Stereochemically Nonrigid Organometallic Molecules. XXIV. Preparation and Nuclear Magnetic Resonance Study of Some Fluxional Cyclooctatetraene Derivatives of Ruthenium Carbonyl[1a,2]

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Abstract: The preparation and characterization of four fluxional organometallic molecules derived from the reaction of $Ru_3(CO)_{12}$ with cyclooctatetraene are reported. The molecules are $C_8H_8Ru(CO)_3$, $C_8H_8Ru_2(CO)_6$, $C_8H_8Ru_2(CO)_5$, and $(C_8H_8)_2Ru_3(CO)_4$. The limiting low-temperature pmr spectrum of $C_8H_8Ru(CO)_3$ has been observed at about $-140°$ and shows that the instantaneous structure is of the 1,2,3,4-*tetrahapto* type. The qualitative nature of the line-shape changes at intermediate temperatures shows that rearrangement takes place mainly by 1,2 shifts. Detailed analysis using computer-simulated spectra confirms this and enables us to set an upper limit of about 30% on the occurrence of 1,3 or other shift processes. The Arrhenius activation energy is 9.4 ± 0.5 kcal/mol. For $C_8H_8Ru_2(CO)_6$ the pmr spectrum has been recorded down to $-120°$. The limiting low-temperature spectrum confirms that the dissymmetric structure previously observed (Cotton and Edwards) in the crystalline substance persists as the instantaneous structure in solution. Spin-decoupling experiments on the room-temperature pmr spectrum show that a time-average mirror plane exists. These results, along with the changes observed in the spectra at intermediate temperatures, are interpreted in terms of an oscillation of the $(OC)_3Ru-Ru(CO)_3$ group relative to the C_8H_8 ring such that the enantiomers are rapidly interconverted at room temperature. $C_8H_8Ru_2(CO)_6$ readily loses CO at higher temperatures giving $C_8H_8Ru_2(CO)_5$. This is a fluxional molecule (single, sharp proton line at 25°) presumably isostructural with $C_8H_8Fe_2(CO)_5$. Because of its very low solubility at lower temperatures efforts to observe a limiting low-temperature spectrum have failed. The preparation and characterization of $(C_8H_8)_2Ru_3(CO)_4$ are fully described. This fluxional molecule has also failed to yield a low-temperature spectrum because of a severe solubility problem.

In recent years there have been many investigations of compounds containing metal carbonyl moieties, $M_m(CO)_c$, either mono- or polynuclear, bound to cyclooctatetraene[2-20] or substituted cyclooctatetraenes.[21-26]

Of particular interest are those containing iron[3-12,23-26] or ruthenium.[2,13-17] For several of the iron compounds there have remained unresolved questions regarding their structures and/or the nature of the fluxional processes[27] which occur in solution. Two of the chief problems have been the following.

(1) *The instantaneous structure of $C_8H_8Fe(CO)_3$ in solution and the nature of the intramolecular rearrangement which accounts for the single line nmr spectrum at higher temperatures.* Although the most recently published studies[6,26] have lent considerable support to the view that the instantaneous structure in solution is the same as the molecular structure which occurs in crystal,[9] namely, the 1,2,3,4-*tetrahapto*cyclooctatetraene[28] structure, definitive proof for $C_8H_8Fe(CO)_3$ as such has so far eluded all investigators. Further, even granting the correctness of this structure in solution, there have been no experimental data to show what is the principal pathway of intramolecular rearrangement.

(2) *The structure of that one of the isomeric $C_8H_8Fe_2(CO)_6$ molecules for which Keller, Emerson, and Pettit proposed the structure shown schematically as I.* As reported in an earlier paper,[17] the ruthenium analog to this compound does not have structure I and it is therefore doubtful that the iron compound has such a structure. However, the structure found for the $C_8H_8Ru_2(CO)_6$ molecule in the crystal cannot account for the

(1) (a) Research Supported by the National Science Foundation under Grants GP-7034X and GP-6672; (b) Fellow of the Alfred P. Sloan Foundation; (c) National Science Foundation Predoctoral Fellow, 1966–1969

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type of nmr spectrum which has been observed for both $C_8H_8Fe_2(CO)_6$[7] and $C_8H_8Ru_2(CO)_6$[15] in solution.

Since the various $C_8H_8Fe_x(CO)_y$ compounds seemed generally to be difficult subjects for study owing to their relative instability (especially under irradiation by X-rays, in some instances) or because of the rapidity of the fluxional processes which makes the recording of limiting low-temperature spectra difficult or impossible, it was hoped that their ruthenium analogs might be more amenable to study. Therefore, a program of preparation, X-ray structural study, and nmr study of compounds derived from the reactions of C_8H_8 with $Ru_3(CO)_{12}$ was undertaken. Analogs to nearly all the reported $C_8H_8Fe_x(CO)_y$ compounds have been obtained, as reported in an earlier note.[15] Nmr study of C_8H_8-$Ru(CO)_3$ has revealed the instantaneous structure and the pathway of fluxional rearrangement for this molecule, as also reported briefly in an earlier communication.[14] The crystal structure of $C_8H_8Ru(CO)_3$ has also been determined[2] with the result that the $C_8H_8Ru(CO)_3$ and $C_8H_8Fe(CO)_3$ molecules in their respective crystals are strictly isostructural, each having the (1,2,3,4-*tetrahapto*cyclooctatetraene)tricarbonylmetal constitution.

In addition the remarkable fluxional molecule $(C_8H_8)_2$-$Ru_3(CO)_4$, which at present has no known iron analog, has been made and structurally characterized.[15,16] The structure in the crystal of the molecule $C_8H_8Ru_2(CO)_6$, mentioned earlier, has also been described;[17] it will be shown in this report that the instantaneous structure of $C_8H_8Ru_2(CO)_6$ in solution is the same skew structure found in the crystal and that the molecule is a fluxional one undergoing an oscillatory intramolecular rearrangement which gives time-average mirror symmetry.

It is the purpose of this paper to describe in detail the preparation, purification, and chemical characterization of all the $(C_8H_8)_wRu_x(CO)_y$ molecules presently known to us and to report and interpret their nmr spectra in terms of their structures and fluxional deportment in as much detail as these are presently understood.

Results and Discussion

The general procedure for the preparation of the compounds described here is to reflux a hydrocarbon solution of cyclooctatetraene and $Ru_3(CO)_{12}$. Separation and purification of the products is achieved by suitable combinations of chromatography, sublimation, and recrystallization. Using heptane as the reaction solvent the three compounds $C_8H_8Ru(CO)_3$, *cis*-$C_8H_8Ru_2(CO)_6$, and $C_8H_8Ru_2(CO)_5$ were obtained. Traces of a yellow solid tentatively identified by its infrared spectrum as *trans*-$C_8H_8[Ru(CO)_3]_2$ were isolated in some preparations. The analogous iron compound also forms in only minute amounts as a by-product in the preparation[3,7] of $C_8H_8Fe(CO)_3$. The compound $(C_8H_8)_2$-$Ru_3(CO)_4$ has not been observed as a product of reaction in heptane, but when octane is used as the reaction solvent it is the principal product.

Each of these four molecules has been shown by pmr study to be fluxional.[27] In two cases, $C_8H_8Ru(CO)_3$ and $C_8H_8Ru_2(CO)_6$, a limiting low-temperature pmr spectrum has been recorded, thus establishing the instantaneous structure in solution, and the rearrangement pathway has been inferred from the observed manner of collapse of the limiting spectrum. In both of these cases the instantaneous structure inferred from
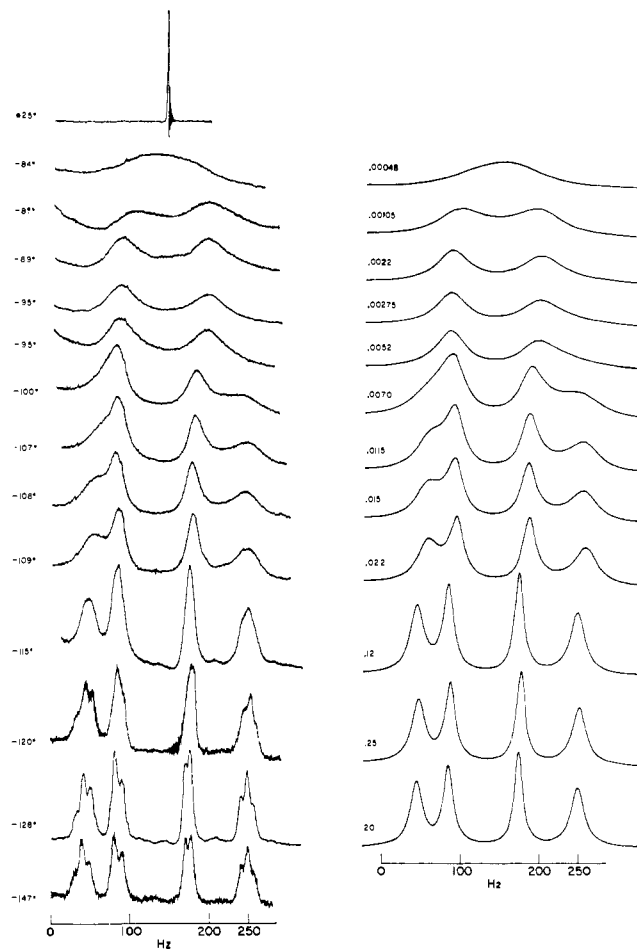

Figure 1. The 100 MHz pmr spectra of (C_8H_8) $Ru(CO)_3$ in $CFHCl_2$: CF_2Cl_2 (1:1 v/v) solution at various temperatures (left) and computer-simulated spectra at various mean residence times (right). The temperatures and residence times have been chosen to achieve the closest possible match between pairs of spectra. The frequency scale starts at +100 Hz to the high-field side of the internal lock signal, which is the low-field component of the $CFHCl_2$ doublet.

the limiting low-temperature spectrum is the same as the structure observed in the crystalline compound. Indeed, it is worthwhile emphasizing that, so far, among organometallic molecules, the molecular structures have always been the same in the crystalline and solution phases. The data concerning the structural and dynamical properties of each of the four molecules will now be presented.

$(C_8H_8)Ru(CO)_3$. This complex has been shown[2] to be isostructural in the crystalline state with its iron analog.[9] Unlike the iron compound, however, its pmr spectrum over the complete range from limiting low- to limiting high-temperature behavior is accessible. These spectra are shown in Figure 1. An examination of these spectra has enabled us to deduce the main pathway by which the intramolecular rearrangement of the molecule takes place to give the time-average equivalence of the protons and the appearance of the single sharp line spectrum at room temperature.

The limiting spectrum is clearly in accord with the results of the X-ray crystallographic study. There are four main regions of resonance of equal intensity corresponding to the environments α, β, γ, and δ as defined in Figure 2. We can, with a high degree of certainty, make the assignment that the two sets of resonances at
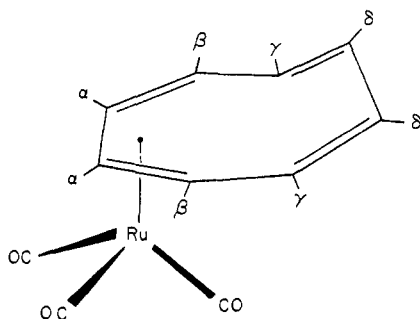
Figure 2. A diagram of the instantaneous structure of C_8H_8Ru-$(CO)_3$ showing designations of the four different proton sites.
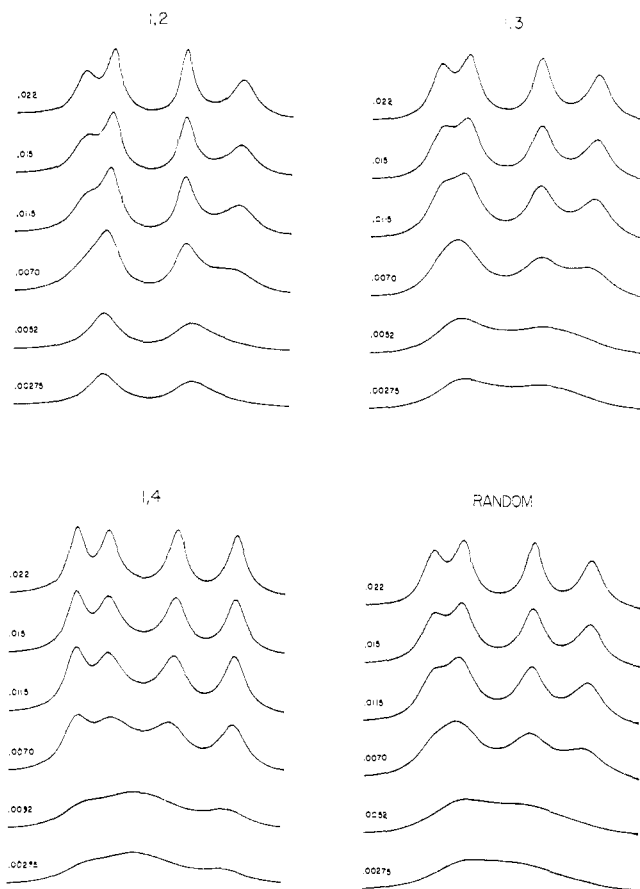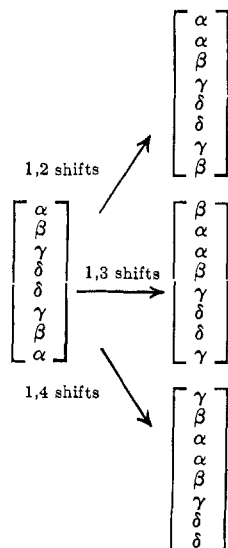

Figure 3. Spectra computed at various mean residence times in the range of major spectral change for four pathways of rearrangement, 1,2 shifts, 1,3 shifts, 1,4 shifts, and any process, such as a random mixture of different shifts, leading to equal rates of site exchange for all protons.

highest field are associated with the 1–3 diene fragment bonded to the $Ru(CO)_3$ group. The unsymmetrical doublet at 172 Hz is due to the α protons while the unsymmetrical triplet at 251 Hz is due to the β protons. The assignments of γ and δ resonances will depend upon an analysis of the intermediate spectra in the markedly exchange-broadened region as discussed below. The fact that certain resonances in the limiting spectrum collapse more rapidly than others as the temperature rises is extremely significant and provides the clues for deducing, in a topological sense, the predominant pathway for the intramolecular rearrangement which will lead to a time-average single-line spectrum.

In principle there are five possible pathways which could be considered for the intramolecular rearrangement process: (1) a sequence of 1,2 shifts of the $Ru(CO)_3$ moiety relative to C_8H_8; (2) a sequence of 1,3 shifts; (3) a sequence of 1,4 shifts; (4) a sequence of 1,5 shifts or transannular jumps; (5) a random sequence of the foregoing shifts. We immediately eliminate random shifts because this would cause all the resonances to collapse at approximately the same rate contrary to that which is observed. Furthermore, a sequence of 1,5 shifts would average α with δ (or γ) and β with γ (or δ) and could not therefore give a single-line spectrum at the high-temperature limit. This leaves three pathways to be considered and we have the problem of distinguishing between (1), (2), and (3). In order to do so we must examine in detail how the protons are permuted among the four environments α, β, γ, and δ by

Scheme I

each of the three paths. We can illustrate this symbolically as shown in Scheme I.

In two cases (viz. 1,2 shifts and 1,4 shifts), only six of the protons change their environment in each step while two do not. The difference between these two cases lies in the fact that for 1,2 shifts the unchanged environments are of types α and δ while for 1,4 shifts they are of types β and γ. The consequences of these observations are that for 1,2 shifts the β and γ resonances will collapse most rapidly with increasing temperature whereas for 1,3 shifts it will be α and δ resonances. Our assignments of the α and β resonances as previously described and the observation that it is the high-field β resonance which broadens most rapidly in the markedly unsymmetrical collapse of the high-field portion of the spectrum are therefore clearly only consistent with the pathway involving 1,2 shifts. The 1,3-shift pathway, in which all environments change at each step, would lead to initial symmetrical collapse, while the pathway involving 1,4 shifts would require the unsymmetrical doublet due to the α protons to broaden first. This qualitative analysis requires only the assignment of the chemical shifts for the α and β protons but enables us to derive an assignment of the γ and δ protons once the predominant pathway has been deduced. The 1,2-shift pathway is only consistent with an assignment in the low-field region of the spectrum such that the unsymmetrical triplet at 42 Hz is ascribed to the γ protons and the unsymmetrical doublet 87 Hz to the δ protons.

Employing the method of Kubo[29a] and Sack[29b] as implemented in the computer program NMRCTL written by Professor G. M. Whitesides, we have calculated the line shapes for 1,2, 1,3, 1,4, and random shift sequences at various values of the preexchange lifetimes with the chemical shift assignments derived above. An extensive sequence of computed spectra based on 1,2 shifts is matched to the observed spectra in Figure 1, while the spectra for each mechanism through the region of critical change are displayed in Figure 3. As expected the 1,2-shift sequence gives excellent agreement with the observed spectra.

As an additional test for the conclusion that a sequence of 1,2 shifts is the major cause of the observed spectral changes, we have computed spectra for varying admixtures of the 1,2 and 1,3 shifts, e.g., a 1:1 mixture and a 2:1 mixture. Even at the 2:1 ratio there is a clear difference between the observed and calculated spectra. However, the incorporation of lesser proportions of the 1,3-shift mechanism provides spectra which substantially agree with observed spectra. Consequently we cannot rule out the possibility that 1,3 shifts provide a minor pathway of rearrangement, perhaps up to 30%, though we do not suggest that they do.

Assuming that the major process causing the observed changes in line shape is a sequence of 1,2 shifts of the $Ru(CO)_3$ moiety, we can obtain kinetic data by visually comparing computed spectra for 1,2 shifts with the experimental spectra. Figure 1 shows computed spectra which are considered to be the best possible match to the experimental spectra. Analysis of these data by the method of least squares yielded a straight Arrhenius plot with E_a equal to 9.4 ± 0.5 kcal/mol and log A equal to 14.0 ± 0.7.

cis-$(C_8H_8)Ru_2(CO)_6$. As noted in the introductory section structure I was first proposed for the iron analog of this molecule[7] on the basis of nmr and Mössbauer spectra. However, X-ray study[17] has shown that in the crystal this molecule has the asymmetric structure II. It has further been demonstrated[30] that $C_8H_{10}Fe_2(CO)_6$, the 1,3,5-cyclooctatriene analog, also possesses a skew structure entirely analogous to II. As will be shown below, $C_8H_8Ru_2(CO)_6$ in C_6D_{12} solution has a pmr spectrum indicative of the existence of a plane of symmetry
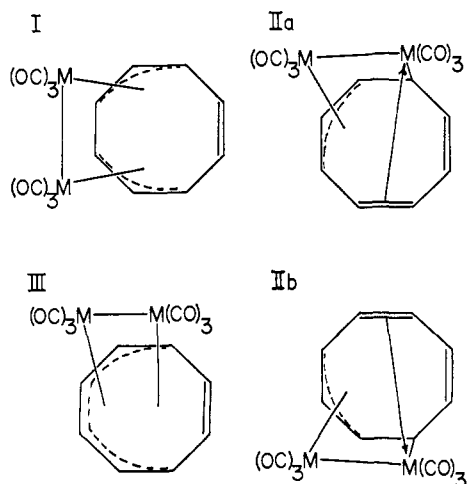
I IIa

III IIb
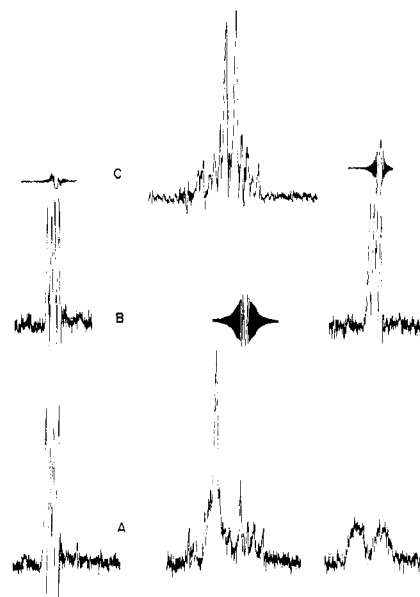
Figure 4. (A) The nmr spectrum of $(C_8H_8)Ru_2(CO)_6$ in C_6D_{12} solution at 35°. (B) The spectrum when the central multiplet is irradiated. (C) The spectrum when the low- and high-field resonances are irradiated simultaneously.

bisecting two opposite edges of the C_8H_8 ring. There are then three principal possibilities to be considered with respect to the structure and dynamic character of this molecule in solution. (1) It may have structure I in solution. (2) It may have structure III in solution; III, obtained from II by a relatively slight shift of the nuclei, has a symmetry plane which contains the two metal atoms and bisects the uncoordinated double bond. (3) Structure II may persist as the preferred structure of the molecule in solution but a rapid interconversion of this and its mirror image (most likely proceeding by way of III as a transition state or short-lived intermediate) may occur.

The pmr evidence that $C_8H_8Ru_2(CO)_6$ has an apparent plane of symmetry at room temperature is presented in Figure 4. The spectrum in its entirety consists of three regions of absorption at $\tau \sim 4.2$, ~ 5.7, and ~ 7.4, with relative intensities 2, 4, and 2, respectively. Irradiation of the intense multiplet at $\tau \sim 5.7$ causes the other two multiplets to form jointly an AA'XX' spectrum in which A to X couplings are much less than the chemical shift difference between A and X protons. The τ 4.2 multiplet is essentially unchanged from its form in the undecoupled spectrum while the τ 7.4 multiplet is greatly simplified and sharpened. This shows that the τ 4.2 protons have appreciable coupling only to the τ 7.4 protons, while the latter are also coupled to protons which contribute to the τ 5.7 multiplet. When both the τ 4.2 and 7.4 multiplets are irradiated, the central multiplet assumes a structure attributable to an AA'BB' set of protons.[31] From these observations two conclusions are drawn. (1) The eight protons behave on the pmr time scale at ambient temperature as though they are distributed pairwise over four different sites. This is equivalent to saying that there is a (time-average) plane of symmetry bisecting opposite edges of the ring. (2) From the positions of the multiplets and

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Figure 5. Nmr spectra (60 MHz) of cis-(1,2,6-trihapto:3,4,5-trihaptocyclooctatetraene)hexacarbonyldiruthenium. An approximately 0.1 M solution in $\sim$3:2 v/v mixture of $CD_3C_6D_5$–CF_2Cl_2. The peak marked T is due to toluene-d_7 and peaks marked X are due to impurities. Numbers indicate assignments as represented in Figure 6.

the relative magnitudes of the couplings it is highly probable that the τ 4.2 protons are those of the uncoordinated double bond, the τ 7.4 protons are those immediately adjacent to the uncoordinated double bond, and the τ 5.7 multiplet is due to the remaining sequence of four protons belonging to coordinated carbon atoms.

A study of the pmr spectrum of $C_8H_8Ru_2(CO)_6$ dissolved in a $C_6D_5CD_3$–CF_2Cl_2 mixture at lower temperatures corroborates the assignment just suggested and demonstrates that the molecule actually has the structure II with the apparent symmetry plane being attributable to the interconversion, which is rapid at room temperature, of two enantiomorphous structures, IIa and IIb. The low-temperature spectra are shown in Figure 5. Peaks marked with crosses are due to impurities, while the small multiplet marked with a T is due to the proton of $C_6D_5CD_2H$. Numbers indicate assignments in terms of the numbering scheme shown in Figure 6.

The absorption in the room-temperature spectrum due to the 1 and 6 protons begins to broaden noticeably at about $-35°$ and is completely collapsed in the range -65 to $-75°$. The growth of separate 6 and 1 resonances at approximately τ 7.0 and 8.9, respectively, is observed between -80 and $-90°$. Separation of the resonance due to the 7 and 8 protons does not occur until about $-90°$ since, as shown by the $-120°$ spectrum, the chemical shift difference between these is relatively small ($\sim$35 Hz compared $\sim$115 Hz for the 1 and 6 protons). Changes in the large resonance due to protons 2, 3, 4, and 5 are relatively subtle due to the fact that the chemical shifts for all of these protons are within
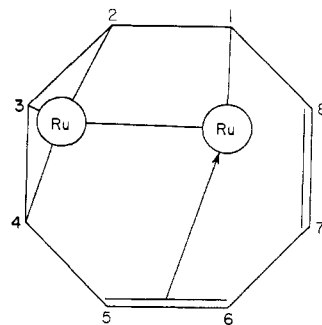

Figure 6. A diagrammatic representation of the $(C_8H_8)Ru_2(CO)_6$ structure giving the numbering scheme used to discuss and interpret the spectra of Figure 5.

a narrow range. All of the observed changes are consistent with the postulated oscillatory motion and, so far as we can see, they will admit of no other interpretation.

$C_8H_8Ru_2(CO)_5$. At room temperature, the pmr spectrum of this molecule in CS_2 consists of a single line at τ 5.30. Attempts to obtain a limiting low-temperature spectrum have been unsuccessful because the complex is virtually insoluble at temperatures below $-80°$. Above this temperature the resonance remains a sharp singlet.

The analogous iron compound,[7] $C_8H_8Fe_2(CO)_5$, also has a single-line pmr spectrum down to $-80°$. Both $C_8H_8Fe_2(CO)_5$ and its 1,3,5,7-tetramethylcyclooctatetraene analog (which has nmr-equivalent ring protons and methyl groups at room temperature) have been shown to have structures[8,24] in the crystal in which the eight vertices of the ring are sorted into three sets containing 4, 2, and 2. The observed nmr equivalence is thus attributable to fluxional behavior. We pressume that the $C_8H_8Ru_2(CO)_5$ molecule is structurally and dynamically analogous to the iron compound.

$(C_8H_8)_2Ru_3(CO)_4$. This complex was produced exclusively by the reaction of C_8H_8 and $Ru_3(CO)_{12}$ in refluxing octane. It forms lustrous red air-stable crystals which are sparingly soluble in organic solvents. The structure of this organometallic cluster compound has been determined[16] and shows that each of the two C_8H_8 rings is attached to an Ru_2 fragment of the Ru_3 cluster.

The mass spectrum is complex but the parent ion multiplet and a fragmentation scheme which involves stepwise removal of CO from the cluster are evident from the appearance of both singly charged ions, $(C_8H_8)_2$-$Ru_3(CO)_n^+$, $n = 0$–4, and doubly charged ions $(C_8H_8)_2$-$Ru_3(CO)_n^{2+}$, $n = 0$–3.

The nmr spectrum in $CDCl_3$ shows a single sharp line at τ 6.26 from room temperature to about $-40°$. Attempts to record spectra in toluene–Freon mixtures at low temperatures were frustrated by the very low solubility of the material. However, the molecule is clearly fluxional and is simultaneously a metal atom cluster compound. The four-band infrared spectrum has been shown to be in accord with the molecular structure.[16]

Experimental Section

Preparation of Compounds. Reaction of $Ru_3(CO)_{12}$ with C_8H_8 in Boiling Heptane. A mixture of freshly distilled cyclooctatetraene (1.5 ml), triruthenium dodecacarbonyl (0.64 g), and heptane (80 ml) was gently refluxed under nitrogen for 20 hr. Efficient sitrring was maintained to avoid local overheating. The solvent was then removed at 25° and 0.05 Torr; the orange residue was extracted with 25 ml of petroleum ether (37–51°) giving an orange solution and

leaving a solid orange residue. The solution was chromatographed on an alumina column. Using additional petroleum ether as eluent, two bands, one orange and one yellow, were carried through the column and collected, while at the top of the column there remained two more bands, one orange and one yellow. The alumina column was then treated with a 1:3 benzene–petrol mixture, thereby eluting the yellow band which had remained at the top. Evaporation of the eluent afforded a very small amount of a yellow, crystalline compound which has not yet been conclusively identified. The orange band is believed to consist of a small amount of $C_8H_8Ru_2$-$(CO)_5$ which was mechanically transferred to the top of the alumina column; it was not eluted at this time. No further effort was made to remove it.

$C_8H_8Ru(CO)_3$. The solution of the orange band which was eluted with petroleum ether was evaporated to give a crude sample of $C_8H_8Ru(CO)_3$. Purification was effected by sublimation at 47° and 0.05 Torr. About 30 mg was obtained in a typical run. The residue from the sublimation consisted of a few milligrams of a yellow solid believed to be mainly trans-$C_8H_8[Ru(CO)_3]_2$, on the basis of its infrared spectrum (three strong bands, in heptane, at 2067, 2000, and 1992 cm⁻¹). The purity of the sublimed C_8H_8Ru-$(CO)_3$ was monitored by its infrared spectrum and resublimation was carried out as necessary to remove extraneous bands. The spectrum of the pure compound, in heptane, consists of three strong bands at 2070, 2010, and 1996 cm⁻¹; mp 75–76°.

Anal. Calcd for $C_{11}H_8RuO_3$: C, 45.67; H, 2.79. Found: C, 45.2; H, 2.96.

cis-$C_8H_8Ru_2(CO)_6$. The solution containing the yellow band eluted by petroleum ether was evaporated to give a yellow crystalline solid. The solid was recrystallized from pentane or hexane by cooling to −70° to give about 150 mg of yellow crystals. Recrystallization was sometimes repeated to eliminate extraneous bands from the infrared spectrum. The authentic spectrum in heptane consists of bands at 2078 s, 2048 vs, 2011 vs, 2006 sh, 1988 s, and 1978 sh cm⁻¹, all ±5 cm⁻¹; mp 95–99° dec.

Anal. Calcd for $C_{14}H_8Ru_2O_6$: C, 35.45; H, 1.70. Found: C, 35.4; H, 1.71.

$C_8H_8Ru_2(CO)_5$. The orange solid remaining after extraction of the residue from the reaction with petroleum ether consists of about 150 mg of the relatively insoluble $C_8H_8Ru_2(CO)_5$. It was recrystallized from hot toluene; mp ~160° dec.

Anal. Calcd for $C_{13}H_8Ru_2O_5$: C, 34.98; H, 1.81. Found: C, 34.1; H, 1.84.

$(C_8H_8)_2Ru_3(CO)_4$. This compound is prepared by reaction of C_8H_8 with $Ru_3(CO)_{12}$ in refluxing octane. Freshly distilled C_8H_8 (2 ml), $Ru_3(CO)_{12}$ (1.0 g), and octane (100 ml) were mixed and refluxed for 24 hr in a nitrogen atmosphere. The red mixture was then cooled and allowed to stand several hours at 25°. It was filtered through a glass frit, affording about 850 mg of sparkling, red, air-stable crystals. The red filtrate was discarded. The product may be further purified by recrystallization from boiling benzene or CH_2Cl_2. It is but sparingly soluble in common organic liquids at room temperature; mp 165–170° dec. Its infrared spectrum (CS_2 solution) contains the following bands (all ±5 cm⁻¹): 2032 vw, 1996 s, 1956 ms, and 1920 s cm⁻¹.

Anal. Calcd for $C_{20}H_{16}Ru_3O_4$: C, 38.52; H, 2.59. Found: C, 38.8; H, 2.55.

Nmr Spectra. Spectra at 60 MHz were obtained with Varian Associates A-60 or HA60 IL 6340 nuclear magnetic resonance spectrometers. Homonuclear spin-decoupling experiments were performed using two Hewlett–Packard Model 200 CD audio oscillators. Temperature control was accomplished with a V-6040 variable-temperature controller. The temperature scale was calibrated using a copper–constantan thermocouple inserted into a glass tube resembling an ordinary sample tube but having a small hole in the bottom through which the thermocouple junction projected. This tube was then inserted in the standard sample-tube spinner and the entire assembly inserted in the instrument probe so as to locate the thermocouple junction at the position normally occupied by a sample. The nitrogen flow was set at the same rate as that used in actual measurements. The spectra at 100 MHz were recorded at JEOLCO, Medford, Mass., using a JNM-44-100 spectrometer. We thank Messrs. D. Stratouly and Y. Ogawa for these spectra.

In sample preparation toluene-d_8 and $(CH_3)_4Si$ were first degassed by freeze–thaw cycles under vacuum and distilled on the vacuum line directly into the nmr sample tube already containing the solute. Next, the CCl_2F_2 was trap-to-trap distilled, degassed by freeze–thaw cycles and distilled into the sample tube, which was then sealed off under vacuum.

Mass Spectra. These were recorded on a Hitachi–Perkin-Elmer R MU6-D mass spectrometer.