Crystal Structure of Di-μ-chloro-bis{chloro[2-(hydroxymethyl)pent-4-enyl]rhodium(III)}–Methanol

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Crystals of the title compound are orthorhombic, space group $Pc2_1n$, with $a = 11{\cdot}88(1)$, $b = 15{\cdot}00(2)$, $c = 10{\cdot}70(1)$ Å, $Z = 4$. The structure was determined by Patterson and Fourier methods from photographic data and was refined by least squares with allowance for anisotropic temperature factors to a final R of 7·6% for 2948 independent reflections. The complex is dimeric but the central Rh_2Cl_2 ring is non-planar. The OH groups of the organic ligands and of the solvent methanol molecule are involved in hydrogen bonding.

A number of transition metals will react catalytically with allyl alcohol to give a variety of organic products.[1-5] A solution of rhodium trichloride trihydrate in allyl alcohol evolves propene and traces of ethylene.[4,5] In the reaction solution propionaldehyde, propionaldehyde diallyl acetal, and acraldehyde are formed. When a solution of rhodium trichloride trihydrate in a mixture of allyl alcohol and methanol is heated under reflux for 1 min and allowed to cool, yellow-brown crystals of $[RhCl_2(C_6H_{11}O)]_n,\frac{n}{2}MeOH$ are deposited. The i.r. spectrum of this compound shows absorptions in the regions characteristic of a bridging chloride system and of a hydroxy-group, but its ^1H n.m.r. spectrum is very complex. The structure of the compound has been determined by single-crystal X-ray diffraction. A preliminary account has appeared.[6]

EXPERIMENTAL

Crystal Data.—$C_{13}H_{26}Cl_4O_3Rh_2$, $M = 578{\cdot}0$, Orthorhombic, $a = 11{\cdot}88(1)$, $b = 15{\cdot}00(2)$, $c = 10{\cdot}70(1)$ Å (consistent with the Crystal Data[7] convention $c < a < b$), $U = 1906{\cdot}3$ Å^3, $D_m = 1{\cdot}98$, $Z = 4$, $D_c = 2{\cdot}01$ g cm^{-3}, $F(000) = 1144$. Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å; μ(Mo-K_α) $= 22$ cm^{-1}, $\mu R = 0{\cdot}3$. Space group $Pc2_1n$ (No. 33, C^9_{2v}) from structure analysis.

Structure Determination.—Intensity data were recorded on equi-inclination Weissenberg photographs of the reciprocal lattice layers $hk0$—16, by use of Mo-K_α radiation, and by visual estimation 2948 independent structure amplitudes were obtained. No absorption corrections were applied.

Although the systematic absences were consistent with either space group $Pcmn$ (No. 62) or $Pc2_1n$ (No. 33) the Patterson synthesis was compatible only with $Pc2_1n$. The structure was determined by standard Patterson and Fourier techniques. In space group $Pc2_1n$ the origin is not fixed in the y direction by reference to symmetry elements, and it was necessary during refinement to fix the y co-ordinate of one of the rhodium atoms [$y = \frac{1}{4}$ for Rh(1)].

Least-squares refinement of co-ordinates, isotropic temperature factors, and 17 layer scale-factors gave R 8·7%. Atomic scattering factors for rhodium were taken from ref. 8, with inclusion of the real part ($\Delta f'$) of anomalous scattering, and for other atoms from ref. 9. Block-diagonal refinement was continued with allowance for anisotropic temperature factors, initially for the rhodium atoms alone, then for

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the rhodium and chlorine atoms, and finally for all non-hydrogen atoms and the significance of the improved agreement was confirmed at each stage by use of Hamilton's [10] tests. As a result of attempting to refine anisotropic temperature factors and layer scale-factors of data taken about a single axis the matrix of normal equations would be singular since only the relative values of U_{33} can be determined in this way; [11] accordingly U_{33} for Rh(1) was not allowed to vary. The final R was 7·6%. The weighting scheme used in the last cycles was $w = 1/(17 + |F_o|)$.

It has been pointed out by Cruickshank and McDonald [12] that in the polar class $mm2$, co-ordinate errors in the direction of the polar axis can be caused by the neglect of the imaginary component $\Delta f''$ of the anomalous scattering. In space group $Pc2_1n$ the measurement of data with all indices non-negative implies, by symmetry, the measurement of the hkl, $\bar{h}kl$, $\bar{h}k\bar{l}$, and $hk\bar{l}$ reflections. As there are no negative k values the structure would be liable to errors Δy. In the present work, however, data were collected for the non-symmetry related octants hkl and $\bar{h}\bar{k}l$ for which the errors will be in opposite directions so that there will be no net co-ordinate errors. Thus by using as structure amplitudes the averages of the hkl and $\bar{h}\bar{k}l$ data, $\Delta f''$ may be neglected and the polar dispersion error avoided.

Final co-ordinates with their estimated standard deviations are given in Table 1. Observed and calculated structure amplitudes and thermal parameters are listed in Supplementary Publication No. SUP 21041 (19 pp., 1 microfiche).*

TABLE 1

Final atomic fractional co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses

Atom	x	y	z
Rh(1)	−707(1)	2500(0)	760(1)
Rh(2)	763(1)	1796(1)	3673(1)
Cl(1)	916(3)	1469(3)	1510(3)
Cl(2)	−498(3)	3099(3)	2821(3)
Cl(3)	−2033(3)	1466(3)	1387(4)
Cl(4)	2441(4)	2545(5)	3624(5)
O(1)	387(10)	3429(8)	77(11)
O(2)	−728(11)	1074(10)	3809(12)
O(3)	2135(13)	3806(11)	1405(14)
C(1)	−1853(14)	3514(13)	422(17)
C(2)	−1326(19)	3933(12)	−764(18)
C(3)	−149(19)	4238(11)	−373(18)
C(4)	−1274(19)	3222(14)	−1787(16)
C(5)	−1340(17)	2284(13)	−1156(15)
C(6)	−393(17)	1785(15)	−947(13)
C(7)	1481(17)	593(13)	4081(18)
C(8)	601(20)	184(17)	4917(20)
C(9)	−509(20)	122(15)	4193(23)
C(10)	486(19)	786(17)	6071(16)
C(11)	914(16)	1720(13)	5737(13)
C(12)	261(23)	2409(19)	5374(17)
C(13)	1921(24)	4583(17)	2206(33)

RESULTS AND DISCUSSION

Figure 1 shows a projection of the molecule on the plane (160) and the arrangement of molecules in the unit cell is shown in Figure 2. The molecule is dimeric with the rhodium atoms bridged by two chlorine atoms. The terdentate $C_6H_{11}O$ ligand is held to the metal *via* a σ-bonded carbon, a π-bonded olefin, and a co-ordinated OH group. Rh–Cl bond lengths are 2·612 Å (mean of 2) *trans* to the σ-bonded carbon, 2·383 Å (mean of 2) *trans* to the π-bonded olefin, and 2·299 Å (mean of 2) *trans* to the co-ordinated oxygen. The Rh–Cl–Rh angle is 96·4° (mean of 2). Rh–C is 2·06 Å (mean of 2). This may be compared with other Rh^{III}–C bond lengths of 2·048(16) in

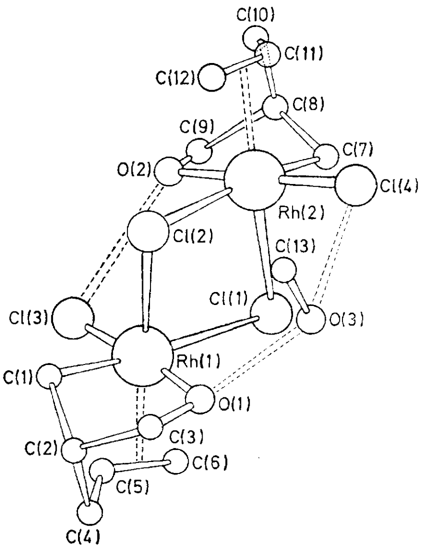

FIGURE 1 A projection of the dimeric molecule on the plane (160)

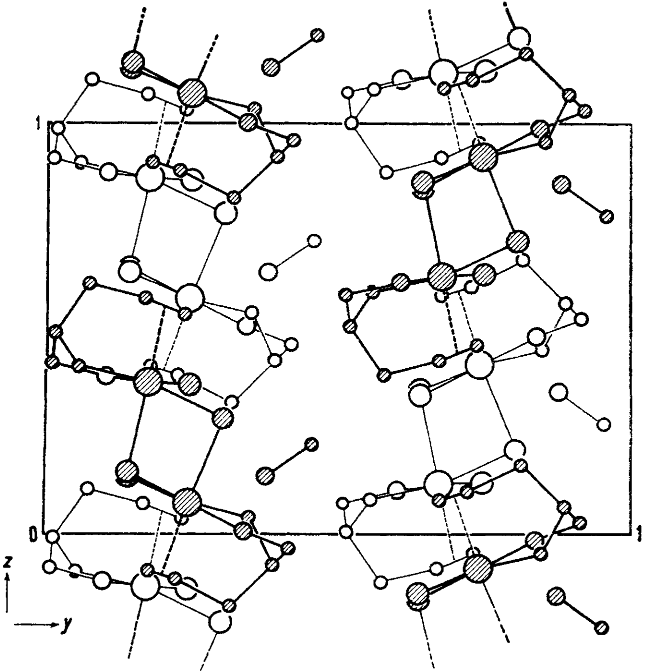

FIGURE 2 The contents of the unit cell projected down the *a* axis

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue.

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$[RhEt(NH_3)_5]^{2+}$ (ref. 13), 2·083(7) in $[RhI_2Me(PPh_3)_2]$,-C_6H_6,[14] 2·08 in $[Rh_2I_2(SMe_2)_3Me_4]$,[15] and 2·083(16) Å in $[RhCl_2(C_6H_5N)_2\{P(o\text{-}C_6H_4CH_3)_2(o\text{-}C_6H_4CH_2)\}]$.[16] The C=C bond length (π-bonded olefin) is 1·36 Å (mean of 2). Around the metal atoms no inter-bond angle (as calculated from the atomic positions, neglecting standard deviations) deviates by more than 9° from a right angle (where the centre of the co-ordinated C=C is taken as the sixth co-ordination site). The principal molecular dimensions are given in Table 2. There are no intermolecular contacts <3·3 Å.

TABLE 2

Principal molecular dimensions with estimated standard deviations in parentheses

(*a*) Bond lengths (Å)

Rh(1)–Cl(1)	2·598(4)	Rh(2)–Cl(1)	2·372(4)
Rh(1)–Cl(2)	2·394(4)	Rh(2)–Cl(2)	2·626(4)
Rh(1)–Cl(3)	2·311(4)	Rh(2)–Cl(4)	2·288(6)
Rh(1)–O(1)	2·04(1)	Rh(2)–O(2)	2·08(1)
Rh(1)–C(1)	2·07(2)	Rh(2)–C(7)	2·04(2)
Rh(1)–C(5)	2·21(2)	Rh(2)–C(11)	2·22(2)
Rh(1)–C(6)	2·15(2)	Rh(2)–C(12)	2·13(2)
C(1)–C(2)	1·55(3)	C(7)–C(8)	1·51(3)
C(2)–C(3)	1·53(3)	C(8)–C(9)	1·53(3)
C(3)–O(1)	1·45(2)	C(9)–O(2)	1·51(3)
C(2)–C(4)	1·53(3)	C(8)–C(10)	1·53(3)
C(4)–C(5)	1·56(3)	C(10)–C(11)	1·53(3)
C(5)–C(6)	1·37(3)	C(11)–C(12)	1·35(3)
O(3)–C(13)	1·47(3)		
O(1) · · · O(3)	2·58(2)		
O(2) · · · Cl(3)	3·08(2)		
O(3) · · · Cl(4)	3·06(2)		

(*b*) Angles (°)

Cl(1)–Rh(1)–Cl(2)	82·1(0·1)	Cl(1)–Rh(2)–Cl(2)	81·9(0·1)
Cl(1)–Rh(1)–Cl(3)	90·9(0·1)	Cl(1)–Rh(2)–Cl(4)	90·7(0·2)
Cl(1)–Rh(1)–O(1)	92·5(0·3)	Cl(1)–Rh(2)–C(7)	89·7(0·5)
Cl(2)–Rh(1)–Cl(3)	93·2(0·1)	Cl(1)–Rh(2)–O(2)	91·5(0·4)
Cl(2)–Rh(1)–C(1)	87·3(0·5)	Cl(2)–Rh(2)–Cl(4)	97·1(0·2)
Cl(2)–Rh(1)–O(1)	90·5(0·3)	Cl(2)–Rh(2)–O(2)	85·8(0·4)
Cl(3)–Rh(1)–C(1)	95·5(0·5)	Cl(4)–Rh(2)–C(7)	94·3(0·6)
C(1)–Rh(1)–O(1)	81·7(0·6)	C(7)–Rh(2)–O(2)	83·1(0·7)
Rh(1)–Cl(1)–Rh(2)	97·0(0·1)	Rh(1)–Cl(2)–Rh(2)	95·7(0·1)
Rh(1–C(1)–C(2)	100·1(1·1)	Rh(2)–C(7)–C(8)	101·4(1·3)
C(1)–C(2)–C(3)	105·5(1·4)	C(7)–C(8)–C(9)	108·7(1·7)
C(1)–C(2)–C(4)	108·7(1·4)	C(7)–C(8)–C(10)	107·5(1·7)
C(3)–C(2)–C(4)	111·6(1·5)	C(9)–C(8)–C(10)	111·4(1·7)
C(2)–C(3)–O(1)	104·0(1·4)	C(8)–C(9)–O(2)	103·3(1·6)
C(3)–O(1)–Rh(1)	114·2(1·0)	C(9)–O(2)–Rh(2)	111·4(1·1)
C(2)–C(4)–C(5)	108·5(1·3)	C(8)–C(10)–C(11)	108·7(1·5)
C(4)–C(5)–C(6)	121·4(1·6)	C(10)–C(11)–C(12)	125·2(1·8)

An interesting feature of the structure is the folding of the central Rh_2Cl_2 ring. Across the line of the bridging chlorine atoms the fold angle is 18·4°. Thus the O(2) · · · Cl(3) distance is reduced to 3·08 Å, a typical value for known O–H · · · Cl hydrogen-bonded distances.[17] On the other side of the molecule the separation of O(1) and Cl(4) to 4·7 Å allows the solvent methanol molecule to bridge O(1) and Cl(4) by the formation of two more hydrogen bonds; O(1) · · · O(3) is 2·58 Å, in agreement with known O–H · · · O distances; O(3) · · · Cl(4) is 3·06 Å. A projection of the molecule along the line of the bridging chlorine atoms is shown in Figure 3.

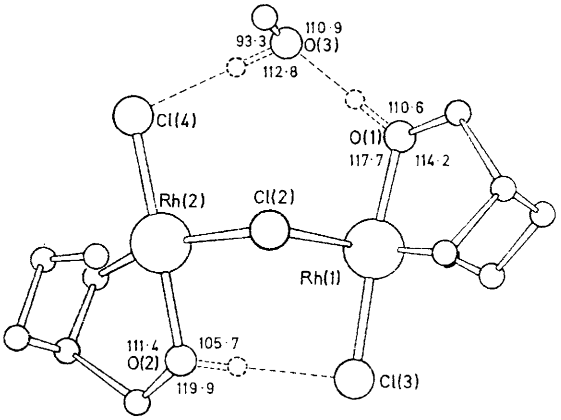

FIGURE 3 The molecule projected along the Cl(2) · · · Cl(1) line

Hydrogen atoms could not be located in the structure analysis as the rhodium atoms dominate the scattering, but likely positions, assuming linear O–H · · · A hydrogen bonds (A = O or Cl), are shown, together with interbond angles around the oxygen atoms. In fact, neutron diffraction studies on hydrogen-bonded systems indicate that linearity is more the exception than the rule [17] and therefore these angles may not be appropriate to the hydrogen atoms themselves.

The stability of the complex can thus be attributed not only to the terdentate nature of the organic ligand but also to the hydrogen bonding.

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