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Fluxional Organometallic Molecules

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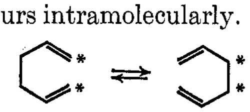
Within the past few years chemists have become actively interested in the phenomena exhibited by some molecules which, unlike the majority, have more than one thermally accessible structure and which, under conditions (especially temperatures) of interest, pass from one to another of these structures fairly rapidly. That the interest is active rather than passive is due chiefly to the availability of a good experimental method, *viz.*, observation of nmr line shapes as a function of temperature and other system variables. Of particular interest are molecules for which the several configurations of the nuclei are *equivalent*, in structure and bonding, and hence of equal free energy content. Such molecules are called, following Doering and Roth,[1] fluxional.[2] In many (but not all) cases, as these molecules pass from one configuration to another, atoms of a given chemical species pass among several different environments within the molecule. This *site exchange* process provides a basis for convenient experimental detection and mechanistic study of fluxional behavior by means of nmr spectroscopy. In this article only fluxional organometallic molecules amenable to this method of study will be considered.

It is worthwhile to emphasize, however, that fluxional molecules occur widely; there are purely organic ones and purely inorganic ones, as well as organometallic and organometalloidal ones. Muetterties[3] has called attention to a number of inorganic ones, and organic ones range from such familiar molecules as cyclohexanes[4–6] to more exotic types such as those which undergo "degenerate Cope rearrangements" (as illustrated schematically in **1**). Among the latter the most arresting is, undoubtedly, Doering's spectacular invention,[1] bullvalene (**2**).

The purpose of this article is to review some of the work which has been done on fluxional organometallic compounds. Detailed discussion will be reserved for the molecules containing unsaturated carbocycles. The chief objectives will be to summarize the methods which have been most useful and to see what generalizations can be made on the basis of existing data. In these discussions, the most stable structure, *i.e.*, the overwhelmingly predominant one (in its various nuclear permutations), will be called the *instantaneous* structure. This is the only structure which would be "seen" by the shortest time scale methods such as X-ray, neutron and electron diffraction, or vibrational spectroscopy. The set of concerted displacements of nuclei as the molecule passes from the instantaneous structure with a given permutation of the nuclei to an equivalent instantaneous structure with a different permutation of nuclei will be called the rearrangement *pathway*. In all cases it will be either known or assumed that the rearrangement occurs intramolecularly. Rearrangements known or believed to occur by dissociation–recombination processes will not be discussed here.[7]



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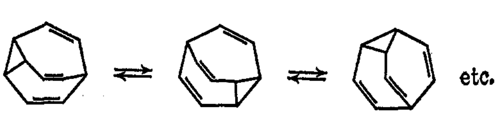

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(1) W. von E. Doering and W. R. Roth, *Angew. Chem. Intern. Ed. Engl.*, **2**, 115 (1963).

(2) When the structures are not equivalent they are properly called tautomers, the interconversion is called tautomerization, and the state of equilibrium is called tautomeric equilibrium. In a tautomeric system molecules with different instantaneous identities are present. In a fluxional system all molecules have at all times the same chemical identity. Tautomerism is, of course, a well-known classical phenomenon. In reference to fluxional molecules the literature contains such terms as "degenerate tautomerism" and "valence tautomerism." The former, while not without redeeming logic, is cumbersome; the latter is an uninformative tautology since *all* tautomerism involves changes or differences in valence. In this writer's view prompt and general adoption of the word fluxional would be useful.

(3) E. L. Muetterties, *Inorg. Chem.*, **4**, 769 (1965). Muetterties has proposed the phrase "stereochemically nonrigid" as a synonym for fluxional. Since it is more cumbersome and, according to some of my colleagues in organic chemistry, tends to have an unintended connotation of "flexible," the word fluxional is preferable. However, as a completely general phrase to embrace all kinds of molecules which undergo rapidly reversible intramolecular rearrangements, *i.e.*, tautomeric systems as well as fluxional molecules, it fills a need and has been so used in papers from this writer's laboratory.

(4) J. E. Anderson, *Quart. Rev.* (London), **19**, 426 (1965).

(5) J. D. Roberts, *Chem. Brit.*, 529 (1966).

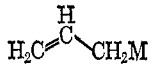
(6) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," John Wiley and Sons, Inc., Interscience Division, New York, N. Y., 1965.

(7) For a recent review dealing with nmr studies of some dissociation–recombination phenomena in organometallic molecules see T. L. Brown, *Accounts Chem. Res.*, **1**, 23 (1968).

Types of Fluxional Organometallic Molecules

The major classes are: (1) complexes of acyclic olefins, *e.g.*, allene, allyl radical or anion, and some α,ω-diphenylpolyenes; (2) compounds with a cyclopolyene σ bonded to a metal atom; (3) compounds with a cyclopolyene bonded to a metal atom through its π system; (4) compounds with one or more cyclopolyenes π bonded or σ and π bonded to several metal atoms.

Some examples of molecules in class 1 are the many allyl complexes of both transitional and nontransitional metals in which the instantaneous structure may have either localized σ bonding (**3**) or delocalized π bonding (**4**). The fluxional character of the molecules is such that each of the four terminal protons passes between the two environments available to them rapidly. Already there is an extensive literature on fluxional allyl–metal systems, sufficient to require an entire article for adequate coverage. The reader is referred to a recent article[8] which discusses certain π-allylpalladium complexes in detail and gives references to the literature on related topics.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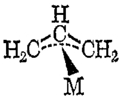
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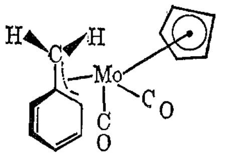
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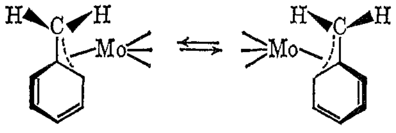
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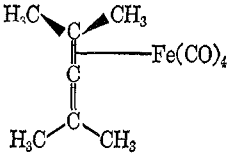
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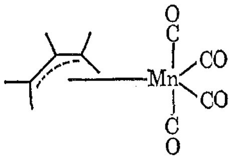
One rather special (π-allyl)metal system will be mentioned specifically here. It has been known for some time that allyl groups can become attached to metal carbonyl moieties initially through a σ bond to the α-carbon atom and then, upon heating or irradiation, a carbonyl group can be expelled with the allyl group assuming the role of a π ligand, as illustrated in eq 1. A rather unusual example of this process was reported in 1966 by King and Fronzaglia,[9] who found that, when the σ-benzyl compound, $(\pi\text{-}C_5H_5)Mo(CO)_3\text{-}CH_2C_6H_5$, is irradiated, a CO group is expelled. It seemed reasonable though a little surprising to postulate that again a π-allyl complex had been formed; in order for this to happen, delocalization of the ring π electrons must be at least partially sacrificed, as in structure **5**, which was suggested as the most likely one. But even more surprising, the molecule is fluxional; it has an nmr spectrum at −30° which is consistent with structure **5**, but at temperatures above ~60° the spectrum reveals that over a time average the 2,6 ring protons, the 3,5 ring protons, and the pair of methylene protons are equivalent. The separate resonances of the members of these pairs collapse and coalesce to sharp signals at the higher temperatures.

$$CH_2{=}CHCH_2Cl + NaMn(CO)_5 \longrightarrow$$

$$CH_2{=}CHCH_2Mn(CO)_5 \xrightarrow{\Delta \text{ and/or } h\nu}$$


+ CO (1)

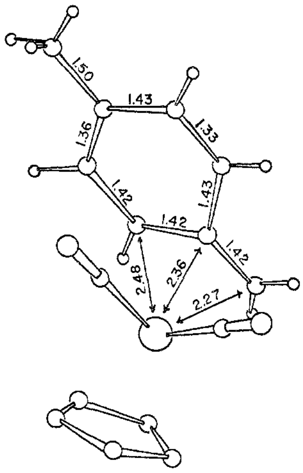


Figure 1. The molecular structure of $(\pi\text{-}C_5H_5)Mo(CO)_2(p\text{-}CH_2C_6H_4CH_3)$ as observed in the crystal at 25°.

A recent X-ray study[10] of the similar p-xylyl compound has confirmed the proposed type of instantaneous structure and provided a quantitative picture of how the benzene resonance is disturbed to make way for the (π-allyl)metal bonding, as shown in Figure 1. The rearrangement pathway was not elucidated by King and Fronzaglia, but recent work in this laboratory[11] has provided evidence for a four-site rearrangement process. The experimental data for the benzyl[9] and p-xylyl[11] compounds may be explained by the simple suprafacial jump process shown as **6** ↔ **7**. However, there are two more equivalent sites for the $(C_5H_5)\text{-}Mo(CO)_2$ group on the obverse of the benzyl ring plane and the question naturally arises as to whether the $(C_5H_5)Mo(CO)_2$ does, indeed, visit all four sites. Detailed study[11] of the temperature dependence of the proton resonance spectrum of the 3,5-diisopropylbenzyl compound permits us to conclude that this does occur. The intermediacy of a short-lived σ-benzyl intermediate seems a reasonable mechanistic possibility.

A unique molecule in the acyclic category is the tetramethylallene complex **8**, recently described by Ben-Shoshan and Pettit.[12] According to the instantaneous structure shown, the molecule should exhibit three sets of methyl proton resonances with a 1:1:2 ratio of intensities, and such a spectrum is observed below −60°. As the temperature rises this spectrum collapses, and

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[8] J. Powell and B. L. Shaw, *J. Chem. Soc., A*, 1839 (1967).

[9] R. B. King and A. Fronzaglia, *J. Am. Chem. Soc.*, **88**, 709 (1966).

[10] F. A. Cotton and M. D. LaPrade, *ibid.*, in press.

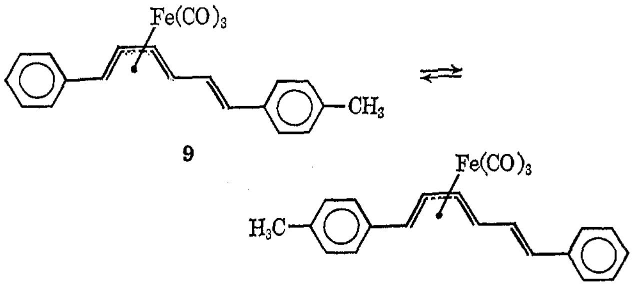
[11] F. A. Cotton and T. J. Marks, manuscript in preparation.

[12] R. Ben-Shoshan and R. Pettit, *J. Am. Chem. Soc.*, **89**, 2231 (1967).

at ~25° and above a single sharp signal is observed. The spectral changes are independent of the presence of excess tetramethylallene, thus proving that the rearrangement process is a nondissociative one. A plausible assumption is that the Fe(CO)$_4$ group moves relative to the allene in a quasihelical manner from end to end.

One other system involving an acyclic olefin will be mentioned here. While not fluxional in the same sense as the other molecules, it provides an instructive comparison with molecules to be described later.

Whitlock and coworkers[13] have shown that the tautomeric rearrangement **9** → **10** does occur, but only slowly and at elevated temperatures ($k_0 \approx 10^{-3}$ min^{-1} at 100°). The activation energy[13b] is about 32 kcal/mol. It is to be emphasized that the rearrangements **9** ↔ **10** involve 1,3 shifts in which the midway point must involve a substantially excited electronic state. Thus, to put it in simple (hopefully not oversimple) terms, the rearrangement requires a long jump over a high barrier and thus occurs only infrequently.



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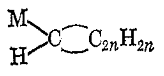

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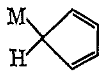

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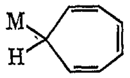

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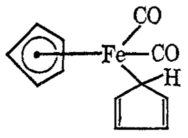
Compounds with σ-Bonded Cyclopolyenes. The molecules of interest in this section may be represented by the general formula **11**; particular examples are σ-cyclopentadienyl- and σ-cycloheptatrienylmetal compounds **12** and **13**, respectively. In actual fact, only σ-cyclopentadienyls have been prepared and studied.

The first fluxional σ-cyclopentadienylmetal compounds were discovered in 1956 by Piper and Wilkinson,[14] who also postulated, with remarkable intuition, an undetailed but essentially correct description of them as fluxional molecules.[14] The molecules in question are **14–16**. In each case infrared evidence (complex spectra in the C–H stretching region and in the fingerprint region) and chemical reactivity indicative of the 1,3-diene system supported these structures, which were entirely reasonable on the basis of valence concepts and comparison with analogous compounds. However, the proton nmr spectra contained only a single peak for $(C_5H_5)_2Hg$, a single one for each ring in $(\pi\text{-}C_5H_5)Fe(CO)_2C_5H_5$, and a single peak for all five ring protons in $(C_2H_5)_3PCuC_5H_5$. Piper and Wilkinson proposed that the appearance of single resonances for all protons in presumably σ-bonded cyclopentadienyl rings could be attributed to a rapid shifting of the metal–carbon bond among the five possible positions. It is strange that for nearly 10 years this distinctly novel situation was ignored—at least as far as the literature indicates.



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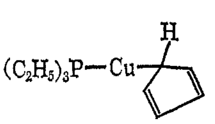

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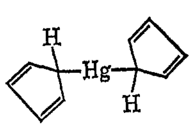

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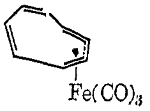

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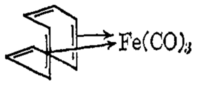

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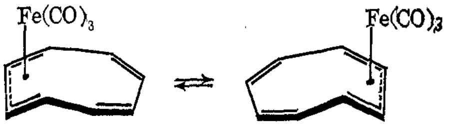

19a **19b**

In early 1965, Professor A. Davison and I discussed the work of Piper and Wilkinson and decided that the phenomena supposedly involved deserved more detailed study. An X-ray crystallographic study[15] of $(\pi\text{-}C_5H_5)Fe(CO)_2C_5H_5$ showed that the molecular structure was that assumed by Piper and Wilkinson. The temperature dependence of the proton nmr spectrum of this molecule was then studied over the range +30 to −100°. The results are presented in Figure 2. It was first shown that the spectrum which develops at about −80° and does not significantly change on further cooling to −100° (the limiting spectrum[16]) provides strong evidence that the molecule has the instantaneous structure **14** in solution. This phase of the work—establishing definitely the instantaneous structure of the molecule—will normally be the first objective in any study of a fluxional molecule, but, having done this, one would hope next to learn something about the pathway of rearrangement.

For $(\pi\text{-}C_5H_5)Fe(CO)_2C_5H_5$ the reasoning used to deduce the pathway may be briefly summarized as follows. First, the *un*symmetrical collapse of the low-field pattern (τ 3.6–4.2) eliminates any pathway in which site exchange occurs either randomly or *via* any configuration in which all sites become equivalent. The reasonable possibilities can in fact be reduced to only two, a succession of 1,2 shifts or a succession of 1,3 shifts (but not a mixture of both), in either of which the relative motions of the metal atom and the ring will

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[13] (a) H. W. Whitlock, Jr., and Y. N. Chuah, *J. Am. Chem. Soc.*, **87**, 3605 (1965); (b) C. Reich, Ph.D. Thesis, University of Wisconsin, 1968.

[14] (a) G. Wilkinson and T. S. Piper, *J. Inorg. Nucl. Chem.*, **2**, 32 (1956); T. S. Piper and G. Wilkinson, *ibid.*, **3**, 104 (1956). (b) To the best of my knowledge, these molecules are the first fluxional organometallic molecules of *any* kind to be discovered and recognized as such.

[15] 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).

[16] The resolved structure due to spin–spin coupling is another good indication, though not a proof, that a true limiting spectrum has been recorded.

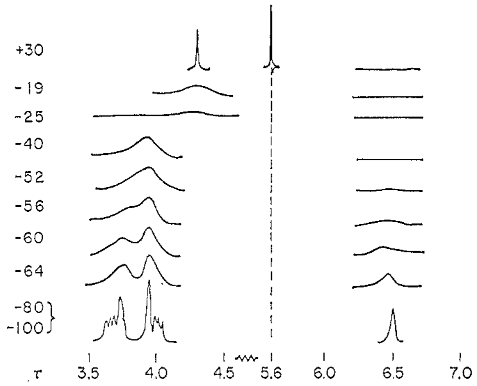

Figure 2. The proton magnetic resonance spectra of (π-C_5H_5)-$Fe(CO)_2C_5H_5$ in CS_2 at various temperatures. The position and width of the (π-C_5H_5) resonance at $\tau \sim 5.6$ are essentially invariant.

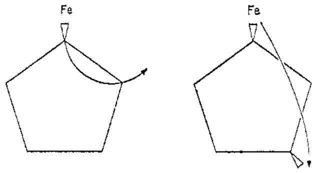

Figure 3. The most probable 1,2- and 1,3-shift pathways for rearrangement of the FeC_5H_5 groups in (π-C_5H_5)$Fe(CO)_2C_5H_5$.

most likely be such that interaction through the ring π electrons is continuously maintained, as indicated in Figure 3. The observations embodied in Figure 2 permit us to distinguish between the two paths provided the two parts of the complex low-field multiplet can be assigned.

If the proton position on the carbon atom to which the iron atom is attached is called H, the two adjacent (α) proton positions are called A and the remaining two (β) are called B, the low-field multiplet may be described as an AA′BB′ resonance, the downfield side of which is broadened more by interaction with H than is the upfield side. An assignment of predominant A and B character to the two sides of the multiplet on the basis of chemical shifts was considered too risky, but the assumption that the A protons would be more strongly coupled to H ($J_{AH} \approx 2$ Hz) than would the B protons ($J_{BH} < 0.5$ Hz) seemed fairly safe on empirical grounds. Therefore it was assumed that the downfield part of the multiplet, which obviously collapses faster than the upfield half, has predominantly A character. From this it follows that the rearrangement pathway must cause protons to enter and leave the A environments more often than they enter and leave the B environments.

Since it is easy to show[15] that a sequence of 1,2 shifts causes redistribution of protons among A environments twice as often as among B environments (whereas 1,3 shifts do just the opposite), the 1,2 pathway is proved to be correct *if the assignment of the multiplet is correct.* More recently, a study of the nonfluxional molecule (π-C_5H_5)$Fe(CO)_2$(1-indenyl) has provided further support for the assignment from which the 1,2-shift pathway is deduced.[17] The isoelectronic molecule (π-C_5H_5)$Cr(NO)_2C_5H_5$ has been shown[17] to behave very similarly to (π-C_5H_5)$Fe(CO)_2C_5H_5$.

The compound $(C_2H_5)_3PCuC_5H_5$ has also been studied;[18] the spectrum at −70° is consistent with structure **15**. Its behavior at intermediate temperatures differs from that of (π-C_5H_5)$Fe(CO)_2C_5H_5$ in that the upfield portion of the AA′BB′ multiplet collapses more rapidly. Since the upfield portion was here assigned to the B protons, the pathway was deduced to be 1,3 shifts. The assignment is only tentative, however.[19]

Compounds with Cyclic Polyolefins π Bonded to One Metal Atom. There are many compounds consisting of a metal atom partly coordinated by some carbonyl groups, $M(CO)_x$, but not enough of them to satisfy entirely its usual coordination requirements, and a cyclic polyolefin which furnishes enough π electrons to fulfill the remaining bonding capacity of the metal atom. In many cases the polyolefin, which may be either an even-membered ring such as C_4H_4 or C_6H_6 or an odd-membered one such as C_5H_5 or C_7H_7, has available precisely the number of electrons required by the metal. In such cases, the metal interacts equally with all carbon atoms of the ring, and the C_nH_nM group has C_{nv} symmetry, as in $C_4H_4Fe(CO)_3$, $C_5H_5Mn(CO)_3$, $C_6H_6Cr(CO)_3$, and $[C_7H_7Mo(CO)_3]^+$. However, when the polyolefin has one or more double bonds beyond the number required to meet the needs of the metal atom, fluxional behavior may occur. In the general case, the ring system, $C_{2n}H_{2n}$ or $C_{2n+1}H_{2n+1}$, is bound to a metal atom requiring fewer than $2n$ or fewer than $2n + 1$ electrons, so that one, two, or more double bonds remain uncoordinated to the metal atom. There are then a number of equivalent positions for the $M(CO)_x$ group relative to the ring, and the question is whether intramolecular interconversions between them can occur and how rapidly. The most thoroughly studied molecules are those containing cyclooctatetraene, but there are some examples containing C_5H_5 and C_7H_7.

The story of fluxional cyclooctatetraene (COT) complexes begins with reports of the preparation of (COT)-$Fe(CO)_3$ in 1959.[20-22] Manuel and Stone observed that the proton nmr spectrum at room temperature consisted of only a single line. After several false attempts had been made to explain this observation in terms of static structural equivalence of all protons,

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(17) F. A. Cotton, A. Musco, and G. Yagupsky, *J. Am. Chem. Soc.*, **89**, 6136 (1967).

(18) G. M. Whitesides and J. S. Fleming, *ibid.*, **89**, 2855 (1967).

(19) Resolution in the low-temperature spectrum was too poor to reveal spin–spin coupling. The basis for the assignment is such that, if correct, it requires a reversal of the assignment made[15,17] for (π-C_5H_5)$Fe(CO)_2C_5H_5$, and hence implies that 1,3 shifts are operative in that case also. This seems doubtful to me. It is entirely possible, of course, that the assignment made by Whitesides and Fleming for $(C_2H_5)_3PCuC_5H_5$ might be correct, for reasons other than those which they adduced. In that event, the 1,3-shift pathway would be operative for that compound alone. It seems to me that there is also at least a 50:50 chance that the assignment ought to be reversed, and thus 1,2 shifts would be deduced.

(20) T. A. Manuel and F. G. A. Stone, *Proc. Chem. Soc.*, 90 (1959); *J. Am. Chem. Soc.*, **82**, 336 (1960).

(21) M. D. Rausch and G. N. Schrauzer, *Chem. Ind.* (London), 957 (1959).

(22) A. Nakamura and N. Hagihara, *Bull. Chem. Soc. Japan*, **32**, 880 (1959).

X-ray study[23] showed that in the crystal the molecule has the (1,3-diene)metal structure shown schematically in **17**. It was suggested then[23] that in solution at room temperature the locus of the metal–C_8H_8 interaction changes rapidly enough to give time-average equivalence to all eight protons, but no particular rearrangement pathway was proposed.

In 1966 three publications[24–26] appeared which attempted to define more closely the nature and the behavior of the $C_8H_8Fe(CO)_3$ molecule in solution. Although secondary lines of evidence were used, the crux of each publication was the appearance of the nmr spectrum at *about* −145° (Figure 4a). Essentially the same spectrum was discussed by the three groups, and yet each came to a different conclusion. Kreiter, *et al.*, contended that this spectrum supported the assumption that the instantaneous structure in solution is **17**; they did not propose any specific rearrangement pathway. Cotton, *et al.*,[25] and Keller, *et al.*[26] argued that the observed spectrum was in fact "clearly inconsistent" with **17** on the basis that the partially resolved splitting ($\sim$0.3 Hz) of the upfield resonance (assigned to the four protons of the coordinated 1,3-diene) is much too small compared to the splittings between inner and outer protons of such groups *consistently* observed in dozens of other cases (>1.2 Hz). Cotton, *et al.*, then proposed that an instantaneous structure of the 1,5-diene type, **18**, could better explain the spectrum shown in Figure 4a and that the rearrangement process would then involve flipping the coordinated bonds out and the uncoordinated bonds in.[27] Keller, *et al.*, proposed that while the molecule does have the instantaneous structure **17** in solution, even at $\sim -145°$ it is still undergoing a rapid rearrangement, namely, the "molecular broad jump" shown as **19a** ↔ **19b** (a 1,5 shift).

Following this first round of attacks, there have appeared several more attempts to resolve the problem—and rebut the arguments of others—by further study and discussion of molecules containing iron and either C_8H_8 itself or substituted cyclooctatetraenes. Anet, *et al.*,[28] pointed out that infrared evidence on the whole favors structure **17** over **18** and also raised objections to the molecular broad jump. In a clever piece of work, Anet[29] provided persuasive evidence that the instantaneous structure of $CH_3C_8H_7Fe(CO)_3$ is of the (1,3-diene)metal type, with the methyl group at an inner position of the bound diene. Later[30] it was shown that at (perhaps) a slightly lower temperature than −145° and with the better resolution obtained at 100 MHz, the spectrum of $C_8H_8Fe(CO)_3$ is that shown in Figure 4b. This spectrum is qualitatively inconsistent with both **18** and with the **19a** ↔ **19b** scheme; it is not qualitatively inconsistent with **17**, but quantitatively still has the difficulty that the splitting in the upfield absorption is anomalously small.

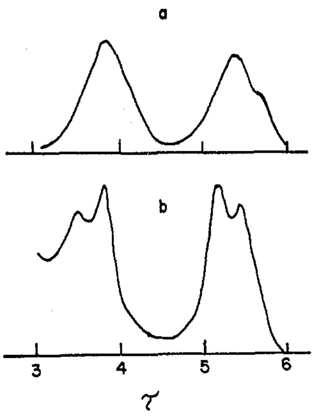

Figure 4. (a) The proton nmr spectrum of $C_8H_8Fe(CO)_3$ at $\sim -145°$ (60 MHz); (b) the spectrum at $\sim -150°$ (100 MHz).

Thus, at this stage, the weight of evidence favored structure **17**, although there were disquieting inconsistencies, but there was no evidence at all regarding the rearrangement pathway. In the hope of obtaining independent evidence on the first point and possibly some evidence on the second, we at Massachusetts Institute of Technology decided to prepare and study $C_8H_8Ru(CO)_3$. It seemed a safe assumption that its behavior would parallel that of $C_8H_8Fe(CO)_3$, and the hope was that the rate of rearrangement would be slow enough to permit truly definitive study at low temperatures. These hopes were fulfilled,[31,32] as indicated by Figures 5 and 6.

The most obvious conclusions to be drawn from the observed spectra are the following. (1) For the iron compound, the spectra observed at −145 to −155° are very far indeed from being limiting spectra. They correspond to the spectra of $C_8H_8Ru(CO)_3$ seen in the −95 to −110° temperature range. Thus, of the three original attempts to elucidate the structure and behavior of $C_8H_8Fe(CO)_3$ in solution from the low-temperature nmr spectrum, two[24,25] were based on the implicit assumption, which is now seen to be fallacious, that these spectra are limiting spectra (or nearly enough to afford structural characterization). In the third case,[26] this error was not made, but the suggestion that 1,5 shifts are required to explain the observations at −145°, with some more general averaging process supervening at higher temperatures, is unnecessarily elaborate and apparently incorrect (see below). (2) The spectra of $C_8H_8Ru(CO)_3$ at the lowest temperatures are essentially limiting spectra (even spin–spin hyperfine structure may be seen), and as such do, fully and without anomalies or ambiguities, demonstrate that the

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(23) B. Dickens and W. N. Lipscomb, *J. Am. Chem. Soc.*, **83**, 4062 (1961); *J. Chem. Phys.*, **37**, 2084 (1962).

(24) C. G. Kreiter, A. Maasbol, F. A. L. Anet, H. D. Kaesz, and S. Winstein, *J. Am. Chem. Soc.*, **88**, 3444 (1966).

(25) F. A. Cotton, A. Davison, and J. W. Faller, *ibid.*, **88**, 4507 (1966).

(26) C. E. Keller, B. A. Shoulders, and R. Pettit, *ibid.*, **88**, 4760 (1966).

(27) Just this kind of rearrangement may well occur in the isoelectronic molecule (π-C_5H_5)CoC_8H_8, although not with great facility, according to S. Otsuka and A. Nakamura, *Inorg. Chem.*, **5**, 2059 (1966).

(28) F. A. L. Anet, H. D. Kaesz, A. Maasbol, and S. Winstein, *J. Am. Chem. Soc.*, **89**, 2489 (1967).

(29) F. A. L. Anet, *ibid.*, **89**, 2491 (1967).

(30) R. Grubbs, R. Breslow, R. Herber, and S. J. Lippard, *ibid.*, **89**, 6864 (1967).

(31) F. A. Cotton, A. Davison, and A. Musco, *ibid.*, **89**, 6796 (1967).

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

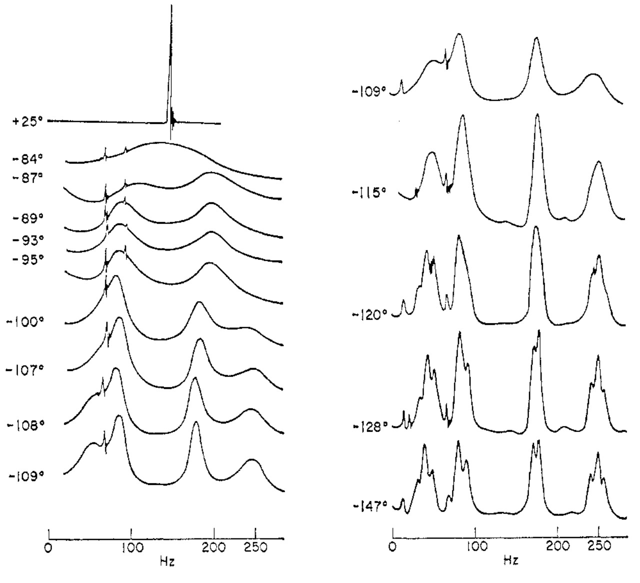


Figure 5. The measured spectra of $C_8H_8Ru(CO)_3$ at temperatures from +25° to −147°.

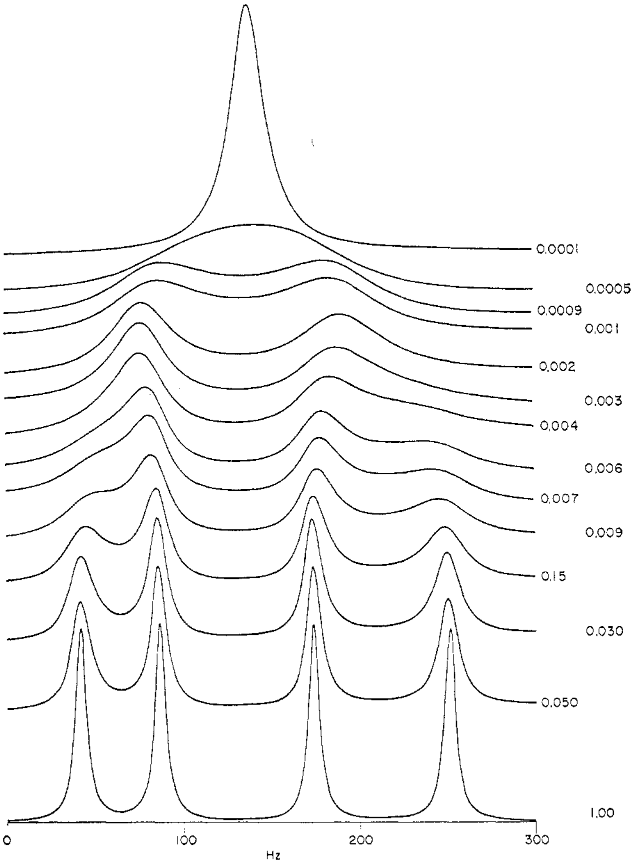


Figure 6. Computer-simulated spectra for $C_8H_8Ru(CO)_3$ assuming a 1,2-shift rearrangement pathway.

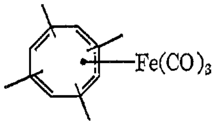
instantaneous structure is of the (1,3-diene)metal type, **17**.

In order to ascertain the rearrangement pathway, the technique of computer simulation of spectra was employed.[33] Various possible pathways were considered, *e.g.*, 1,2, 1,3, 1,4, and random shifts. The computed spectra for all but 1,2 shifts were in gross qualitative disagreement with the observed spectra. For the 1,2 shifts, the agreement is very close, as comparison of Figures 5 and 6 will show. Thus, despite the fact that there is rather a complicated set of changes occurring successively as the single-line, high-temperature spectrum evolves into the complex low-temperature spectrum, it is only necessary to invoke *one* process, a sequence of 1,2 shifts, in order to account for *all* the observations.

It is worth emphasizing that when the position of metal attachment undergoes a 1,2 shift, the entire double bond system of the ring must undergo an accompanying, concerted shift.

As an interesting aside to the study of the $C_8H_8Fe(CO)_3$ problem, an attempt was made to prepare the analogous molecule with 1,3,5,7-tetramethylcyclooctatetraene (**20**). Instead, a complex, **21**, containing the bicyclo[4.2.0] isomer is obtained.[34]

Cyclooctatetraene complexes of the $Cr(CO)_3$, $Mo(CO)_3$, and $W(CO)_3$ groups have proved to be as inherently interesting as those of $Fe(CO)_3$ and $Ru(CO)_3$, but, fortunately, more amenable to study and not provocative of controversy. The three compounds $(C_8H_8)M(CO)_3$, M = Cr, Mo, W, all have complex spectra[24,35] at −40° consistent with the structure **22**,



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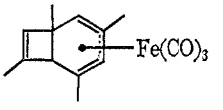

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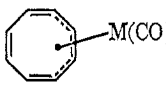

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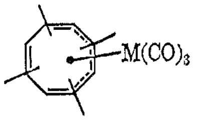

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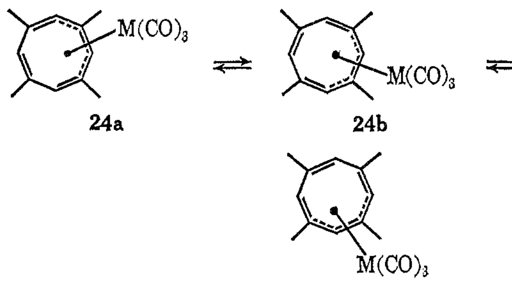
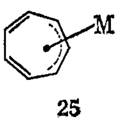


24a **24b** **24c**



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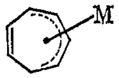

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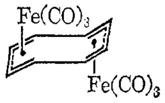

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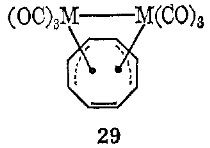

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[33] This was accomplished using a computer program written by G. M. Whitesides (*cf.* ref 18) based on matrix equations developed by R. Kubo, *Nuovo Cimento Suppl.*, **6**, 1063 (1957), and R. A. Sack, *Mol. Phys.*, **1**, 163 (1958).

[34] F. A. Cotton and A. Musco, *J. Am. Chem. Soc.*, **90**, 1444 (1968).

[35] R. B. King, *J. Organometal. Chem.* (Amsterdam), **8**, 129 (1967).

and that structure is found for $C_8H_8Mo(CO)_3$ in the crystal.[36] As the temperature is raised the spectrum broadens and collapses, and at temperatures of 50-100° consists of only a single line. This proves that there is some rearrangement process (or processes) which permutes the eight protons among all four of the different environments of structure **22**. However, studies of the $(C_8H_8)M(CO)_3$ molecules themselves have not yet afforded any direct insight regarding the detailed pathway. This is because the great amount of spin–spin coupling makes the spectra too complex for a dynamical analysis.

In order to avoid the difficulties due to spin–spin coupling in the $C_8H_8M(CO)_3$ molecules, analogous molecules containing 1,3,5,7-tetramethylcyclooctatetraene (TMCOT), **23**, were prepared and studied.[37,38] For these, the limiting low-temperature spectrum consists of four sharp ring proton resonances and four sharp methyl resonances. This spectrum collapses in such a way that there are clearly at least two successive stages of rearrangement. The first one, which affects the spectrum markedly between −30 and +70°, can be unequivocally shown to consist of the particular type of 1,2 shift depicted by **24a** ↔ **24b**. The nature of the second stage is ambiguous. It could involve the acceleration of a second process such as 1,4 and/or 1,5 shifts, which cause a still more extensive but not complete sequence of site exchanges (in which case there is probably still a third stage in which complete exchange takes place), *or* the second stage process could be the second kind of 1,2 shift indicated by **24b** ↔ **24c**. In the latter case it is clearly possible for the $M(CO)_3$ group to make a complete circuit around the ring by alternating the two types of 1,2 shift, and thus complete site exchange, leading eventually to a single line each for ring and methyl protons, will occur. Whatever may be the correct explanation beyond the first stage, the important fact is that the *most* facile process is a kind of 1,2 shift. Such a process in the case of the unsubstituted molecules, $C_8H_8M(CO)_3$, would of course lead immediately, in one stage, to complete site exchange. It seems reasonable to suppose that this is what actually happens.

Fluxional molecules containing π-bonded C_7H_7 have been reported. The compounds $C_7H_7Mo(CO)_2C_5H_5$[39] and its tungsten analog, $[C_7H_7Fe(CO)_3]^+$,[40] and $C_7H_7Co(CO)_3$ are thought to have the instantaneous structures of the types **25**, **25**, **26**, and **25**, respectively, insofar as the metal–C_7H_7 bonding is concerned, but give single-line proton nmr spectra at room temperature. For the molybdenum compound King has shown[9] that the single line broadens markedly at −40°, but in no case has anything approaching a limiting low-temperature spectrum been recorded. The molecules $(\pi\text{-}C_5H_5)Mo(NO)I(C_5H_5)$ and $(\pi\text{-}C_5H_5)Mo(NO)(CH_3)(C_5H_5)$ reported recently by King[41] appear likely to contain one C_5H_5 ring bound in the manner of **27**. All ten ring protons in these molecules give a single resonance in the temperature range −55 to +25°.

One or More Cyclic Polyolefins Bound to Two or More Metal Atoms. In addition to the $C_8H_8Fe(CO)_3$ and $C_8H_8Ru(CO)_3$ molecules which have been the subject of so much study and controversy, there are other more complex products which arise from the reactions of C_8H_8 or substituted COT's with the several iron carbonyls ($Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$) and with $Ru_3(CO)_{12}$.

In their original report of $(COT)Fe(CO)_3$, Manuel and Stone[20] also reported a yellow crystalline substance, $(COT)Fe_2(CO)_6$. This lacks bridging carbonyl absorption in the infrared and has a proton nmr spectrum[42] consisting of two equally intense absorptions at τ 4.2 and 6.7. Its structure in the crystal[23] is that shown schematically as **28**, and it evidently retains this structure, undergoing rearrangement (if at all) too slowly at 25° to affect its nmr spectrum.

Keller, *et al.*,[42] have reported a second and a third isomer of $(COT)Fe_2(CO)_6$, which I shall designate as X and Y here for simplicity. Still later, two isomers of $(COT)Ru_2(CO)_6$ were reported,[31] one being the analog of the iron compound with structure **28** and the other being the analog of X. I shall designate the latter as XRu. The nmr spectra of X and XRu are extremely similar.[31] No more will be said here about compound Y which is stated[42,43] to exist in a slowly established equilibrium with X in solution. As for X, Keller, *et al.*,[42] proposed a structure of the type **29** on the grounds that (a) this is consistent with the nmr spectrum and (b) the Mössbauer spectrum of the solid was considered to show that the two iron atoms are in identical environments. Spin-decoupling studies[31] of XRu were also consistent with structure **29**, since they point very strongly to the conclusion that the eight ring protons ought to be described as an AA′BB′-CC′DD′ set.

However, structure **29** is incorrect for XRu and hence almost certainly incorrect for X. An X-ray study[44] of XRu revealed the structure shown in Figure 7. When this structure was first solved but not refined, we tentatively considered that it would turn out to be that schematically shown as **30**. This, like **29**, has a plane of symmetry and can thus also explain the AA′BB′CC′DD′ character of the nmr spectrum.[45] However, from Figure 7 it is clear that, while **30** is topologically correct (as opposed to **29**, which is topologically incorrect), in detail **30** does not correctly

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[36] J. S. McKechnie and I. C. Paul, *J. Am. Chem. Soc.*, **88**, 5927 (1966).

[37] F. A. Cotton, J. W. Faller, and A. Musco, *ibid.*, **88**, 4506 (1966); **90**, 1438 (1968).

[38] The crystal structure of $(TMCOT)Cr(CO)_3$ was shown to be of type **23** by M. J. Bennett, F. A. Cotton, and J. Takats, *ibid.*, **90**, 903 (1968).

[39] R. B. King and M. B. Bisnette, *Inorg. Chem.*, **3**, 785 (1964).

[40] J. E. Mahler, D. A. K. Jones, and R. Pettit, *J. Am. Chem. Soc.*, **86**, 3589 (1964).

[41] R. B. King, *Inorg. Chem.*, **7**, 90 (1968).

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

[43] Compound Y has not been observed by us, nor have we seen any indication of a ruthenium analog of it, although there are some minor products in the reactions of $Ru_3(CO)_{12}$ with COT which have not been characterized.

[44] F. A. Cotton and W. T. Edwards, *J. Am. Chem. Soc.*, in press.

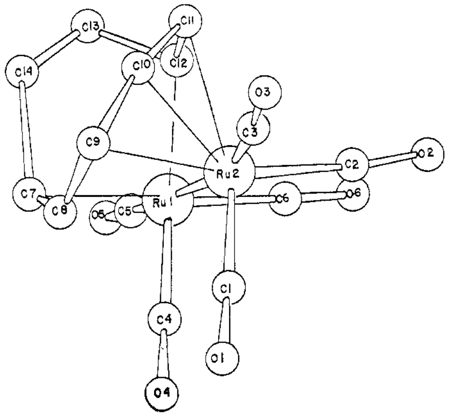
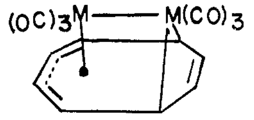


Figure 7. The structure of the $C_8H_8Ru_2(CO)_6$ molecule designated XRu.

represent the structure. In actuality, *in the crystal of XRu,* the $M_2(CO)_6$ group lies not along a potential symmetry plane but oblique to it, so that the molecule is quite far from having mirror symmetry. Indeed, some pairs of metal–carbon distances which would be equivalent in **30** differ by 0.60–0.70 Å.

In order to explain the appearance of mirror symmetry in the solution nmr spectrum at room temperature one could assume that the molecules rearrange to the static structure **30** (or even **29**) or that the instantaneous structure in solution is essentially that in the crystal, with the molecules flipping rapidly between the two equivalent forms which are related by a kind of 1,2 shift. The latter postulate of fluxional character seems more probable, but proof is lacking.



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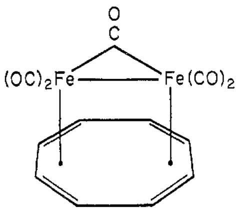

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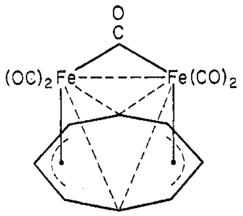

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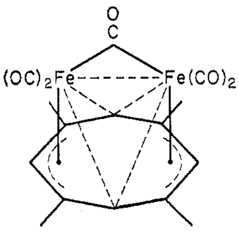

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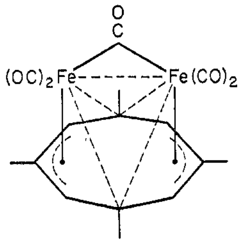

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Both X and XRu readily lose one molecule of CO, giving the substances $(COT)Fe_2(CO)_5$ and $(COT)Ru_2(CO)_5$. Both of these are fluxional molecules, having single-line proton nmr spectra at room temperature and infrared spectra in the CO stretching region consistent with the presence of $(OC)_2M(CO)M(CO)_2$ groups with C_{2v} symmetry. The two molecules are very probably isostructural. On this evidence, the very reasonable structure **31** was proposed.[42] However, an X-ray study[46] of $(COT)Fe_2(CO)_5$ revealed that, in fact, the structure is that shown schematically as **32**. This is a very curious structure. Very crudely, the bonding can be described by first postulating that each metal atom is bound to three ring atoms in a kind of (π-allyl)metal complex. Because of the short Fe–Fe distance, a metal–metal single bond can also be assumed to exist. After allowing also for the metal–CO bonds, each atom has one half-occupied orbital in its valence shell, and the two carbon atoms of the ring which have not been included in the allyl groups each have a half-occupied orbital. These four atoms, four orbitals, and four electrons combine to produce a four-center–four-electron delocalized bonding system.

The very fact that a molecule is fluxional means that there may be at least one additional type of structure which is only a little (10–15 kcal/mol) less stable than the most stable type, the set of second most stable configurations providing the lowest energy pathways for interconversion of the equivalent most stable ones. Thus a fluxional molecule is particularly likely to suffer structural change with change of environment, and it might well be asked whether the surprising structure found for $(COT)Fe_2(CO)_5$ is that which is inherently most stable or whether it is perhaps due in part to intermolecular forces. The results of several other studies indicate that **32** is inherently the most stable structure for $(COT)Fe_2(CO)_5$.

One of the complexes[34] made with 1,3,5,7-tetramethylcyclooctatetraene (TMCOT) is $(TMCOT)Fe_2(CO)_5$. Its structure has been determined in the crystal[47] and found to be of the same type as that of $(COT)Fe_2(CO)_5$. Since intermolecular forces are unlikely to operate with analogous effect in these two molecules, this result very strongly indicates that the novel structure found in each one is inherently preferable. Why it *should* be inherently preferable is an interesting question. Incidentally, for $(TMCOT)Fe_2(CO)_5$ two structures analogous to **32** are possible, differing in the placement of the methyl groups. These are shown as **33** and **34**. It is **33** which actually occurs.

It may be noted here that while studying the $(TMCOT)Fe_2(CO)_5$ molecule just mentioned, with the idea

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(45) It differs from 29 in having nonequivalent metal atoms, and thus if X has this structure, there would be an apparent inconsistency with the Mössbauer spectrum. However, as shown in ref 44, the absence of a resolved splitting due to chemical shift difference does not *prove* that the environments of the iron nuclei are identical, and there are other cases where different environments for iron atoms lead to only slightly resolved or even unresolved splittings in the Mössbauer spectra.

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

(47) F. A. Cotton and M. D. LaPrade, *ibid.*, **90**, 2026 (1968).

that it should be a genuine analog of $(COT)Fe_2(CO)_5$, as indeed it turns out to be, a second compound with the formula $(TMCOT)Fe_2(CO)_5$ was prepared.[34] Because of the relative insensitiveness of elemental analyses to a difference of one CO group and because the infrared and nmr spectra were too complex to be informative, it was not certain, prior to X-ray structural study, whether this was actually a pentacarbonyl or a hexacarbonyl. With the idea that the structure of this compound might provide some helpful clues to the natures of the $(COT)Fe_2(CO)_5$ and $(COT)Fe_2(CO)_6$ molecules, which were not at that juncture even as well understood as they are now, the crystal structure of the second $(TMCOT)Fe_2(CO)_5$ (for it did turn out to be a pentacarbonyl) was determined.[48] It is shown in Figure 8.

The compound is not a cyclooctatetraene complex at all. There has been a hydrogen atom shift to give the tautomer 1,3,5-trimethyl-7-methylenecycloocta-1,3,5-triene. Thus, the study of this compound can tell us nothing regarding the nature of any COT complex. This episode provides a very clear warning against the incautious use of a substituted "analog" to learn about the behavior of a given fluxional molecule unless it is demonstrable that the substituted molecule is truly, in all essential respects, an "analog."

Lastly, let us look with wonder on what is, thus far, the most elaborate fluxional organometallic molecule, $(C_8H_8)_2Ru_3(CO)_4$, to be characterized.[31,49] Its structure is shown in Figure 9. It contains a triangle of Ru atoms similar to that in $Ru_3(CO)_{12}$, and two cyclooctatetraene rings, each of which appeared at first[49] to be bound to a pair of Ru atoms in somewhat the same way as the rings are bound to pairs of iron atoms in the $(COT)Fe_2(CO)_5$ and $(TMCOT)Fe_2(CO)_5$ molecules described earlier. When refinement of the structure was completed, however, it was seen that each ring is oriented relative to its neighboring pair of ruthenium atoms in a manner crudely describable as half way between **31** and **32**! It is, of course, the essence of a fluxional molecule that its hould be unusually deformable in the direction corresponding to the pathway of rearrangement, and here, apparently, we see a manifestation of this. For solutions of $(C_8H_8)_2Ru_3(CO)_4$, all 16 protons are nmr-equivalent at room temperature. Finally, in addition to being a fluxional molecule containing a metal atom cluster, $(C_8H_8)_2Ru_3(CO)_4$ is a dissymmetric molecule which crystallizes in enantiomorphous crystals, each containing only one of the molecular enantiomorphs.

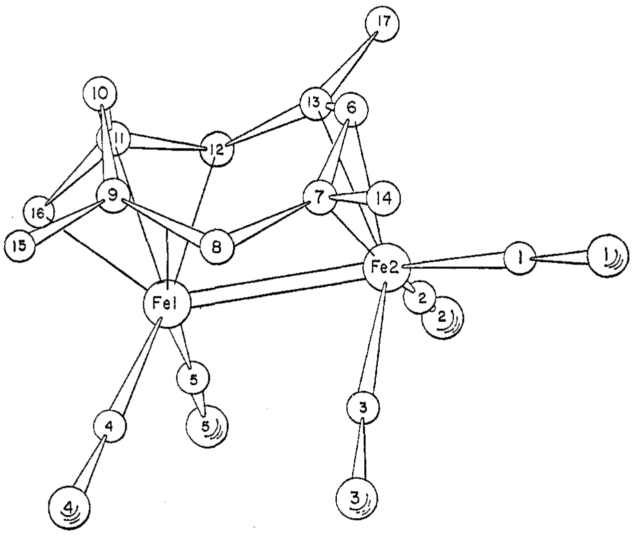

Figure 8. The molecular structure of the $C_{12}H_{16}Fe_2(CO)_5$ isomer which contains 1,3,5-trimethyl-7-methylenecycloocta-1,3,5-triene instead of TMCOT.

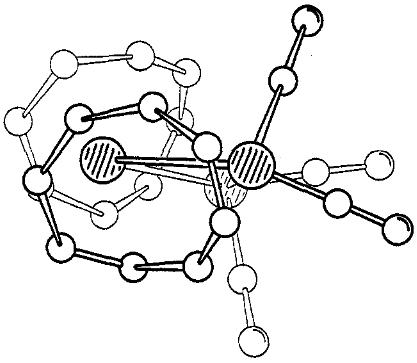

Figure 9. The molecular structure of $(C_8H_8)_2Ru_3(CO)_4$.

A Concluding Generalization

It is undoubtedly a bit early and thus a bit risky to offer any broad generalizations about the types of fluxional molecules discussed here. On the basis of the facts which have just been outlined, however, it does not seem unreasonable to venture the following tentative one. I do this not with the hope of establishing any dogma, but rather with the hope that it will stimulate more research aimed at proving, disproving, or qualifying its validity. It would appear that, in general, the easiest and preferred pathways for rearrangement in these molecules are based on 1,2 shift processes. In other words, a kind of "principle of least action" is in effect. There may, of course, be instances in which some topologically different pathway will turn out to be more economical in distance and activation energy, but I know of none which has yet been validated experimentally. "Molecular broad jumps," unless they can occur through some symmetric intermediate, seem particularly unlikely.

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