The Reaction of Cyclopentadiene with Dodecacarbonyltriruthenium: The Isolation and Crystal Structure of Tetracarbonylbis[dicarbonyl(η-cyclopentadienyl)ruthenio]ruthenium, [$\{Ru(\eta\text{-}C_5H_5)(CO)_2\}_2Ru(CO)_4$]

By **Neil Cook, Lesley E. Smart,** and **Peter Woodward,*** Department of Inorganic Chemistry, The University, Bristol BS8 1TS
John D. Cotton,* Department of Chemistry, University of Queensland, Brisbane, Australia 4067

The new title compound (1) has been isolated, in addition to the normal product [$\{Ru(\eta\text{-}C_5H_5)(CO)_2\}_2$] (2) from the reaction of cyclopentadiene and [$Ru_3(CO)_{12}$] in refluxing heptane. Its formation, which may represent an early stage of the reaction of the diene with the triruthenium cluster, is enhanced by short reaction times and by a low relative concentration of cyclopentadiene. Crystals of (1) are monoclinic, space group $P2_1/c$, with $Z = 2$ in a unit cell of dimensions $a = 6.819(3)$, $b = 11.757(3)$, $c = 13.085(5)$ Å, and $\beta = 110.84(2)°$. The molecules are therefore centrosymmetric. The structure has been determined by heavy-atom methods from diffractometer data and refined to R 0.027 for 1 563 independent reflections. The three ruthenium atoms form a linear array [Ru–Ru 2.889(1) Å] with the cyclopentadienyl rings in a mutually *trans* relationship on the terminal metal atoms. The central metal atom has four equatorial carbonyl groups, while the terminal metal atoms each carry two carbonyl groups which are eclipsed relative to those on the central atom. The metal–carbonyl distances on the central atom are significantly longer than those on the terminal atoms.

THE reaction between cyclopentadiene and [$Ru_3(CO)_{12}$] in refluxing heptane has been studied previously by Humphries and Knox[1] who observed the formation of the η-cyclopentadienyl hydride [$Ru(\eta\text{-}C_5H_5)H(CO)_2$], in essentially quantitative yield, in the absence of air. Interestingly, the hydride is thermally stable (unlike the corresponding iron compound which decomposes to [$\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2$], but it can be converted into the dimer, [$\{Ru(\eta\text{-}C_5H_5)(CO)_2\}_2$] (2), by oxidation. The overall reaction between cyclopentadiene, [$Ru_3(CO)_{12}$], and oxygen, carried out by simple reflux in air, or, more reliably, by oxidation of preformed [$Ru(\eta\text{-}C_5H_5)H(CO)_2$], has been developed as a convenient high-yield synthesis of (2).[1]

The detection, under milder reaction conditions, of the cyclopentadiene complex, [$Ru(\eta^4\text{-}C_5H_6)(CO)_3$], which decomposes thermally to the cyclopentadienyl hydride,[1] and the isolation of [$Fe(\eta^4\text{-}C_5H_6)(CO)_3$], which decomposes to [$\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2$],[2] from the reaction between cyclopentadiene and [$Fe_2(CO)_9$] in diethyl ether,[3] support a common reaction scheme [1,4] in which the cyclopentadiene complex, formed initially, yields the hydride, essentially by oxidative addition of a C–H bond at the metal centre, with concomitant loss of carbon monoxide. There is no evidence for the intermediacy of polynuclear species in the reactions with metal–metal bonded carbonyls: a small and unpredictable amount of the trinuclear η^3-allyl derivative, [$Ru_3(\eta^3\text{-}C_5H_5)H(CO)_9$], was isolated from the [$Ru_3(CO)_{12}$] reactions, but its formation by a secondary pathway was suggested.[1]

Our work in this area was initiated by the unexpected isolation, in the course of a preparation of (2), of an additional product, [$\{Ru(\eta\text{-}C_5H_5)(CO)_2\}_2Ru(CO)_4$] (1), the trinuclear nature of which suggested that it might be an early product in the reaction, formed by the addition of cyclopentadiene to the intact Ru_3 cluster. The possibility was of interest in view of recent studies of the interaction of small organic molecules with metal clusters which could model the interactions of such molecules with metal surfaces.[5]

This report describes the characterisation and crystal-structure analysis of the new product, and discusses its possible involvement in the overall reaction scheme.

RESULTS AND DISCUSSION

The isolation of (1) occurred in a routine reaction of cyclopentadiene and [$Ru_3(CO)_{12}$] in refluxing heptane, over 2 h and with limited access to air. The orange crystals which formed in the cooled reaction mixture were separated off and were shown, by i.r. spectroscopy in the carbonyl-stretching region, to be largely (2). However, a pronounced and relatively broad absorption was also observed at 1 999 cm^{-1} which was incompatible with any other previously reported product of the reactions. Absorbance comparisons indicated that the new compound was present in a *ca.* 1 : 3 mixture with (2). The two compounds unfortunately could not be separated by column chromatography (alumina, hexane), but a pure sample of the new compound, (1), was obtained, in 5% yield, after repeated fractional crystallisation of the mixture from methylene chloride–hexane. Its formulation was established by mass spectrometry which showed the characteristic Ru_3 isotope pattern and stepwise loss of eight CO groups from the parent molecular ion, and by the ^1H n.m.r. spectrum which contained only one η-C_5H_5 resonance (τ 4.75 in $CDCl_3$) and no resonance characteristic of a metal hydride (up to τ 50). No bridging-carbonyl absorptions were observed in the i.r. spectrum in cyclohexane (2 084w, 2 030vw, 1 999s, 1 978m, and 1 943m cm^{-1}). Further chemical evidence for this formulation was obtained by the isolation of a small amount of the same compound (identical spectroscopically) from the complex mixture from the reaction of [$Ru(\eta\text{-}C_5H_5)I(CO)_2$] and [$Ru(CO)_4$]$^{2-}$ in tetrahydrofuran (thf).

Crystallographic investigations have served to confirm completely the formulation of the compound as [$\{Ru(\eta\text{-}C_5H_5)(CO)_2\}_2Ru(CO)_4$]. The overall packing of the molecules and the atom-numbering system are shown in Figure 1, while Tables 1 and 2 summarise the crystallo-

TABLE 1

Atomic positional parameters (fractional co-ordinates) with estimated standard deviations in parentheses

Atom	*X*	*Y*	*Z*
Ru(1)	0.0 *	0.0 *	0.0 *
Ru(2)	0.017 35(6)	0.213 49(3)	0.112 24(3)
C(11)	−0.073 7(12)	0.396 9(5)	0.094 9(6)
H(11)	−0.162 *	0.431 *	0.136 *
C(12)	−0.147 9(9)	0.347 5(5)	−0.011 7(5)
H(12)	−0.303 *	0.335 *	−0.061 *
C(13)	0.031 0(10)	0.314 6(5)	−0.034 8(4)
H(13)	0.029 *	0.279 *	−0.106 *
C(14)	0.208 0(10)	0.339 2(5)	0.054 7(5)
H(14)	0.362 *	0.324 *	0.062 *
C(15)	0.143 1(12)	0.390 1(5)	0.135 2(5)
H(15)	0.239 *	0.418 *	0.209 *
C(1)	0.218 4(8)	0.146 9(5)	0.233 8(4)
O(1)	0.343 7(6)	0.110 5(4)	0.311 9(3)
C(2)	−0.195 7(8)	0.154 9(4)	0.154 6(4)
O(2)	−0.328 4(6)	0.125 1(4)	0.183 7(3)
C(3)	0.221 1(8)	0.068 4(4)	−0.040 6(4)
O(3)	0.349 9(6)	0.109 2(3)	−0.064 9(3)
C(4)	−0.211 3(8)	0.076 6(5)	−0.121 1(4)
O(4)	−0.332 9(6)	0.122 8(4)	−0.192 8(3)

* Restricted.

graphic results. The three ruthenium atoms adopt a linear configuration [Ru–Ru 2.889(1) Å], and as the central metal atom lies on a crystallographic centre of inversion the molecules are constrained to be centrosymmetric. The Ru–Ru distance is within the range of distances measured for other unbridged polynuclear ruthenium compounds.[6] The η-cyclopentadienyl fragments occupy the usual three co-ordination sites on each terminal Ru atom and are, of necessity, *trans* to one another. The other two sites on each terminal Ru atom, and the four equatorial sites on the central Ru atom, are all occupied by carbonyl groups, and these are in an eclipsed orientation to one another (see Figure 2).

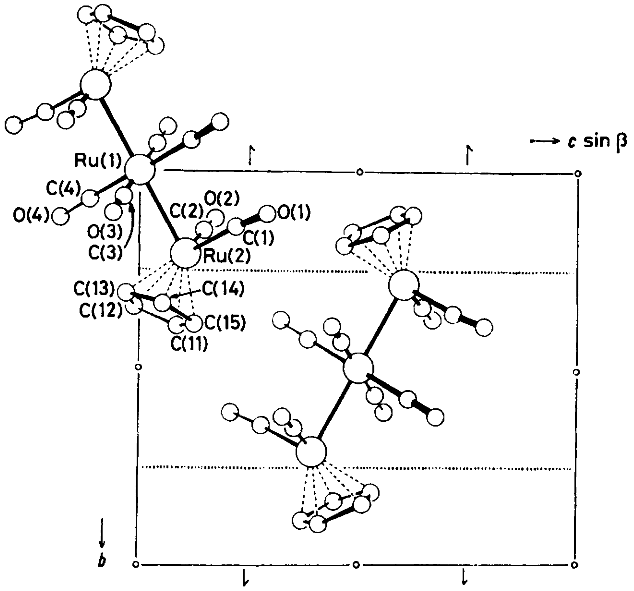

FIGURE 1 The packing of the molecules of compound (1) in the monoclinic unit cell, and the atom-numbering system

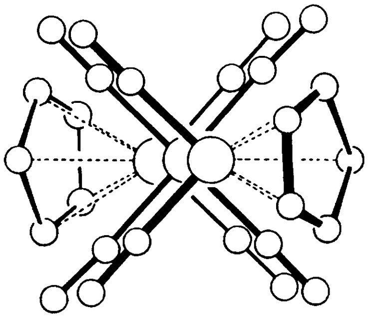

FIGURE 2 A view of the molecule (1) showing the linear Ru_3 spine and the eclipsed configuration of the carbonyl groups

A feature commonly found in linear metal carbonyls is that equatorial groups on terminal metal atoms tend to bend towards the centre of the molecule.[7] The title compound conforms with this pattern [mean Ru(1)–Ru(2)–CO 86.8°], but it is interesting that the equatorial groups on the central metal atom are also not strictly orthogonal to the molecular axis; these carbonyl groups lean towards the nearest cyclopentadienyl ring [mean Ru(2)–Ru(1)–CO 83.7°]. Moreover, the metal–carbonyl bond lengths are significantly greater for the central metal atom [mean Ru(1)–CO 1.942 Å] than for the terminal metal atom [mean Ru(2)–CO 1.863 Å], while the corresponding CO distances show the opposite trend. Furthermore, the Ru–C distances for the C_5 ring also show significant differences; atoms C(11) and C(15), which lie most nearly *trans* to the Ru–Ru bond, are nearer to the metal atom (mean Ru–C 2.229 Å) than are C(12), C(13), and C(14), which lie most nearly *trans* to the carbonyl groups (mean Ru–C 2.271 Å). Finally, while the Ru–C–O links on terminal Ru(2) are significantly non-linear, those for central Ru(1) are straight. The shortest intramolecular contacts of significance are those between corresponding atoms of eclipsed pairs of carbonyl groups (all close to 3 Å), and those between the oxygen atoms of the central equatorial carbonyl groups and the nearest hydrogen atom of the cyclopentadienyl ring [H(13)–O(3) 2.86, H(13)–O(4) 2.96 Å]. The shortest intermolecular contacts also involve the H atoms of the C_5 ring: H(11)–O(4) 2.94, H(11)–O(1)

TABLE 2

Bond lengths (Å) and angles (°)

(*a*) Distances

Ru(1)–Ru(2)	2.889(1)	C(15)–C(11)	1.384(11)
Ru(2)–C(11)	2.233(6)	Ru(2)–C(1)	1.863(4)
Ru(2)–C(12)	2.255(6)	C(1)–O(1)	1.156(5)
Ru(2)–C(13)	2.292(6)	Ru(2)–C(2)	1.862(6)
Ru(2)–C(14)	2.267(7)	C(2)–O(2)	1.154(8)
Ru(2)–C(15)	2.226(6)	Ru(1)–C(3)	1.942(6)
C(11)–C(12)	1.428(9)	C(3)–O(3)	1.141(7)
C(12)–C(13)	1.411(10)	Ru(1)–C(4)	1.942(5)
C(13)–C(14)	1.381(7)	C(4)–O(4)	1.144(6)
C(14)–C(15)	1.413(10)		

(*b*) Angles

Ru(1)–Ru(2)–C(1)	87.3(2)	C(14)–C(15)–C(11)	108.4(5)
Ru(1)–Ru(2)–C(2)	86.3(2)	C(15)–C(11)–C(12)	107.9(7)
C(1)–Ru(2)–C(2)	90.3(2)	Ru(2)–Ru(1)–C(3)	83.3(2)
Ru(2)–C(1)–O(1)	176.6(5)	Ru(2)–Ru(1)–C(4)	84.0(2)
Ru(2)–C(2)–O(2)	175.8(5)	C(3)–Ru(1)–C(4)	90.4(2)
C(11)–C(12)–C(13)	106.8(5)	Ru(1)–C(3)–O(3)	179.5(4)
C(12)–C(13)–C(14)	108.8(5)	Ru(1)–C(4)–O(4)	178.7(5)
C(13)–C(14)–C(15)	108.0(6)		

2.66; H(12)–O(1) 2.48; and H(15)–O(2) 2.77, H(15)–O(3) 2.80, H(15)–O(4) 2.78 Å.

Although pure (1) was obtained in relatively low yield, it was present in a significant amount in the crude reaction mixture and, on this basis, would seem more likely to be an intermediate in the formation of the mononuclear hydride rather than a side product. Its formation in our experiment was probably enhanced by the short period of reflux employed, and by the lower cyclopentadiene : Ru ratio and higher overall concentration compared with the conditions used in the previous study.[1] To test the effect of these several variables, several small-scale experiments were carried out, using i.r. spectroscopy in the carbonyl-stretching region to monitor the reaction. Although absorbance comparisons can give only an approximate evaluation of relative yields, the method provides a reliable and sensitive indicator of the reaction course.

In one series of experiments, cyclopentadiene and $[Ru_3(CO)_{12}]$, in relative amounts of $C_5H_6 : Ru = 0.5$—$10 : 1$, were allowed to react, over 1 h in gently refluxing heptane (solution temperature 95 °C), with rigorous exclusion of air. In each mixture, the characteristic absorptions of $[Ru(\eta\text{-}C_5H_5)H(CO)_2]$ and (1) were observed, together with those of unchanged $[Ru_3(CO)_{12}]$, the amount of which decreased steadily with increasing amount of cyclopentadiene used. The relative amounts of the hydride and (1) were somewhat variable, but in each case compound (1) was the minor component (*e.g. ca.* 30% of the amount of the hydride at a C_5H_6 : Ru ratio of 2.0 : 1). At higher ratios, the yield of (1) decreased significantly. At lower temperatures (*e.g.* 83 °C), the overall rate of reaction was very low and no detectable enhancement in the relative amount of (1) occurred. These experiments demonstrated clearly that oxygen intervention is not necessary for the formation of (1) whereas, as shown earlier,[1] it is required for the conversion of the hydride into (2). Similar experiments carried out either with reflux in air or with reflux under oxygen showed, as expected, the formation of both (1) and (2) but, interestingly, $[Ru(\eta\text{-}C_5H_5)H(CO)_2]$ was still the major product of reaction, indicating the substantial blanketing effect of the refluxing heptane. Similar conditions, *i.e.* limited access to oxygen, obtained in the original preparation of (1). We note that the rate of input of oxygen, either to the refluxing solution or to the preformed hydride, plays a crucial part in determining the overall yield of (2) by the published method; high yields of crystalline material are produced by gradual oxidation, but substantial amounts of decomposition to other oxidised species occurs if, for example, oxygen is blown through the solution.

In experiments which used an excess of cyclopentadiene the period of reflux was an important factor and, after 2—3 h, any (1) formed initially had reacted further to produce $[Ru(\eta\text{-}C_5H_5)H(CO)_2]$. This observation was supported by a direct reaction carried out between (1) and cyclopentadiene which again yielded the hydride. For C_5H_6 : Ru ratios of $\leqslant 1 : 1$, the reaction was complicated by the additional trace formation of $[Ru_4H_4(CO)_{12}]$, identified by its characteristic i.r. spectrum,[8] but this could be converted into the hydride by the addition of more cyclopentadiene and further reflux, thus confirming the earlier observation.[1] The formation of the hydrides $[Ru_4H_4(CO)_{12}]$ and $[Ru_4H_2(CO)_{13}]$ from $[Ru_3(CO)_{12}]$ in refluxing hydrocarbons has recently been ascribed to reaction with trace amounts of water in the solvents.[9]

Even though the formation of (1) in the absence of oxygen logically precludes it, the possibility that (1) may have been formed by insertion of a $Ru(CO)_4$ fragment into (2) was explored. However, no conversion into (1) was observed even after extended reflux of a solution of $[Ru_3(CO)_{12}]$ and (2) in heptane. Likewise, no reaction of $[Ru(\eta\text{-}C_5H_5)H(CO)_2]$ and $[Ru_3(CO)_{12}]$ was detected under similar conditions.

The cooling of solutions after the small-scale reactions of cyclopentadiene and $[Ru_3(CO)_{12}]$ resulted in the precipitation of a mixture of unchanged $[Ru_3(CO)_{12}]$ and (1), leaving the hydride as the major solution species. The separation of the supernatant by decantation, under an inert atmosphere, avoided the possibility of the later contamination of (1) by (2). Since $[Ru_3(CO)_{12}]$ and (1) are readily separated chromatographically, the sequence is appropriate for the deliberate preparation of (1).

While we are cautious in proposing a reaction scheme in view of the ready rearrangements known for metal carbonyls in solution, we believe that the initial stage of the reaction might involve the co-ordination of cyclopentadiene to one ruthenium atom of the triangular cluster, with displacement of carbon monoxide, to give $[Ru_3(\eta^4\text{-}C_5H_6)(CO)_{10}]$. In this regard, we note that a cyclohexadiene complex, $[Os_3(\eta^4\text{-}C_6H_8)(CO)_{10}]$, has recently been isolated from the reaction of cyclohexadiene and $[Os_3H_2(CO)_{10}]$ under mild conditions.[10] Hydrogen transfer from ring to ruthenium could then occur, with concomitant breaking of one Ru–Ru bond, to give $[(CO)_2(\eta^5\text{-}C_5H_5)Ru{\cdot}Ru(CO)_4{\cdot}RuH(CO)_4]$, which could then react similarly with another molecule of cyclopentadiene at the unsubstituted terminal ruthenium. The final stage of the process would require elimination of molecular hydrogen and isomerisation to the linear arrangement. Under vigorous conditions, and in the presence of a significant excess of cyclopentadiene, breakdown to $[Ru(\eta\text{-}C_5H_5)H(CO)_2]$ could occur at almost any step.

EXPERIMENTAL

Manipulations under nitrogen or argon were carried out using standard Schlenk techniques and all solvents were dried and distilled under nitrogen before use. Infrared spectra were recorded on a PE457 spectrophotometer, ^1H n.m.r. spectra for solution in $CDCl_3$ on a Jeolco PS100 spectrometer, and mass spectra on an A.E.I. MS 902 spectrometer.

Preparation of $[\{Ru(\eta\text{-}C_5H_5)(CO)_2\}_2Ru(CO)_4]$ (1).—(*a*) *From* $[Ru_3(CO)_{12}]$.—Dodecacarbonyltriruthenium (4.0 g) and freshly cracked cyclopentadiene (5 cm^3) were allowed to react in refluxing heptane (200 cm^3) for 2 h in air. Orange crystals (*ca.* 2 g) formed when the solution was cooled, and were shown (i.r. spectroscopy) to be a mixture of $[\{Ru(\eta\text{-}C_5H_5)(CO)_2\}_2]$ and the product. Repeated fractional crystallisation from methylene chloride–hexane (made difficult by the larger amount of the slightly less soluble $[\{Ru(\eta\text{-}C_5H_5)(CO)_2\}_2]$) gave the pure *product* (0.2 g, 5%) [Found: C, 33.2; H, 1.5%; *M* (mass spectrometry) 660. $C_{18}H_{10}O_8Ru_3$ requires C, 32.9; H, 1.5%; *M* 660 (for ^{102}Ru)].

(*b*) *From* $[Ru(\eta\text{-}C_5H_5)I(CO)_2]$ *and* $[Ru(CO)_4]^{2-}$. Dodecacarbonyltriruthenium (0.12 g) in liquid ammonia (10 cm^3) was treated with small pieces of sodium until a pale fawn suspension was obtained.[11] Ammonia was pumped off and thf (10 cm^3) added to the residue. A solution of $[Ru(\eta\text{-}C_5H_5)I(CO)_2]$ (0.5 g) in thf (5 cm^3) was added dropwise under nitrogen over 1 h. The solvent was pumped off and the residue extracted with methylene chloride (5 cm^3). Addition of hexane yielded (i.r. spectrum) a small amount (2 mg) of orange crystals of (1), contaminated by $[\{Ru(\eta\text{-}C_5H_5)(CO)_2\}_2]$ (2). The i.r. spectrum of the air-sensitive filtrate showed, in addition, the characteristic peaks of $[Ru(\eta\text{-}C_5H_5)Cl(CO)_2]$ and $[Ru(\eta\text{-}C_5H_5)I(CO)_2]$.

Reactions between Cyclopentadiene and $[Ru_3(CO)_{12}]$.—Solutions of $[Ru_3(CO)_{12}]$ (0.25 g) and freshly cracked cyclopentadiene (in amounts appropriate to the mol ratios, $C_5H_6 : Ru$, of 0.5, 1.0, 2.0, 3.0, and 10 : 1) in heptane (25 cm^3) were degassed by the freeze–thaw method and heated gently under reflux, initially for 1 h, under argon. Samples of the refluxing solution were withdrawn with a degassed syringe and injected into i.r. solution cells under argon. Reflux was continued for an additional 1—2 h and a further sample taken. Similar reactions (mol ratio 1.0 : 1) were carried out in air, and under oxygen.

Attempted Reaction of $[Ru_3(CO)_{12}]$ *and* $[\{Ru(\eta\text{-}C_5H_5)(CO)_2\}_2]$.—Dodecacarbonyltriruthenium (0.045 g) and $[\{Ru(\eta\text{-}C_5H_5)(CO)_2\}_2]$ (0.097 g) were dissolved in heptane (25 cm^3), the system degassed and then heated under reflux under nitrogen. The colour of the orange solution slowly turned brown, with slight formation of $[Ru_4H_4(CO)_{12}]$, but no reaction between the starting materials was observed after 4 h.

Reaction between (1) *and Cyclopentadiene*.—A sample of (1) (0.3 g) was heated under reflux under nitrogen in heptane with cyclopentadiene (1 cm^3) for 2 h. Complete conversion into $[Ru(\eta\text{-}C_5H_5)H(CO)_2]$ was noted (i.r. spectrum).

Attempted Reaction between $[Ru(\eta\text{-}C_5H_5)H(CO)_2]$ *and* $[Ru_3(CO)_{12}]$.—Dodecacarbonyltriruthenium (0.25 g) and cyclopentadiene (0.10 cm^3) in heptane (25 cm^3) were carefully degassed and heated under reflux under nitrogen for 2.5 h. An i.r. spectrum of the reaction mixture showed the presence of small amounts of unchanged $[Ru_3(CO)_{12}]$ and $[Ru_4H_4(CO)_{12}]$ with $[Ru(\eta\text{-}C_5H_5)H(CO)_2]$ as the major product. More $[Ru_3(CO)_{12}]$ (0.25 g) was added to the cooled solution, which was again degassed, and refluxed for another 5 h. No (1) was observed (spectroscopically) and the only change was a deepening of the brown colour of the solution as more $[Ru_4H_4(CO)_{12}]$ was produced.

X-*Ray Data Collection and Structure Determination*.—Crystals of (1) grow as yellow prisms. Diffracted intensities were collected from a crystal of dimensions 0.30 × 0.09 × 0.13 mm on a Syntex $P2_1$ four-circle diffractometer according to methods described earlier.[12] Of the total 1 777 reflections (complete for $2.9 < 2\theta < 50.0°$), 1 563 satisfied the criterion $I \geqslant 1.0\sigma(I)$ and only these were used in the solution and refinement of the structure.

Crystal data. $C_{18}H_{10}O_8Ru_3$, $M = 657.4$, Monoclinic, $a = 6.819(3)$, $b = 11.757(3)$, $c = 13.085(5)$ Å, $\beta = 110.84(2)°$, $U = 980.3$ Å^3, $D_m = 2.24$ g cm^{-3}, $Z = 2$, $D_c = 2.24$ g cm^{-3}, $F(000) = 378$, space group $P2_1/c$, Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 10.2$ cm^{-1}.

The structure was solved by conventional heavy-atom methods and, in the final refinement by full-matrix least squares, anisotropic thermal parameters were used for all non-hydrogen atoms. Hydrogen atoms were incorporated at calculated positions, but neither their positional nor thermal (*B* 6.0 Å) parameters were refined. Weights were applied according to the scheme $1/w = 2.28 - (8.7 \times 10^{-2})F + (1.7 \times 10^{-3})F^2 - (8.0 \times 10^{-6})F^3$. The refinement converged to *R* 0.027 (*R'* 0.029), and a final electron-density difference synthesis showed no peaks >0.3 or <-0.4 e Å^{-3}. The data were not corrected for the effects of *X*-ray absorption. Atomic scattering factors were taken from ref. 13 for hydrogen and from ref. 14 for all other atoms. In the case of Ru these were corrected for the real and imaginary parts of anomalous dispersion.[15] Positional parameters are in Table 1, bond lengths and angles in Table 2. All computational work was carried out at the University of London Computer Centre with the '*X*-Ray System' of programs.[16] Observed and calculated structure factors together with all thermal parameters are listed in Supplementary Publication No. SUP 22480 (9 pp.).*

We thank the S.R.C. (P. W.) and the A.R.G.C. (J. D. C.) for support, Dr. S. A. R. Knox (Bristol) for valuable comment and criticism, and the University of British Columbia (J. D. C.) for facilities during the completion of this work.

[8/1329 *Received*, 17*th July*, 1978]

REFERENCES

[1] A. P. Humphries and S. A. R. Knox, *J.C.S. Dalton*, 1975, 1710.
[2] M. L. H. Green, C. N. Street, and G. Wilkinson, *Z. Naturforsch.*, 1959, **B14**, 738.
[3] R. K. Kochhar and R. Pettit, *J. Organometallic Chem.*, 1966, **6**, 272.
[4] P. L. Pauson, *Proc. Chem. Soc.*, 1960, 297.
[5] E. L. Muetterties, *Science*, 1977, **196**, 839.
[6] J. A. K. Howard, S. C. Kellett, and P. Woodward, *J.C.S. Dalton*, 1975, 2332 and refs. therein.
[7] R. Bau, S. W. Kirtley, T. N. Sorrell, and S. Winarko, *J. Amer. Chem. Soc.*, 1974, **96**, 988 and refs. therein.
[8] F. Piacenti, M. Bianchi, P. Frediani, and E. Benedetti, *Inorg. Chem.*, 1971, **10**, 2759.
[9] C. R. Eady, B. F. G. Johnson, and J. Lewis, *J.C.S. Dalton*, 1977, 838.
[10] E. G. Bryan, B. F. G. Johnson, and J. Lewis, *J.C.S. Dalton*, 1977, 1328.
[11] J. D. Cotton, M. I. Bruce, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 2162.
[12] A. Modinos and P. Woodward, *J.C.S. Dalton*, 1974, 2065.
[13] R. F. Stewart, E. R. Davidson, and W. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.
[14] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.
[15] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.
[16] Technical Report TR 192, Computer Science Centre, University of Maryland, June 1972.

---

* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.