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CARBON COMPOUNDS OF THE TRANSITION METALS
IX. EVIDENCE FOR AND STRUCTURE OF DICYCLOPENTADIENYLTRICARBONYLDIRHODIUM

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It has been reported[1] that when a pentane solution of cyclopentadienyldicarbonylrhodium[2] is allowed to stand for some weeks, dimerisation occurs. The IR spectrum of this dark red crystalline compound showed a close similarity to that of bis(cyclopentadienyldicarbonyliron) whose structure, in the solid[3], contains two bridging and two terminal carbonyl groups in a centrosymmetric molecule. As a result of our request for a sample of this dimer, a further preparation was put in hand. However, in an attempt to hasten the reaction, the solution was irradiated with ultraviolet light. In this paper we report the analysis of the dark red compound formed during this irradiation and show that these crystals are the previously unknown $Cp_2Rh_2(CO)_3$.

DISCUSSION

The analysis of the photolysis product has demonstrated that during irradiation one carbonyl group has been lost from two monomer units. The product is the first example of a binuclear species which contains a single bridging carbonyl group. A sketch of the molecule is shown in Fig. 1. Atomic coordinates are listed in Table 1 and details of the molecular geometry in Table 2.

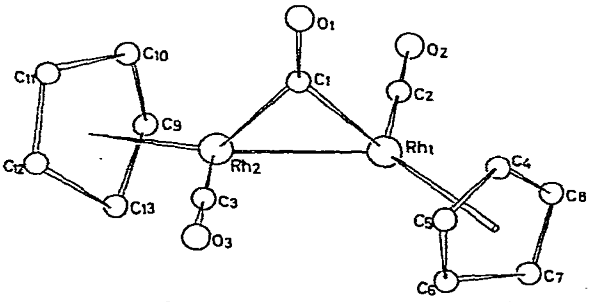

Fig. 1. Sketch of molecule showing atom numbering.

The structure consists of discrete molecules with no intermolecular contacts less than 3.4 Å (hydrogen atom positions were not determined). The local environment of each rhodium atom is similar since an approximate two-fold axis passes through the bridging carbonyl group, perpendicular to the Rh–Rh vector. The π-cyclopentadienyl

TABLE 1

ATOMIC PARAMETERS

Atom	*x/a*	*y/b*	*z/c*	$B(\text{Å}^2)$
RH1	0.1422(2)	0.2094(1)	0.0850(1)	
RH2	0.3385(2)	0.2468(2)	0.2729(1)	
C1	0.2829(26)	0.0560(19)	0.2282(16)	3.42(27)
O1	0.3053(22)	−0.0752(16)	0.2691(14)	5.16(30)
C2	−0.0443(28)	0.1945(20)	0.2375(18)	4.03(32)
O2	−0.1526(21)	0.1921(17)	0.3261(15)	5.10(28)
C3	0.5115(32)	0.2808(24)	0.1168(21)	4.94(40)
O3	0.6267(23)	0.2975(17)	0.0258(15)	5.52(30)
C4	0.0281(28)	0.2030(21)	−0.1161(18)	3.95(32)
C5	0.2023(26)	0.1269(20)	−0.1231(16)	3.70(29)
C6	0.3078(28)	0.2313(21)	−0.1312(18)	4.03(32)
C7	0.2183(35)	0.3792(26)	−0.1353(23)	5.60(46)
C8	0.0440(27)	0.3674(20)	−0.1250(17)	3.80(31)
C9	0.1556(25)	0.3773(19)	0.4271(16)	3.38(28)
C10	0.1854(30)	0.2132(22)	0.5013(19)	4.43(36)
C11	0.3665(37)	0.1969(28)	0.5125(24)	5.91(49)
C12	0.4398(41)	0.3451(32)	0.4267(26)	6.88(57)
C13	0.3030(30)	0.4476(23)	0.3849(19)	4.40(35)

ANISOTROPIC TEMPERATURE PARAMETERS ($\times 10^{-5}$)

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Rh1	1112(24)	959(15)	694(11)	−24(26)	−196(15)	−256(10)
Rh2	1257(26)	1425(20)	849(13)	175(31)	−300(17)	−531(13)

The parenthetic quantities are the estimated standard deviations estimated from the inverted least-squares matrix from the final cycle of refinement and are in units of the last place of decimals given.

The expression for the temperature factor used was:

$$\exp -(b_{11}h^2+b_{22}k^2+b_{33}l^2+2b_{12}hk+2b_{13}hl+2b_{23}kl)$$

TABLE 2

MOLECULAR GEOMETRY

Intramolecular distances and estimated standard deviations (Å)

Rh1–Rh2	2.681(2)	C1–O1	1.127(19)
Rh1–C1	2.017(17)	C2–O2	1.105(22)
Rh1–C2	1.894(20)	C3–O3	1.151(25)
Rh1–C4	2.265(18)	C4–C5	1.489(27)
Rh1–C5	2.259(15)	C5–C6	1.317(26)
Rh1–C6	2.223(18)	C6–C7	1.424(28)
Rh1–C7	2.234(22)	C7–C8	1.410(32)
Rh1–C8	2.280(17)	C8–C4	1.469(24)
Rh2–C1	1.990(17)	C9–C10	1.443(24)
Rh2–C3	1.840(23)	C10–C11	1.472(36)
Rh2–C9	2.355(16)	C11–C12	1.474(34)
Rh2–C10	2.263(18)	C12–C13	1.383(33)
Rh2–C11	2.224(22)	C13–C9	1.360(27)
Rh2–C12	2.206(27)		
Rh2–C13	2.306(18)		

Intramolecular angles and estimated standard deviations (degrees)

C1–Rh1–Rh2	47.6(5)	C1–Rh2–Rh1	48.4(5)
C1–Rh1–C2	90.6(8)	C1–Rh2–C3	91.9(8)
C2–Rh1–Rh2	89.5(6)	C3–Rh2–Rh1	88.2(7)
Rh1–C1–Rh2	84.0(6)	Rh1–C2–O2	177.0(17)
Rh1–C1–O1	136.5(17)	Rh2–C3–O3	175.6(19)
Rh2–C1–O1	139.2(16)		
C4–C5–C6	108.6(16)	C9–C10–C11	103.0(20)
C5–C6–C7	110.0(20)	C10–C11–C12	108.8(21)
C6–C7–C8	110.3(19)	C11–C12–C13	104.6(24)
C7–C8–C4	104.8(19)	C12–C13–C9	112.4(19)
C8–C4–C5	106.3(19)	C13–C9–C10	110.5(19)

The angles subtended at a carbon atom by the rhodium atom and adjacent carbon vary between 68.4 and 75.3° with e.s.d. 1.2° and average values of 71.6 and 71.7° for the rings attached to Rh1 and Rh2 respectively. The angles subtended at the rhodium atoms by adjacent carbon atoms vary between 33.9 and 38.9° with e.s.d. 2.0° and mean values 36.8 and 36.6° for Rh1 and Rh2 respectively.

Best least-squares planes defined by atomic positions

In the following equations the quantities X, Y, Z refer to orthogonal coordinates obtained by the transformation

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} a & b\cdot\cos\gamma & c\cdot\cos\beta \\ 0 & b\cdot\sin\gamma & -c\cdot\cos\alpha^{*}\cdot\sin\beta \\ 0 & 0 & c\cdot\sin\beta\cdot\sin\alpha^{*} \end{bmatrix} \begin{bmatrix} x/a \\ y/b \\ z/c \end{bmatrix}$$

(*i*) Plane defined by Rh1, Rh2, C1 and O1:

$$-0.6854\,X + 0.1335\,Y + 0.7155\,Z + 0.2105 = 0$$

Deviations of atoms from this plane (Å):

Rh1	0.006	C1	−0.030
Rh2	0.007	O1	0.017

(*ii*) Plane defined by C4, C5, C6, C7 and C8:

$$0.0583\,X + 0.0406\,Y + 0.9975\,Z + 0.9669 = 0$$

Deviation of atoms from this plane (Å):

C4	0.005	C6	0.010	C8	0.001
C5	−0.009	C7	−0.006	Rh1	1.900

(*iii*) Plane defined by C9, C10, C11, C12 and C13:

$$0.0410\,X + 0.5081\,Y + 0.8603\,Z - 5.6310 = 0$$

Deviations of atoms from this plane (Å):

C9	0.022	C11	0.046	C13	0.008
C10	−0.042	C12	−0.034	Rh2	−1.914

groups are *trans* relative to one another. The structure can be considered as a distortion of that of $Cp_2Fe_2(CO)_4$[3] or $Cp_2Ru_2(CO)_4$[4]. Since the atomic number of rhodium is one more than that of ruthenium, a dimer would nominally require one less bond and it is the metal–metal bond which remains and one of the bridging carbonyl groups which is eliminated. Because of the absence of this bridging group, a space results into which both cyclopentadienyl groups partially move *i.e.* away from the remaining carbonyl bridge. Thus whilst in $Cp_2Ru_2(CO)_4$ the cyclopentadienyl rings are accurately parallel, in the present compound the normals to the rings make an angle of 28° with one another.

The Rh–Rh distance is 2.68 Å which indicates metal–metal bonding. The value is close to that found[5] in the metal, 2.69 Å, but shorter than those reported[6] for $Rh_6(CO)_{16}$, mean 2.78 Å.

The Rh–CO distances show the usual differences associated with terminal and bridging character. The Rh–C(terminal), 1.87 Å, are significantly shorter than the bridging distances, 2.01 Å, and the expected value for a single bond distance after allowance for *sp* character of the carbon ($1.32+0.70=2.02$ Å). The values are comparable with those in $Rh_6(CO)_{16}$[6] and $(Ph_3P)_3Rh(CO)H$[7], 1.86 and 1.81 Å respectively, but this group is shorter than that reported in $CpRh(CO)IC_2F_5$[8], 1.97 Å. These terminal carbonyls are linear within experimental error and the C–O distances, average 1.13 Å, are comparable with those found in $Rh_6(CO)_{16}$ and $(Ph_3P)_3Rh(CO)H$, 1.15 and 1.18 Å, respectively. The Rh–C (bridge) distances are nearer to the single bond expectation value ($1.32+0.74=2.06$ Å) and can be compared to the values found in $Cp_2Ru_2(CO)_4$[4], 1.99 Å. The C–O distance, 1.13 Å, is however rather shorter than would be expected and reflects the inaccuracy in the data which is referred to in the experimental section.

The cyclopentadienyl groups are planar; the maximum deviations from the "best least-squares planes" are 0.01 and 0.05 Å for the rings attached to Rh1 and Rh2 respectively. The metal atoms lie 1.90 and 1.91 Å from these planes. The same values occur in $(CpRhCO)_3$[9]. The corresponding Rh–C(ring) values are 2.25 and 2.27 Å. However the individual C–C distances, and the Rh–C distances, do show variation but this is not related in a systematic way from one half of the molecule to the other. We attribute this to the lack of precision in the data to which we have already referred.

The mass spectrum is in accord with the structure which we find. The main peaks occur at *m/e* values of 420[$Cp_2Rh_2(CO)_3^+$], 392, 364 and 336 (parent ion less 1, 2 and 3 carbonyls), 233 ($RhCp_2^+$), 224[$CpRh(CO)_2^+$], 196 ($CpRhCO^+$) and 168 ($RhCp^+$). In addition a peak occurs at *m/e* 504 which corresponds to $Cp_3Rh_3^+$. Since it is known[9,10] that $Cp_3Rh_3(CO)_3$ is a further photolysis product of $CpRh(CO)_2$, it is possible that the trimer fragment occurred either as a result of decomposition on the probe or as an impurity in the sample (though not in the single crystals used for analysis). We think the former is the more likely.

EXPERIMENTAL

Crystal data

$C_{13}H_{10}O_3Rh_2$ (mol. wt. 420.0), triclinic, $a=8.08\pm0.04$, $b=8.95\pm0.05$, $c=9.46\pm0.05$ Å, $\alpha=73°8'\pm10'$, $\beta=80°33'\pm10'$, $\gamma=83°9'\pm10'$, $U=644$ Å^3, $D_m=2.15\ g\cdot cm^{-3}$ by flotation in aqueous thallous malonate, $Z=2$, $D_c=2.17\ g\cdot cm^{-3}$ (the predicted value for the tetracarbonyl is $2.31\ g\cdot cm^{-3}$), space-group $P\bar{1}$ (C_i^1, No. 2) by intensity statistics and refinement of structure. For Mo–K_α radiation ($\lambda=0.7107$ Å), $\mu=27.9\ cm^{-1}$.

The complex occurs as a dark red solid and was recrystallised from petrol ether. Crystals from more than one preparation were examined to confirm that only one form of material was present and we succeeded in identifying and characterising only this one triclinic species.

For the measurement of intensities, a crystal was chosen whose maximum dimension was 0.15 mm. The data were collected and estimated by a variety of techniques which included integrated Weissenberg and non-integrated precession photographs. The intensities were estimated either visually or by the use of a Joyce–Loebl microdensitometer. In all nearly 3000 measurements were made of 1865 unique reflexions. No corrections were made for absorption.

Structure determination and refinement

The rhodium atom positions were determined from two-dimensional Patterson projections onto planes normal to the [100] and [010] directions. The phase contribution of these two atoms was sufficient to reveal sixteen light atoms in a three-dimensional Fourier synthesis of electron density. These atoms corresponded to the two cyclopentadienyl rings, two terminal carbonyl groups and one bridging carbonyl group. The structure was improved by Fourier refinement but no evidence for a second bridging group, which would have completed the analogy with $Cp_2Ru_2(CO)_4$, could be found. Further we demonstrated that if a second bridging group were present, then the largest minimum distance between the oxygen atom of this group and the atoms of the rest of the molecule would be only 2.2 Å whereas the van der Waals separation should be of the order of 3.2 Å. In confirmation of this expected separation, we note that the shortest non-bonded contact which is made by the oxygen atom of the bridging group which we did find is 3.2 Å. We concluded therefore that the formula of the complex must be $Cp_2Rh_2(CO)_3$.

The structure was refined by least-square methods. During the refinement we experienced some difficulties which we attribute to inaccuracies in the estimation of the intensities and some of the photographs were retaken and measured afresh. The structure is, however, left with rather a high degree of imprecision in the light atom positions. The rhodium atoms were refined with anisotropic thermal parameters but the light atoms were treated isotropically. The final R factor, $= \Sigma||F_o|-|F_c||/\Sigma|F_o|$, was 8.4% when only non-zero intensities were considered and 13.7% when all reflexions were included. This rather large difference is associated with the high threshold to detection associated with the use of the microdensitometer. The scattering factors used during the analysis were those of Thomas and Umeda[11] for rhodium and Berghuis *et al.*[12] for carbon and oxygen.

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SUMMARY

The product of the ultraviolet-light irradiation of a pentane solution of mono-

meric cyclopentadienyldicarbonylrhodium is shown to be dicyclopentadienyltricarbonyldirhodium. The structure is unusual in that it contains a single bridging carbonyl group. The crystals are triclinic with $a = 8.08 \pm 0.04$, $b = 8.95 \pm 0.05$, $c = 9.46 \pm 0.05$ Å, $\alpha = 73° 8' \pm 10'$, $\beta = 80° 33' \pm 10'$, $\gamma = 83° 9' \pm 10'$. The Rh–Rh distance is 2.68 Å, Rh–C(ring) 2.26 Å, Rh–C(terminal carbonyl) 1.87 Å and Rh–C-(bridging carbonyl) 2.01 Å.

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