Contribution from the Department of Chemistry,
The University of Alberta, Edmonton, Alberta, Canada T6G 2G2

Structure of $[Rh_2Br_2(\mu\text{-}CO)((C_6H_5)_2PCH_2P(C_6H_5)_2)_2]$: A Binuclear Rhodium Carbonyl Complex Having an Unusually Low Carbonyl Stretching Frequency

MARTIN COWIE* and STEPHEN K. DWIGHT

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The structure of $[Rh_2Br_2(\mu\text{-}CO)(Ph_2PCH_2PPh_2)_2]$ has been determined by X-ray crystallography. This binuclear, diphospine-bridged species has a bridging carbonyl ligand and terminal bromo ligands and, on the basis of the structural parameters (Rh–Rh = 2.7566 (9) Å, Rh–$C_{carbonyl}$–Rh = 89.4 (4)°), can be formulated as having a metal–metal bond. The unusually low carbonyl stretching frequency (1745 cm^{-1}, Nujol mull), its low-field ^{13}C chemical shift (227.5 ppm), and the short Rh–$C_{carbonyl}$ distances (1.958 (8) and 1.961 (8) Å) suggest a large amount of back-donation from the metals to the carbonyl ligand. The compound crystallizes in the space group C_{2h}^5-$P2_1/n$ with a = 20.429 (2) Å, b = 11.985 (1) Å, c = 18.865 (2) Å, β = 100.275 (9)°, and Z = 4. On the basis of 4718 unique, observed reflections, the structure was refined by full-matrix, least-squares techniques to R = 0.045 and R_w = 0.055 for 205 parameters varied.

Introduction

The reaction of *trans*-$[RhCl(CO)(DPM)]_2$[1] with NaBr initially yields[2] an asymmetric species $[Rh_2Br(CO)(\mu\text{-}CO)(DPM)_2][Br]$ which undergoes a rearrangement in solution to give a symmetric species having an unusually low value for ν(CO) of 1745 cm^{-1}. On the basis of spectral data, elemental analyses, and its chemistry with SO_2, this symmetric product can equally well be formulated as $[Rh_2Br_2(\mu\text{-}CO)_2(DPM)_2]$, containing two bridging ketonic[3] carbonyl ligands or as $[Rh_2Br_2(\mu\text{-}CO)(DPM)_2]$, having one carbonyl ligand and a formal Rh–Rh bond. The low value for ν(CO) is consistent with a ketonic carbonyl formulation, being comparable to the values observed in $[Pd_2Cl_2(\mu\text{-}CO)(DAM)_2]$[1,4] and $[Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-}DMA)(DPM)_2]$,[1,5] which contain ketonic carbonyl ligands, and the $^{31}P\{^1H\}$ NMR spectrum is very similar to that of other symmetric dirhodium species which have no metal–metal bond.[6,7] Furthermore its reaction with SO_2 yields the dicarbonyl species $[Rh_2(CO)_2(\mu\text{-}Br)(\mu\text{-}SO_2)(DPM)_2][Br]$ as one of the final products. However, these data can also be interpreted in terms of the monocarbonyl formulation. An analogous SO_2-bridged compound,[8,9] $[Rh_2Cl_2(\mu\text{-}SO_2)(DPM)_2]$, has a low value for ν(SO) and has $^{31}P\{^1H\}$ NMR parameters very similar to those in the present carbonyl species, although it has a formal Rh–Rh bond. In addition, the formation of a dicarbonyl product in the reaction with SO_2 can be explained by CO transfer from one molecule to another since a carbonyl-free product, $[Rh_2Br_2(\mu\text{-}SO_2)(DPM)_2]$, is also observed.

The structure determination of the title complex was therefore undertaken in order to unambiguously establish the mode of carbonyl bonding.

Experimental Section

All solvents were dried and degassed prior to use under an atmosphere of dinitrogen. Reactions were routinely performed under Schlenk conditions with an atmosphere of either dinitrogen or carbon monoxide. Infrared spectra were recorded on a Perkin-Elmer Model 467 spectrometer using Nujol mulls on KBr plates. $^{31}P\{^1H\}$ and $^{13}C\{^{31}P\{^1H\}\}$ NMR spectra were recorded by using a Bruker HFX-90 spectrometer.

Crystallization of $[Rh_2Br_2(\mu\text{-}CO)(DPM)_2]$. A 50-mg sample of $[Rh_2Br_2(\mu\text{-}CO)_x(DPM)_2]$ (x = 1 or 2), prepared as described previously,[2] was dissolved in 3 mL of CH_2Cl_2 from which well-formed crystals were obtained by slow diethyl ether diffusion. The crystals were analyzed spectrally as either $[Rh_2Br_2(\mu\text{-}CO)(DPM)_2]$ or $[Rh_2Br_2(\mu\text{-}CO)_2(DPM)_2]$.

Data Collection. A clear red plate of the title complex was mounted on a glass fiber. Preliminary film data showed that the crystal belonged to the monoclinic system with extinctions ($h0l$, $h + l$ odd; $0k0$, k odd) characteristic of the centrosymmetric space group $P2_1/n$, a nonstandard setting of $P2_1/c$. Accurate cell parameters were obtained by a least-squares analysis of 12 carefully centered reflections chosen from diverse regions of reciprocal space (60° ≤ 2θ ≤ 70°, Cu Kα, radiation)

Table I. Summary of Crystal Data and Intensity Collection

compd	$Rh_2Br_2(\mu\text{-}CO)(DPM)_2$
fw	1162.4
formula	$C_{51}H_{44}Br_2OP_4Rh_2$
cell parameters	
a	20.429 (2) Å
b	11.895 (1) Å
c	18.865 (2) Å
β	100.275 (9)°
V	4510.7 $Å^3$
Z	4
density	1.711 (calcd) g cm^{-3}
space group	C_{2h}^5-$P2_1/n$ (nonstandard setting of $P2_1/c$)
cryst dimens	0.240 × 0.088 × 0.301 mm
cryst shape	monoclinic prism $\{010\}$, $\{100\}$, $\{001\}$, $\{\bar{1}02\}$, $\{\bar{2}0\bar{1}\}$, $\{\bar{2}\bar{1}\bar{1}\}$, $\{110\}$, $\{101\}$
cryst vol	0.004 42 mm^3
temp	20 °C
radiatn	Cu Kα
μ	98.229 cm^{-1}
range in abs cor factors	0.190–0.476
receiving aperture	6 × 6 mm
takeoff angle	3.9°
scan speed	2° min^{-1}
scan range	1.00° below Kα_1 to 1.00° above Kα_2
bkgd counts, s	10 (3 ≤ 2θ ≤ 45°), 20 (45 < 2θ ≤ 96), 40 (96 < 2θ < 120°)
2θ limits	3-120°
unique data used ($F_o^2 \geq 3\sigma(F_o^2)$)	4718
final no. of variables	205
error in observn of unit weight	1.392
R	0.045
R_w	0.055

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(1) Abbreviations used: DPM, bis(diphenylphosphino)methane; DAM, bis(diphenylarsino)methane; DMA, dimethyl acetylenedicarboxylate; Ph, phenyl.

(2) Cowie, M.; Dwight, S. K. *Inorg. Chem.*, in press.

(3) The term ketonic carbonyl refers to a carbonyl ligand which bridges two metal centers which are not bonded to each other.

(4) Holloway, R. G.; Penfold, B. R.; Colton, R.; McCormick, M. J. *J. Chem. Soc., Chem. Commun.* **1976**, 485. Colton, R.; McCormick, M. J.; Pannan, C. D. *Aust. J. Chem.* **1978**, *31*, 1425.

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Table II. Positional and Thermal Parameters for the Nongroup Atoms of $[Rh_2Br_2(\mu\text{-}CO)(DPM)_2]$

atom	x^a	y	z	$U_{11}{}^b$	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh(1)	0.580 04 (3)	0.09336 (5)	0.32748 (3)	2.10 (3)	2.26 (3)	2.89 (3)	0.06 (2)	0.98 (2)	−0.06 (3)
Rh(2)	0.448 67 (3)	0.15824 (5)	0.31124 (3)	1.99 (3)	2.13 (3)	3.44 (4)	−0.01 (2)	0.61 (2)	0.25 (3)
Br(1)	0.692 72 (4)	0.03208 (8)	0.31204 (6)	3.03 (4)	3.94 (5)	5.79 (6)	0.57 (4)	1.96 (4)	−0.37 (5)
Br(2)	0.331 05 (5)	0.20589 (9)	0.26417 (8)	2.60 (5)	3.90 (5)	13.0 (1)	0.10 (4)	−0.32 (5)	1.93 (7)
P(1)	0.616 19 (9)	0.2724 (2)	0.3085 (1)	2.35 (9)	2.56 (9)	2.7 (1)	−0.21 (8)	1.02 (8)	−0.01 (8)
P(2)	0.473 70 (9)	0.3473 (2)	0.3022 (1)	2.36 (9)	2.32 (9)	3.2 (1)	0.10 (8)	0.67 (8)	−0.06 (9)
P(3)	0.550 03 (9)	−0.0946 (2)	0.3208 (1)	2.5 (1)	2.31 (9)	3.8 (1)	0.14 (8)	1.02 (8)	0.15 (9)
P(4)	0.407 93 (9)	−0.0248 (2)	0.3104 (1)	2.31 (9)	2.37 (9)	3.3 (1)	−0.26 (8)	0.57 (8)	0.45 (9)
O	0.5269 (3)	0.1498 (6)	0.4559 (3)	4.0 (3)	6.5 (4)	2.7 (4)	0.9 (3)	1.3 (3)	−0.9 (3)
C(1)	0.5210 (4)	0.1375 (6)	0.3938 (5)	2.5 (4)	2.2 (4)	4.6 (6)	−0.5 (3)	1.3 (4)	−0.3 (4)
C(2)	0.5613 (4)	0.3818 (6)	0.3346 (4)	2.4 (4)	2.7 (4)	3.0 (5)	−0.2 (3)	0.5 (3)	−0.6 (3)
C(3)	0.4716 (4)	−0.1243 (6)	0.3513 (4)	3.0 (4)	2.5 (4)	3.1 (5)	0.4 (3)	1.2 (3)	0.3 (3)

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables. [b] The form of the thermal ellipsoid is $\exp[-2\pi^{*2}(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl)]$. The quantities given in the table are the thermal coefficients $\times 10^2$.

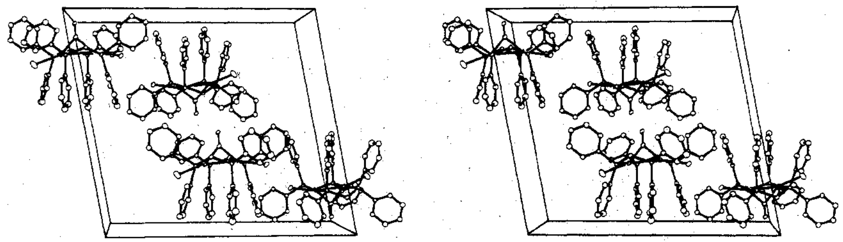

Figure 1. A stereoview of the cell of $[Rh_2Br_2(\mu\text{-}CO)(DPM)_2]$. The x axis is horizontal to the right, the z axis runs from bottom to top, and the y axis goes into the page; 20% thermal ellipsoids are used with the exception of the methylene hydrogen atoms which are drawn artificially small.

and obtained by using a narrow X-ray source. The width at half-height of several strong reflections (ω scan; open counter) lay in the range 0.12–0.17° (see Table I for pertinent crystal data).

Data were collected on an automated Picker four-circle diffractometer equipped with a scintillation counter and pulse-height analyzer tuned to accept 90% of the Cu Kα peak. Background counts were measured at both ends of the scan range with crystal and counter stationary. The intensities of three standard reflections were measured every 100 reflections throughout the data collection. A second set of four standards were monitored twice a day. All remained constant to within 1% of the mean throughout the data collection.

The intensities of 7071 unique reflections ($3° \leq 2\theta \leq 120°$) were measured by using nickel-filtered Cu Kα radiation. Data were processed in the usual manner with a value of 0.05 for p.[10] Absorption corrections were applied to the data using Gaussian integration.[11]

Structure Solution and Refinement. The positions of the Rh, Br, and P atoms were obtained by direct methods using MULTAN.[12] The remaining atoms were located from subsequent least-squares refinements and difference Fourier calculations. Atomic scattering factors were taken from Cromer and Waber's[13] tabulations for all atoms except hydrogen for which the values of Stewart et al.[14] were used. Anomalous dispersion terms[15] for Rh, Br, and P were included in F_c. All carbon atoms of the phenyl rings were refined as rigid groups having D_{6h} symmetry and C–C distances of 1.392 Å. The hydrogen atoms were included as fixed contributions and were not refined. Their idealized positions were calculated from the geometries about their attached carbon atom by using C–H distances of 0.95 Å. Hydrogen atoms were assigned isotropic thermal parameters of 1 Å^2 greater than those of their attached carbon atom. All other nongroup atoms were refined individually with anisotropic thermal parameters.

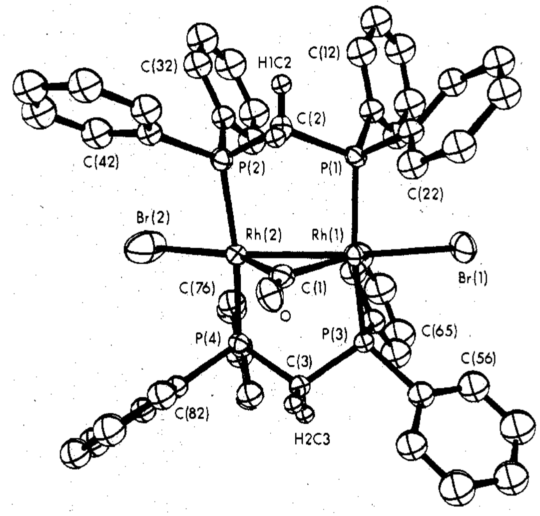

Figure 2. A perspective view of $[Rh_2Br_2(\mu\text{-}CO)(DPM)_2]$ showing the numbering scheme. The numbering on the phenyl carbon atoms starts at the carbon bonded to the phosphorus and increases sequentially around the ring. 50% thermal ellipsoids are used, except for hydrogens which are artificially small.

The final model with 205 parameters varied converged to $R = 0.045$ and $R_w = 0.055$.[16] In the final difference Fourier map the highest 20 peaks were in the vicinities of either the phenyl groups or the Rh and Br atoms (0.45–0.25 e/Å^3). A typical carbon atom on earlier syntheses had an electron density of about 3.5 e/Å^3.

The final positional and thermal parameters of the nonhydrogen atoms and the group atoms are given in Tables II and III, respectively. The derived hydrogen positions and their thermal parameters and a listing of the observed and calculated structure amplitudes used in the refinements are available.[17]

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(10) Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 204.

(11) Besides local programs the following were used in solution and refinement of the structure: FORDAP, the Fourier summation program by A. Zalkin; SFLS-5, structure factors and least-squares refinement by C. J. Prewitt; ORFFE, for calculating bond lengths, angles, and associated standard deviations by W. Busing and H. A. Levy; ORTEP, plotting program by C. K. Johnson; AGNOST, the Northwestern University absorption program which includes the Coppens–Leiserowitz–Rabinowvich logic for Gaussian integration.

(12) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *A27*, 368.

(13) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A.

(14) Stewart, R. F.; Davidson, E. R.; Simpson, W. G. *J. Chem. Phys.* **1965**, *42*, 3175.

(15) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

(16) $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

Table III

Derived Parameters for the Rigid-Group Atoms of $[Rh_2Br_2(\mu\text{-}CO)(DPM)_2]$

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
C(11)	0.6232 (3)	0.3053 (5)	0.2153 (2)	2.5 (1)	C(51)	0.6042 (3)	−0.2070 (4)	0.3643 (5)	3.1 (2)
C(12)	0.6298 (3)	0.4160 (4)	0.1937 (3)	3.8 (2)	C(52)	0.5958 (5)	−0.2493 (5)	0.4308 (3)	3.8 (2)
C(13)	0.6387 (3)	0.4391 (4)	0.1238 (3)	4.3 (2)	C(53)	0.6360 (5)	−0.3367 (5)	0.4626 (4)	5.2 (2)
C(14)	0.6412 (3)	0.3515 (5)	0.0754 (2)	4.6 (2)	C(54)	0.6846 (3)	−0.3817 (4)	0.4278 (5)	5.0 (2)
C(15)	0.6347 (3)	0.2407 (4)	0.0970 (3)	4.8 (2)	C(55)	0.6931 (5)	−0.3393 (5)	0.3612 (3)	5.4 (3)
C(16)	0.6257 (3)	0.2176 (4)	0.1670 (3)	3.5 (2)	C(56)	0.6529 (5)	−0.2520 (5)	0.3295 (4)	4.3 (2)
C(21)	0.6969 (3)	0.3113 (5)	0.3614 (3)	2.3 (1)	C(61)	0.5346 (3)	−0.1274 (6)	0.2240 (3)	3.0 (2)
C(22)	0.7070 (4)	0.2903 (4)	0.4352 (8)	3.1 (2)	C(62)	0.5191 (4)	−0.0366 (4)	0.1774 (4)	3.6 (2)
C(23)	0.7674 (6)	0.3183 (5)	0.4783 (6)	3.6 (2)	C(63)	0.5057 (4)	−0.0540 (5)	0.1033 (3)	5.1 (2)
C(24)	0.8177 (3)	0.3672 (5)	0.4478 (3)	3.4 (2)	C(64)	0.5078 (3)	−0.1622 (6)	0.0757 (3)	5.8 (3)
C(25)	0.8076 (4)	0.3882 (4)	0.3740 (8)	3.4 (2)	C(65)	0.5233 (4)	−0.2530 (4)	0.1222 (4)	6.1 (3)
C(26)	0.7472 (6)	0.3603 (5)	0.3308 (6)	2.9 (2)	C(66)	0.5367 (4)	−0.2356 (5)	0.1963 (3)	4.7 (2)
C(31)	0.4569 (3)	0.3856 (5)	0.2071 (3)	2.4 (1)	C(71)	0.3700 (3)	−0.0935 (5)	0.2259 (2)	2.4 (1)
C(32)	0.4441 (3)	0.4956 (4)	0.1836 (3)	3.5 (2)	C(72)	0.3549 (3)	−0.2076 (5)	0.2272 (3)	3.7 (2)
C(33)	0.4321 (3)	0.5198 (4)	0.1103 (3)	4.7 (2)	C(73)	0.3229 (3)	−0.2606 (4)	0.1648 (3)	4.0 (2)
C(34)	0.4329 (3)	0.4338 (5)	0.0603 (3)	5.0 (2)	C(74)	0.3059 (3)	−0.1997 (5)	0.1011 (2)	4.3 (2)
C(35)	0.4458 (3)	0.3238 (4)	0.0838 (3)	4.7 (2)	C(75)	0.3211 (3)	−0.0857 (5)	0.0999 (3)	5.0 (2)
C(36)	0.4578 (3)	0.2996 (4)	0.1572 (3)	3.7 (2)	C(76)	0.3531 (3)	−0.0326 (4)	0.1623 (3)	3.9 (2)
C(41)	0.4304 (3)	0.4574 (4)	0.3449 (3)	2.4 (1)	C(81)	0.3454 (4)	−0.0352 (5)	0.3681 (5)	2.1 (1)
C(42)	0.3636 (3)	0.4783 (5)	0.3176 (4)	3.9 (2)	C(82)	0.3619 (2)	0.0074 (4)	0.4378 (5)	3.3 (2)
C(43)	0.3301 (2)	0.5628 (5)	0.3475 (3)	4.5 (2)	C(83)	0.3157 (5)	0.0042 (4)	0.4837 (7)	4.2 (2)
C(44)	0.3633 (3)	0.6264 (4)	0.4048 (3)	4.1 (2)	C(84)	0.2529 (4)	−0.0415 (5)	0.4601 (5)	3.8 (2)
C(45)	0.4301 (3)	0.6054 (5)	0.4321 (4)	3.9 (2)	C(85)	0.2363 (2)	−0.0840 (4)	0.3904 (5)	3.8 (2)
C(46)	0.4636 (2)	0.5209 (5)	0.4021 (3)	3.3 (2)	C(86)	0.2825 (5)	−0.0809 (4)	0.3445 (7)	2.9 (2)

Rigid-Group Parameters

	X_c[a]	Y_c	Z_c	δ[b]	ϵ	η
ring 1	0.6322 (2)	0.3284 (4)	0.1454 (2)	3.201 (4)	1.450 (4)	2.943 (3)
ring 2	0.7573 (2)	0.3393 (3)	0.4046 (2)	4.279 (4)	2.126 (9)	0.605 (8)
ring 3	0.4449 (2)	0.4097 (4)	0.1337 (2)	2.992 (4)	1.717 (4)	2.931 (3)
ring 4	0.3968 (2)	0.5419 (3)	0.3748 (2)	−0.720 (4)	2.782 (5)	4.429 (5)
ring 5	0.6444 (2)	−0.2943 (4)	0.3960 (2)	−0.728 (4)	1.086 (6)	1.553 (5)
ring 6	0.5212 (2)	−0.1448 (4)	0.1498 (3)	3.023 (4)	1.786 (4)	3.292 (4)
ring 7	0.3380 (2)	−0.1466 (4)	0.1635 (2)	0.224 (4)	2.000 (4)	2.658 (3)
ring 8	0.2991 (2)	−0.0383 (3)	0.4141 (2)	1.119 (4)	0.895 (8)	6.345 (8)

[a] X_c, Y_c, and Z_c are the fractional coordinates of the centroid of the rigid group. [b] The rigid-group orientation angles δ, ϵ, and η (radians) are the angles by which the rigid body is rotated with respect to a set of axes X, Y, and Z. The origin is the center of the ring: X is parallel to a^*, Z is parallel to c, and Y is parallel to the line defined by the intersection of the plane containing a^* and b^* with the plane containing b and c.

Description of Structure

The unit cell of $[Rh_2Br_2(\mu\text{-}CO)(DPM)_2]$, shown in Figure 1, contains discrete well-separated molecules of the complex. Figure 2 presents a perspective view of the compound including the numbering scheme (phenyl hydrogen atoms have the same number as their attached carbon atom). The inner coordination sphere is shown in Figure 3 along with some relevant bond lengths.

The coordination about each Rh atom is quasi trigonal bipyramidal. Two transoid DPM ligands bridge the Rh atoms in the axial positions with the bridging carbonyl ligand, a terminal bromo ligand on each Rh atom, and a formal Rh–Rh bond completing the coordination in the equatorial plane. The resulting distorted "A-frame" geometry is similar to that observed in $[Rh_2Cl_2(\mu\text{-}SO_2)(DPM)_2]$.[7,8] The distortions of the "A-frame" geometry arise due to steric interactions between the terminal bromo ligands and the phenyl rings of the DPM ligands (Table IV) and due to the presence of a metal–metal bond, both resulting in a flattening of the "A" configuration. Angles about each Rh atom in the equatorial plane clearly show the distortions from trigonal-bipyramidal coordination (Rh–Rh–Br, Rh–Rh–C(1), and Br–Rh–C(1): 167.06 (4), 45.3 (2), and 147.6 (2)°, respectively).

The Rh–Br distances of 2.481 (1) and 2.474 (1) Å are not unusual and compare well with other determinations.[18]

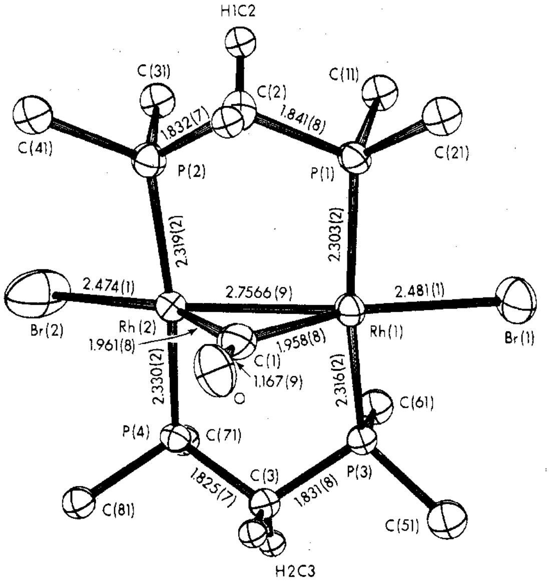

Figure 3. The inner coordination sphere of $[Rh_2Br_2(\mu\text{-}CO)(DPM)_2]$ showing some relevant bond lengths. Only the first carbon atom of each phenyl ring is shown, and 50% thermal ellipsoids are used, except for hydrogens.

Within the Rh–DPM framework most parameters are as expected. The Rh–P distances (average 2.317 (11) Å) and the P–C distances, both methylene and phenyl (average 1.833 (7)

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(17) Supplementary material.

(18) Churchill, M. R.; Julis, S. A. *Inorg. Chem.* **1978**, *17*, 3011. Nave, C.; Truter, M. R. *J. Chem. Soc., Dalton Trans.* **1973**, 2202.

Table IV. Selected Distances (Å) in $[Rh_2Br_2(\mu\text{-}CO)(DPM)_2]$

Bonded Distances

Rh(1)-Rh(2)	2.7566 (8)		P(1)-C(2)	1.841 (8)	1.832 (8)
Rh(1)-Br(1)	2.481 (1)		P(2)-C(2)	1.832 (7)	
Rh(2)-Br(2)	2.474 (1)		P(3)-C(3)	1.830 (8)	
Rh(1)-C(1)	1.958 (8)		P(4)-C(3)	1.825 (7)	
Rh(2)-C(1)	1.961 (8)		P(1)-C(11)	1.831 (5)	1.833 (7)
Rh(1)-P(1)	2.303 (2)	2.317 (11)[a]	P(1)-C(21)	1.828 (4)	
Rh(1)-P(3)	2.316 (2)		P(2)-C(31)	1.824 (5)	
Rh(2)-P(2)	2.319 (2)		P(2)-C(41)	1.844 (4)	
Rh(2)-P(4)	2.330 (2)		P(3)-C(51)	1.833 (5)	
C(1)-O	1.167 (9)		P(3)-C(61)	1.840 (5)	
C(1)-O[b]	1.192 (9)		P(4)-C(71)	1.835 (4)	
			P(4)-C(81)	1.826 (4)	

Nonbonded Distances

P(1)-P(2)	3.026 (3)	C(56)-H(66)	2.68	H2C2-H(46)	2.06		
P(3)-P(4)	2.992 (3)	C(72)-H(86)	2.61	H1C3-H(52)	2.19		
Rh(1)-H(62)	2.65	Br(1)-H(56)	3.15	H2C3-H(72)	2.15		
Rh(2)-H(36)	2.81	Br(2)-H(42)	2.75	H(33)-H(65)[c]	2.21		
C(12)-H(26)	2.59	H1C2-H(12)	2.17	H(35)-H(65)[d]	2.25		

[a] For averaged quantities, the estimated standard deviation is the larger of an individual standard deviation or the standard deviation of a single observation as calculated from the mean. [b] Riding motion corrected; atom O riding on atom C(1). [c] Atom located at $x, 1 + y, z$. [d] Atom located at $1 - x, \bar{y}, \bar{z}$.

and 1.832 (8) Å, respectively), compare well with other determinations.[2,6,8,9,19-21] The Rh–P vectors as viewed down the Rh–Rh axis are slightly staggered (see P–Rh–Rh–P torsion angles in Table V and least-squares planes in Table VI). This skewing of the Rh–DPM framework results in phenyl rings 3 and 6 being forced into the open coordination site opposite the carbonyl ligand, giving rise to close contacts between Rh and the ortho hydrogen atoms (2.65 and 2.81 Å). An almost identical skewing was observed in the chloro/SO_2 analogue $[Rh_2Cl_2(\mu\text{-}SO_2)(DPM)_2]$.[8,9] The Rh–P–C angles, with the exceptions of those for rings 4 and 5 are close to the expected tetrahedral values. In contrast, the Rh–P–C angles involving rings 4 and 5 (121.8 (2)° and 123.1 (2)°, respectively) are significantly larger than the expected tetrahedral values. These distortions seem to arise from steric interactions between the bromo ligand and the phenyl rings, as evidenced by the short Br–H distances involving these rings (Br(1)–H(56) and Br(2)–H(42): 3.15 and 2.75 Å, respectively) which are less than the sums of the van der Waals radii.[22] In the structure of $[Rh_2Cl_2(\mu\text{-}SO_2)(DPM)_2]$[8] where the bromo ligand is replaced by the less bulky chloro ligand these distortions are somewhat less pronounced, with a maximum Rh–P–C angle of 118.9 (2)°. The bromo ligands, in the present compound, are staggered with respect to the DPM phenyl groups, in order to minimize nonbonded contacts between these groups. This staggering is evident in the phenyl–P–Rh–Br torsion angles which range from 40.7 (3) to 80.0 (2)° (Table V).

Formally, the present compound contains a Rh–Rh single bond as suggested by several structural parameters: (i) the Rh–Rh distance of 2.7566 (9) Å falls within the range previously reported for similar Rh–Rh bonded species (2.617 (3)–2.8415 (7) Å)[8,20] and can be contrasted to the distances of 3.1520 (8) and 3.155 (4) Å observed in the "A-frame" species $[Rh_2(CO)_2(\mu\text{-}Cl)(DPM)_2]^+$[6] and $[Rh_2(CO)_2(\mu\text{-}S)(DPM)_2]$,[23] respectively, where no formal metal–metal bond is present; (ii) the Rh–C–Rh bond angle of 89.4 (4)° compares well with other determinations in which a carbonyl ligand bridges a metal–metal bond[19,20,24-27] and is significantly smaller than the values of 119 (3), 106 (3), and 116.4 (6)° observed in $[Pd_2Cl_2(\mu\text{-}CO)(DPM)_2]$[4], $[Pt_2Cl_2(\mu\text{-}CO)(DPM)_2]$,[28] and $[Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-}DMA)(DPM)_2]$,[1,25] respectively, where no metal–metal bond is present; (iii) the Rh–Rh separation is significantly less than the P···P intraligand separations of 3.026 (3) and 2.992 (3) Å as is usually observed in these systems when a Rh–Rh bond is present.[8,20]

Although the above structural parameters suggest a direct metal–metal bond, this formulation is by no means unambiguous. Recent molecular orbital calculations[29] on carbonyl-bridged species with short metal–metal distances have shown that in some cases no metal–metal bond is actually present even though the structural parameters suggest otherwise. Furthermore, these calculations have been substantiated by experimental differential electron density determinations[30] on the compounds in question, showing no significant buildup of electron density along the metal–metal axis.

The carbonyl ligand bridges the two Rh atoms symmetrically as evidenced by the Rh–C distances of 1.958 (8) and 1.961 (8) Å. These distances are significantly shorter than those observed in other Rh systems containing bridging carbonyl ligands where the values of 2.104 (7) and 2.034 (7) Å, observed in $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DPM)_2][BPh_4]$,[1,20] are more typical. Instead, the observed distances are comparable to the values of 1.90 (6) and 1.97 (9) Å obtained in the Pd[4] and Pt[28] analogues $[M_2Cl_2(\mu\text{-}CO)(DAM)_2]$ (M = Pd, Pt) and that of 1.974 (7) Å observed in $[Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-}DMA)(DPM)_2]$.[5] It is notable that these distances correspond to ketonic carbonyl species which show low values for $\nu(CO)$ in the infrared spectrum similar to that observed for the present compound. It is also relevant that the analogous SO_2 species $[Rh_2Cl_2(\mu\text{-}SO_2)(DPM)_2]$ has short Rh–S bonds and a low value for $\nu(SO)$ in the infrared spectrum.[7,8]

In the title compound the C(1)–O distance is not as long as one might expect on the basis of the low value of $\nu(CO)$ but rather is comparable to that observed in "normal" bridging carbonyl ligands which have $\nu(CO)$ ca. 100 cm^{-1} higher. However, carbonyl C–O distances are not overly sensitive to

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Table V. Selected Angles (Deg) in $[Rh_2Br_2(\mu\text{-CO})(DPM)_2]$

Bond Angles

Rh(2)-Rh(1)-Br(1)	167.06 (4)	Rh(1)-P(3)-C(51)	123.1 (2)
Rh(2)-Rh(1)-P(1)	93.24 (5)	Rh(1)-P(3)-C(61)	104.8 (2)
Rh(2)-Rh(1)-P(3)	91.22 (5)	Rh(2)-P(4)-C(71)	121.2 (2)
Rh(2)-Rh(1)-C(1)	45.3 (2)	Rh(2)-P(4)-C(81)	110.3 (2)
Br(1)-Rh(1)-C(1)	147.6 (2)	C(2)-P(1)-C(11)	105.2 (3)
Br(1)-Rh(1)-P(1)	85.62 (5)	C(2)-P(1)-C(21)	102.0 (3)
Br(1)-Rh(1)-P(3)	87.25 (5)	C(2)-P(2)-C(31)	105.8 (3)
P(1)-Rh(1)-P(3)	166.78 (8)	C(2)-P(2)-C(41)	102.2 (3)
P(1)-Rh(1)-C(1)	95.9 (2)	C(3)-P(3)-C(51)	102.2 (3)
P(3)-Rh(1)-C(1)	96.1 (2)	C(3)-P(3)-C(61)	105.5 (3)
Rh(1)-Rh(2)-Br(2)	165.45 (5)	C(3)-P(4)-C(71)	103.7 (3)
Rh(1)-Rh(2)-P(2)	93.24 (5)	C(3)-P(4)-C(81)	103.1 (3)
Rh(1)-Rh(2)-P(4)	94.51 (5)	C(11)-P(1)-C(21)	104.6 (3)
Rh(1)-Rh(2)-C(1)	45.2 (2)	C(31)-P(2)-C(41)	103.4 (3)
Br(2)-Rh(2)-C(1)	149.2 (2)	C(51)-P(3)-C(61)	105.8 (3)
Br(2)-Rh(2)-P(2)	87.96 (5)	C(71)-P(4)-C(81)	104.8 (3)
Br(2)-Rh(2)-P(4)	83.61 (5)	P(1)-C(11)-C(12)	120.7 (3)
P(2)-Rh(2)-P(4)	171.41 (7)	P(1)-C(11)-C(16)	119.2 (3)
P(2)-Rh(2)-C(1)	92.0 (2)	P(1)-C(21)-C(22)	117.3 (3)
P(4)-Rh(2)-C(1)	96.1 (2)	P(1)-C(21)-C(26)	122.7 (3)
Rh(1)-C(1)-Rh(2)	89.4 (4)	P(2)-C(31)-C(32)	122.7 (3)
Rh(1)-C(1)-O	135.3 (6)	P(2)-C(31)-C(36)	117.3 (3)
Rh(2)-C(1)-O	135.3 (6)	P(2)-C(41)-C(42)	118.7 (3)
P(1)-C(2)-P(2)	111.0 (4)	P(2)-C(41)-C(46)	121.2 (3)
P(3)-C(3)-P(4)	109.9 (4)	P(3)-C(51)-C(52)	120.4 (4)
Rh(1)-P(1)-C(2)	112.6 (3)	P(3)-C(51)-C(56)	119.6 (4)
Rh(2)-P(2)-C(2)	114.1 (2)	P(3)-C(61)-C(62)	116.2 (4)
Rh(1)-P(3)-C(3)	114.0 (2)	P(3)-C(61)-C(66)	123.8 (4)
Rh(2)-P(4)-C(3)	112.1 (2)	P(4)-C(71)-C(72)	118.7 (3)
Rh(1)-P(1)-C(11)	115.4 (2)	P(4)-C(71)-C(76)	121.2 (3)
Rh(1)-P(1)-C(21)	115.6 (2)	P(4)-C(81)-C(82)	117.4 (3)
Rh(2)-P(2)-C(31)	108.0 (2)	P(4)-C(81)-C(86)	122.6 (3)
Rh(2)-P(2)-C(41)	121.8 (2)		

Torsion Angles

P(1)-Rh(1)-Rh(2)-P(2)	−5.42 (7)
P(1)-Rh(1)-Rh(2)-P(4)	170.87 (7)
P(2)-Rh(2)-Rh(1)-P(3)	−172.97 (7)
P(3)-Rh(1)-Rh(2)-P(4)	3.32 (8)
C(11)-P(1)-Rh(1)-Br(1)	73.8 (2)
C(21)-P(1)-Rh(1)-Br(1)	−48.7 (2)
C(31)-P(2)-Rh(2)-Br(2)	−65.2 (2)
C(41)-P(2)-Rh(2)-Br(2)	54.1 (2)
C(51)-P(3)-Rh(1)-Br(1)	40.7 (3)
C(61)-P(3)-Rh(1)-Br(1)	−80.0 (2)
C(71)-P(4)-Rh(2)-Br(2)	63.1 (2)
C(81)-P(4)-Rh(2)-Br(2)	−59.7 (2)
C(2)-P(1)-Rh(1)-C(1)	−17.9 (4)
C(2)-P(2)-Rh(2)-C(1)	28.3 (4)
C(3)-P(3)-Rh(1)-C(1)	17.6 (4)
C(3)-P(4)-Rh(2)-C(1)	−24.8 (4)
C(11)-P(1)-P(2)-C(31)	2.6 (3)
C(11)-P(1)-P(3)-C(61)	−6.5 (3)
C(21)-P(1)-P(2)-C(41)	5.2 (4)
C(21)-P(1)-P(3)-C(51)	−9.3 (3)
C(31)-P(2)-P(4)-C(71)	−3.0 (3)
C(41)-P(2)-P(4)-C(81)	−6.6 (3)
C(51)-P(3)-P(4)-C(81)	30.1 (4)
C(61)-P(3)-P(4)-C(71)	19.1 (3)

such changes owing to the relatively large uncertainty in the atomic positions. Therefore the present distance is, within experimental error, comparable to the analogous distances in the ketonic carbonyl species of $[Rh_2Cl_2(\mu\text{-CO})(\mu\text{-DMA})(DPM)_2]$ and $[PdCl_2(\mu\text{-CO})(DPM)_2]$ where the ν(CO) values of 1700 and 1720 cm^{-1}, respectively, are observed. Applying a riding motion correction to the present C(1)–O distance (atom O riding on C(1)) yields a corrected value of 1.192 (9) Å which is closer to the value we had expected on the basis of spectral parameters.

Discussion

The structural determination of the title compound has unambiguously established it to be a monocarbonyl species having a formal Rh–Rh bond and not the alternate dicarbonyl

Table VI

Least-Squares Planes Calculations[a]

plane no.	equation	plane no.	equation	plane no.	equation
1	$0.0657X - 0.1380Y - 0.9883Z + 5.4452 = 0.0$	2	$0.1087X - 0.0040Y - 0.9941Z + 4.8736 = 0.0$	3	$0.2867X + 0.9530Y - 0.0975Z - 3.5520 = 0.0$

Deviation from Planes, Å

plane no.	Rh(1)	Rh(2)	Br(1)	Br(2)	P(1)	P(2)	P(3)	P(4)	C(1)	C(2)	C(3)	O
1	−0.0091 (6)	0.0097 (6)			0.098 (2)	0.100 (2)				−0.639 (8)[b]		
2	−0.0053 (6)	0.0056 (6)					0.063 (2)	−0.060 (2)			−0.683 (8)[b]	
3	−0.0044 (5)	0.0066 (5)	0.0037 (9)	−0.012 (1)					−0.034 (7)			−0.032 (7)

[a] X, Y, and Z are orthogonal coordinates (Å) with X along the a axis, Y in the a-b plane and Z along the c^* axis. [b] Not included in least-squares plane calculations.

species as was originally suggested[2] by the spectral and chemical studies (vide supra). The spectral parameters are consistent with both formulations (mono- and dicarbonyl species), but the reaction of the compound with SO_2, yielding a dicarbonyl product, at first glance actually favors the dicarbonyl formulation. Prompted by the present structural characterization, however, a reinvestigation of the $^{31}P\{^1H\}$ NMR spectra during the slow stepwise addition of SO_2 indicates[2] that the dicarbonyl species results from CO transfer from one monocarbonyl species to another. In fact tricarbonyl species are also obtained by a similar CO transfer and are observed at intermediate times in the reaction. A somewhat analogous, facile CO transfer has been reported[19,31] between $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DPM)_2]^+$ and $[Rh_2(CO)_2(\mu\text{-}Cl)(DPM)_2]^+$. These results clearly indicate the need for further structural and spectral characterizations of related complexes in order to yield the needed correlations between their structural and spectral parameters.

The complex $[Rh_2Br_2(\mu\text{-}CO)(DPM)_2]$ is only the second structurally characterized example with rhodium[32] in which a carbonyl ligand occupies the bridging site in preference to a halide ligand. Generally the reverse is true;[33] yet in binuclear DPM-,[2,5] DAM-,[4,28] and analogous diphosphazane-bridged[32] complexes of the group 8 metals, several complexes have now been characterized with bridging CO and terminal halide ligands. The closely related, SO_2-bridged complex $[Rh_2Cl_2(\mu\text{-}SO_2)(DPM)_2]$ is also anomalous in this regard having bridging SO_2 and terminal chloro groups.[8,9] It seems that in these complexes there is a strong tendency for the better π-acceptor ligand to enter the bridging site, even when initial attack by this ligand is terminal.[8] In the bridging site the π-acceptor ligand can accept electron density from both electron-rich metals, which in the present complex would account for the low value of $\nu(CO)$ and the short rhodium–carbonyl distances. In addition the buildup of electron density on the carbonyl ligand, resulting from the large degree of back-donation from the metal, is also reflected in the low-field chemical shift (227.5 ppm) of the ^{13}C carbonyl resonance. The trend in spectral parameters with increasing metal–carbonyl back-bonding is seen clearly in the series of closely related complexes $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DPM)_2]^+$, $[Rh_2I(CO)(\mu\text{-}CO)(DPM)_2][I]$, and $[Rh_2Br_2(\mu\text{-}CO)(DPM)_2]$, where we observe that the ^{13}C chemical shifts for the bridging carbonyl ligands (203.2,[34,35] 212.8,[34] and 227.5 ppm, respectively) directly parallel the corresponding $\nu(CO)$ values (1850, 1810, and 1745 cm^{-1}, respectively).[36] In contrast, however, the ketonic carbonyl complexes $[Rh_2X_2(\mu\text{-}CO)(\mu\text{-}DMA)(DPM)_2]$ (X = Cl, Br, I),[1] which have even lower values of $\nu(CO)$ of ca. 1700 cm^{-1} have relatively high-field ^{13}C shifts of ca. 190 ppm.[37] It is unclear to us at this time why the ketonic carbonyl species have such different ^{13}C chemical shifts from the present compound when the carbonyl stretching frequencies are comparable, but it is clear that the use of spectral parameters to assign the mode of carbonyl bonding is fraught with difficulties, at least until more complete spectral and structural correlations are available.

Further studies are now under way investigating the chemistry of this interesting carbonyl species in order to obtain further information on the bonding of the carbonyl ligand and other molecules in this and related complexes.

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Supplementary Material Available: Table VII showing idealized hydrogen parameters and a listing of the observed and calculated structure amplitudes (15 pages). Ordering information is given on any current masthead page.

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