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Crystal Structures of (1,5-Cyclooctadiene)di-μ-methoxo-dirhodium(I) and Tetrakis(η^3-allyl)di-μ-hydroxo-dirhodium(III)

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The crystal structures of (1,5-cyclooctadiene)di-μ-methoxo-dirhodium(I) and tetrakis(η^3-allyl)di-μ-hydroxo-dirhodium(III) were determined by the X-ray method. The former belongs to the triclinic space group $P\bar{1}$ with cell dimensions, $a=7.347(4)$, $b=6.471(3)$, $c=9.554(6)$ Å, $\alpha=87.06(4)$, $\beta=82.50(5)$ and $\gamma=77.98(4)$°. The space group of the latter is also $P\bar{1}$ but two crystallographically independent molecules exist in a cell with dimensions, $a=11.704(7)$, $b=9.793(6)$, $c=7.948(5)$ Å, $\alpha=113.49(5)$, $\beta=54.59(5)$, and $\gamma=110.99(5)$°. Both structures were determined by the heavy atom method and refined by the block-diagonal least-squares method. The final R values were 0.054 for the former and 0.075 for the latter. The coordination of the rhodium atom in the former compound is square planar, the cyclooctadiene ligand being regarded as a bidentate donor. The latter coordination is, in a formal sense, octahedral.

Some of the present authors recently reported the preparation of novel dioxygen complexes of palladium1) and rhodium2) which coordinated to both dioxygen and organic substrates, particularly olefins, by means of the anion exchange reaction of corresponding halogen-bridges complexes with potassium superoxide, and concurrently revealed the basic nature of the coordinated dioxygen. μ-Peroxo complexes of palladium and rhodium reacted with active methylene compounds of which pK_a values were less than 20 to result in the abstraction of the proton by the coordinated dioxygen. For example, treatment of μ-peroxo complexes with acetylacetone (pK_a 9), methyl acetoacetate (pK_a 11), dimethyl malonate (pK_a 13), and cyclopentadiene (pK_a 15) gave the acetylacetonato, methyl acetoacetate, dimethyl malonate and cyclopentadienyl complexes, respectively. With alcohols, amines and thiols, the μ-peroxo complexes also reacted to yield the corresponding μ-alkoxo, μ-amido, and μ-alkylthio complexes accompanied by the liberation of hydrogen peroxide. The alkoxo or hydroxo complexes having olefinic ligands have been studied with interest in recent years in connection with the alkoxy metallation reaction of the Wacker reaction.

This paper deals with two crystal structures of (1,5-cyclooctadiene)di-μ-methoxo-dirhodium(I), $[\{Rh(OMe)(1,5\text{-cod})\}_2]$, which was obtained by the reaction of $[\{RhO(1,5\text{-cod})\}_2]$ with methanol, and of tetrakis(η^3-allyl)di-μ-hydroxo-dirhodium(III), $[\{Rh(OH)(\eta^3\text{-}C_3H_5)_2\}_2]$, which was prepared by the treatment of $[\{RhCl(\eta^3\text{-}C_3H_5)_2\}_2]$ with potassium superoxide.2)

Experimental

General. All reactions were run under positive pressure of dry nitrogen. Infrared spectra were recorded on a Shimadzu IR-27G or Hitachi Model 260-50 spectrometer. Proton magnetic resonance spectra were recorded on a Hitachi R-24B instrument. Chemical shifts are reported as δ values in parts per million relative to internal tetramethylsilane. Melting points were obtained on a Yanagimoto micro melting point apparatus. In experiments requiring dry solvents, benzene and ether were distilled from sodium benzophenon ketyl. Dichloromethane was distilled from diphosphorus pentaoxide. Methanol was distilled from magnesium turnings prior to use. Potassium superoxide, KO_2, (Ventron) was commercially available and used without further purification. Starting rhodium complexes, $[\{RhCl(1,5\text{-cod})\}_2]$ and $[\{RhCl(\eta^3\text{-}C_3H_5)_2\}_2]$, were prepared by a standard procedure.

Preparation of $[\{Rh(OMe)(1,5\text{-cod})\}_2]$. To a suspension of finely powdered potassium superoxide (3.48 g, 49 mmol) in 15 cm^3 of CH_2Cl_2 was added the solution of $[\{RhCl(1,5\text{-cod})\}_2]$ (2.10 g, 4.28 mmol) in 30 cm^3 of CH_2Cl_2 under an atmosphere of dry nitrogen at ambient temperature. The mixture was stirred for 4 h. Then the excess KO_2 together with the precipitated KCl were filtered off under nitrogen pressure. Concentration of the filtrate, followed by the addition of 30 cm^3 of pentane, gave $[\{RhO(1,5\text{-cod})\}_2]$ (1.30 g, 67%) as a yellowish brown microprisms. The $[\{RhO(1,5\text{-cod})\}_2]$ was then dissolved in 20 cm^3 of dry benzene. The addition of 1.0 cm^3 of freshly distilled methanol at room temperature instantaneously gave a yellow solution. Evaporation of the solvent followed by recrystallization from a mixed solvent of CH_2Cl_2 and CH_3OH (1:1 vol. ratio) gave $[\{Rh(OMe)(1,5\text{-cod})\}_2]$ as yellow prisms in a 50% yield (1.04 g) based on $[\{RhCl(1,5\text{-cod})\}_2]$. IR and H-NMR spectral data and melting point agreed with those of the authentic sample. Elemental analysis was also consistent with the formula, $C_{18}H_{30}O_2Rh_2$. Calcd: C, 44.65; H, 6.24%. Found: C, 44.50; H, 6.45%.

Preparation of $[\{Rh(OH)(\eta^3\text{-}C_3H_5)_2\}_2]$. To a suspension of finely powdered KO_2 (718 mg, 10.1 mmol) in 10 cm^3 of CH_2Cl_2 was added the solution of $[\{RhCl(\eta^3\text{-}C_3H_5)_2\}_2]$ (200 mg, 0.454 mmol) in 10 cm^3 of CH_2Cl_2 under nitrogen pressure at the ambient temperature. The resulting mixture turned to an orange solution, which was then stirred for 2 h. The excess KO_2 and the precipitated KCl were filtered off under nitrogen pressure and the filtrate was evaporated to dryness. The residue was dissolved in benzene and again filtered. The filtrate was concentrated to *ca.* 4 cm^3 and was allowed to cool to yield $[\{Rh(OH)(\eta^3\text{-}C_3H_5)_2\}_2]$ as yellow prisms in a 70% (128 mg) yield; mp 129 °C (decomp). IR (KBr) OH 3580, 3549 cm^{-1}; ^{1}H-NMR ($CDCl_3$) 1.10 (br.d, 4H), 2.18 (br.d, 4H), 3.02 (br.d, 4H), 4.38 (m, 4H), 4.67 (br.s, 4H), −2.40 (br.s, 2H, OH). Found: C, 35.31; H, 5.40%. Calcd for $C_{12}H_{22}O_2Rh_2$: C, 35.66, H, 5.49%.

X-Ray Data Collection. The X-ray diffraction data were obtained with graphite monochromatized Mo $K\alpha$ ra-

Table 1. Crystal and experimental data

	$[\{Rh(OMe)(1,5\text{-}cod)\}_2]$	$[\{Rh(OH)(\eta^3\text{-}C_3H_5)_2\}_2]$
Chemical formula	$Rh_2C_{18}O_2H_{30}$	$Rh_2C_{12}O_2H_{22}$
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Z	1	2
Cell dimensions		
a/Å	7.347(4)	11.704(7)
b/Å	6.471(3)	9.793(6)
c/Å	9.554(6)	7.948(5)
α/°	87.06(4)	113.49(5)
β/°	82.50(5)	54.59(5)
γ/°	77.98(4)	110.99(5)
D_m/g cm^{-3}	1.80	2.04
D_x/g cm^{-3}	1.82	2.02
Scan range $\Delta\omega$/°	$1.5+0.35\tan\theta$	$1.5+0.35\tan\theta$
Scan speed /° min^{-1} and background count time /s		
$0°<2\theta\leq40°$	10, 3	10, 3
$40°<2\theta\leq50°$	5, 6	5, 6
$50°<2\theta\leq60°$	2, 15	2, 15
Number of reflections	2154	3308
$2\theta_{max}$/°	60	60
Crystal size /mm^3	$0.40\times0.34\times0.08$	$0.30\times0.10\times0.10$

diation on a Rigaku four-circle diffractometer equipped with a rotating anode X-ray generator operated at 50 kV 120 mA. An ω-2θ continuous scanning technique was used for measuring integrated intensities. Background countings were made at each side of the scan. Other experimental details are listed in Table 1 together with the crystal data. Lorentz and polarization corrections were applied but no absorption correction was made.

Structure Determination and Refinement

Both structures were solved by the heavy atom method and refined by the block-diagonal least-squares procedure. Hydrogen atoms were located on difference Fourier maps with the help of geometrical consideration. Anisotropic thermal parameters were assigned to all the nonhydrogen atoms. Hydrogen positional parameters, as well as their isotropic thermal parameters which were made equal to B_{eq} of their carrier atoms, were not refined. The function minimized was $\Sigma\omega(\Delta F)^2$, with $\omega=a$ for $F_o=0$ and $\omega=[\sigma^2(F)+b|F_o|+c|F_o|^2]^{-1}$ for $F_o\neq0$, where $\sigma(F)$ is the estimated standard deviation based on counting statistics. The final R and parameters a, b, and c are 0.054, 0.68, −0.25, and 0.01 for $[\{Rh(OMe)(1,5\text{-}cod)\}_2]$ and 0.075, 0.13, −0.06, and 0.01 for $[\{Rh(OH)(\eta^3\text{-}C_3H_5)_2\}_2]$. The atomic scattering factors were taken from the International Tables for X-Ray Crystallography.[3] The positional parameters are listed in Tables 2 and 3.[4]

Results and Discussion

$[\{Rh(OMe)(1,5\text{-}cod)\}_2]$. The molecule occupies a center of symmetry in the crystal. A stereo-

Table 2. Atomic positional ($\times10^4$) and thermal parameters with their e.s.d.'s in parentheses for $[\{Rh(OMe)(1,5\text{-}cod)\}_2]$

Atom	x	y	z	B_{eq}/Å^2 a)
Rh	3988(0)	1582(0)	1253(0)	3.2(0)
O	3641(6)	701(6)	−711(6)	4.7(3)
C(1)	2091(9)	1353(9)	−1446(9)	4.8(4)
C(2)	4058(10)	1388(10)	3425(10)	4.1(3)
C(3)	4999(10)	2961(10)	2853(10)	4.6(4)
C(4)	4137(16)	5304(16)	3003(16)	7.7(7)
C(5)	2714(15)	6118(15)	2082(15)	8.0(7)
C(6)	2133(9)	4521(9)	1264(9)	4.3(4)
C(7)	1177(8)	2964(8)	1875(8)	4.0(3)
C(8)	606(11)	2722(11)	3436(11)	6.3(5)
C(9)	2147(13)	1789(13)	4253(13)	7.0(6)

a) The equivalent isotropic temperature factor.[12]

Table 3. Atomic positional ($\times10^4$) and thermal parameters with their e.s.d.'s in parentheses for $[\{Rh(OH)(\eta^3\text{-}C_3H_5)_2\}_2]$

Atom	x	y	z	B_{eq}/Å^2
Rh(A)	84(0)	−1743(0)	−1526(0)	2.4(0)
Rh(B)	5047(0)	1785(0)	1306(0)	2.5(0)
O(A)	1484(6)	214(6)	−664(6)	2.8(2)
O(B)	6485(5)	200(5)	−1098(5)	2.5(2)
C(1A)	1683(10)	−3043(10)	−2954(10)	2.4(3)
C(2A)	421(10)	−3593(10)	−1212(10)	3.2(4)
C(3A)	−85(10)	−2647(10)	774(10)	3.2(3)
C(4A)	−1381(10)	−3162(10)	−2446(10)	3.2(4)
C(5A)	−169(9)	−2710(9)	−4226(9)	2.9(3)
C(6A)	257(9)	−1130(9)	−4101(9)	2.9(3)
C(1B)	6785(9)	3569(9)	583(9)	3.3(3)
C(2B)	5880(10)	3712(10)	82(10)	3.1(3)
C(3B)	5570(9)	2555(9)	−1359(9)	3.4(4)
C(4B)	3356(10)	2855(10)	4138(10)	3.5(3)
C(5B)	4293(10)	2738(10)	4607(10)	3.4(3)
C(6B)	4467(9)	1248(9)	4214(9)	3.2(4)

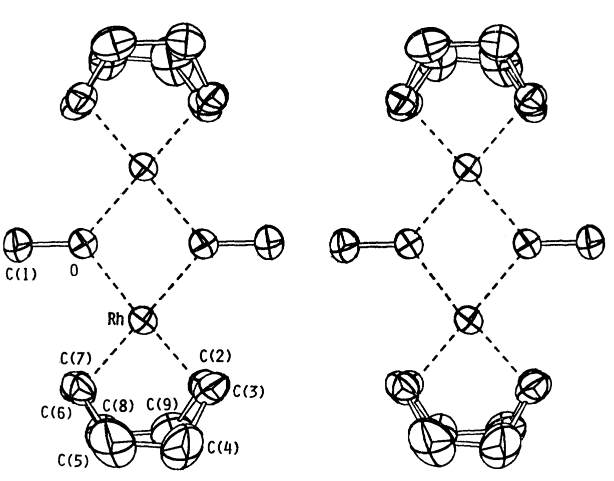

Fig. 1. A stereo drawing of $[\{Rh(OMe)(1,5\text{-}cod)\}_2]$. Thermal ellipsoids are scaled to include 50% probability level.

drawing of the molecule with the numbering of atoms is shown in Fig. 1. The coordination of the Rh atom is essentially square planar, the cyclooctadiene ligand being regarded as a bidentate donor. The geometry of the coordination plane of the Rh atom is given in Table 4. The molecule has an approximate D_{2h} (mmm) symmetry.

The bond lengths and angles are given in Table 5. The two Rh–O lengths, 2.051(5) and 2.063(5) Å, are similar to the values found in previous work, *e.g.* 2.054(5) and 2.066(5) Å for [Rh(acac)(1,5-cod)],[5] or 2.06 and 2.05 Å for [Rh(acac)(CO)$_2$].[6] The C–O length of 1.40(1) Å is shorter than the usual C–O single bond length, 1.43 Å. It indicates that this bond assumes a slight double bond character as a result of the coordination.

The cyclooctadiene ring acquires a tub form of approximate symmetry C_{2v} (2mm), the Rh–Rh vector being the twofold axis. The lengths of the two C=C double bonds participating in the coordination are 1.40(1) and 1.41(1) Å, which are in good agreement with the bond lengths of other complexes in the same situation: 1.41(1) Å for [Rh(acac)(1,5-cod)],[5] 1.44(7) Å for [{RhCl(1,5-cod)}$_2$],[7] or 1.40(1) Å for [Ni(1,5-cod)(duroq)] (duroq=duroquinone).[8] These are significantly longer than the corresponding lengths for the free molecule of 1,5-cyclooctadiene, 1.341 Å,[9] due to π-electron coordination. The two C(4)–C(5) and C(8)–C(9) single bonds have relatively shorter lengths 1.45(2) and 1.47(2) Å, which may be attributed to the larger thermal vibration of these atoms. The distance between the midpoint of the C(2)–C(3) bond and that of the C(6)–C(7) bond is 2.74 Å, which is similar to 2.74 Å for [Rh(acac)(1,5-cod)][5] but shorter than 2.91 Å for [Ni(1,5-cod)(duroq)].[8]

TABLE 4. THE BEST PLANE AND DEVIATIONS (d/Å) OF ATOMS FROM THE PLANE IN [{Rh(OMe)(1,5-cod)}$_2$][a]

$-0.5938X-0.6906Y+0.4129Z+2.1814=0$			
Rh	0.00(1)	C(4)	−1.46(1)
O	0.02(1)	C(5)	−1.54(1)
M(1)	0.02(1)	C(6)	−0.71(1)
M(2)	0.00(1)	C(7)	0.70(1)
C(1)	0.13(1)	C(8)	1.54(1)
C(2)	0.72(1)	C(9)	1.60(1)
C(3)	−0.67(1)		

a) The plane is defined by Rh, O, M(1), and M(2), and their centrosymmetric equivalents; M(1) is the midpoint of the C(2)-C(3) bond and M(2) is that of C(6)-C(7). $X=ax+by\cos\gamma+cz\cos\beta$, $Y=by\sin\gamma-cz\cos\alpha^*\sin\beta$, $Z=cz\sin\alpha^*\sin\beta$.

TABLE 5. BOND LENGTHS AND ANGLES IN [{Rh(OMe)(1,5-cod)}$_2$][a]

Bond length	l/Å	Bond angle	θ/°
Rh-O	2.051(5)	O-Rh-O′	76.5(2)
Rh-O′	2.063(5)	O-Rh-M(1)	174.2(3)
Rh-M(1)	1.969(8)	O-Rh-M(2)	97.6(3)
Rh-M(2)	1.974(8)	O′-Rh-M(1)	97.8(3)
Rh-C(2)	2.080(8)	O′-Rh-M(2)	174.0(3)
Rh-C(3)	2.097(8)	M(1)-Rh-M(2)	88.1(3)
Rh-C(6)	2.096(8)	Rh-O-C(1)	128.0(5)
Rh-C(7)	2.094(7)	Rh-O-Rh′	103.5(2)
O-C(1)	1.40(1)	Rh′-O-C(1)	128.2(5)
C(2)-C(3)	1.40(1)	C(2)-C(3)-C(4)	122.2(8)
C(3)-C(4)	1.52(2)	C(3)-C(4)-C(5)	114.7(10)
C(4)-C(5)	1.45(2)	C(4)-C(5)-C(6)	116.1(11)
C(5)-C(6)	1.49(2)	C(5)-C(6)-C(7)	124.2(8)
C(6)-C(7)	1.41(1)	C(6)-C(7)-C(8)	124.0(7)
C(7)-C(8)	1.51(1)	C(7)-C(8)-C(9)	114.8(9)
C(8)-C(9)	1.47(2)	C(8)-C(9)-C(2)	115.1(9)
C(9)-C(2)	1.50(1)	C(9)-C(2)-C(3)	124.8(8)

a) Primed atoms refer to the centrosymmetric equivalents.

The molecular packing viewed along the a axis is shown in Fig. 2. None of the intermolecular distances is short enough to suggest any significant deviation from normal van der Waals interactions.

[{*Rh(OH)*(η^3-C_3H_5)$_2$}$_2$]. There are two crystallographically independent molecules (A and B) in the unit cell, each occupying the center of symmetry in the crystal. The molecular geometry and numbering scheme of atoms are shown in Fig. 3. The molecule has an approximate symmetry of C_{2h} (2/m) with the 2 axis coinciding with the Rh–Rh vector and the m plane passing through the two O atoms

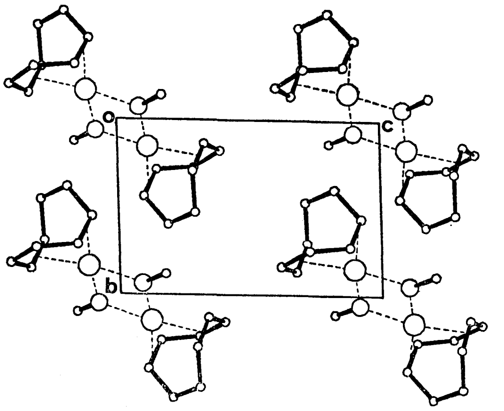

Fig. 2. Molecular packing of [{Rh(OMe)(1,5-cod)}$_2$].

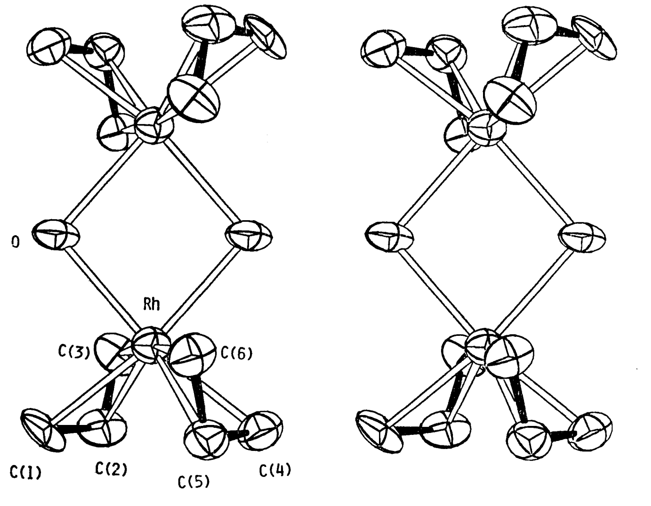

Fig. 3. A stereodrawing of [{Rh(OH)(η^3-C_3H_5)$_2$}$_2$].

Table 6. Bond angles involving Rh atom in $[\{Rh(OH)(\eta^3\text{-}C_3H_5)_2\}_2]$

Bond angle	θ/°		Bond angle	θ/°	
	A	B		A	B
O-Rh-O′	82.6(3)	80.9(3)	C(1)-Rh-C(3)	67.2(5)	67.3(5)
O-Rh-C(1)	87.6(4)	89.4(4)	C(1)-Rh-C(4)	104.8(5)	103.5(5)
O-Rh-C(2)	104.5(4)	105.4(4)	C(1)-Rh-C(5)	90.8(4)	90.4(5)
O-Rh-C(3)	85.4(4)	86.2(4)	C(1)-Rh-C(6)	108.3(3)	109.9(5)
O-Rh-C(4)	164.7(4)	163.8(4)	C(2)-Rh-C(3)	36.4(5)	36.9(4)
O-Rh-C(5)	134.5(4)	133.2(4)	C(2)-Rh-C(4)	90.8(5)	90.9(5)
O-Rh-C(6)	100.2(4)	99.2(3)	C(2)-Rh-C(5)	102.7(5)	103.0(5)
O′-Rh-C(1)	164.8(4)	163.9(4)	C(2)-Rh-C(6)	136.7(5)	137.9(4)
O′-Rh-C(2)	132.8(4)	132.5(4)	C(3)-Rh-C(4)	107.5(5)	108.0(5)
O′-Rh-C(3)	100.3(4)	99.1(4)	C(3)-Rh-C(5)	134.9(4)	135.7(5)
O-Rh-C(4)	86.9(4)	88.8(4)	C(3)-Rh-C(6)	172.8(4)	174.0(4)
O-Rh-C(5)	104.3(4)	105.7(4)	C(4)-Rh-C(5)	38.6(5)	38.4(5)
O′-Rh-C(6)	84.9(4)	84.4(3)	C(4)-Rh-C(6)	67.6(4)	67.1(5)
C(1)-Rh-C(2)	39.4(5)	38.5(5)	C(5)-Rh-C(6)	38.1(4)	38.3(4)

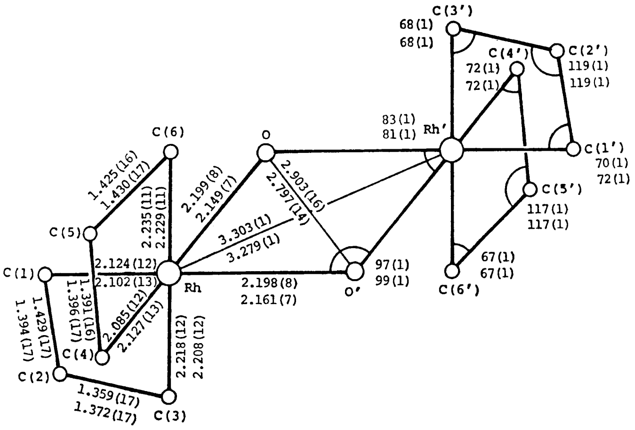

Fig. 4. The bond distances (l/Å) and angles (θ/°) in $[\{Rh(OH)(\eta^3\text{-}C_3H_5)_2\}_2]$.

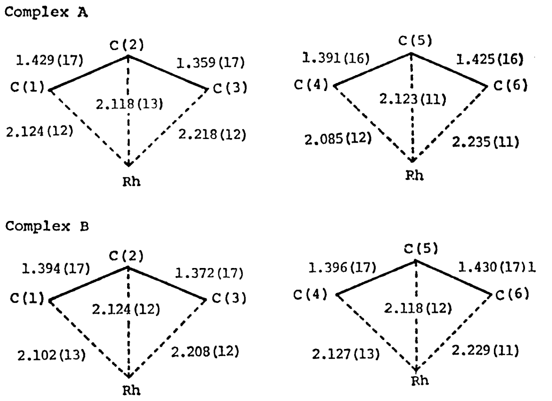

Fig. 5. The bond distances (l/Å) involving Rh and allyl group in $[\{Rh(OH)(\eta^3\text{-}C_3H_5)_2\}_2]$.

Table 7. The best plane and deviations (d/Å) of atoms from the planes in $[\{Rh(OH)(\eta^3\text{-}C_3H_5)_2\}_2]$[a)]

Rh(A) plane			
$0.2283X-0.5635Y+0.7939Z=0$			
Rh(A)	0.00(2)	C(2A)	1.41(3)
O(A)	−0.19(3)	C(3A)	2.09(3)
C(1A)	0.21(3)	C(5A)	−1.37(3)
C(4A)	−0.19(3)	C(6A)	−2.11(3)
RH(B) plane			
$0.6574X-0.3875Y+0.6463Z-3.8469=0$			
Rh(B)	0.00(1)	C(2B)	−1.43(2)
O(B)	0.18(1)	C(3B)	−2.10(2)
C(1B)	−0.26(2)	C(5B)	1.41(2)
C(4B)	0.26(2)	C(6B)	2.11(2)

a) The planes are defined by Rh, O, C(1), and C(4), and their centrosymmetric equivalents.

and perpendicular to the 2 axis. The bond lengths and angles are shown in Table 6 and Figs. 4 and 5.

The coordination of the Rh atom is, in a formal sense, octahedral, if either the two O atoms and the C(1), C(3), C(4), and C(6) atoms or the two O atoms and four midpoints of the C(1)–C(2), C(2)–C(3), C(4)–C(5), and C(5)–C(6) bonds are considered as the ligands. Two atoms C(1) and C(4) of two allyl groups lie roughly on the plane of the Rh and O atoms, and the best plane consisting of the Rh, O, C(1), and C(4) atoms and their centrosymmetric equivalents are given in Table 7 together with the deviations of atoms from that plane. The other two terminal atoms C(3) and C(6) of the allyl groups locate far from the plane on both sides. The bond angle C(3)–Rh–C(6) is 172.8(4)° and 174.0(4)° for the A and B molecules, respectively. The planes of four independent allyl groups, C(1A)–C(2A)–C(3A), C(4A)–C(5A)–C(6A), C(1B)–C(2B)–C(3B), and C(4B)–C(5B)–C(6B), make angles of 57.8(6)°, 59.5(6)°, 57.4(6)°, and 56.5(6)° with the above mentioned plane. These structural characteristics are similar to those found for $[\{RhCl(\eta^3\text{-}C_3H_5)_2\}_2]$[10)] and $[\{RhBr(\eta^3\text{-}C_3H_5)_2\}_2]$,[11)] in which halogen atoms take the place of the OH group of this molecule.

The mean length of the Rh–C(1) and Rh–C(4) bonds, 2.11 Å, is significantly shorter than that of Rh–C(3) and Rh–C(6), 2.22 Å; while that of Rh–C(2) and Rh–C(5) is 2.12 Å. This trend is seen also in $[\{RhCl(\eta^3\text{-}C_3H_5)_2\}_2]$[10)] and $[\{RhBr(\eta^3\text{-}C_3H_5)_2\}_2]$.[11)] On the other hand the mean length of C(1)–C(2) and C(4)–C(5) bonds, 1.40 Å, and that of C(2)–C(3) and C(5)–C(6), 1.40 Å, show no significant asymmetry in the C–C bonds.

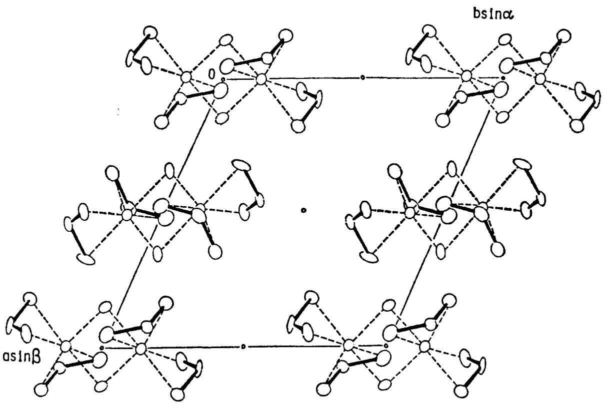

Fig. 6. Molecular packing of $[\{Rh(OH)(\eta^3\text{-}C_3H_5)_2\}_2]$.

The crystal structure is shown in Fig. 6. The molecule A locates at (0,0,0) and B locates at (0.5,0,0). Two Rh–Rh vectors of A and B are roughly parallel with each other, and a slight rotation of A around its Rh–Rh vector gives the orientation of B.

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