symmetrical pentahapto bonding in cyclopentadienyl complexes of the actinides. Presumably the lanthanide complexes also show this geometry. The complicated bridging structure found for $Sm(C_5H_5)_3$ would appear to be anomalous, but the severe experimental difficulties associated with that structure analysis leaves the issue open.

Registry No. $U(C_5H_4CH_2C_6H_5)_3Cl$, 37325-10-3.

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Crystal and Molecular Structure of Tetrakis(triphenylphosphine)di-μ-carbonyl-dirhodium(0)-Bis(dichloromethane) Solvate

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The crystal and molecular structure of tetrakis(triphenylphosphine)di-μ-carbonyl-dirhodium(0)-bis(dichloromethane) solvate, $[Rh(PPh_3)_2CO]_2 \cdot 2CH_2Cl_2$, has been obtained from counter X-ray data. The complex crystallizes in the monoclinic space group $C2/c$ with four dimeric formula units in a cell of dimensions $a = 23.213$ (19), $b = 13.171$ (6), $c = 24.423$ (12) Å, and $\beta = 65.45$ (1)°. The structure was refined by full-matrix least-squares methods to a final value of $R = 0.067$ for 5682 independent reflections having $F^2 > 3\sigma(F^2)$. The complex is dimeric, with the two rhodium(0) atoms linked by two carbonyl bridges; there is a twofold rotation axis passing through the center of the dimer. The Rh–Rh separation of 2.630 (1) Å is indicative of the presence of a metal–metal bond, and the geometry at the metals is very different from other five-coordinate structures. There may be an interaction between the carbonyl groups and the dichloromethane molecules.

Introduction

Complexes having the molecular formulation $[(Ph_3P)_2(S)Rh(CO)]_2$, where S is dichloromethane or ethanol, were first prepared by Wilkinson and coworkers[1] by concentrating a benzene solution of the parent dimer $[(Ph_3P)_2Rh(CO)_2]_2$ under a stream of nitrogen or argon in the presence of dichloromethane or ethanol, which results in the displacement of 2 mol of carbon monoxide per dimer. In contrast to this behavior, these workers found that treatment of a solution of the parent dimer with molecular hydrogen resulted in the reversible formation of the hydrido precursor according to the equilibrium expression

$$[(Ph_3P)_2Rh(CO)_2]_2 \underset{2CO}{\overset{H_2}{\rightleftarrows}} 2RhH(CO)_2(PPh_3)_2 \qquad (1)$$

The solvated complexes are reversibly converted to the parent dimer in the presence of carbon monoxide (eq 2), irreversibly

$$[(Ph_3P)_2(S)Rh(CO)]_2 \underset{2N_2}{\overset{CO}{\rightleftarrows}} [(Ph_3P)_2Rh(CO)_2]_2 + 2S \qquad (2)$$

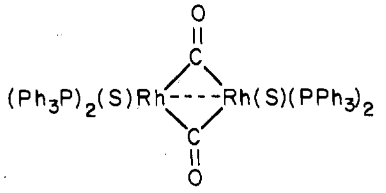
absorb hydrogen in the presence of a large excess of triphenylphosphine to re-form the hydrido starting complex $RhH(CO)(PPh_3)_3$ (eq 3), and readily undergo bridge cleavage

$$[(Ph_3P)_2(S)Rh(CO)]_2 \longrightarrow \left\{ \begin{array}{l} \xrightarrow{H_2\ +\ 2PPh_3} 2RhH(CO)(PPh_3)_3 + 2S \\ \\ \xrightarrow{I_2} 2(Ph_3P)_2(CO)RhI + 2S \end{array} \right. \qquad (3)$$

in the presence of iodine (eq 3).

The solid-state and solution infrared spectra of the parent dimer indicate the presence of *both* terminal and bridging carbonyl groups, whereas the solid-state infrared spectra of the solvated complexes show only bridging carbonyl bands. However, the solution infrared spectrum of the dichloromethane derivative shows the presence of both terminal and bridging carbonyl bands, the appearance of which was attributed to tautomeric isomerization of the complex in solution. This behavior is analogous to that observed for $Co_2(CO)_8$ in solution.[2]

Since the solid-state infrared spectra of the solvated complexes show bands attributable only to bridging carbonyl groups and since it is impossible to precipitate the complexes in the absence of dichloromethane or ethanol, Wilkinson and coworkers[1] suggested that the complexes should be formulated as dimers (I), but in the absence of crystallographic and magnetic data they were unable to present any compelling evidence for the presence of a rhodium–rhodium bond or for an interaction between the solvent molecules and the metal. In order to determine both the coordination geometry about each rhodium(0) atom and the role of the solvent molecules, we have undertaken a three-dimensional structural investigation of the dichloromethane complex.[3]



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Experimental Section

Data Collection and Reduction. Dark red square-biprismatic crystals of $[(Ph_3P)_2Rh(CO)]_2 \cdot 2CH_2Cl_2$ were obtained by treating a solution containing 0.25 g of $RhH(CO)(PPh_3)_3$ in 10 ml of benzene with carbon monoxide for 30 min.[1] The resulting yellow-orange solution was then concentrated to a volume of approximately 5 ml under a stream of nitrogen in the presence of a small amount of dichloromethane, giving a very dark red solution. After standing for several hours in a tightly stoppered erlenmeyer flask, dark red crystals of the complex were isolated by filtration, washed with dichloromethane, and dried by suction. Decomposition occurs upon exposure of the crystals to the atmosphere for several days, necessitating storage in an inert atmosphere.

Precession and Weissenberg photography indicated that the crystals belong to the monoclinic system, and examination of the *hk*0, *h*0*l*, *hk*1, and *h*1*l* zones revealed systematic absences of $h + k$ odd for *hkl* and *l* odd for *h*0*l*, which implies that the space group is either $C_{2h}{}^6$-$C2/c$ or $C_s{}^4$-Cc. Examination of a Wilson plot indicated that the centrosymmetric choice $C2/c$ is the correct space group. The cell constants, obtained by the least-squares procedure of Busing and Levy[4] are $a = 23.213$ (19), $b = 13.171$ (6), $c = 24.423$ (12) Å, and $\beta = 65.45$ (1)°. The observations were made at 25°, with the wavelength assumed as λ(Mo Kα_1) 0.7093 Å. A density of 1.447 g cm^{-3} calculated for four dimeric formula units in the cell is in acceptable agreement with the measured value of 1.42 (2) g cm^{-3} obtained by flotation in dichloromethane-carbon tetrachloride solution. Hence, the dimer is constrained to lie on either a twofold rotation axis $C_2(2)$ or a center of inversion $C_i(\bar{1})$.

Diffraction data were collected on a Picker four-circle automatic diffractometer using Mo Kα radiation. The square-biprismatic crystal had faces (001), (00$\bar{1}$), (101), ($\bar{1}0\bar{1}$), (1$\bar{1}$0), ($\bar{1}$10), (110), and ($\bar{1}\bar{1}$0), the separation between mutually parallel three-sided faces (initial set of four faces) being 0.065 cm and that between mutually parallel four-sided faces (latter set of four faces) being 0.048 cm. The crystal was mounted on a glass fiber roughly parallel to the a^* axis and was coated with a clear adhesive liquid in order to minimize exposure to air. The mosaicity of the crystal was examined by means of the narrow-source, open-counter ω-scan technique described by Furnas.[5] The widths at half-height for eight strong reflections in various regions of reciprocal space were found to lie in the range 0.08–0.14°, which is acceptably low. Slight splitting was observed in many of the ω scans, but in view of the difficulty in growing suitable crystals, we were forced to use this crystal.

Intensity data were collected at a takeoff angle of 2.0°. At this angle the peak intensity was about 90% of the maximum value as a function of takeoff angle. The counter aperture, chosen to minimize extraneous background, was 5.0 mm high and 5.0 mm wide and was positioned 32 cm from the crystal. The data were collected by the θ–2θ scan technique at a scan rate of 2.0°/min. Allowance was made for both Kα_1 and Kα_2 radiations by using a scan range of from 1.0° below the calculated Kα_1 peak to 1.0° above the calculated Kα_2 peak position. Stationary-counter, stationary-crystal background counts of 10-sec duration were taken at each end of the scan.

The Mo radiation was filtered through a 3.0-mil Nb foil after diffraction from the crystal in order to remove the Kβ radiation. The pulse height analyzer was set for approximately a 90% window. A unique data set having 2θ(Mo) $\leqslant 58°$ was gathered, a total of 10,370 intensities being measured. As a check on crystal and electronic stability, the intensities of three standard reflections were measured after every 100 reflections. The results indicated a steady decrease in intensity throughout the run, presumably due to partial decomposition of the crystal in the X-ray beam. The diminution of intensity was plotted against cumulative X-ray exposure, and a least-squares fit was made.[6] The observed intensities of all reflections were appropriately scaled upward to take into account this attenuation, which was such that the intensity of a typical standard reflection at the end of the run was only 88% of its original value. There were very few intensities above background at values of $2\theta > 58°$.

Data processing was carried out as described by Corfield, Doedens, and Ibers.[7] A linear background correction was applied to the data, and the estimated standard deviation in each intensity measurement was calculated by the expression[8]

$$\sigma(I) = [C + 0.25(t_s/t_b)^2(B_h + B_l) + (pI)^2]^{1/2}$$

where C is the total peak count obtained in scan time t_s and where B_h and B_l are background counts obtained in time t_b. The value of p was selected as 0.05 on the basis of values assigned to previously studied crystals.[6,9-11] The values of I and $\sigma(I)$ were corrected for Lorentz-polarization and absorption effects. The linear absorption coefficient, μ, of this crystal for Mo Kα radiation was calculated to be 7.71 cm^{-1}, and for this sample the transmission coefficients evaluated by numerical integration[12] were found to vary from 0.66 to 0.77. Of the 10,370 independent intensities measured, 5862 exceeded 3 times their estimated standard deviations.

Solution and Refinement of Structure. The position of the rhodium atom was determined from a three-dimensional Patterson function, and four cycles of least-squares refinement of this position were run. It was apparent from the Patterson map that the dimer had C_2 symmetry due to the close proximity of the rhodium atom to the C_2 axis. All least-squares calculations in this analysis were carried out on F, the function minimized being $\Sigma w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure amplitudes, and the weights w were taken as $4F_o{}^2/\sigma^2(F_o)^2$. In all calculations of F_c the atomic scattering factors for Rh, Cl, and P were taken from Cromer and Waber,[13] that for H was taken from Stewart, Davidson, and Simpson,[14] and those for C and O were taken from the tabulation of Ibers.[15] The effects of the anomalous dispersion[16] of Rh were included in calculations of F_c, the values of $\Delta f'$ and $\Delta f''$ being taken from Cromer.[17] Only the data set having $2\theta < 40°$ was used in the early stages of refinement.

Initially, a fixed scale factor was used and the rhodium atom was assigned a variable isotropic thermal parameter, both of these parameters being derived from the Wilson plot. After four cycles of least-squares refinement, the agreement factors $R_1 = \Sigma ||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ were 0.456 and 0.573, respectively.

The first difference Fourier map revealed the positions of the two phosphorus atoms. Two cycles of isotropic least-squares refinement on these two positions and that of the rhodium atom gave values of $R_1 = 0.351$ and $R_2 = 0.464$. Subsequent difference Fourier syntheses revealed the positions of the 36 phenyl carbon atoms, the carbon and oxygen atoms of the carbonyl group, and the carbon and two chlorine atoms of the dichloromethane molecule. After two cycles of isotropic least-squares calculations on the positions of all 44 nonhydrogen atoms in the asymmetric unit, the values of R_1 and R_2 reduced to 0.106 and 0.152, respectively. A subsequent difference Fourier map indicated that there may be disorder in the positions of the two chlorine atoms in the dichloromethane moiety, but all attempts to describe this disorder (including twofold and threefold disorder with variable occupancies assigned to Cl) were unsuccessful. At this stage of refinment additional data were utilized, giving a total of 3592 intensities which were greater than 3 times their estimated standard deviations and the phenyl rings were refined as rigid groups of D_{6h} symmetry (C–C = 1.390 Å and C–H = 0.90 Å; the C–H distance, which is shorter than the known average value for such bonds, was chosen to allow for the contraction of bonds involving hydrogen atoms normally calculated in X-ray experiments[18-20]). Variable isotropic thermal parameters were

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Table I. Positional and Group Parameters for $[(Ph_3P)_2Rh(CO)]_2 \cdot 2CH_2Cl_2$

Atom	x	y	z
Rh	0.05866 (2)	−0.01230 (3)	0.20875 (2)
P1	0.12034 (8)	0.11012 (12)	0.22714 (7)
P2	0.12951 (7)	−0.09462 (12)	0.12283 (7)
C38[a]	0.0190 (3)	−0.0558 (5)	0.2974 (3)
O	0.0455 (2)	−0.0866 (5)	0.3259 (2)
C37[a]	0.4631 (8)	0.2051 (16)	0.1079 (8)
Cl1	0.3912 (3)	0.1739 (8)	0.1586 (3)
Cl2	0.4847 (3)	0.1315 (5)	0.0435 (2)

Group	x_c[b,c]	y_c	z_c	ϕ	θ	ρ
Ph1	0.0491 (2)	0.2715 (3)	0.3338 (2)	3.091 (5)	−2.347 (3)	−2.087 (5)
Ph2	0.1806 (2)	0.2578 (3)	0.1119 (2)	1.741 (4)	2.571 (3)	2.130 (4)
Ph3	0.2332 (2)	0.0362 (3)	0.2621 (2)	2.974 (3)	2.825 (3)	−0.659 (3)
Ph4	0.1314 (2)	−0.0292 (3)	−0.0054 (2)	1.133 (4)	−3.026 (3)	1.830 (3)
Ph5	0.2787 (2)	−0.0839 (2)	0.0930 (1)	0.016 (2)	2.885 (3)	−2.874 (3)
Ph6	0.1078 (2)	−0.3376 (2)	0.1350 (2)	−1.863 (6)	1.980 (3)	−2.937 (6)

[a] C38 is the carbonyl carbon; C37 is the methylene chloride carbon. [b] x_c, y_c, and z_c are fractional coordinates of the group centers. The angles ϕ, θ, and ρ are expressed in radians. [c] The numbers in parentheses here and elsewhere in this paper refer to the estimated standard deviations in the least significant figure.

Table II. Thermal Parameters for $[(Ph_3P)_2Rh(CO)]_2 \cdot 2CH_2Cl_2$

Atom	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Rh	0.00144 (1)	0.00360 (3)	0.00125 (1)	−0.00007 (1)	−0.00025 (1)	−0.00002 (1)
P1	0.00188 (4)	0.00370 (9)	0.00143 (3)	−0.00013 (4)	−0.00052 (3)	−0.00001 (4)
P2	0.00153 (3)	0.00437 (9)	0.00120 (3)	−0.00008 (4)	−0.00026 (2)	−0.00016 (4)
C38	0.0021 (2)	0.0049 (4)	0.0014 (1)	−0.0002 (2)	−0.0003 (1)	0.0003 (2)
O	0.0025 (1)	0.0104 (5)	0.0022 (1)	0.0003 (2)	−0.0008 (1)	0.0019 (2)
C37	0.0049 (5)	0.0261 (21)	0.0055 (5)	−0.0009 (8)	−0.0020 (4)	−0.0033 (8)
C11	0.0079 (2)	0.0443 (12)	0.0060 (2)	−0.0077 (4)	−0.0005 (2)	−0.0029 (4)
C12	0.0084 (2)	0.0271 (7)	0.0046 (1)	−0.0018 (3)	−0.0010 (1)	−0.0029 (2)

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

assigned to the carbon atoms in the six phenyl rings and to the carbon and chlorine atoms in dichloromethane, and anisotropic thermal parameters were assigned to the remaining five nonhydrogen atoms. After two cycles of least-squares calculations, the values of R_1 and R_2 reduced to 0.078 and 0.108, respectively.

All of the data were now used, giving 5862 intensities which were greater than 3 times their estimated standard deviations. Assuming no disorder in the dichloromethane moiety, one cycle of least-squares calculations was run on all 44 of the nonhydrogen atoms, allowing the thermal parameters of the Rh atom, the two P atoms, the carbonyl C and O atoms, and the dichloromethane C and two Cl atoms to vary anisotropically and those of the ring carbon atoms to vary isotropically; all of the ring hydrogen atoms were given fixed isotropic thermal parameters of 6.0 Å^2, and none of their parameters were varied. This reduced the values of R_1 and R_2 to 0.073 and 0.101, respectively. It was decided to reject the 180 reflections with $2\theta < 15°$ since agreement for these data was relatively poor ($R_1 = 0.141$), $|F_o|$ being much larger than $|F_c|$; this observation is mainly due to errors in estimating background corrections for the low-angle reflections when niobium filters are used and has been discussed elsewhere.[11,21,22] One cycle of least-squares refinement gave values of $R_1 = 0.068$ and $R_2 = 0.086$. This significant improvement in R_2[23] supports the decision to reject the 180 low-angle reflections.

A final difference Fourier map showed two peaks greater than 1 e/Å^3, the highest being 1.5 e/Å^3, and both peaks were located in the region of dichloromethane. These peaks cannot be assigned as hydrogen atoms on the basis of any reasonable geometry for dichloromethane and are presumably due to the inadequacy of our description of the libration of the chlorine atoms; it was, therefore, impossible to locate the hydrogen atoms of dichloromethane in the final difference Fourier synthesis. An additional cycle of least-squares refinement was run because the previous cycle had not converged and gave values of $R_1 = 0.067$ and $R_2 = 0.086$. In this final cycle of least-squares refinement, no parameter exhibited a shift of more than 0.5 times its estimated standard deviation, which is taken as evidence that the refinement has converged. The value of R_2 showed no apparent dependence on $\sin\theta$ or on $|F_o|$,[12e] which suggests that our choice of $p = 0.05$ is essentially correct. An examination of the final values of $|F_o|$ and $|F_c|$ indicated to us that no correction for secondary extinction was necessary.

The positional and thermal parameters derived from the last cycle of least-squares refinement, along with their associated standard deviations as estimated from the inverse matrix, are presented in Tables I and II. The calculated positional parameters of the ring carbon and hydrogen atoms are presented in Tables III and IV, respectively. The observed and calculated structure amplitudes are available.[24]

Description of the Structure

The crystal structure of $[(Ph_3P)_2Rh(CO)]_2 \cdot 2CH_2Cl_2$ consists of dimeric units being located on a twofold rotation axis and lying in close proximity to two dichloromethane molecules. The principal intramolecular distances and angles are given in Table V. The Rh-Rh separation of 2.630 (1) Å is comparable to the values of 2.69 (1) Å in rhodium metal,[25] 2.618 (5) Å in $[Rh(C_4H_{10}N_2O_2)(C_2H_3O_2)(PPh_3)]_2$,[26] and the average values of 2.663 (2), 2.732 (8), and 2.776 (1) Å found in the cluster compounds $[(\pi\text{-}C_5H_5)(CO)Rh]_3$,[27] Rh_4-

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Table III. Derived Parameters for Group Carbon Atoms

Group	Atom	*x*	*y*	*z*	*B*, Å^2
Ph1	C1	0.0795 (4)	0.2034 (4)	0.2872 (2)	3.6 (1)
	C2	0.0623 (3)	0.1735 (3)	0.3465 (2)	4.8 (2)
	C3	0.0319 (2)	0.2416 (4)	0.3932 (2)	5.7 (2)
	C4	0.0188 (4)	0.3396 (4)	0.3805 (2)	5.7 (2)
	C5	0.0360 (4)	0.3695 (3)	0.3212 (3)	6.1 (2)
	C6	0.0663 (2)	0.3014 (4)	0.2745 (2)	5.2 (2)
Ph2	C7	0.1569 (3)	0.1944 (4)	0.1619 (2)	3.5 (1)
	C8	0.1214 (2)	0.2131 (5)	0.1290 (2)	4.8 (2)
	C9	0.1452 (3)	0.2765 (4)	0.1290 (2)	4.8 (2)
	C10	0.2044 (3)	0.3212 (5)	0.0619 (2)	6.1 (2)
	C11	0.2398 (2)	0.3026 (5)	0.0949 (2)	5.8 (2)
	C12	0.2160 (2)	0.2392 (4)	0.1449 (2)	4.5 (1)
Ph3	C13	0.1840 (2)	0.0700 (4)	0.2485 (2)	3.2 (1)
	C14	0.1995 (2)	−0.0326 (3)	0.2435 (2)	4.2 (1)
	C15	0.2488 (3)	−0.0663 (3)	0.2572 (3)	5.8 (2)
	C16	0.2824 (2)	0.0024 (4)	0.2758 (3)	6.1 (2)
	C17	0.2669 (2)	0.1050 (4)	0.2807 (2)	5.1 (2)
	C18	0.2176 (2)	0.1387 (3)	0.2671 (2)	4.5 (1)
Ph4	C19	0.1309 (2)	−0.0586 (4)	0.0495 (2)	3.6 (1)
	C20	0.0798 (2)	−0.0054 (4)	0.0480 (2)	5.3 (2)
	C21	0.0803 (2)	0.0241 (4)	−0.0069 (3)	7.0 (2)
	C22	0.1319 (3)	0.0003 (5)	−0.0602 (2)	6.4 (2)
	C23	0.1829 (2)	−0.0529 (4)	−0.0587 (2)	5.8 (2)
	C24	0.1824 (2)	−0.0824 (4)	−0.0039 (2)	4.8 (2)
Ph5	C25	0.2153 (2)	−0.0926 (3)	0.1035 (2)	3.3 (1)
	C26	0.2461 (2)	0.0001 (3)	0.0861 (2)	4.1 (1)
	C27	0.3095 (2)	0.0088 (3)	0.0756 (2)	4.9 (2)
	C28	0.3421 (2)	−0.0753 (4)	0.0825 (3)	5.3 (2)
	C29	0.3112 (2)	−0.1680 (3)	0.1000 (2)	5.3 (2)
	C30	0.2478 (2)	−0.1767 (3)	0.1105 (2)	4.3 (1)
Ph6	C31	0.1446 (6)	−0.2330 (3)	0.1278 (2)	3.4 (1)
	C32	0.1329 (3)	−0.2958 (4)	0.0776 (2)	4.9 (2)
	C33	0.1262 (4)	−0.4004 (3)	0.0849 (2)	6.0 (2)
	C34	0.1010 (6)	−0.4423 (3)	0.1423 (2)	5.5 (2)
	C35	0.0827 (3)	−0.3795 (4)	0.1925 (2)	5.0 (2)
	C36	0.0895 (4)	−0.2749 (3)	0.1852 (2)	4.3 (1)

Table IV. Calculated Positional Parameters of Phenyl Hydrogen Atoms

Group	Atom[a]	*x*[b]	*y*	*z*
Ph1	H2	0.0708	0.1101	0.3547
	H3	0.0208	0.2222	0.4315
	H4	−0.0009	0.3837	0.4107
	H5	0.0275	0.4329	0.3130
	H6	0.0775	0.3208	0.2361
Ph2	H8	0.0832	0.1841	0.1400
	H9	0.1223	0.2885	0.0577
	H10	0.2198	0.3622	0.0296
	H11	0.2781	0.3315	0.0838
	H12	0.2389	0.2271	0.1662
Ph3	H14	0.1777	−0.0771	0.2315
	H15	0.2588	−0.1327	0.2540
	H16	0.3143	−0.0194	0.2846
	H17	0.2887	0.1495	0.2928
	H18	0.2076	0.2051	0.2703
Ph4	H20	0.0465	0.0100	0.0825
	H21	0.0473	0.0585	−0.0078
	H22	0.1322	0.0194	−0.0957
	H23	0.2163	−0.0683	−0.0933
	H24	0.2155	−0.1169	−0.0029
Ph5	H26	0.2250	0.0545	0.0816
	H27	0.3295	0.0688	0.0643
	H28	0.3831	−0.0696	0.0758
	H29	0.3323	−0.2224	0.1045
	H30	0.2279	−0.2367	0.1218
Ph6	H32	0.1492	−0.2687	0.0404
	H33	0.1380	−0.4411	0.0524
	H34	0.0967	−0.5100	0.1470
	H35	0.0665	−0.4066	0.2297
	H36	0.0776	−0.2342	0.2177

[a] The digits correspond to the carbon atom to which the H atom is bonded. [b] The hydrogen atom positions were not refined.

Table V. Intramolecular Distances and Angles in $[(Ph_3P)_2Rh(CO)]_2 \cdot 2CH_2Cl_2$

Atoms	Distance, Å	Atoms	Angle, deg
Rh-Rh′	2.630 (1)	P1-Rh-P2	103.7 (1)
Rh-P1	2.321 (2)	P1-Rh-Rh′	112.18 (4)
Rh-P2	2.327 (2)	P2-Rh-Rh′	144.07 (4)
Rh-C	2.051 (6)	C-Rh-Rh′	47.4 (2)
Rh-C′	1.956 (7)	C-Rh-P1	91.9 (2)
C-O	1.175 (8)	C-Rh-P2	131.4 (2)
C-C′	2.80 (1)	C′-Rh-Rh′	50.6 (2)
P-C (Av)	1.843 (6)	C′-Rh-P1	151.7 (2)
C37-Cl1	1.66 (2)	C′-Rh-P2	97.1 (2)
C37-Cl2	1.73 (2)	C′-Rh-C	88.6 (3)
		O-C-Rh	127.3 (5)
		O-C-Rh′	150.7 (5)
		O-C-C′	155.7 (5)
		Rh-C-C′	44.3 (2)
		Rh′-C-Rh	82.0 (3)
		Rh′-C-C′	47.1 (2)
		Cl1-C37-Cl2	111.1 (9)

$(CO)_{12}$,[28] and $Rh_6(CO)_{16}$,[29] respectively, and confirms the existence of a rhodium-rhodium bond. As can be seen in Figure 1, the rhodium(0) atoms are five-coordinated, but their coordination geometries are very different from either trigonal bipyramidal or tetragonal pyramidal. Moreover, the unsymmetrical arrangement of the two carbonyl and two phosphine ligands around the metal precludes any "bent metal-metal bond" deductions of the type proposed[30] in $Co_2(CO)_8$ and $[Rh(CO)_2Cl]_2$, since these four ligands cannot be used as the basis for any reasonable five-coordinated structure irrespective of the location of the fifth bond. The geometry found here is quite different from that found in $Co_2(CO)_8$,[31] $[Fe(NO)_2SC_2H_5]_2$,[32] $[RhCl(O_2)(PPh_3)_2]_2 \cdot 2CH_2Cl_2$,[33] $[(\pi\text{-}C_8H_{12})RhCl_2Rh(PPh_3)_2]$,[34] or any other binuclear complex. Tetrakis(triphenylphosphine)di-μ-carbonyl-dirhodium(0)-bis(dichloromethane) is unique in that it represents the first proven example of a five-coordinate binuclear rhodium(0) complex. While zerovalent rhodium complexes are not unknown,[35] their occurrence in forms other than cluster compounds, such as $Rh_4(CO)_{12}$[28] and $Rh_6(CO)_{16}$,[29] is extremely uncommon.

The Rh-P distances of 2.321 (2) and 2.327 (2) Å fall within the range 2.31-2.39 Å found for five-coordinated d^8 and d^6 rhodium complexes, such as $RhH(PPh_3)_4$,[36] $Rh(CH_3)I_2(PPh_3)_2$,[37] and $RhH(CO)(PPh_3)_3$[38] in which the coordination geometry around the rhodium atom is tetrahedral, tetragonal pyramidal, and trigonal bipyramidal, respectively. The Rh-C distances of 1.956 (7) and 2.051 (6) Å and C-O

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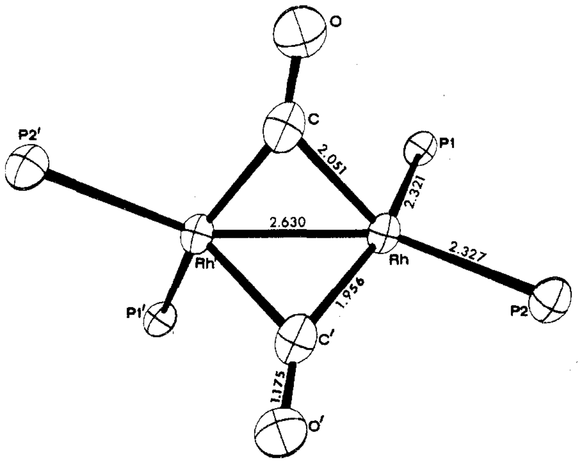

Figure 1. View of the coordination about the Rh(0) atoms. Atoms designated by a prime are related to the reference atom by the twofold rotation.

distance of 1.175 (8) Å compare favorably with those values observed for bridging carbonyl groups in the rhodium cluster compounds $[(\pi\text{-}C_5H_5)(CO)Rh]_3$[27] and $Rh_4(CO)_{12}$.[28] The dihedral angle between the Rh-C-Rh′ and Rh-C′-Rh′ planes is 132.8 (5)°.

Solvent-to-Metal Interaction

The pertinent intermolecular contact distances and angles are given in Table VI. There is clearly no interaction between the metal atoms and the solvent molecules, the shortest Rh-Cl approach being 5.662 (7) Å. The complex is, therefore, coordinatively unsaturated, and this may explain its chemical properties. In view of the uncertainty in the positions of the chlorine atoms in the dichloromethane molecule, the C-Cl bond lengths of 1.66 (2) and 1.73 (2) Å and Cl1-C37-Cl2 bond angle of 111.1 (9)° cannot be validly compared with those values obtained from a microwave study of the gaseous molecule.[39]

Intramolecular Hydrogen Bonding

As seen in Table VI, the shortest intermolecular contact in $[(Ph_3P)_2Rh(CO)]_2 \cdot 2CH_2Cl_2$ involves the carbon atom of dichloromethane located 3.15 (1) Å from the nearest carbonyl oxygen atom in the dimer; the sum of the van der Waals radii of these atoms is 3.22 Å.[40] The positions of the hydrogen atoms in the dichloromethane molecule were calculated assuming a C-H bond length of 1.09 Å and tetrahedral geometry for dichloromethane. A subsequent calculation of the contact distance between each hydrogen atom and the nearest carbonyl oxygen atom gave H···O contact distances of 3.12 and 2.50 Å, the latter being shorter than the sum of the van der Waals radii of 2.72 Å[40] for these atoms. The corresponding C-H···O bond angles were 81.5 and 117.1°, respectively.

Table VI. Intermolecular Contact Distances and Angles in $[(Ph_3P)_2Rh(CO)]_2 \cdot 2CH_2Cl_2$

Atoms	Distance, Å	Atoms	Angle, deg
Rh···Cl1	5.662 (7)	C37-H37···O	81.5
Rh···Cl2	7.387 (6)	C37-H38···O	117.1
Rh···Cl1′	6.135 (7)		
Rh···Cl2′	6.855 (5)		
C37···O	3.15 (2)		
C37···O′	6.93 (2)		
H37···O	3.12		
H38···O	2.50		

Although occurring less commonly than N-H···O or O-H···O hydrogen bonding,[20,41,42] C-H···O interactions involving methylene or methyl hydrogen atoms and keto oxygen atoms have been reported for some organic molecules such as caffeine, ethylene carbonate, and 1,3,7,9-tetramethyluric acid.[42] For these molecules, C···O and H···O contact distances and C-H···O bond angles were found in the ranges 3.00-3.24 Å, 2.26-2.76 Å, and 103-121°,[42] respectively. The C···O, H···O, and C-H···O values found for $[(Ph_3P)_2Rh(CO)]_2 \cdot 2CH_2Cl_2$ are within the ranges cited for interactions of this type. In view of the "shortness" of the H···O separation and the lack of angular restrictions placed on C-H···O interactions,[42] it is conceivable that a hydrogen bonding interaction may exist between dichloromethane and the dimer, which would explain why dichloromethane or ethanol is necessary for the isolation of the dimer.

Registry No. $[Rh(PPh_3)_2CO]_2 \cdot 2CH_2Cl_2$, 37998-25-7; $RhH(CO)(PPh_3)_3$, 17185-29-4.

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