Stereochemically Nonrigid Organometallic Molecules. XXIII. The Crystal and Molecular Structures of (Cyclooctatetraene)tricarbonylruthenium[1,2]

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Abstract: The compound $C_8H_8Ru(CO)_3$, which exhibits fluxional character in solution, has been characterized structurally in its crystalline form by a single-crystal X-ray diffraction study. The crystals are orthorhombic with dimensions $a = 6.576 \pm 0.001$, $b = 12.955 \pm 0.003$, and $c = 11.635 \pm 0.002$ Å and belong to the space group Pnam. The density calculated for $Z = 4$ is 1.80 g cm^{-3}; that measured by flotation is 1.77 ± 0.03 g cm^{-3}. The structure was solved from 622 observed, independent reflections. The positional and anisotropic temperature parameters of one Ru, six C, and two O atoms and the positional and isotropic thermal parameters of four H atoms were refined by full-matrix least squares. The weighted and unweighted discrepancy indices had final values of 3.1 and 2.3%, respectively. The structure is very isomorphous with that of $C_8H_8Fe(CO)_3$, suggesting that it is safe to regard the ruthenium compound as a close structural and dynamical analog of the iron compound. The molecule may be designated as (1,2,3,4-*tetrahapto*cyclooctatetraene)tricarbonylruthenium, which describes the same structure as that which it has in solution. The Ru–CO distances are 1.908 (8) and 1.924 (6) Å. The Ru to ring carbon distances are: Ru–C(1) = Ru–C(4) = 2.265 (6) Å and Ru–C(2) = Ru–C(3) = 2.182 (6) Å. The C–C distances in the bound "butadiene" moiety are: C(1)–C(2) = C(3)–C(4) = 1.443 (8) Å; C(2)–C(3) = 1.394 (12) Å. C–C distances in the free "butadiene" moiety are: C(5)–C(6) = C(7)–C(8) = 1.332 (10) Å; C(6)–C(7) = 1.536 (14) Å. The mean plane of C(1)–C(2)–C(3)–C(4) makes an angle of 136.3° with the mean plane of C(4)–C(5)–C(6)–C(7)–C(8)–C(1). (The numbering scheme just employed is based on the systematic name of the compound used above.)

Of all fluxional organometallic molecules[3] which have been studied thus far, (cyclooctatetraene)tricarbonyliron, $(C_8H_8)Fe(CO)_3$, has provoked the greatest amount of controversy with regard to the detailed molecular structure in solution and the rearrangement pathway.[3] The molecular structure of the crystalline compound was shown by Dickens and Lipscomb[4] to be that which we would designate[5] (1,2,3,4-*tetrahapto*cyclooctatetraene)tricarbonyliron, but definitive structural and dynamical characterization of the substance in solution was made extremely difficult by the rapidity of the intramolecular rearrangement, even at the lowest accessible temperatures (*ca.* −150°).

With the hope that the analogous ruthenium molecule, $(C_8H_8)Ru(CO)_3$, would be essentially similar in its structural and dynamical characteristics but not quite so rapid in its rearrangement, this substance was prepared[6a] and its pmr spectrum studied as a function of temperature.[6b] This hope was entirely fulfilled and it proved possible to establish conclusively the instantaneous structure of the molecule in solution as (1,2,3,4-*tetrahapto*cyclooctatetraene) tricarbonylruthenium and to demonstrate that the rearrangement pathway is a sequence of 1,2 shifts.[6b] While it seems very reasonable to assume that these conclusions would apply also to $(C_8H_8)Fe(CO)_3$, the validity of this assumption may be substantiated by evidence of other close similarities between the two molecules. In order to establish conclusively one important similarity, namely, that the compounds are isostructural in the solid state, a thorough single-crystal X-ray diffraction study of $(C_8H_8)Ru(CO)_3$ has been carried out. That investigation is reported in detail here.

Procedure

A sample of $(C_8H_8)Ru(CO)_3$, prepared as described,[6a] was obtained from Dr. A. Musco. Attempts to grow suitable crystals from heptane solution were occasionally successful. One such crystal, a rectangular parallelipiped, was mounted in a capillary and placed on a General Electric XRD-5 manual diffractometer. The crystal was found to be orthorhombic. Unit cell parameters and the space group were determined directly on the diffractometer. The observed classes of absent reflections were $0kl$, $l = 2n + 1$ and $hk0$, $h + k = 2n + 1$, consistent with the space groups $Pc2_1n$ or Pcmn. These are nonstandard settings for the standard space groups[7] $Pna2_1$ ($C_{2v}{}^9$, no. 30) or Pnam ($D_{2h}{}^{16}$, no. 62), respectively. Determination of unit cell parameters by least-squares refinement of the 2θ values for Cu $K\alpha_1$ (λ 1.54050 Å) and $K\alpha_2$ (λ 1.54434 Å) peaks for 34 reflections gave the values $a = 6.576 \pm 0.001$, $b = 13.955 \pm 0.003$, and $c = 11.635 \pm 0.002$ Å, where the axes have been selected to be consistent with the space groups $Pna2_1$ or Pnam. Comparison of the space group, unit cell parameters, and density (calculated, 1.799 g/cm^3 for $Z = 4$; measured by flotation, 1.77 ± 0.03 g/cm^3) would suggest that $(C_8H_8)Ru(CO)_3$ is isostructural with $(C_8H_8)Fe(CO)_3$.[4]

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[1] Research supported in part by the National Science Foundation (GP-7034X).

[2] Part XXII: F. A. Cotton and T. J. Marks, *J. Amer. Chem. Soc.*, **91**, 3178 (1969).

[3] F. A. Cotton, *Accounts Chem. Res.*, **1**, 257 (1968).

[4] B. Dickens and W. N. Lipscomb, *J. Chem. Phys.*, 37, 2084 (1962).

[5] F. A. Cotton, *J. Amer. Chem. Soc.*, **90**, 6230 (1968).

[6] (a) F. A. Cotton, A. Davison, and A. Musco, *ibid.*, **89**, 6796 (1967); (b) W. K. Bratton, F. A. Cotton, A. Davison, A. Musco, and J. W. Faller, *Proc. Natl. Acad. Sci. U. S.*, **58**, 1324 (1967).

[7] International Tables for X-Ray Crystallography, Kynoch Press, Birmingham, England, 1962: (a) Vol I; (b) Vol III.

A second crystal, approximately 0.04 × 0.03 × 0.008 cm, was selected for collection of intensity data, mounted in a capillary, and placed on a computer-controlled[8] Picker four-circle diffractometer. Niobium-filtered Mo radiation (μ = 14.17 cm^{-1}) was used in preference to Cu radiation (μ = 122.19 cm^{-1}). The moving-crystal, moving-counter technique was employed with a 2θ scan rate of 1°/min and scan range of $(1° + \Delta)$, where Δ is the 2θ separation of Mo Kα_1 and Kα_2 peaks at the 2θ value for the reflection concerned. A take-off angle of 4° was used, and the pulse–height discriminator was set to accept 95% of the Mo Kα radiation when centered on the Kα peak. The crystal-to-source and crystal-to-detector distances were each approximately 24 cm; using a 1.5-mm diameter collimator on both incident and exit beams, with no further restriction on the aperture, there was no evidence for overlapping peaks. Background counts of 10 sec each were measured at the extremes of the 2θ scan. The observed intensities were taken as $A[P - t/20B]$, where A is a correction factor required when attenuators were inserted (for those reflections with counting rates in excess of the linear counting rate of the detector), P is the number of counts during the scan, B is the sum of the background counts, and t is the counting time for the scan in seconds.

Four octants of data were collected (the forms hkl, $hk\bar{l}$ and the center-of-symmetry related $\overline{hk}l$ and $\overline{hkl}$) having $\theta_{\mathrm{Mo\,K}\alpha} \leq 25°$, after which the octants hkl and $\overline{hkl}$ were recollected. Three standard reflections which were measured after each 50 reflections gave evidence of slow but appreciable decreases in intensity (up to ~8%) during this period. Since the decrease during the collection of any one octant was less than ~4%, which was only slightly greater than the estimated time-independent error, ±3%, no correction was made for this effect.

The six equivalent octants collected contained 6751 reflections, of which 3545 were accepted according to the criteria (a) $I > 0$ and (b) $I \geq 3\sigma(I)$. All reflections required to be absent by the symmetry elements of the space groups had been measured and none was accepted under these criteria, confirming the choice of possible space groups. While no statistical studies were carried out, there was very good agreement between the intensities of equivalent reflections; the calculated value for $\sigma(I) = [P + t/20B + (0.045I)^2]^{1/2}$ was nearly always considerably larger than the observed standard deviation of the six equivalent intensity measurements.

The observed intensities were corrected for Lorentz and polarization effects and the values for equivalent sets of reflections were averaged, giving a total of 622 observed independent reflections. The value for $\sigma(F)$ was taken as either the observed standard deviation of the n values used to calculate the average, or $n^{-1/2}$ times the average value of $\sigma(F)$ for the n (usually six) equivalent reflections, whichever was larger. In nearly every case it was the latter.

Solution and Refinement of the Structure. Calculation of a set of structure factors[9] using the atomic positions and anisotropic temperature factors reported[4] for $(C_8H_8)Fe(CO)_3$ confirmed that the ruthenium analog is isostructural and gave a residual, $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, of 0.106. After four cycles of full-matrix least squares refinement[10] using a unit weighting scheme this dropped to 0.049. Absorption corrections, giving calculated transmission factors in the range 0.66 to 0.89, were then made and refinement continued, reducing R_1 to 0.039. Three of the four strongest peaks in the difference Fourier map, having electron densities of 0.4 to 0.5 e/Å^3, were in reasonable positions for hydrogen atoms. A fourth hydrogen peak, density 0.3 e/Å^3, was also apparent. The strongest nonhydrogen peak, 0.5 e/Å^3, was in the vicinity of the ruthenium atom. The hydrogen atoms were assigned thermal parameters of 5.5 Å^2 and a cycle of refinement, including the positional but not the thermal parameters for the hydrogen atoms and all parameters for the nonhydrogen atoms, reduced R_1 to 0.033. Attempts to refine hydrogen temperature parameters gave negative values until the hydrogen scattering factors of Mason and Robertson[11] were used, whereupon reasonable values were obtained.

Reflections having very large structure amplitudes (particularly 002) apparently suffered strong extinction effects. A cycle of refinement which omitted the 17 strongest reflections (in terms of structure amplitudes, not intensities) gave R_1 = 0.020 while no parameter shifted more than 1.3 times its esd. Extinction was therefore neglected and these reflections were included in a final cycle in which all parameters were varied giving R_1 = 0.023, $R_2 = \{\Sigma w[|F_o| - |F_c|]^2/\Sigma w|F_o|^2\}^{1/2}$ = 0.031. The weighting factors, w, for each reflection are given by $w = 4F^2/L\sigma(I)$), where L is the reciprocal Lorentz-polarization correction, and $\sigma(I)$ is calculated according to Doedens and Ibers.[12a] The final stand-

Table I. Final Atomic Coordinates for $(C_8H_8)Ru(CO)_3$[a]

Atom	x	y	z	Equivalent B[b]
Ru	0.76314 (8)	−0.06182 (4)	0.75	2.78
C(5)	0.4889 (13)	−0.1065 (7)	0.75	4.07
O(5)	0.3236 (11)	−0.1261 (6)	0.75	7.69
C(6)	0.8667 (10)	−0.1444 (4)	0.6312 (5)	4.05
O(6)	0.9320 (8)	−0.1928 (3)	0.5625 (4)	6.54
C(1)	0.7360 (9)	0.0583 (4)	0.6200 (5)	4.06
C(2)	0.9160 (8)	0.0675 (4)	0.6901 (5)	3.89
C(3)	0.5554 (11)	0.1170 (5)	0.6133 (6)	4.44
C(4)	0.4433 (11)	0.1654 (4)	0.6890 (6)	4.81
H(1)	0.790 (7)	0.032 (4)	0.583 (4)	4.2 (10)
H(2)	1.051 (9)	0.061 (4)	0.642 (5)	5.7 (13)
H(3)	0.505 (7)	0.117 (4)	0.534 (5)	4.7 (12)
H(4)	0.339 (9)	0.203 (4)	0.663 (4)	4.6 (12)

[a] The numbering scheme, which is the same as that used for $(C_8H_8)Fe(CO)_3$, is shown in Figure 1. Estimated standard deviations (in parentheses) in this and other tables occur in the last significant digit in each case. [b] For hydrogen atoms the isotropic B is listed.

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[8] The Busing and Levy programs for four-circle diffractometers (*Acta Crystallogr.*, 22, 457 (1967)) were used to collect intensities.

[9] The scattering factors and corrections for anomalous scattering for ruthenium are from D. T. Cromer and J. T. Waber, *ibid.*, 18, 104 (1965); D. T. Cromer, *ibid.*, 18, 17 (1965). For the other atoms values were used from ref 7b.

(10) The computer programs used for the solution and refinement of the structure are fully described by A. L. Beauchamp, M. J. Bennett, and F. A. Cotton, *J. Amer. Chem. Soc.*, 90, 6775 (1968).

(11) R. Mason and G. B. Robertson in "Advances in Structure Research by Diffraction Methods," Vol 2, R. Brill and R. Mason, Ed., Wiley-Interscience, New York, N. Y., 1966, p 57.

(12) (a) R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, 6, 204 (1967). The coefficient p in the "ignorance factor," $(pI)^2$, was assigned a value of 0.045 in our work. (b) To procure a copy of this table, order NAPS Document No. 00632 from ASIS National Auxiliary Pubications Service,

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

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ru	164.0 (15)	32.4 (3)	55.2 (4)	−0.6 (9)	0	0
C(5)	218 (25)	38 (5)	101 (9)	−6 (9)	0	0
O(5)	199 (18)	86 (6)	240 (11)	−22 (8)	0	0
C(6)	257 (17)	46 (4)	76 (5)	2 (7)	8 (8)	7 (4)
O(6)	506 (17)	72 (3)	97 (4)	33 (7)	73 (8)	−24 (4)
C(1)	286 (16)	44 (3)	70 (4)	−10 (10)	25 (9)	11 (3)
C(2)	200 (14)	42 (3)	91 (5)	−16 (7)	26 (7)	7 (4)
C(3)	290 (20)	44 (4)	90 (6)	−7 (7)	−48 (10)	18 (4)
C(4)	225 (16)	36 (3)	144 (7)	1 (6)	−40 (9)	12 (4)

[a] These are of the form exp $[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$; standard deviations occurring in the last significant digits are given in parentheses.

Table III. Root Mean Square Amplitudes of Vibration and Their Direction Cosines

Atom	Minor axis	Medium axis	Major axis
Ru	0.179	0.190	0.194
	(0.067, 0.998, 0.000)	(0.998, −0.067, 0.000)	(0.000, 0.000, 1.000)
C(5)	0.191	0.220	0.264
	(0.226, 0.974, 0.000)	(0.974, −0.226, 0.000)	(0.000, 0.000, 1.000)
O(5)	0.203	0.294	0.405
	(0.974, 0.227, 0.000)	(−0.227, 0.974, 0.000)	(0.000, 0.000, 1.000)
C(6)	0.206	0.229	0.243
	(0.039, 0.874, −0.484)	(−0.648, 0.390, 0.653)	(0.760, 0.289, 0.582)
O(6)	0.188	0.297	0.353
	(−0.387, 0.572, 0.723)	(0.150, 0.812, −0.563)	(0.910, 0.109, 0.400)
C(1)	0.182	0.232	0.259
	(0.314, 0.701, −0.640)	(−0.306, 0.713, 0.631)	(0.899, −0.002, 0.438)
C(2)	0.177	0.222	0.259
	(0.664, 0.668, −0.335)	(−0.652, 0.737, 0.177)	(0.366, 0.101, 0.925)
C(3)	0.182	0.224	0.292
	(−0.278, 0.759, −0.589)	(0.711, 0.574, 0.405)	(−0.645, 0.306, 0.700)
C(4)	0.182	0.213	0.323
	(−0.203, 0.960, −0.191)	(0.942, 0.244, 0.228)	(−0.266, 0.134, 0.955)

ard deviation of an observation of unit weight was 1.6, which could be reduced by a value higher than 0.045 for p in the expression for $\sigma(I)$. However, the successful refinement to a very low residual, giving reasonable values for the positional and thermal parameters of the hydrogen atoms, does not suggest that the intensities are less reliable than usual. On the contrary $\sigma(I)$ values, calculated directly by averaging six equivalent measurements for each data point, are consistently lower than those calculated by the Doedens and Ibers formula with $p = 0.045$. We did not, therefore, undertake to manipulate the statistical reliability calculations any further.

A table of the calculated and observed structure amplitudes has been deposited with the ASIS National Auxiliary Publications Service.[12b] Final atomic fractional coordinates and equivalent isotropic temperature factors are given in Table I. Anisotropic temperature factors for nonhydrogen atoms are given in Table II. Root-mean-square vibrational amplitudes and their direction cosines are listed in Table III. The intramolecular dimensions are presented in Table IV. Figure 1 shows the structure schematically and presents the atom numbering scheme, which has been kept the same as the one used by Dickens and Lipscomb for $C_8H_8Fe(CO)_3$. Figure 2 presents two perspective views of the molecule.

Discussion

The main result of this study is that crystalline $C_8H_8Ru(CO)_3$ is extremely similar in both its molecular and crystal structures to $C_8H_8Fe(CO)_3$. This, then, leads to the main conclusion, which is that the assumption, made elsewhere,[6b] that the two molecules have analogous structural and dynamical properties in solution is a reasonable one. Thus, from the fluxional behavior of $C_8H_8Ru(CO)_3$, which is relatively easy to observe and interpret, we may safely make inferences as to the nature of the rearrangement pathway for $C_8H_8Fe(CO)_3$, whose fluxional behavior is, on the contrary, not readily observed or interpreted in a complete way due to its greater rate of rearrangement.

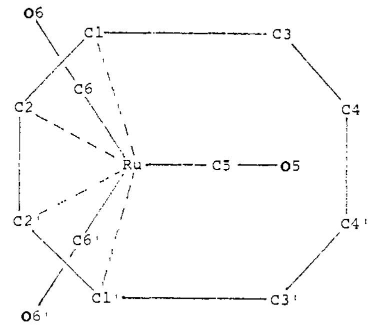

Figure 1. A schematic representation of the structure indicating the atom-numbering scheme.

The configuration of the molecule is seen in Figure 2. It possesses a plane of symmetry, *viz.*, the (001) mirror of the crystallographic space group. The $Ru(CO)_3$ group is bound to a sequence of four carbon atoms. The arrangement of double bonds in the remaining se-

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Table IV. Molecular Dimensions of $C_8H_8Ru(CO)_3$, with Some Dimensions of $C_8H_8Fe(CO)_3$ for Comparison[a]

A. Bond Lengths, A

$C_8H_8Ru(CO)_3$		$C_8H_8Fe(CO)_3$[b]
Ru-C(5)	1.908 (8)	
Ru-C(6)	1.924 (6)	
Ru-C(1)	2.265 (6)	2.18 (1)
Ru-C(2)	2.182 (6)	2.05 (1)
C(5)-O(5)	1.121 (11)	1.12 (2)
C(6)-O(6)	1.132 (8)	1.13 (1)
C(1)-C(2)	1.443 (8)	1.42 (1)
C(1)-C(3)	1.445 (9)	1.45 (2)
C(2)-C(2′)	1.394 (12)	1.42 (2)
C(3)-C(4)	1.332 (10)	1.34 (2)
C(4)-C(4′)	1.536 (14)	1.49 (3)
H(1)-C(1)	1.08 (5)	
H(2)-C(2)	1.05 (6)	
H(3)-C(3)	0.98 (6)	
H(4)-C(4)	0.91 (6)	

B. Bond Angles, Deg

$C_8H_8Ru(CO)_3$		$C_8H_8Ru(CO)_3$		$C_8H_8Fe(CO)_3$
C(1)-Ru-C(1′)	83.8 (3)	C(2′)-C(2)-C(1)	124.4 (6)	124.6 (5)
C(1)-Ru-C(2)	37.8 (3)	C(2)-C(1)-C(3)	130.8 (5)	132.4 (10)
C(2)-Ru-C(2′)	37.3 (3)	C(1)-C(3)-C(4)	134.9 (6)	133.2 (12)
C(1)-Ru-C(5)	99.6 (3)	C(3)-C(4)-C(4′)	131.4 (8)	131.8 (17)
C(1)-Ru-C(6)	89.5 (2)	H(1)-C(1)-C(2)	104 (3)	
C(1)-Ru-C(6′)	162.0 (2)	H(1)-C(1)-C(3)	115 (3)	
C(2)-Ru-C(5)	134.9 (3)	H(2)-C(2)-C(2′)	122 (3)	
C(2)-Ru-C(6)	95.9 (2)	H(2)-C(2)-C(1)	112 (3)	
C(2)-Ru-C(6′)	124.2 (2)	H(3)-C(3)-C(1)	109 (4)	
C(5)-Ru-C(6)	98.0 (2)	H(3)-C(3)-C(4)	116 (3)	
C(6)-Ru-C(6′)	91.9 (4)	H(4)-C(4)-C(3)	119 (4)	
Ru-C(5)-O(5)	175.0 (4)	H(4)-C(4)-C(4′)	109 (4)	
Ru-C(6)-O(6)	178.4 (6)			

[a] Estimated standard deviations occurring in the last quoted digit of each parameter are given in parentheses. [b] Taken from ref 4.

quence of four carbon atoms which are not bound to the Ru atom is unambiguous from the carbon to carbon distances and allows the adoption of a unique numbering scheme from which the systematic name[5] (1,2,3,4-*tetrahapto*cyclooctatetraene)tricarbonylruthenium is derived. It is also clearly evident from Figure 2 that in this molecule the C_8H_8 moiety defines two planes, one containing the four bound carbon atoms and the other the two outermost bound atoms together with the sequence of four free carbon atoms lying between them. This is exactly the kind of arrangement found in the iron analog and, as shown by Dickens and Lipscomb,[4] it permits appreciable overlap between the two π systems. In the iron compound the dihedral angle is 137.5 ± 0.5° while in $C_8H_8Ru(CO)_3$ it is 136.3 ± 0.3°.

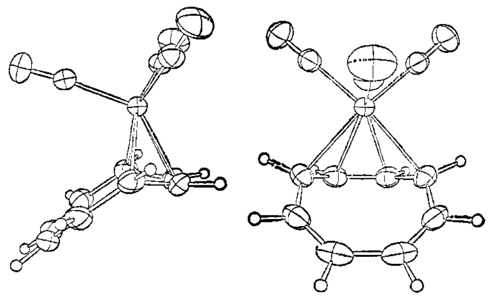

Figure 2. Two perspective views of the molecule. Atoms other than hydrogen are represented by their thermal vibration ellipsoids. Right: A view along the *a* axis, in which the mirror plane is vertical and perpendicular to the plane of the paper. Left: A view along the *c* axis, *i.e.*, perpendicular to the mirror plane.

Because of the slightly smaller standard deviations of carbon to carbon distances in this work (0.008 to 0.014 Å) as compared to those in the study of $C_8H_8Fe(CO)_3$ (0.01 to 0.03 Å), certain aspects of the bonding may be examined a little more closely. The C═C and C—C distances in the free butadiene moiety are not significantly (in a statistical sense) different between the two molecules. However, the length of the central C-C "single" bond distance here is 1.536 (14) Å which differs from the usual central C-C distance[13] of a *cis*-1,3-butadiene group (1.46–1.47 Å) by an amount which is 4–5 times the estimated standard deviation. The exceptional length of the central bond here thus seems very likely to be real.

If we assume that the carbon atom C(4) employs a coplanar set of orbitals for σ bond formation[14] the length of the C(4)-C(4′) bond may perhaps be accounted for in terms of a grossly uneven apportioning of s and p character among the three σ orbitals which must be constructed on C(4), in terms of an appreciably bent C(4)-C(4′) bond, or both. At any rate, the very large C(3)-C(4)-C(4′) angle (131.4°) betokens some anomalous character in the bonds formed by C(4).

With respect to the mode of interaction of the bound "butadiene" residue with the metal atom, the results for the ruthenium compound point more strongly to predominance of the "octahedral" model over the "seven-coordinate" model (to follow the nomenclature of

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(13) *Cf.* "Tables of Interatomic Distances and Configuration in Molecules and Ions, Supplement," Special Publication No. 18, The Chemical Society, London, 1965, p S15s.

(14) This assumption is reasonable and not inconsistent with the observed position of the hydrogen atom, which is such that the sum of the three angles C(3)-C(4)-C(4′), C(3)-C(4)-H(4), and C(4′)-C(4)-H(4) equals 359 ± 9°.

Dickens and Lipscomb) than was the case in the iron compound. For the latter, the C(1)–C(2) and C(2)–C(2′) distances were each 1.42 Å with esd's of 0.01 and 0.02 Å, respectively, whereas for the "octahedral" model, in which the donors (in addition to the three CO groups) are C(1), C(1′), and the C(2)–C(2′) π electrons, a shorter C(2)–C(2′) distance would be expected. In the present case the C(2)–C(2′) bond is 0.05 Å shorter than the C(1)–C(2) bond, with the sum of their esd's being 0.02 Å. Dickens and Lipscomb's conclusion that the "true" picture of the bonding lies between the "octahedral" and "seven-coordinate" extremes, probably nearer the former, is buttressed by the present results.

The structures of two other compounds (both also fluxional) containing cyclooctatetraene bound to ruthenium atoms have been reported.[15,16] While extensive comparisons are not possible due to the gross, qualitative differences in the several structures, certain explicit comparisons of similar structural elements are appropriate. The mean length of the Ru–CO bonds in the present case, 1.916 ± 0.007 Å, is very similar to the average value for $C_8H_8Ru_2(CO)_6$ (1.89 ± 0.02 Å). This is not expected since the ratios of olefin ligand atoms (6) to Ru atoms (2) to CO groups (6) in the latter, 3:1:3, is quite similar to the corresponding ratios, 4:1:3 in $C_8H_8Ru(CO)_3$. The CO groups in the two compounds thus engage in quite similar amounts of π bonding to Ru. In $(C_8H_8)_2Ru_3(CO)_4$, on the other hand, the ratio of olefin ligand atoms to Ru atoms is very high, 16:3, while the ratio of Ru atoms to CO groups is also quite high, 3:4, in comparison to the two previous cases. Because olefin ligands are not nearly as effective in back accepting electrons from the metal atoms as are CO groups,[17] we should expect the four CO groups in $(C_8H_8)_2Ru_3(CO)_4$ to be much more heavily engaged in π bonding to Ru atoms than are the CO groups in the other two compounds and, therefore, that the Ru–CO distances would be appreciably shorter. This is indeed the case; the mean Ru–CO distance in $(C_8H_8)_2Ru_3(CO)_4$ is 1.81 ± 0.02Å, shorter by approximately 0.1 Å, in a range where bond order is a relatively sensitive function of bond distance.[18]

In each of the two compounds just discussed, the molecular symmetry is such that the *n* CO groups give rise to *n* nondegenerate, infrared-active CO stretching fundamentals. Under such circumstances a satisfactory index of the relative mean strengths of the CO bonds is afforded by the mean of the several CO stretching frequencies in each of the compounds. For $C_8H_8Ru(CO)_3$ and $C_8H_8Ru_2(CO)_6$, which ought to have very similar Ru–C bond orders, and thus very similar C–O bond strengths, these mean frequencies are 2025 and 2018 cm^{-1}, respectively. For $C_8H_8Ru_3(CO)_4$, in which considerably stronger Ru–C bonds are indicated, the C–O bonds should then be considerably weaker. In complete accord with this, the mean CO stretching frequency for this compound is 1976 cm^{-1}, that is, some 46 cm^{-1} less than the average of those for the other two compounds.

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