

pellet. The ultraviolet spectrum was measured with a dilute solution of the dimer ($1.6 \times 10^{-3} M$) in spectral grade methanol (Eastman Kodak Co.). The molecular weight could not be determined due to the insolubility of the dimer.

Anal. Calcd. for $C_{22}H_{20}O_2$: C, 83.51; H, 6.37. Found: C, 83.34; H, 6.29.¹¹

Quenching Experiment and Emission Spectra.—A mixture of 0.5 g. of benzophenone and 0.5 g. of methyl β -naphthyl ether in 5 ml. of the benzene-isopropyl alcohol mixture was divided into two portions. One part (degassed) was irradiated using the uranium glass filter and the other without. No product was observed in either case. The emission spectrum of this solution exhibited no fluorescence or phosphorescence. The emission spectrum of the naphthyl ether at 77°K. exhibited a weak 0–0 band at 4595 Å. (21,700 cm^{-1} , 62 kcal.). At room temperature the emission spectrum in cyclohexane showed a broad fluorescence band with the maximum at 3530 Å. (28,300 cm^{-1}) and no phosphorescence. A mixture of methyl β -naphthyl ether (0.05 M) and benzophenone (0.01 M) in cyclohexane gave the same emission spectrum as that reported above for the naphthyl ether in cyclohexane except the intensity was reduced by about 90%.

(11) Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y.

Attempted Preparation of Other Naphthalenic Dimers.—Solutions, each containing 2 g. of substrate in a mixture of 10 ml. of benzene and 10 ml. of isopropyl alcohol, were prepared and irradiated as before. The naphthalene derivatives used in this study were: naphthalene, methyl α -naphthyl ether, α - and β -methylnaphthalenes, α - and β -bromonaphthalenes, α - and β -naphthylamines, and α - and β -naphthols. No products were formed in any of these experiments. Comparisons of the ultraviolet absorption spectra of the solutions after at least 1 week of irradiation with that of the starting material indicated that no reaction had taken place.

Attempted Preparation of Cross Photoadducts.—Mixtures of 0.5 g. of methyl β -naphthyl ether and, in one case, 0.5 g. of maleic anhydride and, in a second experiment, with 0.5 g. of dimethyl acetylenedicarboxylate, in 5 ml. of the benzene-isopropyl alcohol mixture were prepared and irradiated as before. No products were formed. Comparison of the ultraviolet absorption spectra of the solutions after at least 1 week of irradiation with those of solutions before irradiation indicated that no reaction had taken place.

Acknowledgments.—This work was supported in part by the National Science Foundation. We are indebted to Mr. Angelo Lamola for measurement of the emission spectra.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, THE UNIVERSITY OF TEXAS, AUSTIN, TEXAS]

Organo-Iron Complexes. II.¹ π -Pentadienyl- and π -1,5-Dimethylpentadienyliron Tricarbonyl Cations

BY J. E. MAHLER AND R. PETTIT

RECEIVED JUNE 7, 1963

Stable salts of π -pentadienyl- and π -1,5-dimethylpentadienyliron tricarbonyl cations have been prepared by reaction of *trans*-dienol-iron tricarbonyl complexes with strong acids. Evidence favoring a completely cisoid disposition of the five sp^2 hybridized carbon atoms of the pentadienyl ligand in these cationic complexes is presented. A mechanism is proposed to account for the stereochemistry observed in the reaction of the hydrolysis of the cations and their formation from *trans*-dienol-iron tricarbonyl complexes.

Introduction

Several cationic complexes in which an iron tricarbonyl residue is π -bonded to a pentadienyl grouping have recently been reported. Stable salts of the cyclohexadienyliron tricarbonyl cation (I) were first reported in 1960 by Fischer and Fischer²; this cation was formed, together with triphenylmethane, upon reaction of cyclohexadieneiron tricarbonyl with triphenylmethyl fluoroborate. A similar hydride ion abstraction reaction utilizing the triphenylmethyl cation had previously been employed by Dauben and Honnen³ for the conversion of cycloheptatrienemolybdenum tricarbonyl to salts of the tropyliummolybdenum tricarbonyl cation.

More recently, salts of the cycloheptadienyliron tricarbonyl cation have been prepared by means of a similar reaction involving hydride ion abstraction from cycloheptadiene iron tricarbonyl⁴; this same cation is also formed upon protonation of the free double bond in cycloheptatrieneiron tricarbonyl.^{4,5} Addition of strong acids to cyclooctatetraeneiron tricarbonyl also gives rise to stable salts^{6,7} which have recently been shown to contain the bicyclooctadienyliron tricarbonyl cation.⁷

The type of reaction employed in these preparations typically gives rise to carbonium ions and, from one extreme viewpoint, the cationic complexes just described might formally be considered as being derived

from an iron atom having, as ligands, three carbonyl groups and a substituted pentadienyl carbonium ion. Viewed in this way, the stability of the cation I is then of particular interest for its mode of formation suggests that it is more stable (less electrophilic) than the triphenylmethyl cation; this is also evident from the fact that salts of I can be recrystallized from water. The reverse order of stability holds for the cyclohexadienyl cation when it is not complexed to a metal.

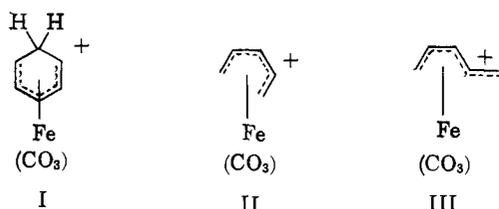
Although no X-ray data for these dienyl-iron tricarbonyl complex cations are available, it seems most probable that in each case the iron atom would lie below a plane defined by the five carbon atoms of the dienyl system and, as in the case of the diene-iron tricarbonyl complexes,⁸ would be situated approximately equidistant from these five carbon atoms. In common then with other organometallic systems, the two factors involved in the union of the dienyl moiety to the iron atom will be the forward coordination arising from interaction of bonding orbitals of the pentadienyl ligand with vacant iron orbitals and the back donation of electrons from iron to the ligand *via* interaction of filled orbitals on iron with low-lying, vacant molecular orbitals of the dienyl system. In these particular systems the back donation would be of special significance, for not only would it increase the ligand-metal bonding and decrease the electron density on iron, but it would also result in a decrease in the electrophilicity of the carbonium ion ligand.

Now, in each of the cationic complexes mentioned before, the dienyl ligand is part of a cyclic system and necessarily possesses a completely cisoid arrangement of sp^2 hybridized carbon atoms. This geometrical restriction need not necessarily be imposed upon an

(1) Part I: R. Pettit, *J. Am. Chem. Soc.*, **81**, 1266 (1959).
 (2) E. O. Fischer and R. D. Fischer, *Angew. Chem.*, **72**, 919 (1960).
 (3) H. J. Dauben and L. R. Honnen, *J. Am. Chem. Soc.*, **80**, 5570 (1958).
 (4) H. J. Dauben and D. J. Bertelli, *ibid.*, **83**, 497 (1961).
 (5) R. Burton, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 594 (1961).
 (6) G. N. Schrauzer, *J. Am. Chem. Soc.*, **83**, 2966 (1961).
 (7) A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 4821 (1962), and references therein.

(8) O. S. Mills and G. Robinson, *Proc. Chem. Soc.*, 241 (1960).

acyclic pentadienyl system and the two isomeric complex cations II and III could conceivably exist as stable species.⁹ The ligands in each case possess the same



low-lying, vacant molecular orbitals, though only in the system II could the iron atom be strongly bonded simultaneously to each of the five carbon atoms. Nevertheless, it is conceivable that bonding in III could be provided through interaction with four carbon atoms as in diene-iron tricarbonyl complexes.¹⁰

The present paper describes investigations leading to the preparation of certain such acyclic pentadienyl-iron tricarbonyl cations. In particular, the studies have been directed toward investigation of the geometrical problem afforded by isomers of the type exemplified by II and III.

Results and Discussion

The triphenylmethyl cation fails to abstract a hydride ion from *trans*-1,3-pentadieneiron tricarbonyl (IV) under the same conditions that it is found to react with cyclohexadieneiron tricarbonyl to give the cation I. This would immediately suggest that the cation III, if it is stable, is less so than the triphenylmethyl cation.



It was of interest to determine whether *cis*-1,3-pentadieneiron tricarbonyl (V) would behave similarly; however, at this stage, this compound was not available. The reaction of *cis*-1,3-pentadiene with iron pentacarbonyl leads to the formation of the *trans* complex IV. The *cis* isomer V has subsequently been obtained by an indirect route and, as will be discussed below, it is found that the hydride abstraction reaction does proceed in this case.

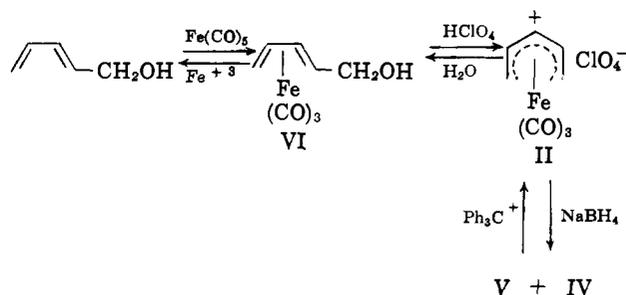
For preparative purposes, the method of preparing salts of stable carbonium ions developed by Dauben and co-workers¹¹ is restricted to those systems which are more stable than the triphenylmethyl cation. In view of the failure of the *trans* complex IV to undergo reaction with triphenylmethyl fluoroborate, attention was therefore directed to the reaction of alcohol complexes with strong acids.

As indicated in the reaction scheme below, *trans*-2,4-pentadien-1-ol-iron tricarbonyl (VI) has been prepared from the reaction of *trans*-pentadienol with iron pentacarbonyl. Treatment of this *trans* alcohol complex with perchloric acid affords an almost quantitative yield of the perchlorate salt of a pentadienyliron tricarbonyl cation; it has been shown, however, that this cation possesses the *cisoid* structure II rather than the *transoid* one III.

(9) In view of the recent isolation of salts of π -allyliron tricarbonyl cations [G. F. Emerson and R. Pettit, *J. Am. Chem. Soc.*, **84**, 4591 (1962)] a third isomer, namely, the *syn*-1-vinyl- π -allyliron tricarbonyl cation, might also be stable.

(10) Weak bonding of iron to the fifth carbon of the dienyl ligand in III, analogous to that postulated in α -metallocenyl carbonium ions [E. A. Hill and J. H. Richards, *ibid.*, **83**, 3840 (1961)], is conceivable.

(11) H. J. Dauben, F. A. Gadecki, K. M. Harmon, and D. L. Pearson, *ibid.*, **79**, 4557 (1957).



Convincing evidence showing that geometrical isomerization has occurred in the formation of the cation is seen in the proton n.m.r. spectrum of the salt (Fig. 1). Four widely separated bands of relative areas 1:2:2:2 are seen in the spectrum. The number of bands and the symmetrical nature of each one is clearly in accord with structure II rather than structure III for the cation. The two pairs of protons H_a and H_s give rise to the two sets of doublets at 7.83 and 6.25 τ , respectively, the former pair being assigned the higher value from analogy with acyclic diene-iron tricarbonyl complexes in which *anti*-protons are found to absorb at higher fields than *syn* protons.^{12,13} The symmetrical octet centered at 3.74 τ is associated with the two protons H_d , while the proton H_c shows as a triplet at 2.78 τ .

Other salts of cation II, for example, the tetrafluoroborate and the hexafluorophosphate, can be prepared in a similar manner from VI and the appropriate strong acid. The salts are all yellow, crystalline, diamagnetic solids, being soluble only in polar solvents such as nitromethane. They all possess strong carbonyl absorption in the infrared at 2120 and 2072 cm^{-1} . This high frequency of absorption is also found for the related cyclic species mentioned^{4,5} before and presumably reflects a reduction of back donation of electrons into the anti-bonding orbitals of the carbonyl groups due to the increased affinity of the pentadienyl ligand for these electrons.

Salts of the cation II, unlike those of the cyclohexadienyliron tricarbonyl cation I, are readily decomposed in water. The product of this reaction is the *trans* alcohol complex VI: the formation of VI must involve the reverse type of geometrical inversion noted before. The *trans* configuration of the complex VI is seen from its n.m.r. spectrum.¹⁵

Geometrical inversion apparently does not always accompany the reaction of the cation II with nucleophiles. Treatment of the salts of II with sodium borohydride gives a mixture of pentadiene-iron tricarbonyl complexes; degradation of this mixture with ceric or ferric salts liberates a mixture consisting of 80% *cis*- and 20% *trans*-1,3-pentadiene. This same ratio is confirmed by inspection of the n.m.r. spectrum of the mixture of complexes; *cis*-1,3-pentadieneiron tricarbonyl possesses a unique absorption at 7.33 τ , due to the *syn* proton on the substituted terminal carbon atom of the diene ligand, which allows an independent method of analysis.

This reaction with sodium borohydride affords the only route so far for the preparation of *cis*-1,3-penta-

(12) J. E. Mahler and R. Pettit, unpublished observations.

(13) Following the nomenclature used for π -allylmetal complexes,¹⁴ the terms *syn* and *anti* are used here to indicate the configurations of groups on the terminal positions of π -pentadienyl- and π -1,3-diene-iron tricarbonyl complexes. The groups attached to the internal carbons are taken as the point of reference.

(14) W. R. McClellan, H. H. Hoehn, H. N. Cripps, E. L. Muetterties, and B. W. Howk, *J. Am. Chem. Soc.*, **83**, 1601 (1961).

(15) The n.m.r. spectrum of VI does not exhibit a band in the region expected (6.8–7.6 τ) for a *syn* proton on a substituted terminal carbon atom of the diene-iron tricarbonyl complex. Instead, the proton (on the carbon atom) adjacent to the CH_2OH group gives absorption at 8.93 τ , which is the region expected for an *anti* proton.¹²

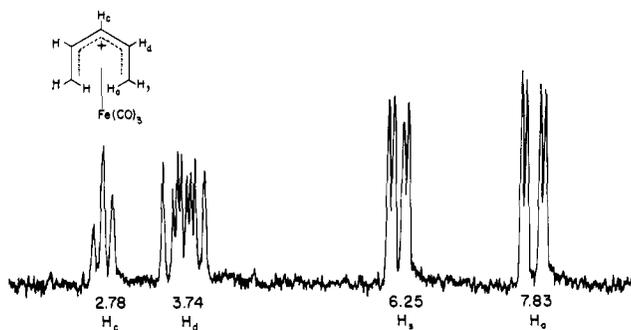
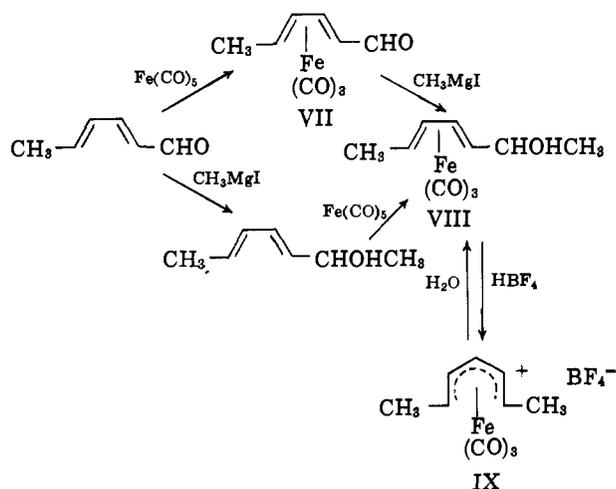


Fig. 1.—Proton nuclear magnetic resonance spectrum of pentadienyliron tricarbonyl fluoroborate; peak positions are given in τ -units.

dieneiron tricarbonyl. In contrast to the *trans* isomer, the *cis* complex V reacts readily with the triphenylmethyl cation to give salts of the complex ion II together with triphenylmethane. It is therefore apparent that the cation II is more stable than both the triphenylmethyl cation and the isomeric *trans* complex cation III. This order of stability for the two isomeric cations undoubtedly is due to the fact that only the *cisoid* configurations of the dienyl ligand allow the iron atom to be strongly bonded simultaneously to each of the five carbon atoms.

The failure to observe hydride ion abstraction from *trans*-1,3-pentadieneiron tricarbonyl by the triphenyl carbonium ion, to produce the cation II, must involve kinetic rather than thermodynamic factors.

Further evidence indicating the stability of the pentadienyliron tricarbonyl cation, and the prevalence of the occurrence of the type of geometrical inversion discussed earlier, is seen in the accompanying reactions pertaining to the 1,5-dimethyl derivative of II.



trans-trans-2,4-Hexadienal is converted, upon reaction with iron pentacarbonyl, to the corresponding diene-iron tricarbonyl complex VII. This compound also has been prepared by Stone and co-workers, using triiron dodecacarbonyl in place of iron pentacarbonyl.¹⁶ Treatment of the complex VII with methylmagnesium iodide affords *trans-trans*-3,5-heptadien-2-ol-iron tricarbonyl (VIII). The alcohol complex is also obtained by an alternative route through reaction of 2,4-hexadienal with methylmagnesium iodide and treatment of the resulting heptadienol with iron pentacarbonyl. For purposes of the subsequent discussion it is important to note that the product (VIII) in each synthesis consists of a mixture of diastereoisomers; the two asym-

(16) R. B. King, T. A. Manuel, and F. G. A. Stone, *J. Inorg. Nucl. Chem.*, **16**, 233 (1961).

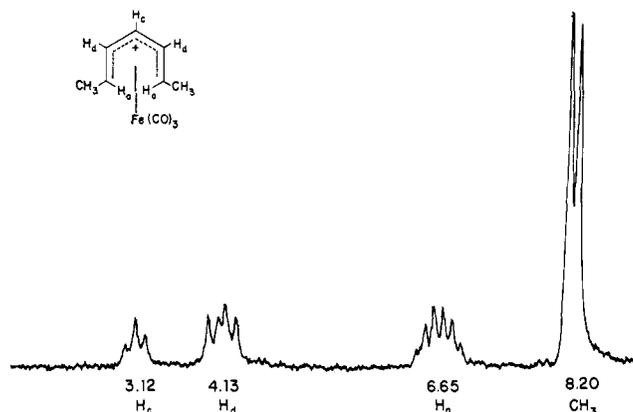


Fig. 2.—Proton nuclear magnetic resonance spectrum of *syn-syn*-1,5-dimethylpentadienyliron tricarbonyl fluoroborate; peak positions are given in τ -units.

metric centers responsible for the existence of these being the carbon atom bearing the hydroxyl group and the unsymmetrical diene-iron tricarbonyl unit. One of the racemates has a m.p. of 85° while the other, produced here in greater amounts, melts at 70° .

Treatment with fluoroboric acid of either diastereoisomer of VIII, or a mixture of the two, produced in almost quantitative yield one single compound. This material has been shown to be the fluoroborate salt of the *syn-syn*-1,5-dimethylpentadienyliron tricarbonyl cation (IX). The n.m.r. spectrum of the salt is shown in Fig. 2. The four bands of area 1:2:2:6 are clearly in accord with the symmetrical structure IX with the assignments being as indicated. On this basis the only other structure which could be contemplated for the cation would be the isomeric system having the two terminal methyl groups on the dienyl system in an *anti* configuration. For steric reasons such a structure seems unlikely. Furthermore, the terminal protons of the dienyl unit show absorption at 6.65 τ , which is 1.5 τ units higher than the analogous protons are found to absorb in the cycloheptadienyliron tricarbonyl cation, in which of course they are fixed in a *syn* configuration.⁷

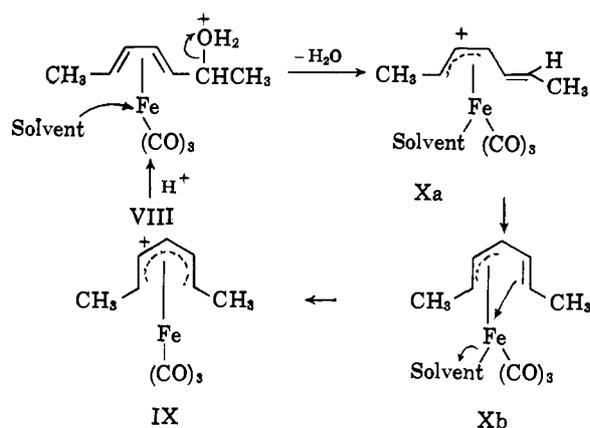
Other salts of the cation IX can be prepared in a similar manner from VIII and strong acids. Again, these salts are air-stable, crystalline solids which display carbonyl absorption at 2111 and 2060 cm.^{-1} in the infrared.

Of particular interest is the reaction of the cation IX with water; this leads to the formation of a single alcohol complex VIII in yields of better than 90%. The two significant features of this reaction are the geometrical inversion which must accompany the formation of VIII and the fact that only one of the two diastereoisomers, m.p. 85° , is formed. As seen in the following paper, the same stereospecificity is also observed in the reaction of the 1-methyl derivative of II with water.

From the foregoing discussion it is clear that cations of type II are more stable than those of type III and the question as to whether the latter cations will form stable salts remains unanswered.

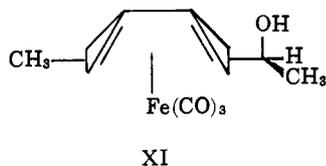
Another interesting question raised by the foregoing results concerns the mechanism of the formation of the *cisoid* cations from *trans* alcohol complexes and *vice versa*. The mechanism as outlined in the following scheme for the case of the 1,5-dimethyl derivative of II would seem to adequately account for these reactions.

In the first step in the formation of IX from VIII, it is proposed that dehydration of each diastereoisomer leads to the formation of the hydrated vinyl- π -allyliron tricarbonyl cation (Xa) in which a *trans* configuration



exists about the double bond. External attack of solvent on the iron atom is suggested in this step in order to maintain the inert gas configuration of krypton for the iron atom. In the interests of writing a reversible reaction to account for the formation of only one alcohol complex from IX, it is proposed that both diastereoisomers of VIII yield the same *trans* olefin derivative (Xa) though they do so at different rates. Free rotation about the appropriate single bond in Xa to give Xb, followed by intramolecular displacement of solvent from iron by coordination of the vinyl bond, leads to the observed product.

The reverse of these reaction steps could then account for the formation of the single *trans* alcohol complex upon reaction of IX with water. In this reverse reaction it is logical to suppose that water will attack the species (Xa) from the side opposite that of the iron tricarbonyl group. In this case then, it is predicted that the alcohol complex formed upon hydrolysis, m.p. 85°, will be a racemate, one enantiomer of which will have the configuration shown in formula XI. The relative configurations about the two asymmetric centers



C-2 and C-3 in XI can be described as S. and S.¹⁷ The other diastereoisomer, m.p. 70°, must then have the relative configuration R.S. and S.R. for its enantiomeric forms.

The formation of *cis*-1,3-pentadieneiron tricarbonyl from the reaction of II with sodium borohydride would require a different type of reaction sequence; however, it should be noted that this is a heterogeneous reaction run under conditions quite different from those of the reaction of II with water.

Experimental

The proton n.m.r. data were obtained with a Varian A60 spectrometer using tetramethylsilane as an internal standard, and peak positions are reported in parts per million relative to tetramethylsilane as 10 p.p.m. (τ). The infrared spectra were taken with a Beckman IR7 instrument. All boiling points and melting points are uncorrected.

***trans*-2,4-Pentadien-1-ol Iron Tricarbonyl.**—*trans*-2,4-Pentadien-1-ol was prepared by lithium aluminum hydride reduction of *trans*-2,4-pentadienoic acid.¹⁸ A solution containing 16.0 g. of *trans*-2,4-pentadien-1-ol, 160 g. of iron pentacarbonyl, and 160 g. of ethylcyclohexane was refluxed under nitrogen for 36 hr. The solution was cooled and the unchanged reactants were removed under reduced pressure (30 mm.). The residual red oil was distilled *in vacuo* to yield 26.0 g. of *trans*-2,4-pentadien-1-ol iron tricarbonyl, b.p. 91–98° (0.3 mm.), n_D^{20} 1.5934.

(17) For the purpose of assigning relative configurations in unsymmetrical diene-iron tricarbonyl complexes, it is assumed that each carbon atom of the diene ligand is bonded to iron.

(18) A. D. Mebane, *J. Am. Chem. Soc.*, **74**, 5227 (1952).

Anal. Calcd. for $C_8H_8O_4Fe$: C, 42.89; H, 3.59. Found: C, 43.29; H, 3.28.

The infrared spectrum exhibited bands at 3360 cm^{-1} (OH) and at 2054, 1989, and 1978 cm^{-1} ($C=O$).

Pentadienyliron Tricarbonyl Perchlorate.—A solution containing 0.60 g. of 70% perchloric acid in acetic anhydride, prepared by adding the acid dropwise to 5 ml. of cooled (0°) acetic anhydride, was added slowly to 0.36 g. of *trans*-2,4-pentadien-1-ol-iron tricarbonyl in 5 ml. of acetic anhydride at 0°. When about half of the acid solution was added, yellow crystals began to separate from the solution. After the addition, the solution was stirred for 15 min. and then poured into excess dry ethyl ether. Filtration of the suspension provided 0.41 g. of yellow crystalline pentadienyliron tricarbonyl perchlorate. The salt crystallizes from nitromethane in fine yellow needles; it explodes violently when heated.

Anal. Calcd. for $C_8H_7O_7ClFe$: C, 31.35; H, 2.30. Found: C, 31.48; H, 2.40.

The infrared spectrum of the salt in a hexachlorobutadiene mull showed absorption at 2120 and 2072 cm^{-1} ($C\equiv O$).

The n.m.r. spectrum of the salt in liquid sulfur dioxide, with the various proton assignments, is given in Fig. 1 of the text. The coupling constants as determined from the spectrum are $J_{cd} = 6.8$, $J_{ad} = 9.8$, $J_{bd} = 13$, and $J_{aa} = 3.5$ c.p.s. Although the coupling between H_a and H_c was not obtained accurately, it seems to be of the order of 1 c.p.s.

Reaction of Pentadienyliron Tricarbonyl Perchlorate with Water.—Pentadienyliron tricarbonyl perchlorate, 1.0 g., was added to 50 ml. of water at room temperature with stirring; after 30 min. the reaction mixture was extracted several times with ether. The combined extracts were washed with water and dried over magnesium sulfate. The infrared spectrum of the oil that remained, after removal of the ether, was identical with the spectrum of *trans*-2,4-pentadien-1-ol-iron tricarbonyl.

Reaction of Pentadienyliron Tricarbonyl Fluoroborate with Sodium Borohydride.—To a stirred suspension of 13.0 g. of pentadienyliron tricarbonyl fluoroborate in 150 ml. of dry tetrahydrofuran, 1.7 g. of sodium borohydride was added over a 10–15-min. period. During the addition and for 1.5 hr. following, the temperature of the reaction mixture was maintained between –25 and –30°. The reaction mixture was then warmed to ca. 10°, poured into excess water, and extracted three times with petroleum ether. The combined extracts were washed twice with water and dried over magnesium sulfate. Distillation of the oil which remained after removal of the solvent afforded 4.95 g. of pentadieneiron tricarbonyl, b.p. 29–30° (0.1 mm.), n_D^{20} 1.5705.

Anal. Calcd. for $C_8H_8O_3Fe$: C, 46.19; H, 3.88. Found: C, 46.24; H, 3.90.

A portion of the complex was degraded with ceric ammonium nitrate in water and the liberated diene was shown to consist of 80% *cis*- and 20% *trans*-1,3-pentadiene by gas chromatography (on a silver nitrate column that was previously shown to separate *cis*- and *trans*-1,3-pentadienes).

***trans*-1,3-Pentadieneiron Tricarbonyl.**—This compound has previously been reported by Stone and co-workers.¹⁶ Degradation (in the same manner mentioned earlier) of a sample prepared from the reaction of iron pentacarbonyl and commercial 1,3-pentadiene gave only *trans*-1,3-pentadiene as shown by gas chromatography.

Reaction of *cis*- and *trans*-1,3-Pentadieneiron Tricarbonyl with Triphenylmethyl Fluoroborate.—A solution of 1.88 g. of triphenylmethyl fluoroborate in 7 ml. of nitromethane was added to 1.04 g. of 1,3-pentadieneiron tricarbonyl (containing 80% of the *cis* and 20% of the *trans* isomer) in 2 ml. of nitromethane. The solution was heated at 50° for 8 min. and then poured into 200 ml. of dry ether. The suspension in ether was stirred for 10 min. to decompose any unreacted triphenylmethyl fluoroborate and then filtered. The salt, 0.66 g., was crystallized from nitromethane. The infrared spectrum, taken as a mull in Nujol and also in hexachlorobutadiene, was identical with that of an authentic sample of pentadienyliron tricarbonyl fluoroborate.

A sample of *trans*-1,3-pentadieneiron tricarbonyl was treated with triphenylmethyl fluoroborate in the same manner. However, no pentadienyliron tricarbonyl salt could be isolated.

***trans*-2,4-Hexadienyliron Tricarbonyl.**—A solution of 55 g. of freshly distilled *trans-trans*-2,4-hexadienal and 225 g. of iron pentacarbonyl was refluxed under nitrogen for 46 hr. The reaction mixture was cooled and the unchanged reactants removed by distillation (20 mm.). Distillation of the residual oil *in vacuo* yielded 61.0 g. of *trans-trans*-2,4-hexadienyliron tricarbonyl, b.p. 112° (1.3 mm.), n_D^{20} 1.5982. The complex formed yellow crystals from ether, m.p. 26–27°. This complex has previously been prepared from the reaction of *trans-trans*-2,4-hexadienal and triiron dodecacarbonyl.¹⁶

Anal. Calcd. for $C_8H_8O_4Fe$: C, 45.80; H, 3.42. Found: C, 45.94; H, 3.84.

The infrared spectrum exhibited absorption at 2064, 2002, and 1987 cm^{-1} ($C=O$) and at 1685 and 1697 cm^{-1} ($C=O$).

The 2,4-dinitrophenylhydrazone derivative, prepared in the normal manner, crystallized from ethanol-ethyl acetate solutions in red needles, m.p. 192–193° dec.

Anal. Calcd. for $C_{15}H_{11}O_7N_4Fe$: C, 43.29; H, 2.91; N, 13.46. Found: C, 43.18; H, 2.82; N, 13.70.

trans-trans-3,5-Heptadien-2-ol-iron Tricarbonyl from Reaction of Methylmagnesium Iodide with trans-trans-2,4-Hexadienaliron Tricarbonyl.—An ethereal solution of methylmagnesium iodide (prepared from 9.72 g. of magnesium and 39.8 g. of iodomethane) was added slowly to a cooled solution (0°) of 57.0 g. of trans-trans-2,4-hexadienaliron tricarbonyl in 1 l. of dry ether. The reaction mixture became very viscous during the addition. The mixture was stirred for 30 min. and hydrolyzed with a saturated ammonium chloride solution. The ether layer was separated and the aqueous solution extracted twice with ether. The combined ether extracts were washed with 5% sodium carbonate and water and then were dried over magnesium sulfate. Removal of the solvent left a thick red oil which was distilled to yield 31.3 g. of complex, b.p. 110–115° (0.3 mm.). An infrared spectrum of the distillate indicated the presence of small amounts of unreacted aldehyde complex. Crystallization of the crude product from pentane yielded the alcohol complex VIII, m.p. 68–70°. Repeated recrystallizations from petroleum ether gave fine yellow needles, m.p. 70–71.5°.

Anal. Calcd. for $C_{10}H_{12}O_4Fe$: C, 47.66; H, 4.80. Found: C, 47.44; H, 4.99.

Repeated crystallization of the material obtained following evaporation of the mother liquors afforded a small amount of the other diastereoisomer of VIII, m.p. 85–86°.

A portion of the isomer, m.p. 70°, was dissolved in light petroleum and chromatographed over alumina. It was found, after solvent removal, that the complex now melted at 85°.

A solution obtained upon dissolving 1.0 g. of the alcohol complex, m.p. 70°, in 20 ml. of 10% fluoroboric acid was diluted with water and extracted with ether. Evaporation of the ether afforded 0.90 g. of alcohol complex, m.p. 85°.

A small portion of the isomer, m.p. 70°, was degraded with ceric ammonium nitrate; gas chromatography indicated that the liberated dienol was the same as the dienol liberated by degradation of the isomer, m.p. 85°.

A comparison of the infrared spectra of the two isomers is given in this Experimental section which describes the reaction of the dimethyl salt with water.

trans-trans-3,5-Heptadien-2-ol-iron Tricarbonyl from the Reaction of Iron Pentacarbonyl with trans-trans-3,5-Heptadien-2-ol.—trans-trans-3,5-Heptadien-2-ol was prepared by addition of 96.0 g. of trans-trans-2,4-hexadienal to methylmagnesium iodide (from 150.0 g. of methyl iodide and 32 g. of magnesium) in 600 ml. of ether. Treatment of the mixture in the usual manner afforded 70.0 g. of product, b.p. 87–90° (25 mm.). The infrared spectrum did not display strong carbonyl absorption.

A solution containing 70.0 g. of crude trans-trans-3,5-heptadien-2-ol and 200 g. of iron pentacarbonyl was refluxed gently under nitrogen for 58 hr. After cooling, the volatile materials

were removed under reduced pressure and the remaining oil was distilled to yield 35.7 g. of trans-trans-3,5-heptadien-2-ol-iron tricarbonyl, b.p. 110–115° (0.3 mm.). The complex became solid upon cooling and several crystallizations from pentane afforded yellow needles, m.p. 85°.

An infrared spectrum of the complex exhibited absorptions at 3425 cm^{-1} (OH) and 2045, 1979, and 1971 cm^{-1} ($C\equiv O$).

syn-syn-1,5-Dimethylpentadienyliron Tricarbonyl Fluoroborate.—A solution of 17.8 g. of 40% fluoroboric acid in 90 ml. of propionic anhydride (prepared by adding the aqueous acid to the anhydride cooled in an ice bath) was added slowly to a cooled (0°) solution of 20.0 g. of trans-trans-3,5-heptadien-2-ol-iron tricarbonyl (m.p. 85°) in 80 ml. of propionic anhydride. The syn-syn-1,5-dimethylpentadienyliron tricarbonyl fluoroborate salt crystallized from the solution and, after stirring for 30 min. at 0°, was filtered, washed with ether, and dried. The salt, 21.4 g., was recrystallized from nitromethane to give yellow needles, which decomposed without melting above 220°.

Anal. Calcd. for $C_{10}H_{11}BO_3F_4Fe$: C, 37.32; H, 3.44; B, 3.36; F, 23.61. Found: C, 37.06; H, 3.59; B, 3.20; F, 23.30.

An infrared spectrum of the salt as a mull in hexachlorobutadiene showed bands at 2111 and 2060 cm^{-1} ($C\equiv O$).

The n.m.r. spectrum of this salt in liquid sulfur dioxide is shown in Fig. 2 of the text and from this spectrum, the following coupling constants are evaluated: $J_{cd} = 7.0$; $J_{ad} = 11.5$ –12; $J_{CH_3,a} = 6.2$ c.p.s.

Treatment of the isomer, m.p. 70°, with fluoroboric acid, in the same manner as before, afforded a 94% yield of syn-syn-1,5-dimethylpentadienyliron tricarbonyl fluoroborate.

Reaction of syn-syn-1,5-Dimethylpentadienyliron Tricarbonyl Fluoroborate with Water. To 300 ml. of water was added 13.5 g. of syn-syn-1,5-dimethylpentadienyliron tricarbonyl fluoroborate. The reaction mixture was stirred for 20 min. and then extracted with pentane. The pentane extracts were washed with water and dried over magnesium sulfate. One crystallization from pentane afforded trans-trans-3,5-heptadien-2-ol-iron tricarbonyl as yellow needles, m.p. 83–85°. A second crystallization from pentane gave the pure material (8.0 g.), m.p. 85°.

Anal. Calcd. for $C_{10}H_{12}Fe$: C, 47.66; H, 4.80. Found: C, 47.44; H, 4.97.

The infrared spectrum of this complex, m.p. 85°, is almost identical with that of the isomer melting at 70°; the only differences are the appearance of medium absorption bands at 683 and 1000 cm^{-1} in the spectrum of the latter compound which are not present in that of the other isomer.

The n.m.r. spectra of the alcohol complex, m.p. 85°, and of the isomer, m.p. 70°, in carbon tetrachloride exhibit absorptions at 4.84, 6.45, 6.87, 8.4, 8.6, and 9.06 τ with respective areas of 2:1:1:1:6:1.

Acknowledgments.—We wish to thank the National Science Foundation and the Robert A. Welch Foundation for financial support. We also thank Antara Chemicals for a generous gift of iron carbonyl.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS, AUSTIN, TEXAS]

Organo-Iron Complexes. III.^{1,2} Reactions of the syn-1-Methylpentadienyliron Tricarbonyl Cation

By J. E. MAHLER, DOROTHY H. GIBSON, AND R. PETTIT

RECEIVED JUNE 7, 1963

The synthesis and reactions of salts of the syn-1-methylpentadienyliron tricarbonyl cation are discussed. A high degree of selectivity is seen in the reactions of the cation with water, alcohols, and zinc dust; it is not seen, however, in the case of sodium borohydride.

As shown in the previous paper the reaction of 2,4-dien-1-ol-iron tricarbonyl complexes with strong acids affords a convenient synthesis of salts of pentadienyliron tricarbonyl cations. In this paper we report the preparation of salts of the syn-1-methylpentadienyliron tricarbonyl cation (I) utilizing this method and discuss several chemical reactions of these salts. Reactions of the unsymmetrical cation I could, in principle, lead to a larger number of products than would be expected from the symmetrical systems discussed previously, and it is

(1) Part II: J. E. Mahler and R. Pettit, *J. Am. Chem. Soc.*, **85**, 3955 (1963).

(2) A preliminary account of some of this work has been published: J. E. Mahler and R. Pettit, *ibid.*, **84**, 1511 (1962).

of interest to determine the degree of selectivity which might be attained in such reactions.

Results and Discussion

Salts of the syn-1-methylpentadienyliron tricarbonyl cation have been prepared by means of the reactions indicated in the scheme shown at the top of the next page.

trans-trans-2,4-Hexadien-1-ol-iron tricarbonyl (II) is prepared through the reaction of 2,4-hexadienol with iron pentacarbonyl; an alternative route is provided by reduction of 2,4-hexadienaliron tricarbonyl (III) with sodium borohydride. Treatment of the alcohol complex with perchloric acid affords syn- π -1-methylpenta-