Trimethylenemethaneiron Tricarbonyl Complexes[1]

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Received July 2, 1971

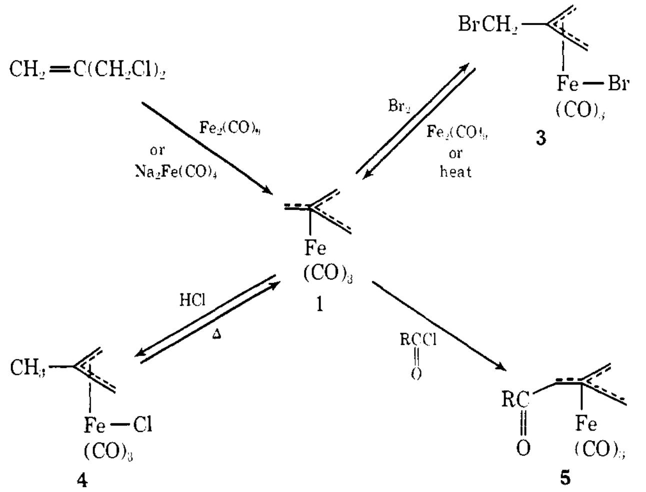
Abstract: Various trimethylenemethaneiron tricarbonyl complexes were prepared by either dehalogenation of 3-halo-2-halomethylpropenes with diiron nonacarbonyl or by disproportionation of 2-methallyliron tricarbonyl complexes. The former procedure was used to prepare the phenyl-, carbomethoxy-, 1,1-dimethyl-, 1,1-dicarboethoxy-, and the parent trimethylenemethaneiron tricarbonyl complexes. The dehalogenation of tris(bromomethyl)ethylene with excess diiron nonacarbonyl gave the dimeric complex, bis(methylenetrimethylenemethaneiron tricarbonyl). The disproportionation procedure was used to prepare the phenyl, chloro, and unsubstituted trimethylenemethane complexes. Methyltrimethylenemethaneiron tricarbonyl was obtained as a mixture with isopreneiron tricarbonyl in the disproportionation of *syn*-1,2-dimethallyliron tricarbonyl bromide. The same mixture was obtained by the reduction of carbomethoxytrimethylenemethaneiron tricarbonyl with lithium aluminum hydride in the presence of aluminum chloride. Addition of benzoyl chloride to trimethylenemethaneiron tricarbonyl followed by disproportionation of the intermediate allyl complex yielded benzoyltrimethylenemethaneiron tricarbonyl. Addition of bromine to trimethylenemethaneiron tricarbonyl gave 2-bromomethylallyliron tricarbonyl bromide which, on disproportionation, regenerated the starting trimethylenemethane complex. The behavior of trimethylenemethaneiron complexes upon protonation in strong acids was also investigated.

Trimethylenemethanes have been the subjects of numerous theoretical and synthetic studies.[4] To date, only two trimethylenemethanes have been detected by electron spin resonance and trapping experiments.[5] As with a number of other unstable molecules, for example, *o*-xylylene,[6] norbornadienone,[7] and cyclobutadiene,[8] trimethylenemethane can be isolated as its iron tricarbonyl complex.[1] Such complexes are potentially valuable both as models for the structures and properties of the ligands and as a means of generating the unstable ligands, either by oxidative,[9] thermal,[10] or photochemical[11] decomposition of the complexes. Complexes of unstable organic species may be used in lieu of the uncomplexed compound in synthetic reactions which require the species as an intermediate.[9] Also, they may allow certain otherwise unmeasurable values of the ligand (such as ionization potentials[12]) to be estimated empirically. In this paper we present the first full report concerning the preparation and properties of various trimethylenemethaneiron tricarbonyl complexes.[13]

Results

Trimethylenemethaneiron Tricarbonyl. Several different methods have been used to prepare trimethylenemethaneiron tricarbonyl (**1**) (TMM-Fe(CO)$_3$). These are illustrated in Scheme I. The reaction of 3-chloro-2-chloromethylpropene (**2**) with 2 equiv of Fe$_2$(CO)$_9$ in diethyl ether or pentane for 10–20 hr at room temperature gave TMM-Fe(CO)$_3$ in 70% yield. As the reaction progressed the initially golden mixture gradually became light green and finally bright yellow. At this time (after 20 hr) evolution of carbon monoxide became very slow. The ferrous chloride which formed was removed by filtration, and iron pentacarbonyl and TMM-Fe(CO)$_3$ were isolated by distillation. As an alternate procedure, the reaction of **2** with Na$_2$Fe(CO)$_4$ gave a 30% yield of **1**.

Scheme I



TMM-Fe(CO)$_3$ was obtained by the thermal decomposition of 2-methallylirontricarbonyl chloride (**4**), either as a solid or in solution in yields up to 39% (cal-

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(1) Part of this work has appeared as communications: G. F. Emerson, K. Ehrlich, W. P. Giering, and P. C. Lauterbur, *J. Amer. Chem. Soc.*, **88**, 3172 (1966); G. F. Emerson and K. Ehrlich, *Chem. Commun.*, 59 (1969).

(2) National Institutes of Health Predoctoral Fellow, 1966–1969; address correspondence to this author at the Department of Chemistry, Columbia University, New York, N. Y. 10027.

(3) Deceased March 20, 1968.

(4) F. Weiss, *Quart. Rev., Chem. Soc.*, **24**, 278 (1970).

(5) (a) P. Dowd, *J. Amer. Chem. Soc.*, **88**, 2587 (1966); (b) P. Dowd and K. Sachdev, *ibid.*, **89**, 715 (1967); (c) P. Dowd, A. Gold, and K. Sachdev, *ibid.*, **90**, 2715 (1968); (d) J. A. Berson, R. J. Bushby, J. M. McBride, and M. Tremelling, *ibid.*, **93**, 1545 (1971).

(6) W. R. Roth and J. D. Meier, *Tetrahedron Lett.*, 2053 (1967).

(7) J. M. Landesberg and J. Sieczkowski, *J. Amer. Chem. Soc.*, **90**, 1655 (1968).

(8) G. F. Emerson, L. Watts, and R. Pettit, *ibid.*, **87**, 131 (1965).

(9) L. Watts, J. D. Fitzpatrick, and R. Pettit, *ibid.*, **87**, 3253 (1965).

(10) P. H. Li and H. A. McGee, *Chem. Commun.*, 497 (1967).

(11) J. M. Landesberg and J. Sieczkowski, *J. Amer. Chem. Soc.*, **91**, 2120 (1969).

(12) M. J. S. Dewar and S. D. Worley, *J. Chem. Phys.*, **51**, 1672 (1969).

(13) Other studies of trimethylenemethane complexes have been published: (a) R. Noyori, T. Nishimura, and H. Takaya, *Chem. Commun.*, 89 (1969); (b) A. N. Nesmeyanov, I. S. Astakhova, G. P. Zol'nikova, I. I. Kritskaya, and Yu T. Struchkov, *ibid.*, 85 (1970); (c) D. J. Ehntholt and R. C. Kerber, *ibid.*, 1451 (1970); (d) J. S. Ward and R. Pettit, *ibid.*, 1419 (1970); (e) S. Otsaka, A. Nakamura, and K. Tani, *J. Chem. Soc. A.*, 154 (1971).

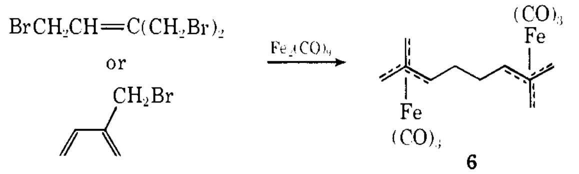
culated on the assumption that the reaction proceeds by disproportionation in which 2 equiv of **4** can give only 1 equiv of **1**). Besides TMM-Fe(CO)$_3$, ferrous chloride and isobutylene were isolated.

Treatment of TMM-Fe(CO)$_3$ with hydrogen chloride gas gave **4** as the only product. Similarly, the reaction of TMM-Fe(CO)$_3$ with 1 equiv of bromine gave the allyl complex **3** in 86% yield. TMM-Fe(CO)$_3$ could be generated quantitatively from **3** by treatment with $Fe_2(CO)_9$. It was also isolated when a hexane solution of **3** was heated at reflux. In the latter reaction, in addition to $FeBr_2$, isolated products included $CH_2{=}C(CH_2Br)_2$ and $(BrCH_2)_3CBr$. The reaction of TMM-Fe(CO)$_3$ with benzoyl of acetyl chloride in the presence of aluminum chloride (Friedel-Crafts acylation) yielded small amounts (5–10%) of the acyltrimethylenemethaneiron tricarbonyl complexes (**5**). Besides unidentified products, $C_6H_5COCH{=}C(CH_3)_2$ was isolated from the reaction of C_6H_5COCl with TMM-Fe(CO)$_3$.

Other attempts to generate substituted TMM-Fe(CO)$_3$ complexes by electrophilic substitution reactions under conditions similar to those used to prepare the corresponding cyclobutadieneiron tricarbonyl complexes[14] were unsuccessful. Neither the carboxaldehyde nor the chloromercury derivative could be isolated from the reaction of TMM-Fe(CO)$_3$ with $POCl_3$ and *N*-methylformanilide or with $HgCl_2$, respectively.

Substituted Trimethylenemethaneiron Tricarbonyl Complexes. Substituted TMM complexes were prepared by methods similar to those used to prepare TMM-Fe(CO)$_3$. The phenyl-, carbomethoxy-, 1,1-dicarboethoxy-, and 1,1-dimethyltrimethylenemethaneiron tricarbonyl complexes were obtained in yields ranging from 30 to 60% by dehalogenation of the appropriately substituted 2-bromomethylallyl bromides with $Fe_2(CO)_9$. The reaction of tris(bromomethyl)ethylene with excess $Fe_2(CO)_9$ gave the dimeric complex **6** (Scheme II). This complex was also obtained in the reaction of 2-bromomethylbutadiene with $Fe_2(CO)_9$.

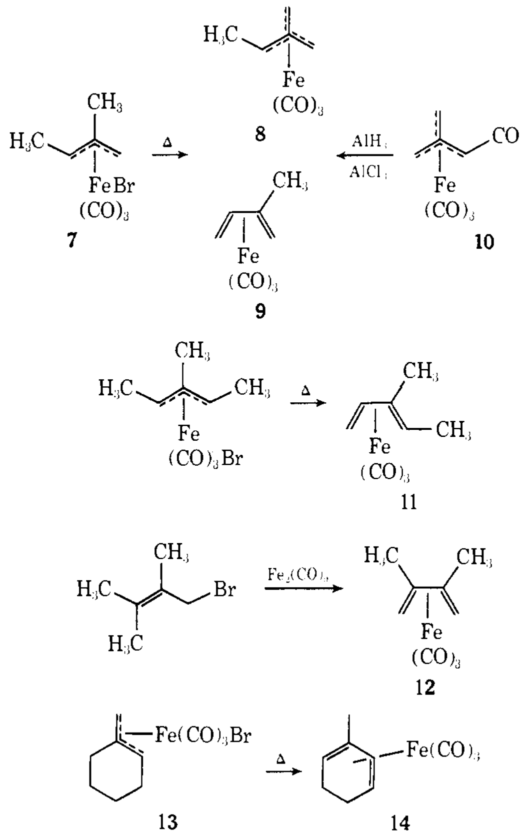
Scheme II



Substituted TMM-Fe(CO)$_3$ complexes could also be prepared by the reaction of certain allyl halides with $Fe_2(CO)_9$. With 1-phenyl-2-methylallyl chloride, C_6H_5TMM-Fe(CO)$_3$ was obtained in 36% yield together with a 33% yield of a mixture of $C_6H_5CH{=}C(CH_3)_2$ (19%) and $C_6H_5CH_2C(CH_3){=}CH_2$ (14%). Unlike the preparation of TMM-Fe(CO)$_3$ from the decomposition of **4**, the intermediate allyl complex was not isolable but instead partially decomposed to the TMM complex under the conditions of the reaction (stirring in hexane at 40°). Chlorotrimethylenemethaneiron tricarbonyl was obtained in low yield in the reaction of *cis*- and *trans*-$ClCH{=}C(CH_3)CH_2Cl$[15] with $Fe_2(CO)_9$. Again, the allylirontricarbonyl chloride complex could not be isolated.

The reaction of *cis*-$CH_3CH{=}C(CH_3)CH_2Br$ with $Fe_2(CO)_9$ gave the allyl complex **7**. Decomposition of **7** upon heating gave a mixture (1:2) of methyltrimethylenemethane (**8**) and isopreneiron tricarbonyl (**9**). Upon dissolving this mixture in concentrated sulfuric acid a red solution of the allyliron tricarbonyl salt formed, which, when poured onto ice, gave only **9** (90% recovery). Treatment of the trimethylallyl bromides, *cis*-$CH_3CH{=}C(CH_3)CH(CH_3)Br$ and $(CH_3)_2C{=}C(CH_3)CH_2Br$, with $Fe_2(CO)_9$ followed by thermal decomposition of the intermediate allyl halide complexes led only to the diene complexes **11** and **12** (Scheme III), respectively. Similarly, thermal decomposition of the allyl complex **13** gave the cyclohexadiene complex **14**, and no TMM-type complex could be detected.

Scheme III



Whereas reduction of carbomethoxytrimethylenemethaneiron tricarbonyl (**10**) with lithium aluminum hydride caused extensive decomposition of the complex, reduction of **10** with AlH_3 in the presence of $AlCl_3$ gave a 31% yield of a mixture (1:2) of **8** and **9**. Reduction of the ketones, benzoyl- and acetyltrimethylenemethaneiron tricarbonyl, with sodium borohydride proceeded in high yields to give the corresponding alcohol complexes. Upon treatment with strong acids hydroxyethyltrimethylenemethaneiron tricarbonyl gave a 4:1 mixture of the isomeric diene–iron tricarbonyl–alcohol complex and the starting trimethylenemethane complex.

As previously noted, methyltrimethylenemethaneiron tricarbonyl quantitatively rearranges to isoprene-

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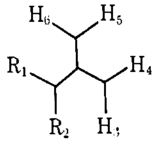
(14) J. D. Fitzpatrick, L. Watts, G. F. Emerson, and R. Pettit, *J. Amer. Chem. Soc.*, **87**, 3255 (1965).

(15) J. T. Gragson, K. W. Greenlee, J. M. Derfer, and C. E. Boord, *ibid.*, **75**, 3344 (1953).

Table I. Chemical Shifts (τ) and Coupling Constants (Hz) for the Trimethylenemethane Protons in Substituted Trimethylenemethaneiron Tricarbonyl Complexes[a]



R_1	R_2	H_2	H_3	H_4	H_5	H_6	$J_{H_2H_5}$	$J_{H_3H_6}$	Solvent
CH_3	H	6.86	8.37	8.23	7.89	7.49	2.5	4.5	*b*
CH_3	CH_3		7.77	8.28	8.28	7.77			CCl_4
CH_3	C_6H_5		7.59	8.09	8.15	7.89		4.2	CS_2
TMM–Fe(CO)$_3$(CH$_2$)$_2$	H	7.09	8.31	8.36	7.86	7.51	1.9	3.8	$CDCl_3$
CH_3CHOH	H	7.07	8.37	8.27	7.91	7.56	2.0	4.0	CCl_4
C_6H_5	H	5.72	8.16	8.16	7.70	7.13	3.3	5.4	CCl_4
Cl	H	5.80	8.33	8.15	7.61	6.92	3.0	4.3	CS_2
C_6H_5CO	H	5.90	7.47	8.00	7.83	6.27	4.1	1.9	CCl_4
CH_3CO	H	6.12	7.51	7.93	7.88	6.84	4.0	2.0	CCl_4
CO_2CH_3	H	6.09	7.58	8.03	7.98	7.13	4.2	2.3	CCl_4
$CO_2C_2H_5$	$CO_2C_2H_5$		6.82	7.90	7.90	6.82			CCl_4
CO_2H	H	6.00	7.39	7.84	7.78	7.08	3.5	2.0	CD_2Cl_2

[a] Spectra were recorded at 60 MHz; tetramethylsilane was used as internal standard. [b] Obtained as a mixture with isopreneiron tricarbonyl.

iron tricarbonyl upon protonation in concentrated sulfuric acid followed by dilution of the acid solution with water. Similarly, 1,1-$(CH_3)_2$TMM–Fe(CO)$_3$ and 1-CH_3-1-Ph-TMM–Fe(CO)$_3$ are converted to the diene complexes upon such treatment. However, TMM–Fe(CO)$_3$ could not be regenerated on dilution of its solution in sulfuric acid.

Properties. The TMM complexes were bright yellow, volatile substances which were fairly stable to air oxidation as solids but considerably more sensitive as liquids or in solution. Oxidation with ceric ammonium nitrate was found to occur more slowly than similar oxidations of cyclobutadiene[9] and diene–iron tricarbonyl complexes.[16] The complexes are distillable under reduced pressure and some, such as C_6H_5TMM–Fe(CO)$_3$ and TMM–Fe(CO)$_3$, sublime readily, even on standing at 0° and atmospheric pressure. They do not decompose on alumina (neutral) and hence, can be readily purified by column chromatography. Since most of the complexes mentioned in this report are quite nonpolar, elution with pentane or benzene is sufficient.

Spectra. The elucidation of the structures of several trimethylenemethaneiron tricarbonyl complexes by X-ray[13b,17] or electron diffraction[18] has shown these complexes to be distinct from allyl-type complexes (in which one of the CH_2 groups of the TMM ligand would be σ bonded to the iron rather than π bonded) and therefore to represent a new type of organometallic π complex. A convenient method for identifying TMM–Fe(CO)$_3$ complexes is by their characteristic infrared (ir) and nuclear magnetic resonance (nmr) spectra given in Tables I and II, respectively.

The ir absorptions for the iron carbonyls in TMM–Fe(CO)$_3$ complexes appear as two distinct peaks in the region 1950–2100 cm^{-1}. The first is a broad, intense peak at frequencies from 1980 to 2010 cm^{-1}, and the second is a sharper, less intense peak at 2054–2075 cm^{-1}. These absorptions are similar to those of other Fe(CO)$_3$ complexes but occur at slightly higher energy than their identically substituted analogs indicating that more metal backbonding occurs to the TMM-type ligand than to the diene-type ligand. As with diene–iron tricarbonyl complexes,[19] substitution of the ligand with alkyl or phenyl groups causes a decrease in the frequencies whereas substitution with electron-withdrawing groups such as benzoyl or chlorine causes an increase in the frequencies for carbonyl absorption. Unlike diene complexes, however (but like cyclobutadieneiron complexes[20]), no splitting of the broad carbonyl band occurs in unsymmetrically substituted complexes. A very weak absorption occurs at lower frequencies (1953–1978 cm^{-1}) than those of the broad carbonyl peak and may be characteristic of TMM–Fe(CO)$_3$ complexes.

Monosubstituted TMM–Fe(CO)$_3$ complexes may be readily identified by their characteristic proton nmr spectra. Whereas the protons in TMM–Fe(CO)$_3$

Table II. Carbonyl Infrared Stretching Frequencies for the Trimethylenemethaneiron Tricarbonyl Complexes

Substituent on TMM–Fe(CO)$_3$	Frequencies, cm^{-1} (s)	(s)	(w)	Solvent
H	2061	1995	1966	Hexane
CH_3[a]	2058	1979		Hexane
1,1-$(CH_3)_2$	2056	1985	1953	Hexane
1-CH_3-1-Ph[b]	2054	1993	1960	CCl_4
TMM–Fe(CO)$_3$(CH$_2$)$_2$	2059	1991	1960	Hexane
CH_3CHOH	2062	1992	1963	Hexane
Ph	2061	1993	1962	Hexane
Cl	2071	2001	1967	Hexane
PhCO	2070	2003	1970	Hexane
CH_3CO	2069	2003	1971	Hexane
CO_2CH_3	2074	2009	1978	Hexane
1,1-$(CO_2C_2H_5)_2$	2075	2011	1978	Hexane

[a] Obtained as a mixture with isopreneiron tricarbonyl. [b] Reference 13a.

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(16) Ward and Pettit[13d] have found that the oxidation of 1 with ceric ammonium nitrate in the presence of tetracyanoethylene gives a 4% yield of an adduct which could result from addition of trimethylenemethane to tetracyanoethylene.

(17) M. R. Churchill and K. Gold, *Inorg. Chem.*, 8, 401 (1969).

(18) A. Almenningen, A. Haaland, and K. Wahl, *Acta Chem. Scand.*, 23, 1145 (1969).

(19) R. Pettit, G. Emerson, and J. Mahler, *J. Chem. Educ.*, 40, 175 (1963).

(20) J. D. Fitzpatrick, Ph.D. Thesis, The University of Texas, Austin, Tex., 1966.

appear as a sharp singlet, monosubstitution causes all of the ligand protons to become nonequivalent. Although four types of coupling are possible [geminal (H_3H_4, H_5H_6), cis (H_2H_3, H_4H_5), cis–trans (H_2H_4, H_3H_5, H_4H_6), trans (H_2H_5, H_3H_6)], only coupling of the latter type fits the observed spectra. Preferential coupling of protons held in such a geometry has been observed in other organic systems.[21] Like allyl complexes,[22] but unlike diene complexes,[23] geminal coupling in TMM–$Fe(CO)_3$ complexes is not observed.

The assignments for the chemical shifts and couplings of the TMM protons listed in Table II are made as follows. In monosubstituted complexes the lowest field doublet may be assigned to the proton on the same carbon as the substituent (H_2). The fact that this proton is the lowest field signal may not only be caused by electron withdrawal by the substituent but also by decreased shielding of this proton by the iron, possibly because of steric repulsion between the iron and the substituent. In the X-ray structure of C_6H_5TMM–$Fe(CO)_3$, it is found that the bond distance between the iron and the carbon bearing the substituent is significantly greater than that between the iron and the methylenes.[17] The proton, H_2, couples with H_5 by long-range trans coupling (W coupling). The singlet resonance found in the spectra of monosubstituted TMM–$Fe(CO)_3$ complexes may be assigned to H_4 since it is located over a W configuration from the substituent. The doublets observed for the remaining protons, H_3 and H_6, may not be as definitely assigned, but from comparisons of chemical shifts with those observed in the 1,1-disubstituted complexes it is likely that the lower field doublet is due to resonance of the proton adjacent to the substituent, H_6.

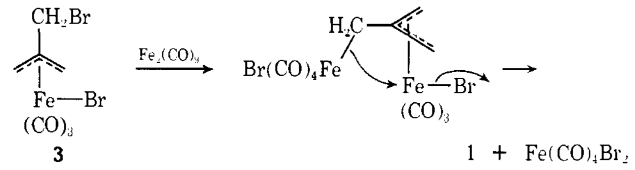
Two trends may be noted for the chemical shifts and couplings of the protons in monosubstituted TMM–$Fe(CO)_3$ complexes. If the substituent has little or no conjugative interaction with the TMM ligand, the chemical shift difference between H_3 and H_4 is less than that between H_4 and H_5 and $J_{H_2H_5} < J_{H_3H_6}$. When the substituent contains a carbonyl group (and presumably where conjugation with the TMM is substantial), the chemical shift difference between H_3 and H_4 is more than that between H_4 and H_5 and $J_{H_2H_5} > J_{H_3H_6}$. Such substituent effects may reflect a difference in hybridization of the carbon bearing the substituent.

Discussion

Synthesis of TMM–$Fe(CO)_3$ Complexes from Allylic Dihalides. Previous studies have shown that diiron nonacarbonyl can dehalogenate benzylic[6,8,24] and allylic[25] halides with or without formation of an iron complex. The use of $Fe_2(CO)_9$ as a dehalogenating agent has been particularly important for the preparation of iron tricarbonyl complexes of unstable species[6,8] since the procedure of generating the unstable species and then trapping it may be avoided. This method has been particularly convenient for the preparation of a variety of TMM–$Fe(CO)_3$ complexes and, to date, the only limitation in the method appears to be the availability of the starting allylic dihalide.

Although the mechanism for the dehalogenation of 2-halomethyl-3-halopropenes by $Fe_2(CO)_9$ has not been rigorously determined, it probably involves the initial formation of a 2-halomethylallyliron tricarbonyl halide complex. This intermediate complex can react with a second mole of $Fe_2(CO)_9$ by the route shown in Scheme IV. This pathway involves the oxidative addition of the coordinatively unsaturated species, $Fe(CO)_4$ (generated from the breakdown of $Fe_2(CO)_9$), to the C–Br bond of **3**. The intermediate diiron complex can collapse to TMM–$Fe(CO)_3$ (**1**) by loss of $Fe(CO)_4Br_2$, a species which would lose carbon monoxide under the reaction conditions to give the observed $FeBr_2$. The fact that 2-bromomethylallyliron tricarbonyl bromide (**3**), prepared by the reaction of TMM–$Fe(CO)_3$ with bromine, quantitatively yields TMM–$Fe(CO)_3$ upon treatment with 1 mol of $Fe_2(CO)_9$ is consistent with such a pathway. A less likely pathway involving the formation of uncomplexed TMM in the transition state of the dehalogenation reaction (a pathway which has been observed for the dehalogenation of 1,4-dichloro-2-butene with $Fe_2(CO)_9$ in which uncomplexed butadiene is formed[26]) might be expected to lead to a greater variety of final products.

Scheme IV



The dimeric complex **6** could be formed by the insertion of $Fe(CO)_4$ into the C–Br bond of 2-bromomethyltrimethylenemethaneiron tricarbonyl which then can dimerize by loss of $Fe(CO)_4Br_2$. It is possible that another sequence may be involved since the reaction of 2-bromomethylbutadiene with $Fe_2(CO)_9$ also gives **6**.[27]

Synthesis of TMM Complexes from Allyl Halides. The thermal decomposition of 2-methylallyliron tricarbonyl halide complexes involves a bimolecular disproportionation of the type previously observed by Impastato and Ihrman for the formation of butadieneiron tricarbonyl from 1-methylallyliron tricarbonyl chloride.[28] From the results of the present study two conclusions concerning this procedure as a method of preparing TMM–$Fe(CO)_3$ complexes can be made.

When the substituent in the 1 position of the allyl halide is trans to the 2 substituent (anti), the allyl complex formed upon reaction of the allyl halide with $Fe_2(CO)_9$ cannot be isolated but instead partially decomposes under the reaction conditions to give the TMM complex and a mixture of olefins. For example, the intermediate allyl complex in the reaction of *trans*-1-phenyl-2-methylallyl chloride with $Fe_2(CO)_9$ to give phenyltrimethylenemethaneiron tricarbonyl cannot be isolated. The relative instability of anti-substituted allyliron tricarbonyl halide complexes had previously

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[21] M. Barfield and B. Chakrabarti, *Chem. Rev.*, **69**, 757 (1969).

[22] M. L. H. Green and P. L. I. Nagy, *Advan. Organometal. Chem.*, **2**, 325 (1964).

[23] M. L. Maddox, S. L. Stafford, and H. D. Kaesz, *ibid.*, **3**, 1 (1965).

[24] I. Rhee, M. R. Yang, and S. Tsutsumi, *J. Organometal. Chem.*, **9**, 361 (1967).

[25] (a) H. D. Murdoch and E. Weiss, *Helv. Chim. Acta*, **45**, 1927 (1962); (b) A. Nakamura, *Bull. Chem. Soc. Jap.*, **39**, 543 (1966).

[26] K. Ehrlich, Ph.D. Thesis, The State University of New York at Stony Brook, Dec 1969.

[27] A related process has been observed by Nesmeyanov, *et al.*[13b]

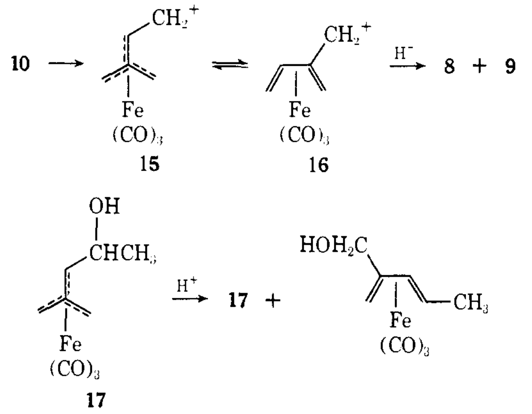
[28] F. J. Impastato and K. G. Ihrman, *J. Amer. Chem. Soc.*, **83**, 3726 (1961).

been noted by Emerson during attempts to prepare cyclic allyliron halide complexes.[29] This instability also accounts for the lower temperature necessary to achieve disproportionation of such complexes.

In the disproportionation of a 1,2-dialkylallyliron tricarbonyl halide which can give either a diene or a TMM complex, the formation of the diene-type complex is preferred and, in some cases, occurs exclusively. The preference for the formation of a diene complex over a TMM complex may be governed either by a closer proximity of a 1-methyl substituent to the reactive center in the transition state or to a possibly greater thermodynamic stability of a diene complex compared to its isomeric TMM–Fe(CO)$_3$ complex.

An argument in favor of thermodynamic factors controlling the formation of products in the disproportionation reaction is the fact that the same product mixture is obtained in the reduction of carbomethoxytrimethylenemethaneiron tricarbonyl by aluminum hydride as in the disproportionation of *syn*-1,2-dimethylallyliron tricarbonyl bromide. The products in the former reaction most likely arise *via* an equilibrium between a trimethylenemethaneiron tricarbonyl carbinyl cation (**15**) and a 2-methylenebutadieneiron tricarbonyl cation (**16**), and therefore the reaction would be expected to be thermodynamically controlled. An equilibrium of this sort is probably responsible for the partial rearrangement of **17** to **18** on treatment of **17** with sulfuric acid (Scheme V).

Scheme V



Reactions of TMM–Fe(CO)$_3$ Complexes with Electrophiles. Although electrophilic substitution reactions occur readily with cyclobutadieneiron tricarbonyl[14] and occur in certain cases with butadieneiron tricarbonyl,[30] similar attempts to prepare substituted TMM–Fe(CO)$_3$ complexes by electrophilic substitution have been unsuccessful with the exception of the preparation of acyltrimethylenemethaneiron tricarbonyl complexes by treatment of TMM–Fe(CO)$_3$ with acyl chlorides in the presence of aluminum chloride. The formation of PhCOCH=C(CH$_3$)$_2$ in the reaction of PhCOCl with TMM–Fe(CO)$_3$ indicated that the reaction probably proceeded by the formation of 2-benzoylmethylallyliron tricarbonyl chloride which then gave benzoyltrimethylenemethaneiron tricarbonyl by disproportionation.

Since one might anticipate that the same low-energy pathway *via* an allyliron tricarbonyl cation[31] is available for the electrophilic substitution of TMM–Fe(CO)$_3$ and diene- and cyclobutadieneiron tricarbonyl complexes, some special property of TMM–Fe(CO)$_3$ complexes or of 2-methallyliron tricarbonyl cations must account for the different results upon reaction with electrophiles.

Although protonation of TMM–Fe(CO)$_3$ in concentrated sulfuric acid occurred readily to give the 2-methallyliron tricarbonyl cation, upon dilution of this solution with water, TMM–Fe(CO)$_3$ was not regenerated. Deprotonation of 1-methallyliron tricarbonyl cation upon dilution of its sulfuric acid solution had been found to occur readily.[29] Furthermore, when solutions of either CH$_3$TMM–Fe(CO)$_3$ or 1,1-(CH$_3$)$_2$-TMM–Fe(CO)$_3$ in sulfuric acid were diluted with water, only recovery of the rearranged product, isoprene or 2,3-dimethylbutadieneiron tricarbonyl, was possible. From these results it may be concluded that either deprotonation of a 2-methyl group in methallyliron tricarbonyl cations is very slow compared to deprotonation of a 1-methyl group or that the reaction cannot occur. The latter possibility would explain the lack of formation of TMM complexes in the deprotonation studies as well as the different behavior of TMM and diene complexes in electrophilic substitution reactions.

Experimental Section

Melting points were measured on a Mel-Temp melting point apparatus and are uncorrected. The values for the infrared absorptions given in Table I were measured on a Perkin-Elmer Model 521 double beam spectrometer. The nmr spectra were measured on a Varian Model A-60 spectrometer with tetramethylsilane as internal standard. Microanalyses were obtained by Schwarzkopf Microanalytical Laboratories. Those for the TMM–Fe(CO)$_3$ complexes are given in Table III. Diiron nonacarbonyl was prepared by the method described by King.[32] All solvents used were reagent grade and were not further purified unless otherwise noted.

Table III. Analytical Data for the Trimethylenemethaneiron Tricarbonyl Complexes

Substituent on TMM-Fe(CO)$_3$	% C		% H	
	Calcd	Found	Calcd	Found
H	43.41	43.29	3.12	2.90
1,1-(CH$_3$)$_2$	48.68	48.50	4.55	4.58
TMM–Fe(CO)$_3$(CH$_2$)$_2$	46.41	46.68	3.41	3.58
CH$_3$CHOH	45.41	45.03	4.24	4.79
Ph	57.81	58.13	3.71	3.73
Cl	36.89	36.81	2.22	2.33
PhCO	56.41	56.44	3.39	3.38
CH$_3$CO	45.80	46.45	3.42	4.07
CO$_2$CH$_3$	42.89	43.09	3.21	3.26
1,1-(CO$_2$C$_2$H$_5$)$_2$	46.17	46.83	4.18	4.35

Preparation of Trimethylenemethaneiron Tricarbonyl (1). A. A mixture of 125 g (0.34 mol) of Fe$_2$(CO)$_9$ and 18.3 g (0.15 mol) of 2-chloromethyl-3-chloropropene[33] in 500 ml of anhydrous ethyl ether was stirred for 24 hr at room temperature. During this time

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(29) G. F. Emerson, Ph.D. Thesis, The University of Texas, Austin, Tex., 1964.

(30) (a) G. G. Ecke (to Ethyl Corp.), U. S. Patent, 3,149,135 (c 1260–439) (Sept 15, 1945); *Chem. Abstr.*, **62**, 4054 (1965); (b) M. R. Churchill, J. Wormald, D. A. T. Young, and H. D. Kaesz, *J. Amer. Chem. Soc.*, **91**, 7201 (1969); (c) E. O. Greaves, G. R. Knox, and P. L. Pauson, *Chem. Commun.*, 1124 (1969).

(31) G. F. Emerson and R. Pettit, *J. Amer. Chem. Soc.*, **84**, 4591 (1962).

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the reaction mixture turned successively greenish yellow and yellow. The filtered mixture was evaporated on a rotary evaporator (bath temperature 40°) to remove most of the ether and iron pentacarbonyl. Distillation of the residue gave **1**, bp 53–54° (16 mm), 19.27 g (0.10 mol). This distillate, which contained a small amount of iron pentacarbonyl, was sufficiently pure for most work. Analytical samples were prepared by several crystallizations from pentane at −78°. prisms, mp 28-29°.

B. Treatment of 1.0 g (8 mmol) of 2-chloromethyl-3-chloropropene with disodium tetracarbonylferrate (prepared from 1.4 g of sodium in 11 ml of mercury and 3.85 g of triiron dodecacarbonyl in 10 ml of dry tetrahydrofuran) under nitrogen gave 0.35 g (1.7 mmol) of **1**.

C. A mixture of 100 g (0.28 mol) of $Fe_2(CO)_9$ and 30 ml of 2-methylallyl chloride was stirred for 3 hr at room temperature in 100 ml of cyclohexane. The solution was then heated at reflux for 3 hr, filtered. and distilled to give 4.3 g (0.02 mol) of **1**.

D. A solution of 2.85 g (0.012 mol) of 2-methylallyliron tricarbonyl chloride (**4**)[31] in 20 ml of cyclohexane was heated at reflux for 3 hr. The filtered solution was concentrated to an oil which yielded 0.47 g of **1** (0.002 mol). If the reflux condensor was attached to a cold trap cooled by Dry Ice–acetone, a small amount of isobutylene was produced (nmr: septet at τ 5.35; lit.[34] τ 5.35 (septet), 8.28 (triplet)). The high-field nmr peak was obscured by cyclohexane which also condensed in the trap.

E. A mixture of 0.4 g (1.1 mmol) of **3** and 0.5 g (1.4 mmol) of $Fe_2(CO)_9$ was stirred for 24 hr at room temperature in ethyl ether. The filtered solution gave 0.2 g (1.0 mmol) of **1**.

F. A 1.0-g (2.8 mmol) sample of **3** in cyclohexane was heated under reflux for 30 min. The filtered solution was concentrated to a yellow liquid, 0.3 g. From nmr (CCl_4) this liquid was a mixture of TMM–$Fe(CO)_3$ (47%), $CH_2{=}C(CH_2Br)_2$ (τ 4.69 (s, 2 H, $=CH_2$), 5.95 (s. 4 H. CH_2Br)) (47%), and $(CH_2Br)_3CBr$ (τ 6.05, s) (6%).

Protonation of 1. A solution of 0.3 g of **1** in 3 ml of concentrated (96%) sulfuric acid gave nmr τ 8.0, 7.3, 5.0 (3:2:2). Addition of 100 ml of water gave a yellow solution. No product was extracted with ether. However. when 10 ml of concentrated hydrochloric acid (or lithium chloride) was added, extraction with ether gave a yellow solid. mp 90–93° dec; nmr (CCl_4) τ 7.98, 6.69, 5.62, identical in all respects with an authentic sample of 2-methylallyliron tricarbonyl chloride.[31]

Bromination of 1. A solution of 0.6 ml (1.6 g, 0.01 mol) of bromine in 9 ml of carbon tetrachloride was added dropwise to a solution of 2 g (0.01 mol) of **1** in 11 ml of carbon tetrachloride under nitrogen while externally cooling with an ice bath. After 2 hr dark brown needles precipitated. 1.8 g. Evaporation of the mother liquor left 1.3 g. Recrystallization from hexane gave 2.9 g of brown needles: mp 78–79° dec; ir (CCl_4) 2086, 2039, 2007 cm^{-1}; nmr ($CDCl_3$) τ 5.60, 5.36, 4.75 (singlets of equal intensity). *Anal.* Calcd for $C_4H_6Br_2Fe(CO)_3$: C, 23.76; H, 1.71; Br, 45.17. Found: C, 23.87; H, 1.55; Br. 45.40.

Preparation of Benzoyltrimethylenemethaneiron Tricarbonyl. A solution of 5.0 g of **1** in 20 ml of carbon disulfide was added dropwise with stirring under nitrogen to a slurry of 6.8 g of anhydrous aluminum chloride and 3.74 g of benzoyl chloride in 50 ml of carbon disulfide while cooling to 5°. On warming to room temperature two layers formed: the mixture was heated at reflux for 2 hr. The upper CS_2 layer was discarded and the lower, dark red layer was hydrolyzed on ice. Extraction with ether left a red oil which was purified by chromatography on neutral alumina. Elution with 1:1 hexane–benzene gave a yellow oil which crystallized on cooling its solution in 15 ml of 1:10 ether–pentane at −78°, 0.51 g, mp 54–56°.

A second chromatographic fraction was obtained (benzene–methylene chloride) which, from its nmr spectrum (CCl_4) τ 2.1–2.9 (m, 5 H, PhH), 3.49 (septet, 1 H, J = 1.0 Hz, $CH{=}$), 7.99, 8.25 (d, 6 H, J = 1.0 Hz, CH_3)] was identified as dimethylacrylophenone.[35]

Preparation of Acetyltrimethylenemethaneiron Tricarbonyl. As above the reaction of 10 g of **1**, 3.8 g of acetyl chloride, and 8.2 g of aluminum chloride in carbon tetrachloride gave 0.83 g of CH_3-COTMM–$Fe(CO)_3$, bp 55–59° (0.05 mm).

Preparation of α-Hydroxyethyltrimethylenemethaneiron Tricarbonyl (17) and Its Reactions with Acids. Treatment of 0.28 g of CH_3-COTMM–$Fe(CO)_3$ with 0.5 g of sodium borohydride in methanol at 0° gave 0.28 g of **17**. On dissolving **17** in 5 ml of 96% sulfuric acid a red solution resulted. This solution was added to ice and extracted with ether. The dried ether extracts left 0.092 g of a yellow oil: ir (CCl_4) 2062, 2048, 1990, 1978 cm^{-1}; nmr (CCl_4) τ 4.71 (d, J = 8 Hz), 5.6–5.9 (m), 7.5–9.3 (m), 9.89 (d, J = 8 Hz). Chromatography on alumina failed to eliminate the impurities in the peaks at τ 7.5–9.3 and 5.6–5.9. From the areas of the ir peaks at 2048 and 2062 cm^{-1} the ratio of diene to TMM product was 4:1. When **17** (47 mg) was dissolved in 70% perchloric acid, a brownish red precipitate formed which rapidly turned gummy on exposure to air. This precipitate showed peaks for the carbonyls in the ir (Nujol) at 2146, 2105, 2058, 1984 cm^{-1}.

Preparation of Phenyltrimethylenemethaneiron Tricarbonyl. A. 1-Phenyl-2-bromomethylallyl bromide (29.4 g, 0.10 mol), which was prepared by the reaction of 2 mol of *N*-bromosuccinimide (NBS) with 1 mol of α,α-dimethylstyrene[36] and used without further purification [nmr (CCl_4) τ 2.80 (s, 5 H, PhH), 3.40 (s, 1 H, CH), 5.82, 5.86 (s, 4 H, CH_2)]. was stirred with 85 g (0.23 mol) of $Fe_2(CO)_9$ in 250 ml of hexane for 10 hr. The filtered solution was distilled; PhTMM–$Fe(CO)_3$ was collected at bp 110–114° (0.5 mm). The distillate crystallized to a yellow solid, mp 59–61°. Recrystallization from 95% ethanol gave plates, 11.5 g (0.04 mol), mp 63.5–64.2°.

B. α-Methylcinnamyl chloride[37] (20 g, 0.12 mol) and 60 g (0.16 mol) of diiron nonacarbonyl were stirred for 4 hr in 100 ml of hexane at room temperature. The solution was then heated at reflux for 1 hr to complete the reaction. The mixture was filtered and distilled to give a colorless liquid, bp 25–29° (0.45 mm), 0.28 g, and PhTMM–$Fe(CO)_3$, bp 109–115° (0.05 mm). 4.8 g (0.018 mol). The colorless liquid gave nmr (CCl_4) τ 2.92, 2.98 (s, PhH), 3.79 (m, CH), 5.27 (m, $CH_2{=}$), 8.28, 8.42 (s, CH_3), indicating, by comparison with authentic samples, that the mixture contained α,α-dimethylstyrene [nmr (CCl_4) τ 2.92, 3.79, 8.28] and 2-methyl-3-phenylpropene [nmr (CCl_4) τ 2.98, 5.27, 6.81, 8.42].[36,38] From integration of the peak at τ 3.79 (1 H, rel area 1) and 5.27 (1 H, rel area 1.5), the ratio of products is 4:3.

Preparation of Carbomethoxytrimethylenemethaneiron Tricarbonyl (10). 1-Carbomethoxy-2-bromomethyl allyl bromide (35.2 g, 0.13 mol), prepared by the reaction of NBS with 1-carbomethoxy-2-methylpropene[39] [nmr (CCl_4) τ 3.91 (CH), 5.24, 5.78 (CH_2Br), 6.41 (OCH_3)], was allowed to stir with 100 g (0.27 mol) of $Fe_2(CO)_9$ in 300 ml of hexane at 40–60°. After 6 hr the mixture was filtered and the filtrate fractionally distilled to give 7.1 g (0.028 mol) of the desired product, bp 34–37° (0.04 mm).

Reduction of 10. To 1.75 g (0.046 mol) of lithium aluminum hydride in 100 ml of anhydrous ethyl ether maintained under an atmosphere of nitrogen was added 0.62 g (0.022 mol) of anhydrous aluminum chloride in small portions. The complex, **10** (5.0 g, 0.02 mol), in 40 ml of ethyl ether was added slowly to the stirred solution. After addition the mixture was heated under reflux for 3 hr. Excess hydride was destroyed with 50 ml of wet ether, and the solution was treated with 30 ml of a saturated magnesium sulfate solution. After several hours a gray paste formed. The ether was decanted and the paste triturated with ether several times. After washing with water and drying over magnesium sulfate the ether portion was concentrated to 2.6 g, which was subjected to chromatography on alumina. Elution with pentane gave 1.3 g of a mixture of methyltrimethylenemethane and isopreneiron tricarbonyl which were present in the ratio 1:2 from nmr integration.

Preparation of 1,1-Dicarboethoxytrimethylenemethaneiron Tricarbonyl. 1,1-Dicarboethoxy-2-bromomethylallyl bromide (10 g, 0.03 mol), prepared by NBS bromination of diethyl isopropylidenemalonate[40] [nmr (CCl_4) τ 5.56 (s, CH_2Br), 5.72 (q, OCH_2), 8.62 (t, CH_3)], was allowed to stir with 30 g (0.08 mol) of $Fe_2(CO)_9$. After the usual work-up, 3.6 g (0.012 mol) of the diester was collected, bp 69–70° (0.006 mm). Crystallization from 15 ml of 1:10 ether–pentane at −78° gave yellow crystals, mp 27–29°.

Preparation of 1,1-Dimethyltrimethylenemethaneiron Tricarbonyl. Reaction of 3 g (0.01 mol) of 2-bromomethyl-3-methylbromobut-2-ene[41] and 10 g (0.03 mol) of $Fe_2(CO)_9$ gave 1.3 g

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(0.006 mol) of product purified by chromatography on alumina (pentane).

Preparation of Bis(methylenetrimethylenemethaneiron tricarbonyl) (6). **A.** The treatment of 1 mol of 1,1-dimethylallyl bromide[42] with 2 mol of NBS gave a mixture of bromides, which, from its nmr spectrum [τ 3.5–4.1 (CH), 5.8–6.3 (CH_2Br), 8.0–8.2 (CH_3), rel areas 2:6:3], consisted of equimolar quantities of $BrCH_2C(CH_3){=}CHCH_2Br$ and $(BrCH_2)_2C{=}CHCH_2Br$. This mixture (30 g) was allowed to react with 90 g of $Fe_2(CO)_9$ in 300 ml of hexane. The resulting solution was fractionally distilled to remove all components with bp 120° (0.3 mm) or lower. The resulting residue was chromatographed on a column of neutral alumina. Elution with pentane and pentane–benzene (1:1) separated a yellow band, which was concentrated to 1.1 g of a solid. Recrystallization from 1:10 ether–pentane at −20° gave a yellow powder, mp 112–116°.

B. A mixture of 4.9 g of 2-bromomethylbutadiene[43] and 30 g of $Fe_2(CO)_9$ was allowed to stir in hexane for 24 hr. After filtration, the residue upon concentration of the filtrate (2.5 g) was dissolved in 1 ml of ether and 14 ml of pentane and cooled at −78°. The product had mp 114–116° and was identical in all respects with that obtained by method A.

Preparation of Chlorotrimethylenemethaneiron Tricarbonyl. A mixture of 3- and 1-chloro-2-chloromethylpropene (60 g), prepared by the method of Gragson,[15] was stirred with 200 g of $Fe_2(CO)_9$ in 600 ml of anhydrous ethyl ether. After 24 hr the mixture was filtered and the filtrate distilled. Distillates of $Fe(CO)_5$, bp 30–35° (30 mm), and TMM–$Fe(CO)_3$, 9.1 g, bp 58–59° (30 mm), were initially obtained. When the pot temperature reached 95° vigorous gas evolution occurred. A red liquid distilled at 78–89° (15 mm). This liquid, upon chromatography on neutral alumina (elution with pentane), gave a yellow oil which crystallized from its pentane solution on cooling to −78° but melted at room temperature. Its ir and nmr spectra are consistent with its identification as ClTMM–$Fe(CO)_3$.

Preparation of the Allyliron Tricarbonyl Halide Complexes. The new allyliron tricarbonyl halide complexes which were used in the present study were prepared by the methods described by Murdoch and Weiss[25] and Emerson and Pettit.[31] *syn*-1,2-Dimethylallyliron tricarbonyl bromide (**7**) was obtained in 22% yield from tiglyl bromide:[37] mp 59–60° dec; nmr (CCl_4) τ 5.78 (q, 1 H, J = 6 Hz), 5.88 (s, 1 H), 6.94 (s, 1 H), 8.08 (d, 3 H, J = 6 Hz); ir (CCl_4) 2083, 2037, 2000 cm^{-1}. *Anal.* Calcd for $C_8H_9O_3BrFe$: C, 33.25; H, 3.15; Br, 27.65. Found: C, 33.37; H, 3.39; Br, 27.30.

syn,syn-1,2,3-Trimethylallyliron tricarbonyl bromide was obtained in 16% yield from the reaction of 1,2,3-trimethylallyl bromide with $Fe_2(CO)_9$: mp 52.5–53.0° dec; nmr (CCl_4) τ 6.04 (q, 2 H, J = 8 Hz), 8.01, 8.10 (s, d, 9 H, J = 8 Hz); ir (CCl_4) 2084, 2033, 1996 cm^{-1}. *Anal.* Calcd for $C_9H_{11}O_3BrFe$: C, 35.7; H, 3.63; Br, 26.4. Found: C, 35.70; H, 3.65; Br, 26.65.

Methylenecyclohexenyliron tricarbonyl bromide (**13**) was prepared in 8% yield from α-bromomethylenecyclohexane:[44] mp 46–48° dec; ir (CCl_4) 2081, 2035, 1994 cm^{-1}. *Anal.* Calcd for $C_{10}H_{11}O_3BrFe$: C, 38.14; H, 3.49; Br, 25.38. Found: C, 38.26; H, 3.46; Br, 25.25.

Disproportionation Studies. Samples of the above allyliron tricarbonyl bromides were decomposed by heating their solutions in cyclohexane for several hours under reflux. The products obtained were identified by the nmr and ir spectra of the crude product mixture. Decomposition of **7** gave an oil (36% yield), bp 65–74° (12 mm), which had an identical nmr spectrum with that of the product mixture obtained by the reduction of carbomethoxytrimethylenemethaneiron tricarbonyl. The product obtained from the thermal decomposition of *syn,syn*-1,2,3-trimethylallyliron tricarbonyl bromide had nmr (CCl_4) τ 4.97 (m, 1 H), 7.91 (s, 3 H), 8.62 (d, J = 6 Hz), 9.95, 10.11 (d of d, 1 H, J = 2, 9 Hz). Other absorptions occur under the peaks at τ 8.62 and at 8.9–9.5; ir (CCl_4) at 2047, 1985, 1972 cm^{-1}. Disproportionation of **13** gave an oil which was identified as mostly 2-methylcyclohexadieneiron tricarbonyl from its nmr spectrum (CS_2) [τ 4.80 (d of d, J = 6 and 1 Hz), 6.8–7.2 (m), 7.92 (s, CH_3), 8.38 (CH_2), in relative areas 1:2:3:4] and ir spectrum [(liquid film) 2049, 1976 cm^{-1}]. Treatment of trimethylallyl bromide[45] with $Fe_2(CO)_9$ gave a product after work-up which was identical with an authentic sample of 2,3-dimethylbutadieneiron tricarbonyl[46] (60% yield): nmr (CCl_4) τ 7.85 (s, CH_3), 8.32 (d, trans H, J = 1.9 Hz), 9.92 (d, cis H, J = 1.9 Hz); ir (CCl_4) 2049, 1986, 1974 cm^{-1}.

Protonation Reactions. The mixture of methyltrimethylenemethane- and isopreneiron tricarbonyl (1:2, 1.0 g) was dissolved in 5 ml of 86% sulfuric acid. The red solution was diluted to 50 ml with water and extracted with ether. Concentration of the ether extracts left 0.9 g of **9**. Similar treatment of 1,1-dimethyltrimethylenemethaneiron tricarbonyl gave a 95% yield of 2,3-dimethylbutadieneiron tricarbonyl.

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