Neutron-diffraction Study of a Symmetrical Ruthenium–Hydrogen–Ruthenium Bond in Nonacarbonylhydrido(t-butylethynyl)-*triangulo*-triruthenium

By **Michele Catti**, Istituto di Mineralogia, Cristallografia e Geochimica dell'Università, Via S. Massimo 24, 10123 Torino, Italy
Giuliana Gervasio,* Istituto di Chimica Generale ed Inorganica dell'Università, C.so Massimo d'Azeglio 48, 10125 Torino, Italy
Sax A. Mason, Institut Laue-Langevin, 156X, 38042 Grenoble, France

Neutron-diffraction investigation of the title compound has confirmed the presence of an hydridic hydrogen atom, as suggested by n.m.r. measurements. The compound crystallizes in the triclinic system, space group $P\bar{1}$, with $Z = 2$ in a unit cell of dimensions $a = 9.024(3)$, $b = 12.893(4)$, $c = 9.026(1)$ Å, $\alpha = 105.25(7)$, $\beta = 100.38(4)$, and $\gamma = 92.20(8)°$. Reflection intensities have been measured (λ 1.212 Å) with a step-scan technique up to $2\theta \leqslant 68°$. The anisotropic least-squares refinement, with 1 339 observed reflections, has led to R 0.028. The hydride atom lies on a pseudo-plane of symmetry out of the cluster plane, and forms a symmetrical bent Ru–H–Ru tricentric bond, confirmed by thermal-motion analysis. Extensions of the two axial Ru–C(carbonyl) bonds *trans* to the hydride atom clearly intersect at a point very close to the hydride atom; the Ru–H–Ru bond should thus be classified as ' open ', unlike other W–H–W bonds previously studied. The observation that the Ru_3 cluster has equilateral geometry shows that there is an exact balance between the lengthening effect of the hydride atom and the shortening effect of the organic ligand on the bridged Ru–Ru bond.

RECENT papers [1-3] have reported neutron-diffraction studies and reviewed the main features of the tricentric bond M–H–M (M = Mo or W). No similar investigation has been carried out for M = Ru although many ruthenium carbonyl hydrides are known, and only a few X-ray studies [4-10] have been able to determine the H position.

The presence of a hydrido-hydrogen atom in $[Ru_3H(CO)_9(C{\equiv}CBu^t)]$ was supported by n.m.r. measure-

---

[1] J. P. Olsen, T. F. Koetzle, S. W. Kirtley, M. Andrews, D. L. Tipton, and R. Bau, *J. Amer. Chem. Soc.*, 1974, **96**, 6621.

[2] J. L. Petersen, L. F. Dahl, and J. M. Williams, *J. Amer. Chem. Soc.*, 1974, **96**, 6610.

[3] T. F. Koetzle and R. Bau, *Proc. Conf. Neutron Scattering*, Tennessee, 6—10th June, 1976.

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

[5] A. J. P. Domingos, B. F. G. Johnson, J. Lewis, and G. M. Sheldrick, *J.C.S. Chem. Comm.*, 1973, 912.

[6] R. Bau, B. Don, R. Greatrex, R. J. Haines, R. A. Love, and R. D. Wilson, *Inorg. Chem.*, 1975, **14**, 3021.

[7] G. M. Sheldrick and J. P. Yesinowski, *J.C.S. Dalton*, 1975, 873.

[8] M. R. Churchill, B. G. De Boer, J. R. Shapley, and J. B. Keister, *J. Amer. Chem. Soc.*, 1976, **98**, 2357.

[9] M. R. Churchill, B. G. De Boer, and F. J. Rotella, *Inorg. Chem.*, 1976, **15**, 1843.

[10] G. Gervasio, D. Osella, and M. Valle, *Inorg. Chem.*, 1976, **15**, 1221.

ments,[11,12] but the *X*-ray analysis [13] could not locate it because of the poor quality of the data. The criterion of triruthenium cluster distortion did not help in this case, owing to the influence of the organic ligand. A neutron-diffraction study of this compound was suggested also by the interest in obtaining a more accurate characterization of the co-ordination of the organic ligand.

TABLE 1

Atomic fractional co-ordinates (Å) for $[Ru_3H(CO)_9(C{\equiv}CBu^t)]$ with estimated standard deviations in parentheses

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Ru(1)	0.084 0(2)	0.336 4(2)	0.682 5(2)
Ru(2)	0.099 7(2)	0.182 2(2)	0.850 6(2)
Ru(3)	0.303 2(2)	0.188 6(2)	0.653 3(2)
C(1)	−0.071 2(3)	0.269 2(2)	0.501 2(3)
C(2)	−0.053 1(3)	0.423 3(2)	0.785 4(3)
C(3)	0.161 8(3)	0.437 9(2)	0.590 6(3)
C(4)	0.143 8(2)	0.056 4(2)	0.924 4(3)
C(5)	0.032 2(3)	0.258 9(2)	1.034 6(3)
C(6)	−0.103 5(3)	0.139 0(2)	0.739 1(3)
C(7)	0.211 6(3)	0.146 0(2)	0.436 0(3)
C(8)	0.462 7(3)	0.275 1(2)	0.617 9(3)
C(9)	0.417 1(3)	0.064 8(2)	0.663 0(3)
C(10)	0.248 9(2)	0.319 9(2)	0.843 9(2)
C(11)	0.339 1(2)	0.263 1(2)	0.916 1(2)
C(12)	0.468 9(2)	0.277 0(2)	1.051 3(3)
C(13)	0.423 1(6)	0.342 8(5)	1.198 6(4)
C(14)	0.602 8(5)	0.337 1(4)	1.022 0(6)
C(15)	0.513 0(8)	0.170 8(4)	1.075 8(7)
O(1)	−0.160 0(5)	0.225 7(3)	0.396 1(5)
O(2)	−0.135 8(4)	0.472 3(3)	0.849 4(5)
O(3)	0.211 5(4)	0.498 4(4)	0.538 5(5)
O(4)	0.168 5(4)	−0.019 8(3)	0.958 5(4)
O(5)	−0.008 0(4)	0.302 6(3)	1.143 5(5)
O(6)	−0.225 3(5)	0.114 6(3)	0.676 1(5)
O(7)	0.158 5(4)	0.120 8(3)	0.306 2(4)
O(8)	0.557 1(5)	0.326 1(4)	0.596 5(4)
O(9)	0.473 3(4)	−0.011 3(3)	0.666 9(4)
H(1)	0.151 2(5)	0.103 6(3)	0.675 4(5)
H(2)	0.390 3(12)	0.418 3(9)	1.187 3(10)
H(3)	0.330 8(12)	0.302 6(11)	1.226 7(9)
H(4)	0.516 3(10)	0.358 7(7)	1.298 0(9)
H(5)	0.573 0(10)	0.415 4(9)	1.002 7(13)
H(6)	0.696 5(10)	0.354 9(7)	1.121 0(11)
H(7)	0.641 5(8)	0.289 1(10)	0.923 3(13)
H(8)	0.423 7(15)	0.131 3(10)	1.107 2(15)
H(9)	0.610 7(11)	0.181 6(6)	1.170 5(11)
H(10)	0.545 0(15)	0.118 4(9)	0.974 3(14)

EXPERIMENTAL

A crystal of $[Ru_3H(CO)_9(C{\equiv}CBu^t)]$, tabular along {010}, with well developed {100} and {001} forms (0.56 × 4.07 × 3.95 mm, 5.8 mm^3 volume), was grown by slow recrystallization at room temperature from a saturated solution in n-heptane. Neutron-diffraction intensities were collected on the D8 automatic four-circle diffractometer at the Institut Laue-Langevin. The following conditions were used: $\lambda = 1.212$ Å with a Cu(200) monochromator; neutron flux on the crystal, 10^7 n cm^{-2} s^{-1}; step-scan technique ($\omega - 2\theta$) with 31 steps for each reflection, pre-set monitor counting, and scan width increasing linearly with 2θ (4.2 — 4.8° in 2θ); $2\theta \leqslant 68°$; two reference reflections (333 and 318) were measured every 50 reflections. The method of minimum $\sigma(I)/I$ value [14] was used for locating peaks in the 1 723 measured intensity profiles. Since the intensities of the reference reflections increased after a reactor shutdown, owing to a slight change in the neutron flux, the last 302 measurements had to be rescaled with a factor of 0.80. After rejecting 254 intensities which were not statistically significant $[I \leqslant 3\sigma(I)]$, and averaging the centrosymmetrical ones, a final set of 1 339 independent observations was obtained.

The following cell parameters reported in the *X*-ray structural study [13] were used: $a = 9.024(3)$, $b = 12.893(4)$, $c = 9.026(1)$ Å, $\alpha = 105.26(7)$, $\beta = 100.38(4)$, $\gamma = 92.20(8)°$. Other crystal data are: space group $P\bar{1}$, $Z = 2$, $U = 992.45$ Å^3, $M = 637.45$, $D_c = 2.13$ g cm^{-3}, $D_m = 2.11$ g cm^{-3}, calculated linear absorption coefficient $\mu = 0.968$ cm^{-1}. (A value of 37 b * was used for the incoherent scattering cross section of hydrogen.) An absorption correction was applied using the program GONO9.[15]

TABLE 2

Root-mean-square displacements (Å) of atoms along the principal axes of their vibration ellipsoids for $[Ru_3H(CO)_9(C{\equiv}CBu^t)]$

	$(\bar{U}^2)_{\text{min.}}^{\frac{1}{2}}$	$(\bar{U}^2)_{\text{av.}}^{\frac{1}{2}}$	$(\bar{U}^2)_{\text{max.}}^{\frac{1}{2}}$
Ru(1)	0.148	0.189	0.214
Ru(2)	0.162	0.176	0.194
Ru(3)	0.166	0.175	0.196
C(1)	0.146	0.239	0.241
C(2)	0.166	0.213	0.250
C(3)	0.155	0.218	0.280
C(4)	0.160	0.192	0.228
C(5)	0.168	0.211	0.223
C(6)	0.152	0.212	0.249
C(7)	0.169	0.204	0.238
C(8)	0.172	0.209	0.260
C(9)	0.169	0.195	0.233
C(10)	0.138	0.168	0.183
C(11)	0.139	0.180	0.189
C(12)	0.143	0.207	0.220
C(13)	0.161	0.226	0.392
C(14)	0.172	0.239	0.369
C(15)	0.134	0.246	0.455
O(1)	0.163	0.312	0.325
O(2)	0.195	0.284	0.318
O(3)	0.197	0.277	0.380
O(4)	0.171	0.249	0.302
O(5)	0.180	0.287	0.300
O(6)	0.167	0.275	0.336
O(7)	0.162	0.265	0.320
O(8)	0.183	0.279	0.367
O(9)	0.170	0.254	0.309
H(1)	0.195	0.204	0.245
H(2)	0.230	0.300	0.498
H(3)	0.220	0.281	0.561
H(4)	0.190	0.312	0.436
H(5)	0.225	0.293	0.539
H(6)	0.177	0.328	0.440
H(7)	0.208	0.312	0.500
H(8)	0.227	0.322	0.531
H(9)	0.134	0.341	0.480
H(10)	0.192	0.272	0.666

The structure refinement was started from the *X*-ray parameters of the non-hydrogen atoms;[13] subsequent difference-Fourier maps revealed the positions of the H atoms. A correction for secondary extinction by least-squares fitting of the function $I_c/I_o = k(1 + gI_c)$ yielded $k = 0.978$ and $g = 1.37 \times 10^{20}$ cm^{-2}. The final cycle of full-matrix least-squares refinement with anisotropic temperature factors for all the atoms converged to R 0.028; unit

---

* Throughout this paper: 1 b = barn = 10^{-28} m^2.

[11] E. Sappa, O. Gambino, L. Milone, and G. Cetini, *J. Organometallic Chem.*, 1972, **39**, 169.

[12] S. Aime, O. Gambino, L. Milone, E. Sappa, and E. Rosenberg, *Inorg. Chim. Acta*, 1975, **15**, 53.

[13] G. Gervasio and G. Ferraris, *Cryst. Struct. Comm.*, 1973, **3**, 447.

[14] M. S. Lehmann and F. K. Larsen, *Acta Cryst.*, 1974, **A30**, 580.

[15] W. C. Hamilton, 'World List of Crystallographic Computer Programs,' 1966, Program no. 225.

TABLE 3

Interatomic distances (Å) for $[Ru_3H(CO)_9(C{\equiv}CBu^t)]$

Ru(1)–Ru(2)	2.795(3)	Ru(1)–Ru(3)	2.799(3)	Ru(2)–Ru(3)	2.792(3)
Ru(1)–C(1)	1.931(4)	Ru(2)–C(4)	1.938(3)	Ru(3)–C(7)	1.910(4)
Ru(1)–C(2)	1.903(3)	Ru(2)–C(5)	1.912(3)	Ru(3)–C(8)	1.911(3)
Ru(1)–C(3)	1.898(3)	Ru(2)–C(6)	1.910(4)	Ru(3)–C(9)	1.944(3)
Ru(1)–C(10)	1.947(3)	Ru(2)–C(10)	2.207(3)	Ru(3)–C(10)	2.214(3)
		Ru(2)–C(11)	2.268(3)	Ru(3)–C(11)	2.271(3)
		Ru(2)–H(1)	1.789(5)	Ru(3)–H(1)	1.796(5)
C(10)–C(11)	1.315(3)	C(12)–C(13)	1.514(5)	C(12)–C(15)	1.500(5)
C(11)–C(12)	1.500(3)	C(12)–C(14)	1.511(5)		
C(1)–O(1)	1.127(5)	C(4)–O(4)	1.124(5)	C(7)–O(7)	1.137(5)
C(2)–O(2)	1.136(5)	C(5)–O(5)	1.126(5)	C(8)–O(8)	1.132(5)
C(3)–O(3)	1.129(5)	C(6)–O(6)	1.134(5)	C(9)–O(9)	1.128(5)
C(13)–H(2)	1.054(14)	C(14)–H(5)	1.104(12)	C(15)–H(8)	1.057(14)
C(13)–H(3)	1.067(12)	C(14)–H(6)	1.082(11)	C(15)–H(9)	1.088(12)
C(13)–H(4)	1.083(10)	C(14)–H(7)	1.067(11)	C(15)–H(10)	1.079(14)

weights were used, owing to the satisfactory constant value of Δ^2 averaged over groups of $|F_o|$ and sin θ. The scattering lengths were[16]: Ru, 7.30; C, 6.65; O, 5.80; and H, -3.74×10^{-13} cm; calculations were made with a modified version of the ORFLS program.[17]

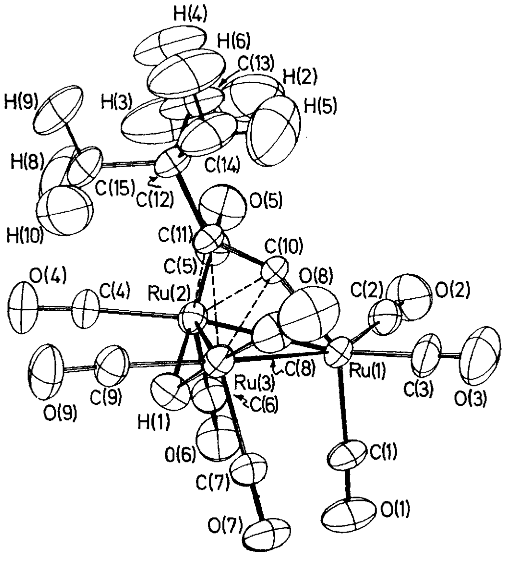

FIGURE 1 ORTEP plot of the molecule, showing 50% probability thermal ellipsoids. The H(7) atom is not shown, for the sake of clarity; bold lines represent bonds of the Ru_3 cluster, and broken lines are π bonds of the organic ligand

The final fractional co-ordinates are reported in Table 1 and root-mean-square vibrational displacements are in Table 2. Observed and calculated structure factors and final temperature factors are available as Supplementary Publication No. SUP 22133 (13 pp.).*

RESULTS AND DISCUSSION

Interatomic distances and bond angles are in Tables 3 and 4, respectively. The molecule (Figure 1) contains a triruthenium cluster (arranged as an equilateral triangle within experimental error), with two equatorial and one axial carbonyl groups bonded to each Ru atom; an acetylenic ligand is co-ordinated to the metallic cluster *via* a three-centre μ-type bond between Ru(2), Ru(3), and C(10)–C(11), and a σ bond between C(10) and Ru(1). The molecule has $C_s(m)$ pseudo-symmetry (Figure 2) as in the related compound $[Ru_3H(CO)_{10}(C{=}NMe_2)]$.[9] This symmetry is obeyed exactly (within the estimated standard deviations) by the Ru_3 cluster and by the atoms H(1), C(10), C(11), and C(12), while it is approximate for the carbonyl and methyl groups; the largest deviations are observed for C(15), which is 0.101 Å distant from the mirror pseudo-plane, and for the pseudo-symmetrical pairs H(8)–H(10) (1.027 and 0.705 Å), H(4)–H(5) (1.191 and 1.368 Å), O(2)–O(3) (2.378 and 2.243 Å), and H(2)–H(6) (1.170 and 1.276 Å).

The Triruthenium Cluster.—The three Ru–Ru bonds are shorter than those found in $[Ru_3(CO)_{12}]$ (2.85 Å)[18] but are within the range of ruthenium–ruthenium distances reported in the literature. The Ru(1) atom

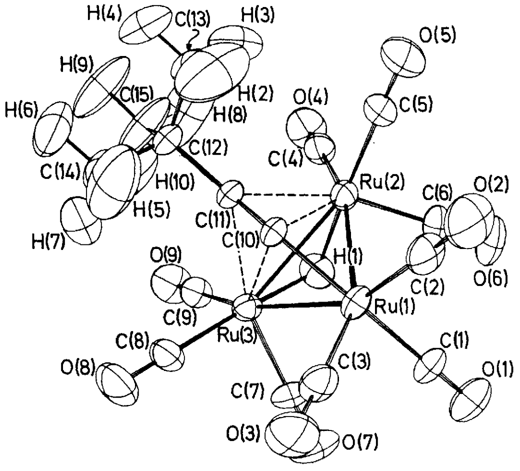

FIGURE 2 View of the molecule, emphasizing the pseudo-mirror plane

---

* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue.

[16] G. E. Bacon, *Acta Cryst.*, 1972, **A28**, 357.

[17] W. R. Busing, K. O. Martin, and H. A. Levy, 'ORFLS, a Fortran Crystallographic Least-Squares Program,' Report ORNL TM 305, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1962.

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

TABLE 4

Bond angles (°) for $[Ru_3H(CO)_9(C\equiv CBu^t)]$

Ru(2)–Ru(1)–Ru(3)	59.9(1)	Ru(1)–Ru(3)–Ru(2)	60.0(1)
Ru(1)–Ru(2)–Ru(3)	60.1(1)		
Ru(2)–Ru(1)–C(1)	102.3(1)	Ru(3)–Ru(2)–C(5)	145.2(1)
Ru(2)–Ru(1)–C(2)	98.0(1)	Ru(3)–Ru(2)–C(6)	112.8(1)
Ru(2)–Ru(1)–C(3)	155.9(1)	Ru(3)–Ru(2)–C(10)	50.9(1)
Ru(2)–Ru(1)–C(10)	51.8(1)	Ru(3)–Ru(2)–C(11)	52.1(1)
Ru(3)–Ru(1)–C(1)	101.6(1)	Ru(1)–Ru(3)–C(7)	85.1(1)
Ru(3)–Ru(1)–C(2)	155.6(1)	Ru(1)–Ru(3)–C(8)	100.0(1)
Ru(3)–Ru(1)–C(3)	100.1(1)	Ru(1)–Ru(3)–C(9)	162.9(1)
Ru(3)–Ru(1)–C(10)	51.9(1)	Ru(1)–Ru(3)–C(10)	43.8(1)
Ru(1)–Ru(2)–C(4)	163.9(1)	Ru(1)–Ru(3)–C(11)	76.9(1)
Ru(1)–Ru(2)–C(5)	100.9(1)	Ru(2)–Ru(3)–C(7)	113.6(1)
Ru(1)–Ru(2)–C(6)	83.6(1)	Ru(2)–Ru(3)–C(8)	144.1(1)
Ru(1)–Ru(2)–C(10)	43.9(1)	Ru(2)–Ru(3)–C(9)	103.4(1)
Ru(1)–Ru(2)–C(11)	77.0(1)	Ru(2)–Ru(3)–C(10)	50.7(1)
Ru(3)–Ru(2)–C(4)	104.4(1)	Ru(2)–Ru(3)–C(11)	52.0(1)
Ru(3)–Ru(2)–H(1)	38.9(2)	Ru(2)–Ru(3)–H(1)	38.8(2)
Ru(1)–Ru(2)–H(1)	81.0(2)	Ru(1)–Ru(3)–H(1)	80.8(2)
C(1)–Ru(1)–C(2)	92.7(1)	C(6)–Ru(2)–C(10)	127.4(1)
C(1)–Ru(1)–C(3)	94.6(1)	C(6)–Ru(2)–C(11)	159.9(1)
C(1)–Ru(1)–C(10)	148.4(2)	C(10)–Ru(2)–C(11)	34.1(1)
C(2)–Ru(1)–C(3)	98.3(1)	C(7)–Ru(3)–C(8)	91.9(1)
C(2)–Ru(1)–C(10)	107.3(1)	C(7)–Ru(3)–C(9)	99.4(1)
C(3)–Ru(1)–C(10)	106.1(1)	C(7)–Ru(3)–C(10)	128.8(1)
C(4)–Ru(2)–C(5)	94.7(1)	C(7)–Ru(3)–C(11)	161.2(1)
C(4)–Ru(2)–C(6)	100.0(1)	C(8)–Ru(3)–C(9)	96.3(1)
C(4)–Ru(2)–C(10)	131.3(1)	C(8)–Ru(3)–C(10)	93.8(1)
C(4)–Ru(2)–C(11)	97.2(1)	C(8)–Ru(3)–C(11)	96.6(1)
C(5)–Ru(2)–C(6)	91.6(1)	C(9)–Ru(3)–C(10)	130.2(1)
C(5)–Ru(2)–C(10)	94.7(1)	C(9)–Ru(3)–C(11)	96.3(1)
C(5)–Ru(2)–C(11)	97.3(1)	C(10)–Ru(3)–C(11)	34.1(1)
C(4)–Ru(2)–H(1)	83.7(2)	C(7)–Ru(3)–H(1)	85.2(2)
C(5)–Ru(2)–H(1)	175.8(2)	C(8)–Ru(3)–H(1)	176.9(1)
C(6)–Ru(2)–H(1)	84.9(2)	C(9)–Ru(3)–H(1)	83.3(2)
C(10)–Ru(2)–H(1)	89.2(2)	C(10)–Ru(3)–H(1)	88.8(2)
C(11)–Ru(2)–H(1)	86.7(2)	C(11)–Ru(3)–H(1)	86.5(2)
Ru(1)–C(10)–Ru(2)	84.3(1)	Ru(2)–C(10)–Ru(3)	78.3(1)
Ru(1)–C(10)–Ru(3)	84.3(1)	Ru(2)–C(11)–Ru(3)	75.9(1)
Ru(1)–C(10)–C(11)	153.7(2)	Ru(3)–C(11)–C(10)	70.6(1)
Ru(2)–C(10)–C(11)	75.5(1)	Ru(2)–C(11)–C(12)	135.2(2)
Ru(3)–C(10)–C(11)	75.3(1)	Ru(3)–C(11)–C(12)	135.0(2)
Ru(2)–C(11)–C(10)	70.4(1)		
Ru(1)–C(1)–O(1)	176.9(1)	Ru(2)–C(6)–O(6)	178.3(1)
Ru(1)–C(2)–O(2)	177.5(1)	Ru(3)–C(7)–O(7)	179.2(1)
Ru(1)–C(3)–O(3)	178.3(1)	Ru(3)–C(8)–O(8)	179.9(1)
Ru(2)–C(4)–O(4)	176.0(3)	Ru(3)–C(9)–O(9)	175.0(3)
Ru(2)–C(5)–O(5)	179.0(1)		
C(10)–C(11)–C(12)	141.0(2)	C(13)–C(12)–C(14)	108.9(3)
C(11)–C(12)–C(13)	108.8(2)	C(13)–C(12)–C(15)	108.4(4)
C(11)–C(12)–C(14)	109.1(3)	C(14)–C(12)–C(15)	109.5(3)
C(11)–C(12)–C(15)	112.1(3)		
C(12)–C(13)–H(2)	111.5(6)	C(12)–C(14)–H(7)	109.8(6)
C(12)–C(13)–H(3)	112.0(6)	C(12)–C(15)–H(8)	110.2(8)
C(12)–C(13)–H(4)	111.0(6)	C(12)–C(15)–H(9)	111.4(6)
C(12)–C(14)–H(5)	110.9(6)	C(12)–C(15)–H(10)	112.8(7)
C(12)–C(14)–H(6)	111.8(6)		
H(2)–C(13)–H(3)	107.8(1.0)	H(6)–C(14)–H(7)	107.5(7)
H(2)–C(13)–H(4)	106.9(8)	H(8)–C(15)–H(9)	106.9(1.0)
H(3)–C(13)–H(4)	107.7(8)	H(8)–C(15)–H(10)	109.6(1.1)
H(5)–C(14)–H(6)	106.5(9)	H(9)–C(15)–H(10)	105.6(1.0)
H(5)–C(14)–H(7)	110.2(1.0)		
Ru(2)–H(1)–Ru(3)	102.3(2)		

has a distorted-octahedral environment, whereas Ru(2) and Ru(3) achieve distorted-octahedral co-ordination by including the π interaction with the C(10)–C(11) bond, and excluding the Ru(2)–Ru(3) bond as in the compounds $[Ru_3H_3(CO)_9(\mu_3\text{-CMe})]$ [7] and $[Ru_3H(CO)_{10}(\mu_1\text{-C=NMe}_2)]$.[9] The observation that the triangular cluster has equilateral geometry shows that there is an exact balance between the lengthening effect of the hydride atom and the shortening effect of the organic ligand on the bridged Ru(2)–Ru(3) bond. In other compounds of this type, either the ligand or the hydride effect prevails, so that the cluster is observed to have isosceles geometry, with the bridged Ru–Ru side of the triangle shorter or longer, respectively, than the other sides; see, for example, $[Ru_3H(CO)_{10}(\mu_2\text{-C=NMe}_2)]$ [9] and $[Os_3H(CO)_{10}(\mu_2\text{-CHCH}_2PMe_2Ph)]$ [8] for the former case, and $[Fe_3H(CO)_9(\mu_3\text{-SR})]$ [6] for the latter.

The Hydride Atom.—H(1) is shown by the results of this study to bridge Ru(2) and Ru(3), forming a symmetrical bent Ru–H–Ru tricentric bond. Indeed, each Ru–H distance differs from the average value (1.793 Å) by less than the estimated standard deviation, so that this can be considered as the first case of a really symmetrical bent metal–hydrogen–metal bond. In one of the previous examples studied by neutron diffraction, $[Mo_2H(\eta\text{-}C_5H_5)_2(CO)_4(PMe_2)]$,[2] the Mo–H–Mo bond was claimed to be symmetrical, although a slight but significant asymmetry was present since the two Mo–H distances [1.851(4) and 1.869(4) Å] differed from their average value by more than the estimated standard deviation. However, as it has been shown for O–H–O and F–H–F bonds,[19] symmetrical and slightly asymmetrical configurations of M–H–M bonds should reflect essentially similar bonding schemes.

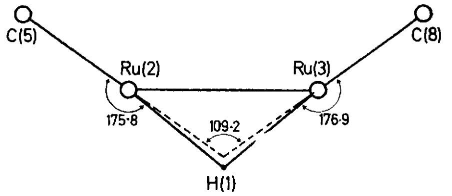

FIGURE 3 Sketch of the three-centre two-electron Ru–H–Ru bond

An analysis of the thermal motion of H(1) provides evidence that the hydride atom of the Ru–H–Ru system vibrates in a single-well potential. The size of its thermal ellipsoid (Table 2) is much smaller than those of the other hydrogen atoms; the ellipsoid is only slightly anisotropic, and its longest axis is nearly perpendicular to the Ru(2)–H(1) (88°) and Ru(3)–H(1) (87°) bond directions.

The problem of a possible Ru–Ru overlap in the three-centre two-electron Ru–H–Ru bond will now be considered. The system H(1)Ru(2)Ru(3)C(5)C(8), essentially coplanar, is represented in Figure 3; extensions of the two axial Ru–C(carbonyl) bonds *trans* to the hydride atom intersect at a point very close to H(1) itself, so that no appreciable (or very little) Ru–Ru interaction should be present, and the Ru–H–Ru bond should be classified as ' open '.[3] This result is different

---

[19] M. Catti and G. Ferraris, *Acta Cryst.*, 1976, **B32**, 2754.

from that found in $[W_2H(CO)_9(NO)]$ and $[W_2H(CO)_8(NO)\{P(OMe)_3\}]$,[1,3] where the decrease in the H-W-C(carbonyl) angles (163.8 and 166.2° for the former compound) causes the extensions of the W-C(carbonyl) bonds *trans* to H to intersect near the centre of the W-H-W triangle, and the W-H-W bonds were considered to be ' closed '. The configuration with large H-Ru-C(carbonyl) angles (176.9 and 175.8°) observed in the present compound should be mainly controlled by minimizing intercarbonyl repulsions, in view of the large steric crowding shown by the molecule.

TABLE 5

Some relevant distances and angles in ruthenium carbonyl hydrides

Compound	Bond/Å Ru-H	Bond/Å Ru-Ru	Angle/° Ru-H-Ru	Source
$[Ru_2H(CO)_6(C_{10}H_9O)]$	1.85(12)	2.862(3)	110(6)	*X*-Ray [5]
	1.64(11)			
$[Ru_3H_3(CO)_9(CMe)]$	1.72(7)	2.842(6)	112(7)	*X*-Ray [7]
	1.812		103.3	N.m.r. [7]
$[Ru_3H(CO)_9(C_6H_9)]$	1.61(7)	2.994(1)	125(4)	*X*-Ray [10]
	1.77(7)			
$[Ru_3H(CO)_{10}(C{=}NMe_2)]$	1.93(5)	2.7997(5)	95.4(25)	*X*-Ray [9]
	1.85(5)			
	1.80(3)	2.8016(6)	101.3(17)	
	1.82(3)			
$[Ru_3H(CO)_9(C{\equiv}CBu^t)]$	1.789(5)	2.792(3)	102.3(3)	Neutron diffraction (this work)
	1.796(5)			

Table 5 compares some relevant distances and angles of the Ru-H-Ru bond obtained from *X*-ray studies with the results of our neutron study. It should be borne in mind that the information concerning hydrogen atoms is of low accuracy in the *X*-ray studies referred to.

The Ru(2)Ru(3)H(1) plane forms an angle of 115.0° with the Ru_3 cluster plane; the hydride atom thus lies in a non-planar configuration with respect to the cluster, just as in the compounds $[Fe_2H(CO)_9(\mu\text{-SR})]$,[6] $[Ru_3H(CO)_{10}(\mu_2\text{-C=NMe}_2)]$,[9] and $[Os_3H(CO)_{10}(\mu_2\text{-CHCH}_2\text{PMe}_2\text{Ph})]$.[8] This configuration is caused by the organic ligand bridging the two hydride-bridged metal atoms, so that its barycentre is shifted towards that side of the cluster and a planar arrangement of the H atom is sterically hindered. In contrast, in $[Ru_3H(CO)_9(C_6H_9)]$ [10] the hydride atom lies on the cluster plane, because the allenic ligand is shifted towards the cluster corner opposite to the hydride-bridged side.

H(1) is approximately equidistant from the four atoms C(4), C(6), C(7), and C(9) of the carbonyl groups [2.489(5), 2.498(5), 2.508(5), and 2.487(5) Å, respectively], and it lies very close (0.041 Å) to the plane formed by them; this plane forms an angle of 84.7° with the Ru(2)-Ru(3)H(1) plane. The orientation of the RuRuH plane with respect to the cluster is then likely to obey the requirement of least hindrance between H(1) and the neighbouring carbonyl groups.

The Organic Ligand.—The C(10)-C(11) acetylenic bond length is typical of a double bond, and can be compared with that present in $[Fe_3(\eta\text{-C}_5H_5)(CO)_7(C_2Ph)]$; [20] indeed an electron pair of the original triple bond has been diverted and is involved in a double π-co-ordination bond from C(10)-C(11) to Ru(2) and Ru(3). The interaction between the acetylenic moiety and the Ru_3 cluster is completed by C(10)-Ru(1) σ bonding; however, the C(10)-Ru(1) distance is comparable with the longest Ru-C(carbonyl) bond lengths and is then just slightly longer than the average Ru-C(carbonyl) value (1.917 Å), so that in fact a partial double-bond character can be ascribed to such bonding. Therefore, the organic ligand can be represented by the formula $\overline{\cdots}C(10)\overline{\overline{\cdots}}C(11)\text{-}CMe_3$.

The Carbonyl Groups.—The longest Ru-C(carbonyl) bond distances are those of the two equatorial carbonyl groups adjacent to the hydride atom, CO(4) and CO(9); this effect, which did not appear in the *X*-ray study, could be ascribed to steric hindrance of the atoms bridging Ru(2)-Ru(3). No similar phenomenon is present in the related complex $[Ru_3H(CO)_{10}(C{=}NMe_2)]$,[9] where the two axial carbonyl groups *trans* to the organic ligand have the longest Ru-C(carbonyl) distances. CO(5) and CO(8), *trans* to the hydride atom, are tilted towards the ligand as in $[Ru_3H(CO)_{10}(C{=}NMe_2)]$,[9] $[Ru_3H_3(CO)_9(CMe)]$,[7] $[Fe_3H(CO)_9(SR)]$,[6] and $[Os_3H(CO)_{10}(\mu_2\text{-CHCH}_2\text{PMe}_2\text{Ph})]$.[8] Opening of the Ru(2)-Ru(3)-C(9) and Ru(3)-Ru(2)-C(4) angles with respect to the other equatorial carbonyls also occurs, as in the related compounds.

CO(1), which is nearly *trans* to C(10), shows a significant lengthening of the Ru-C bond with respect to CO(2) and CO(3), and the bond Ru(1)-CO(1) is closer to being normal to the cluster plane than the bonds of the other axial carbonyl groups.

[7/898 *Received, 24th May,* 1977]

---

[20] K. Yasufuku, K. Aoki, and H. Yamazaki, *Bull. Chem. Soc. Japan*, 1975, **48**, 1616.