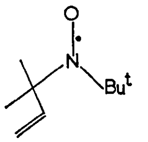
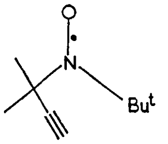
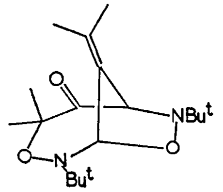
nitroxide radical (II) (Craig & Roberts, 1972), and the structure of the product could not be deduced by comparison with this reaction.


(I)


(II)


(III)

The X-ray analysis was undertaken to find the molecular structure of the unexpected product, and has shown it to be (III). A speculation has been made as to the mechanism of its formation and the origin of the additional oxygen atom (Craig *et al.*, 1973), but confirmation of this requires more experimental work with isotopically substituted molecules. The bicyclic ring system was hitherto unknown, but its detailed geometry does not appear to be remarkable. The five-membered ring and isopropylidene group should all be planar, and the least-squares plane is given in Table 4. The N–O bond lengths are consistent with other determinations of this distance (Murray-Rust, Murray-Rust & Riddell, 1974) in cyclic molecules, and the other lengths and angles are within typical ranges for organic compounds. There are no molecular contacts less than 3·5 Å, so packing forces are unlikely to affect the geometry.

Table 4. *Least-squares best plane through the five-membered ring and isopropylidene group*

Equation of plane: $13{\cdot}63x+7{\cdot}61y-0{\cdot}04z=3{\cdot}48$

Atom	Distance from plane (Å)
C(1)	−0·30
C(2)	−0·12
C(3)	−0·22
N(1)	0·18
O(1)	0·23
C(8)	0·03
C(9)	0·08
C(10)	0·11

We thank R. L. Craig for supplying the crystals.

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The Crystal and Molecular Structure of 1,5-Cyclooctadieneacetylacetonatorhodium(I)

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Abstract. $C_{13}H_{19}O_2Rh$, monoclinic, space group Cc, with $a=6{\cdot}854$ (5), $b=18{\cdot}645$ (10), $c=9{\cdot}864$ (7) Å, $\beta=93{\cdot}1$ (2)°, $U=1258{\cdot}7$ Å^3, $Z=4$, $D_c=1{\cdot}64$ g cm^{-3}. R is 0·040 for 1884 counter reflexions. Mean Rh–O and Rh–C bond lengths are 2·060 and 2·103 Å respectively.

Introduction. The yellow transparent crystals commonly have the forms {100}, {021} and {0$\bar{2}$1}. The cell dimensions were determined from precession photographs. The intensities of reflexions with $\theta<30°$ were measured on a Stoe Weissenberg diffractometer in ten layers, $0kl$ through $9kl$, with monochromatic Mo $K\alpha$ radiation and an ω-scan technique. A crystal of approximate dimensions $0{\cdot}081\times0{\cdot}031\times0{\cdot}017$ cm was used. The 1884 reflexions with significant intensity $[I<3\sigma(I)]$ and with $\sin\theta/\lambda>0{\cdot}1$ Å^{-1} were corrected for Lorentz and polarization effects. An absorption correction was applied [$\mu(\text{Mo } K\alpha) = 13{\cdot}03 \text{ cm}^{-1}$] by the method of de Meulenaer & Tompa (1965), as programmed by Alcock (1969).

Scattering factors were taken from Cromer & Waber (1965). The position of the rhodium atom was deduced from a Patterson synthesis and the remaining non-hydrogen atoms from a difference synthesis. Block-diagonal least-squares refinement reduced R to 0·040 [$R_w = \sum w(|F_o| - |F_c|)/\sum w|F_o| = 0{\cdot}044$ where $w = (1{\cdot}0 + 0{\cdot}114|F_o| + 0{\cdot}0004|F_o|^2)^{-1}$]. The function minimized was $\sum w(|F_o| - |F_c|)^2$, the weighting scheme introduced in order that $w(|F_o| - |F_c|)^2$ be approximately independent of $|F_o|$. In addition to refinement of positional and anisotropic thermal parameters of the non-hydrogen atoms, the positional parameters of the four olefinic protons were refined. The remaining hydrogen atoms were included at positions derived from a difference synthesis calculated after several cycles of refinement. All hydrogen atoms were given temperature factors of $B = 5{\cdot}0$ Å^2. A correction to the structure factors for the anomalous dispersion (Cromer, 1965) of Rh was applied. The maximum shift in the final cycle was 0·3σ. The final atomic parameters are listed in Tables 1 and 2.* The molecular geometry and atom numbering are shown in Fig. 1.

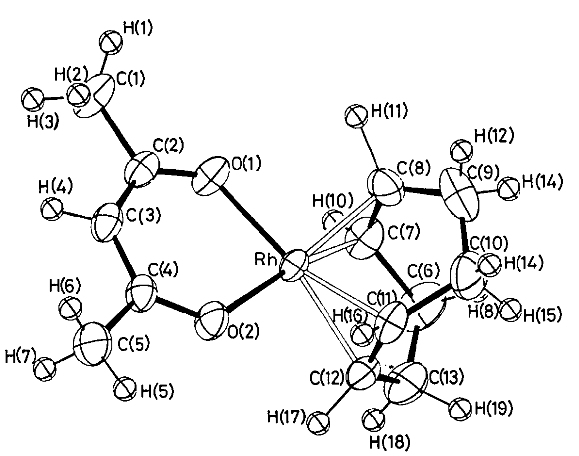

Fig. 1. The molecular geometry and numbering of the atoms. Thermal ellipsoids for atoms other than hydrogen are scaled to include 50% probability. The hydrogen atom ellipsoids are scaled arbitrarily.

Table 2. *Hydrogen-atom coordinates*

Where appropriate standard deviations (in parentheses) are given.

	x	y	z
H(1)	0·496	−0·021	0·272
H(2)	0·607	0·043	0·353
H(3)	0·515	−0·022	0·435
H(4)	0·236	−0·003	0·533
H(5)	−0·219	0·063	0·631
H(6)	−0·092	−0·011	0·629
H(7)	−0·004	0·059	0·709
H(8)	0·106	0·340	0·108
H(9)	−0·060	0·303	0·007
H(10)	0·249 (20)	0·236 (7)	0·125 (13)
H(11)	0·163 (20)	0·121 (8)	0·010 (13)
H(12)	−0·173	0·116	−0·078
H(13)	−0·144	0·200	−0·118
H(14)	−0·439	0·151	0·010
H(15)	−0·372	0·235	0·010
H(16)	−0·336 (24)	0·154 (6)	0·247 (16)
H(17)	−0·217 (22)	0·249 (7)	0·374 (14)
H(18)	−0·075	0·341	0·273
H(19)	−0·251	0·335	0·156

Discussion. In connexion with recent work in this laboratory on the reaction products of hexafluorobut-2-yne with metal diene complexes (Jarvis, Kemmitt,

Table 1. *Final atomic parameters with standard deviations* (*in parentheses*)

Temperature factor is in the form $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{23}klb^*c^* + 2B_{12}hka^*b^* + 2B_{13}hla^*c^*]$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
Rh	0·0*	0·15699 (2)	0·25*	2·59 (2)	2·03 (2)	3·33 (2)	0·40 (2)	−0·05 (1)	0·17 (2)
O(1)	0·2540 (8)	0·0972 (3)	0·2669 (6)	3·1 (2)	3·0 (2)	5·5 (3)	0·9 (2)	0·3 (2)	0·5 (2)
O(2)	−0·0863 (9)	0·1142 (3)	0·4291 (5)	4·1 (2)	3·4 (2)	3·9 (2)	1·3 (2)	0·6 (2)	0·6 (2)
C(1)	0·4796 (13)	0·0096 (5)	0·3452 (12)	3·5 (3)	3·8 (3)	7·5 (5)	0·9 (3)	0·3 (3)	0·9 (3)
C(2)	0·2941 (11)	0·0514 (4)	0·3588 (8)	2·8 (2)	2·3 (2)	4·9 (3)	−0·2 (2)	−0·5 (2)	−0·1 (2)
C(3)	0·1844 (12)	0·0350 (4)	0·4692 (8)	4·0 (3)	2·5 (2)	4·4 (3)	0·5 (2)	−0·7 (2)	0·2 (2)
C(4)	0·0083 (12)	0·0669 (4)	0·4994 (7)	4·0 (3)	2·7 (2)	3·6 (3)	0·5 (2)	−0·2 (2)	0·1 (2)
C(5)	−0·0855 (18)	0·0432 (5)	0·6261 (10)	6·8 (6)	4·6 (4)	4·5 (4)	1·8 (3)	1·2 (4)	1·0 (4)
C(6)	0·0077 (19)	0·2996 (5)	0·0973 (14)	6·7 (6)	3·0 (3)	9·2 (7)	2·3 (4)	2·0 (5)	0·1 (4)
C(7)	0·1159 (12)	0·2282 (4)	0·1081 (9)	3·7 (3)	3·7 (3)	5·3 (4)	1·4 (3)	0·8 (3)	−0·3 (3)
C(8)	0·0367 (17)	0·1669 (5)	0·0416 (8)	6·2 (5)	4·4 (3)	3·0 (3)	0·6 (2)	1·0 (3)	0·6 (3)
C(9)	0·1514 (26)	0·1637 (8)	0·0396 (11)	8·5 (9)	8·4 (8)	3·4 (4)	0·3 (4)	−1·1 (4)	−0·9 (6)
C(10)	−0·3272 (16)	0·1848 (7)	0·0370 (11)	4·7 (4)	6·3 (5)	5·7 (5)	−0·4 (4)	−2·0 (4)	0·2 (4)
C(11)	−0·2899 (11)	0·1829 (4)	0·1883 (9)	2·9 (3)	3·8 (3)	5·1 (4)	0·8 (3)	−0·5 (2)	0·3 (2)
C(12)	−0·2055 (12)	0·2400 (4)	0·2629 (8)	4·2 (3)	3·3 (3)	4·1 (3)	0·3 (2)	0·4 (2)	1·4 (3)
C(13)	−0·1355 (19)	0·3089 (4)	0·2003 (11)	7·6 (6)	2·5 (3)	6·6 (5)	0·6 (3)	0·4 (4)	1·2 (3)

* Parameters fixed by choice of origin.

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* A list of observed and calculated structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30712 (12 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Kimura, Russell & Tucker, 1974) we wished to have accurate data on the geometry of coordination of 1,5-cyclooctadiene to rhodium(I).

Bond lengths and angles for the title compound are listed in Table 3 and the molecular packing is shown in Fig. 2. The mean Rh–O length is similar to that reported in other molecules either with olefinic bonds [*e.g.* 2·075 Å in bis(tetramethylallene)acetylacetonatorhodium(I) (Hewitt & De Boer, 1971)] or carbonyl groups [*e.g.* 2·06 Å in dicarbonylacetylacetonatorhodium(I) (Bailey, Coater, Robinson, Bonati & Ugo, 1967)] *trans* to oxygen.

The bond lengths and angles in the rhodiumacetylacetonate ring are equal, within experimental error, to those reported in molecules containing similar rings (Hewitt & De Boer, 1971; Bailey *et al.*, 1967). As expected for a delocalized system the C–O bonds are significantly longer than ketonic bonds (1·215 Å; Sutton, 1965) and the C–C rhodiumacetylacetonate ring bonds are equal and significantly shorter than the accepted C–C(=C) length (1·510 Å; Sutton, 1965). These C–O and C–C lengths imply π-bond orders of about 0·7 (Popov, Kogan & Zheltnova, 1970). The angles at C and O are larger than 120° reflecting the strain imposed by the small angle at the metal and the requirement, for maximum electron delocalization, of ring planarity. The rhodiumacetylacetonate ring is approximately planar (Table 4) with the Rh atom furthest

Table 3. *Bond lengths* (Å) *and angles* (°) *with estimated standard deviations in parentheses*

Rh—O(1)	2·054 (5)
Rh—O(2)	2·066 (5)
Mean	2·060
Rh—C(7)	2·115 (7)
Rh—C(8)	2·092 (8)
Rh—C(11)	2·101 (7)
Rh—C(12)	2·101 (7)
Mean	2·103
C(2)—O(1)	1·28 (1)
C(4)—O(2)	1·27 (1)
C(2)—C(3)	1·39 (1)
C(3)—C(4)	1·39 (1)
C(2)—C(1)	1·50 (1)
C(4)—C(5)	1·50 (1)
C(7)—C(8)	1·41 (1)
C(11)–C(12)	1·40 (1)
C(8)—C(9)	1·49 (2)
C(7)—C(6)	1·53 (1)
C(11)–C(10)	1·50 (1)
C(12)–C(13)	1·51 (1)
Mean	1·51
C(9)—C(10)	1·51 (2)
C(6)—C(13)	1·46 (2)
C(7)—H(10)	0·9 (1)
C(8)—H(11)	1·3 (1)
C(11)–H(16)	1·0 (1)
C(12)–H(17)	1·0 (1)

Rh—O(1)—C(2)	125·1 (5)
Rh—O(2)—C(4)	125·2 (5)
O(1)—C(2)—C(3)	127·2 (7)
O(2)—C(4)—C(3)	127·0 (7)
C(2)—C(3)—C(4)	125·6 (6)
O(1)—Rh—O(2)	89·8 (2)
O(1)—C(2)—C(1)	116·2 (7)
C(3)—C(2)—C(1)	116·6 (7)
O(2)—C(4)—C(5)	115·4 (7)
C(3)—C(4)—C(5)	117·6 (7)
C(6)—C(7)—C(8)	120 (1)
C(7)—C(8)—C(9)	126 (1)
C(10)–C(11)–C(12)	123 (1)
C(11)–C(12)–C(13)	124 (1)
Mean	123
C(7)—C(6)—C(13)	113 (1)
C(8)—C(9)—C(10)	114 (1)
C(9)—C(10)–C(11)	113 (1)
C(12)–C(13)–C(6)	115 (1)
Mean	114
C(8)—C(7)—H(10)	124 (8)
C(7)—C(8)—H(11)	114 (6)
C(12)–C(11)–H(16)	106 (10)
C(11)–C(12)–H(17)	124 (8)
C(6)—C(7)—H(10)	110 (8)
C(9)—C(8)—H(11)	115 (6)
C(10)–C(11)–H(16)	129 (10)
C(13)–C(12)–H(17)	108 (7)

Table 4. *Parameters of mean planes through sets of atoms and* (*in square brackets*) *distances of atoms from the planes*

The equation of a plane is $lx+my+nz=p$ with coordinates and distances (Å) referred to orthogonal axes a, b and c'.

	l	m	n	p
(i) O(1), O(2), C(2), C(3), C(4), [O(1) 0·01, O(2) −0·01, C(2) −0·01, C(3) −0·01, C(4) 0·02, C(1) −0·05, C(5) 0·05, Rh −0·08, C(6) 1·05, C(9) −1·94, C(7) 0·50, C(8) −0·90, C(13) 1·24, C(10) −1·82, C(12) 0·43, C(11) −0·96]	0·4581	0·7087	0·5366	3·428
(ii) C(6), C(7), H(9)	0·1746	0·0171	−0·9845	−0·847
(iii) C(9), C(8), H(10)	0·3900	0·6466	−0·6556	1·835
(iv) C(13), C(12), H(16)	0·9417	−0·2971	0·1580	−2·364
(v) C(10), C(11), H(17)	0·7733	−0·6243	−0·1107	−3·940
(vi) O(1), O(2), M* (1), M(2) [O(1) 0·01, O(2) −0·01, M(1) 0·01, M(2) −0·01, Rh 0·03]	0·4178	0·7629	0·4934	3·367
(vii) M*(1), M(2), M(3)	0·3922	0·7929	0·4664	3·459
(viii) C(7), C(8), C(11), C(12) [C(7) −0·03, C(8) 0·03, C(11) −0·03, C(12) 0·03]	0·3788	−0·6155	0·6912	−1·574

Dihedral angles between planes

(ii) and (iii) 43° (iv) and (v) 26° (i) and (vii) 7° (vi) and (viii) 88°

* M(1) is the midpoint of the C(7)–C(8) bond, M(2) is the midpoint of the C(11)–C(12) bond and M(3) is the centroid of the four atoms C(6), C(9), C(10) and C(13).

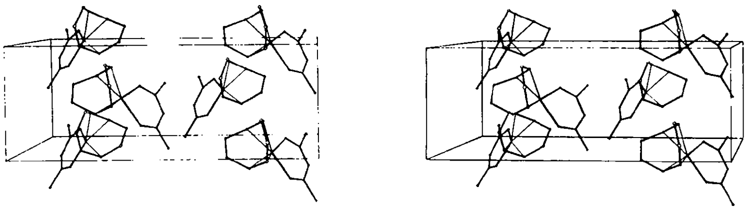

Fig. 2. A stereoscopic drawing of the molecular packing looking along **c**.

from the mean plane. The non-planarity is effected by small torsion angles about the C–O and C–C bonds.

The cyclooctadiene ligand has a skewed conformation as observed in the free molecule (Hedberg & Hedberg, 1964) and when coordinated to other metals. It has approximate symmetry 2. The angle between the projections of C(6)–C(13) and C(9)–C(10) on the plane passing through the midpoints of C(7)–C(8), C(11)–C(12), C(9)–C(6) and C(3)–C(10) is approximately 17°. The mean C=C length of 1·41 Å is longer than in the free molecule (1·341 Å; Hedberg & Hedberg, 1964) and in 1,5-cyclooctadiene-duroquinonenickel (1·325 Å; Glick & Dahl, 1965) but equal, within experimental error, to the equivalent lengths in 1,5-cyclooctadienerhodium(I) chloride (1·44 Å; Ibers & Snyder, 1962) and 1,5-cyclooctadienecopper(I) chloride (1·41 Å; Van den Hende & Baird, 1963). The C(sp^2)–C(sp^3) lengths and the ring angles are not significantly different from those reported in the free molecule or in other metal complexes of the ligand. C(6)–C(13) is shorter than is usually found, but as C(6) and C(13) have relatively large thermal parameters and no corrections for librational effects have been made, this observation may not be significant.

The geometry of the cyclooctadiene ligand is altered slightly on coordination and this is reflected in the cross-ring distances. The distance between the midpoints of C(7)–C(8) and C(11)–C(12) is 3·05 Å in the free molecule, 2·91 Å in cyclooctadiene-duroquinone nickel, a complex in which it is suggested that cyclooctadiene is only weakly bonded (Glick & Dahl, 1965), and 2·74 Å in the title compound. The skewing of the diene makes the C(6)···C(10) and C(9)···C(13) distances non-equivalent at 3·60 and 3·17 Å respectively. The difference between these two values decreases as the ligand becomes more strongly bonded to a metal, the difference being 0·68 Å in the free molecule, 0·58 Å in the duroquinonenickel complex and 0·43 Å in the title compound.

The extent of rehybridization of the olefinic carbon atoms on coordination to the metal may be measured by the angle between the two planes, each defined by an olefinic carbon atom and the carbon and hydrogen atoms bonded to it, of each olefinic bond. The poorly determined hydrogen-atom coordinates lead to an inaccurate determination of this quantity (Table 4) but the mean value of 35° compares well with the value reported for the angle between the two CH_2 planes of the ethylene ligand in the neutron diffraction study of Zeise's salt, $K[Pt(C_2H_4)Cl_3]$ (35°; Hamilton, Klanderman & Spratley, 1969).

The deviations of the carbon atoms in the cyclooctadiene ring from the mean rhodiumacetylacetonate plane show that this plane does not contain the approximate twofold axis of the cyclooctadiene ligand. The angle between this axis and its projection on the acetylacetonato plane is about 7°. The entire molecule is therefore without symmetry.

There are no exceptionally short intermolecular contacts; those shorter than the sum of van der Waals atomic radii (Pauling, 1960) are H(4)···H(11^{I}), 2·27 Å and H(5)···H(8^{II}), 2·17 Å, where the superscripts refer to atoms related to those in Table 1 by the operations $(x,-y,\frac{1}{2}+z)$ for (I) and $(x-\frac{1}{2},\frac{1}{2}-y,\frac{1}{2}+z)$ for (II). The shortest Rh···Rh contact is 6·80 Å.

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