Synthesis and crystal structure of the new near-linear Rh$_2$Mo trinuclear complex [(η^5-C$_5$H$_5$)Rh(μ-CO)-(μ-Ph$_2$PC$_5$H$_4$N)Rh(CO)Mo(CO)$_3$(η^5-C$_5$H$_5$)]

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Abstract

Addition of [Mo(η^5-C$_5$H$_5$)(CO)$_3$]Na to a solution of the complex [η^5-C$_5$H$_5$)Rh(μ-CO)(μ-Ph$_2$PC$_5$H$_4$N)Rh(CO)Cl] (1) in THF results in the replacement of the terminal chloride by the anion [Mo(η^5-C$_5$H$_5$)(CO)$_3$]$^-$, to give the near-linear trinuclear complex [(η^5-C$_5$H$_5$)Rh(μ-CO)(μ-Ph$_2$PC$_5$H$_4$N)Rh(CO)Mo(CO)$_3$(η^5-C$_5$H$_5$)] (3) in a good yield. The crystal structure of 3 has been determined by an X-ray diffraction study.

Introduction

We recently reported [1] the synthesis and some reactions of the unsymmetrically rhodium–rhodium bonded complex [η^5-C$_5$H$_5$)Rh(μ-CO)(μ-Ph$_2$PPy)Rh(CO)Cl] (1) (Ph$_2$PPy = 2-(diphenylphosphino)pyridine). It was found remarkably, to react with alkynes activated by electron-withdrawing groups such as COOR (R = Me, Et) to give the tetranuclear species {[η^5-C$_5$H$_5$)Rh(μ-alkyne)(μ-Ph$_2$PPy)Rh(CO)(μ-Cl)]$_2$} (2), containing two bimetallic units linked by two chloride ligands bridging the rhodium atoms not directly involved in a metal–metal bond [2]. In each bimetallic unit the alkyne ligand adopts a *cis*-dimetallated olefin, μ,η^2-‖, coordination; the structural parameters and the solution behaviour of 2 support the view that its formation occurs by an intermolecular nucleophilic attack of chlorine on the coordinatively unsaturated 16-electron rhodium(II) in the bimetallic species [(η^5-C$_5$H$_5$)Rh(μ-alkyne)(μ-Ph$_2$PPy)Rh(CO)Cl]. As an extension of this study we thought it of interest to determine the effect of the replacement of the chloride ligand in 1 by

carbonylmetallate anions since the most likely product would be a near-linear trinuclear species. Complexes containing a linear arrangement of transition metals are the subject of much current interest [3,4]. Study of these complexes is relevant to understanding of the reactivities and site selectivities exhibited by heterometallic complexes, particularly in activation of species such as alkynes and dienes [3,4]. Here we report the synthesis, the crystal structure, and some reactions of the title compound.

Results and discussion

Addition of $[Mo(\eta^5\text{-}C_5H_5)(CO)_3]Na$ to a solution of the complex $[\eta^5\text{-}C_5H_5)Rh(\mu\text{-}CO)(\mu\text{-}Ph_2PPy)Rh(CO)Cl]$ (1) in THF resulted in the replacement of the terminal chloride by the anion $[Mo(\eta^5\text{-}C_5H_5)(CO)_3]^-$, to give the near-linear trinuclear complex $[(\eta^5\text{-}C_5H_5)Rh(\mu\text{-}CO)(\mu\text{-}Ph_2PC_5H_4N)Rh(CO) \quad Mo(CO)_3(\eta^5\text{-}C_5H_5)]$ (3) in a good yield. Attempts to obtain linear trinuclear complexes analogous to 3 by treating 1 with the sodium salt of the carbonylmetallate anions $[Co(CO)_4]^-$, $[Mo(CO)_5]^-$, $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]^-$ failed; in all cases mixtures of intractable products not containing the $\overline{Rh(\mu\text{-}CO)Rh}$ moiety were obtained. Breaking of the $\overline{Rh(\mu\text{-}CO)Rh}$ moiety was also observed when 1 was treated with the short bite bidentate ligands Ph_2PPy and dppm (dppm = bis(diphenylphosphino)methane), the A-frame complexes $[Rh_2(Ph_2PPy)_2(CO)Cl_2]$ [5] and $[Rh_2(dppm)_2(CO)Cl_2]$ [6] and $[Rh(\eta^5\text{-}C_5H_5)(CO)(Ph_2PPy)]$ [1] being formed.

Complex 3 is a brown solid, stable in the air, moderately soluble in diethyl ether and soluble in benzene and chlorinated solvents. Its IR spectrum exhibits very strong $\nu(CO)$ bands at 1970, 1895, 1843, 1805 cm^{-1}. The $^{31}P\{^1H\}$ NMR spectrum of a $CDCl_3$ solution at 298 K shows resonance at δ 50.50 ppm as doublet of doublets ($^1J(RhP)$ 175.9; $^2J(RhP)$ 2.80 Hz); the ^1H NMR spectrum shows two sets of resonances in the η^5-cyclopentadienyl region, a singlet at δ 5.27 ppm and a triplet at δ 5.23 ppm ($^2J(RhH) = {}^3J(PH) = 0.8$ Hz). The low-temperature spectra do not differ from those at room temperature indicating that the structure in solution is static and the same as that in the crystal.

Under mild conditions, in contrast to 1, the compound 3 does not react with the alkynes $RC\equiv CR$ (R = Me, Et). If the temperature is raised or a very large excess of the alkyne used, fragmentation of 3 occurs by breaking of the metal–metal bonds, to form intractable material.

Crystal structure of $[(\eta^5\text{-}C_5H_5)Rh(\mu\text{-}CO)(\mu\text{-}Ph_2PC_5H_4N)Rh(CO)Mo(CO)_3(\eta^5\text{-}C_5H_5)]$ (3). The crystal structure of 3 consists of heterotrinuclear complexes and disordered heptane molecules of solvation. A view of the Rh_2Mo complex is shown in Fig. 1, together with the atomic numbering scheme. Selected bond distances and angles are listed in Table. The metal atoms are in a near-linear arrangement, the $Rh(2)–Rh(1)–Mo$ angle being of $162.6(1)°$. The Rh–Rh and Rh–Mo separations, $2.686(2)$ and $2.888(2)$ Å, respectively, fall within the range normally associated with Rh–Rh and Rh–Mo single bonds [1,7]. The Ph_2PPy ligand bridges the two Rh atoms through the P and N atoms ($Rh(1)–N = 2.17(1)$ and $Rh(2)–P = 2.212(4)$ Å) with a bite P...N separation of $2.73(1)$ Å, slightly longer than the Rh–Rh separation. The Ph_2PPy group is "twisted" about the Rh–Rh bond (the N–Rh(1)–Rh(2)–P torsion angle is $22.4(3)°$), probably in order to minimize steric interactions and the five-membered ring $Rh(1)–N–C(6)–P–Rh(2)$ adopts an "envelope" confor-
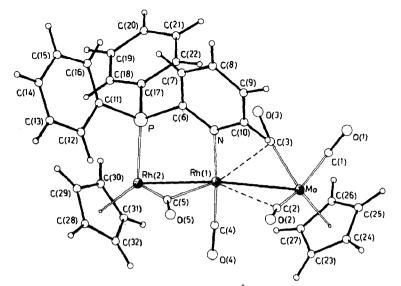
Fig. 1. View of the molecular structure of $[(\eta^5\text{-}C_5H_5)Rh(\mu\text{-}CO)(\mu\text{-}Ph_2PC_5H_4N)Rh(CO)Mo(CO)_3(\eta^5\text{-}C_5H_5)]$ (3) with the atomic numbering scheme.

Table 1

Selected bond distances (Å) and angles (°) [a]

Mo–Rh(1)	2.888(2)	Rh(1)–Rh(2)	2.686(2)
Mo–C(1)	1.92(1)	Rh(1)–C(4)	1.81(1)
Mo–C(2)	1.97(1)	Rh(1)–C(5)	2.14(1)
Mo–C(3)	1.94(1)	Rh(2)–P	2.212(4)
Mo–M(1)	2.04(2)	Rh(2)–C(5)	1.88(1)
Rh(1)–N	2.17(1)	Rh(2)–M(2)	1.92(2)
Rh(1)–C(2)	2.53(1)	P–C(6)	1.84(1)
Rh(1)–C(3)	2.48(1)	C(6)–N	1.35(2)
M(1)–Mo–C(1)	119.0(7)	C(4)–Rh(1)–Rh(2)	84.1(5)
M(1)–Mo–C(2)	124.2(7)	C(4)–Rh(1)–Mo	81.3(4)
M(1)–Mo–C(3)	125.9(6)	C(4)–Rh(1)–C(2)	91.9(5)
M(1)–Mo–Rh(1)	130.7(5)	C(4)–Rh(1)–C(3)	102.2(6)
C(1)–Mo–C(2)	84.9(6)	C(4)–Rh(1)–C(5)	95.2(6)
C(1)–Mo–C(3)	82.8(6)	C(5)–Rh(1)–Rh(2)	44.0(4)
C(1)–Mo–Rh(1)	110.3(4)	C(5)–Rh(1)–C(2)	105.5(5)
C(2)–Mo–C(3)	105.4(6)	C(2)–Rh(1)–Mo	42.1(3)
C(2)–Mo–Rh(1)	59.1(4)	Mo–Rh(1)–C(3)	41.5(3)
C(3)–Mo–Rh(1)	57.9(4)	C(3)–Rh(1)–Rh(2)	134.8(3)
Mo–Rh(1)–Rh(2)	162.61(6)	M(2)–Rh(2)–P	129.5(5)
N–Rh(1)–C(4)	176.6(5)	M(2)–Rh(2)–C(5)	132.7(7)
N–Rh(1)–Rh(2)	92.8(3)	M(2)–Rh(2)–Rh(1)	137.4(5)
N–Rh(1)–C(5)	81.6(5)	P–Rh(2)–C(5)	92.5(5)
N–Rh(1)–Mo	102.1(3)	P–Rh(2)–Rh(1)	84.8(1)
N–Rh(1)–C(2)	90.1(4)	C(5)–Rh(2)–Rh(1)	52.4(5)
N–Rh(1)–C(3)	81.1(4)		

[a] M(1) and M(2) are the centroids of the two C(23)–C(27) and C(28)–C(32) cyclopentadienyl rings.

mation, with the Rh(2) atom lying 0.818(2) Å out of the mean plane through the other four atoms. The two Rh atoms are also unsymmetrically bridged by a carbonyl group (Rh(2)–C(5) 1.88(1) and Rh(1)–C(5) 2.14(1) Å, Rh(2)–C(5)–O(5) 153(1) and Rh(1)–C(5)–O(5) 123(1)°). The carbonyl bridge is almost perpendicular to the Ph_2PPy bridge, the dihedral angle between the Rh(1)–C(5)–Rh(2) and Rh(2)–P–C(6)–N–Rh(1) planes being 93.1(4)°. The coordination around Rh(2) displays a severely distorted tetrahedral geometry if the M(2) centroid of the cyclopentadienyl ring is regarded as a single coordination site. The Rh(1) is in a distorted square pyramidal coordination environment, with the basal plane occupied by the N, Mo, Rh(2) and C(4) (from a carbonyl group) atoms, with the bridging C(5) at the apex, markedly bent towards the Rh–Rh vector. Two long interactions with the C(2) and C(3) atoms of carbonyls bonded to the Mo atom complete the coordination of Rh(1) (Rh(1)–C(5) 2.53(1) and Rh(1)–C(3) 2.48(1) Å). The semi-bridging behaviour of these carbonyls is also revealed by the Mo–C(2)–O(2) and Mo–C(3)–O(3) angles (both of 168(1)°), and may be due to the demand for charge redistribution from the electron poor Rh(1) (16-electron).

When the M(1) centroid of the cyclopentadienyl ring, the carbonyl carbon atoms C(1), C(2), C(3) and Rh(1) are considered, the coordination around the Mo atom can be described as four-legged piano stool, the angles between the Mo–M(1) vector and the atoms C(1), C(2), C(3) and Rh(1) ranging from 119.0(7) and 130.7(5)°. The four atoms are approximately coplanar, and the mean plane passing through them is almost parallel to the mean plane through the cyclopentadienyl ring (the dihedral angle is 16.9(5)°.

The structural features of the $[\eta^5\text{-}C_5H_5)Rh(\mu\text{-}CO)(\mu\text{-}Ph_2PPy)Rh(CO)]$ moiety of 3 are closely comparable to those in 1 [1].

Experimental

Previously reported methods were used to prepare the compounds $[(\eta^5\text{-}C_5H_5)Rh(\mu\text{-}CO)(\mu\text{-}Ph_2PPy)Rh(CO)Cl]$ [1], $Na[Co(CO)_4]$ [8], $Na[Mo(\eta^5\text{-}C_5H_5)(CO)_3]$ [9], $Na[Mn(CO)_5]$ [10], $Na[Fe(\eta^5\text{-}C_5H_5)(CO)_2]$ [11], and Ph_2PPy [12]. All other reagents were purchased and used as supplied. Solvents were dried by standard procedures. All experiments were performed under purified nitrogen. IR spectra were recorded with Nujol mulls on a Perkin Elmer 783 spectrophotometer. ^1H and ^{31}P NMR spectra were recorded on a Bruker WP80-SY spectrometer, operating at 80.13 and 32.442 MHz, respectively. Elemental C, H, and N analyses were carried out at the Istituto di Chimica Organica dell'Università di Milano; other analyses were performed by Malissa and Reuter Analytische Laboratorien, Elbach, West Germany.

Preparation of $[(\eta^5\text{-}C_5H_5)Rh(\mu\text{-}CO)(\mu\text{-}Ph_2PC_5H_4N)Rh(CO)Mo(CO)_3(\eta^5\text{-}C_5H_5)]$ (3). A tetrahydrofuran solution (25 cm³) of $Na[Mo(\eta^5\text{-}C_5H_5)(CO)_3]$ (obtained from 0.54 g, 1.10 mmol, of $[Mo(\eta^5\text{-}C_5H_5)(CO)_3]_2$ and sodium amalgam) was added to one of $[(\eta^5\text{-}C_5H_5)Rh(\mu\text{-}CO)(\mu\text{-}Ph_2PPy)Rh(CO)Cl]$ (1.39 g, 2.22 mmol) in the same solvent (30 cm³). The colour solution immediately turned from orange to brown. The volume of the solution was then reduced to ca. 15 cm³ under reduced pressure, and diethyl ether (30 cm³) was added to give a brown precipitate. This was filtered off, and extracted into benzene (15 cm³) and 25 cm³ of hexane was added to the extract. The solution was set aside, and compound 3 separated as brown

Table 2

Fractional atomic coordiantes ($\times 10^4$) with e.s.d.s in parentheses

	x	y	z
Mo	4026(1)	3557(1)	3168(1)
Rh(1)	3028(1)	2690(1)	3326(1)
Rh(2)	2130(1)	1887(1)	2420(1)
P	1724(1)	2797(2)	4015(4)
O(1)	4194(5)	4629(7)	6416(14)
O(2)	3974(4)	2203(8)	5962(15)
O(3)	2971(5)	4536(7)	2810(15)
O(4)	3457(5)	1859(8)	223(16)
O(5)	2801(5)	1222(7)	5378(15)
N	2673(4)	3208(6)	5626(12)
C(1)	4123(6)	4231(10)	5185(18)
C(2)	3934(5)	2685(10)	4881(18)
C(3)	3338(6)	4094(8)	2995(17)
C(4)	3294(5)	2210(9)	1418(19)
C(5)	2625(6)	1644(9)	4234(19)
C(6)	2136(5)	3244(7)	5799(15)
C(7)	1908(6)	3576(9)	7254(15)
C(8)	2239(6)	3839(9)	8634(16)
C(9)	2782(6)	3754(8)	8464(16)
C(10)	2980(5)	3476(9)	6990(15)
C(11)	1157(5)	2392(8)	5235(15)
C(12)	1177(6)	1592(9)	5688(16)
C(13)	765(7)	1278(10)	6656(20)
C(14)	367(7)	1717(11)	7215(20)
C(15)	355(6)	2518(12)	6761(23)
C(16)	739(5)	2874(9)	5782(18)
C(17)	1440(5)	3650(7)	2878(16)
C(18)	1034(7)	3545(11)	1693(22)
C(19)	824(8)	4192(12)	768(26)
C(20)	1029(8)	4947(11)	905(25)
C(21)	1465(8)	5052(11)	2034(22)
C(22)	1670(5)	4426(8)	3041(16)
C(23)	4595(7)	2840(11)	1331(22)
C(24)	4910(6)	3345(14)	2374(20)
C(25)	4791(7)	4124(12)	1974(24)
C(26)	4412(7)	4138(12)	689(21)
C(27)	4260(7)	3355(13)	222(20)
C(28)	1791(9)	730(11)	1368(21)
C(29)	1438(6)	1315(11)	1028(21)
C(30)	1649(6)	1881(11)	−160(17)
C(31)	2162(7)	1594(11)	−499(19)
C(32)	2258(7)	911(10)	520(20)
C(33)	3904(24)	252(41)	3706(103)
C(34)	4437(24)	575(36)	4376(90)
C(35)	4861(26)	−60(43)	3897(71)
C(36)	5303(22)	11(40)	5102(98)
C(37)	5380(24)	−650(41)	6394(88)
C(38)	5981(26)	−760(41)	6738(90)

microcrystals. (Found: C, 46.08; H, 2.96; N, 1.70; Mo, 11.40. $C_{32}H_{24}NO_5PMoRh_2$ calcd.: C, 46.01; H, 2.89; N, 1.68; Mo, 11.48%).

A similar procedure was carried out for reactions of **1** with the sodium salts of the carbonylmetalate anions $[Co(CO)_4]^-$, $[Mn(CO)_5]^-$, $[Fe(\eta^5-C_5H_5)(CO)_2]^-$, but we could not separate and characterize the products.

Reactions of 1 with Ph$_2$PPy and dppm. Solid Ph$_2$PPy (0.029 g; 0.11 mmol) was added to a dichloromethane solution of **1** (0.072 g; 0.11 mmol). The brown solution was stirred at room temperature for 40 min, during which the solution became dark orange. The volume was reduced to ca. 10 cm^3 and diethyl ether (20 cm^3) was added, to produce an orange precipitate of $[Rh_2(Ph_2PPy)_2(CO)Cl_2]$ [5]. The mother liquor was evaporated under reduced pressure to give $[Rh(\eta^5-C_5H_5)(CO)(Ph_2PPy)]$ [1].

A similar procedure, involving reaction of **1** with dppm gave the complexes $[Rh_2(dppm)_2(CO)Cl_2]$ [6] and $[Rh(\eta^5-C_5H_5)(CO)(Ph_2PPy)]$ [1].

Determination of the crystal structure of [(η^5-C$_5$H$_5$)Rh(μ-CO)(μ-Ph$_2$PC$_5$H$_4$N)Rh (CO)Mo(CO)$_3$(η^5-C$_5$H$_5$)] · $\frac{1}{2}$C$_7$H$_{16}$ (3). Brown crystals of **3** were obtained by slow evaporation of dichloromethane/heptane solutions. A crystal of dimensions ca. $0.17 \times 0.20 \times 0.25$ was used.

Crystal data. $C_{32}H_{24}MoNO_5PRh_2 \cdot \frac{1}{2}C_7H_{16}$, $M = 885.37$, monoclinic, space group $P2_1/a$, a 24.990(5), b 16.667(9), c 7.658(3) Å, β 91.72(2)°, V 3188(2) Å^3 (by least-squares refinement from the θ values of 28 accurately measured reflections, λ 0.71073 Å), $Z = 4$, D_c 1.845 g cm^{-3}, $F(000) = 1756$, $\mu(Mo-K_\alpha)$ 14.79 cm^{-1}.

Data collection, structure solution and refinement. A Siemens AED single-crystal diffractometer ($\theta/2\theta$ scan mode, niobium-filtered Mo-K_α radiation) was employed. Reflections were measured in the range θ 3–25°; of 5640 independent reflections, 2786 with $I > 2\sigma(I)$ were considered observed, and used in the analysis. The individual profiles were analyzed by Lehmann and Larsen's method [13]. No absorption correction was applied.

The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares with anisotropic thermal parameters in the last cycles for all the non-hydrogen atoms. The final Fourier difference map revealed the presence of a disordered heptane molecule distributed in two positions of occupancy factors 0.5 near an inversion centre. All efforts to localize the terminal carbon atom were unsuccessful. All the hydrogen atoms, except those of the solvent, were placed in calculated positions (C–H 1.00 Å) and refined riding on the corresponding carbon atoms. A weighting scheme $\omega = K[\sigma^2(F_o) + gF_o^2]^{-1}$ was used in the last cycles of refinement, with $K = 0.386$ and $g = 0.0053$. Final R and R' values were 0.0514 and 0.0530, respectively. The SHELX system of computer programs was used [14]. Atomic scattering factors, corrected for anomalous dispersion, were taken from ref. 15. Final atomic coordinates for the non hydrogen atoms are given in Table 2. All calculations were carried out on the Cray X-MP/12 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Bologna and on the Gould Powernode 6040 of the Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Parma.

Additional data (H-atom coordinates, thermal parameters, and structure factors) are available from the authors.

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