

tion from chloroform-pentane gave 0.79 g (78%) of large colorless plates; mp 58°; ir (neat) 3000, 2940, 2260, 1420, 1320, 1150, 880, 750 cm<sup>-1</sup>; nmr (CDCl<sub>3</sub>) δ 2.3 (2 H, m), 2.6 (2 H, t, *J* = 7 Hz), 3.3 (2 H, t, *J* = 7 Hz), 4.5 (2 H, s).

*Anal.* Calcd for C<sub>8</sub>H<sub>8</sub>ClNO<sub>2</sub>S: C, 33.06; H, 4.44; N, 7.71. Found: C, 32.88; H, 4.24; N, 7.54.

(e) *p*-Toluenesulfonyl Chloride. A solution of 1.0 g of oxime **10** and 1.8 g of *p*-toluenesulfonyl chloride in 25 ml of pyridine was stirred at room temperature for 24 hr. The reaction mixture was poured onto ice, acidified with dilute hydrochloric acid, and extracted with chloroform. After the mixture was washed with water and dried, concentration of the chloroform extracts left a residue which showed both nitrile and lactam absorption in the ir. Two recrystallizations from chloroform-pentane yielded 0.11 g (11%) of lactam **15**, colorless needles; mp 141° (lit.<sup>20</sup> mp 141–142.5°); ir (KBr) 3220, 2910, 1655, 1490, 1430, 1290, 1155, 950, 760 cm<sup>-1</sup>;

nmr (CDCl<sub>3</sub>) δ 1.9–2.1 (2 H, m), 2.8 (2 H, m), 3.2 (2 H, s), 3.1–3.3 (2 H, m).

*Anal.* Calcd for C<sub>8</sub>H<sub>9</sub>NOS: C, 45.77; H, 6.91; N, 10.68. Found: C, 45.73; H, 6.89; N, 10.61.

Concentration of the filtrates from recrystallization of the lactam left an oily nitrile, whose ir and nmr spectra were identical with those of the mercaptal **13** obtained in part c.

The same product mixture of lactam and mercaptal resulted when the oxime tosylate was formed separately in acetone and aqueous sodium hydroxide at room temperature and then heated in ethanolic aqueous sodium hydroxide.

**Hydrolysis of Lactam 15.** A solution of 100 mg of lactam **15** in 2 ml of concentrated hydrochloric acid was heated at 100° for 2 hr. The reaction mixture, after cooling and diluting with water, deposited needles of the amino acid hydrochloride **16**, mp 138° (lit.<sup>21</sup> mp 137–138.5°).

## Iron Carbonyl Complexes of Heptafulvene<sup>1</sup>

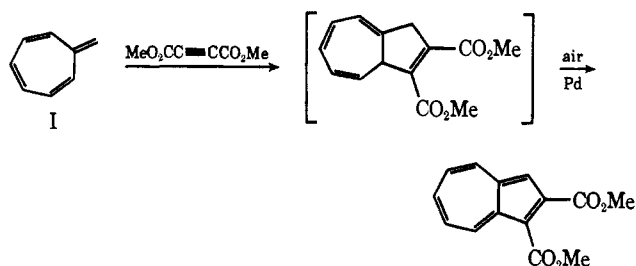
Robert C. Kerber\* and Daniel J. Ehntholt

Contribution from the Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11790. Received August 5, 1972

**Abstract:** The preparation of three iron carbonyl complexes of heptafulvene is described. (Cycloheptatrienylmethyl)- $\pi$ -cyclopentadienyldicarbonyliron hexafluoroantimonate (IIa) has been prepared from 7-(hydroxymethyl)cycloheptatriene (IV) by preparation of the benzenesulfonate ester, displacement by cyclopentadienyldicarbonyliron anion, and hydride removal. 1,6,7,8-Tetrahydroheptafulveneiron tricarbonyl (VII) has been prepared by reaction of IV with diiron nonacarbonyl, followed by distillation at 115°. Further reaction with diiron nonacarbonyl gave heptafulvenediiron hexacarbonyl (XIII). VII appears to be more stable than its 1,2,3,4-*H* isomer, IXa.

Heptafulvene (I) is one of a group of unsaturated hydrocarbons known as fulvenes, many of which are not isolable because of their high reactivity toward oxygen or tendency to polymerize.<sup>2</sup> In many cases, however, fulvenes can be stabilized as ligands in transition metal complexes.<sup>3</sup>

Heptafulvene was first prepared by Doering and Wiley,<sup>4</sup> who found it to be unisolable even at -80°. It polymerized quickly on contact with acids; the only other reactions reported were hydrogenation to methylcycloheptane and cycloaddition with dimethyl acetylenedicarboxylate. A variety of derivatives of I having



electron-withdrawing groups on the exocyclic carbon

(1) (a) Abstracted from the Ph.D. Thesis of D. J. Ehntholt, State University of New York at Stony Brook, March 1971. (b) Preliminary accounts of the research have appeared: D. J. Ehntholt, G. F. Emerson, and R. C. Kerber, *J. Amer. Chem. Soc.*, **91**, 7547 (1969); D. J. Ehntholt and R. C. Kerber, *Chem. Commun.*, 1451 (1970).

(2) E. D. Bergmann, *Chem. Rev.*, **68**, 41 (1968).

(3) R. C. Kerber and D. J. Ehntholt, *Synthesis*, 449 (1970).

(4) W. von E. Doering and D. W. Wiley, *Tetrahedron*, **11**, 183 (1960); D. W. Wiley, Ph.D. Thesis, Yale University, Sept 1954.

have also been prepared.<sup>5</sup> These are generally unstable substances which decompose on warming or on exposure to air. Nonetheless, fairly extensive studies of their chemistry have been made.<sup>5,6</sup>

It appeared to be of value to prepare a stable transition metal derivative of I, from which I itself might be liberated to allow more thorough study of its properties.<sup>7</sup> Moreover, the polyene system of I appeared to offer a variety of sites for metal coordination, so that the organotransition metal complexes themselves were expected to possess interesting properties.

Since acid-catalyzed polymerization of I is thought to involve protonation of the exocyclic double bond,<sup>4</sup> we first sought to prepare a complex in which that re-

(5) See, for example, (a) T. Nozoe, T. Mukai, K. Osaka, and N. Shishido, *Bull. Chem. Soc. Jap.*, **34**, 1384 (1961); (b) H. Kafner, H. W. Riedel, and M. Danieliss, *Angew. Chem., Int. Ed. Engl.*, **2**, 215 (1963); (c) D. J. Bertelli, C. Golino, and D. L. Dreyer, *J. Amer. Chem. Soc.*, **86**, 3329 (1964); (d) C. Jutz, *Chem. Ber.*, **97**, 2050 (1964); (e) P. Bladon, P. L. Pauson, G. R. Proctor, and W. J. Rodger, *J. Chem. Soc. C*, 926 (1966); (f) M. Oda and Y. Kitahara, *Chem. Commun.*, 352 (1969); (g) *Chem. Ind. (London)*, 920 (1969); (h) W. M. Jones and C. L. Ennis, *J. Amer. Chem. Soc.*, **91**, 6391 (1969).

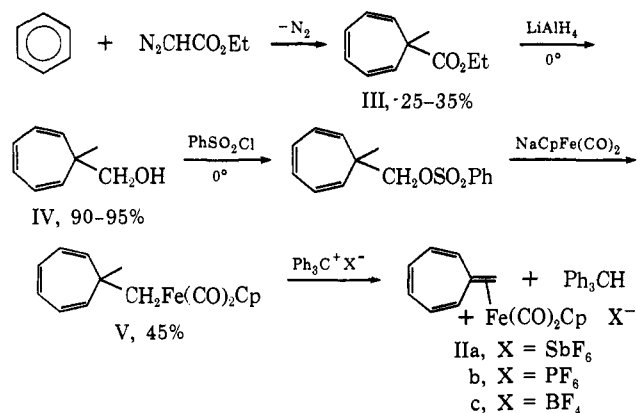
(6) Y. Kitahara and M. Oda in "Aromaticity, Pseudoaromaticity and Antiaromaticity," (Proceedings of Jerusalem Symposium), Israel Academy of Science and Humanities, Jerusalem, 1971, pp 284–294.

(7) (a) A recent preparation of I, with spectra: M. Neuenschwander and W. K. Schenk, *Chimia*, 194 (1972). (b) For calculations on the properties of I, see, for example, D. H. Lo and M. A. Whitehead, *Tetrahedron*, **25**, 2615 (1969); D. Bertelli, T. Andrews, and P. Crews, *J. Amer. Chem. Soc.*, **91**, 5286 (1969); R. Brown, F. Burden, and G. Williams, *Aust. J. Chem.*, **21**, 1939 (1968); H. Kurod and T. Kunii, *Theor. Chim. Acta*, **7**, 220 (1967); R. D. Brown and B. A. W. Coller, *ibid.*, **7**, 259 (1967); N. Tyutyutkov and F. Fratev, *ibid.*, **8**, 62 (1967); M. Titz and P. Hochmann, *Collect. Czech. Chem. Commun.*, **32**, 3028 (1967); and N. L. Allinger, *Tetrahedron*, **22**, 1367 (1966).

active double bond was coordinated to a transition metal.

The Complex (Cycloheptatrienylmethyl)- $\pi$ -cyclopentadienyldicarbonyliron Hexafluoroantimonate (IIa). A number of complexes of simple alkenes, formed by removal of a  $\beta$  hydrogen from alkyl transition metal compounds, are known.<sup>8,9</sup> An analogous route to a heptafulvene complex *via* a (7-cycloheptatrienyl)methyl  $\sigma$ -bonded complex appeared quite feasible (Scheme I).

Scheme I. Synthesis of II



Formation of III by reaction of ethyl diazoacetate with benzene has been achieved both thermally<sup>10,11</sup> and photochemically,<sup>4</sup> using sun lamps. The more convenient photochemical process has been found, however, to yield III contaminated by ethyl phenylacetate and by hydrogen positional isomers;<sup>12</sup> these contaminants arise both photochemically during the reaction<sup>10,13</sup> and thermally during work-up.<sup>12</sup> However, we were able to obtain essentially pure III by photolyzing ethyl diazoacetate in benzene solution using *G.E. 250-W infrared lamps*, by keeping temperatures below 30° during work-up, and then by *rapid* distillation of the product III. Evidently the infrared lamps emit sufficient energy in the visible or near-ultraviolet to excite the light yellow ethyl diazoacetate but not the colorless ester III. The pmr spectrum of III obtained in this manner was identical with that reported<sup>10</sup> for pure III obtained by a more arduous route, no evidence of isomers being discernible.

Reduction of III with lithium aluminum hydride at room temperature using normal addition gave the carbinol IV contaminated with about 20% of material which appeared from pmr to have resulted from reduction of C=C bonds, perhaps by base-catalyzed isomerization of III, followed by conjugate reduction. However, reduction by inverse addition at 0° gave pure IV, whose pmr was identical with that prepared by another route.<sup>12b</sup> Thermolysis of IV at 130° gave principally styrene<sup>4</sup> rather than isomeric alcohols.

The benzenesulfonate ester of IV, prepared at 0°,

(8) M. L. H. Green and P. L. I. Nagy, *J. Organometal. Chem.*, **1**, 58 (1963).

(9) M. L. H. Green and P. L. I. Nagy, *Proc. Chem. Soc., London*, **74** (1962).

(10) G. Linstrumelle, *Bull. Soc. Chim. Fr.*, 920 (1970).

(11) C. Grundmann and G. Ottmann, *Justus Liebig's Ann. Chem.*, **582**, 163 (1953).

(12) (a) F. L. Hedberg, Ph.D. Thesis, University of Massachusetts, Amherst, Mass., 1965; (b) G. D. Sargent, N. Lowry, and S. Reich, *J. Amer. Chem. Soc.*, **89**, 5985 (1967).

(13) G. Linstrumelle, *Tetrahedron Lett.*, 85 (1970).

decomposed exothermically to a black tarry residue when allowed to warm to room temperature. Consequently, the freshly prepared ester was treated with a solution of sodium *h*<sup>5</sup>-cyclopentadienyliron dicarbonyl in THF at -78°.<sup>14</sup> Alumina chromatography gave V in 45% yield as a yellow-orange air-sensitive oil. Spectroscopic data and comparison with similarly synthesized model compounds confirmed the structure of V, particularly the absence of rearrangement to styryl compounds (Table I).

Table I. Spectroscopic Data for RFe(CO)<sub>2</sub>(*h*<sup>5</sup>-Cp)

R	$\nu_{C=O}$ , cm <sup>-1</sup>	( <i>h</i> <sup>5</sup> -Cp) pmr <sup>a</sup> ( $\tau$ )	-CH <sub>2</sub> -Fe pmr <sup>c</sup> ( $\tau$ )
(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> -	2013, 1945 <sup>a</sup>	5.36	8.53
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> - <sup>c</sup>	2011, 1952 <sup>b</sup>	5.59	7.40
C <sub>6</sub> H <sub>5</sub> C(CH <sub>3</sub> )H-	2014, 1953 <sup>a</sup>	5.67	
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> -	2006, 1951 <sup>b</sup>	5.44	8.40
V, C <sub>7</sub> H <sub>7</sub> CH <sub>2</sub> -	2008, 1953 <sup>a</sup>	5.38	8.20

<sup>a</sup> CS<sub>2</sub> solution. <sup>b</sup> CH<sub>2</sub>Cl<sub>2</sub> solution. <sup>c</sup> Synthesis: A. Nakamura and N. Hagihara, *Nippon Kagaku Zasshi*, **84**, 344 (1963).

Reaction of V with trityl salts gave salts, II, which were expected to contain the cation (*h*<sup>5</sup>-cyclopentadienyl)(7,8-*h*<sup>2</sup>-heptafulvene)iron(I) dicarbonyl. The tetrafluoroborate and hexafluorophosphate salts were deep red oils which could not be induced to crystallize. The hexafluoroantimonate salt, however, crystallized as reddish-black crystals, mp 98-101°. All three salts showed identical infrared (except for anion absorptions) and pmr spectra. However, the data were not fully consistent with those to be expected by comparison with other *h*<sup>2</sup>-alkene iron complexes (Table II). In par-

Table II. Spectroscopic Data for Alkene-Fe(CO)<sub>2</sub>(*h*<sup>5</sup>-Cp)<sup>+</sup> Complexes

Alkene	$\nu_{C=O}$ , cm <sup>-1</sup>	( <i>h</i> <sup>5</sup> -Cp) pmr ( $\tau$ )	=CH <sub>2</sub> pmr ( $\tau$ )	$\Delta\nu_{CO}$ ( $\sigma \rightarrow \pi$ ) <sup>a</sup>	$\Delta\tau_{Cp}$ ( $\sigma \rightarrow \pi$ ) <sup>b</sup>
CH <sub>2</sub> =CH <sub>2</sub> <sup>c</sup>	2083, 2049	4.37 <sup>e</sup>	6.46	73, 99	1.03
CH <sub>3</sub> CD=CH <sub>2</sub> <sup>d</sup>	2089, 2055 <sup>f</sup>	4.40 <sup>e</sup>	6.06, 6.53	77, 104	1.01
(CH <sub>3</sub> ) <sub>2</sub> C=CH <sub>2</sub>	2090, 2051 <sup>g</sup>	4.19 <sup>h</sup>	5.98	77, 106	1.17
PhCH=CH <sub>2</sub>	2082, 2040 <sup>f</sup>	4.13 <sup>h</sup>	5.6	76, 89	1.31
Heptafulvene	2033, 1986 <sup>g</sup>	4.73 <sup>h</sup>	6.51	25, 33	0.60

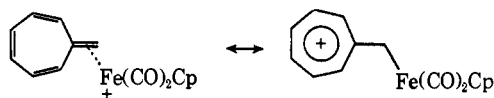
<sup>a</sup> Shift in carbonyl frequencies upon converting *h*<sup>1</sup>-alkyl complex to *h*<sup>2</sup>-alkene complex by hydride removal. <sup>b</sup> Shift in pmr of *h*<sup>5</sup>-cyclopentadienyl ring upon converting *h*<sup>1</sup>-alkyl complex to *h*<sup>2</sup>-alkene complex by hydride removal. <sup>c</sup> Data from E. O. Fischer and K. Fichtel, *Chem. Ber.*, **94**, 1200 (1961), except nmr from this work. <sup>d</sup> Reference 8. <sup>e</sup> SO<sub>2</sub> solution. <sup>f</sup> Nujol mull. <sup>g</sup> CH<sub>2</sub>Cl<sub>2</sub> solution. <sup>h</sup> Acetone-*d*<sub>6</sub> solution.

ticular, the increase in carbonyl frequencies and shift of cyclopentadienyl resonance to lower field, which normally accompany conversion of *h*<sup>1</sup>-alkyl complex to *h*<sup>2</sup>-alkene complex, occur to a smaller extent in converting V to II than in the other cases. Since these shifts are presumably consequences of the increased positive charge on iron in the alkene complexes, they suggest greater dispersal of that charge away from iron in II than in other alkene complexes. Consistent with that view are the chemical shifts of the remaining

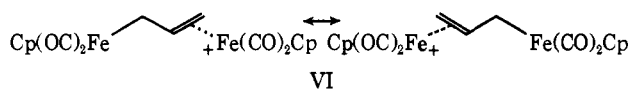
(14) W. P. Giering, Ph.D. Thesis, State University of New York at Stony Brook, Stony Brook, N. Y., 1969, p 124.

protons in II. Those in the seven-membered ring give rise to a resonance at about  $\tau$  2.2, substantially downfield from those of tropone ( $\tau$  3.0),<sup>15</sup> heptafulvalene ( $\tau$  4.09),<sup>16</sup> or even 8,8-dicyanoheptafulvene ( $\tau$  2.8),<sup>15</sup> but upfield from tropylium ( $\tau$  0.86),<sup>17</sup> allyltropylium ( $\tau$  0.97),<sup>15</sup> or cyanomethyltropylium ( $\tau$  0.78)<sup>5f</sup> ions. Similarly, the upfield shift of the methylene protons relative to model  $h^2$ -alkene complexes may be taken to indicate stronger than normal  $\sigma$ -bonding between the iron and the methylene group. The pmr spectrum is unchanged at  $-60^\circ$ .

In short, the spectroscopic data require that II be represented as a hybrid structure (the ir data exclude an equilibrium) rather than as a simple  $h^2$ -alkene complex, the two structures seemingly contributing about



equally. This is further demonstrated by ir and nmr comparison with the ion VI, prepared by King and Bisnette.<sup>18</sup> In VI, each iron must have a net charge of



about  $+1/2$ ; the similarity in  $\tau_{Cp}$  (4.6) and  $\nu_{C=O}$  (2044, 2019  $cm^{-1}$ ) with II indicates a similar charge on iron in II.

These deductions were confirmed by Churchill and Fennessey, based on an X-ray crystallographic study of IIa.<sup>19</sup> Their results showed the iron to be substantially bonded only to the methylene carbon ( $r_{Fe-C(1)}$ , 2.16  $\pm$  0.05  $\text{\AA}$ ;  $r_{Fe-C(2)}$ , 3.00  $\pm$  0.05  $\text{\AA}$ ), so that the compound is structurally best described as a tropylium ion bearing a  $-CH_2Fe(CO)_2Cp$  substituent. The  $Fe-C(1)-C(2)$  bond angle is  $109^\circ$ , and the iron occupies a position on the twofold axis of the heptafulvene moiety. These results, together with the infrared and nmr evidence cited above, show that the positive charge must be distributed between the tropylium ring and the iron without direct bonding interaction between them. This constitutes the firmest evidence available for hyperconjugative (vertical) stabilization of a carbonium ion by a metalloalkyl substituent.<sup>20, 21</sup>

The chemical properties of IIa were consistent with this hybrid structure. Thus, IIa was resistant to hydrogenation, being recovered unchanged after 24 hr under 45 psi of hydrogen in the presence of a platinum on carbon catalyst. It also failed to react with tetracyanoethylene, either by insertion into the  $Fe-C$  bond<sup>22</sup> or addition across the seven-membered ring. Reaction

(15) D. J. Bertelli, C. Golino, and D. L. Dreyer, *J. Amer. Chem. Soc.*, **86**, 3329 (1964).

(16) W. M. Jones and C. L. Ennis, *ibid.*, **91**, 6391 (1969).

(17) G. Fraenkel, R. E. Carter, A. McLachlan, and J. H. Richards, *ibid.*, **82**, 5846 (1960).

(18) R. B. King and M. B. Bisnette, *J. Organometal. Chem.*, **7**, 311 (1967). These authors described interconversion of the two forms as a rapid equilibration, but our results on II favor a true hybrid structure as shown.

(19) M. R. Churchill and J. P. Fennessey, *Chem. Commun.*, 1056 (1970).

(20) For an extensive discussion, see T. G. Traylor, W. Hanstein, H. J. Berwin, N. A. Clinton, and R. S. Brown, *J. Amer. Chem. Soc.*, **93**, 5715 (1971), and references therein.

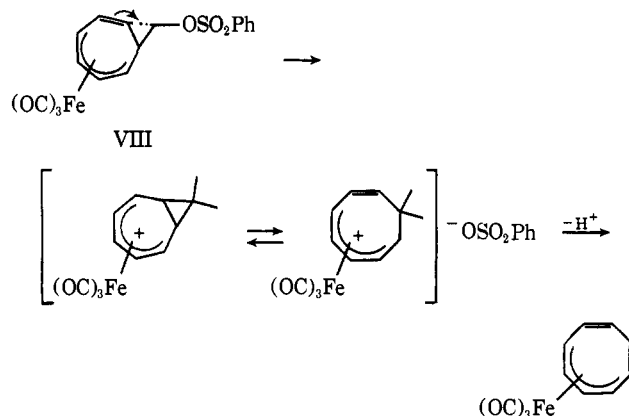
(21) A more recent X-ray crystallographic structure, for bis(cyclobutadienyliron tricarbonyl)phenylcarbonium fluoroborate, provides further such evidence: R. E. Davis, H. D. Simpson, N. Grice, and R. Pettit, *J. Amer. Chem. Soc.*, **93**, 6688 (1971).

(22) S. R. Su, J. A. Hanna, and A. Wojcicki, *J. Organometal. Chem.*, **21**, P 21 (1970).

did occur, however, with nucleophiles: triphenylphosphine and IIa reacted slowly to produce the salt  $[Ph_3PFe(CO)_2Cp]^+ SbF_6^-$  in quantitative yield.<sup>23</sup> The fate of the heptafulvene moiety remains unclear. IIa also reacted with sodium borohydride to give V in admixture with its hydrogen positional isomers; analogous mixtures were obtained in borohydride reduction of the closely related ferrocenyltropylium ion.<sup>24</sup>

Our inability to obtain evidence of free heptafulvene from decomposition of IIa, and our desire for a more easily handled uncharged complex, led to efforts to prepare a heptafulveneiron tricarbonyl complex.

**The Complex 1,6,7,8- $h^4$ -Heptafulveneiron Tricarbonyl (VII).** Our approach to this complex was by reaction of the carbinol IV or its benzenesulfonate derivative with iron carbonyl reagents. Reaction of the benzenesulfonate ester of IV with diiron nonacarbonyl at  $40^\circ$  in hexane gave a product mixture from which could be isolated styrene (26%), styreneiron tetracarbonyl<sup>25, 26</sup> (21%), and cyclooctatetraeneiron tricarbonyl<sup>27, 28</sup> (15%). The formation of styrene and its iron tetracarbonyl derivative was not surprising in view of the production of styrene on thermal dehydration of IV,<sup>4</sup> the formation of styrene on solvolysis of esters of IV,<sup>12b</sup> and the facile complexation of styrene under the reaction conditions.<sup>25, 26</sup> The ring expansion to the cyclooctatetraene complex was, however, unanticipated and does not occur in the absence of the iron tricarbonyl group.<sup>29</sup> This suggests that this reaction initially results in formation of an iron tricarbonyl complex VIII of the starting ester, which rearranges *via*



iron-stabilized carbonium ion intermediates.<sup>30, 31</sup> Reaction of the benzenesulfonate ester of IV with sodium tetracarbonylferrate<sup>32</sup> yielded only styrene and styreneiron tetracarbonyl.

(23) Analogous displacement of propene and butene from their complexes: M. L. H. Green and P. L. I. Nagy, *J. Chem. Soc.*, 189 (1963).

(24) M. Cais and A. Elsenstadt, *J. Amer. Chem. Soc.*, **89**, 5468 (1967).

(25) E. Koerner von Gustorf, M. C. Henry, and C. DiPietro, *Z. Naturforsch. B*, **21**, 42 (1966).

(26) R. Victor, R. Ben-Shoshan, and S. Sarel, *Tetrahedron Lett.*, 4257 (1970).

(27) R. Grubbs, R. Breslow, R. Herber, and S. J. Lippard, *J. Amer. Chem. Soc.*, **89**, 6864 (1967).

(28) T. A. Manuel and F. G. A. Stone, *ibid.*, **82**, 336 (1960).

(29) For a possibly related ring expansion, see J. Lewis and A. W. Parkins, *Chem. Commun.*, 1194 (1968).

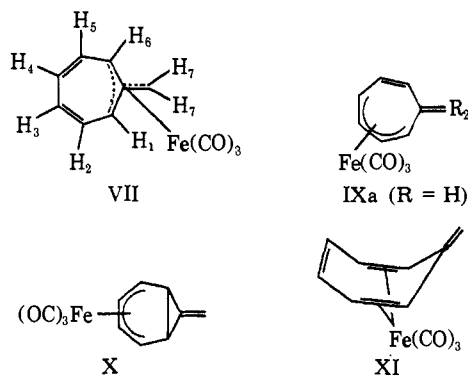
(30) M. Brookhart and E. R. Davis, *J. Amer. Chem. Soc.*, **92**, 7622 (1970).

(31) Formation of cyclooctatetraeneiron tricarbonyl by loss of a proton from the indicated cations: A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 4821 (1962); G. N. Schrauzer, *J. Amer. Chem. Soc.*, **83**, 2966 (1961).

(32) M. P. Cooke, *ibid.*, **92**, 6080 (1970).

The desired complex VII was obtained in 48% yield by reaction of carbinol IV with excess diiron nonacarbonyl in ether, followed by reduced pressure distillation of the crude product at 115°. Further purification by sublimation gave red crystals, mp 38–41°, which gave a correct analysis for  $C_8H_8Fe(CO)_3$ . The complex showed two strong carbonyl stretching frequencies at 2049 and 1980  $cm^{-1}$  ( $CH_2Cl_2$ ), consistent with either a diene- or trimethylenemethane-iron tricarbonyl complex.

The pmr spectrum of the complex ( $CS_2$ ) showed a multiplet at  $\tau$  4.13 (4 H), a doublet of doublets at  $\tau$  6.30 (2 H,  $J = 6$  and 1 Hz), and a sharp singlet at  $\tau$  8.60 (2 H). The simplicity of this spectrum rules out unsymmetrical structures such as IXa, and the chemical



shifts, coupling pattern, and general chemical implausibility rule out the symmetrical structures X and XI. The spectrum is fully consistent with structure VII, however, the uncomplexed diene unit ( $H_2, H_3, H_4, H_5$ ) giving rise to the  $\tau$  4.13 multiplet,  $H_1$  and  $H_6$  the resonance at  $\tau$  6.30, and the exocyclic protons the singlet at  $\tau$  8.60. The latter may be compared with the singlet at  $\tau$  8.00 in trimethylenemethaneiron tricarbonyl;<sup>33</sup> no long-range coupling is anticipated or found due to lack of a "W" bond pattern which is required for such coupling in trimethylenemethane complexes.<sup>34</sup> The  $H_1$  (and  $H_6$ ) proton shows a moderate coupling (*ca.* 6 Hz) to  $H_2$  and a small one (*ca.* 1 Hz) to  $H_3$ ; the chemical shift of this proton agrees well with other substituted trimethylenemethane complexes,  $XC-CH(CH_2)_2Fe(CO)_3$ :  $X = C_6H_5$ ,  $\tau$  5.72;  $X = CO_2CH_3$ ,  $\tau$  6.09.<sup>34</sup>

The mass spectrum of VII (Table III) shows the expected parent peak at  $m/e$  244, and characteristic stepwise losses of carbon monoxide to give ultimately a peak at  $m/e$  160 for  $C_8H_8Fe^+$ . The base peak appears at  $m/e$  104 ( $C_8H_8^+$ ), followed by a further fragmentation pattern with large fragments at  $m/e$  103, 91, 78, 77, 52–50, 40, and 39.<sup>35</sup>

The chemical properties of VII are characterized by low reactivity. Thus, it does not undergo cycloaddition with tetracyanoethylene (TCNE) at room temperature for 14 hr, although the isomeric cyclooctatetraeneiron tricarbonyl reacts completely in less than 1 hr under these conditions.<sup>36</sup> Nor does it react upon 8 hr reflux

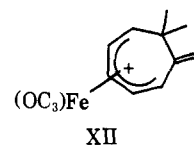
(33) G. F. Emerson, K. Ehrlich, W. P. Giering, and P. C. Lauterbur, *J. Amer. Chem. Soc.*, **88**, 3172 (1966).

(34) K. Ehrlich and G. F. Emerson, *ibid.*, **94**, 2464 (1972).

(35) This cracking pattern does not resemble those of other  $C_8H_8$  isomers recently studied: J. L. Franklin and S. R. Carroll, *ibid.*, **91**, 5940 (1969); it is similar to that of free I.<sup>7a</sup>

(36) D. J. Ehntholt and R. C. Kerber, *J. Organometal. Chem.*, **38**, 139 (1972), and references therein.

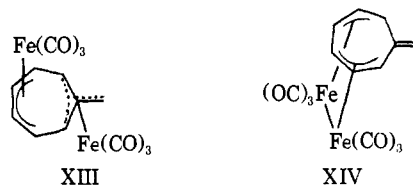
in benzene-acetone solution, conditions which were used for reaction of 1,3-cyclooctadiene with TCNE.<sup>37</sup> An attempted hydrogenation (20 psi  $H_2$ , 25°, 5 hr, 10% Pd-C) also gave only recovered starting material. VII underwent immediate decomposition with gas evolution on addition of  $HBF_4$  to a nitromethane solution. The resulting black solution gave no pmr spectrum; thus, no evidence of formation of either the methyltropyliumiron tricarbonyl fluoroborate<sup>38</sup> or the known complex XII<sup>39</sup> could be obtained.



Thermolysis of VII at about 140° led to its decomposition, giving a yellow iron carbonyl complex having a complicated pattern of pmr resonances. Thermolysis in the presence of dimethyl acetylenedicarboxylate (DMAD) gave in addition an organic product which, upon dehydrogenation with Pd on C, gave a purple product with uv maxima similar to those reported for dimethyl azulene-1,2-dicarboxylate, obtained from heptafulvene and DMAD.<sup>4</sup> Similar attempts to trap heptafulvene with TCNE at 142° gave a complex mixture of products. However, it does appear that VII can function as a stable source of heptafulvene (I), making further study of that highly reactive species practical.

**The Complex Heptafulvenediiron Hexacarbonyl (XIII).** The only reaction which we observed involving the diene grouping of VII was its facile complexation by reaction with diiron nonacarbonyl, to give XIII in 77% yield. This orange-red product was highly insoluble in organic solvents, making purification difficult. The pmr spectrum (acetone- $d_6$ ) showed resonances of equal intensity at  $\tau$  4.0, 6.0, 8.4, and 8.6. Those at  $\tau$  6.0 and 8.6 are similar to those in VII and again show the complexed trimethylenemethane unit. The resonances at  $\tau$  4.0 and 8.4 are consistent with the formation of a dieneiron tricarbonyl unit on the free diene portion of VII, to give XIV. The alternative structure XIV appears to be excluded by the infrared spectrum, which shows only two strong carbonyl stretching frequencies, at 2040 and 1980  $cm^{-1}$ , rather than the five observed for complexes of type XIV.<sup>40</sup> The trans orientation of the iron tricarbonyl groups in XIII is assigned purely for steric reasons.

The mass spectrum of XIII shows a very small parent



ion at  $m/e$  384, and the expected series of ions  $C_8H_8-Fe_2(CO)_n$ ,  $n = 1-6$ , and  $C_8H_8Fe(CO)_m$ ,  $m = 0-2$ .

(37) P. Scheiner and W. R. Vaughan, *J. Org. Chem.*, **26**, 1923 (1961).

(38) Tropyliumiron tricarbonyl fluoroborate: J. E. Mahler, D. A. K. Jones, and R. Pettit, *J. Amer. Chem. Soc.*, **86**, 3589 (1964).

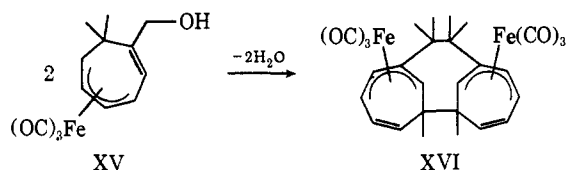
(39) B. F. G. Johnson, J. Lewis, P. McArdle, and G. L. P. Randall, *J. Chem. Soc., Dalton Trans.*, 456 (1972).

(40) F. A. Cotton, B. G. DeBoer, and T. J. Marks, *J. Amer. Chem. Soc.*, **93**, 5069 (1971).

Hydrocarbon fragments similar to those given by VII were also found.

### Discussion

Since the initial report of the synthesis of VII,<sup>1b</sup> Lewis and coworkers<sup>41</sup> have reported the preparation of a number of 8-substituted heptafulveneiron tricarbonyl complexes, all of which possess the unsymmetrical structures IX. However, attempts to prepare the parent complex IXa by dehydration of XV gave a dimeric product which has been found to possess the unexpected structure XVI.<sup>42</sup> IXa has been obtained by



Hunt and coworkers, by treating XII with triethylamine in methylene chloride solution.<sup>43</sup> Reaction of XII with triethylamine in ether solution, however, gave a dimer, presumably XVI.<sup>44</sup>

More recently, Lewis' group has also obtained VII, in 27% yield, by reaction of IV with (benzylideneacetone)iron tricarbonyl in refluxing benzene for 8 hr.<sup>45</sup> They have also reported preparation of *h*<sup>6</sup>-heptafulvene-chromium tricarbonyl.<sup>46</sup>

In contrast to VII, a sample of which has been stored unchanged for more than 2 years, IXa slowly dimerizes at room temperature. Also in contrast to VII, it undergoes cycloaddition with DMAD, and reversible protonation with acids.<sup>43</sup> It is thus evidently more reactive than VII.

It is tempting to infer that, in contrast to the usual situation,<sup>34</sup> the trimethylenemethane complex VII is more thermodynamically stable than the 1,3-diene complex IXa. In any case, the apparent lack of interconversion of the two heptafulveneiron tricarbonyl isomers stands in dramatic contrast to the fluxional character of the isomeric cyclooctatetraeneiron tricarbonyl,<sup>47</sup> apparently reflecting the lack of a practical sequence of 1,2 shifts which will interconvert the heptafulvene complexes.

### Experimental Section<sup>48</sup>

**Materials.** Benzene was distilled from calcium hydride before use; tetrahydrofuran was degassed and distilled from lithium aluminum hydride on a vacuum line; methanol and methylene chloride were spectrophotometric grade (Baker) and were used

(41) B. F. G. Johnson, J. Lewis, P. McArdle, and G. L. P. Randall, *Chem. Commun.*, 177 (1971); *J. Chem. Soc., Dalton. Trans.*, 2076 (1972).

(42) R. Mason, *Proc. Int. Congr. Pure Appl. Chem. (Spec. Lectures)*, 6, 55 (1971).

(43) G. T. Rodeheaver, G. C. Farrant, and D. F. Hunt, *J. Organometal. Chem.*, 30, C22 (1971).

(44) D. F. Hunt, personal communication, Dec 1970.

(45) J. A. S. Howell, B. F. G. Johnson, P. L. Josty, and J. Lewis, *J. Organometal. Chem.*, 39, 329 (1972).

(46) J. A. S. Howell, B. F. G. Johnson, and J. Lewis, *ibid.*, 42, C54 (1972).

(47) F. A. Cotton, *Accounts Chem. Res.*, 1, 257 (1968).

(48) Melting points were measured on a Mel-Temp apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 137 NaCl spectrophotometer or, for the iron carbonyl regions (1900–2100 cm<sup>-1</sup>), on a Perkin-Elmer Model 521 spectrometer. The nuclear magnetic resonance spectra were obtained on a Varian A-60 spectrometer. The mass spectra were obtained on a Hitachi Perkin-Elmer RMU-6D spectrometer. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn.

directly. All other solvents were reagent grade. All reactions were run under an atmosphere of nitrogen and stirred magnetically unless otherwise noted. Solutions were dried using MgSO<sub>4</sub>.

Ethyl diazoacetate was originally prepared according to the method of Searle;<sup>49</sup> later preparations utilized the method of Moser.<sup>50</sup> [ $\pi$ -CpFe(CO)<sub>2</sub>]<sub>2</sub>,<sup>51</sup>  $\pi$ -CpFe(CO)<sub>2</sub>Na,<sup>14</sup> Na<sub>2</sub>Fe(CO)<sub>4</sub>,<sup>52</sup> and Fe<sub>2</sub>(CO)<sub>9</sub>,<sup>52</sup> were prepared by published methods.

**7-(Carbethoxy)cycloheptatriene (III).** A solution of ethyl diazoacetate (50 g, 0.44 mol) in 2750 ml of benzene was stirred and irradiated with two 250-W G.E. infrared heat lamps for 7 days under reflux. Benzene was removed at 30° under reduced pressure. The red liquid products from two similar runs were combined and distilled rapidly at reduced pressure to give (1) 20 ml of ethyl diazoacetate, bp 40–45° (4.0 mm); (2) 18.0 g (23%) of 7-(carbethoxy)cycloheptatriene, bp 90–97° (4.0 mm), lit.<sup>10</sup> bp 56° (0.5 mm); nmr (neat)  $\tau$  3.40 (t, 2 H), 3.83 (m, 2 H), 4.62 (4-line multiplet, 2 H), 5.81 (q, 2 H), 7.56 (m, 1 H), 8.79 (t, 3 H).

**7-(Hydroxymethyl)cycloheptatriene (IV).** Solid lithium aluminum hydride (2.4 g, 0.063 mol) was added very slowly to 7-(carbethoxy)cycloheptatriene (10.0 g, 56 mmol) in 200 ml of ethyl ether at 0°. The solution was then allowed to warm to room temperature over a period of 5 hr. Water (5 ml) was added cautiously with stirring, the ether layer was decanted, and the remaining white paste was triturated with three 40-ml portions of ether. The ether solution was dried and evaporated at reduced pressure to give a yellow oil. Distillation yielded 6.3 g (93%) of 7-(hydroxymethyl)cycloheptatriene (IV): bp 94–98° (3.5 mm), lit.<sup>4</sup> bp 83–85° (3.5 mm); ir (thin film) 3247 (m, OH), 2945 (m), 2854 (w), 2799 (m), 1608 (vw), 1410 (w), 1106 (m), 1052 (m), 1012 (m), 968 (w), 956 (w), 910 (w), 764 (m), 730 (s), 704 (m) cm<sup>-1</sup>; nmr (CCl<sub>4</sub>)  $\tau$  3.48 (t, 2 H), 3.90 (m, 2 H), 4.85 (4-line multiplet, 2 H), 5.60 (br, s, 1 H), 6.30 (d, 2 H, *J* = 6 Hz), 8.15 (m, 1 H).

**7-(Benzenesulfonyloxymethyl)cycloheptatriene.** Benzenesulfonyl chloride (1.47 g, 8.3 mmol) was added dropwise with stirring over a 1-hr period to a solution of IV (1.0 g, 8.2 mmol) in 3 ml of  $\gamma$ -collidine at 0°. After an additional 20 min, 10 ml of methylene chloride and 8 ml of 10% H<sub>2</sub>SO<sub>4</sub> were added. The organic layer was separated and washed with 100 ml of water, 100 ml of 5% NaHCO<sub>3</sub> solution, and again with 100 ml of water, and dried, and the solvent was removed under reduced pressure at 0° to give 1.5 g (70%) of a slightly yellow oil: ir (thin film) 3072 (w), 3025 (m), 2980 (w), 1626 (w), 1592 (w), 1446 (m), 1403 (w), 1365 (s), 1311 (w), 1290 (w), 1210 (w), 1188 (s), 1176 (s), 1128 (w), 1096 (m), 1070 (w), 998 (w), 969 (s), 934 (m), 904 (m), 822 (m), 779 (w), 754 (s), 709 (m), 685 (m) cm<sup>-1</sup>; nmr (CCl<sub>4</sub>)  $\tau$  2.30 (m, 5 H), 3.50 (m, 2 H), 3.90 (m, 2 H), 4.82 (m, 2 H), 5.85 (d, 2 H, *J* = 6 Hz), 7.75 (m, 1 H). It was necessary to keep the ester cold, as it decomposed violently several times upon warming to room temperature.

**(*h*<sup>5</sup>-Cyclopentadienyl)(*h*<sup>1</sup>-7-cycloheptatrienyl)methyl]iron Dicarboxylate (V).** The flask containing the benzenesulfonate (1.5 g, 5.7 mmol) at 0° was purged with nitrogen, stoppered with a serum cap, and cooled to -78°. Then  $\pi$ -CpFe(CO)<sub>2</sub>Na (8.1 ml of a 0.8 M solution in THF, 6.5 mmol) was added through the serum cap. The reaction mixture was allowed to warm to room temperature, solvent was removed, and the hexane-soluble portion was chromatographed on 50 g of neutral alumina, using hexane eluent. A yellow band was collected to yield 0.73 g (45%) of V as an air-sensitive, orange-yellow oil which could be crystallized at -78° from hexane: mp 33.0–34.5°; ir (CS<sub>2</sub>) 3040 (m), 2932 (m), 2872 (m), 2008 (vs), 1953 (vs), 1626 (m), 1402 (w), 1065 (w), 1002 (w), 971 (m), 889 (s), 807 (m), 672 (s) cm<sup>-1</sup>; nmr (CS<sub>2</sub>)  $\tau$  3.45 (t, 2 H), 3.95 (m, 2 H), 4.85 (4-line multiplet, 2 H), 5.38 (s, 5 H), 8.20 (m, 3 H).

**(*h*<sup>5</sup>-Cyclopentadienyl)(*h*<sup>1</sup>-2-phenylethyl)iron Dicarboxylate.**  $\pi$ -Cp-Fe(CO)<sub>2</sub>Na (20.0 ml of a 0.8 M solution in THF, 16 mmol) was added through a serum cap to a sample of 2-phenylethyl bromide (3.0 g, 16 mmol) at -78° under nitrogen. The reaction mixture was allowed to warm to room temperature over a 1-hr period. The solvent was evaporated, and the gummy solid was triturated with three 75-ml portions of hexane. The hexane was evaporated to about 20 ml, and this was chromatographed on 50 g of neutral alumina, eluting with hexane. A yellow band was collected, and the hexane was evaporated to give 3.5 g (78%) of slightly air-sensitive yellow crystals, which were recrystallized from pentane at -78°:

(49) N. E. Searle, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 424.

(50) W. R. Moser, *J. Amer. Chem. Soc.*, 91, 1135 (1969).

(51) R. B. King, "Organometallic Syntheses," Vol. 1, Academic Press, New York, N. Y., 1965, p 114.

(52) Reference 51, p 93.

mp 73–74°; ir (CH<sub>2</sub>Cl<sub>2</sub>) 3020 (vw), 2949 (m), 2872 (w), 2006 (vs), 1951 (vs), 1600 (w), 1487 (w), 1448 (w), 1248 (m), 1106 (w), 995 (w), 828 (m), 704 (s) cm<sup>-1</sup>; nmr (CS<sub>2</sub>)  $\tau$  2.93 (s, 5 H), 5.44 (s, 5 H), 7.35 (m, 2 H), 8.40 (m, 2 H).

Anal. Calcd for C<sub>15</sub>H<sub>14</sub>FeO<sub>2</sub>: C, 63.85; H, 5.00. Found: C, 64.15; H, 5.26.

The isobutyl (61%, liquid), ethyl (87%, liquid), and benzyl (91%, mp 45–47°, lit.<sup>53</sup> mp 54°) complexes were made in the same manner as above.

**Attempted Preparation of (*h*<sup>5</sup>-Cyclopentadienyl)(*h*<sup>1</sup>-1-phenylethyl)iron Dicarbonyl.** Reaction of 1-phenylethyl bromide as above gave about 1.0 g of an unstable yellow oil. Attempts at low-temperature crystallization were unsuccessful. Samples used to obtain spectral data for the complex were contaminated with a considerable amount of decomposition product, but absorptions for the complex could be discerned: ir (CS<sub>2</sub>) 3035 (vw), 2955 (m), 2014 (s), 1953 (s), 1384 (w), 1296 (w), 1259 (s), 1084 (w), 1041 (w), 921 (w), 876 (s), 842 (w), 789 (w), 834 (m), 712 (s) cm<sup>-1</sup>; nmr (CS<sub>2</sub>)  $\tau$  2.97 (m, C<sub>6</sub>H<sub>5</sub>), 5.67 (s, 5 H), 6.40 (q, 1 H, *J* = 8 Hz), 8.38 (d, 3 H, *J* = 8 Hz). The impurity was identified as 2,3-diphenylbutane by comparison of its nmr absorptions with the literature values: nmr (CS<sub>2</sub>)  $\tau$  2.97 (m, C<sub>6</sub>H<sub>5</sub>), 7.2 (m, CH), 8.75 and 9.00 (m, CH<sub>3</sub>); literature values are essentially identical.<sup>54</sup> An nmr absorption due to [ $\pi$ -CpFe(CO)<sub>2</sub>]<sub>2</sub> was also observed at  $\tau$  5.35. This compound was recovered pure from another column chromatography.

**Triphenylcarbonium Hexafluoroantimonate.** Hexafluoroantimonic acid (65%, 3.65 g) was dissolved in 5 ml of acetic anhydride at 0°. Then a suspension of triphenylcarbinol (2.5 g, 10 mmol) in 7 ml of acetic anhydride was added slowly with swirling. The reaction mixture was left in an ice bath for 15 min, filtered quickly, and washed with three 30-ml portions of ether. The resulting 2.8 g (58%) of light yellow crystals, mp 195–200°, were stored under nitrogen and used as quickly as possible.

The other salts used (Ph<sub>3</sub>C<sup>+</sup>PF<sub>6</sub><sup>-</sup> and Ph<sub>3</sub>C<sup>+</sup>BF<sub>4</sub><sup>-</sup>) were prepared similarly.

**(Cycloheptatrienylmethyl)- $\pi$ -cyclopentadienyldicarbonyl-iron Hexafluoroantimonate (IIa).** The  $\sigma$ -complex V (1.0 g, 3.5 mmol) dissolved in 5 ml of CH<sub>2</sub>Cl<sub>2</sub> was added to a solution of freshly prepared trityl hexafluoroantimonate (1.67 g, 3.5 mmol) in a minimum amount of CH<sub>2</sub>Cl<sub>2</sub> at 0°. The solution rapidly turned deep red in color; it was then washed with 10 ml of water and dried and the solvent evaporated at reduced pressure. The resulting red oil was extracted with three 20-ml portions of ethyl ether to remove triphenylmethane, which could be isolated almost quantitatively. The red oil was dissolved in 10 ml of CH<sub>2</sub>Cl<sub>2</sub>, and ether was added until a trace of cloudiness persisted. The flask was stoppered under nitrogen and left overnight at 0°. Crystals formed and were collected (1.15 g, 63%); after several recrystallizations, reddish-black crystals, mp 98–101°, were obtained: ir (CH<sub>2</sub>Cl<sub>2</sub>) 3096 (w), 2033 (s), 1986 (s), 1616 (m), 1498 (s), 1469 (s), 1419 (m), 1212 (s), 947 (m), 845 (w), 825 (s) cm<sup>-1</sup>; uv (CH<sub>2</sub>Cl<sub>2</sub>) 257 nm ( $\epsilon$  11,200), 402 (9700), 517 (2000). The nmr spectrum (see text) did not change on lowering the temperature to -60°.

Anal. Calcd for C<sub>15</sub>H<sub>18</sub>F<sub>6</sub>FeO<sub>2</sub>Sb: C, 34.81; H, 2.51; Fe, 10.80. Found: C, 35.10; H, 2.57; Fe, 10.68.

**(*h*<sup>5</sup>-Cyclopentadienyl)(*h*<sup>2</sup>-styrene)iron Dicarboxyl Hexafluorophosphate.** Freshly prepared triphenylcarbonium hexafluorophosphate (3.1 g, 8.0 mmol), dissolved in the minimum amount of CH<sub>2</sub>Cl<sub>2</sub>, was added with swirling to a solution of 2-phenylethyl complex (3.0 g, 10.6 mmol) in CH<sub>2</sub>Cl<sub>2</sub>. A large amount of yellow solid formed immediately. The solution was filtered to give 2.4 g (71%) of yellow-gold crystals: mp dec >165°; ir (Nujol mull) 3135 (m), 2914 (vs), 2082 (s), 2039 (s), 1524 (w), 1454 (s), 1373 (s), 880 (m), 840 (s), 818 (s), 765 (w), 742 (m), 715 (w), 682 (m) cm<sup>-1</sup>; nmr (acetone)  $\tau$  2.55 (m, 5 H), 3.55 (4-line multiplet, 1 H), 4.13 (s, 5 H), 5.60 (3-line multiplet, 2 H); uv (CH<sub>2</sub>Cl<sub>2</sub>) 225 nm ( $\epsilon$  12,000), 285 (8500), 345 (2800).

Anal. Calcd for C<sub>15</sub>H<sub>13</sub>F<sub>6</sub>FeO<sub>2</sub>P: C, 42.25; H, 3.06. Found: C, 42.80; H, 3.27.

**(*h*<sup>5</sup>-Cyclopentadienyl)(*h*<sup>2</sup>-isobutene)iron Dicarboxyl Tetrafluoroborate.** The isobutyl complex (2.2 g, 9.4 mmol) in a minimum of CH<sub>2</sub>Cl<sub>2</sub> was added to a solution of freshly prepared triphenylcarbonium tetrafluoroborate (3.2 g, 10 mmol) in the minimum amount of CH<sub>2</sub>Cl<sub>2</sub>. The mixture was washed with 5 ml of water and dried, and the solvent was evaporated to give an orange solid.

(53) A. Nakamura and N. Hagihara, *Nippon Kagaku Zasshi*, **84**, 344 (1963).

(54) A. A. Bothner-By and C. Naar-Colin, *J. Amer. Chem. Soc.*, **84**, 743 (1962).

This was recrystallized from a CH<sub>2</sub>Cl<sub>2</sub>-Et<sub>2</sub>O mixture to give 2.1 g (70%) of orange crystals: mp 101–102° dec; ir (CH<sub>2</sub>Cl<sub>2</sub>) 3110 (w), 2090 (vs), 2051 (vs), 1593 (w), 1505 (m), 1456 (w), 1414 (w), 1382 (w), 1368 (m), 1248 (w), 1052 (s), 859 (m), 782 (w), 679 (m) cm<sup>-1</sup>; nmr (acetone-*d*<sub>6</sub>)  $\tau$  4.19 (s, 5 H), 5.98 (s, 2 H), 8.05 (s, 6 H); uv (CH<sub>2</sub>Cl<sub>2</sub>) 226 nm ( $\epsilon$  14,000), 363 (800).

Anal. Calcd for C<sub>11</sub>H<sub>13</sub>BF<sub>4</sub>FeO<sub>2</sub>: C, 41.25; H, 4.06. Found: C, 41.05; H, 4.02.

**(*h*<sup>5</sup>-Cyclopentadienyl)(*h*<sup>2</sup>-ethylene)iron Dicarboxyl Tetrafluoroborate.**<sup>55</sup> The ethyl complex (1.9 g, 9.2 mmol) was added to triphenylcarbonium tetrafluoroborate (1.4 g, 4.4 mmol) in the minimum amount of CH<sub>2</sub>Cl<sub>2</sub>. There was an immediate formation of a yellow precipitate, 1.2 g (95%, based on (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>C<sup>+</sup>BF<sub>4</sub><sup>-</sup>). These crystals were dissolved in an nmr tube in liquid SO<sub>2</sub>, the tube was sealed, and a nmr spectrum taken:  $\tau$  4.37 (s, 5 H), 6.16 (s, 4 H).

**Attempted Hydrogenation of [ $\pi$ -CpFe(CO)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]<sup>+</sup>SbF<sub>6</sub><sup>-</sup> (IIa).** The heptafulvene salt IIa (0.45 g, 0.87 mmol) was dissolved in 30 ml of methanol, about 200 mg of Pt/C was added, and the system was rocked at room temperature in a Parr hydrogenator under a 45 psi pressure of hydrogen for 24 hr. At the end of this period, there had been essentially no drop in pressure. The system was opened to air, the solution filtered through infusorial earth, and the methanol was evaporated to give 0.40 g (90% recovery) of starting material, identified by its ir spectrum.

**Attempted Reaction of [ $\pi$ -CpFe(CO)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]<sup>+</sup>SbF<sub>6</sub><sup>-</sup> (IIa), with Tetracyanoethylene.** A solution of 0.50 g (0.97 mmol) of heptafulvene salt and 0.12 g (0.97 mmol) of freshly sublimed TCNE in 20 ml of CH<sub>2</sub>Cl<sub>2</sub> was stirred for 3 hr, then 20 ml of ethyl ether was added, and the solution was decanted. A nmr of the red-brown precipitate and of the red product remaining after evaporation of the solvents showed only absorptions due to the starting complex.

**Attempted Liberation of Heptafulvene from [ $\pi$ -CpFe(CO)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]<sup>+</sup>SbF<sub>6</sub><sup>-</sup> (IIa) Using (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P.** Triphenylphosphine (0.16 g, 0.61 mmol) was added to a solution of the heptafulvene salt (0.30 g, 0.58 mmol) in 25 ml of CH<sub>2</sub>Cl<sub>2</sub>. After the mixture was stirred for 10 min, the deep red solution turned yellow-orange. When ether was added, a yellow precipitate of [ $\pi$ -CpFe(CO)<sub>2</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]<sup>+</sup>SbF<sub>6</sub><sup>-</sup> was formed and collected (0.35 g, 91%): mp 235–238° dec (recrystallized from CH<sub>2</sub>Cl<sub>2</sub>-Et<sub>2</sub>O mixture); ir (CH<sub>2</sub>Cl<sub>2</sub>) 3076 (w), 2889 (w), 2057 (s), 2011 (s), 1599 (w), 1480 (w), 1428 (m), 1306 (w), 1187 (w), 1116 (m), 1092 (s), 1069 (w), 1028 (w), 999 (w), 866 (m) cm<sup>-1</sup>.

Anal. Calcd for C<sub>25</sub>H<sub>20</sub>F<sub>6</sub>FeP<sub>2</sub>Sb: C, 45.13; H, 3.01; Fe, 8.40. Found: C, 44.99; H, 2.93; Fe, 8.15.

The addition of TCNE or DMAD to the filtrate after all of the [ $\pi$ -CpFe(CO)<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P]<sup>+</sup>SbF<sub>6</sub><sup>-</sup> had been removed did not result in the isolation of any other compounds. These dienophiles cannot be used as *in situ* trapping agents because of facile reaction with triphenylphosphine. An attempt to distill heptafulvene into a -178° trap containing DMAD on a vacuum line (10<sup>-3</sup> mm), with reaction at 0°, gave no indication of the adduct as observed in subsequent work.

**Reduction of [ $\pi$ -CpFe(CO)<sub>2</sub>CH<sub>2</sub>=CHPh]<sup>+</sup>PF<sub>6</sub><sup>-</sup> by NaBH<sub>4</sub>.** Small portions of NaBH<sub>4</sub> (0.1 g, 2.6 mmol) were added to 1.0 g (2.3 mmol) of styrene complex in 100 ml of methanol at 0°, and the solution was stirred for 30 min. After the solvent was removed on a rotary evaporator, the red solid residue was chromatographed on 25 g of neutral alumina. Hexane eluted a slow-moving yellow band. Evaporation of this eluate gave 0.15 g (23%) of a yellow liquid. This was identified by its nmr (CS<sub>2</sub>) as a 2:1 mixture of  $\pi$ -CpFe(CO)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub> and  $\pi$ -CpFe(CO)<sub>2</sub>CH(CH<sub>3</sub>)C<sub>6</sub>H<sub>5</sub>.

**Reduction and Regeneration of [ $\pi$ -CpFe(CO)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]<sup>+</sup>SbF<sub>6</sub><sup>-</sup> (IIa).** NaBH<sub>4</sub> (0.5 g, 13 mmol) was added in small portions to a solution of IIa (4.0 g, 7.7 mmol) in 80 ml of THF at -78°. The solution was stirred at -78° for 3 hr and then allowed to warm to room temperature. The solvent was stripped off at 32°, and the red solid residue was dissolved in hexane and chromatographed on 30 g of neutral alumina to give the following fractions.

**Fraction 1.** A hexane eluent, containing an orange-yellow air-sensitive liquid (0.6 g), identified by nmr and ir as a mixture of V and its double-bond positional isomers: ir (CS<sub>2</sub>) iron carbonyl absorptions at 2009 and 1950 cm<sup>-1</sup>; nmr (CS<sub>2</sub>) multiplets at  $\tau$  3.0, 4.0, 4.8, 5.4, 7.5, and 8.3.

**Fraction 2.** A benzene eluent, containing 0.45 g of red crystals identified as [ $\pi$ -CpFe(CO)<sub>2</sub>]<sub>2</sub> by its characteristic<sup>51</sup> nmr and ir: nmr (CS<sub>2</sub>)  $\tau$  5.40 (s); ir (CS<sub>2</sub>) iron carbonyl absorptions at 1998, 1951, and 1778 cm<sup>-1</sup>.

(55) E. O. Fisher and K. Fichtel, *Chem. Ber.*, **94**, 1200 (1961).

When fraction 1 was added to a solution of  $(C_6H_5)_3C^+SbF_6^-$  (0.2 g, 0.42 mmol) in  $CH_2Cl_2$ , a deep red color immediately formed. Ethyl ether was added to give a red precipitate. The nmr and ir data for the precipitate confirmed the regeneration of  $[\pi-CpFe(CO)_2C_6H_5]^+SbF_6^-$  (IIa).

**Reaction of the Benzenesulfonate Ester of 7-(Hydroxymethyl)cycloheptatriene with  $Fe_2(CO)_9$ .** The benzenesulfonate ester (2.5 g, 9.5 mmol) was added to 25 g of freshly prepared  $Fe_2(CO)_9$  (66 mmol) in 100 ml of hexane, and the solution was stirred at 40° for 3 hr. It was then allowed to cool to room temperature and filtered through infusorial earth, and the hexane was removed on a rotary evaporator. The resulting liquid was chromatographed on 40 g of neutral alumina in hexane to give the following fractions.

**Fraction 1.** An air-sensitive, orange-yellow oil (ca. 0.8 g) which was identified by its ir and nmr spectra as a mixture (1:2) of styrene and styreneiron tetracarbonyl: ir ( $CH_2Cl_2$ ) 3021 (w), 2915 (w), 2092 (s) (CO), 2019 (vs) (CO), 1983 (s) (CO), 1599 (m), 1497 (m), 1479 (m), 1226 (m), 1072 (m), 1018 (w), 986 (w), 907 (w)  $cm^{-1}$ ; nmr ( $CS_2$ )  $\tau$  2.9 (m,  $C_6H_5$ ), 3.4 (4-line multiplet), 4.5 (4 doublets), 5.5 (4-line multiplet), 7.04 (4 doublets). This nmr spectrum was identical with that of a mixture prepared by reaction of styrene with diiron nonacarbonyl, but with different relative intensities for the two compounds.

**Fraction 2.** An orange band (0.3 g), which was identified by its nmr spectrum as cyclooctatetraeneiron tricarbonyl, nmr ( $CS_2$ )  $\tau$  4.88 (s) (column sample, mp 82–84°; mixture mp 82–86°; authentic sample, 86–88°; lit.<sup>56</sup> mp 93–95°).

**Reaction of the Benzenesulfonate Ester of 7-(Hydroxymethyl)cycloheptatriene with  $Na_2Fe(CO)_4$ .** A solution containing  $Na_2Fe(CO)_4$  (15 mmol) in 75 ml of THF was introduced through a serum cap into 3.7 g of ester (14 mmol) under nitrogen at 0°. The solution was left for 10 min at 0° and then the THF was stripped off.

The benzene-soluble portions of the residue were chromatographed on 30 g of neutral alumina in hexane to give a yellow band (0.4 g) identified by its nmr and ir spectra as a mixture (ca. 2:1) of styrene and styreneiron tetracarbonyl.

**1,6,7,8-*h*-Heptafulveneiron Tricarbonyl (VII).** The alcohol IV (7.0 g, 57.5 mmol) was stirred in 250 ml of ethyl ether with  $Fe_2(CO)_9$  (74 g, 203 mmol), prepared 2 months earlier and washed with hexane before use. After stirring at room temperature for 17 hr, the solution was refluxed for 4 hr and then stirred at room temperature for 2 days. It was then filtered through infusorial earth to remove a green solid, and solvent was stripped from the deep red solution. Chromatography of a small sample of the reaction mixture on neutral alumina at this time did not reveal any products which eluted in hexane. The reaction mixture was distilled at reduced pressure to yield the following fractions.

**Fraction 1.** A yellow-orange liquid (1.0 g), bp 62–84° (0.25 mm). A nmr spectrum showed that this fraction contained mostly starting alcohol IV, and a phenyl-substituted product: nmr ( $CDCl_3$ )  $\tau$  2.9 (m), 3.4 (m), 3.8 (m), 4.2 (4-line multiplet), 5.8 (m), 6.2 (m), 7.1 (m), 8.0 (m), all of approximately equal intensity.

**Fraction 2.** A red liquid, bp 84–115° (0.2 mm), which crystallized on standing at 0°. The resulting red crystals (6.7 g, 48%) were further purified by sublimation at 40° (0.1 mm): mp 38–41°; ir ( $CH_2Cl_2$ ) 2959 (m), 2049 (s) (CO), 1980 (s) (CO), 1855 (w), 1790 (w), 1778 (w), 1699 (w), 1622 (w), 1552 (w), 1484 (w), 1456 (m), 1410 (m), 1322 (m), 1158 (w), 961 (w), 933 (w), 918 (w), 879 (s), 798 (s)  $cm^{-1}$ ; uv ( $CH_2Cl_2$ ) 272 nm ( $\epsilon$  25,600), 355 (2100), long tail into visible region; the mass spectrum is tabulated in Table III.

*Anal.* Calcd for  $C_{11}H_8FeO_3$ : C, 54.09; H, 3.28; Fe, 22.95. Found: C, 54.10; H, 3.32; Fe, 22.60.

**Fraction 3.** An orange liquid (0.5 ml), bp 120–128° (0.2 mm), which may be a (hydroxymethyl)cycloheptatrieneiron tricarbonyl: ir (film) 3288 (m), 2874 (m), 2050 (s) (CO), 1970 (s) (CO), 1678 (m), 1600 (w), 1456 (m), 1413 (w), 1346 (w), 1075 (w), 1054 (w), 1029 (m), 874 (w)  $cm^{-1}$ ; nmr ( $CDCl_3$ )  $\tau$  4.6 (m, 2 H), 6.7 (m, 4 H), 7.8 (m, 4 H).

**Attempted Reaction of VII with TCNE. Method A.** The heptafulvene complex VII (0.20 g, 0.82 mmol) was stirred with freshly sublimed TCNE (0.09 g, 0.73 mmol) in benzene at room temperature for 14 hr with no apparent change. The solvent was stripped off, and the black residue was chromatographed on 15 g of neutral alumina in benzene to give back 0.20 g of the starting complex, identified by its nmr spectrum.

**Method B.**<sup>37</sup> The complex (0.20 g, 0.82 mmol) and freshly sub-

**Table III.** Mass Spectra of Heptafulvene Complexes VII and XIII

<i>m/e</i>	Rel Inten- sity, VII, 7.5 eV	Rel Inten- sity, VII, 75 eV	Rel Inten- sity, XIII, 75 eV	Interpretation
384			0.5	$C_8H_8Fe_2(CO)_6^+$
356			5.4	$C_8H_8Fe_2(CO)_5^+$
328			5.4	$C_8H_8Fe_2(CO)_4^+$
300			2.2	$C_8H_8Fe_2(CO)_3^+$
272			3.1	$C_8H_8Fe_2(CO)_2^+$
244	1	3	17	$C_8H_8Fe_2(CO)^+$ , $C_8H_8Fe(CO)_3^+$
242			2.3	$C_8H_8Fe_2(CO)^+$
216	5	14	18	$C_8H_8Fe(CO)_2^+$
214			2.9	$C_8H_8Fe(CO)_2^+$
188	3	8	8.3	$C_8H_8Fe(CO)^+$
168	9	15		$C_8H_7Fe(CO)_3^+$
160	4	37	52	$C_8H_8Fe^+$
158			5.4	$C_8H_8Fe^+$
140			7.0	$Fe(CO)_3^+$
135	3		7.8	$C_8H_7Fe^+$
134	2	35	20	$C_8H_8Fe^+$
133			5.3	$C_8H_8Fe^+$
132			11	$C_8H_7Fe^+$
121			10	$C_8H_7Fe^+$
112			29	$Fe(CO)_2^+$ , $Fe_2^+$
106	12	14	4	$C_8H_6CO^+$
105	35	38	6	$C_8H_5CO^+$ , $C_8H_9^+$ ?
104	100	87	19	$C_8H_4CO^+$ , $C_8H_8^+$
103	25	53	19	$C_8H_7^+$
102	3	32	7.0	$C_8H_6^+$
94			9.6	
91	5	32	1.0	$C_7H_7^+$
89		14	3.5	$C_7H_8^+$
84			66	$Fe(CO)^+$ , $C_2H_4Fe^+$
82			24	$C_8H_7Fe^+$
81			33	$C_2HFe^+$
78	31	51	31	$C_8H_8^+$
77		100	21	$C_8H_5^+$
68		19	48	$FeC^+$ , $C_3O_2^+$
65		14	36	$C_8H_5^+$
63		35	11	$C_8H_3^+$
57	1	10	14	$FeH^+$
56	1	35	100	$Fe^+$

limed TCNE (0.10 g, 0.78 mmol) in 55 ml of benzene and 10 ml of acetone were refluxed for 8 hr. The solvent was stripped off and the residue chromatographed on 15 g of neutral alumina in benzene to give 0.14 g of the starting complex (70%).

**Attempted Hydrogenation of VII.** Heptafulveneiron tricarbonyl (VII, 0.21 g, 0.6 mmol) and 50 mg of 10% Pd/C, in 50 ml of methanol, were rocked at room temperature for 5 hr under 20 psi of hydrogen. The solution was filtered and the methanol evaporated at reduced pressure to give red crystals (0.19 g, 90%) which had an nmr spectrum identical with the starting material.

**Reaction of Heptafulveneiron Tricarbonyl with  $HBFe_4$ .** Four drops of  $HBFe_4$  (48%) were added to a nmr sample tube containing VII in nitromethane. Gas was evolved at once, and the organic layer turned black. No nmr signal could be observed.

**Attempted Photolysis of VII.** The complex (0.33 g, 1.3 mmol) was dissolved in 3.0 ml of *n*-butyl ether in a flask on a vacuum line. DMAD (0.18 g, 1.3 mmol) was added to the trap in the apparatus. Both liquids were frozen in liquid nitrogen, and the system was evacuated on a vacuum line to  $10^{-3}$  mm. The system was then closed, and the liquids were allowed to warm to room temperature. The flask containing the complex was irradiated with a medium-pressure mercury lamp (G.E. UA-3), while the contents were stirred magnetically.

After 1 hr, there was no evident decomposition of the complex, so the system was opened and the reaction mixture was chromatographed and then sublimed to give 0.28 g of VII (85%).

**Thermolysis of VII. Method A. Without Trapping Agent.** The complex VII (0.095 g, 0.4 mmol) in 15 ml of xylene was heated in an oil bath at 150° for 7 hr. The solution was then cooled to room temperature and filtered through infusorial earth, and the

(56) T. A. Manuel and F. G. A. Stone, *J. Amer. Chem. Soc.*, **82**, 366 (1960).

solvent was stripped off. The yellow residue was chromatographed on 10 g of neutral alumina. Nothing eluted with hexane, indicating the disappearance of the starting VII. Benzene eluted an air-sensitive yellow liquid (45 mg):  $\text{ir}$  ( $\text{CH}_2\text{Cl}_2$ ) 3496 (w), 2953 (w), 2869 (m), 2790 (w), 2040 (s), 1973 (s), 1029 (m)  $\text{cm}^{-1}$ ;  $\text{nmr}$  ( $\text{CDCl}_3$ ) broad absorptions at  $\tau$  2.8, 4.0, 4.5, 6.6, 7.5, and 8.6 (br s). This product may be dimeric in nature, as evidenced by the intricate  $\text{nmr}$  spectrum.

**Method B. With DMAD Present.** VII (0.20 g, 0.6 mmol) and DMAD (0.20 g 1.4 mmol) in 50 ml of xylene were stirred in an oil bath at  $150^\circ$  for 8 hr. The mixture was cooled to room temperature, the solvent stripped off, and the residue chromatographed on 25 g of neutral alumina. Benzene eluted a yellow compound (70 mg) with an  $\text{ir}$  spectrum similar to that described above. A brown band eluted in methanol; the solvent was evaporated from this product, 25 ml of benzene and *ca.* 100 mg of 10% Pd/C were added, and air was bubbled through the mixture for 2 days. The residue after stripping the benzene was placed on 20 g of neutral alumina. Ethyl ether eluted a slow-moving purple band (0.031 g, 16%). Purification by  $\text{tlc}$  on a 2 mm  $\times$  20 cm  $\times$  20 cm silica gel plate gave a blue band. Extraction of the center portion of this band with 95% ethanol gave a uv-visible spectrum with the following maxima: 555 nm (rel absorbance 0.16), 344 (0.16), 298 (1.6), 290 (0.95), 236 (0.45); *cf.* 1,2-dicarbomethoxyazulene.<sup>4</sup>

**Method C. With TCNE Present.** The complex VII (0.20 g, 0.6 mmol) and TCNE (0.10 g, 0.25 mmol) were refluxed for 10 hr in 40 ml of *n*-butyl ether. A black-brown solid (0.2 g) was then filtered off, and the brown solution was evaporated under reduced pressure. The residue was chromatographed on 20 g of neutral alumina to yield the following fractions.

**Fraction 1.** Hexane eluted a yellow-orange liquid (*ca.* 0.03 g):  $\text{ir}$  (film) 2976 (m), 2890 (m), 2833 (m), 2045 (s), 1972 (vs), 1499 (s), 1456 (m), 1445 (m), 1435 (m), 868 (w), 742 (w), 706 (w)  $\text{cm}^{-1}$ .

**Fraction 2.** Ethyl acetate eluted an orange, waxy oil (*ca.* 0.05 g):  $\text{ir}$  (film) 3367 (w), 2890 (m), 2882 (s), 2817 (m), 2024 (w), 1957 (w), 1835 (w), 1730 (s) ( $\text{CO?}$ ), 1701 (m), 1664 (m), 1621 (m), 1484 (m),

1435 (m), 1366 (m), 1236 (m), 1174 (w), 1109 (w), 1072 (w), 1034 (w), 912 (w), 872 (w), 759 (m), 701 (m), 682 (w)  $\text{cm}^{-1}$ .

**Fraction 3.** Methanol eluted a red-brown viscous liquid (*ca.* 0.03 g):  $\text{ir}$  (film) 3425 (s), 2941 (m), 2066 (m), 1992 (m), 1742 (s) ( $\text{CO?}$ ), 1724 (w), 1456 (m), 1385 (m), 1263 (m), 703 (m)  $\text{cm}^{-1}$ .

The black-brown precipitate which had been filtered from the reaction mixture was insoluble in organic solvents:  $\text{ir}$  (KBr) 3300 (m), 2941 (m), 2865 (m), 2217 (m), 2114 (w), 2062 (m), 1988 (m), 1592 (s), 1453 (m), 1387 (w), 1280, 1107 (w)  $\text{cm}^{-1}$ .

**Heptafulvnediiron Hexacarbonyl (XIII).** The heptafulvneiron tricarbonyl complex VII (0.20 g, 0.8 mmol) was dissolved in 50 ml of hexane and stirred overnight with 15 g (41 mmol) of  $\text{Fe}_2(\text{CO})_9$ . The solution was then heated to reflux for 1 hr to decompose the small amount of  $\text{Fe}_2(\text{CO})_9$  still remaining. After cooling, the reaction mixture was filtered through infusorial earth, the hexane was evaporated, and the green residue was chromatographed on 15 g of neutral alumina. Benzene eluted an orange band which, upon solvent removal, yielded 0.24 g (77%) of orange-red crystals, mp  $177\text{--}180^\circ$  dec (recrystallized from a  $\text{CH}_2\text{Cl}_2$ -hexane mixture at  $-78^\circ$ ). The crystals were very insoluble in organic solvents. Attempted purification by sublimation ( $80^\circ$ , 0.1 mm) led to mixtures of VII and XIII. The mass spectrum of XIII is recorded in Table III:  $\text{ir}$  ( $\text{CH}_2\text{Cl}_2$ ) 2967 (w), 2890 (m), 2817 (w), 2040 (s) ( $\text{CO}$ ), 1980 (s) ( $\text{CO}$ ), 1580 (w), 1464 (w), 1443 (w), 1361 (w), 1099 (m), 1015 (m), 873 (m), 810 (m)  $\text{cm}^{-1}$ ;  $\text{nmr}$  (acetone-*d*<sub>6</sub>)  $\tau$  4.0 (m, 2 H), 6.0 (m, 2 H), 8.4 (m, 2 H), 8.6 (s, 2 H).

**Acknowledgment** is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research, in the form of an ACS-PRF Graduate Fellowship (1969-1970) to D. J. Ehntholt. We also gratefully acknowledge financial support by the Graduate School, State University of New York at Stony Brook.

## Preparation of Metallocenes from Hydrocarbon Dianions

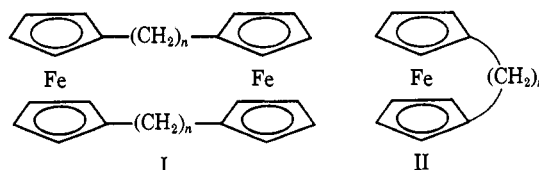
Thomas J. Katz,\* Nancy Acton, and Geoffrey Martin

Contribution from the Department of Chemistry,

Columbia University, New York, New York 10027. Received October 20, 1972

**Abstract:** Transition metal halides and hydrocarbon dianions composed of two linked cyclopentadienyl residues might yield polymers in which metal atoms and hydrocarbon residues alternate. Procedures are described for preparing a series of cyclic oligomers by treating iron salts with the dianion of bis(cyclopentadienyl)methane. Analogously, dimers are prepared from the dianions of 1,4-bis(cyclopentadienyl)but-2-yne and 1,4-bis(cyclopentadienyl)but-2-ene. The latter also gives a bridged monomer. The dianion of bis(cyclopentadienyl)methane with titanium tetrachloride gives 1,1'-methyleneitanocene dichloride, and this material is used with lithium naphthalenide to fix nitrogen and with diethylaluminum chloride to polymerize ethylene.

The metallocene nucleus has been incorporated into a large number of polymers, the usual procedures beginning with monomeric metallocenes.<sup>1</sup> An alternative, to react a ligand having two cyclopentadienyl moieties with a transition metal halide, a procedure that might generate both the metallocene nucleus and the polymer in one step, has been tried only rarely. The disodium salt of 1,4-bis(cyclopentadienyl)butane with ferrous chloride gives the dimer, I ( $n = 4$ ), [4.4]-ferrocenophane, and possibly related higher polymers that were not characterized, as well as the bridged



monomeric ferrocene, II ( $n = 4$ ), [4]ferrocenophane,<sup>2,3</sup> while analogous experiments wherein  $n = 2$ ,<sup>4</sup> 3,<sup>2</sup> and 5<sup>2</sup> give II, but neither I nor higher polymers. The dilithium salt of the *as*-indacenyl anion with ferrous

(2) A. Lüttringhaus and W. Kullick, *Makromol. Chem.*, **44-46**, 669 (1961).

(3) Ferrocenophanes were reviewed by W. E. Watts, *Organometal. Chem. Rev.*, **2**, 231 (1967).

(4) H. L. Lentzner and W. E. Watts, *Tetrahedron*, **27**, 4343 (1971)

(1) (a) H.-J. Lorkowski, *Fortschr. Chem. Forsch.*, **9**, 207 (1967); (b) E. Neuse and H. Rosenberg, *J. Macromol. Sci., Rev. Macromol. Chem.*, **4**, 1 (1970).