m.p. 72–73°. *Anal.* Calcd. for $(C_8H_{16})_2PtCl_2$: C, 39.1; H, 6.5; Pt, 40. Found: C, 39.1; H, 6.4; Pt, 39.2.

Infrared spectra were measured in KBr disks; n.m.r. spectra in perdeuteriobenzene.

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H, H Coupling in Diene–Iron Carbonyl Complexes[1]

BY H. S. GUTOWSKY AND J. JONÁŠ[2]

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High resolution nuclear magnetic resonance spectra recently have been used extensively for the study of transition metal complexes of various organic unsaturated compounds.[3] Among such applications, the iron carbonyl complexes of different dienes[4] have been investigated and several interesting features have been observed in their high resolution proton spectra. In a diene–iron carbonyl complex, shown schematically in Figure 1, the "terminal" hydrogens X, X′, which are nearest to and most directly affected by the bonding to iron, exhibit a large upfield shift.[4] On the other hand, the resonance of the central hydrogens A, A′ appears in the normal region for olefinic protons (usually around 5.0 p.p.m. downfield from TMS). The two central and two terminal hydrogens give proton spectra characteristic of A_2X_2 spin systems as reported for a number of these complexes,[4] such as cyclohepta-1,3-dieneiron tricarbonyl, cyclohexa-1,3-dieneiron tricarbonyl, and bicyclo[4.2.0]octa-2,4-dieneiron tricarbonyl. Besides the chemical shifts, the magnitudes of the H, H coupling constants have been reported[4] for protons in the diene moiety, and it has been noted[5] that the vicinal coupling constants are "smaller than usual."

Several authors have commented on the significance of the n.m.r. results. For example, Sternhell[5] has suggested that the small vicinal coupling constants result from delocalization of the π-electrons, and Manuel[6] has proposed that the proton spectra of tricarbonyl-(1,1′-bicycloalkenyl)iron(0) complexes favor a structure involving 1,4 addition of the iron atom across the dienic system, as implied in Figure 1. However, in the previous discussions, no consideration seems to have been given to the effects upon the proton spectra of the nonplanarity of the H and C atoms in the diene–iron carbonyl complex. The main purpose of this note is to call attention to the existence and importance of such effects in these complexes.

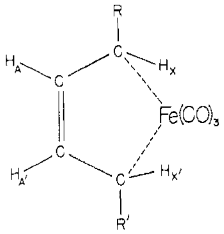

Figure 1.—The diene–iron carbonyl complex. The four carbon atoms which were the 1,4-diene before complex formation are in the plane of the paper, the Fe is below, H_X and $H_{X'}$ are above, and H_A and $H_{A'}$ are perhaps somewhat below.

Our interest in this type of system was stimulated by Frankel,[7] who very kindly gave us a sample of the iron carbonyl complex obtained from methyl linoleate as well as a spectrum of it obtained with a Varian Associates A-60 spectrometer. At that time, only the magnitudes of the coupling constants had been reported. However, it is possible to obtain the relative signs of J_{AX} and $J_{AX'}$ from an A_2X_2 spectrum,[8] and we thought it worthwhile to make such an analysis. Therefore, we reran the A_2X_2 part of the proton spectrum of the linoleate complex on the A-60 spectrometer in our laboratory and analyzed it by means of the Swalen–Reilly computer programs.[9] The appearance and assignment of the spectrum are very similar to those reported[4] for other diene–iron carbonyl complexes. The central hydrogen atoms (A and A′ in Figure 1) give a well-defined low-field multiplet 5.00 p.p.m. downfield from TMS, whereas the terminal hydrogens (X and X′ in Figure 1) give the high-field half of the A_2X_2 spectrum, which overlaps the intense structureless bands of the CH_2 groups. Further details of the spectrum and of the properties of the complex have been reported by Frankel.[7]

Our analysis, based mainly on the unobscured low-field multiplet, gave the following results: $\nu_A = -300.0 \pm 2.0$, $\nu_X = -110.3 \pm 20.0$, $J_{AA'} = 4.4 \pm 0.2$, $J_{XX'} = 0.0 \pm 0.2$, $J_{AX} = J_{A'X'} = +8.4 \pm 0.2$, $J_{AX'} = J_{A'X} = -1.7 \pm 0.2$, all in c.p.s. with the ν values referred to TMS. The large uncertainty in ν_X is due to overlap of the high-field half (X_2) of the spectrum by the strong CH_2 bands. The widths of the downfield lines were exceptionally large, about 3 c.p.s. at half-maximum intensity. In spite of the broadening and the fact that only the downfield multiplet could be analyzed, the results show conclusively that J_{AX} and $J_{AX'}$ are of opposite sign. The broadening of the A_2X_2 lines most likely results from the fact that the sample is actually a mixture of diene–iron carbonyl complexes, with slightly different shifts and coupling constants which give overlapping transitions. That is, in Figure 1, R and R′ are[7] $CH_3(CH_2)_y$– and –$(CH_2)_x$-$COOCH_3$ with $x + y = 12$ and $x, y = 4, 8; 5, 7; \ldots 10, 2$.

In any event the chemical shifts and coupling constants obtained in our analysis are comparable with

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[3] G. Wilkinson, "Hydrogen and Organic Derivatives of Transition Metals," in "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, p. 50.

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[5] R. Sternhell, *Rev. Pure Appl. Chem.*, **14**, 15 (1964).

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[8] D. M. Grant, R. C. Hirst, and H. S. Gutowsky, *J. Chem. Phys.*, **38**, 470 (1963).

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those reported for other diene–iron carbonyl complexes, so they will serve as the basis for our discussion. The chemical shifts have been considered in most detail, as reviewed by Wilkinson,[3] with attention centered on the large upfield shift of the X_2 protons upon complex formation. The shift assignment of A_2 and X_2 protons has been verified by means of deuterated compounds, so the main question is the relation of the shifts to the nature of the diene–iron bonding. Here the difficulty is that upfield shifts of the X_2 protons can be produced not only by their more or less direct involvement in the diene–iron bonding but also by the magnetic anisotropy of neighboring bonds. In the latter connection, we wish to point out that the anisotropy effects of the CO groups cannot be neglected. The X-ray structural studies have not revealed the proton positions, but the structures found from the heavier atoms[10,11] are such that there could be large upfield CO anisotropy shifts of the X_2 protons and also appreciable ones for the A_2 protons. In brief, there does not appear to be any simple relation between the shifts of the X_2 and A_2 protons and the extent of π-delocalization or localization in the diene complexes.

The situation with respect to the H, H coupling constants is somewhat more favorable because of our better understanding of the relevant structural factors.[12–14] For example, the vicinal H, H coupling is known to be 6–10 c.p.s for *cis* protons in an ethylenic group and 10–18 c.p.s. for *trans*.[12] Thus, the 4.4 c.p.s. value of $J_{AA'}$ and the 8.4 c.p.s. value of J_{AX} and $J_{A'X'}$ are both too small for either the 2,3 or the 1,2 and 3,4 C–C bonds to be normal ethylenic bonds in the complex. But it is an oversimplification to ascribe the differences to delocalization of the π-electrons,[15] because coupling of vicinal protons is dominated by the σ-electron contribution and its angular dependence.[12–14]

It is more instructive to compare the H, H coupling constants in the diene–iron carbonyl complex with those in the heterocyclic five-membered ring compounds[14] such as thiophene, as summarized in Table I. Thiophene was chosen for the comparison because the heteroatom is relatively electropositive and the size of S is not too different from that of Fe. The differences between the two sets of data are surprisingly small, and most of them can be attributed to the diene–iron heterocycle being nonplanar while thiophene is planar. Consider the fact that J_{AX} is larger (8.4 c.p.s.) than $J_{\alpha\beta}$ (5.0 c.p.s.). In the complex, the CCH angles in the H_ACCH_X group probably are smaller than the 125° for thiophene and this would tend to increase J_{AX}.[14] However, as shown in Figure 1, the X-ray structural studies[10,11] make it seem improbable that the group is planar; instead the dihedral angle ϕ between the H_A–C and C–H_X bonds is perhaps 135°, which would make J_{AX} smaller[12] than what it would be if $\phi = 180°$. So, independently of the π-character of the 1,2 and 3,4 C–C bonds, we would not expect J_{AX} to differ greatly from $J_{\alpha\beta}$, as is indeed the case.

TABLE I

COMPARISON OF H, H COUPLING CONSTANTS (C.P.S.) IN THE DIENE–IRON CARBONYL COMPLEX WITH THE CORRESPONDING COUPLING CONSTANTS IN A REPRESENTATIVE HETEROCYCLIC FIVE-MEMBERED RING COMPOUND, THIOPHENE[a]

Diene–iron carbonyl		Thiophene	
J_{AX}	+8.4	$J_{\alpha\beta}$	5.0[b]
$J_{AA'}$	4.4	$J_{\beta\beta'}$	3.3
$J_{AX'}$	−1.7	$J_{\alpha\beta'}$	1.1
$J_{XX'}$	0.0	$J_{\alpha\alpha'}$	2.7

[a] Taken from R. Abraham and H. Bernstein, *Can. J. Chem.*, **37**, 2095 (1959). [b] These values are of the same sign and presumably all are positive: R. Freeman and D. H. Whiffen, *Mol. Phys.*, **4**, 32 (1961), and A. D. Cohen and A. D. McLauchlan, *Discussions Faraday Soc.*, **34**, 132 (1962).

The negative value (−1.7 c.p.s.) found for $J_{AX'}$ is of particular interest in connection with the dependence of the π-electron contribution to the H, H coupling, in the HCC═CH′ fragment, upon the dihedral angle ϕ between the C–H bonds. This has been predicted[13] to be $J_{HH'}{}^{\pi} = -3.4 \cos^2 (\phi + 90°)$. Thus, for the usual little or no σ-contribution,[13,14] the value observed for $J_{AX'}$ indicates that $90° < \phi \lesssim 135°$, which is compatible with the X-ray structural studies of other diene–iron carbonyl complexes.[10,11] As to the difference between $J_{XX'} \cong 0$ and $J_{\alpha\alpha'} = 2.7$ c.p.s., only the obvious statement can be made; the diene–iron bonding differs in the complex from the diene–S bonding in thiophene.

In summary, it seems fair to say that the n.m.r. data, particularly the H, H coupling constants, are compatible with 1,4 addition of the Fe to the diene to form a nonplanar complex.

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(15) This discrepancy is excessively large because both $J_{HH}{}^{cis}$ and $J_{HH}{}^{trans}$ increase greatly with decreasing electronegativity of the element directly bonded to a vinyl group. See, *e.g.*, J. S. Waugh and S. Castellano, *ibid.*, **35**, 1900 (1961).

Stability Constants of the Acetylacetone–Chromium(II) Complexes[1a]

BY WILLIAM P. SCHAEFER AND MAURICE E. MATHISEN[1b]

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The stability constants of the acetylacetone complexes of all of the divalent cations of the first-row transition elements, except vanadium and chromium,

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