atom. This is shown by the formalism of three bonds going to two bonds with the addition of a pair of electrons by the entering nucleophile, to one bond with the addition of a second ligand, and finally arene leaves with the addition of the third ligand and the third pair of electrons. Such a suggestion is in keeping with the somewhat general observation[8,14] that whereas simple metal carbonyls react by first-order processes, the

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π complexes of metal carbonyls react by second-order mechanisms.

Carbon-13 Magnetic Resonance of Diene–Iron Tricarbonyl Complexes[1]

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Abstract: The ^{13}C nmr spectra of butadiene–iron tricarbonyl and methyl octadecadienoate–iron tricarbonyl were obtained to elucidate the structure of these complexes. The ^{13}C–H coupling constants indicate that all of the C–H bonds in the butadiene complex are essentially sp^2 hybrids. This observation, the ^{13}C and proton chemical shifts, the H–H coupling constants, and other data are consistent with a structure in which the bonding of Fe at $C_{2,3}$ in the diene complexes is very similar to that in ferrocene, but in which the terminal CH_2 and CHR groups are rotated about the C_1–C_2 and C_3–C_4 bonds of the ligand. This steric distortion of the ligand from planarity makes the bonding of the Fe at $C_{1,4}$ differ somewhat from that at $C_{2,3}$, but both instances involve π orbitals on the carbons.

Recent interest in the structure of diene–iron tricarbonyl complexes has prompted us to obtain and analyze the ^{13}C nmr spectra of butadiene–iron tricarbonyl and methyl octadecadienoate–iron tricarbonyl. It has been uncertain whether these complexes involve delocalization of the π electrons in the diene system (structure I) or 1,4 addition of iron to the diene (structure II). We define structure I to be a butadiene system containing only sp^2-hybridized carbon atoms which are π bonded to the iron, and II to be a structure which has some localized bonding between iron and carbon atoms 1 and 4 with the bonding orbitals of the latter being sp^3 hybrids.
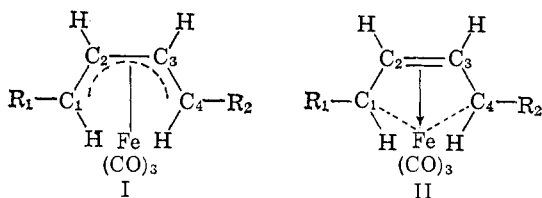
Much chemical and other evidence indicates that the structure represented by I is the most appropriate.[3]

However, the nmr spectra of protons in such complexes exhibit features which can be interpreted as supporting or being consistent with structure II. Thus, the resonance of the central hydrogen atoms in butadiene–iron tricarbonyl appears in the normal region for olefinic protons, whereas those of the terminal atoms exhibit large upfield shifts into the region generally associated with aliphatic protons.[4] But it has been pointed out[5] that this result has little bearing on the bonding in methyl octadecadienoate–iron tricarbonyl[6] because the upfield shifts could result from magnetic anisotropy effects of the CO groups, or of the Fe to diene bonds, rather than from any aliphatic character of the terminal protons.

Recent interpretations of the proton spectra of the iron tricarbonyl complexes of 1,1′-bicycloalkenyls[7] favor structure II. On the other hand, the infrared and ultraviolet spectra of various conjugated diene–iron tricarbonyl complexes have been considered[8] to indicate no loss of conjugation, in support of structure I. Also, electron absorption studies of various metal complexes of cyclopentadienone derivatives[9,10] show that the π-electron system of the ligand is not sufficiently perturbed to support a structure involving

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(3) For current reviews citing leading references, see R. Pettit and G. F. Emerson, Advan. Organometal. Chem., 1, 1 (1964); and M. Cais, "The Chemistry of Alkenes," S. Patai, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, p 335.

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(5) H. S. Gutowsky and J. Jonas, Inorg. Chem., 4, 420 (1965).

(6) E. N. Frankel, E. A. Emken, H. Peters, V. L. Davison, and R. O. Butterfield, J. Org. Chem., 29, 3292 (1964).

(7) T. A. Manuel, Inorg. Chem., 3, 510 (1964).

(8) M. Cais and N. Maoz, J. Organometal. Chem., in press.

(9) G. N. Schrauzer and G. Kratel, ibid., 2, 336 (1964).

(10) G. N. Schrauzer, Inorg. Chem., 4, 264 (1965).

both σ and π bonding of metal to carbon as in II. In this connection, a molecular orbital description of the π-cyclopentadienyl–metal–diene system has been proposed[11] to reconcile X-ray evidence which supports structures involving both sp^2- and sp^3-hybridized carbons as in II, and chemical evidence supporting structures in which all carbons of the "butadiene" residue are sp^2 as in I. The overlap between the first antibonding molecular orbital of butadiene and the metal d_{yz} orbital gives a bonding scheme in which the terminal carbons have "pseudo-sp^3 character."

The vicinal H–H coupling constants in the butadiene and substituted butadiene–iron tricarbonyl complexes[5,12,12a] are dominated by the σ-electron contribution and its angular dependence, and they do not provide any very direct evidence on the extent and nature of π-electron localization or delocalization. They do show that the hydrogen atoms are not coplanar with the plane defined by the four carbon atoms and that the dihedral angle between the *anti* C–H bonds may be as small as 135°. Such a structure would be consistent with X-ray results[13] which show that the trigonal axis of the carbonyl groups makes an angle of 61° with the four-carbon plane. One might expect that a large rotation of the terminal CH_2 groups about the 1,2 and 3,4 C–C bonds would be associated with rehybridization of the carbon orbitals in the sp^2 σ bonds as well as with a change in the nature of the π bonding. In this sense, it was stated earlier[5] that the H–H coupling constants are compatible with 1,4 addition of Fe to the diene to form the complex. However, a more direct and much better indication of the hybridization of C–H bonds is given by the ^{13}C–H coupling constant which, to a good approximation, is directly proportional to the s character of the bond.[14] The attractiveness of this approach to an improved understanding of the electronic structure of the diene–iron carbonyl complexes was the main motivation of the present work.

Results and Discussion

The ^{13}C spectrum of butadiene–iron tricarbonyl consists of a low-field singlet for the metal carbonyl carbon, a central doublet for $C_{2,3}$, and a high-field triplet for $C_{1,4}$, a result of spin–spin coupling between ^{13}C and no, one, and two directly bonded protons, respectively. Chemical shifts and coupling constants are given in Table I along with those of butadiene.

A low signal-to-noise ratio in the spectra of the methyl octadecadienoate–iron tricarbonyl prevented accurate measurements of the chemical shifts and precluded measurements of the coupling constants. Heteronuclear double resonance experiments, however, revealed two doublets centered at $\sim$108 and $\sim$129 ppm which may be assigned to $C_{2,3}$ and $C_{1,4}$, respectively. The assignment for this ester complex is not unambiguous, but appears reasonable in view of

Table I. Carbon Chemical Shifts and ^{13}C–H Coupling Constants in 1,3-Butadiene and Its Iron Tricarbonyl Complex

Position		Butadiene	Butadiene–iron tricarbonyl
$C_{1,4}$	δ_C, ppm from CS_2	76.2[a]	151.7
	J_{C-H}, cps	158[b]	160 ± 5
$C_{2,3}$	δ_C, ppm from CS_2	55.6[a]	107.0
	J_{C-H}, cps	158[c]	170 ± 5
$C=O$	δ_C, ppm from CS_2	...	−18.9[d]

[a] See ref 15. [b] H. L. Retcofsky and R. A. Friedel, unpublished results. [c] See ref 17. [d] The ^{13}C chemical shift of the carbonyl group is not significantly different from those of $Fe(CO)_5$, −16.8 ppm, and $C_5H_5Fe(CO)_2I$, −20.9 ppm, reported by Lauterbur and King.[20]

chemical shift trends reported for a variety of olefinic hydrocarbons.[15]

Although there are deviations from[14] and exceptions to[16] a simple, direct proportionality between ^{13}C–H coupling constants and hybridization of the C–H bond,[14] the relatively small differences in the coupling constants of C_1 and C_4 in butadiene–iron tricarbonyl ($J = 160$ cps) and the parent diene ($J = 158$ cps)[17] strongly suggest that the bond hybridizations are very similar in the two compounds. The magnitude of the coupling constants is that expected for sp^2 C–H bonds. The coupling constant for C_2 and C_3 ($J = 170$ cps) may be slightly larger than that for C_1 and C_4 and is comparable to that in ferrocene ($J = 174$ cps),[18] both being greater than the coupling constants observed[17] for the corresponding atoms in 1,3-butadiene ($J = 158$ cps) and cyclopentadienyl anion ($J = 157$ cps). Thus, the C–H bonding at C_2 and C_3 in the diene–iron tricarbonyl complex is very similar to that in ferrocene. It is concluded from these data that all of the C–H bonds in the complex are essentially sp^2 hybrids.

Further evidence consistent with this conclusion is provided by the geminal H–H coupling constant of the terminal CH_2 groups in butadiene–iron tricarbonyl. The magnitude of this constant has been reported[12] to be 2.5 cps, in good agreement with the value of about +3 cps predicted for sp^2 hybridization from coupling constants and their dependence upon reported electronegativities of substituents on ethylenes.[19]

Both the central and terminal ^{13}C chemical shifts in the butadiene complex (107 and 151.7 ppm upfield from CS_2) are substantially upfield from the corresponding values in butadiene and from any values reported[15] for unsaturated carbons in olefinic hydrocarbons. For the methyl octadecadienoate complex, both chemical shifts ($\sim$108 and $\sim$129 ppm) lie between the olefinic and aliphatic spectral regions. In fact, the chemical shifts for the two complexes are in the general range of the carbon shielding in ferrocene ($\delta_C = 123.6$ ppm)[18] in which the ^{13}C resonance is found at much higher field than in cyclopentadiene ($\delta_C = 60.8$ ppm)[17] or in the cyclopentadienyl anion ($\delta_C = 90.7$ ppm).[17]

(11) M. R. Churchill, *J. Organometal. Chem.*, **4**, 258 (1965).

(12) S. Sternhell, *Rev. Pure Appl. Chem.*, **14**, 15 (1964). This article cites unpublished results of J. C. Davis, Jr.

(12a) NOTE ADDED IN PROOF. Details of the latter, as well as a brief report of ^{13}C data, have now been published by J. C. Davis, Jr., *J. Am. Chem. Soc.*, **88**, 1585 (1966).

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(15) R. A. Friedel and H. L. Retcofsky, *J. Am. Chem. Soc.*, **85**, 1300 (1963).

(16) G. J. Karabatsos and C. E. Orzech, *ibid.*, **86**, 3574 (1964).

(17) H. Spiesecke and W. G. Schneider, *Tetrahedron Letters*, 468 (1961).

(18) P. C. Lauterbur, *J. Am. Chem. Soc.*, **83**, 1838 (1961).

(19) See, *e.g.*, H. S. Gutowsky and C. Juan, *Discussions Faraday Soc.*, **34**, 52 (1962), and references therein.

Lauterbur and King have recently shown that a plot of the carbon shieldings of transition metal cyclopentadienyl derivatives against the shieldings of the associated protons is nearly linear.[20] Two of the compounds studied, $(C_5H_5)_2Fe$ and $CH_3COFe(CO)_2C_5H_5$, contained iron atoms. A least-squares treatment of their data using the proton chemical shift as the independent variable yields the equation

$$\delta_C = 197.7 - 18.06\delta_H \qquad (1)$$

where δ_C is the ^{13}C chemical shift with respect to carbon disulfide ($\delta_C = 0$ ppm) and δ_H is the proton shift referred to tetramethylsilane ($\delta_H = 0$ ppm). Substitution in eq 1 of the published value for δ_H of $H_{2,3}$ in the butadiene complex[4] yields a calculated ^{13}C shift of 102.3 ppm which is only slightly less than the observed value, 107.0 ppm. For the methyl octadecadienoate complexes, the observed value, $\sim$108 ppm, agrees well with that calculated from eq 1, 107.6 ppm. Thus, not only the ^{13}C but also the proton shifts indicate that the bonding at $C_{2,3}$ in the diene complex is similar to that in ferrocene.

However, the situation with respect to the terminal proton and ^{13}C shifts is not nearly as straightforward. Use of eq 1 to calculate the ^{13}C shift for the terminal carbons in the butadiene complex from the literature value[4] for the shift of the *syn* proton at $C_{1,4}$ leads to a value which is higher than that observed (164.4 vs. 151.7 ppm). For the methyl octadecadienoate complex, the deviation between the ^{13}C shift calculated from the shift of the *anti* proton and the observed value is even larger (163.9 vs. $\sim$129 ppm), but the calculated value is nonetheless much smaller than the ^{13}C shift (193.7 ppm) calculated from the δ_H observed for the *anti* proton in the butadiene complex. These differences in the terminal proton and ^{13}C shifts between the butadiene and methyl octadecadienoate complexes are indicative of structural differences at $C_{1,4}$ in the two complexes. Thus, unless eq 1 is a very poor approximation for terminal carbons of acyclic diene systems,[21] it appears that the methyl octadecadienoate complex is more similar to ferrocene than is the butadiene complex. Differences in angular distortion of the ligand are the most likely cause of the differences in the complexes.

A reasonably self-consistent picture emerges from the various results. The bonding of Fe at $C_{2,3}$ in the diene complexes is very similar to that in ferrocene. However, steric effects[22] at the terminal CH_2 or CHR

groups twist them about the C_1–C_2 and C_3–C_4 bonds. This steric effect leads to a smaller rotational displacement in the substituted butadiene system of the methyl octadecadienoate complex. In the rotation the sp² hybridization at both carbons is relatively unaffected, presumably because the carbon p_z orbitals involved in the C–C π bonds of the butadiene residue are used to form three-center π bonds to the Fe, such as those described by Churchill for a Co complex.[11] Nonetheless, the rotation of the $C_{1,4}$ p_z orbitals leads to differences in the bonding of the Fe to $C_{1,2}$ (and $C_{3,4}$) and to $C_{2,3}$ such that the latter is similar to the bonding in ferrocene but the former differs. This interpretation is consistent with the differences in the Fe–C bond distances[13] and in the ^{13}C and proton shifts as well as with the H–H and ^{13}C–H coupling constants.

In summary it may be said that the ^{13}C spectra of these two diene–iron tricarbonyl complexes support a structure approaching I in which all four carbon atoms of the butadiene system have essentially sp² hybridization. ^{13}C magnetic resonance studies therefore provide a valuable diagnostic tool of the bond type in these organometallic compounds.

Experimental Section

(20) P. C. Lauterbur and R. B. King, *J. Am. Chem. Soc.*, 87, 3266 (1965).

(21) Equation 1 should, of course, be more applicable to the *syn* H than to the *anti* H of the complexes, because the former is more comparable to the hydrogen atoms of cyclopentadienyl complexes.

(22) A similar effect has been invoked by Cais and Maoz[3] to account for the variation in stability of various iron tricarbonyl complexes of β-ionones. They suggest that molecular overcrowding at the terminal positions results in twisting around the "essential single bond" (C_2–C_3). This deviation from coplanarity would account for the instability of certain substituted butadiene–iron tricarbonyl complexes. Also Emerson, et al.,[23] have pointed out that the reaction of acyclic dienes with Fe(CO)₅ favors complexes with *trans* (or *syn*) substituents on the diene ligand which are more stable and subject to less steric strain than those with *cis* (or *anti*) substituents.

(23) G. F. Emerson, J. E. Mahler, R. Kochhar, and R. Pettit, *J. Org. Chem.*, 29, 3620 (1964).

(24) H. Reihlen, A. Gruhl, G. V. Hessling, and O. Pfrengle, *Ann.*, 482, 161 (1930).