The structure of $(C_8H_{10})Fe_2(CO)_6$ in the solid state is of very particular interest because this is precisely the compound which initiated the postulation of structures such as II and III on the basis of Mössbauer data.[5] We thus have a direct and irrefutable invalidation of the Mössbauer criterion as applied to the case of $(C_8H_{10})Fe_2(CO)_6$ and, by direct implication, in the case of $(C_8H_8)Fe_2(CO)_6$. It is perhaps a little less certain that the structure postulated for $(C_7H_8)Fe_2(CO)_6$ is also incorrect, because the change in ring size *could* lead to significantly different bonding proclivities in the C_7 system as compared to the C_8 systems. However, it seems to us that the correct structure of $(C_7H_8)Fe_2(CO)_6$ is likely to be similar to those we have found for $(C_8H_8)Ru_2(CO)_6$ and $(C_8H_{10})Fe_2(CO)_6$.

It is now abundantly clear, if indeed it was not already so, that in Mössbauer spectroscopy as in all other types of spectroscopy there is great danger in using negative evidence (absence of bands, failure to observe splittings, etc.) to infer structures.

We know of at least one instance[19] in which a structure has been assigned by analogy with II. Presumably a structure analogous to V should be assigned instead.

[19] G. N. Schrauzer and P. W. Glockner, *J. Am. Chem. Soc.*, 90, 2800 (1968).

Stereochemically Nonrigid Organometallic Molecules. XIX.[1a] (1,2,3-*Trihapto*:4,5,6,7-*tetrahapto*cycloheptatrienyl)-[(*pentahapto*cyclopentadienyl)dicarbonylmolybdenum]-[tricarbonyliron].[1b] Preparation, Structure, and Temperature-Dependent Proton Magnetic Resonance Spectrum[2]

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Contribution from the Department of Chemistry,
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Received August 26, 1968

Abstract: A compound containing both the $C_5H_5)(CO)_2Mo$ and $Fe(CO)_3$ groups bound to a cycloheptatrienyl ring, C_7H_7, has been prepared by photochemical reaction of $(C_7H_7)(C_5H_5)Mo(CO)_2$ with$Fe(CO)_5$ and/or $Fe_2(CO)_9$. This red crystalline compound, $(C_5H_5)(CO)_2Mo(C_7H_7)Fe(CO)_3$, appears to have a structure in which the $(C_5H_5)(CO)_2Mo$ group lies over one face of the C_7H_7 ring and interacts wth a sequence of three carbon atoms (a π-allyl-type complex) of the C_7H_7 ring, while the $Fe(CO)_3$ lies over the other face and interacts with a butadiene-like sequence of four carbon atoms. The molecule is fluxional and gives a pmr spectrum consistent with this structure only at temperatures below about −50°. Above this temperature the complex pattern of resonances due to the C_7H_7 ring collapses, and at room temperature and above these seven protons give only a single resonance. The Arrhenius activation energy for the rearrangement (in 4:1 $CDCl_3/CD_3C_6D_5$) is 13 ± 1 kcal/mol. The low-temperature spectrum collapses unsymmetrically and detailed analysis, including comparison with computer-simulated spectra, permits us to exclude all rearrangement pathways except 1,2 shifts or a mixture of 1,2 and 1,3 shifts.

One way of classifying fluxional organometallic molecules[4] is according to the number of metal atoms bonded to the organic moiety, usually a cyclic olefin, which is intramolecularly mobile. There are a number of molecules known with two such metal atoms, but in all cases in which fluxional character is definitely established, these two metal atoms are on the same side of the ring and are connected to each other.

It was the objective of the investigation reported here to prepare and characterize a fluxional compound with two separate, unconnected metal atoms lying on opposite sides of a cyclic polyolefin.[5] In fact, the molecule we have studied, shown schematically as I, contains two different metal atoms in different environments. It is of particular interest because it combines two mononuclear systems, *viz.*, II[8] and III,[9] each of which is already known to be fluxional.

A point of particular interest is how the simultaneous attachment of both metal-containing moieties will affect the rate of rotation of the cycloheptatrienyl ring, as

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[1] (a) Part XVIII: F. A. Cotton and P. Legzdins, *J. Am. Chem. Soc.*, **90**, 6232 (1968). (b) For an explanation of the nomenclature see F. A. Cotton, *ibid.*, **90**, 6230 (1968).

[2] This study was supported in part by Grant No. GP 7034X from the National Science Foundation.

[3] National Institutes of Health Postdoctoral Fellow, 1968.

[4] F. A. Cotton, *Accounts Chem. Res.*, 1, 257 (1968).

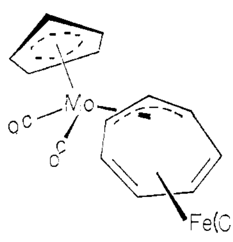
[5] The only well-characterized[6,7] molecule of this type which has been previously reported is *trans*-$C_8H_8[Fe(CO)_3]_2$, but this does not show fluxional character,[7] at least up to room temperature.

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

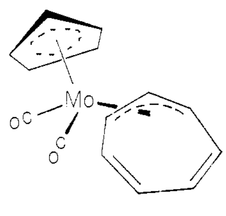
[7] C. E. Keller, G. F. Emerson, and R. Pettit, *J. Am. Chem. Soc.*, **87**, 1388 (1965).

[8] R. B. King and M. B. Bisnette, *Inorg. Chem.*, 3, 785 (1964). In this paper an unsuccessful attempt to prepare I from II is mentioned.

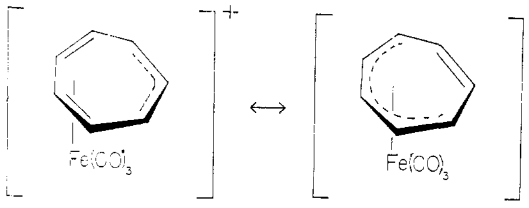
[9] J. E. Mahler, D. A. K. Jones, and R. Pettit, *J. Am. Chem. Soc.*, **86**, 3589 (1964).



I



II



III

compared to the rates in the mononuclear systems. It might be expected that more energy would be required to move the ring so as to displace simultaneously two metal–ring interactions from their most stable configurations to less stable ones (activated state or unstable intermediate) than to do this for either of the metal-to-ring interactions separately. Thus, an increase in activation energy and a decrease in rate would be expected. This effect could, if too extreme, cause the molecule to lose its fluxional character. Hopefully, however, a moderate effect of this sort would have the beneficial result of slowing the rearrangement just sufficiently to make it more amenable to study. Thus, for II, King and Fronzaglia[10] found that even at −40° the C_7H_7 resonance had only broadened by a factor of about 5 relative to its width at 25°. Subsequently, however, Faller[11a] has carried out studies at temperatures down to −118°, whereby he has obtained spectra with well-resolved spin–spin couplings and established that rearrangement proceeds, as in the majority of fluxional olefin-metal complexes,[11b] by a sequence of 1,2 shifts. Because Faller's low-temperature spectra raise the possibility that this molecule in solution may contain a *monohapto-* rather than the *trihapto*cycloheptatrienyl ring shown in II, we have refrained from giving it a systematic name.

A second interesting and useful feature expected of I compared to II is that the resonances of the four protons in the butadiene moiety should be separated into a low-field resonance due to the inner pair and a high-field resonance due to the outer pair. On the basis of a great deal of empirical knowledge,[12] assignment of these resonances should be unequivocal and their great separation (~2 τ units) should aid in interpreting line-shape changes in the temperature range of intermediate exchange rates.

Experimental Section

All operations were carried out in an atmosphere of prepurified nitrogen.

Cycloheptatrienylcyclopentadienyldicarbonylmolybdenum. This compound was prepared according to the method of King and Bisnette.[8]

(1,2,3-*Trihapto*: 4,5,6,7-*tetrahapto*cycloheptadienyl)[(*pentahapto*-cyclopentadienyl)dicarbonylmolybdenum][tricarbonyliron]. A mixture of 2.0 g (0.065 mole) of cycloheptatrienylcyclopentadienyldicarbonylmolybdenum, 50 ml of iron pentacarbonyl, and 100 ml of ether was degassed in a photolysis vessel and then irradiated, under nitrogen with stirring, with a 450-W Hanovia high-pressure mercury vapor lamp equipped with a water-jacketed quartz immersion well and a Pyrex filter. After 4 days of irradiation, the reaction mixture was filtered from about 5 g of diiron enneacarbonyl (formed from irradiation of iron pentacarbonyl). The residue was washed with methylene chloride. The filtrate was concentrated at 20 torr (50°) to remove iron pentacarbonyl. The residue was placed on a chromatography column packed with 100 g of alumina (Woelm, neutral grade). Elution with methylene chloride removed a red band, which yielded 1.6 g (55% yield) of a red solid. The nmr spectrum (deuteriochloroform) showed a broad singlet at τ 5.43 (7 H) and a sharp singlet at τ 4.87 (5 H) as well as sharp singlets at τ 5.05 (7 H) and 4.78 (5 H) corresponding to about 15% of the initial molybdenum complex.

A portion of the crude product was purified by crystallization from methylene chloride–*n*-hexane solution upon rapid cooling to −70°. Red crystals, mp 176° dec, stable to air, were obtained. The infrared spectrum of a cyclohexane solution had CO stretching maxima at 1880, 1950, 1975, 1980, and 2040 cm^{-1} (all ±5 cm^{-1}).

Anal. Calcd for $C_{17}H_{12}O_5FeMo$: C, 45.56; H, 2.70; Mo, 21.41; Fe, 12.47; mol wt, 448.1. Found: C, 45.6; H, 2.85; Mo, 21.5; Fe, 12.7; mol wt ($CHCl_3$), 452.

Reaction of $(C_5H_5)(C_7H_7)(CO)_2Mo$ with $Fe_2(CO)_9$ in *n*-heptane for 24 hr at 80° gave very small amounts (about 5% yield) of the iron tricarbonyl complex, as detected by nmr analysis.

Instrumental Measurements. Infrared 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 chart supplied by Varian Associates.

The sample for recording nmr spectra was placed in a standard nmr tube and a mixture of deuteriochloroform with toluene-d_8 (4:1) containing 2% tetramethylsilane, which had previously been degassed by pumping and freezing on the vacuum line, was distilled under high vacuum onto the solid. The tube was then sealed under vacuum and spectrum measured immediately.

Melting points were determined on a Buchi melting point apparatus calibrated with USP standard samples.

Analyses and molecular weight were determined by Galbraith Laboratories, Inc., Knoxville, Tenn.

Results

The Instantaneous Structure. The pmr spectra of the molecule at various temperatures are shown in Figure 1. These results show clearly that the molecule is fluxional, and this aspect of its behavior will be discussed in detail presently. We shall first consider the evidence pertaining to the instantaneous structure.

The lowest temperature spectrum (−71°) is in good accord with structure I. It must be conceded that we have no substantive evidence for the postulated *trans*

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

[11] (a) J. W. Faller, *Inorg. Chem.*, in press; (b) F. A. Cotton, *Accounts Chem. Res.*, **1**, 257 (1968).

[12] (a) C. E. Keller, B. A. Shoulders, and R. Pettit, *J. Am. Chem. Soc.*, **88**, 4760 (1966); (b) R. Pettit and G. F. Emerson, *Advan. Organometal. Chem.*, **1**, 12 (1964); (c) M. L. Maddox, S. L. Stafford, and H. D. Kaesz, *ibid.*, **3**, 1 (1965).

arrangement of the metal atoms as against a *cis* one, but it seems very unlikely that the crowded *cis* structure could be more stable than the *trans* one since the metal-to-ring bonding potentialities would be essentially the same for both. Also, the representation I is a schematic one and is not intended to specify in detail finer features such as puckering of the C_7H_7 ring and the rotational orientations of the $(C_5H_5)Mo(CO)_2$ and $Fe(CO)_3$

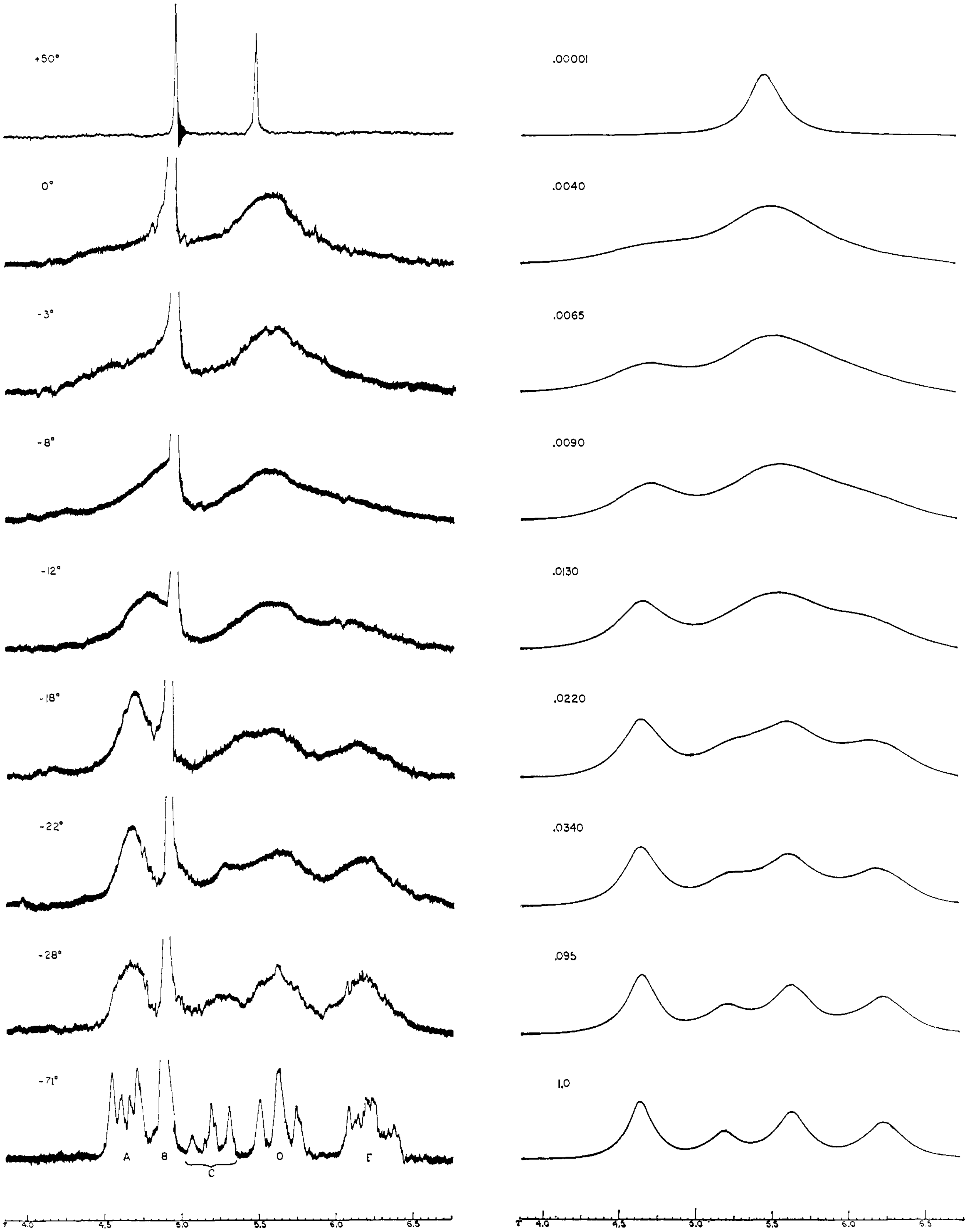


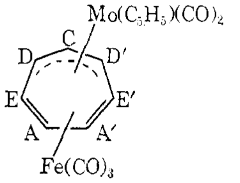
Figure 1. (a) Left side: observed pmr spectra at various temperatures. (b) Right side: spectra computed for various mean residence times in seconds assuming rearrangement exclusively by a sequence of 1,2 shifts.

groups. An X-ray study of the crystalline compound has been undertaken in order to confirm the *trans* structure and gain information on the structural details, particularly bending or puckering of the ring, which may be critical to the fluxional character of the molecule.

The low-temperature spectrum is seen to consist of five multiplets, labeled in Figure 1 as A, B, C, D, and E, which have relative intensities of 2,5,1, 2, 2. The resonance B, a singlet of relative intensity 5, is obviously due to the cyclopentadienyl protons. The remaining resonances must be assigned to the C_7H_7 ring. Relevant characteristics of these resonances are summarized in Table I.

The multiplet A may be unambiguously assigned to the inner protons of the butadiene group bound to $Fe(CO)_3$ on the basis of its chemical shift.[12] The peculiar pattern of intensities has also been observed in resonances due to these protons in other compounds having butadiene-to-$Fe(CO)_3$ moieties and adds further weight to the assignment. The assignment of multiplet C to the unique proton of the allylic grouping bound to the molybdenum atom is evident from its intensity. The triplet structure is due to splitting by the pair of equivalent protons (the D protons, as will be seen, with $J_{CD} \approx 7.0$ cps) and is distorted from the first-order 1:2:1 intensity distribution by second-order coupling with the proximate D protons.

The assignment of the D and E multiplets is based on the following considerations. Empirical data[12] on chemical shifts and couplings in butadiene–$Fe(CO)_3$ moieties indicate that for the outer protons the resonance should occur at least 80 cps higher than that of the inner protons and generally above τ 6, and that the effects of both strong coupling to the adjacent inner proton ($\sim$7 cps) as well as weaker coupling ($\sim$3 cps) to the nonadjacent inner proton should be observed. Since each outer proton of the butadiene–$Fe(CO)_3$ grouping would also experience splitting from the adjacent proton of the allyl-$Mo(C_5H_5)(CO)_2$ grouping, we may expect that the resonance due to the outer butadiene–$Fe(CO)_3$ protons should be a complex multiplet lying at upwards of τ 6. Clearly resonance E fits this description, while resonance D does not. The chemical shifts for the *syn* outer protons of π-allyl complexes are variable, but the D resonance is within the observed range. Moreover, the triplet structure of D has a satisfactory interpretation in terms of essentially equal splitting ($\sim$7 cps) of the resonance of each outer allyl proton by coupling with the unique allyl proton and with the adjacent outer butadiene–$Fe(CO)_3$ proton. These assignments are summarized diagrammatically in IV.



IV

The low-temperature pmr spectrum as well as the other spectra to be discussed below were run in the solvent mixture $CDCl_3/CD_3C_6D_5$ (4/1) in order to avoid having the C_5H_5 line overlap the A resonance. In pure $CDCl_3$ the C_5H_5 line occurs at τ 4.79, partially obscuring the A resonance, whereas in the mixed solvent, it is at τ 4.91, and this falls between the A and C resonances as may be seen in Figure 1. As Table I shows, the other resonances also suffer appreciable shifts on introducing 20% toluene into the chloroform. The use of mixed solvents containing benzene or toluene to make desirable shifts in line positions may well be a useful trick in other cases.

Table I. The Low-Temperature Pmr Spectrum of the C_7H_7 Ring

Multiplet[a]	Chemical shifts (τ) $CDCl_3$	 $CDCl_3$/$CD_3C_6D_5$[b]	Rel intensity	Pattern
A	4.60	4.63	2	Double doublet
C	5.02	5.18	1	Distorted triplet
D	5.50	5.63	2	Triplet
E	6.17	6.23	2	Complex

[a] Line B is due to C_5H_5. [b] $CDCl_3/CD_3C_6D_5$ ratio is 4:1.

The infrared spectrum is also in accord with a structure of type I in showing five CO stretching bands. By comparison with the reported spectra of II[13] and of $C_8H_8Fe(CO)_3$,[14] the $(C_5H_5)Mo(CO)_2$ absorptions may be either 1880 and 1950 cm^{-1} or 1880 and 1975 cm^{-1}, while the bands due to the $Fe(CO)_3$ group may be either those at 1975, 1980, and 2040 cm^{-1} or those at 1950, 1980, and 2040 cm^{-1}.

Of particular importance is the fact that only the expected five bands for a single structure of type I are seen. This indicates that there is only one isomer present in detectable quantity, whereas in several other molecules having allylic residues bound to the $(C_5H_5)Mo(CO)_2$ group[13,15] the infrared spectrum (and sometimes also the nmr spectrum) shows the presence of two isomers. The isomerism is believed[15] to depend upon the rotational orientation of the $(C_5H_5)(CO)_2Mo$ group relative to the allylic moiety.

Fluxional Behavior. The set of spectra presented in Figure 1 shows that $(C_5H_5)(CO)_2Mo(C_7H_7)Fe(CO)_3$ is a fluxional molecule. As the temperature rises above about $-50°$, broadening of the resonances associated with the C_7H_7 ring becomes noticeable. Broadening continues until finally at about $+10°$ the entire spectrum has coalesced into one line which then narrows with increasing temperature. At $+50°$ a measurement of the areas of the two resonances using the instrument integrator gave a ratio of 5.0:7.0. In the $+50°$ spectrum the line due to C_7H_7 lies at τ 5.43 $\pm$ 0.01 while the weighted average of the positions of the four multiplets in the limiting low-temperature spectrum is τ 5.45 $\pm$ 0.05.

A line-shape analysis was carried out in order to learn something about the pathway of the intramolecular rearrangement responsible for the observed changes in the spectrum. While there is no experimental proof that the site exchanges do in fact arise intramolecularly, the possibility that some intermolecular process is responsible seems too remote to merit consideration. Dissociation and recombination of the metal-containing moieties and the C_7H_7 ring or interchanges of two such rings between two molecules would seem certain to re-

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(13) R. B. King, *Inorg. Chem.*, **5**, 2242 (1966).

(14) E. T. Bailey, E. R. Lippincott, and D. Steele, *J. Am. Chem. Soc.*, **87**, 5346 (1965).

(15) A. Davison and W. C. Rode, *ibid.*, **6**, 2124 (1967).

quire activation energies far too high to permit rapid site exchange at temperatures below 0°.

Four intramolecular processes were considered: 1,2 shifts, 1,3 shifts, 1,4 shifts, and random shifts. By a 1,2 shift we mean a movement of the ring relative to the metal atoms which shifts the points of attachment of the metal atoms from their starting positions to the next nearest equivalent ones. 1,3 and 1,4 shifts carry the metal–ring attachments to the second and third nearest positions to the starting one. Each of these shifts is of course reversible. By random shifts we mean *either* of two things: a random mixture of 1,2, 1,3, and 1,4 shifts (each occurring in both directions) or a process whereby the seven protons simultaneously reach a common

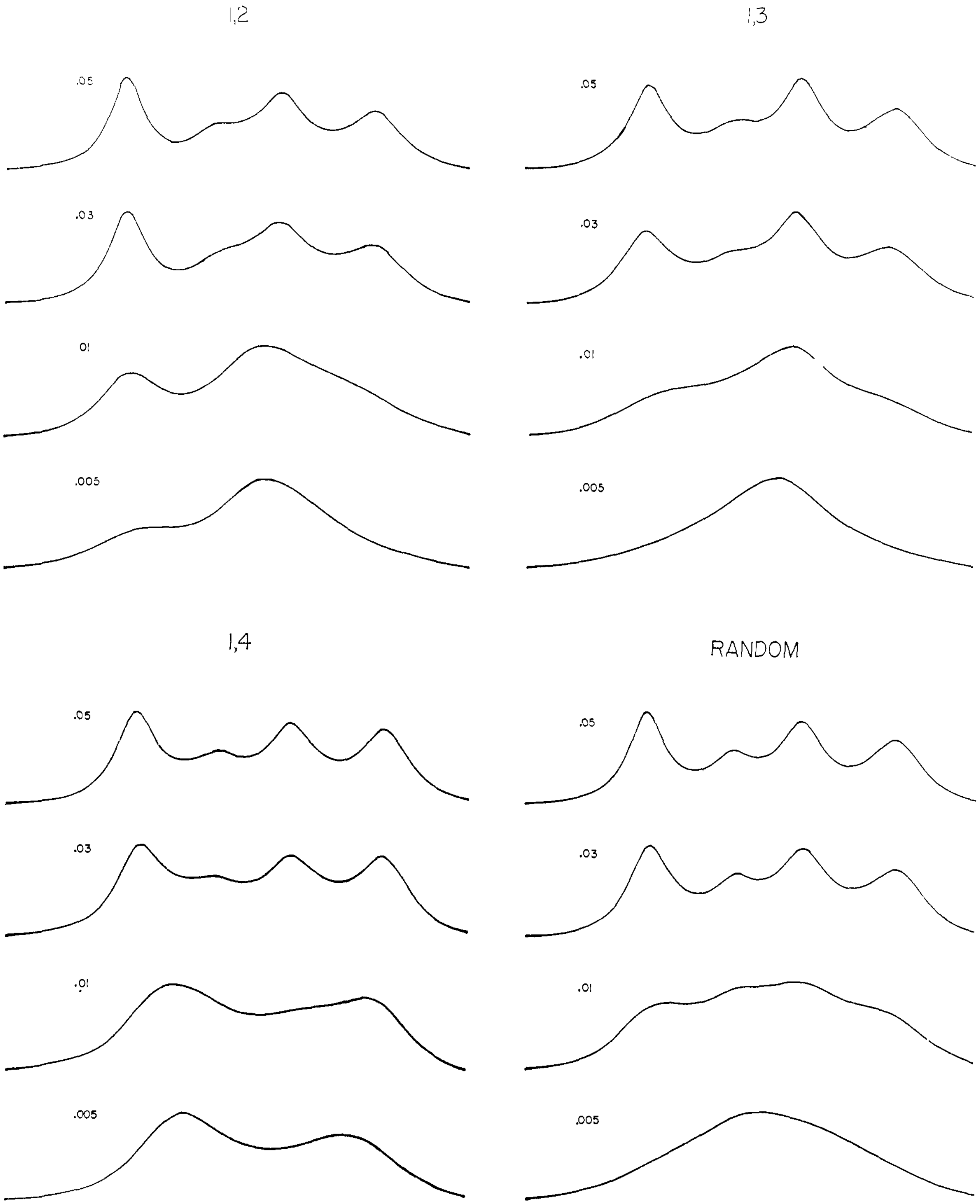

Figure 2. A comparison of sets of spectra computed at the same four mean residence times assuming sequences of each of four possible shifts as the exclusive pathway for rearrangement.

environment from which they may return to any one of the ground-state environments with equal probability. Insofar as our experimental results and calculations are concerned, these two interpretations of the term random shifts are indistinguishable so long as the intermediate affording momentary equivalence of all protons is short-lived. Physically, this second process might occur if the two metal-containing groups were to move from their off-center positions to positions along the C_7 axis of a plane heptagonal ring, whence they could return to each of the seven sets of off-center positions with equal probability.

The discrete shift processes (1,2, 1,3, and 1,4) are in principle qualitatively distinguishable because each process causes a different type of site to participate in exchange with only half the frequency of the others. This will tend to cause the resonance of protons at that site to collapse more slowly than the other resonances. The following lists of before-shift and after-shift site labels show that for 1,2 shifts, 1,3 shifts, and 1,4 shifts it is A, D, and E sites, respectively, which have the slower exchange.

$$\begin{bmatrix}A\\E\\D\\C\\D'\\E'\\A'\end{bmatrix}\longrightarrow\begin{bmatrix}A'\\A\\E\\D\\C\\D'\\E'\end{bmatrix}$$

1,2

$$\begin{bmatrix}A\\E\\D\\C\\D'\\E'\\A'\end{bmatrix}\longrightarrow\begin{bmatrix}E'\\A'\\A\\E\\D\\C\\D'\end{bmatrix}$$

1,3

$$\begin{bmatrix}A\\E\\D\\C\\D'\\E'\\A'\end{bmatrix}\longrightarrow\begin{bmatrix}D'\\E'\\A'\\A\\E\\D\\C\end{bmatrix}$$

1,4

In practice, the use of the qualitative criterion is restricted by the fact that the broadening of a resonance is affected not only by the mean lifetime of nuclei in the corresponding environment but also by the frequency separation between the resonance for that environment and the resonances for the environments with which direct site exchanges occur. It is difficult to make proper allowance mentally for these two factors and thereby to deduce with certainty a predominant shift sequence by simply inspecting experimental spectra. In the present case, the A resonance appears to collapse more slowly than the C, D, and E resonances, thus suggesting that 1,2 shifts are predominant. However, the A resonance is also further removed from the mean position of the other three than they are from each other, so that this conclusion is not a certainty.

The way to avoid these ambiguities is to utilize a digital computer to simulate spectra for each of the shift processes assuming various mean residence times in the preferred configuration; these sets of computed spectra are then compared with the observed spectra to see which process leads to the best over-all agreement. This approach has been used several times[16,17] before in dealing with fluxional organometallic molecules. Details of the method and references to earlier literature may be found in the papers cited.

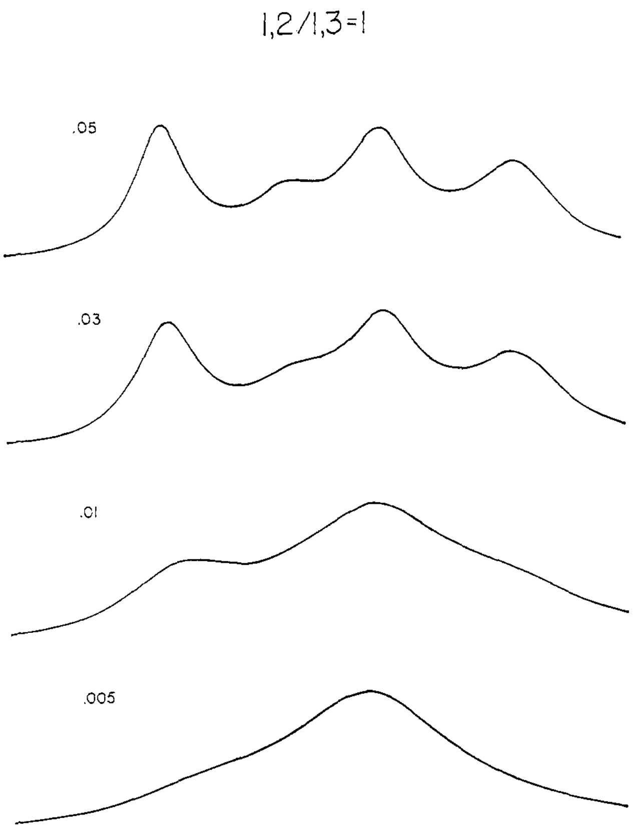

Figure 3. Spectra computed at several mean residence times for a random mixture in equal proportions of 1,2 and 1,3 shifts.

On the right side of Figure 1 are spectra computed at different mean residence times for the sequence of 1,2 shifts. It will be seen that the pattern of calculated line-shape changes is very similar indeed to that observed and strongly supports the conclusion that 1,2 shifts play a prominent role in the fluxional behavior of the molecule. In Figure 2 the computed spectra for 1,2 shifts through the critical range of residence times, 0.005–0.05 sec, are compared with spectra computed through the same range of residence times for the other three processes. It is obvious that pure 1,4 shifts and random shifts give grossly dissimilar patterns, and they can each be ruled out as accounting in themselves for the observed behavior of the molecule.

The pattern of changes given by pure 1,3 shifts differs less drastically from the observed pattern (and from that calculated for 1,2 shifts) but still fails to match in certain crucial respects. In particular, as the earlier qualitative considerations would suggest, it gives too rapid a collapse of the A resonance while permitting the D resonance to survive too long. However, even though it seems quite clear that *pure* 1,3 shifts fail to account for the observations, the question is raised as to whether 1,3 shifts may occur *along with* and perhaps a little less frequently than 1,2 shifts.

In order to test the possibility of mixed mechanisms short of the completely random mixing of all three types of shift in equal proportions, spectra were computed for 1,2 + 1,4 in equal proportions, 1,3 + 1,4 in equal proportions, 1,2 + 1,3 in equal proportions, and

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(16) G. M. Whitesides and J. S. Fleming, *J. Am. Chem. Soc.*, **89**, 2855 (1967).

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

1,2 + 1,3 in a ratio of 4/1. The first two mixtures could be rejected quite confidently. The 1,2 + 1,3 mixture in the ratio 4/1 gave spectra scarcely distinguishable from those for pure 1,2 shifts, and the mixture must be considered to provide an acceptable explanation for the observed spectra. For an equal mixture of 1,2 and 1,3 shifts, the spectra shown in Figure 3 are obtained. We think that these spectra are slightly but definitely less satisfactory than those given by pure 1,2 shifts and feel that the proportion of 1,3 shifts cannot be as high as 50%. However, the reader may inspect Figure 3 and make his own judgment.

In summary, comparison of computed and observed spectral changes shows that the latter can only be accounted for by a rearrangement pathway which either consists exclusively of 1,2 shifts or consists mainly of 1,2 shifts with 1,3 shifts occurring no oftener than about 40% of the time.

If we make the reasonable assumption that rotation of the C_7H_7 ring occurs without significant movement of the metal atoms relative to each other, then the points obtained by dropping a perpendicular from each metal atom onto the mean C_7H_7 ring plane will trace out circles concentric with the heptagon approximating to the time-average ring conformation. It would then be impossible for a 1,3 shift (or a 1,4 shift either) to occur as distinct from two (or three) 1,2 shifts. On this basis, we would come to the final conclusion that the overwhelmingly predominant intramolecular rearrangement process in this molecule is the 1,2 shift and that the averaging of proton resonance signals may be attributed to a rapid sequence of 1,2 shifts.

By choosing residence times which permit the closest practical match of a computed spectrum (for 1,2 shifts) to each of several observed spectra (specifically, those at 0, −3, −8, −12, −18, and −22°; see Figure 1 for the goodness of fit), a set of rate constants at various temperatures was obtained. These data gave a good Arrhenius plot from which the following activation parameters were extracted: $E_a = 13 \pm 1$ kcal/mole; $\log A = 12.7 \pm 0.8$; $\Delta S^* = -2$ eu at 273° and +2 eu at 251°.

Local Orbital and Bond Index Characterization of Hybridization

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Contribution from the Sterling Chemistry Laboratory, Yale University, New Haven, Connecticut. *Received June 3, 1968*

Abstract: Hybridization, a local property of the wave function, is discussed in terms of the molecular orbital theory. Two methods for prediction of hybridization are introduced, one based on orbital localization and the other on an extension of Wiberg's bond index. When a localized description of the wave function is possible, a situation which allows unambiguous definition of hibridization, the two methods give indistinguishable results. Calculations employing the complete neglect of differential overlap approximation for a variety of molecules, including alkanes, alkenes, ethers, alcohols, and carboxylic acids, give a reliable qualitative account of trends in hybridization. Agreement between the calculated p character X_p and estimates of X_p from nmr coupling constants is good. Correspondingly, a local orbital estimate of the hybridization can be used to predict the coupling between carbon-13 nuclei and directly bound protons in molecules for which the experimental data are not available.

The valence-bond treatment of the molecular charge distribution provided an intuitively appealing description of bonds in terms of ionic character, hybridization, and resonance.[2a] Many molecular properties, including dipole moments, bond lengths, force constants, quadrupole coupling constants, and certain nuclear magnetic resonance shifts, could be understood using these ideas.[2b] It is desirable to define intuitively meaningful quantities parallel to these earlier ideas in terms of the molecular orbitals.

In this report we consider the notion of hybridization.[3] Several particular problems are examined: conditions requisite to the unambiguous definition of hybridization are sought. Two methods affording numerical characterization of hybridization, expressed in terms of the molecular orbitals, are introduced. Finally the reliability of predictions of hybridization based on semiempirical wave functions is indicated by comparison to an experimental reference, the carbon-13–proton coupling, for a variety of molecules including alkanes, alkenes, alcohols, ethers, and carboxylic acids.

Definition of Hybridization

The idea of hybridization is the result of an assumption that an atom retains its identity within a molecule and makes only slight adjustments to the molecular environment. This assumption has two main implications. First, the total wave function may be represented in terms of orbitals formed by combination of atomic functions. Since each atom then has s, p, etc., orbitals unambiguously associated with it, it is possible to define atomic s and p populations. Such a definition is essential for any discussion of hybridization. Wave functions expressed in terms of floating Gaussian

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(1) National Science Foundation Postdoctoral Fellow, 1967–1968.

(2) (a) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960—of course; (b) W. Kauzman, "Quantum Chemistry," Academic Press, New York, N. Y., 1957.

(3) H. A. Bent, *Chem. Rev.*, 61, 275 (1961).