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Crystallographic Identification of Azulenetriruthenium Heptacarbonyl

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The reaction of azulene with $Ru_3(CO)_{12}$ leads, *inter alia*, to the formation of azulenetriruthenium heptacarbonyl, $(C_{10}H_8)Ru_3(CO)_7$, whose identity and stereochemistry have been elucidated *via* a single-crystal X-ray diffraction study. The complex is obtained as thin red plates crystallizing in the centrosymmetric monoclinic space group $P2_1/c$ (C_{2h}^5; No. 14) with $a = 17.183$ (8), $b = 13.357$ (11), and $c = 16.410$ (5) Å; $\beta = 108.7$ (1)°; $\rho_{\text{obsd}} = 2.19$ (3) and $\rho_{\text{calcd}} = 2.336$ g cm^{-3} for $M = 627.46$ and $Z = 8$. The structure was solved by means of Patterson and Fourier syntheses and was refined, by the method of least squares, to a final discrepancy index of $R_F = 8.9\%$ for 2285 independent nonzero reflections (Mo Kα radiation; $\sin\theta_{\max} = 0.36$) collected with a Supper-Pace automated diffractometer. The two $(C_{10}H_8)Ru_3(CO)_7$ molecules which define the crystallographic asymmetric unit are equivalent and have C_s symmetry within the limits of experimental error. Within each molecule the three ruthenium atoms define an isosceles triangle with Ru(1)–Ru(2) ≡ Ru(1)–Ru(3) = 2.937 (4)–2.949 (4) and Ru(2)–Ru(3) = 2.740 (4)–2.741 (4) Å. Each ruthenium atom is bonded to two terminal carbonyl ligands, with the seventh carbonyl group symmetrically bridging Ru(2) and Ru(3). Atom Ru(1) interacts with all atoms of the five-membered carbocyclic ring of the azulene ligand; Ru(2) and Ru(3) lie below the seven-membered ring and are linked, in a delocalized manner, to the remaining five carbon atoms of the azulene system. Relationships between $(C_{10}H_8)Ru_3(CO)_7$ and the tetrahedral cluster complex $[(CH_3)_3C_{10}H_5]Ru_4(CO)_9$ are also discussed.

Introduction

We have previously reported the results of crystallographic studies on such azulene complexes as $(C_{10}H_8)Fe_2(CO)_5$,[1] $(C_{10}H_8)Mo_2(CO)_6$,[2] $[(i\text{-}C_3H_7)(CH_3)_2C_{10}H_5]Mo_2(CO)_6$,[3] $[(C_{10}H_8)Mo(CO)_3(CH_3)]_2$,[4] $(C_{10}H_8)Mn_2(CO)_6$,[5] $(C_{10}H_8)_2Fe_4(CO)_{10}$,[6] and $(C_{10}H_8)_2Fe$.[7] In each of these species the ten azulene π electrons are "factored into groups," giving rise to conventional π-cyclopentadienyl→metal, π-dienyl→metal, π-diene→metal, π-allyl→metal, and/or simple (σ) carbon-carbon bonds.

We have also described the synthesis and the crystal structures of the monoclinic and triclinic modifications of $[4,6,8\text{-}(CH_3)_3C_{10}H_5]Ru_4(CO)_9$—a complex in which a substituted azulene ligand interacts (*via* delocalized "ligand-to-cluster" bonding) with three atoms of a tetrahedral $Ru_4(CO)_9$ cluster.[8–10] The mechanism whereby 4,6,8-trimethylazulene and $Ru_3(CO)_{12}$ react to form a *tetra* nuclear complex is, however, puzzling, and led us to investigate further the reaction of $Ru_3(CO)_{12}$ with azulene and with a variety of substituted azulenes.[11] From this latter work we obtained $(C_{10}H_8)Ru_3(CO)_7$, the synthesis of which has been described previously.[12] We now report details of the crystallographic identification and molecular structure of this new complex.

Unit Cell and Space Group

The complex crystallizes as thin red platelets. Optical examination indicated that the crystals belonged to the monoclinic system. A careful survey of (0–1)kl, h(0–1)l, and hk(0–2) precession photographs revealed the systematic absences $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$, which uniquely determine the space group as $P2_1/c$ (C_{2h}^5; No. 14).[13] Unit cell parameters, from a least-squares analysis of high angle reflections on calibrated (NaCl, $a_{25°} = 5.6410$ Å)[14,15] precession photographs, are $a = 17.183$ (8) Å, $b = 13.357$ (11) Å, $c = 16.410$ (5) Å, and $\beta = 108.7$ (1)°. The unit cell volume is $V = 3567.6$ Å^3. The observed density, by flotation in aqueous zinc iodide, was 2.19 ± 0.03 g cm^{-3}; that calculated for $M = 627.46$ (consistent with the stoichiometry $(C_{10}H_8)Ru_3(CO)_7$, as determined later) and $Z = 8$ is 2.336 g cm^{-3}.

Collection and Unification of X-Ray Diffraction Data

Intensity data were recorded with a 0.01°-incrementing Supper-Pace "Buerger automated diffractometer" using Mo Kα radiation (*i.e.*, molybdenum radiation filtered through a 3-mil Zr foil at the source; $\bar{\lambda}$ 0.7107 Å), a "stationary-background, ω-scan, stationary-background" counting sequence, and equiinclination Weissenberg geometry.[16]

Two crystals were used in the collection of intensity data. Crystal 1 (0.20 × 0.04 × 0.26 mm, referred to $\vec{a}, \vec{b}, \vec{c}$) was mounted on its c axis; crystal 2 (0.24 × 0.04 × 0.32 mm, for $\vec{a}, \vec{b}, \vec{c}$) was aligned along a.

Details specific to the present analysis (*cf.* ref 16) were as follows: (i) generator power 49.3 kV/19.2 mA; (ii) $d\omega/dt = 2°$/min; (iii) scan range $\omega = [1.8 + 0.7/L]°$; (iv) $t_{B_1} = t_{B_2} = 0.25t_C$; (v) standard reflections collected after every 20 reflections; (vi) $I(hkl) = C(hkl) - 2[B_1(hkl) + B_2(hkl)]$.

Standard deviations were assigned according to the following scheme: $I(hkl) \geq 4900$, $\sigma[I(hkl)] = 0.1[I(hkl)]$; $I(hkl) < 4900$, $\sigma[I(hkl)] = 7.0[I(hkl)]^{1/2}$; $I(hkl) \leq 3.0[C(hkl) + 4B_1(hkl) + 4B_2(hkl)]^{1/2}$, reflection rejected as less than 3σ above background.

Of 4081 reflections ($\sin\theta_{\max} = 0.36$) in quadrants hkl and $\bar{h}kl$ of levels hk(0–12) collected from crystal 1, 1770 were rejected as being less than 3σ above background; of 2936 reflections in quadrants hkl and $hk\bar{l}$ from levels (0–10)kl collected from crystal 2, 1452 were similarly rejected. Reflections in the range $0 \leq \theta \leq 4°$ were not collected since they were shielded from the counter by a lead backstop.

All data were corrected for Lorentz, polarization, and absorption[17] effects ($\mu = 24.848$ cm^{-1}); transmission coefficients ranged 0.623–0.905 for crystal 1 (volume 2.08×10^{-6} cm^3) and 0.582–0.905 for crystal 2 (volume 3.07×10^{-6} cm^3).

Symmetry-equivalent reflections within a given level were averaged and data from the 24 Weissenberg levels were placed on a

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(1) M. R. Churchill, *Inorg. Chem.*, 6, 190 (1967).

(2) M. R. Churchill and P. H. Bird, *Chem. Commun.*, 746 (1967).

(3) M. R. Churchill and P. H. Bird, *Inorg. Chem.*, 7, 1545 (1968).

(4) P. H. Bird and M. R. Churchill, *Inorg. Chem.*, 7, 349 (1968).

(5) M. R. Churchill and P. H. Bird, *Inorg. Chem.*, 7, 1793 (1968).

(6) M. R. Churchill and P. H. Bird, *Inorg. Chem.*, 8, 1941 (1969).

(7) M. R. Churchill and J. Wormald, *Inorg. Chem.*, 8, 716 (1969).

(8) M. R. Churchill and P. H. Bird, *J. Amer. Chem. Soc.*, 90, 800 (1968).

(9) M. R. Churchill, K. Gold, and P. H. Bird, *Inorg. Chem.*, 8, 1956 (1969).

(10) M. R. Churchill, *Progr. Inorg. Chem.*, 11, 58 (1970); see, especially, pp 78–81.

(11) M. R. Churchill and F. R. Scholer, unpublished work.

(12) M. R. Churchill, F. R. Scholer, and J. Wormald, *J. Organometal. Chem.*, 28, C21 (1971).

(13) "International Tables for X-Ray Crystallography," Vol. 1, 2nd ed, Kynoch Press, Birmingham, England, 1965, p 99.

(14) "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962, p 122.

(15) Note that $a_{NaCl} = [5.62800 + 0.000227(t - 18)]$ kX, where t is temperature in degrees centigrade and 1 kX = 1.00202 Å.

(16) Details of the apparatus and experimental technique have been given previously: M. R. Churchill and J. P. Fennessey, *Inorg. Chem.*, 7, 1123 (1968).

(17) Using IMBIBE, a Fortran IV program by J. Wormald; see also C. W. Burnham, *Amer. Mineral.*, 51, 159 (1966).

Table I. Final Atomic Parameters for $(C_{10}H_8)Ru_3(CO)_7$

1. Positional and Isotropic Thermal Parameters

Atom	*x*	*y*	*z*	*B*, Å^2
Molecule A, Ru_3 Cluster Centered at 0.128, 0.270, 0.378				
Ru(1)	0.12916 (22)	0.23337 (27)	0.48027 (23)	
Ru(2)	0.04329 (23)	0.28646 (27)	0.29916 (25)	
Ru(3)	0.21160 (23)	0.29085 (27)	0.35567 (24)	
O(1)	0.2551 (22)	0.3725 (27)	0.6016 (23)	5.3 (6)
O(2)	0.0063 (19)	0.3690 (24)	0.5123 (20)	3.9 (4)
O(3)	−0.1020 (23)	0.3868 (27)	0.3359 (34)	5.4 (6)
O(4)	−0.0274 (21)	0.3678 (26)	0.1214 (23)	4.9 (5)
O(5)	0.2870 (23)	0.3843 (27)	0.2321 (24)	5.3 (5)
O(6)	0.3629 (27)	0.3827 (31)	0.4839 (26)	6.1 (6)
O(7)	0.1246 (22)	0.4861 (27)	0.3535 (22)	4.6 (6)
C(1)	0.2018 (27)	0.0921 (23)	0.5146 (30)	2.9 (7)
C(2)	0.1314 (28)	0.0797 (34)	0.5481 (30)	2.8 (7)
C(3)	0.0572 (28)	0.0962 (33)	0.4811 (29)	3.0 (7)
C(4)	0.0317 (29)	0.1076 (35)	0.3172 (32)	2.7 (7)
C(5)	0.0491 (26)	0.1330 (32)	0.2399 (28)	2.6 (7)
C(6)	0.1273 (36)	0.1780 (44)	0.2410 (37)	4.1 (8)
C(7)	0.2096 (26)	0.1351 (31)	0.2976 (27)	2.6 (7)
C(8)	0.2301 (26)	0.1125 (32)	0.3824 (28)	2.8 (7)
C(9)	0.1738 (36)	0.0992 (42)	0.4206 (37)	5.4 (9)
C(10)	0.0827 (29)	0.1037 (34)	0.3998 (30)	3.1 (7)
C(11)	0.2055 (30)	0.3173 (37)	0.5467 (32)	3.7 (8)
C(12)	0.0548 (35)	0.3237 (42)	0.4955 (36)	5.0 (8)
C(13)	−0.0490 (28)	0.3419 (35)	0.3218 (39)	3.1 (8)
C(14)	−0.0010 (30)	0.3344 (36)	0.1860 (33)	3.0 (8)
C(15)	0.2606 (35)	0.3437 (44)	0.2779 (38)	6.7 (9)
C(16)	0.3031 (42)	0.3481 (51)	0.4403 (42)	5.9 (9)
C(17)	0.1248 (33)	0.4000 (41)	0.3450 (34)	3.7 (8)
H(1)	0.2654	0.0955	0.5546	5.0
H(2)	0.1365	0.0609	0.6136	5.0
H(3)	−0.0039	0.1022	0.4858	5.0
H(4)	−0.0316	0.0888	0.3084	5.0
H(5)	0.0030	0.1184	0.1786	5.0
H(6)	0.1270	0.1818	0.1751	5.0
H(7)	0.2557	0.1217	0.2671	5.0
H(8)	0.2942	0.1050	0.4198	5.0
Molecule B, Ru_3 Cluster Centered at 0.629, 0.248, 0.377				
Ru(1′)	0.62664 (23)	0.28198 (27)	0.27452 (25)	
Ru(2′)	0.71356 (22)	0.22909 (27)	0.45529 (24)	
Ru(3′)	0.54522 (23)	0.23344 (27)	0.40233 (24)	
O(1′)	0.5040 (23)	0.1382 (28)	0.1582 (23)	5.1 (5)
O(2′)	0.7493 (38)	0.1380 (46)	0.2418 (38)	9.1 (7)
O(3′)	0.8600 (28)	0.1546 (33)	0.4181 (27)	6.3 (6)
O(4′)	0.7858 (21)	0.1351 (26)	0.6300 (23)	4.7 (5)
O(5′)	0.4702 (27)	0.1351 (33)	0.5259 (29)	6.7 (7)
O(6′)	0.3902 (27)	0.1689 (33)	0.2663 (29)	7.4 (6)
O(7′)	0.6235 (19)	0.0323 (24)	0.3966 (20)	4.0 (5)
C(1′)	0.5608 (31)	0.4234 (37)	0.2412 (33)	3.9 (7)
C(2′)	0.6250 (33)	0.4271 (37)	0.2002 (34)	3.9 (7)
C(3′)	0.6981 (27)	0.4298 (32)	0.2886 (29)	3.0 (6)
C(4′)	0.7331 (28)	0.4077 (33)	0.4486 (29)	3.1 (7)
C(5′)	0.7150 (31)	0.3802 (38)	0.5197 (33)	3.8 (8)
C(6′)	0.6333 (27)	0.3444 (35)	0.5159 (29)	3.2 (7)
C(7′)	0.5574 (25)	0.3826 (30)	0.4720 (26)	2.3 (7)
C(8′)	0.5311 (28)	0.4066 (33)	0.3882 (29)	3.0 (7)
C(9′)	0.5841 (24)	0.4209 (28)	0.3339 (26)	1.8 (6)
C(10′)	0.6703 (24)	0.4161 (29)	0.3532 (27)	2.0 (7)
C(11′)	0.5514 (42)	0.1884 (52)	0.2081 (46)	6.7 (9)
C(12′)	0.7055 (40)	0.1918 (49)	0.2600 (41)	6.2 (8)
C(13′)	0.8040 (42)	0.1838 (50)	0.4376 (42)	6.7 (9)
C(14′)	0.7579 (34)	0.1710 (42)	0.5607 (37)	4.6 (8)
C(15′)	0.4969 (32)	0.1716 (40)	0.4855 (35)	4.7 (8)
C(16′)	0.4469 (24)	0.1917 (29)	0.3173 (25)	1.9 (8)
C(17′)	0.6233 (31)	0.1205 (41)	0.4049 (33)	1.8 (8)
H(1′)	0.4968	0.4226	0.2024	5.0
H(2′)	0.6232	0.4277	0.1338	5.0
H(3′)	0.7619	0.4415	0.2947	5.0
H(4′)	0.7965	0.4260	0.4573	5.0
H(5′)	0.7624	0.3847	0.5815	5.0
H(6′)	0.6348	0.3467	0.5822	5.0
H(7′)	0.5152	0.3942	0.5078	5.0
H(8′)	0.4658	0.4163	0.3579	5.0

Table I. Final Atomic Parameters for $(C_{10}H_8)Ru_3(CO)_7$ *(Continued)*

II. Anisotropic Thermal Parameters ($\times 10^4$) for Ruthenium Atoms[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ru(1)	25.5 (1.7)	34.2 (2.4)	26.4 (2.0)	2.4 (3.1)	12.6 (2.6)	2.3 (3.4)
Ru(2)	20.5 (1.7)	47.1 (2.5)	26.1 (2.0)	−4.8 (3.2)	9.1 (2.8)	8.3 (3.4)
Ru(3)	18.2 (1.6)	41.9 (2.6)	34.0 (2.0)	−1.5 (3.1)	15.1 (2.7)	3.5 (3.4)
Ru(1′)	24.0 (1.8)	37.8 (2.5)	33.0 (1.9)	3.0 (3.3)	17.4 (3.0)	5.4 (3.6)
Ru(2′)	15.8 (1.7)	42.5 (2.5)	33.0 (1.9)	−0.8 (3.1)	10.3 (2.7)	6.0 (3.5)
Ru(3′)	17.6 (1.5)	42.0 (2.5)	36.6 (1.9)	−0.2 (3.1)	16.8 (2.9)	7.0 (3.5)

III. Direction Cosines for Thermal Ellipsoids of Ruthenium Atoms[b,c]

Atom	B_{max}, Å^2 (dc's major axis)	B_{med}, Å^2 (dc's median axis)	B_{min}, Å^2 (dc's minor axis)
Ru(1)	2.93	2.61	2.40
	(0.902, 0.057, −0.693)	(0.280, 0.675, 0.556)	(−0.328, 0.735, −0.459)
Ru(2)	3.64	2.53	2.06
	(−0.338, 0.863, 0.463)	(−0.518, −0.503, 0.822)	(0.786, 0.040, 0.332)
Ru(3)	3.40	2.93	1.90
	(−0.221, 0.369, 0.926)	(0.007, 0.926, −0.360)	(0.975, 0.077, −0.116)
Ru(1′)	3.32	2.69	2.46
	(−0.162, 0.333, 0.932)	(0.592, 0.786, −0.359)	(0.790, −0.521, 0.054)
Ru(2′)	3.56	2.85	1.66
	(−0.296, 0.491, 0.871)	(0.140, 0.871, −0.491)	(0.945, 0.025, 0.006)
Ru(3′)	3.72	2.85	1.82
	(−0.183, 0.400, 0.909)	(−0.038, 0.910, −0.379)	(0.982, 0.110, −0.172)

[a] The anisotropic thermal parameter is defined as $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. [b] The major, minor, and median axes of the thermal vibration ellipsoids are defined in terms of the familiar isotropic thermal parameter, B, which is related to the root-mean-square displacement, $(\overline{U}^2)^{1/2}$, by $(\overline{U}^2)^{1/2} = [B/8\pi^2]^{1/2}$. [c] Direction cosines (dc's) refer to the natural monoclinic axes.

common scale by a least-squares analysis of common reflections.[18] The "R factor" for interlevel scaling was 4.55%. The resulting 2285 symmetry-independent nonzero reflections were used in a Wilson plot,[19] from which were obtained the approximate absolute scale and the overall isotropic thermal parameter $\overline{B} = 2.4$ Å^2.

Elucidation of Molecular Formula and Refinement of the Structure

At the onset of the structural analysis (early in 1969) we did not know the stoichiometry of the material under investigation. Furthermore, mass spectral data[12] (which showed series of peaks based on successive loss of $^{12}C^{16}O$ from $C_{10}H_8Ru_4(CO)_9^+$, $C_{10}H_8Ru_3(CO)_7^+$, and $C_{10}H_8Ru_2(CO)_4^+$) were somewhat misleading. Application of Sayre's equation to the 282 reflections with $E \geqslant 1.5$ yielded no chemically sensible solution but gave results suggestive of a disordered structure either with a "Star of David" pattern or with two triangles sharing a common edge (depending upon the solution selected!). Initial attempts to solve the structure by the Patterson technique were also unsuccessful. It seemed that this structural analysis was destined to become one of the "hidden embarrassments" of the crystallographic world.

The key to the solution of this problem was found some two years later, during a structural study of $[Me_4N^+]_2[Fe_6(CO)_{16}C^{2-}]$, in which the asymmetric unit contains two Fe_3 triangles (from different anions) which are related by pseudosymmetry.[20,21] A very detailed examination of the Patterson map of the azuleneruthenium carbonyl species revealed a set of peaks around the origin which were consistent with the presence of two Ru_3 triangles in different, but related, orientations. An examination of complex patterns of peaks around $^1/_4$, $^1/_2$, $^1/_4$ and $^1/_2$, 0, $^1/_2$ revealed that the two symmetry-independent Ru_3 triangles were centered at approximately (0.13, 0.25, 0.38) and (0.63, 0.25, 0.38).

The positions of the six ruthenium atoms were refined by the method of least-squares, yielding $R_F = 28.8\%$.[22] A difference-Fourier synthesis quickly revealed the positions of carbon atoms of an azulene skeleton and of seven carbonyl groups about each Ru_3 cluster. The molecular formula was now established as $(C_{10}H_8)Ru_3(CO)_7$. Full-matrix least-squares refinement of positional and isotropic thermal parameters for all 54 nonhydrogen atoms converged in four cycles to $R_F = 10.0\%$, $R_{wF^2} = 6.2\%$.

Refinement was continued using anisotropic thermal parameters for the ruthenium atoms and isotropic thermal parameters for all other nonhydrogen atoms, with hydrogen atoms introduced at (fixed) calculated positions[23] and assigned thermal parameters of 5.0 Å^2. Two cycles of refinement resulted in convergence ($\Delta/\sigma < 10\%$) at $R_F = 8.9\%$ and $R_{wF^2} = 5.0\%$. [Refinement *without* hydrogen atoms led to $R_F = 9.0\%$, $R_{wF^2} = 5.1\%$.] Hamilton R factor ratio tests[24] indicate that the refinement of anisotropic thermal parameters of the ruthenium atoms is meaningful at a 98% level of confidence.

The standard error in an observation of unit weight was 1.81, indicating a slight underestimate in the assigned standard deviations. Peak heights on a final "observed" Fourier synthesis were as follows (e Å^{-3}): Ru, 55.5–72.8; O, 4.9–8.4; C(azulene), 2.9–7.1; C(carbonyl), 3.2–5.4. A final "difference" Fourier map showed no significant features, thus validating the results of the least-squares refinement process and confirming the essential correctness of the determined molecular structure.

During the analysis all calculations were (unless otherwise specified) performed on the Harvard University IBM 360/65 computer, using a locally modified version of Marsh's CRYM system of crystallographic routines. Scattering factors for neutral oxygen, carbon, and hydrogen were used;[25a] the scattering curve for neutral ruthenium[25b] was corrected for both the real and imaginary components of anomalous dispersion ($\Delta f' = -1.2$ e, $\Delta f'' = +1.1$ e).[25c] The residual minimized in the least-squares refinement process was $\Sigma w(|F_o|^2 - |F_c|^2)^2$, where $w(hkl) = [\sigma[F^2(hkl)]]^{-2}$ and $\sigma[F^2(hkl)] = \sigma[I(hkl)]\,|F^2(hkl)|/[I(hkl)]$.

A table of observed and calculated structure factor amplitudes is available.[26] Final atomic parameters are listed in Table I.

The Molecular Structure

The asymmetric unit contains *two* molecules of $(C_{10}H_8)$-

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(18) Using MATE, a Fortran IV program by J. Wormald; this program is based on the method of A. D. Rae, *Acta Crystallogr.*, 19, 683 (1965).

(19) A. J. C. Wilson, *Nature (London)*, 150, 152 (1942).

(20) M. R. Churchill, J. Wormald, J. Knight, and M. J. Mays, *J. Amer. Chem. Soc.*, 93, 3073 (1971).

(21) M. R. Churchill and J. Wormald, in preparation.

(22) $R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_{wF^2} = \Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o|^4$.

(23) Hydrogen atoms other than H(6) were positioned with sp^2 geometry and d(C–H) = 1.08 Å. Atom H(6) was positioned assuming pseudo-sp^3 geometry about C(6), with the other "bond directions" being defined by C(6)–C(5), C(6)–C(7), and C(6)–[midpoint of Ru(2)–Ru(3)]. The assumption of approximate sp^3 geometry is based upon the position of the 6-methyl group in 4,6,8-$[(CH_3)_3C_{10}H_5]Ru_4(CO)_9$—see Figure 3 and ref 9.

(24) W. C. Hamilton, *Acta Crystallogr.*, 18, 502 (1965).

(25) "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England: (a) pp 202–203, (b) p 211, (c) p 216.

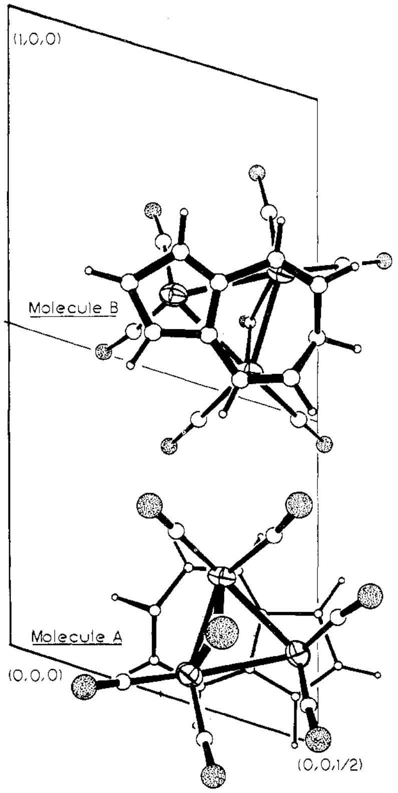

Figure 1. The two $(C_{10}H_8)Ru_3(CO)_7$ molecules in the asymmetric unit and their positions in the unit cell, viewed down *b*. The thermal vibration ellipsoids of the ruthenium atoms are also shown.

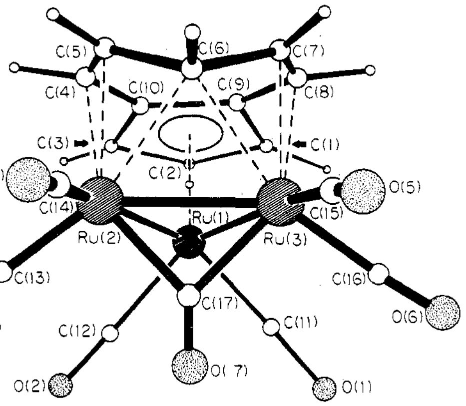

Figure 2. An "end-on" view of the $(C_{10}H_8)Ru_3(CO)_7$ molecule, showing the atomic numbering scheme, the bridging carbonyl group, and the azulene-to-cluster bonding.

$Ru_3(CO)_7$, which, although crystallographically distinct and independent, are chemically similar--see Figure 1. Furthermore, each molecule has *approximate* $C_s(m)$ symmetry. Atoms within the two molecules are numbered similarly, save that those of molecule A are unprimed, while those of molecule B are primed. The geometry and atomic labeling are illustrated in Figure 2.

The numbering of the different kinds of atoms is quite systematic: the azulene fragment is labeled in the conventional fashion [C(1) through C(10)]; Ru(1), the unique ruthenium atom, is bonded to carbonyl groups C(11)-O(1) and C(12)-O(1); the terminal carbonyl ligands are labeled cyclically as C(10 + *n*)-O(*n*) (*n* = 1-6), with the bridging carbonyl group being C(17)-O(7).

Table II. Interatomic Distances (Å) for $(C_{10}H_8)Ru_3(CO)_7$

Atoms	Molecule A	Molecule B	Mean[a]
	(a) Ruthenium-Ruthenium Distances		
Ru(1)-Ru(2)	2.949 (4)	2.947 (4)	2.944 ± 0.005
Ru(1)-Ru(3)	2.937 (4)	2.942 (4)	
Ru(2)-Ru(3)	2.740 (4)	2.741 (4)	2.741 ± 0.001
	(b) Ruthenium-Azulene Distances		
Ru(1)-C(2)	2.329 (35)	2.285 (43)	2.307 ± 0.031
Ru(1)-C(1)	2.232 (35)	2.179 (42)	2.231 ± 0.050
Ru(1)-C(3)	2.213 (36)	2.298 (43)	
Ru(1)-C(10)	2.169 (37)	2.195 (32)	2.243 ± 0.072
Ru(1)-C(9)	2.289 (49)	2.320 (31)	
Ru(2) · · · C(10)	2.902 (37)	2.965 (32)	2.925 ± 0.028
Ru(3) · · · C(9)	2.924 (49)	2.908 (31)	
Ru(2)-C(4)	2.423 (35)	2.417 (37)	2.398 ± 0.046
Ru(3)-C(8)	2.424 (40)	2.329 (37)	
Ru(2)-C(5)	2.285 (33)	2.274 (40)	2.279 ± 0.006
Ru(3)-C(7)	2.283 (37)	2.273 (33)	
Ru(2)-C(6)	2.445 (39)	2.478 (37)	2.472 ± 0.018
Ru(3)-C(6)	2.483 (39)	2.481 (37)	
	(c) Carbon-Carbon Distances in the Azulene Ligand		
C(1)-C(2)	1.489 (50)	1.465 (59)	1.487 ± 0.073
C(2)-C(3)	1.408 (50)	1.586 (60)	
C(3)-C(10)	1.535 (52)	1.307 (53)	1.438 ± 0.095
C(9)-C(1)	1.465 (61)	1.444 (52)	
C(9)-C(10)	1.493 (62)	1.413 (44)	1.453 ± 0.056
C(10)-C(4)	1.359 (51)	1.595 (48)	1.438 ± 0.124
C(8)-C(9)	1.321 (64)	1.475 (48)	
C(4)-C(5)	1.435 (48)	1.350 (54)	1.370 ± 0.043
C(7)-C(8)	1.354 (54)	1.342 (50)	
C(5)-C(6)	1.466 (51)	1.464 (55)	1.458 ± 0.067
C(6)-C(7)	1.532 (54)	1.370 (50)	
	(d) Ruthenium-Carbonyl Distances		
Ru(1)-C(11)	1.803 (40)	1.875 (51)	1.848 ± 0.038
Ru(1)-C(12)	1.831 (45)	1.884 (48)	
Ru(2)-C(13)	1.891 (39)	1.776 (52)	1.865 ± 0.059
Ru(3)-C(16)	1.894 (51)	1.897 (33)	
Ru(2)-C(14)	1.879 (40)	1.824 (44)	1.892 ± 0.069
Ru(3)-C(15)	1.876 (55)	1.989 (45)	
Ru(2)-C(17)	2.037 (37)	2.091 (38)	2.047 ± 0.034
Ru(3)-C(17)	2.051 (37)	2.010 (38)	
	(e) Carbon-Oxygen Distances		
C(11)-O(1)	1.261 (51)	1.165 (60)	1.176 ± 0.057
C(12)-O(2)	1.132 (53)	1.146 (64)	
C(13)-O(3)	1.174 (50)	1.173 (62)	1.149 ± 0.032
C(16)-O(6)	1.144 (62)	1.105 (48)	
C(14)-O(4)	1.103 (50)	1.184 (52)	1.115 ± 0.060
C(15)-O(5)	1.132 (65)	1.040 (58)	
C(17)-O(7)	1.159 (46)	1.186 (46)	1.173 ± 0.019

[a] The "scatter" from the mean value is calculated from the formula

$$\sigma = \left[\sum_{i=1}^{i=N} (\chi_i - \overline{\chi})^2/(N-1)\right]^{1/2}$$

Here χ_i is the *i*th value and $\overline{\chi}$ is the mean of *N* "equivalent" observations.

Interatomic distances are given in Table II, while bond angles are presented in Table III. All geometric data in the tables are given for both molecules A and B but are arranged according to the pairing of dimensions produced by the approximate C_s symmetry. Individual estimated standard deviations are shown in parentheses, while values of the "scatter" from the mean (see footnote *a* of Table II) are preceded by "±."

The precision of the location of carbon and oxygen atoms is not high due principally to (i) the presence of six heavy

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(26) A listing of observed and calculated structure factor amplitudes will appear immediately following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth Street, N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-191.

Table III. Angles (deg) within the $(C_{10}H_8)Ru_3(CO)_7$ Molecules

Atoms	Molecule A	Molecule B	Mean[a]
(a) Angles within Ru_3 Framework			
Ru(2)-Ru(1)-Ru(3)	55.5 (0.1)	55.5 (0.1)	55.5 ± 0.0
Ru(1)-Ru(2)-Ru(3)	62.0 (0.1)	62.2 (0.1)	62.3 ± 0.2
Ru(1)-Ru(3)-Ru(2)	62.5 (0.1)	62.4 (0.1)	
(b) Other Angles within the $Ru_3(CO)_7$ Cluster			
Ru(2)-Ru(1)-C(11)	119.5 (1.3)	117.3 (1.6)	117.8 ± 1.8
Ru(3)-Ru(1)-C(12)	115.8 (1.4)	118.4 (1.5)	
Ru(2)-Ru(1)-C(12)	80.4 (1.4)	79.7 (1.5)	80.9 ± 1.2
Ru(3)-Ru(1)-C(11)	80.7 (1.3)	82.6 (1.6)	
C(11)-Ru(1)-C(12)	84.9 (1.9)	83.7 (2.2)	84.3 ± 0.7
Ru(1)-Ru(2)-C(13)	94.4 (1.2)	96.0 (1.7)	94.4 ± 1.2
Ru(1)-Ru(3)-C(16)	93.9 (1.6)	93.2 (1.0)	
Ru(1)-Ru(2)-C(14)	172.2 (1.2)	168.2 (1.4)	170.4 ± 2.6
Ru(1)-Ru(3)-C(15)	173.0 (1.7)	168.1 (1.3)	
Ru(3)-Ru(2)-C(13)	141.7 (1.2)	147.7 (1.7)	144.5 ± 2.8
Ru(2)-Ru(3)-C(16)	142.7 (1.3)	145.8 (1.4)	
Ru(3)-Ru(2)-C(14)	112.1 (1.2)	112.8 (1.4)	113.6 ± 1.5
Ru(2)-Ru(3)-C(15)	115.6 (1.7)	113.8 (1.3)	
C(13)-Ru(2)-C(14)	87.8 (1.7)	83.6 (2.2)	85.1 ± 1.9
C(15)-Ru(3)-C(16)	84.1 (2.3)	85.0 (1.6)	
Ru(1)-Ru(2)-C(17)	75.3 (1.2)	72.3 (1.4)	74.1 ± 1.5
Ru(1)-Ru(3)-C(17)	75.3 (1.1)	73.4 (1.1)	
Ru(3)-Ru(2)-C(17)	48.2 (1.2)	46.8 (1.2)	48.0 ± 1.0
Ru(2)-Ru(3)-C(17)	47.7 (1.1)	49.3 (1.1)	
C(13)-Ru(2)-C(17)	99.0 (1.6)	106.0 (2.0)	102.2 ± 3.0
C(16)-Ru(3)-C(17)	100.7 (1.9)	103.0 (1.5)	
C(14)-Ru(2)-C(17)	97.1 (1.6)	96.4 (1.8)	96.9 ± 1.3
C(15)-Ru(3)-C(17)	98.5 (2.0)	95.5 (1.7)	
Ru(2)-C(17)-Ru(3)	84.1 (1.3)	83.9 (1.4)	84.0 ± 0.1
(c) Angles between the $Ru_3(CO)_7$ Cluster and Azulene			
C(1)-Ru(1)-C(2)	38.0 (1.3)	38.2 (1.5)	38.2 ± 1.8
C(2)-Ru(1)-C(3)	36.0 (1.3)	40.5 (1.5)	
C(9)-Ru(1)-C(1)	37.8 (1.5)	37.3 (1.3)	37.5 ± 3.0
C(10)-Ru(1)-C(3)	41.0 (1.4)	33.7 (1.4)	
C(9)-Ru(1)-C(10)	39.0 (1.6)	36.4 (1.1)	37.7 ± 1.8
C(4)-Ru(2)-C(5)	35.3 (1.2)	33.3 (1.1)	33.8 ± 1.0
C(8)-Ru(3)-C(7)	33.3 (1.3)	33.1 (1.2)	
C(5)-Ru(2)-C(6)	35.9 (1.3)	35.6 (1.3)	35.7 ± 1.4
C(7)-Ru(3)-C(6)	37.2 (1.3)	33.9 (1.2)	
Ru(2)-C(6)-Ru(3)	67.5 (1.1)	67.1 (1.0)	67.3 ± 0.3
(d) Angles within the Azulene Ligand			
C(1)-C(2)-C(3)	109.5 (3.1)	94.2 (3.2)	101.9 ± 10.8
C(2)-C(1)-C(9)	111.4 (3.3)	119.3 (3.5)	111.4 ± 6.1
C(2)-C(3)-C(10)	104.4 (3.0)	110.5 (3.5)	
C(1)-C(9)-C(10)	102.1 (3.6)	98.9 (2.8)	107.2 ± 8.1
C(3)-C(10)-C(9)	111.7 (3.2)	116.2 (3.4)	
C(1)-C(9)-C(8)	117.7 (4.2)	128.5 (3.1)	123.1 ± 5.2
C(3)-C(10)-C(4)	126.6 (3.3)	119.8 (3.2)	
C(10)-C(9)-C(8)	139.4 (4.4)	131.5 (3.0)	129.0 ± 8.1
C(9)-C(10)-C(4)	121.5 (3.6)	123.7 (2.8)	
C(9)-C(8)-C(7)	121.8 (4.0)	125.4 (3.3)	125.9 ± 3.3
C(10)-C(4)-C(5)	129.8 (3.4)	126.5 (3.3)	
C(8)-C(7)-C(6)	126.3 (3.5)	125.4 (3.4)	124.1 ± 2.0
C(4)-C(5)-C(6)	122.4 (3.1)	122.4 (3.6)	
C(5)-C(6)-C(7)	121.2 (3.2)	129.7 (3.5)	125.5 ± 6.0
(e) Angles within the Carbonyl Ligands			
Ru(1)-C(11)-O(1)	172.0 (3.4)	171.5 (4.4)	171.5 ± 1.1
Ru(1)-C(12)-O(2)	169.9 (4.0)	172.5 (4.5)	
Ru(2)-C(13)-O(3)	172.3 (3.5)	173.9 (4.5)	174.1 ± 2.9
Ru(3)-C(16)-O(6)	171.8 (4.5)	178.2 (3.3)	
Ru(2)-C(14)-O(4)	176.0 (3.7)	178.4 (3.8)	175.9 ± 2.1
Ru(3)-C(15)-O(5)	173.3 (4.8)	175.9 (4.3)	
Ru(2)-C(17)-O(7)	139.0 (3.1)	134.9 (3.0)	137.7 ± 2.4
Ru(3)-C(17)-O(7)	136.4 (3.0)	140.3 (3.1)	

[a] See footnote *a* to Table II.

(ruthenium) atoms in the asymmetric unit and (ii) the use of small crystals of concomitantly low diffracting power (volume (~2-3) × 10^{-6} cm^3, *vide supra*). Larger crystals were simply not obtainable. We will therefore discuss mean values of parameters within this text.

Each molecule is based on a triangular cluster of ruthenium atoms, centered on (0.128, 0.270, 0.378) for molecule A and on (0.629, 0.248, 0.377) for molecule B. Each ruthenium atom carries two normal terminal carbonyl groups, while the seventh carbonyl group bridges (symmetrically) Ru(2) and Ru(3). The azulene ligand arches over the metal cluster, providing ten p_π electrons. The compound can be regarded as a derivative of $Ru_3(CO)_{12}$, with azulene replacing five of the carbonyl groups and with some reorientation and reorganization of the remaining seven such groups.

The metal-metal bonds that are not bridged by carbonyl groups, *i.e.*, Ru(1)-Ru(2) and Ru(1)-Ru(3), have a mean length of 2.944 ± 0.005Å, while the carbonyl-bridged Ru(2)-Ru(3) bonds average 2.741 ± 0.001Å in length. For comparison we may note that ruthenium-ruthenium distances in other polynuclear carbonyl-containing species include the following: 2.848 (6) Å for nonbridged Ru-Ru bonds in $Ru_3(CO)_{12}$;[27] 2.827 (5)-3.034 (5) for nonbridged and 2.855 (6) Å for carbonyl-bridged Ru-Ru bonds in $Ru_6(CO)_{17}C$;[28] 2.854 (7)-2.956 (7) for nonbridged and 2.853 (7) Å for carbonyl-bridged Ru-Ru bonds in $Ru_6(CO)_{14}C$(mesitylene);[29] 2.858 (3)-2.874 (3) for nonbridged and 2.950 (3)-2.959 (3) Å for μ_3-hydrido-bridged Ru-Ru bonds in $H_2Ru_6(CO)_{18}$;[30,31] 2.702 (5)-2.902 (5) Å for nonbridged Ru-Ru bonds in monoclinic $[(CH_3)_3C_{10}H_5]Ru_4(CO)_9$;[8,9] 2.698 (3)-2.908 (3) Å for nonbridged Ru-Ru bonds in triclinic $[(CH_3)_3C_{10}H_5]Ru_4(CO)_9$;[9] 2.771 (7)-2.818 (7) Å for nonbridged, 2.762 (6)-2.786 (7) Å for (asymmetrically) carbonyl-bridged, and 2.915 (7)-2.947 (6) Å for μ_2-hydrido-bridged Ru-Ru bonds in α-$H_2Ru_4(CO)_{13}$;[32] 2.777 (7)-2.816 (8) Å for nonbridged and 2.885 (8)-2.914 (9) Å for μ_2-hydrido-bridged Ru-Ru bonds in $H_2FeRu_3(CO)_{13}$,[33] 2.775 (4)-2.779 (4) Å for nonbridged and 2.929 (4) Å for μ_2-hydrido-bridged Ru-Ru bonds in $HRu_3(CO)_9(C_{12}H_{15})$;[34,35] 2.772 (6)-2.852 (6) Å for nonbridged Ru-Ru bonds in $(C_{12}H_{16})Ru_4(CO)_{10}$.[36]

Within the $(C_{10}H_8)Ru_3(CO)_7$ molecule, all three ruthenium atoms are bonded directly to the azulene ligand. Atom Ru(1) is involved in the customary π-cyclopentadienyl→metal linkage that prevails in azulene complexes of the transition metals. Individual carbon-carbon distances within the five-membered ring range from C(3′)-C(10′) = 1.307 (53) to C(2′)-C(3′) = 1.586 (60) Å; however, the mean carbon-carbon distances (*i.e.*, those averaged over the two molecules, assuming ideal C_s symmetry for each molecule—see last column of Table II) are C(1)-C(2) ≡ C(2)-C(3) = 1.487 ± 0.073, C(3)-C(10) ≡ C(9)-C(1) = 1.438 ± 0.095, and C(9)-C(10) = 1.453 ± 0.056 Å [*cf.* the accepted C-C(π-cyclopentadienyl) distance of ~1.43 Å].

The ten independent Ru-C(π-cyclopentadienyl) distances range from 2.169 (37) to 2.329 (35) Å, with mean values being Ru(1)-C(2) = 2.307 ± 0.031, Ru(1)-C(1) ≡ Ru(1)-

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

[28] A. Sirigu, M. Bianchi, and E. Benedetti, *Chem. Commun.*, 596 (1969).

[29] R. Mason and W. R. Robinson, *Chem. Commun.*, 468 (1968).

[30] M. R. Churchill, J. Wormald, J. Knight, and M. J. Mays, *Chem. Commun.*, 458 (1970).

[31] M. R. Churchill and J. Wormald, *J. Amer. Chem. Soc.*, 93, 5670 (1971).

[32] D. B. W. Yawney and R. J. Doedens, *Inorg. Chem.*, 11, 838 (1972).

[33] C. J. Gilmore and P. Woodward, *J. Chem. Soc. A*, 3453 (1971).

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

[35] M. I. Bruce, M. A. Cairns, A. Cox, M. Green, M. D. H. Smith, and P. Woodward, *Chem. Commun.*, 735 (1970).

[36] R. Belford, M. I. Bruce, M. A. Cairns, M. Green, H. P. Taylor, and P. Woodward, *Chem. Commun.*, 1159 (1970).

Table IV. Important Least-Squares Planes in the Two $(C_{10}H_8)Ru_3(CO)_7$ Molecules

(A) Equations of the Planes[a]

Plane	Atoms	C_1	C_2	C_3	D
	(i) In Molecule A				
I	C(1)-C(2)-C(3)-C(9)-C(10)	+0.0025	+0.9931	+0.1170	−2.109
II	C(4)-C(8)-C(9)-C(10)	−0.0407	+0.9942	+0.0992	−1.981
III	C(4)-C(5)-C(7)-C(8)	−0.0920	+0.9716	+0.2180	−2.576
IV	C(5)-C(6)-C(7)	−0.2805	+0.6029	+0.7469	−3.973
V	Ru(1)-Ru(2)-Ru(3)	−0.1104	+0.9587	+0.2620	−4.978
VI	Ru(1)-C(2)-C(6)-Ru(2-3)[b]	+0.9503	+0.0106	+0.3112	−2.066
	(ii) In Molecule B				
I	C(1′)-C(2′)-C(3′)-C(9′)-C(10′)	−0.0306	+0.9984	+0.0470	−5.570
II	C(4′)-C(8′)-C(9′)-C(10′)	−0.0305	+0.9925	+0.1185	−5.906
III	C(4′)-C(5′)-C(7′)-C(8′)	−0.0746	+0.9640	+0.2552	−6.257
IV	C(5′)-C(6′)-C(7′)	−0.2302	+0.5708	+0.7881	−7.066
V	Ru(1′)-Ru(2′)-Ru(3′)	−0.0585	+0.9654	+0.2540	−4.174
VI	Ru(1′)-C(2′)-C(6′)-Ru(2′-3′)[b]	+0.9554	−0.0097	+0.2951	−10.122

(B) Interplanar Angles

Planes	A	B	Mean
I-II	2° 48′	4° 06′	3° 27′
I-III	8° 06′	12° 24′	10° 15′
I-IV	46° 44′	52° 07′	49° 25′
II-III	7° 32′	8° 24′	7° 58′
II-IV	46° 46′	48° 10′	47° 28′
III-IV	39° 14′	39° 46′	39° 30′
V-VI	89° 15′	89° 27′	89° 21′

(C) Deviations from the Planes (Å)[c]

Atom	Molecule A	Molecule B	Mean[d]
	(i) From Plane I		
C(2)*	−0.057 (36)	−0.025 (42)	−0.016
C(1)*	+0.051 (36)	−0.003 (42)	+0.001
C(3)*	+0.038 (36)	+0.053 (43)	
C(9)*	−0.026 (50)	+0.034 (31)	−0.002
C(10)*	−0.007 (37)	−0.059 (32)	
C(8)	+0.084 (40)	−0.081 (37)	+0.044
C(4)	−0.107 (35)	−0.118 (37)	
C(7)	+0.230 (37)	−0.341 (34)	+0.268
C(5)	+0.091 (34)	−0.412 (40)	
C(6)	+0.693 (39)	−0.850 (37)	+0.771
Ru(1)	+1.860 (03)	−1.894 (03)	+1.877
Ru(2)	+2.233 (03)	−2.484 (03)	+2.376
Ru(3)	+2.401 (03)	−2.385 (03)	
	(ii) From Plane II		
C(4)*	−0.017 (35)	+0.014 (37)	+0.005
C(8)*	+0.023 (40)	−0.017 (37)	
C(9)*	−0.047 (50)	+0.037 (31)	−0.005
C(10)*	+0.041 (37)	−0.034 (32)	
	(iii) From Plane III		
C(4)*	−0.001 (35)	+0.010 (37)	+0.000
C(8)*	+0.001 (40)	−0.010 (37)	
C(5)*	+0.001 (34)	−0.012 (40)	+0.000
C(7)*	−0.001 (37)	+0.013 (34)	
	(iv) From Plane V		
C(2)	−1.657 (36)	+1.556 (42)	−1.607
C(1)	−1.787 (36)	+1.748 (42)	−1.762
C(3)	−1.617 (36)	+1.895 (43)	
C(9)	−2.080 (50)	+2.087 (31)	−2.033
C(10)	−1.947 (37)	+2.020 (32)	
C(8)	−2.195 (40)	+2.187 (37)	−2.205
C(4)	−2.184 (35)	+2.256 (37)	
C(7)	−2.261 (37)	+2.207 (34)	−2.235
C(5)	−2.253 (34)	+2.221 (40)	
C(6)	−1.820 (39)	+1.826 (37)	−1.823
C(11)	+1.240 (40)	−1.413 (52)	+1.331
C(12)	+1.368 (46)	−1.304 (49)	
O(1)	+2.108 (32)	−2.226 (31)	+2.143
O(2)	+2.118 (27)	−2.119 (42)	
C(13)	+0.990 (39)	−0.751 (52)	+0.874
C(16)	+0.954 (52)	−0.802 (33)	
O(3)	+1.732 (31)	−1.266 (34)	+1.435
O(6)	+1.486 (35)	−1.255 (36)	
C(14)	+0.172 (40)	−0.345 (45)	+0.283
C(15)	+0.222 (55)	−0.394 (45)	
O(4)	+0.349 (31)	−0.541 (28)	+0.509
O(5)	+0.479 (35)	−0.667 (38)	
C(17)	+1.512 (38)	−1.524 (38)	+1.518
O(7)	+2.655 (27)	−2.698 (26)	+2.676
	(v) From Plane VI (Mean Values Are Algebraic)		
Ru(1)*	−0.002 (03)	+0.008 (03)	0.005
C(2)*	+0.001 (36)	−0.004 (42)	0.003
C(6)*	−0.001 (39)	+0.004 (37)	0.003
Ru(2-3)*[b]	+0.002 (03)	−0.008 (03)	0.005
C(1)	+1.158 (36)	−1.076 (43)	1.147
C(3)	−1.198 (36)	+1.156 (31)	
C(9)	+0.718 (50)	−0.735 (32)	0.723
C(10)	−0.766 (37)	+0.673 (37)	
C(8)	+1.644 (40)	−1.626 (37)	1.675
C(4)	−1.585 (35)	+1.664 (34)	
C(7)	+1.327 (37)	−1.229 (40)	1.295
C(5)	−1.284 (34)	+1.338 (37)	
C(11)	+1.245 (40)	−1.185 (52)	1.239
C(12)	−1.206 (46)	+1.322 (49)	
O(1)	+2.054 (32)	−1.936 (31)	2.010
O(2)	−1.994 (27)	+2.055 (42)	
C(13)	−2.871 (39)	+2.862 (52)	1.886
C(16)	+2.861 (52)	−2.949 (33)	
O(3)	−3.732 (31)	+3.793 (34)	3.804
O(6)	+3.835 (35)	−3.856 (36)	
C(14)	−2.066 (40)	+2.051 (45)	2.107
C(15)	+2.192 (55)	−2.120 (45)	
O(4)	−2.482 (31)	+2.485 (28)	2.564
O(5)	+2.636 (35)	−2.651 (38)	
C(17)	−0.028 (38)	−0.082 (38)	0.055
O(7)	−0.020 (27)	−0.064 (26)	0.042
Ru(2)	−1.368 (03)	+1.363 (03)	1.370
Ru(3)	+1.372 (03)	−1.378 (03)	

[a] The planes are defined in cartesian coordinates, where the equation is $C_1X + C_2Y + C_3Z + D = 0$ and the relationships to unit cell axes are $X = xa + zc \cos\beta$, $Y = yb$, $Z = zc \sin\beta$. [b] Ru(2-3) is the midpoint of the Ru(2)-Ru(3) bond. [c] In the tables of deviations, the defining atoms are marked with an asterisk and have unit weight; all others have zero weight. [d] The mean value incorporates the necessary sign reversal for molecule B. [The absolute sign is irrelevant, since it refers only to the unit cell origin.]

C(3) = 2.231 ± 0.050, and Ru(1)-C(9) ≡ Ru(1)-C(10) = 2.243 ± 0.072 Å.

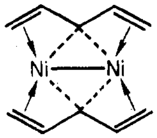
We thus conclude that the azulene-Ru(1) bonding may be described as an *essentially symmetric* π-cyclopentadienyl→metal linkage. [While the "scatter" on mean distances is large, the Ru(1)-C(2) distances are the greatest of the three nonequivalent metal-carbon vectors; in the $[(CH_3)_3C_{10}H_5]$-$Ru_4(CO)_9$ molecules,[9] the longest distances are Ru-C(9) and Ru-C(10), rather than Ru-C(2). This represents part of a pattern of differences between the trinuclear and tetranuclear azuleneruthenium carbonyl species and is discussed in the final section of this article.]

As shown in Table IV, the ruthenium atoms lie 1.860 Å [Ru(1)] and 1.894 Å [Ru(1′)] from the planes of the five-membered rings in the two $(C_{10}H_8)Ru_3(CO)_7$ molecules.

Bonding among Ru(2), Ru(3), and the atoms of the seven-membered carbocyclic ring is quite complex. First, we observe that the Ru(2)· · ·C(9) and Ru(3)· · ·C(10) distances range from 2.902 (37) to 2.965 (32) Å, with a mean value of 2.925 ± 0.028 Å; this is outside the normal range of significant metal· · ·carbon interactions.

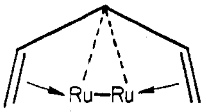
The angle between the five-membered ring and the plane defined by C(4)-C(10)-C(9)-C(8) [*i.e.*, planes I and II of Table IV] is only 3° 27′ (average), so atoms C(4) and C(8) are barely distorted from the five-membered ring plane. [Deviations are from 0.081 to 0.118 Å.] The average of the four independent C(10)-C(4) and C(8)-C(9) bond lengths is 1.438 ± 0.124 Å, while the C(5)-C(6) and C(6)-C(7) bonds have a mean value of 1.458 ± 0.067 Å. The C(4)-C(5) and C(7)-C(8) bonds appear to be slightly shorter, with an average value of 1.370 ± 0.043 Å. There is clearly no prospect of the five p_π electrons in the C(4)-C(5)-C(6)-C(7)-C(8) system forming a regular π-pentadienyl system, since the plane C(5)-C(6)-C(7) makes an angle of 39° 30′ (average) with that defined by C(4)-C(5)· · ·C(7)-C(8). Atom C(6) lies 0.406 Å (mean) below the latter plane and is displaced toward the triangle of ruthenium atoms (see Figure 2).

The mean ruthenium-carbon distances within this part of the molecule are Ru(2)-C(4) ≡ Ru(3)-C(8) = 2.398 ± 0.046 Å, Ru(2)-C(5) ≡ Ru(3)-C(7) = 2.279 ± 0.006 Å, and Ru(2)-C(6) ≡ Ru(3)-C(6) = 2.472 ± 0.018 Å. A similar situation was found by Kruger[37] in bis(pentadienyl)-dinickel, where pertinent data are as follows: Ni(1)-C(1), 1.996 Å; Ni(1)-C(2), 1.987 Å; Ni(1)-C(3), 2.240 Å; Ni(2)-C(3), 2.243 Å; Ni(2)-C(4), 1.994 Å; Ni(2)-C(5), 1.997 Å, with atom C(3) lying 0.23 Å from the plane of atoms C(1)-C(2)· · ·C(4)-C(5). The metal-dienyl bonding in this species was explained by structure I, where each nickel atom is coordinated by two double bonds, participates in two Ni-C-Ni three-center bonds, and forms a regular metal-metal bond.



I

The present situation is analogous and could be represented formally by structure II.



II

The carbonyl ligands appear normal in every respect. Mean ruthenium-carbon distances for the terminal carbonyl groups range from 1.848 ± 0.038 to 1.892 ± 0.069 Å, while the mean carbon-oxygen distances vary from 1.115 ± 0.060 to 1.176 ± 0.057 Å. Mean values for terminal Ru-C-O angles range from 171.5 ± 1.1 to 175.9 ± 2.1°. The bridging C(17)-O(7) ligands are quite symmetrical, with average parameters being Ru-C(17) = 2.047 ± 0.034 Å, C(17)-O(7) = 1.173 ± 0.019 Å, ∠Ru-C(17)-O(7) = 137.7 ± 2.4°, and ∠Ru(2)-C(17)-Ru(3) = 84.0 ± 0.1°. [For comparison, bond distances within the $Ru_6(CO)_{14}$(mesitylene) molecule[29] are Ru-C-(terminal) = 1.92 (4) Å and Ru-C(bridging) = 2.06 (4) Å.]

Table V. Intermolecular Contacts in the $(C_{10}H_8)Ru_3(CO)_7$ Crystal (Å)

Atoms	Dist	Trans[a]	Atoms	Dist	Trans[a]
(a) Between Molecule A and Molecule B (to 3.5 Å)					
O(5) · · · O(6′)	3.33		O(5′) · · · H(8)	2.99	
O(6) · · · C(7′)	3.41		O(6) · · · H(7′)	2.52	
O(6′) · · · C(7)	3.33		O(6′) · · · H(7)	2.40	
O(6′) · · · C(5)	3.27		C(5) · · · H(8′)	3.42	
O(6) · · · H(8′)	3.15		C(5′) · · · H(8)	3.42	
O(5) · · · H(8′)	3.13		C(6′) · · · H(7)	3.26	
(b) With Symmetry-Related Molecules (to 3.0 Å)					
O(1) · · · O(6′)	3.00	I	O(7) · · · H(5)	2.73	II
O(7) · · · H(4)	2.96	II	O(2′) · · · H(5′)	2.73	IV
O(4′) · · · H(2′)	2.94	I	O(1) · · · H(7)	2.71	I
O(3′) · · · H(2)	2.93	III	O(7′) · · · H(1′)	2.63	VI
O(1) · · · H(6)	2.92	I	O(1′) · · · H(7′)	2.57	IV
O(1′) · · · H(6′)	2.91	IV	O(7) · · · H(5′)	2.56	V
O(1) · · · H(4′)	2.90	V	O(7′) · · · H(1)	2.49	III
O(1′) · · · H(1′)	2.89	I	O(4) · · · H(3)	2.42	IV
O(5) · · · H(1)	2.83	IV	O(3′) · · · H(3)	2.35	VII
O(5) · · · H(2)	2.79	IV	O(3) · · · H(3′)	2.33	VIII
O(5′) · · · H(2′)	2.79	IV	C(3′) · · · H(7)	2.92	IX
O(2′) · · · H(6′)	2.73	IV	C(3) · · · H(3)	2.91	X
C(1′) · · · H(6′)	2.91	IV	H(7′) · · · H(7′)	2.87	V
C(1) · · · H(6)	2.84	I	H(3) · · · H(3)	2.78	X
C(2′) · · · H(6′)	2.83	IV	H(7) · · · H(3′)	2.59	VI
C(2′) · · · H(6)	2.81	I			

[a] The transformations are as follows: (I) $x, \frac{1}{2} - y, -\frac{1}{2} + z$; (II) $-x, -\frac{1}{2} + y, \frac{1}{2} - z$; (III) $1 - x, -y, 1 - z$; (IV) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (V) $1 - x, 1 - y, 1 - z$; (VI) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (VII) $-1 + x, y, z$; (VIII) $1 + x, y, z$; (IX) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (X) $-x, -y, 1 - z$.

It is possible to reach an adequate description of the electron distribution within the cluster by invoking the "noble gas rule." Ru(1) is assigned the formal oxidation state of +1 (*i.e.*, d^7) and acquires five electrons from the azulene ligand, two electrons each from C(11)-O(1) and C(12)-O(2), and one electron from each of the bonds Ru(1)-Ru(2) and Ru(1)-Ru(3), giving 18 electrons in all. Ru(2) and Ru(3) must each be assigned a formal oxidation state of $-\frac{1}{2}$; each then gains two electrons from a carbon-carbon double bond, one-half electron from the three-center Ru(2)-C(6)-Ru(3) bond, four from terminal carbonyl groups, one from the bridging C(17)-O(7) ligand, and two from Ru-Ru bonds, again resulting in 18 outer electrons for each metal atom. The molecular orbital treatment that might account for the structure in a more satisfactory fashion is, unfortunately, still out of reach.

The $(C_{10}H_8)Ru_3(CO)_7$ molecules are mutually separated by normal van der Waals distances [see Table V]. Shortest contacts of each type are O· · ·H = 2.33, H· · ·H = 2.59, C· · ·H = 2.81, O· · ·O = 3.00, and O· · ·C = 3.27 Å.

Comparison of $(C_{10}H_8)Ru_3(CO)_7$ with $[(CH_3)_3C_{10}H_5]Ru_4(CO)_9$. Side views of these two species are shown in Figure 3. Structurally, the (azulene)$Ru_3(CO)_7$ molecule is derived from (azulene)$Ru_4(CO)_9$ by substituting a bridging carbonyl group for a basal $Ru(CO)_3$ moiety, along with a concomitant anticlockwise (relative to Figure 3) rotation of all ligands. The most important effect of this small rotation is that the azulene ligand in $(C_{10}H_8)Ru_3(CO)_7$ is shifted laterally from right to left relative to that in the substituted (azulene)$Ru_4(CO)_9$ molecule. This results in C(9) and C(10) interacting with Ru(2) and Ru(3) in the tetranuclear species, but no such interaction in the trinuclear molecule. Ruthenium-to-azulene distances are compared in Table VI. The most striking result is, of course, the Ru(2)-C(9) and Ru(3)-C(10) distance, which is 2.925 ± 0.028 Å for $(C_{10}H_8)Ru_3(CO)_7$ and 2.586 ± 0.038 and 2.592 ± 0.014 Å in the two crystalline modifications of $[(CH_3)_3C_{10}H_5]Ru_4(CO)_9$.

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(37) C. Krueger, *Angew. Chem., Int. Ed. Engl.*, **8**, 678 (1969).

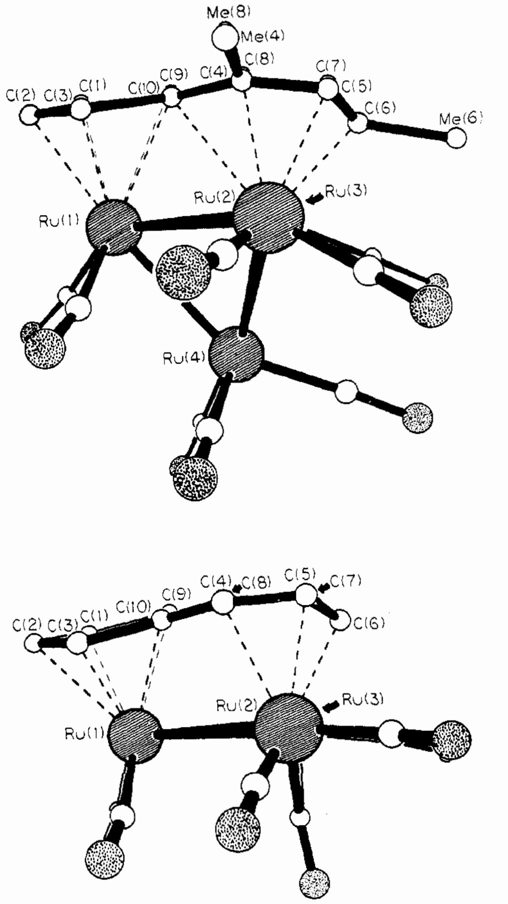

Figure 3. Comparative side views of the $[(CH_3)_3C_{10}H_5]Ru_4(CO)_9$ (top) and the $(C_{10}H_8)Ru_3(CO)_7$ (bottom) molecules. Note the relative lateral displacements of the azulene ligands and the different modes of azulene-to-cluster bonding.

Table VI. Ruthenium-Carbon Distances (Å) in Some Azulene Complexes

Bond	$(C_{10}H_8)Ru_3(CO)_7$	$[(CH_3)_3C_{10}H_5]Ru_4(CO)_9$[a] Triclinic	$[(CH_3)_3C_{10}H_5]Ru_4(CO)_9$[a] Monoclinic
Ru(1)-C(2)	2.307 ± 0.031	2.242 (14)	2.182 (36)
Ru(1)-C(1) Ru(1)-C(3)	2.231 ± 0.050	2.231 ± 0.018	2.224 ± 0.007
Ru(1)-C(9) Ru(1)-C(10)	2.243 ± 0.072	2.342 ± 0.008	2.347 ± 0.021
Ru(2)-C(9) Ru(3)-C(10)	2.925 ± 0.028	2.586 ± 0.038	2.596 ± 0.014
Ru(2)-C(4) Ru(3)-C(8)	2.398 ± 0.046	2.260 ± 0.000	2.263 ± 0.016
Ru(2)-C(5) Ru(3)-C(7)	2.279 ± 0.006	2.198 ± 0.021	2.172 ± 0.015
Ru(2)-C(6) Ru(3)-C(6)	2.472 ± 0.018	2.465 ± 0.034	2.432 ± 0.061

[a] See ref 9.

There is some evidence that $(C_{10}H_8)Ru_3(CO)_7$ may be an intermediate in the formation of $(C_{10}H_8)Ru_4(CO)_9$. Thus the mass spectrum of $C_{10}H_8Ru_3(CO)_7$ shows not one but three fragmentation patterns. One is based on $[C_{10}H_8Ru_4(CO)_9]^+$, the second on $C_{10}H_8Ru_3(CO)_7$, and the third on $[C_{10}H_8Ru_2(CO)_4]^+$. A disproportionation reaction seems to be taking place in the mass spectrometer. Note that the mass spectrum of $[(CH_3)_3C_{10}H_5]Ru_4(CO)_9$ also shows a strong fragmentation pattern based on $[[(CH_3)_3C_{10}H_5]Ru_2(CO)_4]^+$.

The only parallel case of successive aggregation of metal carbonyl fragments on an organic ligand is for the reaction of $Ru_3(CO)_{12}$ with 1,5,9-cyclododecatriene. The intermediate and final products have been isolated and examined by single-crystal X-ray diffraction: they are $HRu_3(CO)_9(C_{12}H_{15})$[34,35] and $(C_{12}H_{16})Ru_4(CO)_{10}$.[36] Ruthenium thus seems to have a so-far unique propensity for forming this kind of cluster, which appears to be favored by flexible cyclic ligands.

Registry No. $(C_{10}H_8)Ru_3(CO)_7$, 11067-30-4.

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