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## Spectroscopic Studies of the Structures of Protonated Dieneiron Tricarbonyl Complexes<sup>1a</sup>

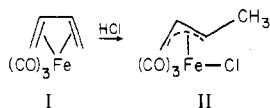
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The species generated from protonation of butadieneiron tricarbonyl and cyclohexadieneiron tricarbonyl in strongly acidic media have been studied by infrared and <sup>13</sup>C NMR spectroscopy. As previously determined, protonation occurs at iron in these systems to yield monoprotonated metal hydride species. Based on the <sup>13</sup>C data reported here, the best description of the bonding between iron and the four-carbon ligand is one in which iron is  $\sigma$  bound to a terminal carbon and  $\pi$  bound to the remaining allyl moiety. <sup>13</sup>C spectra are also reported for  $\pi$ -allyliron tetracarbonyl cations which serve as models for the allyl fragment of the  $\sigma$ - $\pi$  species. Analysis of the <sup>13</sup>C-H coupling constants suggests that the metal hydride may be bridging between iron and carbon in the protonated species. Infrared studies support the proposed structures and further suggest that the 16-electron unsubstituted  $\pi$ -allyliron tricarbonyl cation is not generated by ionization of  $\pi$ -allyliron tricarbonyl trifluoroacetate in strongly acidic media (HBF<sub>4</sub>-TFA).

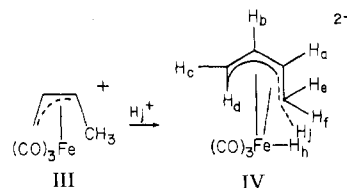
Basic to the elucidation of the reactivity of low-valent polyolefin transition metal complexes is an understanding of their reactions with simple electrophiles, particularly the proton. Investigations of the protonation of simple dieneiron tricarbonyl complexes have revealed a remarkable variety of reactions which depend critically on the exact reaction conditions employed. Protonation of dieneiron tricarbonyl complexes with HCl or HBr where the halide ion is a strongly coordinating anion yields coordinatively saturated  $\pi$ -allyliron tricarbonyl halides.<sup>2</sup> For example, reaction of butadieneiron tricarbonyl, I, with HCl leads to a change in configuration of the diene and production of *syn*-1-methylallyliron tricarbonyl chloride, II.<sup>2b</sup>



In acids with weakly coordinating anions, behavior is somewhat more complex. Gibson<sup>3</sup> has shown that when acyclic dieneiron tricarbonyl complexes are treated with HBF<sub>4</sub> in acetic anhydride at 25 °C, the saturated  $\pi$ -allyliron tetracarbonyl tetrafluoroborate salts could be isolated. Such species are apparently formed from capture of CO by the coordinatively unsaturated  $\pi$ -allyliron tricarbonyl cation. Whitesides<sup>4</sup> has observed similar behavior in trifluoroacetic acid (TFA) and has further shown that in deuterated TFA complete exchange of the terminal protons of the complexed diene occurs before formation of the allyliron tetracarbonyl cation. When cyclohexadieneiron tricarbonyl is treated with TFA, no  $\pi$ -allyl complex is formed; however, Whitesides has demonstrated that the endo protons of the methylene groups undergo rapid and complete exchange in TFA-*d*<sub>1</sub> at 25 °C.<sup>4</sup> The results demonstrate that protonation of the diene ligand is endo and highly stereospecific (probably through an iron hydride intermediate; see below). In early work Pettit<sup>5</sup> reported isolation of tetrafluoroborate salts of substituted  $\pi$ -allyliron tricarbonyl cations at 25 °C; however, in view of the results of Gibson<sup>3</sup> and Whitesides,<sup>4</sup> it is likely such salts are in fact at least principally the tetracarbonyls.

Young, Holmes, and Kaesz<sup>6</sup> studied by <sup>1</sup>H NMR the low-temperature (-78 °C) protonation of a number of

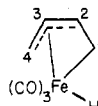
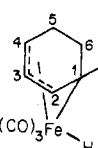
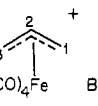
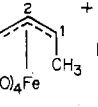
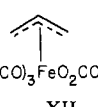
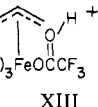
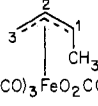
dieneiron tricarbonyl complexes in the highly acidic HSO<sub>3</sub>-F-SO<sub>2</sub> medium. When the complexes were treated with 1 equiv of acid, a  $\pi$ -allyl species was formed which was presumed to be the unsaturated  $\pi$ -allyliron tricarbonyl cation. Upon addition of excess acid, a second species was formed which was postulated to be a diprotonated species. The structure of this diprotonated species is illustrated as structure IV for butadieneiron tricarbonyl; its formation was presumed to occur by attack of the second proton H<sub>j</sub> on the saturated carbon of the  $\pi$ -allyl complex III with shift of H<sub>h</sub> from saturated carbon



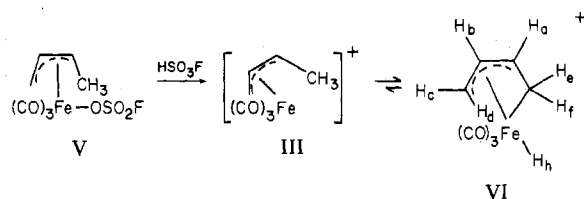
to iron. The low-temperature (-80 °C) <sup>1</sup>H NMR spectrum of IV revealed an iron hydride at  $\tau$  24.59 and one-proton signals at  $\tau$  3.05 (H<sub>a</sub>), 3.56 (H<sub>b</sub>), 6.37 (H<sub>c</sub>), 8.33 (H<sub>d</sub>), 9.00 (H<sub>e</sub>), and 10.96 (H<sub>f</sub>). Measured coupling constants were  $J_{fh} = 22$ ,  $J_{eh} = 14$ ,  $J_{bd} = 11.7$ ,  $J_{cd} = 3.7$ ,  $J_{bc} = 7.8$ ,  $J_{ab} = 6.5$ , and  $J_{cf} \approx 7$  Hz. The H<sub>j</sub> proton was proposed to be in rapid equilibrium with solvent acid and thus not observed in the <sup>1</sup>H NMR spectrum. At higher temperatures the <sup>1</sup>H NMR signals assigned to H<sub>e</sub>, H<sub>f</sub>, and H<sub>h</sub> broaden and eventually merge to a single resonance, indicating rapid intramolecular scrambling of these three protons. This scrambling was presumed to occur via deprotonation back through species III as an intermediate in which the three protons of the methyl group become equivalent.

Brookhart and Harris<sup>7</sup> have recently offered an alternative interpretation of the results of Kaesz.<sup>6</sup> The initially generated species (III) was proposed to be a covalent fluorosulfonate, V. In the presence of excess acid ionization of the fluorosulfate ligand occurs. The final species formed was postulated to be monoprotonated VI rather than diprotonated IV. In structure VI, iron is  $\pi$  bound to an allyl fragment and  $\sigma$  bound to a terminal carbon. This can be viewed as arising from the oxidative addition of a C-H bond of the methyl group to iron. In the formation of VI, the unsaturated  $\pi$ -allyliron tricarbonyl

Table I.  $^{13}\text{C}$  NMR Data for Iron Carbonyl Complexes

Compd	Medium	$T, ^\circ\text{C}$	$^{13}\text{C}$ shifts and assignments <sup>a</sup>
 VI	$\text{HSO}_3\text{F}-\text{SO}_2$ $\text{TFA}-\text{HBF}_4$	-80 and -20 0	$\text{C}_1, -3.0; \text{C}_2, 80.7; \text{C}_3, 100.2; \text{C}_4, 52.7; \text{CO's}, 195.8, 198.9, 202.8$ $\text{C}_1, -1.9; \text{C}_2, 81.7$ (d, 179 Hz); $\text{C}_3, 101.9$ (d, 176 Hz); $\text{C}_4, 54.0$ (t, 161 Hz); $\text{CO's}, 203.0, 199.7, 196.5$
 X	$\text{HSO}_3\text{F}-\text{SO}_2$ $\text{TFA}-\text{HBF}_4$	-80 -20 25	$\text{C}_1, \text{C}_5, 19.0$ or $26.4; \text{C}_2, \text{C}_4, 81.2$ or $83.6; \text{C}_3, 96.4; \text{C}_6, 13.8; \text{CO's}, 196.2, 200.3, 203.0$ $\text{C}_1, \text{C}_5, 23.5$ (averaged); $\text{C}_2, \text{C}_4, 82.9$ (averaged); $\text{C}_3, 97.0, \text{C}_6, 14.4$ $\text{C}_1, \text{C}_5, 24.6$ (averaged, dd, 109, 142 Hz); $\text{C}_2, \text{C}_4, 84.5$ (averaged, d, 178 Hz); $\text{C}_3, 99.0$ (d, 179 Hz); $\text{C}_6, 16.0$ (t, 133 Hz); $\text{CO's}, 201.0$ (averaged, 2 C), $201.5$ (1 C)
 VII	$\text{TFA}-\text{HBF}_4$	25	$\text{C}_1, \text{C}_3, 58.5; \text{C}_2, 100.8; \text{CO's}, 198.5, 200.0$
 VIII	$\text{TFA}-\text{HBF}_4$	25	Methyl, $19.2$ (q, 124 Hz); $\text{C}_1, 84.5$ (d, 168 Hz); $\text{C}_2, 96.8$ (d, 163 Hz); $\text{C}_3, 57.0$ (t, 164 Hz); $\text{CO's}, 200.5, 199.4, 199.2, 198.1$
 XII	TFA	25	$\text{C}_1, \text{C}_3, 70.4; \text{C}_2, 107.1; \text{CO's}, 204.5, 205.7$
 XIII	$\text{TFA}-\text{HBF}_4$	25	$\text{C}_1, \text{C}_3, 72.0; \text{C}_2, 108; \text{CO's}$ not observed
 XIV	TFA	0	Methyl, $15.3$ (q, 128 Hz); $\text{C}_1, 82.8$ (d, 161 Hz); $\text{C}_2, 102.8$ (d, 155 Hz); $\text{C}_3, 70.3$ (d, 160 Hz); $\text{CO's}, 206.5, 205.2, 204.6$

<sup>a</sup> Shifts in  $\text{SO}_2-\text{HSO}_3\text{F}$  are in ppm relative to external TMS (capillary). Shifts in TFA and  $\text{TFA}-\text{HBF}_4$  are in ppm relative to external TMS in benzene- $d_6$  in a coaxial inner tube. In certain cases uncoupled spectra were recorded. Observed coupling constants and multiplicities (d = doublet, t = triplet, q = quartet, dd = doublet of doublets) are shown in parentheses.



cation is a possible intermediate and will be further discussed below. We suggested VI more reasonably accounts for the  $^1\text{H}$  NMR data, especially the large coupling between  $\text{H}_f$  and  $\text{H}_h$  (22 Hz) and between  $\text{H}_e$  and  $\text{H}_h$  (14 Hz) and the high-field chemical shifts of  $\text{H}_e$  ( $\tau$  9.00) and  $\text{H}_f$  ( $\tau$  10.86).<sup>7</sup> The monoprotonated species VI avoids the need for postulating protonation at saturated carbon, and, furthermore, the three-proton scrambling can be nicely accounted for by rapid reductive elimination of VI back to V (and/or III) as an intermediate in which all three protons are equivalent. Making use of titration experiments in TFA, Whitesides and Arhart<sup>8</sup> have recently established that the hydride species is in fact monoprotonated, in accord with the suggested structure VI but not the diprotonated structure IV.

In this paper we wish to report an infrared and  $^{13}\text{C}$  NMR study of the species which are formed in strong acids. These studies firmly establish the suggested  $\sigma-\pi$  structure VI for the hydride species and yield additional insight into the structure

and properties of these unusual  $\sigma-\pi$  cations.

## Results

**Carbon-13 NMR Data.** The  $^{13}\text{C}$  chemical shift data as well as the chemical shift assignments for the iron carbonyl complexes studied are summarized in Table I.

**Butadieneiron Tricarbonyl.** To ensure that the protonated complex that we examined by  $^{13}\text{C}$  NMR was identical with the hydride species observed by Kaesz,<sup>6</sup> an initial  $^1\text{H}$  NMR study was conducted. Protonation of butadieneiron tricarbonyl in  $\text{HSO}_3\text{F}-\text{SO}_2$  under conditions where the acid:complex ratio was large (ca. 15:1) yielded the hydride species to which we have assigned structure VI. The  $^1\text{H}$  NMR spectrum of this species at  $-80^\circ\text{C}$  as well as its temperature dependence proved identical in all respects to that originally reported by Kaesz.<sup>6</sup> The  $^{13}\text{C}$  NMR spectrum of this species recorded in  $\text{HSO}_3\text{F}-\text{SO}_2$  at  $-80$  and  $-20^\circ\text{C}$  is shown in Figure 1; shifts and assignments are summarized in Table I together with corresponding data at  $0^\circ\text{C}$  in  $\text{TFA}-\text{HBF}_4$ . Although  $\text{H}_e$ ,  $\text{H}_f$ , and  $\text{H}_h$  scramble and give rise to a temperature-dependent  $^1\text{H}$  NMR spectrum, the process proposed to account for such scrambling does not give rise to carbon averaging. In accord with this, the proton-decoupled  $^{13}\text{C}$  NMR spectrum shows no temperature dependence.<sup>9</sup> In the uncoupled spectrum of VI the signal at 53 ppm appears as a triplet ( $J_{\text{CH}} = 161$  Hz) while those at 81 and 100 ppm appear as doublets ( $J = 179$

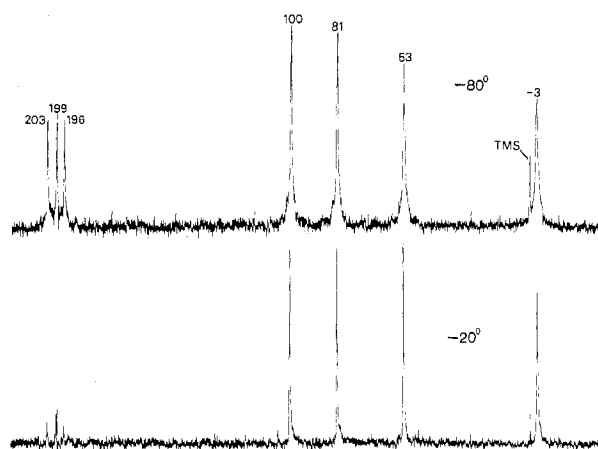
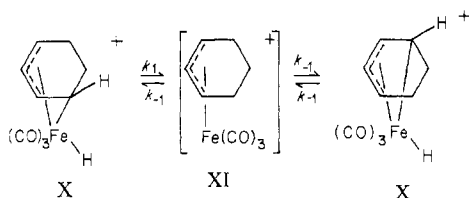


Figure 1.  $^{13}\text{C}$  NMR spectrum of protonated butadieneiron tricarbonyl in  $\text{HSO}_3\text{F-SO}_2$  at  $-80$  and  $-20^\circ\text{C}$ . Numbers indicate band positions in ppm downfield from external capillary TMS.

and 176 Hz, respectively). These signals are assigned to  $\text{C}_4$ ,  $\text{C}_2$ , and  $\text{C}_3$  by comparison with the spectra of the  $\pi$ -allyl tetracarbonyl cations VII and VIII, which were used as models for the  $\pi$ -allyl system in VI. As indicated in Table I, the resonances of VIII, the methylallyliron tetracarbonyl tetrafluoroborate, in particular correspond closely to those of VI, the unsubstituted terminal carbon in VIII giving rise to a signal at 57 ppm, the methyl-substituted terminal carbon a signal at 85 ppm, and the central carbon a signal at 97 ppm. Thus the band at  $-3$  ppm in VI must be assigned to the  $\sigma$ -bound carbon  $\text{C}_1$ . The bands at 196, 199, and 203 ppm for VI are in the range of many other iron carbonyl resonances and are clearly due to three nonequivalent carbonyl carbons.<sup>10</sup>

**Cyclohexadieneiron Tricarbonyl (IX).** Protonation of IX in  $\text{HSO}_3\text{F-SO}_2$  (15:1 molar ratio of  $\text{HSO}_3\text{F}$  to IX) or  $\text{TFA-HBF}_4$  led again to a hydride species whose  $^1\text{H}$  NMR spectrum in the range of  $-80$  to  $-20^\circ\text{C}$  was essentially identical with that reported by Kaesz.<sup>6</sup> In analogy with VI, we reformulate this species as the monoprotonated  $\sigma$ - $\pi$  species X, and this hypothesis is confirmed by titration experiments in TFA similar to those described for VI. The temperature-dependent  $^1\text{H}$  NMR spectrum can then be explained by a mechanism which involves reductive elimination to the symmetrical  $\pi$ -allyl species XI as an intermediate.



The  $^{13}\text{C}$  NMR spectrum of X at  $-80^\circ\text{C}$  as well as shift assignments are summarized in Table I. As expected from this mechanism, the  $^{13}\text{C}$  NMR spectrum is also temperature dependent. As the temperature is raised above  $-80^\circ\text{C}$ , the pair of lines at 81 and 84 ppm ( $\text{C}_2$ ,  $\text{C}_4$ ) and the pair of lines at 19 and 26 ppm ( $\text{C}_1$ ,  $\text{C}_3$ ) broaden and merge. This behavior is illustrated in Figure 2 for the pair of lines at 19 and 26 ppm. From the line widths of the 19- and 26-ppm signals at  $-50^\circ\text{C}$  (ca. 55 Hz at half-height),  $k_1$  can be estimated<sup>11</sup> to be ca.  $1.5 \times 10^2 \text{ s}^{-1}$  which corresponds to a  $\Delta G^\ddagger$  of ca. 11 kcal/mol for conversion of X to XI. The temperature dependence of the carbonyl signals is also of interest. At  $-80^\circ\text{C}$ , three nonequivalent carbonyls can be distinguished, at 196, 200, and 203 ppm. The signal to noise problem<sup>8</sup> in the  $\text{HSO}_3\text{F-SO}_2$  solvent system at  $-20^\circ\text{C}$  was such that the CO resonances could not be clearly resolved. However, at  $25^\circ\text{C}$ , in TFA-

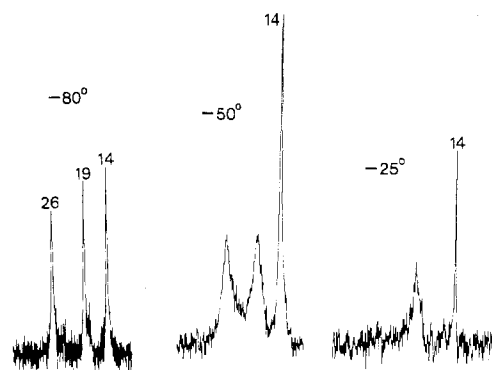


Figure 2.  $^{13}\text{C}$  NMR spectrum in the 10–30-ppm region of protonated cyclohexadieneiron tricarbonyl in  $\text{HSO}_3\text{F-SO}_2$  at  $-80$ ,  $-50$ , and  $-25^\circ\text{C}$ . Numbers indicate band positions downfield from external capillary TMS.

$\text{HBF}_4$ , the spectrum of the averaged species clearly shows two carbonyl signals at 201.0 and 201.5 ppm with relative intensity ratios of 2:1. This observation indicates that the two carbonyl carbons which give rise to the low- and high-field carbonyl resonances become equivalent in X and are thus averaged. Otherwise, the spectrum is very similar to that observed in  $\text{HSO}_3\text{F-SO}_2$  (see Table I) at  $-25^\circ\text{C}$ .

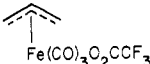
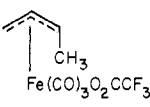
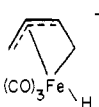
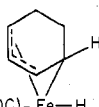
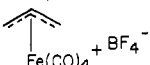
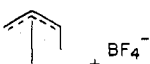
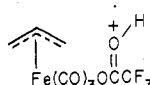
The uncoupled  $^{13}\text{C}$  spectrum was obtained for the rapidly fluxional system at  $25^\circ\text{C}$  in  $\text{HBF}_4\text{-TFA}$ . The observed  $J^{13}\text{C-H}$  coupling constants are summarized in Table I. Of particular note is the appearance of the averaged  $\text{C}_1$ ,  $\text{C}_5$  resonance as a doublet of doublets with couplings of 109 and 142 Hz. Assuming the endo  $\text{C}_5$  hydrogen is coupled to  $\text{C}_5$  by ca. 130–140 Hz, then the value of the coupling between  $\text{C}_6$  and the iron-bound hydrogen must lie between 78 and 88 Hz. This is remarkably high for a geminal C–H coupling constant; possible structural implications are discussed below.

The mechanism shown above, by which  $\text{C}_1$  and  $\text{C}_5$  equilibrate rapidly on the NMR time scale, is not sufficient to explain the incorporation of two deuterium atoms into IX on exposure to TFA-*d*.<sup>4a</sup> This mechanism must be coupled to a slower reversible protonation in order to rationalize this observation.

**$\pi$ -Allyl Complexes.** Included in Table I are  $^{13}\text{C}$  NMR chemical shifts for three complexes containing the unsubstituted  $\pi$ -allyl ligand, which obviously cannot give rise to the  $\sigma$ - $\pi$  structure. Two of these species have been isolated and unambiguously characterized as the covalent, neutral  $\pi$ -allyliron tricarbonyl trifluoroacetate XII and the  $\pi$ -allyliron tetracarbonyl cation VII.<sup>7</sup> The neutral species XII shows resonances at 70.4 and 107.1 ppm for terminal carbons and central carbons respectively, whereas the resonances of the cationic complex are substantially shifted, to 58.5 and 100.8 ppm. Species XII and VII are presumably structurally fairly similar and differ principally in that VII bears a positive charge; hence, we regard the large shift difference between the terminal carbons of these species to be diagnostic of the charge difference. It is therefore interesting that the species formed from the covalent trifluoroacetate on addition of excess  $\text{HBF}_4$  shows resonances at 72 ppm (relative intensity 2;  $\text{C}_1$ ,  $\text{C}_3$ ) and 108 ppm (relative intensity 1;  $\text{C}_2$ ), very close to the corresponding signals for the covalent complex XII and quite distant from those of the cation. We interpret these data to mean that, on protonation, there is only a small change in the charge density at the  $\pi$  ligand and thus that a solvent (TFA) molecule remains coordinated, as shown in XIII (Table I). Further evidence for this hypothesis is derived from ir data (see below).

**Infrared Data.** The metal carbonyl stretching frequencies for several of the complexes discussed here are summarized

Table II. Metal Carbonyl Stretching Frequencies<sup>a</sup>

Compd	Source	$\nu_{\text{MCO}}$ , $\text{cm}^{-1}$
Neutral $\pi$ -allyl trifluoroacetates		
 XII	<i>b</i>	2030, 2068, 2113
 XIV	I dissolved in TFA	2033, 2063, 2112
$\sigma$ - $\pi$ cations		
 VI	I dissolved in TFA-HBF <sub>4</sub>	2087, 2136
 X	VIII dissolved in TFA-HBF <sub>4</sub>	2084, 2128
Tetracarbonyl cations		
 VII	<i>b</i>	2099, 2115, 2156
 VIII	<i>b</i>	2095, 2112, 2155
Solvent-coordinated cation		
 XIII	XII in TFA-HBF <sub>4</sub>	2058, 2082, 2125

<sup>a</sup> TFA solution. <sup>b</sup> Isolated, characterized species dissolved in TFA.

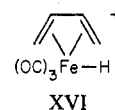
in Table II. The spectra from which these data were derived were obtained on TFA solutions in polyethylene cells at room temperature using a Digilab FTS-20 Fourier transform spectrometer for increased sensitivity. The close similarity between the bands obtained for XII and the species XIV formed from I on solution in TFA and for VI and X provides convincing evidence that the species in each case are similar molecules. That is, the result of TFA addition to I is a covalent trifluoroacetate (and not the tricarbonyl cation) and the structures of VI and X are both of the  $\sigma$ - $\pi$  type. The only unique species in Table II is XIII, from protonation of the covalent trifluoroacetate XII. If this species were the unsaturated tricarbonyl cation XV, a more substantial shift, relative to XII, in the carbonyl stretching frequencies would be expected than is actually observed. In the other series, a shift of approximately 50–60  $\text{cm}^{-1}$  accompanies an increase in positive charge. The observed shifts for XIII are only 12–28  $\text{cm}^{-1}$ , consistent with the presence of a more electron-withdrawing ligand than trifluoroacetate but not a full positive charge, and thus provide further evidence for the coordination of a solvent molecule.

### Discussion

The <sup>13</sup>C NMR and ir spectral data presented here provide substantial insight into the structures of the species formed in highly acid media from complexes I, IX, and XII. First,

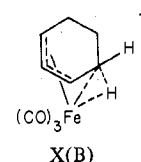
they provide firm support for the formulation of the rapidly exchanging metal hydrides VI and X in terms of the  $\sigma$ - $\pi$  structures proposed by Brookhart and Harris.<sup>7</sup> Particularly compelling is the chemical shift of the C<sub>1</sub> carbon at –2 to –3 ppm in VI. It is well-known that, in general, the  $\alpha$  carbons of transition metal alkyls exhibit high-field <sup>13</sup>C chemical shifts.<sup>12,13</sup> For example, the methyl carbon in CpFe(CO)<sub>2</sub>CH<sub>3</sub> appears at –23 ppm.<sup>13</sup> Considering that species VI bears a positive charge and C<sub>1</sub> bears  $\alpha$  (C<sub>2</sub>) and  $\beta$  (C<sub>3</sub>) carbon substituents, a downfield shift of ca. 20 ppm from CpFe(CO)<sub>2</sub>CH<sub>3</sub> seems reasonable for the  $\sigma$ -bound C<sub>1</sub> species VI.

From the similarities of the C<sub>4</sub> (53 ppm), C<sub>3</sub> (100 ppm), and C<sub>2</sub> (81 ppm) shifts of VI with those of the terminal (58.5 ppm) and internal (100.8 ppm) carbons of the  $\pi$ -allyliron tetracarbonyl VII and the methylallyl complex VIII (C<sub>4</sub>, 57 ppm; C<sub>3</sub>, 97 ppm; C<sub>2</sub>, 85 ppm), it seems clear that the bonding of the C<sub>2</sub>–C<sub>3</sub>–C<sub>4</sub> fragment of VI must approximate a  $\pi$ -allyl unit. The large chemical shift difference of 56 ppm between the terminal carbons C<sub>1</sub> and C<sub>4</sub> indicates a radical difference in their mode of bonding to iron. For example, this difference rules out a structure such as XVI in which the four-carbon



ligand is represented as a  $\pi$ -bound diene. This would result in the shift difference being primarily ascribed to differences in shielding of C<sub>1</sub> and C<sub>4</sub> due to an unsymmetrical (with respect to the diene) arrangement of the hydride and three carbonyl ligands. It is highly unlikely that a chemical shift difference of 56 ppm could be accounted for by remote structural differences of this nature. As pointed out previously,<sup>7</sup> proton chemical shifts and coupling constants also argue against structure XVI.

Although the <sup>13</sup>C shifts of the C<sub>1</sub> carbons of VI and X as well as the C<sub>2</sub>–C<sub>3</sub>–C<sub>4</sub>  $\pi$ -allyl carbons clearly point to ( $\sigma$ - $\pi$ )-allyl type systems, the coupling of ca. 78–88 Hz between C<sub>1</sub> and the iron-bound hydrogen seems unusually large for structure X as written. Two-bond geminal C–X–H couplings are usually much smaller,<sup>14</sup> although no good models exist for the expected <sup>13</sup>C–Fe–H coupling. The coupling between <sup>13</sup>C of coordinated cyanide ligands in metal hydride species can be large as in HRh(CN)<sub>5</sub><sup>3-</sup> (trans  $J_{\text{HRhC}}$  = 56 Hz, cis  $J_{\text{HRhC}}$  = 5.7 Hz);<sup>15</sup> however, in these cases the coordinated carbons are sp hybridized. Such a large  $J_{\text{CFeH}}$  coupling constant in ion X suggests to us the possibility that the hydrogen is partially bound to C<sub>1</sub> and that the best representation of the  $\sigma$ - $\pi$  species might be one in which the hydrogen is bridged between iron and carbon as in X(B). This kind of bridged



interaction has been suggested by Parshall<sup>16</sup> as a possible transition-state structure in the intramolecular ruthenium- and platinum-catalyzed exchange of aliphatic hydrogens in certain alkylphosphine complexes and is also similar to the interaction between an aliphatic hydrogen and molybdenum in pyrazolylborate complexes studied by Cotton<sup>17</sup> and Trofimenko.<sup>18</sup> Confirmation or rejection of a bridged structure such as X(B) must await further experimental results.

The observed carbonyl resonances for VI and X also yield information concerning the structures of these species. It is well established that decreased back-bonding to transition metal carbonyls results in an *upfield* shift of the carbonyl

carbon resonance.<sup>10</sup> In the series of iron tricarbonyl derivatives, the <sup>13</sup>CO resonances for *iron(0)* diene tricarbonyl complexes typically occur in the 210–214-ppm range,<sup>9</sup> while for *iron(II)* species the signals for  $\pi$ -allyliron(II) tricarbonyl iodide appear at ca. 210 and 207 ppm<sup>19</sup> and those for  $\pi$ -allyliron(II) tricarbonyl trifluoroacetate at 204.5 and 205.7 ppm (Table I). The cationic CpFe<sup>II</sup>(CO)<sub>3</sub><sup>+</sup> exhibits a single carbonyl resonance at 203 ppm.<sup>20</sup> On the basis of these examples, there appears to be, in general, a qualitative correlation of <sup>13</sup>CO shifts in tricarbonyl iron derivatives with charge on iron and the extent of back-bonding, although clearly the <sup>13</sup>CO shifts will be sensitive as well to structural differences, as illustrated by the range of <sup>13</sup>CO values in species such as VI. For the  $\sigma$ - $\pi$  species VI and IX, the CO signals at 196 and 200 ppm are the highest field resonances yet reported for iron tricarbonyl derivatives. These high-field shifts give an indication of relatively little back-bonding to the CO ligands in VI and X, consistent with the fact that these species contain iron in the formal oxidation state of IV and are positively charged. On the basis of CO shifts, the extent of back-bonding in VI and X appears qualitatively similar to that in the  $\pi$ -allyliron tetracarbonyl cations VII and VIII, with <sup>13</sup>CO shifts of 198–200 ppm. Infrared studies also support these qualitative arguments. The CO stretching frequencies for the neutral trifluoroacetates XII and XIV are at substantially lower energy ( $\nu_{\text{CO}}$  2030–2033, 2063–2068, and 2112–2113 cm<sup>-1</sup>) than the  $\sigma$ - $\pi$  species VI and X (2084–2087 and 2128–2136 cm<sup>-1</sup>), as expected on the basis of decreased electron density at the metal in the positively charged species. In the absence of detailed force constant calculations, a more quantitative analysis is not warranted, but qualitatively the expected trends are clearly seen.

Earlier in this paper the formation of the  $\sigma$ - $\pi$  species VI and X from the covalent species V and XIV on treatment with excess strong acid was suggested to occur via ionization to the coordinatively unsaturated tricarbonyl cations III and XI. These tricarbonyl complexes also served to rationalize the temperature dependence of the NMR spectra of VI and X. However, there is no direct evidence for the existence of any coordinatively unsaturated complexes in our systems, and the possibility exists that the insertion to yield the metal hydride is concerted with the departure of the protonated or solvated anionic ligand. Assuming, however, that the unsaturated tricarbonyl cations III and XI do account for the fluxional behavior observed, then the energy of these species must lie between ca. 2 and 11 kcal/mol higher than the  $\sigma$ - $\pi$  species. The lower limit results from the fact that neither tricarbonyl is directly observable by NMR or ir spectroscopy, while the upper limit represents the approximate activation energy for hydrogen scrambling in VI and X. The reactivity of these tricarbonyl species is further defined by consideration of the solvated  $\pi$ -allyl cation XIII. The formation of this species to the exclusion of the unsaturated cation XV shows that, even when the formation of the  $\sigma$ - $\pi$  species is precluded, the tricarbonyl cation is still not formed. The further elucidation of the high chemical reactivity of these interesting species is under active investigation.

### Experimental Section

**General Data.** Butadieneiron tricarbonyl and cyclohexadieneiron tricarbonyl were prepared by photolysis of benzene solutions of the

diene and iron pentacarbonyl using standard methods. Complexes were purified by distillation prior to use. All <sup>13</sup>C spectra reported in HSO<sub>3</sub>F–SO<sub>2</sub> media were recorded on a Varian XL-100 NMR spectrometer using a capillary TMS sample as the external reference. <sup>13</sup>C spectra reported in TFA and TFA–HBF<sub>4</sub> media were recorded on a Bruker WH-270 NMR spectrometer using external TMS in benzene-*d*<sub>6</sub> in a coaxial inner tube as a reference. Infrared spectra of species in TFA and TFA–HBF<sub>4</sub> media were recorded in polyethylene cells at room temperature using a Digilab FTS-20 Fourier transform ir spectrometer. All solutions were handled under an atmosphere of dry nitrogen.

**Preparation of NMR Samples.** Preparations of ions in HSO<sub>3</sub>F–SO<sub>2</sub> media were carried out in the following manner. The diene complex was added to a dry NMR tube which was being continuously purged with dry nitrogen. The tube was cooled to –78 °C and SO<sub>2</sub> was condensed onto the complex. This mixture was stirred and HSO<sub>3</sub>F (distilled, degassed) was slowly added. The mixture was stirred until a homogeneous, clear red solution was obtained. These tubes were stored under N<sub>2</sub> at –78 °C for short periods of time until NMR spectra were recorded. Preparations of ions in HBF<sub>4</sub>–TFA media were carried out at 0 °C by dissolving the diene complex in freshly prepared solutions of anhydrous HBF<sub>4</sub> in TFA. The procedure for preparation of anhydrous HBF<sub>4</sub>–TFA solutions has been previously described.<sup>8</sup>

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