decomposition to III and frustrates attempts to observe possible fluxional behavior at elevated temperatures.

III. $C_8H_8Ru_2(CO)_5$. This orange crystalline solid (mp ~160° dec) can be isolated from the reaction mixture in virtually pure form as a solid essentially insoluble in heptane at room temperature. It can also be made by thermal decomposition of II. The infrared spectrum (CS_2 solution) has four terminal and one bridging CO stretching bands (2058 vw, 2035 vs, 2011 vs, 1968 vs, 1813 m cm^{-1}), and the nmr spectrum at $-35°$ in CS_2 consists of a single line at τ 5.3. Thus, the compound is evidently fluxional and presumably isostructural with its iron cyclooctatetraene[2b,12] and 1,3,5,7-tetramethylcyclooctatetraene[3b,13] analogs.

IV. $(C_8H_8)_2Ru_3(CO)_4$. This complex can be produced exclusively by the reaction of C_8H_8 and $Ru_3(CO)_{12}$ in refluxing octane. It forms lustrous red, air-stable crystals (decomposing at 165–170°) and is sparingly soluble in organic solvents. The nmr spectrum consists of one sharp line (τ 6.26 in $CDCl_3$, 35°), and the infrared spectrum has four CO stretching bands (2032 vw, 1996 vs, 1956 m, 1920 vs cm^{-1}). The mass spectrum is complex but the correct parent-ion multiplet and a fragmentation scheme which involves stepwise removal of CO from the cluster is evident from the appearance of both singly charged ions $(C_8H_8)_2Ru_3(CO)_n^+$, $n = 0$–4, and doubly charged ions $(C_8H_8)_2Ru_3(CO)_n^{2+}$, $n = 0$–3.

Clearly IV is a compound of unusual interest as it is simultaneously a metal atom cluster compound and a fluxional molecule. By formal electron counting it can be regarded as a derivative of $Ru_3(CO)_{12}$ in which eight electron pairs formerly supplied by CO groups are now provided by the π systems of two COT molecules. The fluxional behavior implies retention of monocyclic C_8H_8 moieties. A number of plausible structures may be suggested on the evidence at hand. Speculation is unnecessary, however, as the structure has been determined by X-ray crystallography.[14,15]

(11a) Note Added in Proof. The crystal structure has now been solved and is almost completely refined ($R \approx 8\%$). The molecular structure is *not* as postulated by Keller, Emerson, and Pettit[2b] for the iron analog. The Ru–Ru line is *nearly* perpendicular to the direction suggested by these authors for the Fe–Fe line in their compound III. As it occurs in the crystal the $C_8H_8Ru_2(CO)_6$ molecule has no symmetry plane at all. Evidently in solution it has either rearranged to a more symmetrical structure which does have a symmetry plane dividing the eight protons into four sets of two or the molecule is fluxional with the Ru–Ru axis swinging rapidly back and forth so as to give *time-average* mirror symmetry. Studies in progress may lead to a decision between these two explanations.

(12) E. B. Fleischer, A. L. Stone, R. K. B. Dewar, J. E. Wright, C. E. Keller, and R. Pettit, *J. Am. Chem. Soc.*, **88**, 3158 (1966).

(13) F. A. Cotton and M. D. LaPrade, *ibid.*, in press.

(14) M. J. Bennett, F. A. Cotton, and P. Legzdins, *ibid.*, **89**, 6797 (1967).

(15) Support of this research by National Science Foundation Grants GP 7034X and GP 6672 is gratefully acknowledged. We also thank the Badische Anilin- und Soda-Fabrik for a gift of cyclooctatetraene.

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Stereochemically Nonrigid Organometallic Molecules. X. The Structure of Bis(cyclooctatetraene)triruthenium Tetracarbonyl, a Dissymmetric Metal Atom Cluster Compound Which Is Also a Fluxional Organometallic Molecule[1]

Sir:

As reported elsewhere,[1] the reaction of $Ru_3(CO)_{12}$ with cyclooctatetraene (COT) in refluxing octane gives as the principal product a red crystalline substance which is shown by elemental analysis and mass spectrum to be $C_{16}H_{16}Ru_3(CO)_4$. The proton nmr spectrum at 25° consists of one sharp peak, virtually proving that this is another[2] fluxional metal carbonyl derivative of cyclooctatetraene. It seemed clearly of interest to know in detail the structure of this molecule. In this note we report the structure as determined by single-crystal X-ray methods, refined to convergence by least squares using isotropic temperature parameters for all atoms except Ru. We intend to collect additional data to permit further refinement. Upon completion of that work a full report will be published.

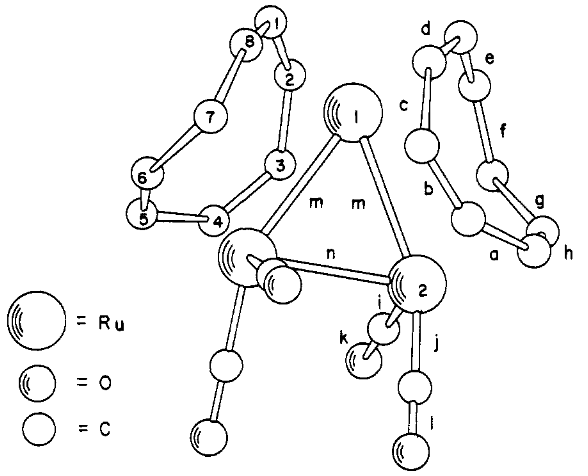

Figure 1. The molecule as seen projected on the *ab* plane.

The crystals are orthorhombic, $P2_12_12_1$, with unit cell dimensions $a = 9.73$ A, $b = 12.59$ A, $c = 15.26$ A; density, calculated for $Z = 4$, 2.21 g cm^{-3} (measured, 2.18 ± 0.05 g cm^{-3}). The 1060 statistically reliable reflections lying within a sphere in reciprocal space corresponding to 1-A interplanar spacings were collected using Mo Kα radiation and an automated General Electric counterdiffractometer. The structure was solved by the usual sequence of Patterson and electron density maps, and refined to a conventional residual of 0.042. The molecule is dissymmetric; by taking into account anomalous dispersion by the ruthenium atoms, the correct enantiomorph has been selected for the crystal studied.

Figure 1 shows the (001) projection of the molecule, and Table I gives some important bond lengths. Crystallographically the molecule is asymmetric, but it has approximately C_2 symmetry, the twofold axis bisecting the Ru(2)–Ru(2)′ line and passing through Ru(1). The bond lengths in Table I are all averages for the two bonds which would be rigorously equivalent under strict C_2 symmetry.

The structure is derived from that of $Ru_3(CO)_{12}$, with π-electron density of the COT rings replacing that of eight CO groups. The $Ru_3(CO)_{12}$ molecule[3] is isostructural with $Os_3(CO)_{12}$[4] with Ru–Ru distances of 2.855, 2.844, and 2.851 A, averaging to 2.85 A. The average of the Ru–Ru distances in the present case,

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(1) Part IX: F. A. Cotton, A. Davison, and A. Musco, *J. Am. Chem. Soc.*, **89**, 6796 (1967).

(2) (a) T. A. Manuel and F. G. A. Stone, *ibid.*, **82**, 366 (1960); (b) C. E. Keller, G. F. Emerson, and R. Pettit, *ibid.*, **87**, 1388 (1965); (c) W. K. Bratton, F. A. Cotton, A. Davison, J. W. Faller, and A. Musco, *Proc. Natl. Acad. Sci. U. S.*, **58**, 1324 (1967).

(3) E. R. Corey and L. F. Dahl, submitted for publication.

(4) E. R. Corey and L. F. Dahl, *Inorg. Chem.*, **1**, 521 (1962).

Table I. Bond Lengths in Angstroms[a]

a	1.38	i	1.81	Ru(1)–C(1)	2.16
b	1.46	j	1.81	Ru(1)–C(2)	2.18
c	1.42	h	1.19	Ru(1)–C(8)	2.16
d	1.44	l	1.19	Ru(1)–C(3)	2.36
e	1.38			Ru(1)–C(7)	2.58
f	1.47	m	2.947	Ru(2)–C(5)	2.21
g	1.46	m′	2.928	Ru(2)–C(4)	2.30
h	1.42	n	2.782	Ru(2)–C(6)	2.17
				Ru(2)–C(3)	2.92
				Ru(2)–C(7)	2.42

[a] Standard deviations are 0.002 A for Ru–Ru, 0.02 A for Ru–C, and 0.03 A for C–C and C–O bonds.

2.89 A, is significantly larger and the difference between the mean Ru(1)–Ru(2) distance, 2.94 A, and the Ru(2)–Ru(2)′ distance, 2.78 A, is notable. Both these differences may be attributed to an inferior ability of cyclooctatetraene in comparison to CO to remove π antibonding electrons from the metal atom cluster.

The mode of attachment of the rings is essentially the same as that in $(C_8H_8)Fe_2(CO)_5$[5] and (1,3,5,7-tetramethylcyclooctatetraene)$Fe_2(CO)_5$,[6] except for some distortions due to intramolecular repulsions. Thus, of the twelve short Ru–C distances, corresponding to π-allyl to metal bonding, all but the two of the Ru(2)–C(4) type are in the range 2.16–2.21 A, while Ru(2)–C(4) is 2.30 A. Again, of the eight long Ru–C distances, corresponding to the multicenter fractional bonding (to C(3) and C(7)), six are in the range 2.34–2.60 A, while the two of type Ru(2)–C(3) are 2.90 and 2.94 A. Both of these distortions arise from repulsion between the CO group on one Ru(2) atom and the C(3) and C(4) atoms of the ring on the other.

Since $C_8H_8Fe_2(CO)_5$ and its 1,3,5,7-tetramethyl analog are both fluxional molecules,[7,8] it is not surprising that in $(C_8H_8)_2Ru_3(CO)_4$, where there is similar metal–ring bonding, fluxional behavior is observed. It is interesting that this unanticipated type of bonding between two metal atoms and a C_8H_8 ring has now been found in three molecules. It may be noted that there are two other molecules, $C_8H_8Ru_3(CO)_8$ and $(C_8H_8)_3Ru_3$, which might exist in view of the stability of $(C_8H_8)_2Ru_3(CO)_4$; these molecules are being sought by us.

This molecule appears to be the first fluxional molecule in which there are two "independent" rings capable of movement. It raises the question of whether the two rings can move entirely independently or whether the two movements must be correlated.

Finally, the reported structure accounts for the characteristic infrared spectrum in the CO stretching region. In C_2 symmetry four infrared-active normal modes are to be expected, with the one consisting mainly of inphase stretching of the two CO groups approximately perpendicular to the Ru_3 plane being very weak.[9]

(5) E. B. Fleischer, A. L. Stone R. B. K. Dewar, J. D. Wright, C. E. Keller, and R. Pettit, *J. Am. Chem. Soc.*, 88, 3158 (1966).

(6) F. A. Cotton and M. D. LaPrade, *ibid.*, in press.

(7) C. E. Keller, G. F. Emerson, and R. Pettit, *ibid.*, 87, 1388 (1965).

(8) F. A. Cotton and A. Musco, *ibid.*, in press.

(9) This work was supported by the National Science Foundation under Grant No. GP 7034X and by the Petroleum Research Fund administered by the American Chemical Society.

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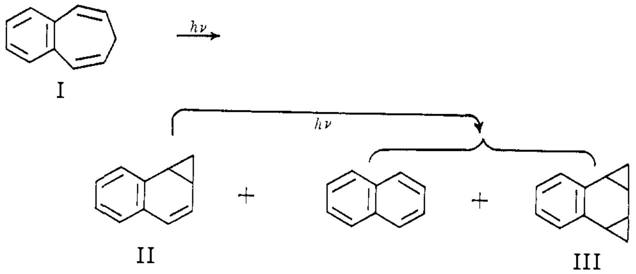
The Photochemical Reorganization of 3,4-Benzotropilidene[1]

Sir:

Our interest in the photochemical behavior of *o*-divinylbenzene[2] led us to examine the photochemistry of 3,4-benzotropilidene (I).[3] Irradiation (100-w G.E. mercury lamp, H100-A4/T; Pyrex filter) of 0.02–0.2% solutions of I in ether led, in rather good yield (70–80%), to benzonorcaradiene (II). Prolonged irradiation produced naphthalene and bismethanonaphthalene (III). The benzonorcaradiene (II) was identified by spectral comparison with authentic material synthesized by the method of Doering,[5] and the naphthalene by comparison of its spectra to those of authentic material. The bismethanonaphthalene (III) was shown to be present by comparing its retention time on three gas chromatography columns with the retention time of authentic material[6] prepared by the reaction of II with methylene iodide and zinc–copper couple.



I

II

III

The mechanism for the conversion of II to naphthalene and III is best rationalized by assuming a photolytic cleavage of II into naphthalene and methylene, for which there is much analogy.[7] This hypothesis was borne out by a trapping experiment in which photolysis of II in cyclohexene gave norcarane and naphthalene.

The mechanism of the photoreorganization was studied by first synthesizing 7,7-dideuterio-3,4-benzotropilidene (IV) by the route shown in Scheme I. Product IV was shown by nmr analysis to contain about 80–83% of two deuterons in the 7 position. It also showed an AB pattern (J = 10 Hz) for the vinyl protons at τ 3.5 and 4.4 ppm.

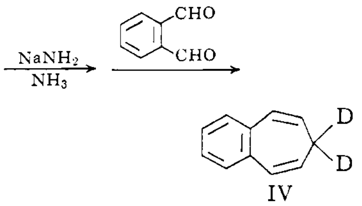
In order to locate the deuterons in photoproduct II

Scheme I

$$CH_2(COOEt)_2 \xrightarrow[\text{Base}]{D_2O,\ THF} CD_2(COOEt)_2 \xrightarrow{LiAlH_4}$$

$$CD_2(CH_2OH)_2 \xrightarrow[H_2SO_4]{HBr} CD_2(CH_2Br)_2 \xrightarrow{Ph_3P}$$

$$\{CD_2(CH_2PPh_3)_2\}^{+2}\ 2Br^- \xrightarrow[NH_3]{NaNH_2}$$



IV

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[1] Presented in part at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, Abstract S25.

[2] M. Pomerantz, *J. Am. Chem. Soc.*, 89, 694 (1967).

[3] 3,4-Benzotropilidene was prepared by the method of Wittig.[4]

[4] G. Wittig, H. Eggers, and P. Duffner, *Ann.*, 619, 10 (1958).

[5] W. von E. Doering and M. J. Goldstein, *Tetrahedron*, 5, 53 (1959).

[6] E. Müller, H. Fricke, and H. Kessler, *Tetrahedron Letters*, 1525 (1964).

[7] See, *e.g.*, D. B. Richardson, L. R. Darrett, J. M. Martin, Jr., W. E. Putnam, S. C. Slaymaker, and I. Dvoretsky, *J. Am. Chem. Soc.*, 87, 2763 (1965).