Crystal and Molecular Structure of Decacarbonyl(cyclododecatrienyl)-tetrahedro-tetraruthenium, $Ru_4(CO)_{10}(C_{12}H_{16})$: a Ruthenium Cluster with a Novel Allyl Bonding System to the Cyclododecatrienyl Ligand

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The *X*-ray crystal structure of the title compound has been elucidated from photographic data by symbolic addition and Fourier methods, and has been refined by least-squares to R 0·086 for 1102 independent reflections. Crystals are monoclinic, space group $P2_1/n$, $Z = 4$, with $a = 14{\cdot}51$, $b = 16{\cdot}71$, $c = 10{\cdot}11$ Å, $\beta = 93{\cdot}0°$. An open C_{12} ring is attached to a ' butterfly ' Ru_4 cluster by means of a unique allyl group which is σ bonded to the cluster ' hinge ' at both ends and π bonded to the cluster ' tips ' on both sides. There is a further attachment from the ring to one of the butterfly tips by a second (normal) π-allyl group.

In the cluster the Ru–Ru bond lengths are all *ca.* 2·78 Å except for the hinge distance Ru(1)–Ru(2) (2·85 Å). There is no direct Ru–Ru bonding across the wing-tips of the butterfly (distance 3·67 Å), but three carbon atoms [C(1), C(12), and C(11)] of the C_{12} ring are held symmetrically between the tips of the cluster Ru(3) and Ru(4), and are coplanar with the hinge Ru atoms. The C_{12} ring is again bonded to Ru(4) through C(5), C(6), and C(7). Ru(4) carries one terminal carbonyl group in an axial position relative to the Ru(1), Ru(2), Ru(4) plane, while each of the other three ruthenium atoms carries three terminal carbonyl groups, of which two are approximately equatorial and one is axial relative to the Ru(1), Ru(2), Ru(3) plane. The nature of the novel bridging allyl group is discussed. Mean Ru–C and C–O distances for the carbonyl ligands are 1·87 and 1·17 Å. All bond lengths have relatively high standard deviations and the details of the geometry of the C_{12} ring are not well defined.

REACTION of cyclododeca-1,5,9-trienes with dodecacarbonyltriruthenium yields four complexes;[1,2] the molecular structure of one of these, $HRu_3(CO)_9(C_{12}H_{15})$, has already been reported,[3] and our preliminary account of the structure of another, $Ru_4(CO)_{10}(C_{12}H_{16})$,[4] is here amplified. We had hoped to collect diffractometer data for $Ru_4(CO)_{10}(C_{12}H_{16})$ because of the intrinsic interest of the bonding situation displayed in this compound, but we have failed to obtain a second crystal good enough for the purpose. What is presented here, therefore, is the refinement to convergence of the structure given by a good but incomplete set of photographic data. The implied limitations in the results obtained are pointed out in the text.

EXPERIMENTAL

Crystals of $Ru_4(CO)_{10}C_{12}H_{16}$ are deep red plates, but the material was available only in minute quantities and is difficult to crystallise. We were able to find only one usable crystal, of cross-section 0·08 × 0·03 × *ca.* 0·17 mm, and this, unfortunately, was lost before data collection was complete. The solution given here is from 1102 independent intensities estimated visually from precession photographs of the six reciprocal layers *hk*0—5 inclusive (Mo-K_α radiation). The sphere of reflection is thus not fully explored, and the data are all from the same crystallographic axial mounting. Standard deviations for bond lengths and angles are therefore predictably high.

The crystal was mounted in a glass capillary with silicone grease, the only manageable mounting medium with which the crystal did not react. Lattice parameters were measured from precession photographs. Exposure times of 48, 24, and 12 h were given for each layer on a Supper precession camera with a precession angle of 30°; Ilford ' Industrial G ' *X*-ray film was used throughout. No absorption corrections were made ($\mu R \simeq 0{\cdot}11$). The crystal density was measured only roughly by flotation of powdery material in aqueous thallium(I) formate.

RESULTS

Crystal Data.—$C_{22}H_{16}O_{10}Ru_4$, $M = 844{\cdot}7$, Monoclinic, $a = 14{\cdot}51(1)$, $b = 16{\cdot}71(1)$, $c = 10{\cdot}11(1)$ Å, $\beta = 93{\cdot}0(2)$, $U = 2505$ Å;[3] D_m (flotation) $= 2{\cdot}1$, $Z = 4$, $D_c = 2{\cdot}25$, $F(000) = 1616$. Space group $P2_1/n$. Mo-K_α *X*-radiation, $\lambda = 0{\cdot}7107$ Å; μ(Mo-K_α) $= 23{\cdot}3$ cm^{-1}.

Study of the three-dimensional Patterson synthesis failed to yield the correct heavy-atom positions, but application of the symbolic addition method[5] produced one solution with the four ruthenium atoms in a butterfly arrangement. The carbon and oxygen atoms were located by successive electron-density difference syntheses. Refinement of this structure with isotropic thermal parameters for all atoms, unit weights for all structure amplitudes, and a separate scale factor for each reciprocal layer, gave R 0·096 (weighted R 0·117). Analysis of the variation of $w(\Delta F)^2$ over various ranges of F and of $\sin\theta/\lambda$, however, showed considerable lack of constancy. Individual weights were reassessed according to the scheme:[6] $1/w = \sigma^2 = a + b|F_0| + c|F_0|^2$ with $a = 246{\cdot}4$, $b = -4{\cdot}13$, $c = 0{\cdot}03$ (the values of a, b, and c having been assessed to keep $w\Delta^2$ as nearly constant as possible over the whole range of observations. As a result, the change in R was small (R 0·093, weighted factor, R', 0·117) but the ' error of fit ' ($= [\Sigma w(\Delta F)^2/(n_o - n_v)]^{\frac{1}{2}}$, where n_o = number of observations and n_v = number of variables) fell to 1·05 and the standard deviations became smaller. At this stage the electron-density difference maps showed evidence of anisotropic thermal motion in the region of the ruthenium atoms, so three cycles of refinement were carried out with anisotropic thermal parameters for the Ru atoms only (B_{33} constant). This gave R 0·090 (R' 0·116) and a much smoother difference map. Finally the hydrogen

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[1] M. I. Bruce, M. A. Cairns, A. Cox, M. D. H. Smith, and P. Woodward, *Chem. Comm.*, 1970, 735.

[2] M. I. Bruce, M. A. Cairns, and M. Green, *J.C.S. Dalton*, 1972, 1293.

[3] A. Cox and P. Woodward, *J. Chem. Soc.* (*A*), 1971, 3599.

[4] Rosemary Belford, M. I. Bruce, M. A. Cairns, M. Green, Helen P. Taylor, and P. Woodward, *Chem. Comm.*, 1970, 1159.

[5] M. M. Woolfson, ' Direct Methods in Crystallography,' Clarendon, Oxford, 1961, pp. 88–92.

[6] D. W. J. Cruickshank, ' Computing Methods and the Phase Problem in *X*-Ray Analysis,' Pergamon, Oxford, 1960, p. 37.

TABLE 1

(*a*) Atomic parameters with standard deviations in parentheses

Atom	*x*/*a*	*y*/*b*	*z*/*c*	B/Å^2
Ru(1)	0·6492(2)	0·2845(2)	0·2530(6)	See
Ru(2)	0·8099(2)	0·3016(2)	0·4247(6)	Table
Ru(3)	0·6794(2)	0·4229(2)	0·4000(6)	1(b)
Ru(4)	0·8163(2)	0·3267(2)	0·1506(6)	

(i) Carbonyl groups

C(101)	0·524(2)	0·306(2)	0·248(6)	3·3(7)
O(101)	0·445(2)	0·323(2)	0·239(6)	7·5(9)
C(102)	0·635(2)	0·187(2)	0·340(7)	3·9(8)
O(102)	0·625(2)	0·127(2)	0·385(6)	6·0(7)
C(103)	0·646(3)	0·232(3)	0·091(9)	4·7(10)
O(103)	0·636(3)	0·195(2)	−0·016(7)	8·2(10)
C(201)	0·890(3)	0·344(2)	0·573(7)	3·6(8)
O(201)	0·932(3)	0·368(2)	0·651(6)	7·1(9)
C(202)	0·764(2)	0·233(2)	0·541(7)	4·0(8)
O(202)	0·740(2)	0·183(2)	0·630(6)	7·2(9)
C(203)	0·902(3)	0·226(2)	0·398(7)	4·3(9)
O(203)	0·960(3)	0·188(3)	0·362(8)	8·9(11)
C(301)	0·723(3)	0·497(2)	0·531(7)	3·8(8)
O(301)	0·748(2)	0·537(2)	0·626(6)	6·2(8)
C(302)	0·627(3)	0·352(2)	0·526(8)	4·5(9)
O(302)	0·584(2)	0·317(2)	0·600(5)	5·5(7)
C(303)	0·570(3)	0·484(2)	0·367(7)	3·8(8)
O(303)	0·501(2)	0·517(2)	0·332(6)	6·4(8)
C(401)	0·845(2)	0·225(2)	0·090(6)	3·5(8)
O(401)	0·865(2)	0·160(2)	0·077(5)	5·8(7)

(ii) The C_{12} ring

C(1)	0·824(2)	0·410(2)	0·320(6)	2·5(6)
C(2)	0·914(3)	0·463(2)	0·340(8)	4·7(9)
C(3)	0·998(2)	0·429(2)	0·304(7)	3·8(8)
C(4)	1·014(3)	0·423(2)	0·145(8)	4·7(9)
C(5)	0·949(3)	0·363(3)	0·093(8)	5·4(11)
C(6)	0·882(3)	0·395(3)	0·000(8)	5·8(11)
C(7)	0·810(3)	0·347(3)	−0·062(9)	6·4(13)
C(8)	0·726(4)	0·385(4)	−0·139(10)	8·0(15)
C(9)	0·680(4)	0·454(3)	−0·041(9)	6·7(13)
C(10)	0·628(3)	0·439(2)	0·058(7)	3·8(8)
C(11)	0·690(2)	0·395(2)	0·165(7)	3·5(8)
C(12)	0·764(2)	0·444(2)	0·226(7)	3·7(8)

(iii) Hydrogen atoms of the ring (not refined, all with B 3·5 Å^2)

H(21)	0·920	0·475	0·451
H(22)	0·902	0·521	0·295
H(31)	1·002	0·369	0·341
H(32)	1·054	0·464	0·348
H(41)	1·084	0·407	0·129
H(42)	0·999	0·481	0·100
H(51)	0·947	0·303	0·139
H(61)	0·891	0·457	−0·034
H(71)	0·814	0·282	−0·052
H(81)	0·674	0·341	−0·169
H(82)	0·748	0·414	−0·230
H(91)	0·645	0·495	−0·102
H(92)	0·742	0·484	0·006
H(101)	0·573	0·403	0·024
H(102)	0·604	0·495	0·096
H(121)	0·769	0·508	0·207

(*b*) Anisotropic thermal parameters for Ru atoms *

	B_{11}	B_{22}	B_{33} (fixed)
Ru(1)	2·8(1)	3·5(1)	6·6
Ru(2)	3·1(1)	2·9(1)	6·0
Ru(3)	3·6(1)	3·1(1)	5·7
Ru(4)	3·5(2)	3·5(1)	6·3

	B_{12}	B_{13}	B_{23}
Ru(1)	−0·3(1)	−0·4(1)	−0·5(2)
Ru(2)	−0·1(1)	−0·0(1)	0·1(1)
Ru(3)	0·4(1)	−0·2(2)	−0·6(2)
Ru(4)	0·2(1)	0·1(1)	−0·5(2)

* These were used in the form: $-\frac{1}{4}(B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + B_{33}c^{*2}l^2 + 2B_{12}a^*b^*hk + 2B_{13}a^*c^*hl + 2B_{23}b^*c^*kl)$.

TABLE 2

Bond lengths (Å) and bond angles (deg) *

(*a*) Distances

(i) Metal cluster

Ru(1)–Ru(2)	2·850(6)	Ru(4)–Ru(1)	2·775(5)
Ru(3)–Ru(1)	2·775(6)	Ru(4)–Ru(2)	2·811(8)
Ru(3)–Ru(2)	2·776(6)	Ru(3)–Ru(4)	3·664(7)

(ii) Carbonyl groups

Ru(1)–C(101)	1·85(4)	Ru(2)–C(203)	1·86(5)
C(101)–O(101)	1·17(5)	C(203)–O(203)	1·13(6)
Ru(1)–C(102)	1·90(5)	Ru(3)–C(301)	1·89(6)
C(102)–O(102)	1·09(6)	C(301)–O(301)	1·23(7)
Ru(1)–C(103)	1·91(8)	Ru(3)–C(302)	1·91(6)
C(103)–O(103)	1·21(9)	C(302)–O(302)	1·18(8)
Ru(2)–C(201)	1·99(6)	Ru(3)–C(303)	1·91(5)
C(201)–O(201)	1·05(7)	C(303)–O(303)	1·19(6)
Ru(2)–C(202)	1·82(6)	Ru(4)–C(401)	1·87(4)
C(202)–O(202)	1·29(8)	C(401)–O(401)	1·13(5)

(iii) The C_{12} ring

Ru(2)–C(1)	2·14(4)	Ru(4)–C(12)	2·28(5)
Ru(1)–C(11)	2·14(5)	Ru(4)–C(11)	2·19(4)
Ru(3)–C(1)	2·34(4)	Ru(4)–C(5)	2·09(6)
Ru(3)–C(12)	2·19(6)	Ru(4)–C(6)	2·20(9)
Ru(3)–C(11)	2·40(7)	Ru(4)–C(7)	2·17(11)
Ru(4)–C(1)	2·17(5)		
C(1)–C(2)	1·58(6)	C(7)–C(8)	1·58(11)
C(2)–C(3)	1·46(7)	C(8)–C(9)	1·69(12)
C(3)–C(4)	1·61(10)	C(9)–C(10)	1·30(10)
C(4)–C(5)	1·46(8)	C(10)–C(11)	1·55(9)
C(5)–C(6)	1·47(11)	C(11)–C(12)	1·47(7)
C(6)–C(7)	1·46(10)	C(12)–C(1)	1·35(8)

(*b*) Angles

Ru(3)–Ru(1)–Ru(2)	59·1(1)	Ru(4)–Ru(2)–Ru(1)	58·7(2)
Ru(3)–Ru(2)–Ru(1)	59·1(1)	Ru(1)–Ru(4)–Ru(2)	61·4(2)
Ru(1)–Ru(3)–Ru(2)	61·8(1)	Ru(3)–Ru(1)–Ru(4)	82·6(2)
Ru(4)–Ru(1)–Ru(2)	60·0(1)	Ru(3)–Ru(2)–Ru(4)	81·9(2)
Ru(1)–C(101)–O(101)	177(5)	Ru(2)–C(203)–O(203)	163(6)
Ru(1)–C(102)–O(102)	177(5)	Ru(3)–C(301)–O(301)	171(5)
Ru(1)–C(103)–O(103)	169(6)	Ru(3)–C(302)–O(302)	169(4)
Ru(2)–C(201)–O(201)	178(7)	Ru(3)–C(303)–O(303)	168(6)
Ru(2)–C(202)–O(202)	173(5)	Ru(4)–C(401)–O(401)	167(6)
C(101)–Ru(1)–C(102)	94(2)	C(12)–C(1)–C(2)	112(4)
C(101)–Ru(1)–C(103)	95(2)	C(1)–C(2)–C(3)	114(4)
C(102)–Ru(1)–C(103)	92(2)	C(2)–C(3)–C(4)	118(5)
C(201)–Ru(2)–C(202)	87(3)	C(3)–C(4)–C(5)	103(5)
C(201)–Ru(2)–C(203)	88(2)	C(4)–C(5)–C(6)	110(5)
C(202)–Ru(2)–C(203)	86(2)	C(5)–C(6)–C(7)	120(6)
C(301)–Ru(3)–C(302)	94(3)	C(6)–C(7)–C(8)	120(6)
C(301)–Ru(3)–C(303)	90(2)	C(7)–C(8)–C(9)	106(8)
C(302)–Ru(3)–C(303)	95(2)	C(8)–C(9)–C(10)	126(6)
Ru(3)–C(12)–Ru(4)	110(2)	C(9)–C(10)–C(11)	107(5)
		C(10)–C(11)–C(12)	114(4)
		C(11)–C(12)–C(1)	119(4)

* Estimated standard deviations include cell parameter errors.

atoms of the C_{12} ring were incorporated at calculated positions, assuming C–H 1·075 Å, and the appropriate hybridisation state for the bonded C atom, with an isotropic thermal parameter of 3·5 Å^2. Neither the positional nor thermal parameters of the hydrogen atoms were refined. The final R 0·086 (R' 0·106) resulted from a refinement in which the average shift to error ratio was 0·16 and the 'error of fit' 0·92. Bond lengths and angles with their respective standard deviations were computed from the full variance-covariance matrix obtained in the last refinement cycle. The final positional and thermal parameters are in Table 1, interatomic distances and angles in Table 2. The atomic scattering factors used were those of ref. 7. All computational work was carried out with the ' *X*-Ray '63 ' system on an Atlas computer.[8] Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20497 (7 pp., 1 microfiche).*

DISCUSSION

A stereoscopic view of the structure of the $Ru_4(CO)_{10}$-$(C_{12}H_{16})$ molecule is given in Figure 1, and shows the relationship between the Ru_4 cluster and the C_{12} ring.[9] The four ruthenium atoms define a ' butterfly ' configuration in which two isosceles triangles share a common base (the ' hinge ') but are not coplanar. The cluster is not bonded across the wing-tips. The two hinge atoms and one of the wing-tip atoms each carry three carbonyl groups, while the fourth metal atom carries only one carbonyl group but is specially related to the C_{12} ring. The bonding between the metal cluster and the C_{12} ring (which remains unbridged) is highly unusual and interesting. Three adjacent carbon atoms of the ring form a unique allyl system which is σ bonded at both ends to the ' hinge ' metal atoms, but is also π-bonded on both sides to each of the wing-tip atoms. The C_{12} ring occupies the region away from the nine carbonyl groups in such a manner that, of the nine remaining ring carbon atoms the central three form a second allyl group which is π bonded back onto the wing-tip ruthenium atom that carries only one carbonyl group. Figure 2 shows a view of the molecule similar to that in the stereoscopic drawing, but with fuller indication of the bonding and the atom numbering system.

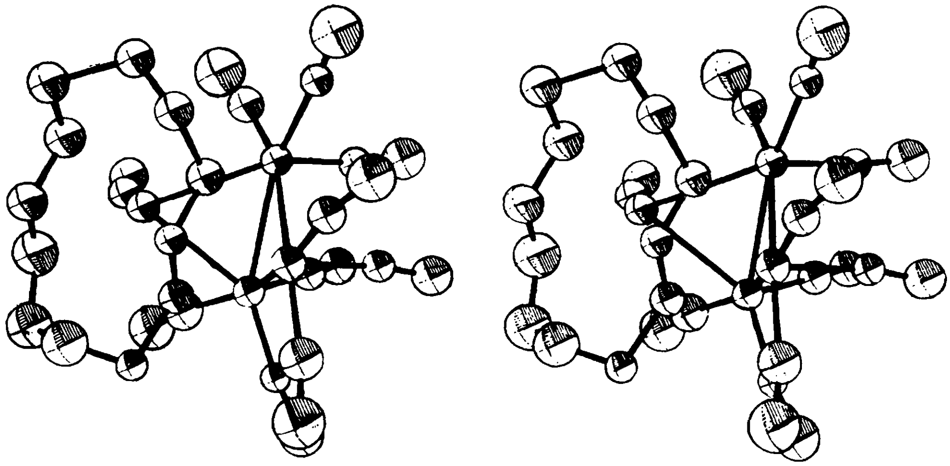

FIGURE 1 A stereoscopic view of the molecule showing the relationship between the Ru_4 butterfly cluster and the C_{12} ring

The Metal Cluster.—In the Ru_4 ' butterfly ' the two isosceles triangles share a basal ' hinge ' Ru(1)–Ru(2) of length 2·850(6) Å. This is significantly longer than the other distances in the metal cluster (Table 2) which have the values 2·775(6), 2·776(6), 2·775(5), and 2·811(8) Å. In comparing these distances, the limitations of the original intensity data should be borne in mind (see earlier). In view of the near equivalence in the environments of Ru(4)–Ru(1) and Ru(4)–Ru(2) with respect to the rest of the molecule, we do not believe that these bond lengths (apart from the hinge) are significantly different from one another, possible though that might appear to be from the standard deviations given. These values may be compared with those obtained for the analogous Ru_3 cluster compound $HRu_3(CO)_9(C_{12}H_{15})$.[3] Similarities are to be expected between the equal sides of the isosceles triangles in the Ru_4 cluster and the two equal sides of the Ru_3 cluster

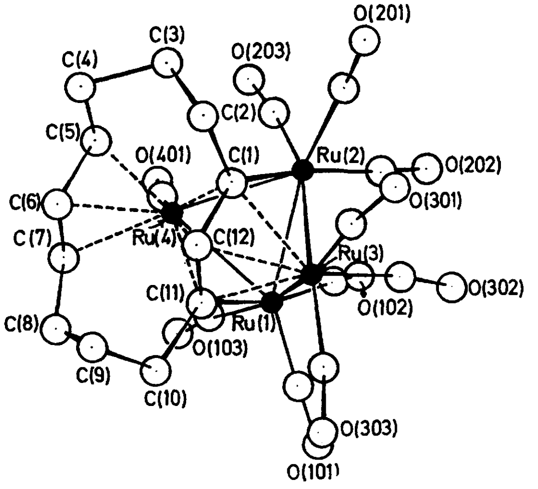

FIGURE 2 The molecule showing the bonding relationships and the atom numbering system

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. will be supplied as full size copies).

[7] H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Cryst.*, 1964, **17**, 1040.

[8] J. M. Stewart and D. High, ' *X*-Ray '63,' (a suite of crystallographic computer programs for use on the Atlas Computer, Chilton, Didcot, Berkshire), University of Maryland Technical Report, TR 64 6.

[9] C. K. Johnson, OR-TEP, a Fortran thermal ellipsoid programme for crystal structure illustrations, Oak Ridge National Laboratory, Report ORNL 3794, 1965.

[2·775(4) and 2·779(4) Å]. Indeed, there is no significant difference in the distances found. It is seen, however, that the 'hinge' bond in Ru_4 [2·850(6) Å], although significantly longer than the other four Ru–Ru bonds, is nevertheless shorter than the basal bond of the Ru_3 cluster [2·929(4) Å]. This gives added weight to our ascription[3] of the H atom in $HRu_3(CO)_9(C_{12}H_{15})$ to a bridging position across the base of the Ru_3 triangle; hydrogen-bridged bonds are commonly longer than direct metal–metal bonds.[10]

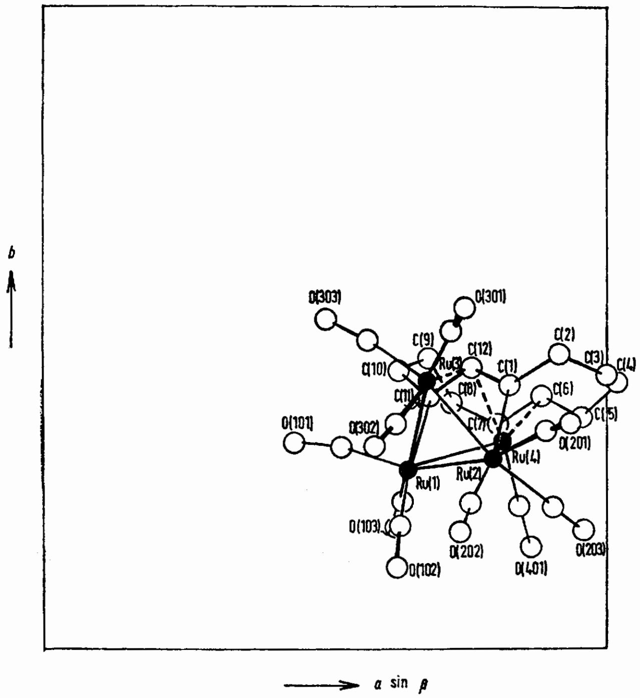

FIGURE 3 The position of the molecule in its monoclinic cell, symmetry $P2_1/n$, in projection down *c* looking towards the origin. For clarity only one molecule is shown

The C_{12} *Ring.*—In the C_{12} ring no less than six of the carbon atoms are bonded to the metal cluster. Around the ring, alternate groups of three atoms are bonded and non-bonded. One of these groups of bonded atoms [C(5), C(6), and C(7)] forms a normal symmetrical π-allyl group bonded to Ru(4) at a mean bonding distance of 2·15 Å. The other three bonded atoms [C(11), C(12), and C(1)], however, are not only bonded, π-allyl fashion, to Ru(4) at a mean distance of 2·21 Å but are also simultaneously symmetrically bonded to Ru(3) at a mean bond distance of 2·31 Å. In $HRu_3(CO)_9(C_{12}H_{15})$, the corresponding mean bonding distance was 2·20 Å; none of the values given here for the Ru_4 compound is significantly different from this value of 2·20 Å because of the large standard deviations in the present determination. Remarkably, however, in addition to this double π-allyl bond, C(11) is σ-bonded to Ru(1) and C(1) to Ru(2); *i.e.* the outermost atoms of the π-allyl group are directly σ-bonded to the two ruthenium atoms of the hinge at a distance of 2·14(4) Å. This bond length is in close agreement with the expected value of 2·13 Å: [radius C(sp^2), 0·71 Å from graphite; radius Ru^0, 1·42 Å from $Ru_3(CO)_{12}$; expected Ru–C *ca.* 2·13 Å]. The agreement may be fortuitous, and it would be interesting to know whether this Ru–C bond really is longer than the corresponding σ-bond in $HRu_3(CO)_9(C_{12}H_{15})$ where a distance of 2·02(3) Å was found;[3] alas, the standard deviations do not allow any conclusion other than the fairly high probability of a difference.

All five of the atoms Ru(1), C(11), C(12), C(1), and Ru(2) are closely coplanar, as shown by the near equivalence of their distances from Ru(3) and Ru(4). This form of bonding has not been observed previously, and is of special interest as it must involve not only interactions between $d_{x^2-y^2}$ orbitals of the wing-tip ruthenium atoms and the b_1 molecular orbital of the allyl group, but also between d_{xy} orbitals on the same ruthenium atoms and the a_2 molecular orbital of the allyl group which in the free radical is non-bonding.[11] We are here considering the group of the four ruthenium atoms Ru(1)—(4) and the allylic carbon atoms C(11), C(12), and C(1) as a cluster of local symmetry C_{2v}, with x as the Ru(3)–Ru(4) direction, y as the C(11)–C(1) direction, and z the two-fold symmetry axis of the group.

The geometry of the C_{12} ring confirms that the number of hydrogen atoms is 16. The existence of allyl moieties at positions C(11), C(12), C(1), and at C(5), C(6), C(7), precludes the existence of double bonds at C(1)–C(2), C(4)–C(5), C(7)–C(8), and C(10)–C(11). The presence of any ethylenic bonds implies that a succession of four carbon atoms, of which the central two are double-bonded, must be coplanar. The sequences which envelop C(2)–C(3), C(3)–C(4), C(8)–C(9), and C(9)–C(10) are all definitely non-planar. We therefore conclude that atoms C(5)–(7) carry one hydrogen atom each, as does also the central atom of the other allyl group, C(12). Atoms C(11) and C(1), of course, carry no hydrogen atom as each is bonded to the Ru_4 cluster. The remaining carbon atoms of the ring C(2)—(4), C(8)—C(10), carry two hydrogen atoms each, making a total of sixteen.

The Carbonyl Groups.—The carbonyl ligands are all terminal; the mean Ru–C and C–O distances are 1·87 and 1·17 Å respectively, and call for no comment except that they fortuitously coincide with the values determined for $HRu_3(CO)_9(C_{12}H_{15})$. To a first approximation the atoms Ru(1), Ru(2), and Ru(3), with their attached carbonyl groups, retain the configuration of the 'parent' molecule $Ru_3(CO)_{12}$ in that one carbonyl group on each ruthenium atom is approximately perpendicular to the metal atom plane, and the two other carbonyl groups on each ruthenium atom are mutually orthogonal and lie close to the metal-atom plane. The fourth ruthenium atom, Ru(4), carries only one carbonyl group, and this lies in an axial relationship to the Ru(1), Ru(2), Ru(4)

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[10] M. R. Churchill, P. H. Bird, H. D. Kaesz, R. Bau, and B. Fontal, *J. Amer. Chem. Soc.*, 1968, **90**, 7135.

[11] D. S. Urch, 'Orbitals and Symmetry,' chap. 2, Penguin, Harmondsworth, 1970.

plane on the side away from the C_{12} ring. The positions where any equatorial carbonyl groups might have been expected are occupied instead by atoms C(5)—(7) of the C_{12} ring to which Ru(4) is bonded.

Finally, we emphasise again that while we have no doubt of the overall correctness of the configuration of this molecule, the detailed quantitative aspects must be treated with the reservations implicit in the original data.

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