan speed	variable according to the intensities	
Scan mode	ω-scan	
Bkgd counts	0.5 scan time at ±0.8°	
Intensity control standards	3 measured every 100 reflections	
2θ Angle (°)	3–50	3–50
Total no. observations	4900	5500
No. unique data with $I \geqslant 2\sigma(I)$	870	1389
Data/parameters	4.2	3.4
No. parameters refined	206	411
R	0.071	0.055
R_w	0.083	0.064

no peaks were localized, which could belong to the atoms of the anion, either in special or in general positions. Therefore only the atoms of the complex cation were refined by full-matrix least-squares procedures with the minimized function $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o^2)$. After convergence of the isotropic refinement at $R = 0.086$ for **1** and $R = 0.095$ for **2**, the hydrogen atoms were introduced into calculated positions and refined riding on the corresponding carbon atoms. All the non-hydrogen atoms in **2** and only the heavier atoms in **1** were allowed to vibrate anisotropically. All the hydrogen atoms of the triphos ligands were given the isotropic thermal factors of the parent carbon atoms but they were not refined. Some cycles of refinement were made with these conditions and then Fourier observed and difference maps were calculated searching for the anion. A few isolated weak peaks in general positions were observed at this stage. One at a time, they were introduced into the refinement with the scattering factor of the carbon atom and 0.5 occupancy. None of them could be accepted after the refinement because of the high values reached by their isotropic thermal factors. Because of the marginal interest of the $[CF_3SO_3]^-$ groups relative to the complex cations, the refinements were completed without the atoms of the counterions, reaching convergence at $R = 0.071$ for **1** and 0.055 for **2** ($R_w = 0.083$ for **1** and 0.064 for **2**). All calculations were performed on the Data General Eclipse MV8000II computer using local programs. Scattering factors and anomalous dispersion terms were taken from the International Tables for X-Ray Crystallography [13]. Final atomic parameters of the non-hydrogen atoms are given in Table 2.

Results and discussion

A view of the molecule of **2** is shown in Fig. 1 and a selection of bond lengths and angles of the two cationic complexes is presented in Table 3. In the $P4/n$ space group Cu in **1** and Ag in **2** lie on the S_4 axis, so that in the two complexes the two halves of each molecule are related by a binary symmetry.

Their structures consist of nearly linear clusters, with Rh–Cu–Rh (**1**) and Rh–Ag–Rh (**2**) arrays lying at an angle of 170 and 168°, respectively. However in each complex the two Rh(triphos) fragments are arranged around the central atom with their C_3 axes forming an angle of about 150° between them, while the triangles defined by the P atoms of the triphos ligands on opposite sides of each molecule adopt an almost staggered conformation (Table 3 and Fig. 2).

Even though the hydride ligands were not located by the X-ray analyses, each rhodium atom can be assumed to be octahedrally coordinated as in the parent $[RhH_3(triphos)]$.

The coordination geometry around the central atom, Cu in **1** and Ag in **2**, is difficult to define without the direct location of the hydride ligands. However, considering the arrangement of the heavy atoms, it appears that the P–Rh–Cu angles in **1** and the P–Rh–Ag angles in **2** are of two kinds. In each case there are two small

TABLE 2. Atomic coordinates and isotropic thermal parameters for non-hydrogen atoms of **1** and **2** with their e.s.d.s in parentheses

	x	y	z	B_{iso}/B_{eq}
Complex **1**				
Cu	−0.2500	0.2500	0.1950(4)	6.3(3)
Rh	−0.2247(2)	0.3705(1)	0.2082(2)	5.7(1)
P(1)	−0.2907(6)	0.4597(6)	0.2216(6)	5.8(4)
P(2)	−0.1660(6)	0.3972(5)	0.3006(6)	5.9(4)
P(3)	−0.1570(5)	0.4360(6)	0.1469(5)	4.8(4)
C(1)	−0.170(2)	0.525(2)	0.253(2)	4(1)
C(2)	−0.143(2)	0.597(2)	0.271(2)	8(1)
C(3)	−0.244(2)	0.525(2)	0.266(2)	3.8(9)
C(4)	−0.130(2)	0.481(2)	0.293(2)	5.0(9)
C(5)	−0.158(2)	0.523(2)	0.180(2)	6(1)
C(6)	−0.369(3)	0.450(2)	0.261(3)	8(1)
C(7)	−0.428(3)	0.445(3)	0.240(3)	13(2)
C(8)	−0.488(3)	0.429(3)	0.278(4)	13(1)
C(9)	−0.480(3)	0.442(3)	0.335(3)	9(1)
C(10)	−0.425(4)	0.449(3)	0.367(4)	13(2)
C(11)	−0.369(4)	0.465(3)	0.325(3)	13(2)
C(12)	−0.318(2)	0.498(2)	0.148(2)	5(1)
C(13)	−0.318(2)	0.569(2)	0.138(2)	7(1)
C(14)	−0.339(2)	0.592(2)	0.084(2)	7(1)
C(15)	−0.358(2)	0.559(2)	0.032(2)	6(1)
C(16)	−0.360(2)	0.493(2)	0.043(2)	6(1)
C(17)	−0.339(2)	0.459(2)	0.097(2)	5(1)
C(18)	−0.097(2)	0.344(2)	0.325(2)	6(1)
C(19)	−0.099(3)	0.274(3)	0.316(2)	10(1)
C(20)	−0.049(3)	0.232(3)	0.335(3)	11(1)
C(21)	−0.000(3)	0.263(3)	0.356(3)	10(1)
C(22)	0.005(3)	0.325(3)	0.369(3)	11(1)
C(23)	−0.043(2)	0.368(3)	0.348(2)	8(1)
C(24)	−0.211(2)	0.400(2)	0.372(2)	6(1)
C(25)	−0.260(3)	0.353(3)	0.392(3)	11(1)
C(26)	−0.298(3)	0.350(3)	0.442(3)	10(1)
C(27)	−0.283(2)	0.398(2)	0.484(2)	7(1)
C(28)	−0.241(3)	0.444(3)	0.483(3)	11(1)
C(29)	−0.204(3)	0.442(3)	0.420(3)	9(1)
C(30)	−0.071(2)	0.419(3)	0.141(2)	8(1)
C(31)	−0.043(2)	0.363(2)	0.165(2)	6(1)
C(32)	0.023(2)	0.350(2)	0.162(2)	7(1)
C(33)	0.061(2)	0.400(2)	0.137(2)	8(1)
C(34)	0.039(2)	0.454(2)	0.109(2)	7(1)
C(35)	−0.031(2)	0.465(2)	0.114(2)	7(1)
C(36)	−0.176(2)	0.438(2)	0.063(2)	5(1)
C(37)	−0.181(2)	0.500(2)	0.029(2)	7(1)
C(38)	−0.201(2)	0.496(2)	−0.037(2)	7(1)
C(39)	−0.208(2)	0.437(3)	−0.064(3)	8(1)
C(40)	−0.199(2)	0.385(3)	−0.031(2)	8(1)
C(41)	−0.184(2)	0.381(2)	0.032(2)	6(1)
Complex **2**				
Ag	0.0000	0.0000	0.1914(2)	5.8(1)
Rh	0.0273(1)	0.1261(1)	0.2046(1)	4.9(1)
P(1)	−0.0386(3)	0.2137(3)	0.2207(4)	4.2(2)
P(2)	0.0859(3)	0.1490(3)	0.2992(5)	5.0(2)
P(3)	0.0943(3)	0.1908(3)	0.1437(4)	4.1(2)
C(1)	0.079(2)	0.277(1)	0.254(1)	5(1)
C(2)	0.103(1)	0.349(1)	0.272(1)	5.0(9)
C(3)	0.004(1)	0.276(1)	0.269(1)	3.2(7)
C(4)	0.122(1)	0.230(1)	0.294(2)	4.9(9)
C(5)	0.092(1)	0.276(1)	0.177(1)	4.2(8)
C(6)	−0.113(2)	0.204(2)	0.266(2)	5(1)
C(7)	−0.172(2)	0.193(3)	0.241(2)	14(2)
C(8)	−0.228(2)	0.185(3)	0.271(4)	15(2)
C(9)	−0.228(2)	0.187(2)	0.332(2)	8(1)
C(10)	−0.170(3)	0.203(3)	0.369(2)	12(2)
C(11)	−0.115(2)	0.215(2)	0.328(3)	11(2)
C(12)	−0.064(1)	0.256(2)	0.147(2)	6(1)
C(13)	−0.064(1)	0.326(1)	0.138(2)	6(1)
C(14)	−0.084(2)	0.353(2)	0.078(3)	8(1)
C(15)	−0.103(2)	0.317(2)	0.028(3)	8(1)
C(16)	−0.110(1)	0.251(2)	0.033(1)	6(1)
C(17)	−0.087(1)	0.220(2)	0.091(2)	6(1)
C(18)	0.157(2)	0.100(2)	0.323(1)	5(1)
C(19)	0.150(2)	0.034(2)	0.312(2)	9(1)
C(20)	0.204(3)	−0.005(2)	0.330(2)	12(2)
C(21)	0.263(2)	0.021(5)	0.354(3)	18(3)
C(22)	0.259(3)	0.077(5)	0.363(4)	25(4)
C(23)	0.211(2)	0.122(2)	0.352(2)	8(1)
C(24)	0.039(2)	0.148(1)	0.377(2)	5(1)
C(25)	−0.010(2)	0.102(2)	0.383(3)	13(2)
C(26)	−0.043(3)	0.100(3)	0.441(4)	14(2)
C(27)	−0.028(3)	0.144(3)	0.488(3)	10(2)
C(28)	0.018(3)	0.193(2)	0.481(3)	11(2)
C(29)	0.048(2)	0.192(3)	0.424(2)	11(2)
C(30)	0.179(1)	0.176(1)	0.139(1)	4.5(9)
C(31)	0.207(1)	0.120(1)	0.162(2)	6(1)
C(32)	0.275(2)	0.109(2)	0.161(1)	6(1)
C(33)	0.316(1)	0.152(2)	0.134(2)	6(1)
C(34)	0.290(2)	0.209(2)	0.109(2)	6(1)
C(35)	0.221(2)	0.220(1)	0.111(2)	6(1)
C(36)	0.075(1)	0.199(1)	0.056(1)	4.0(9)
C(37)	0.068(2)	0.257(1)	0.025(2)	6(1)
C(38)	0.048(2)	0.258(2)	−0.041(3)	7(1)
C(39)	0.043(2)	0.200(3)	−0.074(2)	7(1)
C(40)	0.047(2)	0.143(2)	−0.040(3)	8(1)
C(41)	0.070(2)	0.139(2)	0.024(2)	10(1)

(*continued*)

TABLE 2. (*continued*)

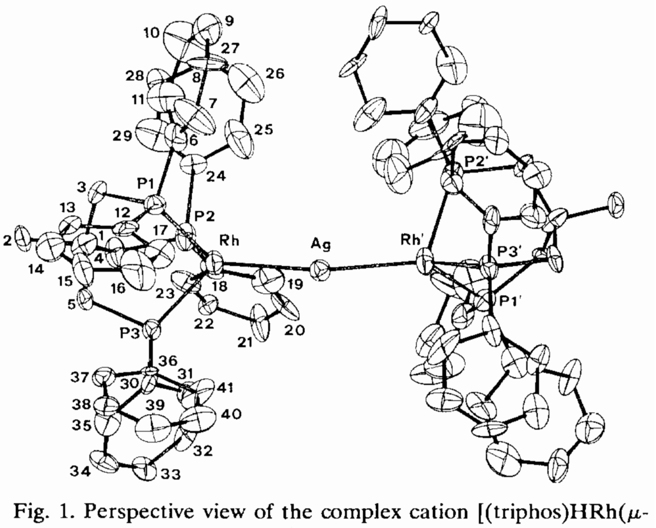


Fig. 1. Perspective view of the complex cation [(triphos)HRh(μ-H)$_2$Ag(μ-H)$_2$RhH(triphos)]$^+$ (**2**). The ellipsoids represent 30% probability.

TABLE 3. Selection of bond distances (Å) and angles (°) for **1** and **2**

	1	**2**
Rh–M	2.534(3)	2.681(2)
Rh–P(1)	2.292(12)	2.290(7)
Rh–P(2)	2.350(13)	2.334(10)
Rh–P(3)	2.322(12)	2.295(8)
P(1)–C(3)	1.89(3)	1.84(2)
P(1)–C(6)	1.83(6)	1.81(4)
P(1)–C(12)	1.82(4)	1.82(3)
P(2)–C(4)	1.87(4)	1.84(2)
P(2)–C(18)	1.85(5)	1.85(3)
P(2)–C(24)	1.76(5)	1.86(3)
P(3)–C(5)	1.92(4)	1.89(3)
P(3)–C(30)	1.80(5)	1.79(3)
P(3)–C(36)	1.81(4)	1.84(3)
C(1)–C(2)	1.59(6)	1.61(4)
C(1)–C(3)	1.54(5)	1.58(4)
C(1)–C(4)	1.48(5)	1.55(4)
C(1)–C(5)	1.57(5)	1.61(4)
Rh–M–Rh	170.3(2)	168.4(2)
P(1)–Rh–M	131.9(3)	131.2(2)
P(2)–Rh–M	113.7(4)	113.0(2)
P(3)–Rh–M	129.8(4)	129.7(2)
P(2)–Rh–P(1)	90.9(4)	91.6(3)
P(3)–Rh–P(1)	87.7(4)	88.7(3)
P(3)–Rh–P(2)	91.0(4)	91.2(3)
C(3)–P(1)–Rh	109(1)	110.2(8)
C(4)–P(2)–Rh	110(1)	110(1)
C(5)–P(3)–Rh	110(1)	109.6(9)
C(1)–C(3)–P(1)	114(2)	112(1)
C(1)–C(4)–P(2)	114(2)	112(1)
C(1)–C(5)–P(3)	112(2)	112(1)
C(6)–P(1)–C(3)	107(2)	102(1)
C(12)–P(1)–C(3)	106(1)	104(1)
C(12)–P(1)–C(6)	100(2)	103(1)
C(18)–P(2)–C(4)	105(1)	101(1)
C(24)–P(2)–C(4)	104(1)	106(1)
C(24)–P(2)–C(18)	101(2)	100(1)
C(30)–P(3)–C(5)	102(2)	102(1)
C(36)–P(3)–C(5)	109(1)	105(1)
C(36)–P(3)–C(30)	99(2)	100(1)
C(3)–C(1)–C(2)	104(3)	106(2)
C(4)–C(1)–C(2)	107(3)	107(2)
C(4)–C(1)–C(3)	116(3)	117(2)
C(5)–C(1)–C(2)	102(3)	101(2)
C(5)–C(1)–C(3)	110(3)	111(2)
C(5)–C(1)–C(4)	116(3)	114(2)
C(7)–C(6)–P(1)	133(4)	127(3)
C(11)–C(6)–P(1)	114(4)	121(3)
C(13)–C(12)–P(1)	123(3)	126(2)
C(17)–C(12)–P(1)	121(2)	120(2)
C(19)–C(18)–P(2)	122(3)	114(2)
C(23)–C(18)–P(2)	122(3)	127(2)
C(25)–C(24)–P(2)	126(3)	118(3)
C(29)–C(24)–P(2)	128(3)	123(2)
C(31)–C(30)–P(3)	123(3)	122(2)
C(35)–C(30)–P(3)	119(3)	122(2)
C(37)–C(36)–P(3)	121(3)	124(2)
C(41)–C(36)–P(3)	118(3)	113(2)
Cu---P and Ag---P distances (Å) and P–Rh---Rh′–P torsion angles (°)		
M′–P(1)	4.41	4.53
M′–P(2)	4.09	4.19
M′–P(3)	4.40	4.51
P(1)–Rh---Rh′–P(1′)	−161.5	−158.7
P(2)–Rh---Rh′–P(3′)	168.8	168.7
P(3)–Rh---Rh′–P(2′)	168.8	168.7

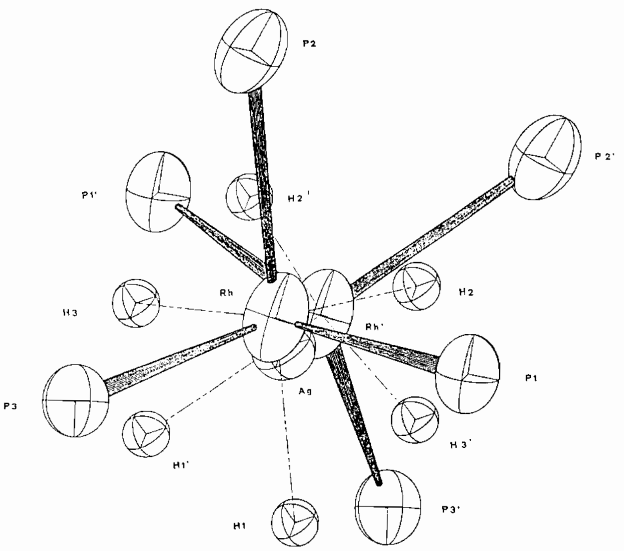


Fig. 2. View down the Rh–Rh direction of complex **2**. The H atoms are at calculated positions with theoretical isotropic thermal parameters.

equal angles (113.7(4)° in **1** and 113.0(2)° in **2**) and four large ones (each pair being 129.8(4) and 131.9(3)° in **1** and 129.7(2) and 131.2(2)° in **2**). This implies that the hydrides, *trans* to the phosphorus atoms with the large P–Rh–M angles, should lie closer to the central atom. Thus, if only the hydride donors are considered, the coordinations around the central atoms seem based on four hydride ligands which interact with the metal, while two hydrides are terminal on the rhodium atoms or interact weakly with the central atoms.

With the program HYDEX [8], the most likely sites for the hydride ligands in a metal complex can be found by minimization of the potential energy of non-bonded interactions involving the hydrides. As the heavy atoms and the IR data showed that both terminal and bridging hydride ligands were present, the potential energy for each complex was minimized optimizing the hydride positions, which were postulated according to two limiting models, i.e. one in which all the H ligands were terminal and the other where all of them were bridging. For this last model several sets of hydride positions were calculated, using different M–H distances. Those sites, which gave the lowest energy minima were then optimized. The best H sites for the two models are collected in Table 4. The first model gives acceptable Rh–H–Ag bond angles only for the H atoms which appear to be terminal on the basis of the heavy atom positions. The second model gives acceptable P–Rh–H angles only for the presumed bridging hydrides. The calculated terminal atom positions, taken from the first model, and those for the bridging atoms taken from the second model are shown in Fig. 3(a). The resulting arrangement of the hydride ligands around the central atom is similar to that found for the SF_4 molecule, i.e. the central metal atom interacts with four hydride ligands, two from each Rh unit, one pair being at about 180° and the other two being on a plane which bisects this axis at approximately right angles (Scheme 1).

Also the analogous Ir/Cu complex $[(Me_2PhP)_3HIr(\mu\text{-}H)_2Cu(\mu\text{-}H)_2IrH(Me_2PhP)_3]^+$ (**3**) [4b] presents a non-symmetrical arrangement of the heavy metal core as in **1** and **2**. In it, only four hydride ligands are close to the Cu atom as in **1** and **2**, but the phosphine ligands are, in this case, eclipsed and oriented with their C_3 axes parallel to each other, though bent to the Ir–Ir direction.

The Rh–Cu distance in **1** and the Rh–Ag distance in **2** are 2.534(3) and 2.681(2) Å, respectively. They are among the shortest metal–metal separations involving coinage metals. Some of the reported M–Cu separations are listed in Table 5, the shortest being the Cu–Cu distance of 2.371(2) Å in $[(\eta^2\text{-triphos})Cu(\mu\text{-}H)_2Cu(\eta^2\text{-triphos})]$ [20] and that of 2.348(2) Å in $[Cu_3(tolylN_5tolyl)]$ [21]. Distances comparable to those found in **1** have been observed in $[(triphos)H_2Rh(\mu\text{-}H)Cu(o\text{-}C_6H_4(CH_2P\{C_6H_{11}\}_2)_2)]^+$ (Ru–Cu = 2.642(1) Å) [14] and in **3** (Ir–Cu = 2.506 Å (av.)).

The Rh–Ag distances in **2** appear to be the shortest for these elements (cf. $[Rh_3Ag_3H_9(triphos)_3]^{3+}$ where the shortest distances are 2.795(4) Å) [3b]. However M–Ag distances have been found to be as short as 2.637(2) Å in $[(C_6F_5)_3(SC_4H_8)PtAg(PPh_3)]$ [29]. These data indicate that strong Rh–Cu and Rh–Ag direct interactions must be assumed.

The Rh–Cu contact (2.534(3) Å), shorter than the Rh–Ag value (2.680(2) Å), may be due to the smaller 'ionic' radius of Cu^+ relative to Ag^+ ($r(Cu^+) = 0.46$, $r(Ag^+) = 0.67$ Å; both values refer to radii for linear complexes. Larger differences have been reported for complexes of higher coordination numbers.)

The Ir–Cu distance in **3** (2.506 Å av.) is considerably shorter than the Rh–Cu distance in **1**, but no reliable interpretation can be given for this observation, since both the Group 9 metal and the phosphine are different and the hydride arrangement in **3** differs from that in **1**. The Cu–H interactions in compound **3** [4b] are described as non-planar and a sketch is given which could be taken as indicating a tetrahedral-type arrangement. Using the crystallographic data, compound **3** was analysed with the HYDEX program as done for **1** and **2**. The results are given in Table 4. These show that the CuH_4 interactions can be regarded as derived from those found for **1** and **2**, and distorted towards a tetrahedral structure (Fig. 3(b)).

In both complexes, the three Rh–P bond distances, which average 2.321 Å in **1** and 2.306 Å in **2** (Table 3), are equivalent in the expected error, though in both complexes the Rh–P(2) bond lengths are the longest

TABLE 4. Calculated H positions and related geometries: distances (Å) and angles (°)

	1	**2**	**3**	
M	Rh	Rh	Ir(1)	Ir(3)
M′	Cu	Ag	Cu	
Geometry with bridging hydrides H_b				
M–H_b	1.85	1.85	1.80	1.80
M′–H_b	1.85	1.85	1.80	1.80
P(1)–M–H(3)	178	174	168	165
P(2)–M–H(1)	161	156	156	147
P(3)–M–H(2)	176	172	167	171
M–H–M′	86	93	88	89
Geometry with terminal hydrides H_t				
M–H_t	1.61	1.60	1.86	1.86
M′–H(1)	2.71	2.77	2.77	2.86
M′–H(2)	2.59	2.63	2.64	2.61
M′–H(3)	2.57	2.62	2.63	2.57
P(1)–M–H(3)	155	159	169	161
P(2)–M–H(1)	168	171	173	178
P(3)–M–H(2)	157	160	165	165
M–H(1)–M′	66	70	62	60
M–H(2)–M′	70	74	65	66
M–H(3)–M′	70	75	65	67

Geometry around the central atom M′

	1	**2**	**3**
M′	Cu	Ag	Cu
H(2)–M′–H(3)	82	75	89
H(2)–M′–H(2′)	97	99	135
H(2)–M′–H(3′)	97	101	95
H(3)–M′–H(2′)	97	101	117
H(3)–M′–H(3′)	178	174	143
H(2′)–M′–H(3′)	82	75	85

Atomic coordinates of the hydrides at calculated positions

	1			**2**		
H_b						
H(1)	−0.2680	0.3217	0.1473	−0.0165	0.0752	0.1455
H(2)	−0.2746	0.3132	0.2560	−0.0300	0.0678	0.2413
H(3)	−0.1729	0.2969	0.1997	0.0728	0.0516	0.1845
H_t						
H(1)	−0.2367	0.1316	0.1416	−0.0121	0.1224	0.1377
H(2)	−0.2260	0.1474	0.2656	−0.0219	0.1042	0.2611
H(3)	−0.3441	0.1671	0.2014	0.0933	0.0854	0.1959

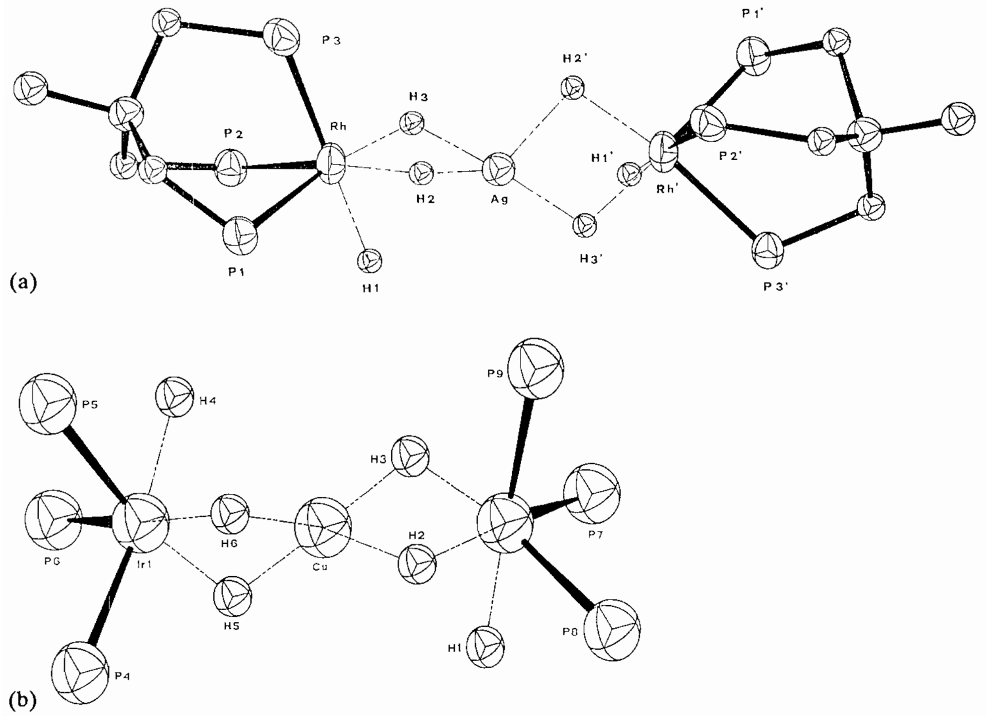
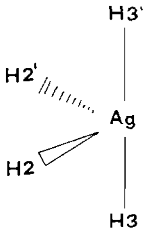


Fig. 3. Arrangement of the hydride ligands around the central atom at calculated positions: (a) in the complex cation [(triphos)HRh(μ-H)$_2$Ag(μ-H)$_2$RhH(triphos)]$^+$ (**2**), (b) in the complex cation [(Me$_2$PhP)$_3$HIr(μ-H)$_2$Cu(μ-H)$_2$IrH(Me$_2$PhP)$_3$]$^+$ (**3**).

TABLE 5. Metal–metal distances (Å) involving Cu and Ag

			Ref.
M–Cu			
[(triphos)H$_2$Rh(μ-H)Cu(o-C$_6$H$_4$(CH$_2$P{C$_6$H$_{11}$}$_2$)$_2$)]$^+$	2.642(1)		14
[(Me$_2$Ph)$_3$HIr(μ-H)$_2$Cu(μ-H)$_2$IrH(Me$_2$Ph)$_3$]$^+$	2.502(4)	2.529(4)	4b
[(PhC-C)(OC)Ir(μ-Ph$_2$PCH$_2$PPh$_2$)$_2$CuCl]	2.832(1)		15
[(Me$_2$PhP)$_2$(CO)IrCu(MeN$_3$Me)Cl]	2.70		16
[Cu$_4$Ir$_2$(PPh$_3$)$_2$(C-CPh)$_8$]	2.776(4)	2.959(4)	17
[(MePh$_2$)$_3$H$_2$Re(μ-H)$_3$Cu(μ-H)$_3$ReH$_2$(MePh$_2$)$_3$]	2.606		18
[Os$_3$Cu$_3$H$_9$(PMe$_2$Ph)$_9$]	2.595(2)	2.636(2)	19
[(η^2-triphos)Cu(μ-H)$_2$Cu(η^2-triphos)]	2.371(2)		20
[Cu$_3$(tolylN$_5$tolyl)$_3$]	2.348(2)		21
M–Ag			
[(PPh$_3$)$_3$Ir(μ_3-H)(μ-H)$_2$Ag$_2$(OSO$_2$CF$_3$)]$^+$	2.764(4)	2.808(4)	22
[PPh$_3$)$_3$Ir(μ-H)$_3$Ag(μ-H)$_3$Ir(PPh$_3$)$_3$]$^+$	2.709(1)		23
[(PPh$_3$)$_3$H$_2$Ir(μ-H)Ag(PPh$_3$)]$^+$	2.758(2)		24
[(PEt$_3$)$_2$(C$_6$Cl$_5$)Pt(μ-H)Ag(μ-H)Pt(C$_6$Cl$_5$)(PEt$_3$)$_2$]	2.791(1)		25
[(triphos)Rh$_3$Ag$_3$H$_9$]$^{3+}$	2.795(4)–2.933(4)		3b
[{PtAgCl$_2$(C$_6$F$_5$)$_2$}$_2$]$^-$	2.772(3)		26
[{Pt(C$_6$F$_5$)(acac)$_2$}Ag]$^-$	2.681(1)	2.667(1)	27
[(C$_6$F$_5$)$_2$(C$_6$Cl$_5$)(SC$_4$H$_8$)PtAg(PPh$_3$)]	2.650(2)		28
[cis-(C$_6$F$_5$)$_2$(C$_6$H$_5$)$_2$(SC$_4$H$_8$)PtAg]$^-$	2.692(2)		28
[(C$_6$F$_5$)$_3$(SC$_4$H$_8$)PtAg(PPh$_3$)]	2.637(1)		29
[(C$_6$F$_5$)$_4$(SC$_4$H$_8$)PtAg]$^-$	2.641(1)		28
[AuAg(C$_6$F$_5$)$_2$(SC$_4$H$_8$)$_n$]	2.726(2)		30
[AuAg(C$_6$F$_5$)$_2$(C$_6$H$_6$)$_n$]	2.702(2)		30

(2.350(13) Å in **1** and 2.334(10) Å in **2**) in accord with the stronger *trans* influence of the terminal versus the bridging hydrides. In the binary complex [(triphos)Rh(μ-H)$_3$Rh(triphos)]$^{2+}$ [1h] the average value of the Rh–P distances is 2.315 Å and in the monomeric [(Et-triphos)RhH$_3$] complex [5] the Rh–P average value is 2.303 Å. Both values are comparable with those found in **1** and **2**.



Scheme 1.

The RhH_3(triphos)–M′ interactions (M′ = Cu or Ag) in compounds **1** and **2** can be described as follows.

(i) Each trihydride unit interacts with M′ with two *cis* hydrides.

(ii) Each of these bridging hydrides binds to M′ through an Rh–H–M′ three-center two-electron interaction.

(iii) Direct Rh–M′ interactions, in addition to those typical of 'closed' M–H–M interactions, seem to arise.

The structural data for **1**, **2** and **3** indicate that the potential for distortions of the $M'H_4$ coordination polyhedron is very low and that, therefore, the hydride character of the mononuclear species, influenced by the donor capacity of the phosphines, the Rh–M′ (or the Ir–M′) interactions, influenced by the total electron density at the Rh or Ir center, or the steric requirements of the mononuclear hydrides, may cause significant changes of the geometry at the central metal atom.

Supplementary material

Hydrogen coordinates, anisotropic temperature factors, calculated and observed structure factors and tables of all bond distances and angles are available from the authors on request.

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