

Stereochemically Nonrigid Organometallic Compounds.

I. π -Cyclopentadienyliron Dicarbonyl σ -Cyclopentadiene¹M. J. Bennett, Jr., F. A. Cotton, A. Davison, J. W. Faller,²
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Abstract: The problem of the nmr equivalence of the protons of the nonsandwich bonded C_5H_5 group of $(\pi-C_5H_5)Fe(CO)_2C_5H_5$ has been investigated by X-ray crystallography and nuclear resonance spectroscopy at low temperatures. In the crystal, the second C_5H_5 group is present as a normal σ -bonded 2,4-cyclopentadienyl group. The unit cell is monoclinic, space group $P2_1/c$, with dimensions $a = 12.53 \pm 0.03$, $b = 7.50 \pm 0.02$, $c = 11.29 \pm 0.02$ Å, and $\beta = 98.0 \pm 0.5^\circ$, and contains four formula units. In solution below about -60° a proton nmr spectrum consisting of three absorption bands at $\tau \sim 4$, 5.6, and 6.5 with relative intensities of 4 : 5 : 1 is observed, the first one having partially resolved structure. This spectrum indicates that in solution the molecular configuration of greatest stability is similar to that in the crystal, which contains a σ -bonded ring. Moreover, from a detailed consideration of the fine structure of the A_2B_2 multiplet of relative intensity four and, particularly, of the unsymmetrical variation in its envelope as a function of temperature, it is concluded that an intramolecular reorientation process occurs by repeated 1,2 shifts, probably passing through a metal-olefin transition state.

The literature presently records several examples of molecules in which all the protons of an unsaturated carbocyclic ring which is bound to a metal atom are nmr equivalent in solution at room temperature despite the fact that elementary valence considerations or the known molecular structure of the crystalline compound would not lead one to expect all of them to be chemically equivalent. Some of these molecules are $(\pi-C_5H_5)Fe(CO)_2C_5H_5$,⁴ $(C_5H_5)_2Hg$,^{4,5} $(C_8H_8)Fe(CO)_3$,^{6,7} and $(C_7H_7)Fe(CO)_3ClO_4$.⁸ The first example of this phenomenon to be discovered appears to have been the $(C_5H_5)_2Hg$ molecule, and, in order to explain the nmr equivalence, Piper and Wilkinson proposed⁴ that each ring was σ bonded to the mercury atom, but that the point of attachment changed from one carbon atom to another rapidly enough that the expected separate proton resonance lines were collapsed to a single sharp peak. The same explanation was proposed⁴ for $(\pi-C_5H_5)Fe(CO)_2C_5H_5$. For some years these interesting phenomena and the equally interesting explanation suggested by Piper and Wilkinson remained the only ones of their kind and apparently excited little active curiosity. Considerably later the $(C_5H_5)Fe(CO)_3$ molecule was prepared,⁶ and when its unsymmetrical structure in the crystalline state was established a similar explanation was suggested⁶ as a possibility. In this instance a rapid shift of a π -orbital-to-metal rather than a σ -orbital-to-metal interaction would be involved. Most recently, the $(C_7H_7)Fe(CO)_3^+$ case has been reported, although here it is perhaps not quite so clear that an inherently unsymmetrical ground configuration must be assumed since few physical data have as yet

been reported. However, it seems probable that this case may be qualitatively similar to the others.

Assuming that the general idea suggested by Wilkinson and Piper is correct (even if the details might be a little different), these molecules constitute examples of stereochemically nonrigid structures.⁹ This paper¹⁰ is the first in a series of reports describing investigations aimed at establishing more precisely the nature of the dynamic processes involved in the nonrigidity of organometallic compounds.^{10a}

Experimental Section

Preparation and Purification. π -Cyclopentadienyliron dicarbonyl σ -cyclopentadiene was prepared using Piper and Wilkinson's method.⁴ The crude product, which was separated from $(\pi-C_5H_5)_2Fe_2(CO)_4$ by chromatography on alumina with benzene as the eluent and finally from ferrocene by chromatography with hexane as the eluent, was a waxy solid. A recrystallization from pentane

(9) Attention has recently been drawn to the importance and possibly widespread occurrence of nonrigidity among inorganic molecules (although the cases under discussion here were not specifically mentioned) by E. L. Muetterties, *Inorg. Chem.*, **4**, 769 (1965). There are also examples of purely organic nonrigid molecules, the case of bullvalene being perhaps the most impressive; cf. W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 751 (1963).

(10) Many of the results described here in detail were first reported in a lecture by F. A. Cotton to the Ninth Robert A. Welch Foundation Conference on Organometallic Chemistry, Nov 17, 1965.

(10a) NOTE ADDED IN PROOF. In the hope of establishing some generally acceptable terminology concerning molecules which undergo relatively rapid intramolecular rearrangements, such as the one discussed in this paper, we offer the following comments and suggestions. E. L. Muetterties (*Inorg. Chem.*, **4**, 769 (1965)) has proposed the term "sterically nonrigid" for some such molecules. W. von E. Doering and W. R. Roth (*Angew. Chem. Intern. Ed. Engl.*, **2**, 115 (1963)) have used the term "fluxional structures" to describe molecules which are distinguished by more than one geometrically identical potential well, e.g., bullvalene. The older term "valence tautomerism" does not apply to such phenomena generally, nor does it apply to intramolecular rearrangements such as planar-tetrahedral equilibria or to the trigonal bipyramidal-square pyramidal-trigonal bipyramidal rearrangements (in PCl_2F_3 , $Fe(CO)_5$, etc.) which permute axial and equatorial positions, nor does it apply to the inversion motions in cyclohexane, amines, sulfides, etc. These allogonic rearrangements (*allo* meaning different and *gon* meaning angle), unlike that in bullvalene, do not involve breaking and re-forming of bonds, but only changes of angles. We therefore propose "stereochemically nonrigid" as a general term which includes all of the intramolecular rearrangements mentioned above. Subdivisions of stereochemical nonrigidity can then be made on the basis of equivalence or nonequivalence of potential wells, the origin of the barriers, and the equivalence or nonequivalence of the barrier heights.

(1) Research supported by the National Science Foundation under Grants GP 3468 and GP 4329.

(2) NSF Predoctoral Fellow, 1963-1966.

(3) NSF Postdoctoral Fellow, 1965-1966.

(4) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956).

(5) T. S. Piper and G. Wilkinson, *ibid.*, **2**, 32 (1956).

(6) T. A. Manuel and F. G. A. Stone, *J. Am. Chem. Soc.*, **82**, 6240 (1960); M. A. Rausch and G. N. Schrauzer, *Chem. Ind. (London)*, 957 (1959); K. Nakamura, *Bull. Chem. Soc. Japan*, **32**, 880 (1959).

(7) B. Dickens and W. N. Lipscomb, *J. Am. Chem. Soc.*, **83**, 4862 (1961).

(8) J. E. Mahler, D. A. K. Jones, and R. Pettit, *ibid.*, **86**, 3589 (1964).

at -78° followed by a slow vacuum sublimation (10 hr at 25° and 10μ) onto a water-cooled probe gave pure crystalline $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\sigma\text{-C}_5\text{H}_5)$. It decomposed very slowly to ferrocene, and samples several weeks old were repurified using the above procedure just prior to use.

Nuclear Resonance Measurements. These were made on solutions in carbon disulfide and in dimethyl ether in the temperature range -100 to $+30^\circ$, using a Varian Associates A-60 spectrometer equipped with a low-temperature probe which was modified to permit operation as low as -100° .

Crystallographic Investigation. The crystals were small red monoclinic prisms. Precession and Weissenberg photographs showed that the unit cell is monoclinic, with the dimensions $a = 12.53 \pm 0.03$, $b = 7.50 \pm 0.02$, $c = 11.29 \pm 0.02$ Å, $\beta = 98.0 \pm 0.5^\circ$, $V = 1061 \pm 6$ Å³. The observed systematic absences $0k0$, $k \neq 2n$, and $h0l$, $l \neq 2n$, identify the space group as $P2_1/c$. The approximate density is 1.5 g cm^{-3} which indicates four molecules per unit cell (d calcd, for $Z = 4$, 1.54 g cm^{-3}).

A small crystal, of dimensions $0.25 \times 0.15 \times 0.25$ mm, was mounted on the c axis and equininclination Weissenberg photographs of the levels $hk0$ – $hk9$ were recorded by the multiple film technique using Mo $K\alpha$ radiation filtered through Zr foil. These data were collected at $ca. 20^\circ$ using approximately 30-hr exposures. Intensities were estimated visually by comparison with a set of timed exposures. Approximately 870 reflections were measured.

The low-angle unobserved reflections were assigned one-half the minimum observed intensity and Lorentz polarization corrections were applied. No absorption corrections were applied since μ was only 15.1 cm^{-1} . The coordinates of the iron atom were estimated from a Patterson synthesis¹¹ and used to calculate the structure factors for a Fourier synthesis.¹¹ At this point it was clear that the iron atoms occupied the general, fourfold equipoint of the cell so that no crystallographic symmetry requirements are imposed on the molecule. The $\sigma\text{-C}_5\text{H}_5$ ring and the two CO groups were located on this Fourier map. A new set of signs was then calculated using these atoms as well as the iron atom from which a second Fourier synthesis was prepared. On this Fourier, the positions of the remaining five carbon atoms were evident. Three cycles of full-matrix least-squares refinement¹² of all positional parameters, isotropic thermal parameters, and scale factors gave a residual ($R = \sum |F_o| - |F_c| / \sum |F_o|$) of 0.141 using unit weights. The small changes in positional parameters in the last cycle and the reasonable temperature factors suggested that satisfactory convergence had been attained. The observed and calculated structure factors are recorded in Table I. The atom parameters obtained are listed in Table II.

Table II. Fractional Atomic Coordinates and Isotropic Temperature Parameters^{a,b}

Atom	x/a	y/b	z/c	B
Fe	0.1849 (2)	0.9917 (4)	0.4282 (2)	2.29 (9)
C ₁	0.744 (2)	0.304 (3)	0.176 (2)	3.1 (5)
C ₂	0.668 (2)	0.188 (3)	0.101 (2)	3.4 (5)
C ₃	0.565 (2)	0.213 (3)	0.137 (3)	3.9 (5)
C ₄	0.574 (2)	0.331 (4)	0.230 (3)	5.3 (6)
C ₅	0.679 (2)	0.392 (4)	0.267 (3)	5.3 (7)
C ₆	0.877 (2)	0.320 (3)	0.007 (3)	3.7 (5)
C ₇	0.916 (2)	0.529 (3)	0.184 (2)	3.2 (5)
C ₈	0.343 (2)	0.092 (3)	0.485 (3)	3.9 (5)
C ₉	0.289 (2)	0.454 (3)	0.083 (3)	4.3 (6)
C ₁₀	0.194 (2)	0.352 (3)	0.072 (3)	4.0 (5)
C ₁₁	0.186 (2)	0.239 (4)	0.983 (3)	4.3 (5)
C ₁₂	0.275 (2)	0.224 (3)	0.417 (3)	4.4 (6)
O ₁	0.920 (1)	0.198 (2)	0.972 (2)	4.2 (4)
O ₂	0.990 (1)	0.559 (2)	0.254 (2)	5.4 (4)

^a Atoms numbered as in Figure 1. ^b Figures in parentheses are the standard deviations occurring in the last recorded figure of each datum.

It should be noted that owing to the instability of the substance some decomposition unquestionably occurred as the photographs

(11) Patterson and Fourier syntheses were computed using MIFR-2, our version of the Sly-Shoemaker-van den Hendé Fourier program for the IBM 7094.

(12) Using SFLSQ-3, a full-matrix least-squares refinement program for the IBM 7094 by C. T. Prewitt, MIT, 1962.

were taken. This could lead to systematic errors such that the estimated standard deviations of atomic parameters underestimate the true uncertainties.

Results

Crystal Structure. The molecular structure is shown in Figure 1, which also gives the atom numbering scheme followed in Tables II–V.

Table III. Intramolecular Distances^{a,b}

Fe–C ₁	2.11 (2)	C ₁ –C ₂	1.46 (3)
Fe–C ₆	1.72 (2)	C ₂ –C ₃	1.42 (3)
Fe–C ₇	1.68 (2)	C ₃ –C ₄	1.37 (4)
Fe–C ₈	2.13 (2)	C ₄ –C ₅	1.40 (4)
Fe–C ₉	2.07 (3)	C ₅ –C ₁	1.54 (4)
Fe–C ₁₀	1.98 (3)	C ₈ –C ₉	1.41 (4)
Fe–C ₁₁	2.12 (3)	C ₉ –C ₁₀	1.40 (3)
Fe–C ₁₂	2.09 (2)	C ₁₀ –C ₁₁	1.30 (4)
C ₈ –O ₁	1.16 (2)	C ₁₁ –C ₁₂	1.45 (4)
C ₇ –O ₂	1.15 (3)	C ₁₂ –C ₈	1.45 (4)

^a In angstrom units; atoms numbered as in Figure 1. ^b Numbers in parentheses are standard deviations in $\text{Å} \times 10^2$.

Table IV. Intramolecular Angles^{a,b}

Fe–C ₁ –C ₂	112 (1)	C ₁ –C ₂ –C ₃	108 (2)
Fe–C ₁ –C ₅	113 (2)	C ₂ –C ₃ –C ₄	109 (2)
Fe–C ₆ –O ₁	174 (2)	C ₃ –C ₄ –C ₅	114 (3)
Fe–C ₇ –O ₂	174 (2)	C ₄ –C ₅ –C ₁	103 (2)
C ₁ –Fe–C ₆	89 (1)	C ₅ –C ₁ –C ₂	107 (2)
C ₁ –Fe–C ₇	92 (1)	C ₈ –C ₉ –C ₁₀	107 (2)
C ₆ –Fe–C ₇	96 (1)	C ₉ –C ₁₀ –C ₁₁	113 (2)
		C ₁₀ –C ₁₁ –C ₁₂	106 (3)
		C ₁₁ –C ₁₂ –C ₈	107 (2)
		C ₁₂ –C ₈ –C ₉	105 (2)

^a In degrees; atoms numbered as in Figure 1. ^b Numbers in parentheses are standard deviations in degrees.

Table V. Mean Planes and Distances

1. Mean plane of $\pi\text{-C}_5\text{H}_5$ ring			
(a) Equation			
$0.511X - 0.708Y + 0.488Z - 0.546 = 0$			
(b) Distances of atoms from plane, Å			
C ₈	–0.01	C ₁₁	–0.04
C ₉	–0.01	C ₁₂	+0.03
C ₁₀	+0.03	Fe	1.70
2. Mean plane of $\sigma\text{-C}_5\text{H}_5$ ring			
(a) Equation:			
$0.621X - 0.760Y + 0.192Z - 0.482 = 0$			
(b) Distances of atoms from plane, Å			
C ₁	–0.02	C ₄	–0.02
C ₂	+0.02	C ₅	+0.03
C ₃	–0.01	Fe	–1.73

In the present context, it is the nature of the structure rather than its precise dimensional details which is of principal importance, and, most particularly, the structural relationship of the non- π -bonded C_5H_5 ring to the iron atom.

Clearly, this ring is present as a $\sigma\text{-C}_5\text{H}_5$ ring. It is the first such ($\sigma\text{-C}_5\text{H}_5$)-to-metal moiety to be structurally characterized in an X-ray study. The ring itself is planar to well within the experimental uncertainties (see Table V) and the three measurable bond angles about C₁ are 107, 112, and 113°. The C₁–Fe bond length, 2.11 ± 0.02 Å, may be compared with the other reported Fe–C σ -bond lengths, namely that in $(\text{OC})_2$ –

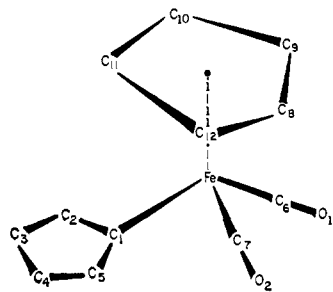


Figure 1. The molecular configuration in crystalline $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$. Atoms are numbered as in Tables II-V.

$\text{Fe}(\pi\text{-C}_5\text{H}_4\text{CH}_2)\text{-Fe}(\text{CO})_4$,¹³ 2.12 Å, those in $(\text{OC})_3\text{-Fe}[\text{C}(\text{OH})=\text{C}(\text{CH}_3)(\text{CH}_3)\text{C}=\text{COH}]\text{Fe}(\text{CO})_3$,¹⁴ and those in $\text{Fe}_2(\text{CO})_8(\text{C}_6\text{H}_5\text{C}_2\text{H})_3$,¹⁵ 2.01, 2.09, 2.10 Å. Although the aptness of all of these comparisons is questionable since there are differences in formal oxidation states of the iron, differences in hybridization of the carbon atoms, and evidences of varying degrees of steric strain in the different molecules, the values are reasonably concordant. The carbon-carbon distances within this ring show some differences from the pattern expected for a cyclopenta-2,4-diene ring but the standard deviations are such that no significance can be attached to this, and the differences cannot be said to be certain.

The $(\pi\text{-C}_5\text{H}_5)\text{Fe}$ part of the molecule has dimensions in good accord with those found for this grouping in numerous other cases.

The dimensions of the iron carbonyl groups are of interest in connection with questions of the metal radius and the Fe-CO bonding. The mean C-O distance, 1.16 ± 0.02 Å, is entirely typical for metal carbonyls in general, and the deviations of the Fe-C-O angles from 180° are also not uncommon nor unexpected when linearity is not demanded by molecular symmetry.¹⁶ The mean Fe-C distance, 1.70 ± 0.02 Å, is shorter than those (~ 1.75 Å) found in derivatives of what is formally Fe(I) and considerably shorter than those found in compounds of formally zero-valent iron, such as $\text{Fe}(\text{CO})_5$ ¹⁷ (1.80 Å) and $(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_3$ ¹⁸ (1.80 Å). This trend may be partly influenced by the differing numbers of CO groups competing for available iron $d\pi$ electrons, but probably reflects at least in part a tendency for the metal radius to decrease as the formal oxidation state increases.

From the Fe-C₁ distance (2.12 Å), we estimate an Fe single bond radius of 1.35 Å. Thus a single bond from iron to sp-hybridized C should have a length of ca. 2.05 Å. The actual Fe-CO distances, averaging 1.70 Å, therefore indicate considerable π character in the Fe-C bonds.¹⁹

(13) J. Meunier-Piret, P. Piret, and M. van Meerssche, *Acta Cryst.*, **19**, 85 (1965).

(14) A. A. Hock and O. S. Mills, *ibid.*, **14**, 139 (1961).

(15) G. S. D. King, *ibid.*, **15**, 243 (1962).

(16) S. F. A. Kettle, *J. Chem. Soc.*, 1661 (1965).

(17) J. Donohue and A. Caron, *Acta Cryst.*, **17**, 663 (1964).

(18) B. Dickens and W. N. Lipscomb, *J. Am. Chem. Soc.*, **83**, 4862 (1961).

(19) It is interesting to note that on comparing these results with those for the $[\text{Fe}(\text{CN})_5\text{NO}]^{2+}$ ion²⁰ in which Fe-N = 1.63 Å and the mean Fe-C distance is 1.91 Å, it seems evident that while the Fe-N bond has a great deal of multiple bond character, the Fe-CN bonds have much less π character than do the Fe-CO bonds in this and other iron carbonyl compounds.

(20) P. T. Manoharan and W. C. Hamilton, *Inorg. Chem.*, **2**, 1043 (1963).

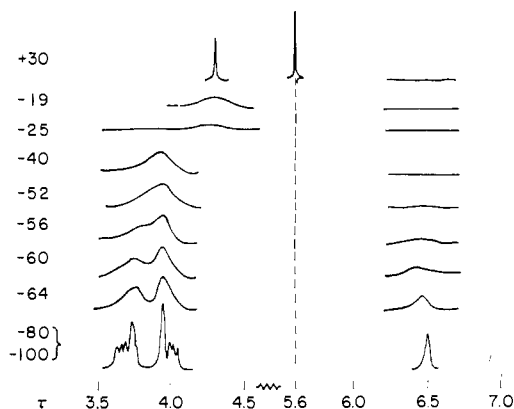


Figure 2. The proton magnetic resonance spectra of $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$ in CS_2 at various temperatures. The dotted line represents the resonance position of the $\pi\text{-C}_5\text{H}_5$ protons at each temperature. The amplitude of the $+30^\circ$ spectrum is shown $\times 0.1$ relative to the others.

Proton Magnetic Resonance Spectra. The proton nmr spectra of $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)$ in CS_2 solution at various temperatures from $+30$ to -100° are displayed in Figure 2. The spectrum at $+30^\circ$ shows two resonances, one at τ 5.60 and another of essentially the same integrated intensity, though noticeably broader, at τ 4.30. These results are the same as those previously reported by Piper and Wilkinson⁴ at $\sim 25^\circ$. The line at τ 5.60 can be assigned²¹ to the $\pi\text{-C}_5\text{H}_5$ protons on the basis of its chemical shift alone, but the low-temperature spectra provide conclusive evidence for this.

As the temperature is lowered, the low-field signal broadens and eventually collapses completely at about -25° . As the temperature drops further two new bands appear. One due to the protons on the four carbon atoms not bonded to the iron atom begins as a single broad, asymmetric band at $\tau \sim 4$ but separates into two bands, each of relative intensity two, this separation becoming clearly evident at $\sim 60^\circ$. The other peak of relative intensity 1 is fairly broad (width at half-height, ~ 5 cps) even at $\sim 100^\circ$ and centered at τ 6.5. During the course of these changes, the peak at τ 5.60 retains its position, shape, and relative intensity of 5, thus confirming its assignment to the $\pi\text{-C}_5\text{H}_5$ group.

In addition, and of great significance (see Discussion), is the fact that the two halves of the absorption at $\tau \sim 4$ vary differently with temperature. The portion at higher τ is higher and narrower at intermediate temperatures, and in the limiting spectrum (that which is reached at -70° and remains essentially unaltered down to -100°) this half shows somewhat better resolved fine structure.

The behavior of the spectrum in dimethyl ether as a function of temperature was essentially identical with that in carbon disulfide except for slight differences in τ values. In particular, the absorption envelopes in the two solvents at each temperature were essentially identical, indicating that there is no specific solvent dependence of the rearrangement process.

Discussion

We believe that the X-ray and nmr results described above clearly show that the molecular configuration of

(21) M. L. H. Green and P. L. I. Nagy, *J. Chem. Soc.*, 189 (1963).

lowest potential energy for this molecule is essentially the one found in the crystal, that is, one in which the non- π -bonded cyclopentadienyl ring is bound through a normal iron-to-carbon σ bond. The stereochemical nonrigidity of the molecule as manifested in the proton nmr spectrum observed at room temperature and above is then a consequence of a relatively rapid shifting of the iron-to-carbon σ bond from one carbon atom of the ring to another, in complete accord with the original suggestion of Piper and Wilkinson. However, the manner in which the shift takes place remains to be specified. While this is not an easy task, we believe the data permit us to draw some definite conclusions. The question we wish to ask is the following: what is the metal-to-ring configuration in the transition state for the predominant shift mechanism? It is not, *a priori*, impossible that there might be two or more mechanisms which contribute significantly to the net result, but, as will be seen, a single process seems to be predominant.

In considering this problem, the detailed behavior of the absorption at $\tau \sim 4$ between ~ -40 and $\sim -70^\circ$ as well as its final, constant character between $\sim -70^\circ$ and $\sim -100^\circ$ will be of critical importance. This absorption is due to the two pairs of protons on the carbon atoms other than that bound to the metal atom. Those in each pair should be instantaneously equivalent and should constitute the A_2 and B_2 members of an HA_2B_2 system. We shall specify the A_2 nuclei as those on the carbon atoms α to the unique carbon atom of the σ - C_5H_5 ring.

In the limit of $J_{HA} = J_{HB} = 0$ the A_2B_2 resonance should be symmetrical, the two halves being mirror images,²² as in thiophene.²³ However, when $J_{HA} \gg J_{HB} \approx 0$, the A_2 portion of the A_2B_2 absorption would be expected to exhibit additional fine structure or, depending on the exact value of J_{HA} relative to J_{AB} , perhaps only a broadening of its structure. In the present case we may infer from the width (~ 5 cycles) of the H resonance at -70 to -100° that J_{HA} is about 2 cycles. We would thus expect this to introduce only broadening rather than additional resolved fine structure in the A portion of the A_2B_2 multiplet. Assuming that proton-proton coupling will attenuate with increasing distance,²⁴ we therefore conclude that the less well-resolved half of the observed A_2B_2 resonance corresponds to the A protons. In the present case, this is the half at lower τ .

We believe there are five mechanisms which might reasonably be considered for the rearrangement process. The first is an intermolecular one, proceeding either by dissociation or by a bimolecular exchange. However, the unsymmetrical manner in which the resonances collapse rules this out conclusively.

There are then four different intramolecular processes, which are indicated diagrammatically in Figure 3. The path indicated in Figure 3a, which borders on being a dissociative process, would presumably have a very high activation energy and is rejected for this reason. The remaining three paths might all preserve substantial

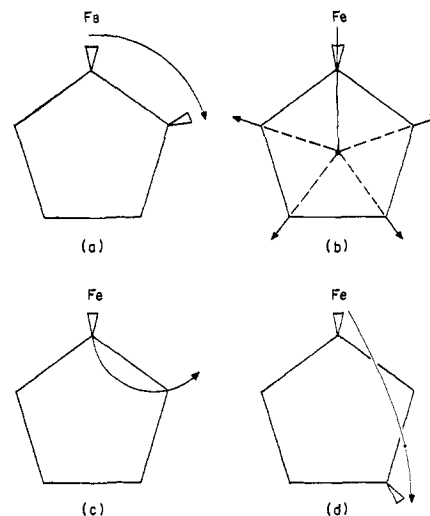
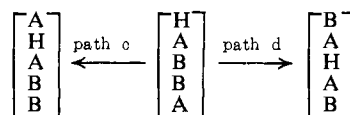


Figure 3. Diagrams showing four possible intramolecular paths leading to the nmr equivalence of the σ - C_5H_5 protons at room temperature.

bonding of the ring to the metal atom and are thus likely to have plausible activation energies. Mechanism b, however, can also be ruled out because it involves a stage in which all protons become equivalent. This in turn would necessitate symmetrical collapse of the spectrum in contradiction to what is observed. This path might, however, be one leading to the irreversible decomposition of the compound to ferrocene, a process which occurs slowly even at low temperatures and more rapidly at high temperatures.

Thus, we have reduced the problem to distinguishing between paths c and d. In order to do so, we must observe in detail how the protons are permuted among the three environments, H, A, B, by the two paths. This is illustrated symbolically as follows.



It will be noted that in each case all protons but one change environment. The difference lies in the fact that for path c the unchanged environment is of type B, while for path d it is of type A. The consequences of these observations are that for path c the A resonance should collapse most rapidly with increasing temperature, whereas for process d the B resonance should collapse soonest, since the averaging depends inversely on the lifetime of a nucleus in a given environment. The observed unsymmetrical collapse of the low-field resonance is clearly compatible with paths c and d. However, since the resonance which collapses most rapidly has been shown on the basis of the limiting low-temperature spectrum to be most likely due to the A protons, we conclude that path c, in which there is a 1,2 shift, is the major path for rearrangement.

The intermediate point in this path could be thought of as one in which the π -electron density of the ring is arranged in a two-center π bond through which the ring is bound to the iron and an allyl anion distribution over the other three carbon atoms. This point in the path may actually constitute a saddle point on the

(22) K. B. Wiberg and B. J. Nist, "The Interpretation of NMR Spectra," W. A. Benjamin, Inc., New York, N. Y., 1962.

(23) N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, NMR Spectra Catalog, Varian Associates, 1962, Spectrum No. 52.

(24) While this assumption cannot perhaps be defended as a universal rule, it seems reasonable and has empirical justification. For example,²¹ in $(\pi-C_5H_5)Fe(CO)_2(\sigma\text{-allyl})$ this is the case.

potential energy *vs.* reaction coordinate graph, with the barrier to rearrangement being slightly higher than the energy difference between this structure and the ground structure.

Since the iron atom in $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$ has only one vacant σ orbital in its valence shell, the intermediate state in this process is consistent with the semiempirical rule which accords maximum stability to a 36-electron configuration for the metal atom in such compounds. In the 1,3 shift, on the other hand, the intermediate stage would involve a free C-C double bond and a bound π -allyl group, the latter having two more than the required number of electrons, with the least stable pair occupying a π -MO not symmetrically suited to overlap with the metal σ orbital.

It is interesting to compare the system studied here with the results recently reported by Fritz and Kreiter²⁵

for some cyclopentadienyl derivatives of the group four metals. In these cases the rate of the rearrangement process is so slow that it can only be observed in the form of a collapse of the σ -cyclopentadienyl spectrum to a single line at temperatures above room temperature for the silicon and germanium compounds, although for tetracyclopentadienyltin the process is rapid and only a single proton resonance line is observed even at -60° . These authors suggested a 1,2-shift mechanism, but no positive experimental evidence was offered to support this as against other possibilities such as those we have considered. The arguments presented here concerning $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$ can in principle be applied to these cases, but the data reported are insufficient actually to do so.

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Hydrogen Bridge Bonding in the $[\text{M}_2\text{H}(\text{CO})_{10}]^-$ Anions (M = Cr, Mo, W)^{1,2}

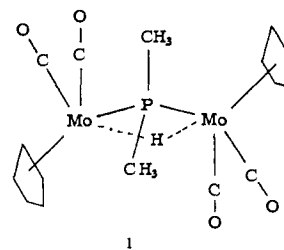
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Abstract: Convenient syntheses have been developed for the $[\text{M}_2\text{H}(\text{CO})_{10}]^-$ and $[\text{M}_2(\text{CO})_{10}]^{2-}$ series of anions and the two series connected by an acid-base relationship. The formation of the mixed complexes $[\text{MM}'\text{H}(\text{CO})_{10}]^-$ has been detected by proton nmr in statistically determined scrambling reactions involving pairs of the $[\text{M}_2\text{H}(\text{CO})_{10}]^-$ anions, or pairs of the group VI metal hexacarbonyls. Infrared and proton nmr studies favor a symmetrical hydrogen-bridged structure for $[\text{M}_2\text{H}(\text{CO})_{10}]^-$ in agreement with a recent X-ray structural investigation of $[(\text{C}_2\text{H}_5)_4\text{N}][\text{Cr}_2\text{H}(\text{CO})_{10}]$.¹⁷ The $[\text{M}_2(\text{CO})_{10}]^{2-}$ series of complexes has been found to contain bridging carbonyl groups and is thus presumably isomeric with the complexes previously reported in the literature.^{4,5}

Previous investigations of the anionic carbonyl complexes of the group VI metals have been carried out almost entirely by Behrens and his co-workers and, in a series of papers, they have reported the species $[\text{M}(\text{CO})_5]^{2-}$,³⁻⁵ $[\text{MH}(\text{CO})_5]$,^{3,4} $[\text{M}_2(\text{CO})_{10}]^{2-}$,^{4,5} $[\text{M}_2\text{H}(\text{CO})_{10}]^-$,⁴⁻⁶ and $[\text{M}_3(\text{CO})_{14}]^{2-}$.^{4,7} The structure of most of these anions, however, remains in doubt owing to the lack of spectroscopic and other physical data. In addition, many of the compounds were synthesized under unusual conditions (for example, in liquid ammonia at elevated temperatures) so that the complexes are not readily accessible for further study.

Our interest in the group VI carbonyl anions arose from a study of the complex $[(\text{C}_5\text{H}_5)_2\text{Mo}_2\text{H}(\text{P}(\text{CH}_3)_2)(\text{CO})_4]^{8-}$ which has recently been shown by Doedens and Dahl⁹ to have structure 1, although the position



of the unique hydrogen was not detected by X-rays. The two molybdenum atoms have identical stereochemical environments, each possessing the "3-4" type of coordination previously found in $[\text{C}_5\text{H}_5\text{Nb}(\text{CO})_4]^{10}$ and $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$.¹¹ In $[(\text{C}_5\text{H}_5)_2\text{Mo}_2\text{H}(\text{P}(\text{CH}_3)_2)(\text{CO})_4]^{8-}$, however, only three of the four basal coordination positions are occupied by ligands which are visible to X-rays, and it is presumed that a bridging hydride ligand occupies the fourth position, thus filling the vacant coordination site of both metal atoms. In such a complex, it is not clear whether or not the hydride ligand plays an important role in binding the two metal atoms together, owing to the simul-

(1) Presented in part at the Second International Organometallic Symposium at Madison, Wis., Aug 29-Sept 3, 1965.

(2) Throughout this paper, M (or M') = Cr, Mo, and W.

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