Low-Temperature Structure of Nonacarbonyl-μ_3-chloromethylidyne-tri-μ-hydrido-*triangulo*-triruthenium

By N. J. Zhu, C. Lecomte, P. Coppens and J. B. Keister

Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214, USA

Abstract. $Ru_3H_3(CO)_9CCl$, orthorhombic, *Pnma*, $a = 17\cdot469$ (2), $b = 14\cdot499$ (2), $c = 6\cdot668$ (1) Å, $V = 1689$ Å^3, $Z = 4$, $D_c = 2\cdot38$ g cm^{-3} at 160 ± 5 K, μ(Mo $K\alpha$) = 28·01 cm^{-1}; $R(F) = 0\cdot018$ for 1979 unique reflections with $F_o > 3\sigma(F_o)$. The molecule has approximate C_{3v} symmetry and lies on a crystallographic mirror plane. The three Ru atoms define an equilateral triangle [$\langle Ru-Ru \rangle = 2\cdot8525$ (5) Å] and are each bonded to three CO ligands. The three H atoms, which have been located from a difference Fourier map, symmetrically bridge the three Ru–Ru edges and are displaced from the Ru plane in a direction away from the CCl ligand.

Introduction. A low-temperature determination of the crystal structure of $Ru_3H_3(CO)_9CCl$ was undertaken as a preliminary to a study of the electron distribution in this second-row transition-metal cluster.

The sample was prepared and recrystallized as described previously (Keister & Horling, 1980). A needle-shaped $Ru_3H_3(CO)_9CCl$ crystal of approximate dimensions 0·1 × 0·1 × 0·26 mm was selected and mounted on an automatic CAD-4 diffractometer, then cooled to 160 ± 5 K with a locally modified Enraf–Nonius low-temperature device.

Cell dimensions were determined by least-squares refinement of the setting angles of 25 reflections with $\theta > 24°$. Intensity measurements of both *hkl* and *h̄kl* octants were carried out up to $\theta = 30°$ in the ω-scan mode with graphite-monochromated Mo $K\alpha$ radiation ($\bar{\lambda} = 0\cdot71069$ Å), with the angle ψ selected such as to minimize absorption in the needle-shaped crystal. The intensities of nine standard reflections were monitored every 3 h and the positions of two reflections were used to check the orientation of the crystal every 200 reflections. 6895 reflections were averaged after correction for Lorentz–polarization and absorption effects (Coppens, Leiserowitz & Rabinovich, 1965) to give 2552 unique reflections. The internal agreement factor between the symmetry-related reflections is $R(F^2) = 0\cdot024$.

This compound is isomorphous with $Ru_3H_3(CO)_9CCH_3$ (*Pnma*, $a = 17\cdot54$, $b = 14\cdot55$, $c =$ 6·766 Å), reported by Sheldrick & Yesinowski (1975). Therefore, the positional parameters of all the heavy atoms but Cl were taken from the earlier paper. The position of the Cl atom was located from a difference Fourier map. In the least-squares refinement $\sum w|F_o - |kF_c||^2$ was minimized with $\sigma^2(F_o^2) = (0\cdot03F_o^2)^2 + \sigma^2_{count}$

Table 1. *Fractional coordinates* ($\times 10^4$, *for* Ru $\times 10^5$) *and isotropic thermal parameters* ($\times 10^4$)

For non-hydrogen atoms $U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j$.

|	x	y	z	U_{eq}/U (Å^2)
Ru(1)	11001 (1)	34838 (1)	30459 (1)	157
Ru(2)	25140 (1)	25000	30882 (1)	152
Cl	1589 (1)	2500	−1435 (1)	243
O(1)	3486 (1)	2500	7023 (3)	351
O(2)	3393 (1)	3970 (1)	784 (3)	439
O(3)	1776 (1)	5157 (1)	934 (3)	497
O(4)	−366 (1)	3658 (1)	615 (3)	375
O(5)	506 (1)	4455 (1)	6909 (3)	416
C(1)	3140 (2)	2500	5606 (5)	238
C(2)	3073 (1)	3432 (2)	1685 (3)	249
C(3)	1517 (1)	4547 (2)	1739 (3)	272
C(4)	172 (1)	3602 (1)	1544 (3)	229
C(5)	734 (1)	4115 (1)	5511 (3)	253
C(6)	1585 (2)	2500	1197 (4)	155
H(1)	739 (22)	2500	4299 (68)	181
H(2)	1974 (16)	3345 (19)	4457 (43)	110
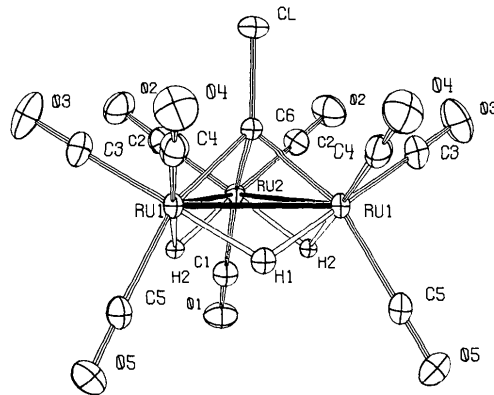
Fig. 1. *ORTEP* drawing (Johnson, 1965) of $Ru_3H_3(CO)_9CCl$ at 160 K. Ellipsoids are 50% probability surfaces.

Table 2. *Bond lengths (Å) and angles (°)*

Ru(1)–Ru(2)	2·8523 (4)		C(1)–O(1)	1·121 (4)
Ru(1)–Ru(1')	2·8527 (5)		C(2)–O(2)	1·132 (3)
			C(3)–O(3)	1·130 (3)
Ru(1)–C(3)	1·915 (2)		C(4)–O(4)	1·129 (3)
Ru(1)–C(4)	1·914 (2)		C(5)–O(5)	1·127 (3)
Ru(1)–C(5)	1·987 (2)			
Ru(2)–C(1)	2·004 (3)		Ru(1)–H(1)	1·77 (3)
Ru(2)–C(2)	1·913 (3)		Ru(1)–H(2)	1·81 (3)
			Ru(2)–H(2)	1·79 (3)
Ru(1)–C(6)	2·067 (2)			
Ru(2)–C(6)	2·056 (2)		Cl–C(6)	1·755 (3)
Ru(1')–Ru(1)–Ru(2)	59·99 (1)		C(3)–Ru(1)–C(4)	90·70 (10)
Ru(1)–Ru(2)–Ru(1')	60·01 (1)		C(3)–Ru(1)–C(5)	97·38 (9)
			C(4)–Ru(1)–C(5)	96·81 (9)
Ru(2)–Ru(1)–C(3)	94·45 (7)		C(1)–Ru(2)–C(2)	97·53 (9)
Ru(2)–Ru(1)–C(4)	141·63 (6)		C(1)–Ru(2)–C(2')	97·53 (9)
Ru(2)–Ru(1)–C(5)	120·06 (6)		C(2)–Ru(2)–C(2')	89·96 (14)
Ru(1')–Ru(1)–C(3)	143·62 (7)			
Ru(1')–Ru(1)–C(5)	95·16 (6)		Ru(1)–C(3)–O(3)	178·0 (2)
Ru(1')–Ru(1)–C(5)	117·40 (6)		Ru(1)–C(4)–O(4)	178·9 (2)
Ru(1)–Ru(2)–C(1)	118·77 (7)		Ru(1)–C(5)–O(5)	177·8 (2)
Ru(1)–Ru(2)–C(2)	94·81 (7)		Ru(2)–C(1)–O(1)	179·47 (2)
Ru(1')–Ru(2)–C(2)	118·76 (7)		Ru(2)–C(2)–O(2)	177·24 (2)
Ru(1')–Ru(2)–C(2)	142·27 (7)			
			Ru(1)–H(1)–Ru(1')	107 (2)
Ru(1)–C(6)–Cl	126·74 (9)		Ru(1)–H(2)–Ru(2)	104 (1)
Ru(2)–C(6)–Cl	127·63 (14)			
			C(3)–Ru(1)–H(1)	178·3 (1)
			C(4)–Ru(1)–H(2)	178·8 (1)
			C(2)–Ru(2)–H(2)	178·1 (1)

and $1/w = [(F_o^2)^2 + \sigma^2(F_o^2)/2]^{1/2} - F_o^2$. Only reflections for which $F_o > 3\sigma(F_o)$ were included in the refinement. After a number of cycles with anisotropic thermal parameters for all the heavy atoms, a difference Fourier map clearly revealed the positions of the H atoms. They were included in the refinement process with isotropic temperature factors. The final values of $R(F)$ $(= \sum |F_o - k|F_c||/\sum F_o)$ and $R_w(F)$ $[= (\sum w|\Delta F|^2/ \sum wF_o^2)^{1/2}]$ are 0·018 and 0·037 respectively. A listing of fractional coordinates and equivalent isotropic temperature factors is given in Table 1.*

Discussion. The molecular structure is shown in Fig. 1. Bond lengths and bond angles are listed in Table 2.

Deviations from C_{3v} molecular symmetry are very small. The three Ru atoms form a triangle of sides

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36510 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

2·8523 (4), 2·8523 (4) and 2·8527 (5) Å. Each Ru atom is bonded to one 'axial' and two 'equatorial' terminal carbonyl ligands. As pointed out by several authors (Sheldrick & Yesinowski, 1975; Leung, Coppens, McMullan & Koetzle, 1981), there are significant differences between the axial and equatorial metal–carbon bond lengths $[Ru-C_{axial} = 1·995 (2)$ Å, $Ru-C_{equatorial} = 1·914 (2)$ Å]. The C–O bond lengths do not vary correspondingly; they show only a small variation from 1·121 (4) to 1·130 (3) Å.

Bridging H atoms are on the opposite side of the plane of the Ru atoms from the CCl moiety. The distances from the plane through the Ru atoms are 0·84 and 0·92 Å for H(1) and H(2) respectively. The average Ru–H distance is 1·79 (2) Å compared with 1·793 Å obtained in a neutron diffraction study of (*tert*-butylethynyl)nonacarbonyl-μ-hydrido-*triangulo*-triruthenium (Catti, Gervasio & Mason, 1977). The Ru(1)–H(1)–Ru(1') and Ru(1)–H(2)–Ru(2) bond angles are 107 (2) and 104 (1)° respectively, compared to 90° deduced from spectroscopic data (Oxton, 1981). It should be noted that the present results from low-temperature X-ray diffraction are likely to be affected by the asphericity of the H electron density due to bonding. But the discrepancy with the spectroscopic results seems too large to be explained in this way. A comparative neutron diffraction study is planned for analysis of the electron density distribution around the H nucleus.

References

CATTI, M., GERVASIO, G. & MASON, S. A. (1977). *J. Chem. Soc. Dalton Trans.* pp. 2260–2264.
COPPENS, P., LEISEROWITZ, L. & RABINOVICH, D. (1965). *Acta Cryst.* **18**, 1035–1038.
JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
KEISTER, J. B. & HORLING, T. L. (1980). *Inorg. Chem.* **19**, 2304.
LEUNG, P., COPPENS, P., MCMULLAN, R. K. & KOETZLE, T. F. (1981). *Acta Cryst.* **B37**, 1347–1352.
OXTON, I. A. (1981). *Spectrochim. Acta.* In the press.
SHELDRICK, G. M. & YESINOWSKI, J. P. (1975). *J. Chem. Soc. Dalton Trans.* p. 873.