A study is in progress[15] to define more completely the scope and breadth of these reactions.

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[15] Nitriles other than *t*-nitriles that have been found to undergo this reaction as well as the analytical procedure for the *t*-nitriles will soon be published.

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Stereochemically Nonrigid Organometallic Molecules. IX.[1] Some Fluxional and Some Nonfluxional Compounds Derived from Cyclooctatetraene and Ruthenium Carbonyl

Sir:

Previous investigations of the reactions of the iron carbonyls with cyclooctatetraene (COT)[2] and its derivatives[3] have provided many interesting compounds, not all of which have been fully characterized as to structure and the nature of the fluxional processes operative in some of them. We have investigated the reaction of $Ru_3(CO)_{12}$ with C_8H_8 hoping to obtain analogs to some of the iron compounds which might lend themselves more readily to answering the major questions regarding structure and fluxional behavior.

The general preparative procedure for all compounds reported here is to reflux a hydrocarbon (generally heptane or octane) solution of $Ru_3(CO)_{12}$ and C_8H_8 and to separate and purify the products by suitable combinations of chromatography, sublimation, and recrystallization. Thus the following major[4,5] products have been isolated and characterized.[6]

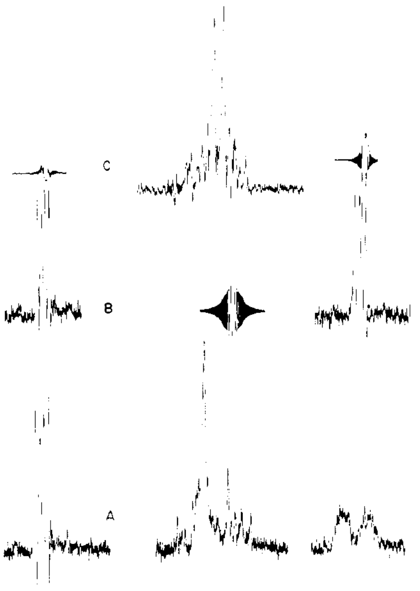

Figure 1. (A) The nmr spectrum of III (C_6H_{12} solution, 35°). Line positions and intensities are τ 4.19 (2), ~5.7 (4), 7.37 (2). (B) The spectrum when the central multiplet is irradiated. (C) The spectrum when the low- and high-field resonances are simultaneously irradiated.

I. $(C_8H_8)Ru(CO)_3$. The isolation of this substance has already been reported by ourselves[7] and others.[8] A thorough study of its nmr spectrum down to $-147°$ coupled with the use of computer-simulated spectra for various models of the intramolecular rearrangement process responsible for its fluxional behavior have enabled us to specify the instantaneous configuration (1,3-diene to metal bonding) and the mechanism of rearrangement (1,2 shifts) with great certainty.[7] The orange crystalline $C_8H_8Ru(CO)_3$ (mp 75–76°) can be readily sublimed at 47° (0.05 mm). A determination of the unit cell and space group suggests that it is isostructural with $(C_8H_8)Fe(CO)_3$.[5,9] The mass spectrum is consistent with the assigned structure, and the ir spectrum is similar to that of $C_8H_8Fe(CO)_3$ (strong peaks in heptane at 2070, 2010, and 1996 cm^{-1}).

II. $(C_8H_8)Ru_2(CO)_6$. The molecular formula of this yellow crystalline substance (mp 90–95° dec) has been confirmed by X-ray crystallographic data.[10] The infrared spectrum in the CO stretching region is complex (in heptane, 2078, 2048, 2011, 2006 sh, 1988, and 1978 sh cm^{-1}); there are no bridging peaks. The nmr spectrum is shown in Figure 1a and is very similar to that reported by Pettit[2b] for a compound $(C_8H_8)_2Fe_2(CO)_6$ (designated in ref 2b as compound III) which suggests that the two compounds are isostructural. The analysis of this complex spectrum is considerably simplified by spin decoupling. Irradiation of the central multiplet (Figure 1b) removes the strong coupling of these protons to the high-field resonance which collapses to one-half of an A_2X_2 spectrum,[11] in which there is appreciable A–X coupling. Simultaneous irradiation of the high- and low-field multiplets (Figure 1c) removes their coupling to the protons of the central multiplet which simplifies to a typical A_2B_2 spectrum.[11]

These data indicate a structure in which the $Ru_2(CO)_6$ moiety is bonded to a sequence of carbon atoms in the carbocyclic ring (which has a free olefinic group, the protons of which give a resonance at τ 4.19) so as to permit a mirror plane which divides the eight ring protons into four equivalent sets ($A_2B_2C_2X_2$). The resonance of the protons at the extremities of the metal-bonded fragment occur at τ 7.37, while those of the central protons account for complex resonance at τ ~5.7. Details of the geometry and bonding will be presented on completion of the X-ray study now in progress.[11a] Heating the complex in solution causes

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[1] Part VIII: F. A. Cotton, A. Musco, and G. Yagupsky, *J. Am. Chem. Soc.*, **89**, 6136 (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).

[3] (a) F. A. L. Anet, *ibid.*, **89**, 2491 (1967); (b) F. A. Cotton and A. Musco, *ibid.*, in press.

[4] At least two other compounds have been isolated in trace amounts. One appears to be the $(C_8H_8)Ru_2(CO)_6$ analog of the *trans*-$(C_8H_8)Fe_2(CO)_6$ compound[2a,5] (ir: 2067, 2000, 1992 (sh) cm^{-1}, all strong, heptane solution).

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

[6] All compounds had satisfactory C and H analyses; all ir frequencies are ±5 cm^{-1}.

[7] W. K. Bratton, F. A. Cotton A. Davison, A. Musco, and J. W. Faller, *Proc. Natl. Acad. Sci. U. S.*, **58**, 1324 (1967).

[8] M. I. Bruce, M. Cooke, M. Green, and F. G. A. Stone, *Chem. Commun.*, 523 (1967).

[9] We thank Dr. Roger Eiss for crystallographic data on $C_8H_8Ru(CO)_3$.

[10] We are indebted to Mr. W. T. Edwards for this determination.

[11] D. M. Grant, R. C. Hirst, and H. S. Gutowsky, *J. Chem. Phys.*, **38**, 470 (1963).

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.

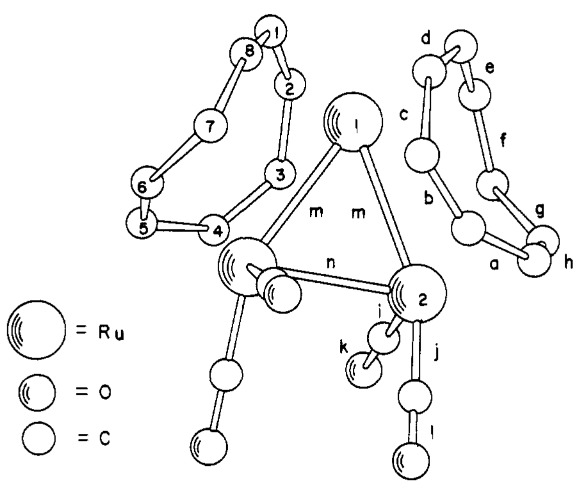

Figure 1. The molecule as seen projected on the *ab* plane.

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).