Stereochemically Nonrigid[1] Organometallic Molecules. XII.[2] The Temperature Dependence of the Proton Nuclear Magnetic Resonance Spectra of the 1,3,5,7-Tetramethylcyclooctatetraene Tricarbonyl Compounds of Chromium, Molybdenum, and Tungsten[3]

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Abstract: The temperature dependence of the proton nmr spectra of the molecules (TMCOT)M$(CO)_3$, where TMCOT is 1,3,5,7-tetramethylcyclooctatetraene and M is Cr, Mo, or W, has been investigated and analyzed. At least two and possibly three phases of intramolecular rearrangement successively acquire sufficient velocity to cause observable averaging of selected sets of proton environments as the temperature is raised from *ca.* $-30°$ to over 115°. The first phase of spectral change can be shown to result from an oscillatory 1,2-shift mechanism. By comparison of observed and computer-simulated spectra it can be shown that the energies of activation for this motion for the three compounds are as follows: for (TMCOT)Cr$(CO)_3$ and (TMCOT)Mo$(CO)_3$, $\Delta E_a = 16.0 \pm 0.6$ kcal/mole, while for (TMCOT)W$(CO)_3$, $\Delta E_a = 19.3 \pm 0.1$ kcal/mole.

There are by now a considerable number of stereochemically nonrigid organometallic molecules known. These include, *inter alia*, systems with cyclopentadienyl rings,[6-10] cycloheptatrienyl rings,[11] allyl groups,[12] and cyclooctatetraene rings. The cyclooctatetraene (COT) compounds include a considerable number of both mono- and dinuclear iron carbonyl derivatives[13] as well as the COT derivatives of the group VI carbonyls, *viz.*, the (COT)M$(CO)_3$ compounds.[14,15]

The COT compounds have proved to be especially interesting in various ways, but, because of the complexity of their nmr spectra, detailed analysis of their behavior has proved difficult. With the object of evading some of the inherent difficulties with COT compounds while, hopefully, still retaining some of their essential features, we have been examining compounds of 1,3,5,7-tetramethylcyclooctatetraene (TMCOT).

This particular substituted derivative of COT was selected for three reasons. (1) It retains much of the symmetry of COT itself. Thus all C=C and C—C bonds in the ring are equivalent; all ring hydrogen atoms are equivalent; all methyl groups are equivalent. (2) The alternation of H atoms and methyl groups around the ring leads to the elimination of pronounced spin–spin coupling effects, thus simplifying nmr spectra and making them susceptible to certain forms of detailed analysis not possible when spin–spin coupling is pronounced. (3) TMCOT can be prepared; this is not a trivial consideration because relatively few substituted COT's are conveniently available.

By using TMCOT, a number of interesting iron carbonyl derivatives have been made[16] as well as the (TMCOT)M$(CO)_3$ (M = Cr, Mo, W) molecules.[17] The structure of (TMCOT)Cr$(CO)_3$ has been reported.[2] The purpose of this paper is to describe the preparation and temperature-dependent nmr spectra of the (TMCOT)M$(CO)_3$ molecules in detail and to discuss the interpretation of the nmr spectra.

Experimental Section

Preparation of Compounds. 1,3,5,7-Tetramethylcyclooctatetraene (TMCOT). The synthesis of this compound was accomplished using the method outlined by de Mayo and Yip.[18] We are grateful to Professor de Mayo for providing us with additional details of the procedure. We found that to obtain a highly pure product the following steps were critical. The purification of the pyrolysate of the 4,6-dimethylcoumalin dimers was accomplished by distillation under vacuum (water pump, 100°). The resultant raw material was sublimed at 0.1 torr and 50° and then recrystallized three

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[1] Although molecules so far discussed in this series of papers could all be called, following Doering, *fluxional*, the series title retains the term *stereochemically nonrigid*. In our view fluxional refers to a molecule undergoing intramolecular rearrangements between equivalent (*i.e.*, equi-energic) structures, while tautomerism (or tautomerization) refers to interconversion of nonequivalent structures. Stereochemically nonrigid is a general term embracing both fluxional and rapidly tautomerizing molecules. It can therefore be used without prior implications regarding the specific nature of the rapid intramolecular rearrangements which are responsible for observed temperature dependence of nmr spectra.

[2] Preceding paper in this series, part XI: M. J. Bennett, F. A. Cotton, and J. Takats, *J. Am. Chem. Soc.*, **90**, 903 (1968).

[3] This research was supported in part by the National Science Foundation under Grants GP-4329 and 7034X and by a grant from the Petroleum Research Fund, administered by the American Chemical Society.

[4] National Science Foundation Predoctoral Fellow, 1963–1966.

[5] Fellow of the F. Giordani Foundation, Rome, 1965–1966.

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[7] M. J. Bennett, F. A. Cotton, A. Davison, J. W. Faller, S. J. Lippard, and S. M. Morehouse, *J. Am. Chem. Soc.*, **88**, 4371 (1966).

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[10] F. A. Cotton, A. Musco, and G. Yagupsky, *ibid.*, **89**, 6136 (1967).

[11] R. B. King and A. Fronzaglia, *ibid.*, **88**, 709 (1966).

[12] There is an enormous number of communications on these systems. A recent one which provides a fair number of prior references is A. Davison and W. C. Rode, *Inorg. Chem.*, 6, 2124 (1967).

[13] C. E. Keller, G. F. Emerson, and R. Pettit, *J. Am. Chem. Soc.*, 87, 1388 (1965).

[14] C. G. Kreiter, A. Maasbol, F. A. L. Anet, H. D. Kaesz, and S. Winstein, *ibid.*, **88**, 3444 (1966).

[15] S. Winstein, H. D. Kaesz, C. G. Kreiter, and E. C. Friedrich, *ibid.*, 87, 3267 (1975).

[16] F. A. Cotton, M. D. LaPrade, A. Musco, and J. Takats, to be published.

[17] A preliminary report of the molybdenum compound has been published: F. A. Cotton, J. W. Faller, and A. Musco, *J. Am. Chem. Soc.*, **88**, 4506 (1966).

[18] P. de Mayo and R. W. Yip, *Proc. Chem. Soc.*, 84 (1964).

times from methanol yielding a white crystalline compound, mp 69–70° (uncor). The purity of the olefin was ascertained by following the gradual disappearance of the band at 1730 cm^{-1} in the infrared spectrum; this band is a strong feature in the spectrum of the chief impurity, 4,6-dimethylcoumalin.

1,3,5,7-Tetramethylcyclooctatetraenemetal Tricarbonyls, (TMCOT)M(CO)$_3$. All (TMCOT)M(CO)$_3$ compounds were prepared and handled in an atmosphere of prepurified nitrogen which was rigorously maintained. All solvents were thoroughly degassed by pumping and freezing on the vacuum line before use and were distilled directly into the reaction vessels.

(TMCOT)Cr(CO)$_3$. A procedure similar to that of King and Fronzaglia[19] was used. One gram of TMCOT and 1.2 g of $(CH_3CN)_3Cr(CO)_3$ in 50 ml of hexane were refluxed for 24 hr. The red reaction mixture was then filtered and the solvent stripped at 0.05 torr (25°). Unreacted TMCOT was removed from the solid by quick sublimation at 0.05 torr (25°). The residue was then sublimed twice at 0.05 torr (60°) giving a good yield (0.82 g, 60% based on $(CH_3CN)_3Cr(CO)_3$) of red, microcrystalline (TMCOT)Cr(CO)$_3$, melting with decomposition at 65–69° (uncor).

Anal. Calcd for $C_{15}H_{16}CrO_3$: C, 60.81; H, 5.48. Found: C, 60.7; H, 5.66.

Strong carbonyl stretching bands are found in the infrared spectrum (recorded in heptane solution) at 1900, 1930, and 1980 cm^{-1} (each ± 3 cm^{-1}).

(TMCOT)Mo(CO)$_3$. A suspension of 1 g of TMCOT and 1 g of diglymemolybdenum tricarbonyl in 25 ml of hexane was refluxed for 16 hr. The reaction mixture was then filtered and, after removal of solvent at 0.05 torr (25°), subjected to a quick sublimation at 0.05 torr (50°) to remove unreacted TMCOT. Sublimation at 0.05 torr (80°) afforded red crystals of (TMCOT)Mo(CO)$_3$ in good yield (typically, 0.55 g, 51% based on diglymemolybdenum tricarbonyl), melting with decomposition at 90–93° (uncor).

Anal. Calcd for $C_{15}H_{16}MoO_3$: C, 52.95; H, 4.73. Found: C, 52.0; H, 4.89. Infrared (in cyclohexane): strong bands at 1903, 1930, 1987 cm^{-1} (all ± 3 cm^{-1}).

(TMCOT)W(CO)$_3$. This was prepared from $(CH_3CN)_3W(CO)_3$ by essentially the same procedure as that used for (TMCOT)Cr(CO)$_3$, using octane as the reaction medium. In refluxing octane, the reaction appears to be complete in 1 hr, whereas, using hexane, little if any reaction was evident after refluxing for 1 week. (TMCOT)W(CO)$_3$ forms clear red crystals (mp 93–95° dec) in good yield, typically 0.70 g/g of $(CH_3CN)_3W(CO)_3$.

Anal. Calcd for $C_{15}H_{16}WO_3$: C, 42.05; H, 3.78. Found: C, 42.1; H, 3.87. Infrared (heptane solution): strong bands at 1900, 1925, and 1995 cm^{-1} (all ± 3 cm^{-1}).

Instrumental Measurements. Infrared spectra were recorded on a Perkin-Elmer 237 spectrograph. The cells were filled in a glove box in a nitrogen atmosphere.

The nmr spectra were measured using a Varian Associates A-60 proton nuclear resonance spectrometer equipped with a variable-temperature accessory. Temperatures were determined by measuring the peak separations in methanol and ethylene glycol samples for low and high temperatures, respectively. Correlation with temperature was based on the shift *vs.* temperature charts supplied by Varian Associates. Calibration of spectra at the lowest temperatures was accomplished with a Krohn-Hite Model 450 oscillator and a Hewlett-Packard Model 524 electronic counter.

To assure rigorous exclusion of oxygen from the nmr samples, solvents ($CDCl_3$ or C_6D_{12}) and tetramethylsilane were degassed and distilled under high vacuum directly onto the solids which had been previously placed in standard size nmr tubes using a nitrogen-filled glove box. The tubes were then sealed under vacuum and stored at −70° until used.

Representative spectra are displayed in Figure 1. Records were made at somewhat closer temperature intervals than those shown in this selection. For each compound about 12 spectra were taken, at ∼−40, ∼−20, ∼−10, and ∼10° intervals from ∼0° to the highest temperatures possible. These were 112, 80, and 90° for the Cr, Mo, and W compounds, respectively.

Treatment of Nmr Data. The rate constant for the rearrangement process at a given temperature was estimated by computing line shapes as a function of rate constant at close intervals over a range of rate constants and matching these to the observed spectra.

The theoretical line shapes were computed using a method developed by Kubo[20] and by Sack.[21] The computations were carried out on an IBM 7094 digital computer using a program whose output is a trace of the line profile drawn on a Calcomp plotter. This program was written by Professor George M. Whitesides to whom we are also grateful for helpful advice on its use.

To summarize briefly, the line-shape function, $I(\omega)$, that is, the intensity, I, as a function of frequency, ω (in cps), is expressed as a function of the physical parameters of the site exchange process by

$$I(\omega) \propto \mathrm{Re}\,(W)(i\omega E_n - i\Omega - \pi - T)^{-1}[1] \qquad (1)$$

Re designates the real part of the following complex function, which is the product of three matrices. [1] is a unit column matrix of order n. W is a row matrix whose n components are proportional to the occupation probabilities of the n available sites. Between these we have the inverse of a square matrix whose elements are made up as indicated. The constituent matrices are as follows.

E_n is a unit matrix of order n.

Ω is a diagonal matrix of order n whose elements, ω_j, are the chemical shifts, in cycles per second, characteristic for each of the n sites. These values are determined from the observed lines in the limiting low-temperature spectrum.

π is a matrix of exchange probabilities, whose elements are defined as

$$\left.\begin{aligned}\pi_{jk} &= p_{jk}\\ \pi_{jj} &= -\sum_k p_{jk}\end{aligned}\right\} j \neq k$$

where j and k are indices over the sites, from 1 to n. Each p_{jk} must be multiplied by the rate constant, expressed as $1/\tau$, τ being the mean residence time at a site.

T is a diagonal matrix with elements defined as

$$\tau_j = 1/T_2(j)$$

$T_2(j)$'s are the relaxation times, T_2, at frequencies ω_j and are determined experimentally from the observed line widths in the limiting low-temperature spectrum.

For the particular molecules and processes studied here, these

$$I^{CH_3}(\omega) \propto$$

$$\mathrm{Re}[3333]\begin{bmatrix}\left[i(\omega-\omega_1)+t_1+\frac{1}{\tau}\right] & -\frac{1}{\tau} & 0 & 0\\ -\frac{1}{\tau} & \left[i(\omega-\omega_2)+t_2+\frac{1}{\tau}\right] & 0 & 0\\ 0 & 0 & \left[i(\omega-\omega_3)+t_3+\frac{1}{\tau}\right] & -\frac{1}{\tau}\\ 0 & 0 & -\frac{1}{\tau} & \left[i(\omega-\omega_4)+t_4+\frac{1}{\tau}\right]\end{bmatrix}\begin{bmatrix}1\\1\\1\\1\end{bmatrix} \qquad (2)$$

$$I^{H}(\omega) \propto \mathrm{Re}[1\ \ 1]\begin{bmatrix}\left[i(\omega-\omega_5)+t_5+\frac{1}{\tau}\right] & -\frac{1}{\tau}\\ -\frac{1}{\tau} & \left[i(\omega-\omega_6)+t_6+\frac{1}{\tau}\right]\end{bmatrix}\begin{bmatrix}1\\1\end{bmatrix}$$

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(19) R. B. King and A. Fronzaglia, *Chem. Commun.*, 547 (1965).

(20) R. Kubo, *Nuovo Cimento Suppl*, 6, 1063 (1957).

(21) R. A. Sack, *Mol. Phys.*, 1, 163 (1958).

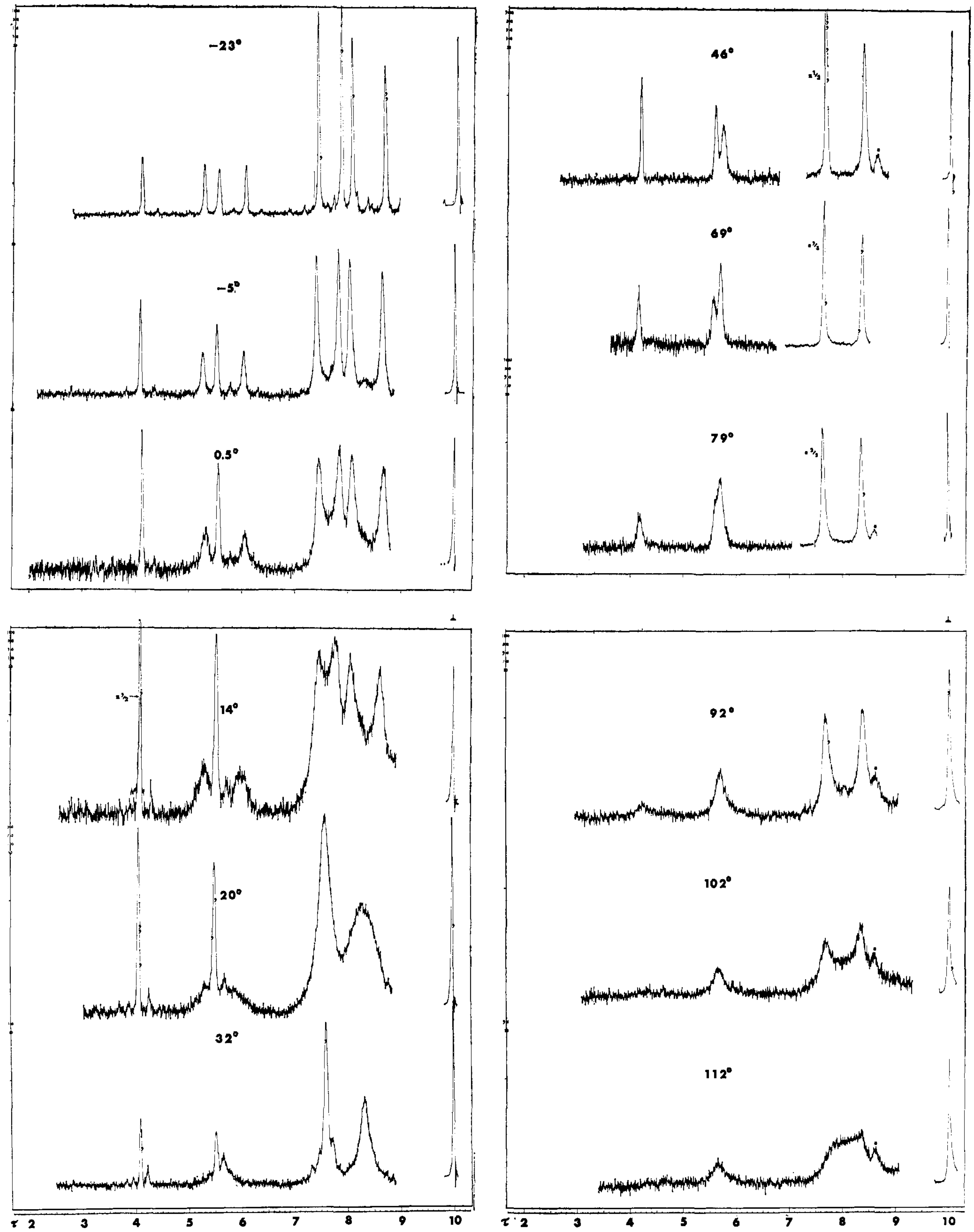

Figure 1. The proton magnetic resonance spectra of 1,3,5,7-tetramethylcyclooctatetraenechromium tricarbonyl. The spectra on the left (-23 to $+32°$) were taken in CCl_3D and those on the right ($+46$ to $+112°$) in C_6D_{12}. The gain settings were varied from run to run to show the most pertinent details.

line-shape functions $I^{CH_3}(\omega)$ and $I^{H}(\omega)$ for the methyl and ring protons, respectively, are as shown in eq 2. Our calculation assumes that neither chemical shifts nor line widths are functions of temperature in the absence of exchange.

Interpretation

The way in which the proton nmr spectra vary with temperature is very much the same for all three of the

(TMCOT)M$(CO)_3$ compounds. Figure 1 presents a selection of representative spectra for the chromium compound; spectra were also recorded at various temperatures between those shown. The chromium compound is actually slightly atypical in that it provides a little bit greater range of data than the other two compounds owing to its slightly greater thermal stability and slightly greater rates of rearrangement. However, aside from such minor, quantitative differences, the observations are so similar in all three cases that it seems reasonably safe to assume that a common mechanism, or set of mechanisms, will apply to all compounds.

We note at the outset that the structure of the (TMCOT)Cr$(CO)_3$ molecule in the crystalline compound has been established firmly by a single-crystal X-ray diffraction study of relatively high accuracy.[2] The structure is shown schematically in Figure 2a. It is important to recognize that all four vinyl protons are in different environments and so also are the four methyl groups. In Figure 2b is shown a topological scheme for the identification of all relevant parts of the complex. The letters A, B, C, D identify ring hydrogen atoms while α, β, γ, δ identify the four methyl groups. The letters S, T, U, ..., Z identify the eight points over which the metal atom may lie in a stable configuration of the molecule. In later discussions, we shall normally assume that position S is initially occupied. Then, crudely speaking, the C–C double bonds would lie at positions S, U, W, and Y, and it is the one at W which would not be coordinated to the metal atom.

At the lowest temperatures in each spectrum one sees eight lines, four of relative intensity 1 at lower fields and four of relative intensity 3 at higher fields. Clearly the first set must be the ring or vinyl protons and the latter the methyl protons. For purposes of identification we shall assign numbers to these peaks as follows, in order of increasing τ values: V(1), V(2), V(3), V(4), Me(5), Me(6), Me(7), and Me(8). We see no basis for assigning the methyl resonances to the various environments (α, β, γ, δ). The vinyl resonances may, however, be assigned, or partly assigned, by comparison with the proposed assignment,[14] which we believe to be correct, for the (COT)Mo$(CO)_3$ molecule. Thus, if the metal occupies site S, the vinyl resonances are assigned as follows.

$$\begin{array}{ll} \mathrm{V}(1) & \text{to}\quad \mathrm{A} \\ \begin{array}{l}\mathrm{V}(2)\\ \\ \mathrm{V}(3)\end{array} & \text{to}\left\{\begin{array}{ccc}\mathrm{C} & & \mathrm{D}\\ & \text{or} & \\ \mathrm{D} & & \mathrm{C}\end{array}\right\} \\ \mathrm{V}(4) & \text{to}\quad \mathrm{B}\end{array}$$

If the (COT)Mo$(CO)_3$ assignment were followed strictly, one could assign V(2) to D, but because of the closeness of the V(2) and V(3) resonances both in our molecules and the reference molecules, there may be some question about this. Since none of our arguments will depend upon the assignments of V(2) and V(3) so long as the assignments of V(1) and V(4) are known, there is no need to pursue this point further.

As Figure 1 shows, the changes which occur in the nmr spectrum as the temperature rises are continuous and, taken altogether, rather elaborate. They can, however, be described in terms of several successive *phases*. In each phase some form of intramolecular rearrangement attains a rate sufficient to cause a particular, well-defined set of proton environments to achieve time-average equivalence. Following this, the next phase, in which another well-defined environmental averaging process attains a high rate, is observed. Naturally, the averaging brought about by an early phase remains in effect as the later one(s) supervenes. *Faute de mieux*, we must assume that two or more rearrangement processes operating at the same time have a kind of orthogonality; that is, each proceeds independently of the other(s). Using this approach the analysis proceeds in two steps. First, we identify the phases in terms of their observable effects on the spectrum. Second, we attempt to deduce mechanisms which can, uniquely if possible, account for the observations.

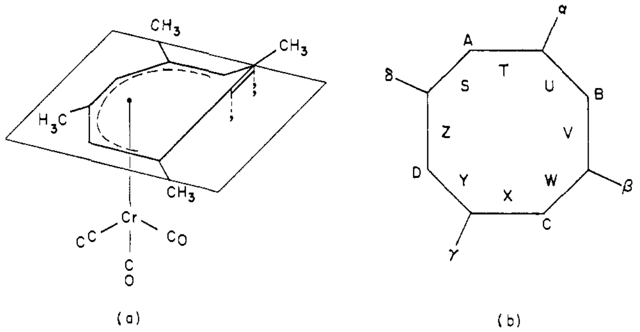

Figure 2. (a) A schematic representation of the structure of (TMCOT)Cr$(CO)_3$. (b) The labeling of methyl groups (α, β, γ, δ), ring protons (A, B, C, D), and points of attachment of the Cr$(CO)_3$ to the TMCOT ring (S, T, . . . , Z).

Phase One. As Observed. The first set of changes in the spectrum occurs between about −15° and about +70°. In the vinyl region V(2) and V(4) broaden and finally collapse (~20°) to a single peak at the mean of the initial V(2) and V(4) chemical shifts, and then this single peak sharpens and reaches its minimum width at about 70°. Up to about 50° there is *no* change in the other vinyl peaks, V(1) and V(3); above ~50° V(1) and V(3) begin to broaden, but the peak resulting from the merger of V(2) and V(4) continues to sharpen. Phase one is observed in the methyl region as a broadening of all the methyl resonances, the eventual collapse of Me(5) with Me(6) and, a little later, the collapse of Me(7) with Me(8), and finally, the sharpening up of the two merged peaks, Me(5,6) and Me(7,8). Again, minimum line widths are achieved at ~70°.

Phase One. Explanation. What we believe to be a unique explanation for the spectral changes which occur in phase one may be deduced by observing first that there are seven distinct reversible shift paths to be considered. These are shown in Figure 3. Of these seven paths, only the two shown at the top of the sketch, S ↔ T and S ↔ X, are in accord with the type of changes observed in phase one. Thus, the S ↔ T exchange would cause an averaging of the shifts of vinyl protons B and D but would leave the absorptions of A and C as distinct resonances. The S ↔ X path would average the environments of vinyl protons A and C but leave B and D distinct. Both of these correspond to the type of change observed. The three paths shown at the lower left of Figure 3 all lead to the simultaneous averaging of two pairs of environments. For example,

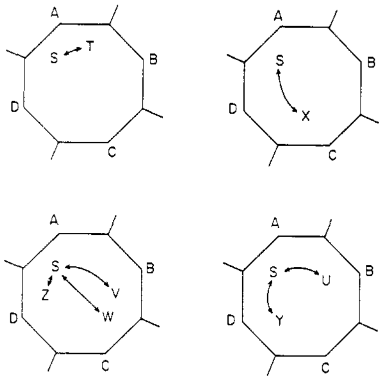

Figure 3. Sketches showing the seven possible one-step shifts which were considered to explain the phase-one spectral changes.

the S ↔ V path averages A with B and, simultaneously, C with D. The two paths indicated in the lower right lead to *complete* averaging because, though reversible, they also represent the initiation of continuous sequences of shifts in the same direction. For example, the S ↔ U shift could as well be followed by a U ↔ W shift as by a reversal (U ↔ S) of the initial shift, and then after U ↔ W there could be W ↔ Y, etc. The S ↔ U and S ↔ Y shifts are not symmetric with respect to any of the symmetry planes of the (idealized) ring and hence permit continuous advance which permutes all environments.

Either of the two paths shown at the top of Figure 3 will satisfactorily account for the changes of the spectrum in the methyl region during phase one, so long as no assignment of the vinyl resonances is made. Thus, we reduce the question of how to account for the observed changes in phase one to that of how to choose between the S ↔ T and S ↔ X paths (1,2 and 1,4 shifts). If the previously proposed assignment of the vinyl resonances is accepted, it is clear that the S ↔ T or 1,2-shift mechanism must be correct, since the A environment must remain distinct.

A Phase or Phases Following Phase One. As Observed. It is clear from Figure 1 that in the temperature range where phase one is nearing, but has not entirely reached, completion (say 50–70°), a second phase begins to be evident. The nature of the changes in this phase is not quite so unequivocal as in the case of phase one. It is clear that V(1) and V(3) begin to broaden while the two merged methyl peaks, Me(5,6) and Me(7,8), continue to narrow. It is also evident that the merged vinyl peak, V(2,4), continues to get higher as V(1) and V(3) are broadening. It is not, however, possible to determine for certain whether V(2,4) continues to *narrow* and actually becomes *narrower* than V(1) and V(3) at any time, while V(1) and V(3) are themselves beginning to collapse. An attempt to settle this point using data obtained at 100 Mc has been inconclusive. Thus, no single, unequivocal explanation for the spectral changes which follow phase one can be defended, and it is necessary to consider two possibilities. In our preliminary communication[17] only the first of these two was put forward.

(1) If V(2,4) does become narrower than V(1) and V(3) as these peaks begin to broaden, then there is a phase two which averages the environments of the protons responsible for V(1) and V(3) with each other, but does *not* exchange them with the environments of the protons responsible for the peak V(2,4). If this is so, then there must be a phase three which subsequently causes all of the vinyl proton environments and all of the methyl environments to be interchanged because, as the last three spectra in Figure 1 show, at temperatures above ∼85° all resonances broaden and collapse. Presumably, if the thermal stability of the molecules permitted observations at still higher temperatures, a single vinyl resonance and a single methyl resonance would eventually appear. Actually, the V(2,4) peak does seem to become narrow in the range 45–65° while V(1) and V(3) are broadening. We therefore seek a mechanism for a phase two in which V(1) and V(3) broaden while V(2,4) continues independently to narrow, and then a mechanism for a phase three in which there is averaging of all vinyl and all methyl environments.

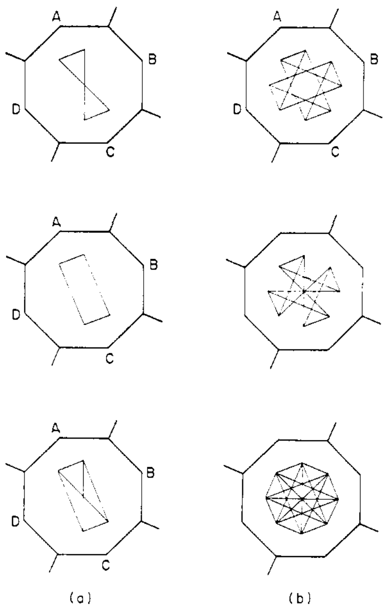

Figure 4. (a) The three possible paths of intramolecular rearrangement which could account for the observed changes immediately following phase one on the assumption that there is a phase two which does not cause complete averaging. (b) Some possible paths for a phase three to follow phase two and cause complete averaging of all ring and methyl environments.

(2) If the V(2,4) peak never actually becomes narrower than the V(1) and V(3) peaks, then, following phase one, there may be only one other phase in which interchange of all vinyl and all methyl environments occurs.

Phase Two. Explanation. Assuming that there *may* be a phase two which does not lead to complete averaging, as discussed under possibility 1 above, we seek a path which averages the A and C environments while keeping B and D (which are already being interchanged by the S ↔ T motion of phase one) separate. This can only be accomplished by some kind of transannular shift; there appear to be three possibilities as shown in Figure 4a. It is to be noted that these sketches indicate the continuance of the S ↔ T motion with the addition thereto of a second, a third, or simultaneously a second *and* a third shift path. The available experimental data do not permit one to choose among these three alternatives.

It will be clear that each of these three shift paths will cause the four methyl proton environments to be interchanged and thus account for the fact that the Me(5,6) and Me(7,8) absorptions broaden and merge as the phase-two motion accelerates.

Complete Averaging Phase. Explanation. If there is a phase two which is intermediate between phase one and a phase in which complete averaging occurs, and it is one of the three possibilities just suggested, then there are quite a number of ways in which additional shift paths might be added to those already accessible so as to allow complete averaging. Some of the possibilities are shown in Figure 4b.

Alternatively, quite independently of what has gone before, complete averaging could be achieved if the metal atom begins frequently to move to a position over the center of the ring, whence it has equal probability of going to any one of the bonding sites, S, T, . . . , Z.

Finally, there is the simplest explanation, and the one which we now consider quite attractive. We may assume that, after the 1,2 shifts of the S ↔ T type have been activated, further increase in thermal energy causes 1,2 shifts of the S ↔ Z type to become rapid. This will lead to complete averaging since, with both types of 1,2 shift able to occur rapidly, the metal atom will have rapid access to all eight possible sites, S, T, . . . , Z.

Relative Rates and Activation Energies. Only for phase one are the experimental data sufficiently complete and unambiguous to permit detailed discussion of rates and activation energies. Even here, however, high precision is difficult to attain because of the difficulties in accurately measuring experimental line widths.

Because of the absence of appreciable spin–spin couplings in the TMCOT compounds, spectra may be computed for different rearrangement rates and assumed mechanisms of rearrangement with a fair degree of rigor by the method described in the Experimental Section. This is not the case for the corresponding COT compounds owing to the sizable spin–spin couplings which are observed. Another advantageous feature of the TMCOT systems is the fact that for stage one there are a number of lines which may be used independently, thus providing strong internal checks on the estimated activation energies and frequency factors.

The results are summarized in Figure 5 and Table I.

Table I. Arrhenius Parameters[a] for Rearrangement Phase One of (TMCOT)M(CO)$_3$ Compounds

Metal, M	Resonance(s)	E_a, kcal/mole	Log A
W	Me(5)	19.3 ± 0.1	15.9 ± 0.1
Mo	Me(5), Me(6)	15.9 ± 0.7	13.4 ± 0.5
Mo	Me(7), Me(8)	16.1 ± 0.6	13.5 ± 0.4
Cr	Me(7)	15.9 ± 0.9	13.9 ± 0.7
Cr	Me(8)	16.2 ± 0.7	14.1 ± 0.7
Cr	Me(5), Me(6)	15.4 ± 1.7	13.8 ± 0.7
Cr	V(2), V(4)	15.4 ± 1.7	13.4 ± 1.2

[a] For the equation rate = $A \exp(E_a/RT)$.

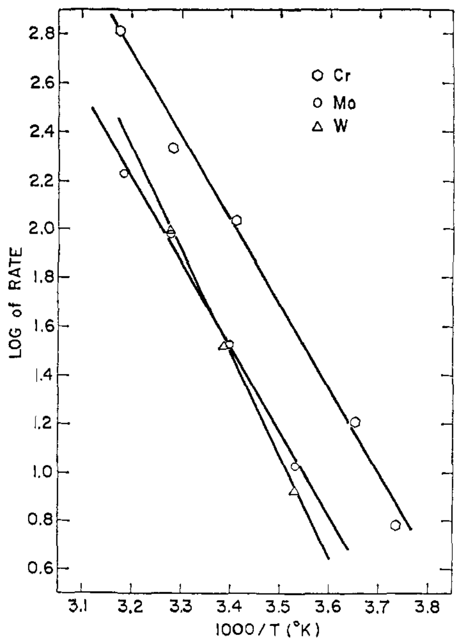

Figure 5. Representative Arrhenius plots for the phase-one intramolecular rearrangement in the (TMCOT)M(CO)$_3$ compounds.

Figure 5 shows a plot of the log (rate) values *vs.* T^{-1} for one peak or pair of peaks for each compound. The lines are the best least-squares fits. Actually for the Mo compound two such plots were made and for the Cr compound four were made. The results of all Arrhenius plots are collected in Table I. The second column of the table indicates which resonance or pair of resonances was used for each plot. When a pair of resonances was used, the widths of the separate lines at low temperature were separately measured and averaged, and the width of the merged peak was used at higher temperatures. Where only a single resonance was used, it was used alone at low temperature and the merged peak to which it contributes was used at higher temperatures.

It is evident that the four different estimates for the Cr compound agree very well considering their estimated standard deviations. The mean of the two E_a values with the lower esd is 16.0 ± 0.6 kcal/mole. For the Mo compound, the mean E_a is also 16.0 ± 0.5 kcal/mole, while for the W compound we have the lone, but significantly higher, value of 19.3 ± 0.1 kcal/mole. The order of activation energies is thus Cr $\approx$ Mo $<$ W. At present we cannot offer any straightforward rationalization for this order.

It is pertinent to give some information on the actual rates of the rearrangements. From the Arrhenius parameters for phase one of (TMCOT)Cr(CO)$_3$ at 102°, one obtains for the unimolecular rate constant, $k_1 \sim 8 \times 10^4$ sec^{-1}. For phase two, one may estimate from the line separation (using the Gutowsky–Holm equation, $k = 2^{-1/2}\pi(\delta\nu)$, as an approximation) that $k_2 \approx 2 \times 10^2$ sec^{-1}. For phase three, we estimate from the line width ($k = \pi W$, where W is the full line width at half-height, corrected for natural line width) that $k_3 \leq 40$ sec^{-1}. If, in fact, there are only two phases, then the rate of the second phase is to be taken as $\sim 2 \times 10^2$ sec^{-1}.

After the completion of this work a report by King[22] concerning the activation parameters of the parent cyclooctatetraene complexes appeared. For the series

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of compounds (COT)M$(CO)_3$ (M = Cr, Mo, W), King estimated E_a's of 6.0, 5.8, and 7.2 kcal/mole, respectively, by applying the Gutowsky–Holm[23] treatment to two of the lines, each subject to appreciable coupling effects, in the low-temperature spectra. King also obtained frequency factors in the range 4.5–16.1 $\times 10^5$ sec^{-1}. Although these parameters *might* refer to a 1,3 shift (without bond shift) rather than the 1,2 shift (with bond shift) corresponding to the phase-one activation parameters calculated in this work for the tetramethyl derivative, and even though one might expect on the basis of steric interactions a slightly higher activation energy for the tetramethyl derivative, a discrepancy of $\sim$10 kcal/mole between the activation energies for the (COT)M$(CO)_3$ compounds on the one hand and the (TMCOT)M$(CO)_3$ compounds on the other seems to deserve some comment. As pointed out by Allerhand, *et al.*,[24] one must use care not to apply equations relating line shapes to rates under certain simple circumstances in more complex circumstances where they do not hold. The Gutowsky–Holm treatment applies rigorously only to a system in which there are two spins exchanging with each other but not coupled. In $(C_8H_8)M(CO)_3$ molecules this is far from the case; there, eight spins are being permuted among four different environments with large coupling effects evident. It would not be surprising, then, to find large systematic errors in results calculated by application of the Gutowsky–Holm treatment in these cases. In particular, it can be seen that, if one neglects coupling, at slow exchange rates the apparent rate calculated from the spectra is greater than the true rate. At intermediate and faster exchange rates this error becomes progressively smaller. The effect upon the Arrhenius calculation is that E_a and log A will both be low. Hence it is hard to say what, if any, significance there is to the apparent difference between the activation parameters for the COT and TMCOT compounds.

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Stereochemically Nonrigid Organometallic Molecules. XIII. Preparation of 1,3,5,7-Tetramethylcyclooctatetraene Derivatives of the Iron Carbonyls[1,2]

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Abstract: The reactions of $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ with 1,3,5,7-tetramethylcyclooctatetraene (TMCOT) have been investigated. Using octane (bp 125°) as the reaction medium, four different compounds have been isolated and characterized. I is a yellow oil, thought to be (1,3,5,7-tetramethylbicyclo[4.2.0]octa-2,4,7-triene)iron tricarbonyl. II, a yellow solid, (TMCOT)$Fe_2(CO)_6$, is considered to be the TMCOT analog of *trans*-(COT)$[Fe(CO)_3]_2$. III, red crystals analyzing as $C_{12}H_{16}Fe_2(CO)_5$, obtained only in minute quantities, contains a tautomer of TMCOT as shown by an X-ray study reported elsewhere. IV, black crystals also analyzing as $C_{12}H_{16}Fe_2(CO)_5$, is a fluxional molecule analogous in structure (as shown by an X-ray study reported elsewhere) to the compound (COT)$Fe_2(CO)_5$ previously reported by Pettit and structurally characterized by Fleischer. Finally, by reaction of TMCOT with $Fe_2(CO)_9$ in refluxing hexane (bp 69°), orange crystals of a compound, (TMCOT)$Fe_2(CO)_6$, which is apparently analogous to Pettit's *cis*-(COT)$[Fe(CO)_3]_2$, are obtained. The compound (TMCOT)$Fe(CO)_3$ was not isolated.

The complexes formed by cyclooctatetraene (COT) with metal carbonyl moieties, $M_m(CO)_c$, have aroused considerable interest recently,[4–14] particularly because a number of then are fluxional. It has been shown[2] that the use of 1,3,5,7-tetramethylcyclooctatetraene (TMCOT) in place of COT may lead to similar or analogous compounds in which the replacement of alternating hydrogen atoms by methyl groups may have some useful consequences, such as altering the rate or even the qualitative nature of the processes responsible for fluxional behavior and effecting a desirable simplification in the limiting low-temperature

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