

Crystal Structure of Nonacarbonyl- μ_3 -ethylidyne-tri- μ -hydrido-triruthenium

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Crystals of the title compound (I) are orthorhombic, space group $Pnma$, $a = 17.54(3)$, $b = 14.55(2)$, $c = 6.766(10)$ Å, $Z = 4$. The structure was solved by the heavy-atom method and refined by full-matrix least-squares to R 0.047 for 1018 unique reflections measured by diffractometer. The molecule lies on a crystallographic mirror plane and possesses approximately C_{3v} ($3m$) symmetry; principal bond lengths (averaged for C_{3v}): Ru \cdots Ru 2.842(6), Ru–C(O) 1.869(15) and 1.956(19), Ru–C(C) 2.083(11), C–O 1.152(16), and C–C 1.511(20) Å. The bridging hydrogen atoms were located in symmetrical positions on the opposite side of the Ru₃ plane from the CMe moiety; their positions were refined from the X -ray data subject to the constraints that all Ru–H and all (C)C–H distances were respectively equal, leading to Ru–H, 1.72(7) Å and Ru–H–Ru, 112(7)°. The nematic-phase proton n.m.r. spectrum has been reinterpreted in the light of the idealised heavy-atom geometry found in the crystal, and used to give calculated values for Ru–H (1.81 Å) and Ru–H–Ru (103°), which are probably more accurate than those calculated only from X -ray data.

In a study of the nematic-phase proton n.m.r. spectrum of nonacarbonyl- μ_3 -ethylidyne-tri- μ -hydrido-triruthenium (I),¹ it was necessary to make a number of geometrical assumptions in order to locate the positions of

the bridging hydrogen atoms relative to the heavy-atom skeleton. It seemed desirable to check these by means

¹ A. D. Buckingham, J. P. Yesinowski, A. J. Canty, and A. J. Rest, *J. Amer. Chem. Soc.*, 1973, **95**, 2732.

of a crystal-structure determination, and also to see if any information about the hydrogen atom positions could be obtained.

EXPERIMENTAL

Intensities were determined on a Stoe Stadi 2 two-circle diffractometer (layers $hk0-4$ and $0-10kl$) with Mo- K_{α} radiation and graphite-crystal monochromator from two crystals (*ca.* $0.03 \times 0.04 \times 0.15$ and $0.08 \times 0.18 \times 0.09$ mm respectively) sealed in Lindemann glass capillary tubes. Data were collected in an approximately 'constant count' mode; where a prescan indicated that the count could not be achieved within a specified time, the reflection was ignored.² A stationary-background- ω scan-stationary-background technique was employed, with variable reflection width, and with the background proportional to the step-measurement time. Of 5147 reflections measured, 678 were rejected because the net count was $< 3\sigma$ based on counting statistics, because of background imbalance, or because of peak centring errors. Lorentz, polarisation, and absorption corrections were applied. Data from different layers were placed on a common scale by linear least-squares, and equivalent reflections averaged to give 1018 unique observed reflections. Unit-cell dimensions were obtained from a least-squares fit to diffractometer zero-layer ω angle measurements for the two crystals.

RESULTS

Crystal Data.— $C_{11}H_6O_9Ru_3$, $M = 585.5$, Orthorhombic, $a = 17.54(3)$, $b = 14.55(2)$, $c = 6.766(10)$ Å, $U = 1726$ Å³, $Z = 4$, $D_c = 2.25$, $F(000) = 1104$. Mo- K_{α} radiation, $\lambda = 0.71069$ Å, $\mu(\text{Mo-}K_{\alpha}) = 25.7$ cm⁻¹. Space group $Pnma$ or $Pn2_1a$ from systematic absences: $0kl$ with $k + l$ odd, $hk0$ with h odd, shown to be the former by subsequent successful refinement.

The asymmetric unit consists of one half of one molecule; one ruthenium, three carbon, one oxygen and two hydrogen atoms lie in the mirror plane at $y/b = 0.25$, and the remaining atoms occupy the eight-fold general positions: $\pm(x, y, z; \frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z; -x, \frac{1}{2} + y, -z; \frac{1}{2} - x, -y, \frac{1}{2} + z)$.

Structure Solution and Refinement.—The ruthenium co-ordinates were obtained from a Patterson function, and the carbon and oxygen atoms found in the first difference electron-density synthesis. The structure was refined by full-matrix least-squares, with complex neutral-atom scattering factors for all atoms,³ and a weighting scheme of the form $w = \Sigma[\sigma^2(N) + 0.001N^2]^{-1}$, where N is the net peak count, and the summation is over equivalent reflections. An isotropic secondary extinction parameter⁴ was included in the refinements, but the value obtained [$10^6 Q_0 \rho^* = 4(3)$ cm⁻¹] was not significantly > 0 . In the first refinement, anisotropic temperature factors were employed for ruthenium, and isotropic temperature factors for the carbon and oxygen atoms; hydrogen atoms were omitted. This converged to $R' 0.0399$ [$R' = \Sigma w^{\frac{1}{2}}|F_o - F_c|/\Sigma w^{\frac{1}{2}}|F_o|$], with a corresponding unweighted index R of 0.0474 , for 61 independent parameters. The resulting difference electron-density synthesis had peaks in the positions expected for symmetrically bridging hydrogen atoms. It was found possible to refine these by imposing the C_{3v} ($3m$) molecular symmetry found in the n.m.r. studies^{1,5} and also found, to a

² W. Clegg and G. M. Sheldrick, unpublished work.

³ D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17; D. T. Cromer and J. T. Waber, *ibid.*, p. 104.

good approximation, for the rest of the molecule in the crystal. This was achieved in practice by assuming that all Ru-H bonds were equal, and that bridging hydrogen atoms were equidistant from C(6). Thus, three new independent variables were introduced: these two distances, which refined to Ru-H $1.72(7)$ and C(6)-H $2.49(12)$ Å, and a common hydrogen-atom isotropic temperature factor, which refined to $U(H) 0.063(35)$ Å². The final value of R' was 0.0395 , and of R 0.0469 . The methyl hydrogen atoms were not located; it is likely that the barrier to torsional motion is low in this compound.

Reinterpretation of Nematic-phase N.m.r. Data.—The analysis of n.m.r. data yielded the ratios of three proton-proton distances: H(C)H, H(Ru)H, and H(C) \cdots H(Ru) averaged by methyl-group rotation. Assuming C_{3v} ($3m$) molecular symmetry and intramethyl H \cdots H 1.780 Å, an intrahydride distance of 2.486 Å and a distance between the planes of the methyl and hydride protons of 4.115 Å was calculated.¹ Assuming (as before) C-H 1.093 Å, but using the nonprotonic molecular dimensions from the crystal structure instead of guessing them, we calculate Ru-H 1.81 Å and Ru-H-Ru 103° , which differ by -0.09 Å and 2° respectively from the estimates made before the diffraction study. Since bond lengths involving hydrogen, obtained from X-ray data by use of a neutral spherical-atom scattering factor for hydrogen, are likely to be systematically shorter than the true internuclear separations by *ca.* 0.1 Å, the foregoing results are consistent with the values obtained directly from the X-ray data [Ru-H $1.72(7)$ Å; Ru-H-Ru $112(7)^\circ$]. The random errors are probably lower for the n.m.r. than for the X-ray results, but it is difficult to estimate them.

TABLE I

Fractional atomic co-ordinates ($\times 10^4$) and isotropic temperature factors (Å² $\times 10^3$)

	x/a	y/b	z/c	U
Ru(1)	1113(1)	3477(1)	3033(1)	*
Ru(2)	2515(1)	2500	3089(2)	*
C(1)	3141(11)	2500	5517(29)	56(4)
O(1)	3471(7)	2500	6947(22)	73(3)
C(2)	3075(7)	3398(8)	1738(20)	60(3)
O(2)	3379(6)	3956(6)	822(15)	84(3)
C(3)	1519(6)	4518(7)	1804(20)	50(3)
O(3)	1783(6)	5148(6)	1023(15)	85(3)
C(4)	216(7)	3600(7)	1672(18)	54(3)
O(4)	-330(6)	3661(5)	614(14)	77(3)
C(5)	747(7)	4101(7)	5395(19)	50(3)
O(5)	514(5)	4426(5)	6822(17)	79(3)
C(6)	1595(6)	2500	1154(7)	30(3)
C(7)	1602(10)	2500	-1079(25)	49(4)
H(1)	753	2500	4407	53(31)
H(2)	1981	3354	4460	53(31)

* Anisotropic temperature factors (Å² $\times 10^3$), in the form: $2\pi^2[h^2a^{*2}U_{11} + h^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hkb^{*c^*}U_{23} + 2hla^{*c^*}U_{13} + 2hka^{*b^*}U_{12}]$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ru(1)	39(1)	26(1)	33(1)	1(1)	-1(1)	4(1)
Ru(2)	33(1)	33(1)	31(1)	0	-2(1)	0

In the final refinement from the X-ray data, Ru-H and C(6) \cdots H distances were fixed at values (1.812 and 2.646 Å) obtained from the reinterpretation of the n.m.r. data. The refinement converged to virtually identical R values to those obtained when these two distances were refined, but with $U(H) 0.053(31)$ Å². The results of this refinement are given

⁴ A. C. Larson, in 'Crystallographic Computing,' ed. F. R. Ahmed, Munksgaard, Copenhagen, 1970, p. 291.

⁵ A. J. Canty, B. F. G. Johnson, J. Lewis, and J. R. Norton, *J.C.S. Chem. Comm.*, 1972, 1331.

in Table 1; the resulting bond lengths and angles are presented in Tables 2 and 3. Estimated standard deviations are random-error estimates calculated by use of the full covariance matrix, and include contributions from the errors in cell dimensions. Observed and calculated structure

TABLE 2

Bond lengths (Å)

Ru(1)-Ru(2)	2.841(6)	Ru(1)-H(1)	1.812
Ru(1)-Ru(1')	2.844(6)	Ru(1)-H(2)	1.812
Ru(1)-C(3)	1.868(14)	Ru(2)-H(2)	1.812
Ru(1)-C(4)	1.865(16)	C(1)-O(1)	1.127(22)
Ru(2)-C(2)	1.873(16)	C(2)-O(2)	1.152(15)
		C(3)-O(3)	1.156(14)
Ru(1)-C(5)	1.946(17)	C(4)-O(4)	1.161(15)
Ru(2)-C(1)	1.976(24)	C(5)-O(5)	1.150(15)
		C(6)-C(7)	1.511(20)
Ru(1)-C(6)	2.086(10)		
Ru(2)-C(6)	2.078(12)		

TABLE 3

Bond angles (°)

C(3)-Ru(1)-Ru(2)	94.7(5)	H(1)-Ru(1)-C(3)	175.4
C(4)-Ru(1)-Ru(2)	141.7(4)	H(1)-Ru(1)-C(4)	93.1
C(5)-Ru(1)-Ru(2)	120.5(5)	H(1)-Ru(1)-C(5)	80.2
C(6)-Ru(1)-Ru(2)	46.9(3)	H(1)-Ru(1)-C(6)	85.2
C(1)-Ru(2)-Ru(1)	119.5(5)	H(2)-Ru(1)-C(3)	89.8
C(2)-Ru(2)-Ru(1)	95.6(6)	H(2)-Ru(1)-C(4)	179.7
C(6)-Ru(2)-Ru(1)	47.1(3)	H(2)-Ru(1)-C(5)	83.4
		H(2)-Ru(1)-C(6)	85.2
C(4)-Ru(1)-C(3)	90.5(7)	H(2)-Ru(2)-C(1)	82.0
C(5)-Ru(1)-C(3)	96.5(7)	H(2)-Ru(2)-C(2)	92.4
C(5)-Ru(1)-C(4)	96.5(7)	H(2)-Ru(2)-C(6)	85.5
C(6)-Ru(1)-C(3)	97.3(5)		
C(6)-Ru(1)-C(4)	94.8(6)	C(7)-C(6)-Ru(1)	127.8(5)
C(6)-Ru(1)-C(5)	162.1(3)	C(7)-C(6)-Ru(2)	128.5(10)
C(2)-Ru(2)-C(1)	96.6(8)		
C(6)-Ru(2)-C(1)	162.8(6)	Ru(2)-C(6)-Ru(1)	86.0(4)
C(6)-Ru(2)-C(2)	95.7(6)		
		O(1)-C(1)-Ru(2)	177.1(17)
H(2)-Ru(1)-H(1)	86.6	O(2)-C(2)-Ru(2)	175.4(12)
H(2)-Ru(2)-H(2')	86.6	O(3)-C(3)-Ru(1)	178.3(10)
		O(4)-C(4)-Ru(1)	177.9(11)
Ru(2)-H(2)-Ru(1)	103.3	O(5)-C(5)-Ru(1)	176.4(10)
Ru(1)-H(1)-Ru(1')	103.4		

factors and shortest non-bonded distances are listed in Supplementary Publication No. SUP 21265 (6 pp., 1 microfiche).*

DISCUSSION

The molecule possess overall C_{3v} ($3m$) symmetry within experimental error (for the atom-numbering system and overall geometry see Figures 1 and 2); the ethylidyne C-C bond makes an angle of 0.4° with the normal to the Ru_3 plane. On each ruthenium atom there are two 'equatorial' carbonyl groups (mean Ru-C 1.87) tilted towards the ethylidyne group, and one 'axial' carbonyl (mean Ru-C 1.96 Å) tilted away from it. The mean Ru-C distance is close to the value [1.91(2) Å] found in $[Ru_3(CO)_{12}]$.⁶ The C-O bond lengths exhibit no significant variations (mean 1.152 Å). If we include the hydrides but ignore any Ru-Ru bond, the co-ordination of ruthenium is close to

* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

⁶ R. Mason and A. I. M. Rae, *J. Chem. Soc. (A)*, 1968, 778.

⁷ P. J. Roberts and J. Trotter, *J. Chem. Soc. (A)*, 1971, 1479.

⁸ R. J. Doedens, W. T. Robinson, and J. A. Ibers, *J. Amer. Chem. Soc.*, 1967, **89**, 4323.

octahedral; the two short Ru-C bonds are *trans* to hydrogen. The mean Ru...Ru distance (2.842 Å) is close to the unbridged Ru...Ru distances in $[Ru_3(CO)_{12}]$ (mean 2.85 Å)⁶ and in $[Ru_3(CO)_{10}L]$ [2.831 Å; L = 1,2-bis-(dimethylarsino)tetrafluorocyclobutene].⁷ Despite the general trend of increased metal-metal distance when there is hydrogen bridging, it is clearly dangerous to use the Ru...Ru distance as a criterion for hydrogen bridging. The bridging-hydrogen geometry reported here is

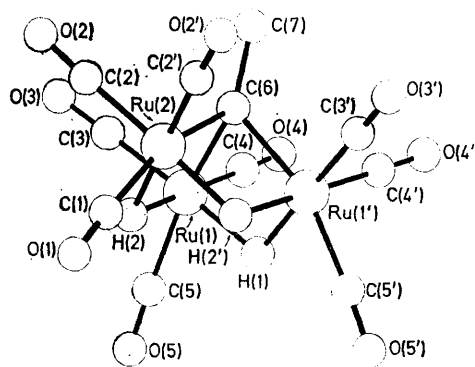
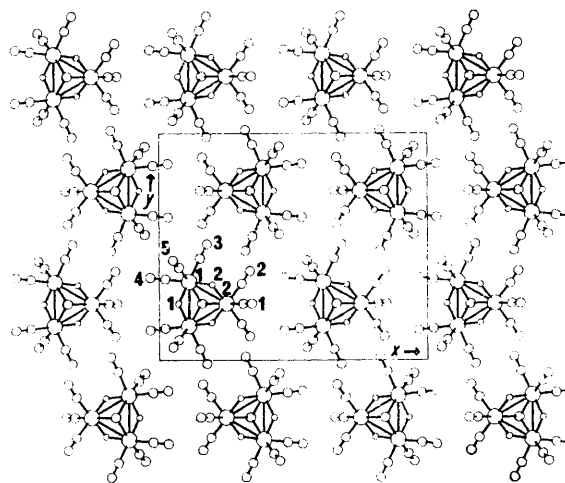


FIGURE 1 The molecule of (I)

FIGURE 2 Projection of the structure perpendicular to z , with the ruthenium, carbonyl, and hydride atoms in the asymmetric unit numbered

similar to that found from X -ray crystallographic studies of $[\{Mn(CO)_4\}_2H(PPh_3)]$ [Mn-H 1.86(6) Å, Mn-H-Mn' 104(5)°],⁸ $\{(CMe)_5RhCl\}_2HCl$ [Rh-H 1.85(5) Å, Rh-H-Rh' 104(4)°],⁹ and $[Et_4N]_2[\{W(CO)_4H\}_2]$ [W-H 1.85(7) Å, W-H-W 110(6)°].¹⁰ An appreciably wider angle at hydrogen is found in $[H_3Mn_3(CO)_{12}]$ [Mn-H 1.72(3) Å, Mn-H-Mn 131(7)°].¹¹ It is too early yet to comment on the differences between bridging and terminal metal-hydrogen distances, especially since the systematic error

⁹ M. R. Churchill and S. W.-Y. Ni, *J. Amer. Chem. Soc.*, 1973, **95**, 2150.

¹⁰ M. R. Churchill, S. W.-Y. Ni Chang, M. L. Berch, and A. Davison, *J.C.S. Chem. Comm.*, 1973, 691.

¹¹ S. W. Kirtley, J. P. Olsen, and R. Bau, *J. Amer. Chem. Soc.*, 1973, **95**, 4532.

introduced by the use of a spherical-atom scattering factor may be different in the two cases.

One possible method of locating the hydrogen atoms more accurately would be to study the nematic-phase proton n.m.r. of $[\text{H}_3\text{Ru}_3(\text{CO})_9(\text{CMe})]$ with ^{13}C substituted for one or more of the carbon atoms. However, an isotropic proton n.m.r. spectrum of the highly substituted derivative obtained by exchange of carbonyl groups with ^{13}C revealed the existence of unanalysed indirect ^{13}CH

couplings, which would considerably complicate the analysis of the nematic-phase spectrum.

Calculations were performed on the Cambridge University IBM 370/165 computer with programs written by G. M. S.; the structural diagrams were drawn by use of Dr. S. Motherwell's program PLUTO. We thank the S.R.C. for providing the diffractometer, and Dr. A. J. Canty for giving us the crystals.

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