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THE SYNTHESIS OF A CATIONIC BINUCLEAR IRON COMPLEX CONTAINING THE η^2 -BUTATRIENE LIGAND AND ITS REACTIONS WITH OXYGEN NUCLEOPHILES

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Summary

The synthesis of the first complex containing the unsubstituted η^2 -butatriene ligand $[\text{Fp}_2(\text{CH}_2=\text{C}=\text{C}=\text{CH}_2)]^{2+}(\text{PF}_6^-)_2$ * (IV) is accomplished in 50% yield by oxidation of $\text{FpCH}_2\text{C}=\text{CCH}_2\text{Fp}$ with trityl hexafluorophosphate. IV reacts with aqueous sodium hydroxide to afford $\text{CH}_2=\text{CFp}-\text{CO}-\text{CH}_3$ (IX) and with aqueous sodium bicarbonate to yield a mixture of IX and $\text{CH}_2=\text{CFpCO}-\text{CH}_2\text{Fp}$ (VIII). The binuclear allene complexes $\text{Fp}^+(\text{CH}_2=\text{C}=\text{CXCH}_2\text{Fp})$ X = OAc, OPh, OPh-*p*-NO₂ are formed by the addition of the respective anions to IV. Ethylation of VIII with triethylxonium hexafluorophosphate gives $\text{CH}_2=\text{CFp}-\text{C}^+(\text{OEt})-\text{CH}_2\text{Fp}$.

The major product resulting from the reaction between IV and methanol is $\eta^3-(\text{CH}_3\text{OCH}_2\text{CFp}=\text{C}(\text{CO}_2\text{Me})=\text{CH}_2)-\eta^5-\text{C}_5\text{H}_5(\text{CO})\text{Fe}$, (XIVa). Methoxide yields $\eta^3-(\text{CH}_2=\text{C}=\text{C}(\text{CO}_2\text{Me})=\text{CH}_2)-(\text{CO})-\eta^5-\text{C}_5\text{H}_5\text{Fe}$ as the major product in addition to smaller yields of XIVa and the isolable *cis* and *trans* isomers (XVI and XVII) of $[\eta^5-\text{C}_5\text{H}_5(\text{CO})-\eta^2-1,2-(\text{CH}_2=\text{CHOMe})\text{Fe}][\text{Fe}(\text{CO})_2-\eta^5-(\text{C}_5\text{H}_5)]$. These isomers equilibrate above 100°C. Ethoxide and isopropoxide give similar results. In contrast, the only characterizable product obtained from the reaction between *t*-butoxide and IV was Fp_2 .

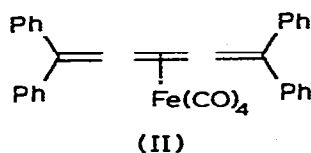
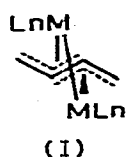
Introduction

The organic and organometallic chemistry of butatriene is little explored. Although butatriene is readily prepared by the debromination of 1,4-dibromo-2-butyne [1] it is an unstable substance which is reported to polymerize explosively at 0°C.

The complexation of butatriene to a transition metal was first reported in

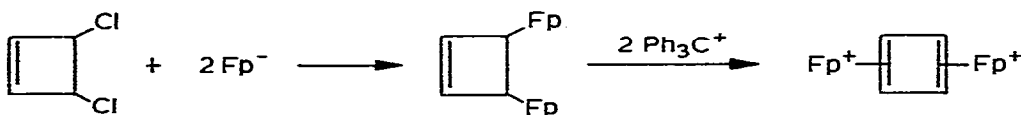
* $\text{Fp} = \eta^5-\text{C}_5\text{H}_5(\text{CO})_2\text{Fe}$

1964 [2]. In this complex as well as most of those butatriene complexes reported subsequently the C_4R_4 moiety functions as a three electron ligand for each metal (I) [3]. Similar binuclear complexes were isolated when the well-behaved tetraalkyl butatrienes were treated with metal carbonyls [2,3]. In at least one instance an intermediate mononuclear complex II was obtained in which the metal group was π -bonded to the center multiple bond [4]. Studies of the transition metal complexes of cumulenes have been extended recently to derivatives of hexapentaene [5].



Several years ago we discovered that complexes of the type $Fe(alkene)^+$, which contain highly reactive unsaturated hydrocarbons (i.e., cyclobutadiene and benzocyclobutadiene) as η^2 -ligands, can be prepared by the oxidation of appropriate neutral binuclear complexes [6,7] (Scheme 1). Our exploration of the gener-

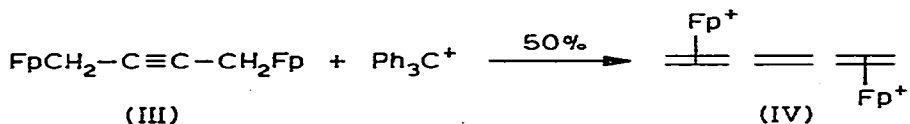
SCHEME 1



ality of this reaction led us to examine the oxidation of the known binuclear complex $FpCH_2C\equiv CCH_2Fp$ (III) [8] with the syntheses of $Fp_2(CH_2=C=C=CH_2)^{2+}$ (IV) and $Fp(CH_2=C=C=CH_2)^{1+}$ (V) as our goal. Herein we report the successful synthesis of IV and its reactions with oxygen nucleophiles.

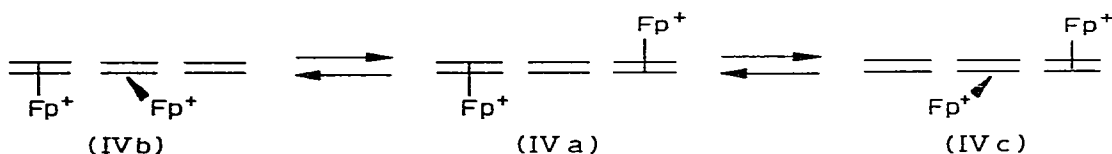
Results and discussion

The binuclear butatriene complex $Fp_2(CH_2=C=C=CH_2)^{2+} (PF_6^-)_2$ (IV) is prepared by oxidizing $FeCH_2C\equiv CCH_2Fp$ (III) with trityl hexafluorophosphate*. IV is generally obtained in 50% yield as a bright yellow powder which is soluble in nitromethane but insoluble in methylene chloride. It is sparingly soluble in acetone and decomposes slowly in this solvent to uncharacterized products. Decomposition is rapid and exothermic in dimethylsulfoxide, pyridine and acetonitrile. IV is stable indefinitely in the atmosphere at 24°C, hence no special precautions are required for its storage and manipulation.



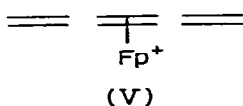
* Part of this work has appeared in preliminary form [9].

Predicated on the spectroscopic properties of IV, it is thought that IV is best depicted as having the static structure IVa in which the Fp^+ groups are π -bonded to the two terminal double bonds of the butatriene ligand rather than the fluxional system involving structures IVa–c. The carbonyl absorptions of IV, which are observed at 2090 and 2065 cm^{-1} , are narrow and symmetrical suggesting that each iron group gives rise to the same symmetric and asymmetric carbonyl stretching frequencies. Complexes such as IVb or IVc would be expected to exhibit four carbonyl absorptions in the IR spectrum since the Fp^+ groups are attached to orthogonal π -orbitals which have different orbital energies [10]. Because the energy of π_2 of the conjugated π -system of butatriene is 9.30 eV, it is a better electron donor than the internal double bond for which the orbital energy is 9.98 eV. Thus, the carbonyl absorptions of the terminal Fp^+ group of IVb and IVc will occur at longer wavelengths than the analogous absorptions of the Fp^+ group bonded to the center double bond.



Either the static or fluxional structure would appear to be consistent with the PMR structure of IV which exhibits sharp singlets at τ 4.04 and 6.10 and a 10 : 4 ratio.

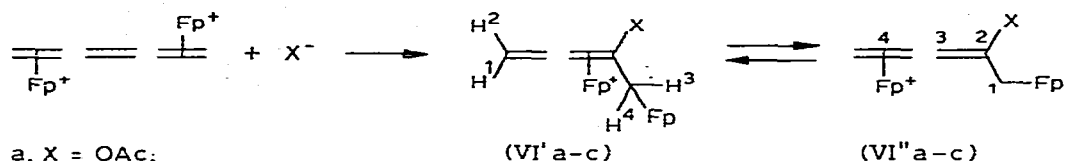
Testing for the existence of fluxionality via low-temperature PMR spectroscopy is not possible since IV is insoluble or decomposes in the appropriate solvents. However, a comparison of the chemical shifts of the methylene protons of IV to those of analogous protons in model compounds lends support to the static structure IVa. The methylene resonances of complexed terminal alkenes in $Fp(\text{alkene})^+$ typically occur in the region τ 6–7. The resonance of the methylene protons of V, which contains the η^2 -2,3-butatriene ligand, occurs as an $AA'BB'$ multiplet centered at τ 3.30 [9]. (The protons of chlorobutatriene [11] also resonate between τ 3 and τ 4. Butatriene [12] exhibits a singlet resonance at τ 4.8.) The methylene protons of the fluxional system would exhibit a chemical shift that would be the average of the chemical shifts of the methylene protons of coordinated and uncoordinated double bonds. Since an average chemical shift of ca. τ 5 seems reasonable for the fluxional structure, the observed value of τ 6.10 is more in accord with the static structure IV.



Reactions between IV and acetate and phenoxides

Acetate, phenoxide and *p*-nitrophenoxide add rapidly to an internal carbon of the butatriene ligand of IV affording the allene complexes VI in moderate yields as lustrous yellow crystalline solids. The IR spectra of VI, which exhibit terminal carbonyl absorptions at 2060, 2020 and 1970 cm^{-1} , support the pre-

sence of Fp^+ and Fp^0 groups in each structure. A band of weak to moderate intensity is observed near 1800 cm^{-1} and is assigned to the allene stretch of the butadienyl ligand. Absorptions observed near 1800 cm^{-1} in the IR spectra of $\text{Fp}(\text{CH}_2=\text{C}=\text{CHMe})^+$ and $\text{Fp}(\text{CH}_2=\text{C}=\text{CHPh})^+$ have been assigned similarly [13].



- a. $\text{X} = \text{OAc}$;
- b. $\text{X} = \text{OPh}$;
- c. $\text{X} = \text{OPh-}p\text{-NO}_2$;
- d. $\text{X} = \text{SPh}$;
- e. $\text{X} = \text{P}(\text{OEt})_3^+$

In solution the adducts VIa, VIb and VIc appear to be mixtures of the rapidly interconverting positional isomers VI' and VI'', of which VI' is thought to be the predominant member of the equilibrium. Thus, the PMR spectra of VI cannot be interpreted in terms of structure VI' alone because both sets of methylene protons give rise to narrow symmetrical triplets ($J = 1.5\text{ Hz}$) * indicating the equivalence on the NMR time scale of the protons in each set. In VI', the *endo* and *exo* protons (H^1 and H^2) and the diastereomeric protons H^3 and H^4 would be spectroscopically distinguishable; hence, a more complex pattern would be expected. These spectroscopic data would appear to be consistent with structure VI'' which possesses a plane of symmetry in one accessible conformation. However, the chemical shift of the vinyl methylene protons of VI argues against VI'' as being the more stable structure. The methylene resonance of methoxypropadiene is observed at τ 4.60 [16]. Significantly, this is similar to the vinyl methylene resonance (τ 4.92–5.03) of VI. If VI'' were the stable form of VI then by analogy to the spectra of the allene complexes reported by Rosenblum [14] the vinyl protons of the allene ligands in VI would be observed in the region between τ 6.8 to 7.0. These disparate spectroscopic properties are reconciled by a dynamic system in which VI', the predominant component, is in rapid equilibrium with a small amount of VI''.

The preference of the Fp^+ group for the internal double bond of VI rather than the terminal double bond as in the case for alkyl substituted allenes, is not unexpected because of the greater electron density associated with the internal π -bond which is conjugated with the $-\text{OR}$ and $-\text{CH}_2\text{Fp}$ groups. Apparently this electronic effect dominates the steric factors that generally favor complexation of the less substituted double bond of substituted allenes [14]. Substitution of poorer electron donor groups for the OR groups in VIa–VIc would be expected then to shift the equilibrium toward VI''. This shift in equilibrium would be reflected in an upfield shift of the resonance of the vinylic methylene protons in the PMR spectra. This is exactly what is observed for VI d and e. The PMR spectrum of VI d is in all respects similar to those of VIa–VIc except that vinylic methylene proton resonance is shifted upfield to τ 5.75 [17]. The change is even more dramatic in the triethoxyphosphonium derivative VI e [17]. In this substance

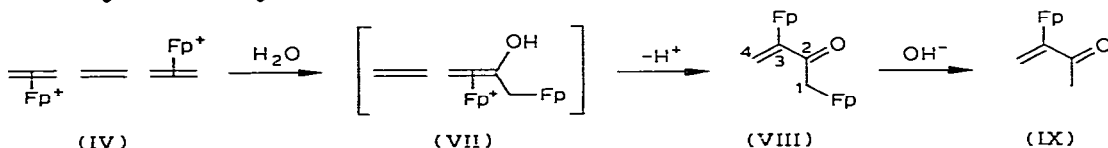
* This small coupling is typical of $\text{Fp}(\text{allene})$ complexes [14,15].

the phosphonium group strongly destabilizes VI' because of the positive charge and size of the phosphorous moiety. Hence the concentration of VI' is reduced and the vinylic methylene proton resonance is observed still further upfield at τ 6.20*.

The phenoxide adducts VIb and VIc exhibit the remarkable stability that appears to be associated with Fp(allene)⁺ complexes in general [14,15]. In contrast, the acetate complex VIa is unusually labile and is demetalated in acetone within minutes at 24°C.

Reactions of IV with water

The reaction between IV and aqueous sodium bicarbonate gives a mixture of the bi- and mononuclear ketones VIII and IX respectively. Aqueous sodium hydroxide affords only the mononuclear ketone IX. It is quite likely that both of these reactions yield initially the binuclear dienol complex VII and subsequently VIII. The binuclear ketone VIII is unstable toward base and is readily demetalated by sodium hydroxide to IX.

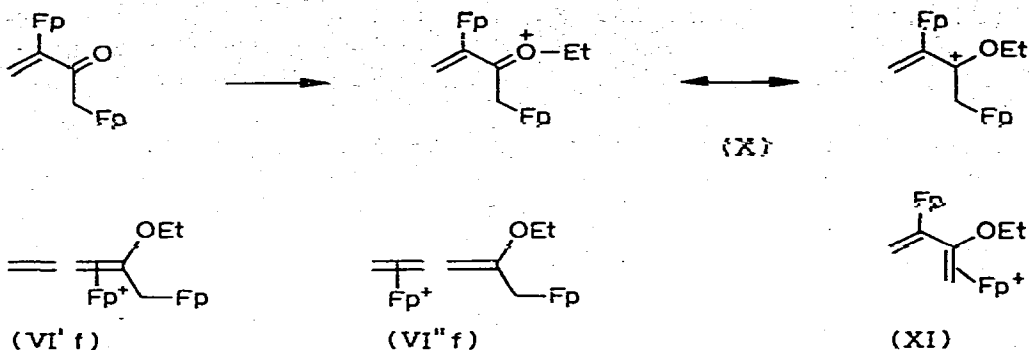


The ketones, VIII and IX, are very similar spectroscopically. Thus, in the PMR spectra of these substances the vinylic methylene protons give rise to two one-proton singlets at τ 3.85, 4.43 and τ 3.85, 4.25, respectively. The respective C(1) methylene protons resonances of VIII and IX are observed at 8.04 and 7.80. Although VIII contains two different Fp groups only one η -cyclopentadienyl resonance (τ 5.19) is observed in carbon disulfide. In benzene-*d*₆ the degeneracy of the cyclopentadienyl groups is removed and they are observed as a pair of singlets at τ 5.60 and 5.62.

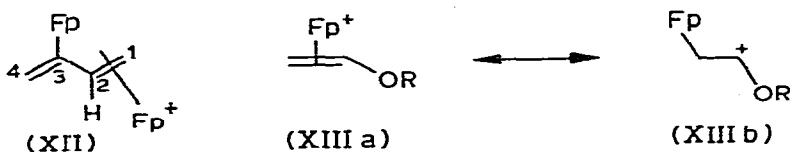
The similarity of the chemical shifts of the cyclopentadienyl groups of VIII suggest that the iron atoms possess similar electron density. Indeed, this contention is supported by the observation of only one set of terminal carbonyl absorptions (2016, 1967 cm⁻¹) for VIII. The ketonic carbonyl absorption of IX is observed at 1945 cm⁻¹ — a value 20 cm⁻¹ lower than carbonyl absorptions considered typical of vinyl ketones [18]. Since the attachment of an Fp group to the α carbon of a ketone lowers the frequency of the carbonyl absorption by 60 cm⁻¹ [20], the iron group of IX is probably only interacting weakly with the ketonic carbonyl. The second Fp group in VIII interacts significantly with the ketonic carbonyl group as evidenced by the shift of this absorption to 1590 cm⁻¹.

Since the allene complex VI_f (X = OEt) could not be prepared by addition of ethanol or ethoxide to the butatriene complex IV (vide infra), an attempt was made to synthesize VI_f via ethylation of the binuclear ketone VIII by triethyl-oxonium hexafluorophosphate. Although VIII is rapidly ethylated at the ketonic oxygen the spectroscopic properties of the resulting product X clearly demonstrate that this substance differs structurally from the allene complexes VI.

* An in-depth study of the stereochemistry of VI and related compounds is in progress.



Firstly, in the PMR spectrum of X the vinyl methylene protons give rise to two one-proton singlets at τ 3.98 and 4.38. The nonequivalence of these protons is in contrast to the analogous C(4) protons of VI which are equivalent on the NMR time scale and weakly coupled to the C(1) methylene group of the butadienyl ligand. Secondly, X does not exhibit an absorption near 1800 cm^{-1} in the IR spectrum. This absorption appears to be characteristic of $\text{Fp}(\text{allene})^+$ complexes [13]. Thirdly, the similar and relatively high field chemical shifts (4.73 and 4.90) of the two Fp groups of X indicate that each bears similar and small portions of the total positive charge. Fourthly, the saturated methylene protons are observed as a two-proton singlet resonance at τ 7.52. The equivalence of these protons eliminates the 1,3-butadiene complex XI as a possible structure since in XI there would be restricted rotation about the C(1)–C(2) bond and the C(1) methylene protons would be nonequivalent. In the butadiene complex XII the C(1) methylene protons are observed as a pair of doublets at τ 6.01 and 6.80. This is typical of terminal alkene complexes of Fp^+ [19]. In Fp^+ complexes (XIII) containing enol ethers as η^2 -ligands, there is restricted rotation about the coordinated π -bond [20], even though canonical form XIIIb is apparently an important contributor to the structure of XIII.



These spectroscopic data are consistent with structure X. Why this substance assumes this structure rather than the allene (VI'f) or butadiene (XI) structures is an open question.

The mononuclear ketone IX failed to react under conditions used successfully to ethylate VIII.

Reactions of IV with alcohols

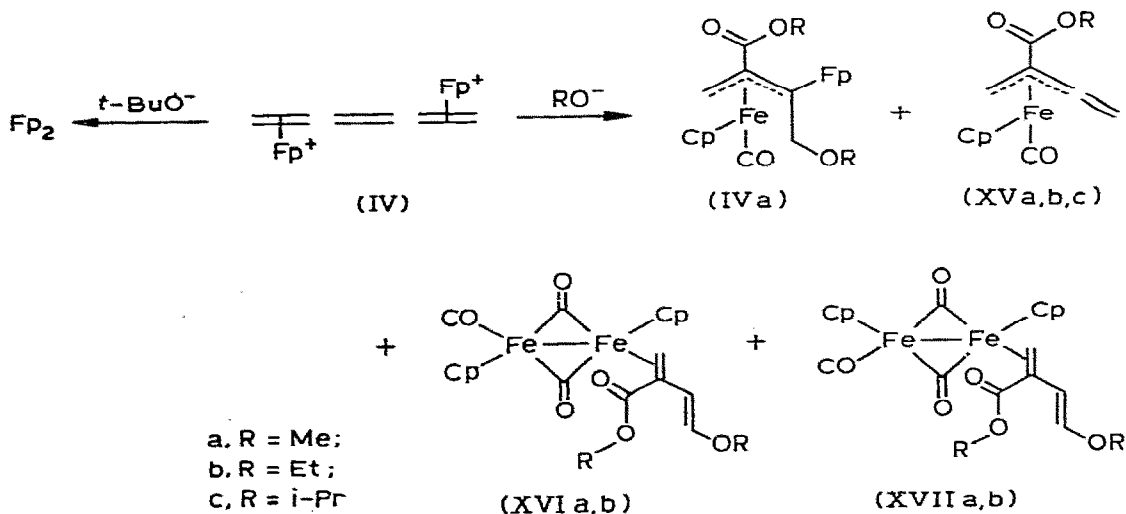
The butatriene complex IV reacts sluggishly with a mixture of sodium bicarbonate and methanol and hardly at all with similar mixtures of ethanol, isopropanol or t-butanol. The only isolated product (49%) obtained from the methanol reaction is the binuclear complex XIVa. The structure of XIVa was

established by an analysis of its PMR and IR spectra. Three terminal carbonyl absorptions were observed in the IR spectrum of XIVa. The high frequency pair (2000, 1951 cm^{-1}) are typical of Fp alkyl compounds and the low frequency absorption (1933 cm^{-1}) is comparable to those observed for other η^3 -allyl cyclopentadienylcarbonyliron compounds [19]. An ester carbonyl absorption is observed also at 1685 cm^{-1} .

The presence of a dicarbonyliron and a monocarbonyliron group is supported also by the presence of cyclopentadienyl resonances at τ 5.36 and 5.55 — chemical shifts that are characteristic of these iron groups [19] — in the PMR spectrum of XIV. The MeOCH_2 resonance is an AB multiplet and thereby supports the chirality of the monocarbonyl iron group. The chemical shift τ 6.01 of this methylene resonance is consonant with a methoxymethylene rather than the Fp-methylene linkage. In carbon disulfide the two methoxy resonances are degenerate. However, in benzene- d_6 this degeneracy is removed.

The addition of alkoxides to IV is rapid and leads to novel products, the distribution and nature of which are dependent on the alkoxide employed. Methoxide gives the mononuclear η^3 -allyl complex XVa in 85% yield in addition to a small amount of XIVa and two other products. The IR spectrum of XVa exhibits the expected single terminal carbonyl absorption at 1975 cm^{-1} and an ester carbonyl absorption at 1700 cm^{-1} . In addition, a relatively weak absorption at 1760 cm^{-1} is assigned to a stretching vibration of the cumulated portion of the butadienyl ligand*.

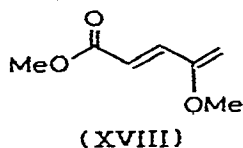
On the basis of their spectroscopic and thermal properties, the last two major products, A and B, from this reaction are assigned the isomeric structures XVI



and XVII although a definite assignment is not possible with the data in hand. The IR spectra of A and B are similar in that each exhibits single terminal, bridging, and ester carbonyl absorptions in the region between 2000 cm^{-1} and 1690

* At least two other complexes containing the butadienyl or related ligands have been reported in the past several years, [5,21].

cm^{-1} . The PMR spectra of A and B are also similar and differ only a small changes of the chemical shifts of the analogous protons. Of particular significance are the high field resonances (7.64, 11.07 and 7.68, 11.57) of the methylene protons of the complexes portion of the butadiene ligand. These chemical shifts agree well with those reported for other neutral iron-butadiene complexes [22]. In contrast the chemical shifts (4.05, 4.90 $J = 18$ Hz; 4.11, 5.01 $J = 16$ Hz) and large coupling constants of the remaining olefinic protons indicate the presence of an uncoordinated double bond containing vicinal *trans* protons. Unfortunately the data in hand are not sufficient to exclude structures containing the isomeric butadiene ligand XVIII in which the positions of the carbomethoxy and methoxy groups are interchanged.



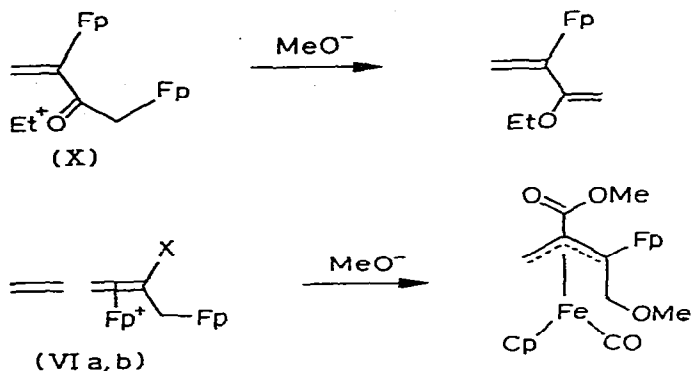
To our knowledge XVI and XVII are the first examples of isolable *cis* and *trans* isomers of this type of compound. The isomers equilibrate at elevated temperatures. In *o*-dichlorobenzene the equilibrium actually favors B ($K_{\text{eq}}(\text{B/A}, 144^\circ\text{C}) = 4$) which is the lesser product from the reaction between IV and methoxide. Attempts to equilibrate A and B in a mixture of methoxide in methanol led to decomposition. A full structural and kinetic study of these substances is underway.

Ethoxide in ethanol gave results similar to the methoxide experiment. Isopropoxide, however, afforded only the mononuclear 1,2-butadienyl complex XIVc. Only Fp_2 was isolated from the reaction between IV and *t*-butoxide.

Several reaction mechanism can be envisaged which account for the formation of the mono- and binuclear alkoxide adducts*. Predicated on the facile formation of the binuclear allene complexes (VIa—C) by the addition of acetate or phenoxide to IV, it appeared possible that alcohols or alkoxides added initially at an internal carbon of the butatriene ligand of IV. Further reaction with the alcohol or alkoxide then afforded the observed products. In apparent support of this hypothesis is the fact that treatment of the acetate or phenoxide adducts (VIa,b respectively) with sodium methoxide does afford the binuclear complex XVa in moderate to good yield. However none of the mononuclear XVa or binuclear complexes (XVI and XVII) were observed. Significantly only demetalation of the ethoxy complex X to $\text{CH}_2=\text{CFpC}(\text{OEt})=\text{CH}_2$ was observed. Hence, the ethoxy adduct (X) and presumably its methoxy analog cannot be intermediates in the formation of XIV—XVII. (This holds true unless the rearrangement of an intermediate alkoxy allene complex (VIc to X) is slow compared to further intermolecular reaction.)

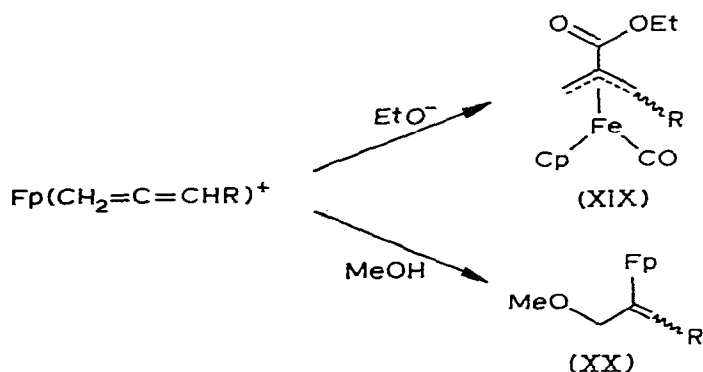
The change in the nature and distribution of the products when alkoxide is substituted for alcohol in the reactions of $\text{Fp}(\text{cumulene})^+$ complexes finds precedent in Wojcicki's [14] and Rosenblum's [15] experiments with $\text{Fp}(\text{allene})^+$ com-

* All the products XIV—XVII are stable under the reaction conditions; hence none of these four compounds is the progenitor of the others.



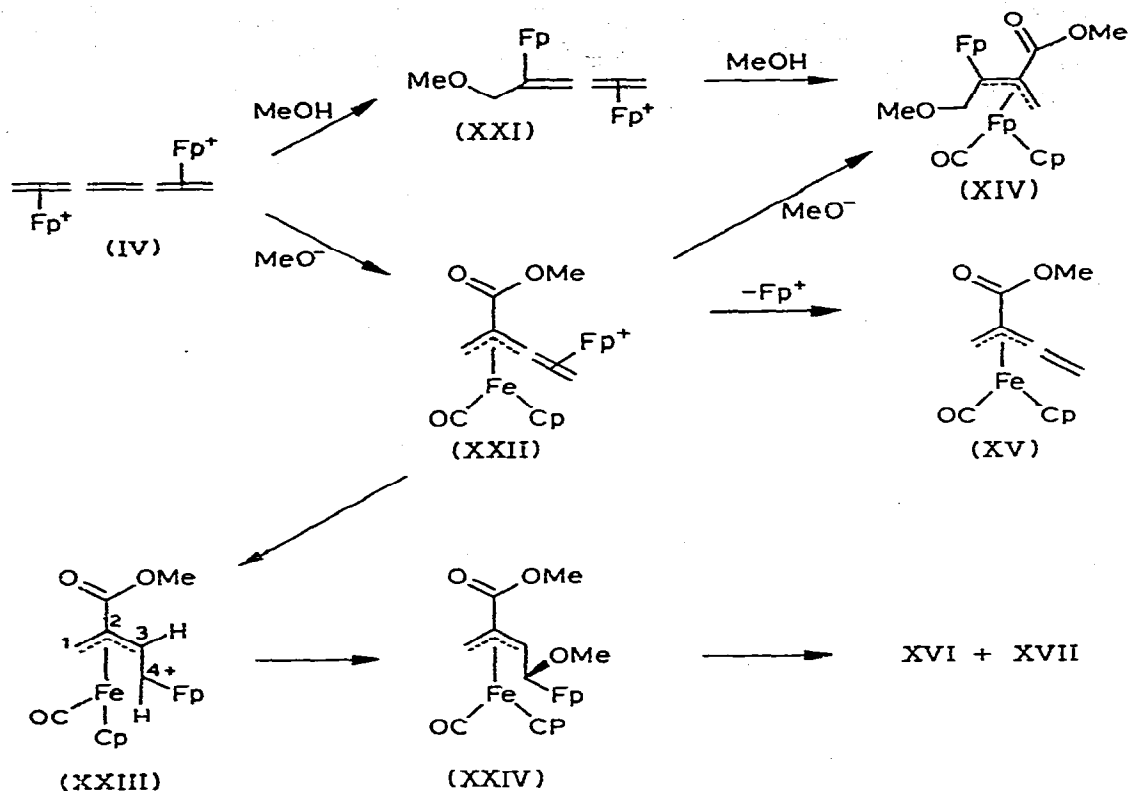
plexes. Wojcicki found that the addition of alkoxide to $\text{Fp}(\text{allene})^+$ afforded the 2-carboalkoxy- η^3 -allyl complex XIX, whereas Rosenblum observed that the methoxy vinyl complex XX results when $\text{Fp}(\text{allene})^+$ was treated with a mixture of sodium bicarbonate and methanol. Similar modes of addition of methoxide and methanol account for the different products obtained when IV is treated with these reagents.

Thus, methanol adds to a terminal carbon of the butatriene ligand of IV yielding the binuclear allene complex XXI*. Addition of a second methanol to a ligating carbonyl of the cationic Fp group gives the observed product XIVa. In contrast methoxide is believed to add directly to a ligating carbon monoxide of IV. The Fp^+ group of the resulting adduct XXII is apparently labile. This is supported by the fact that attempts to prepare XXII by treatment of XIV with acid or by the metalation of XV with $\text{Fp}(\text{isobutylene})^+\text{PF}_6^-$ have been futile. Hence, XXII readily sheds Fp^+ to form the major product XV. Addition of methoxide to C(4) of the butadienyl ligand of XXII accounts for the formation of the small amounts of XIV. Apparently XXII can also rearrange via a hydride shift to XXIII**. The resulting carbonium ion XXIII is stabilized by both the Fp group



* Nucleophilic addition to the terminal carbon has been observed for other nucleophiles such as diethylamine and hydride [17].

** Hydride shifts in these iron complexes finds precedent in formation of $(\text{FpCH}=\text{CH}-\text{CMe}=\text{CH}_2)\text{Fp}^+$ by the methylation of $\text{FpCH}_2\text{C}=\text{CCH}_2\text{Fp}$ with MeOSO_2F [23].



and the adjacent η^3 -allyl system. Addition of methoxide to C(4) of XXIII followed by reorganization of the iron groups leads to the isomers XVI and XVII.

Experimental

General procedures

In general, all reactions were carried out under a nitrogen atmosphere. Iron analyses were performed according to standard procedures.

Physical measurement

Infrared spectra were recorded on a Perkin-Elmer Model 180 spectrophotometer. PMR spectra were obtained on a JEOL C-60 High Resolution spectrometer using tetramethylsilane as an internal standard. Melting points are uncorrected.

Materials

1,4-Dichloro-2-butyne (Aldrich), sodium hydroxide, sodium bicarbonate, sodium acetate (Baker), and lithium phenoxide (Alfa) were used as purchased. Tetrahydrofuran was distilled from lithium aluminum hydride before use. Alu-

mina (Alfa) was baked (250°C) for 4 h and deactivated before use. All other solvents were reagent grade and were used without further purification.

The oxidation of 1,4-bis(η^5 -cyclopentadienyldicarbonyliron)-2-butyne by triphenylcarbenium hexafluorophosphate

Triphenylcarbenium hexafluorophosphate (0.97 g, 2.5 mmol) was added to a solution of 1,4-bis(η^5 -cyclopentadienyldicarbonyliron)-2-butyne [8,20] (0.40 g, 1 mmol) (III) in 10 ml of methylene chloride. The mixture was stirred 1 h, then filtered to yield a brown sludge. This material was extracted with nitromethane. The addition of diethyl ether to the extract precipitated IV as a bright yellow powder (0.35 g, 50% yield): IR (KBr) 2090, 2065 cm^{-1} ($\text{C}\equiv\text{O}$); PMR (CD_3NO_2) τ 4.04 (s, 10, Cp), 6.10 (s, 4, CH_2). (Found: C, 30.84, H, 2.04. $\text{C}_{18}\text{H}_{14}\text{F}_{12}\text{Fe}_2\text{O}_4\text{F}_2$ calcd.: C, 31.03, H, 2.01%.)

The reaction of IV with sodium acetate in acetic acid

To a solution of 2 g of sodium acetate in 15 ml of acetic acid was added a solution of 10.21 g of IV in 150 ml of nitromethane. The mixture was stirred for 1 min and then diethyl ether was added to precipitate unreacted IV. The mixture was filtered and 3.094 g of IV was recovered. More diethyl ether was added to the filtrate to precipitate a golden yellow salt. Filtration afforded 5.16 g of VIa (72% yield based on unrecovered IV): IR (KBr) 2061, 2015, 1968 ($\text{C}\equiv\text{O}$), 1804 ($\text{C}=\text{C}=\text{C}$), 1725 cm^{-1} ($\text{C}=\text{O}$): PMR (CD_3NO_2) τ 4.42 (s, 5, Cp), 4.84 (s, 5, Cp), 5.04 (br, s, 2, CH_2), 7.70 (br, s, 2, CH_2), 7.78 (s, 3, CH_3). (Found: Fe, 17.89. $\text{C}_{20}\text{H}_{17}\text{F}_6\text{Fe}_2\text{O}_6\text{P}$ calcd.: Fe, 18.36%.)

The reaction between IV and lithium phenoxide

Lithium phenoxide (0.184 g, 1.84 mmol) was dissolved in 2 ml of acetone. To this was added IV (0.47 g, 0.7 mmol) dissolved in 10 ml of nitromethane. Diethyl ether was added slowly to precipitate 0.08 g of unreacted IV. The solution was filtered and more diethyl ether was added to precipitate VIb as a lustrous golden salt (0.095 g, 28% yield): IR (KBr) 2060, 2021, 1972 ($\text{C}\equiv\text{O}$), 1803 ($\text{C}=\text{C}=\text{C}$) cm^{-1} ; PMR (CD_3NO_2) τ 2.5–3.0 (m, 5, Ar), 4.45 (s, 5, Cp), 4.79 (s, 5, Cp), 5.06 (t, 2, CH_2 , $J = 2$ Hz), 7.69 (t, 2, CH_2Fp). (Found: Fe, 17.34. $\text{C}_{24}\text{H}_{19}\text{F}_6\text{Fe}_2\text{O}_5\text{P}$ calcd.: Fe, 17.39%.)

A similar reaction using sodium *p*-nitrophenoxide afforded VIc in 47% yield: IR KBr) 1060, 2020, 1972 ($\text{C}\equiv\text{O}$), 1802 cm^{-1} ($\text{C}=\text{C}=\text{C}$); PMR (CD_3NO_2) τ 1.70 (d, 2, Ar), 2.70 (d, 2, Ar), 4.43 (s, 5, Cp), 4.88 (s, 5, Cp), 4.92 (t, 2, CH_2 , $J = 1.5$ Hz), 7.62 (t, 2, CH_2Fp). (Found: Fe, 16.50. $\text{C}_{24}\text{H}_{18}\text{F}_6\text{Fe}_2\text{NO}_7\text{P}$ calcd.: Fe, 16.26 16.26%.)

The reaction between IV and methanolic sodium bicarbonate

Methanol (30 ml), IV (3.0 g, 4.2 mmol) and sodium bicarbonate (0.5 g) were placed in a 50 ml Erlenmeyer flask and stirred for 3 days. The solvent was removed by rotary evaporation. The residue was extracted with methylene

chloride and chromatographed on neutral activity III alumina (4 × 40 cm). Elution with 1 : 1 methylene chloride and petroleum ether afforded, after evaporation of the solvents, η^5 -cyclopentadienyldicarbonyliron dimer and the binuclear complex XIV (0.94 g, 49%). IR (neat) 2000, 1951, 1933 cm^{-1} (C≡O), 1685 cm^{-1} (C=O); PMR (CS_2) τ 5.36 (s, 5, Cp), 5.55 (s, 5, Cp), 6.01 (d of d, 2, CH_2 , AB, $J = 10$ Hz), 6.58 (s, 6, CH_3), 7.75 (d, 1, H, $J = 3.0$ Hz), 8.27 (d, 1, H, $J = 3.0$ Hz). Complex XIV could not be crystallized; hence an analytically pure sample of this substance was not obtained.

The reaction of IV with methanolic sodium methoxide

To a solution of sodium methoxide in methanol (generated by the careful addition of 0.1 g of sodium to 40 ml of methanol) was added IV (10.5 g, 15.1 mmol). The mixture was stirred 10 min and the solvent was removed by rotary evaporation. The residue was extracted with methylene chloride and filtered through Celite. The filtrate was concentrated by rotary evaporation and chromatographed on neutral activity III alumina (2 × 100 cm). Elution with 1 : 1 methylene chloride and petroleum ether afforded four bands. The first band consisted of η^5 -cyclopentadienyldicarbonyliron dimer. The second band was 1,2,3- η^3 -(2-carbomethoxy-1,3-butadien-3-yl)- η^5 -cyclopentadienylcarbonyliron (XVa) as a brown solid (3.26 g, 84%), m.p.: 57–58°C, IR (KBr) 1975 cm^{-1} (C≡O), 1700 cm^{-1} (C=O), 1760 cm^{-1} (C=C); PMR (CS_2) τ 4.01 (d, 1, H, $J = 3$ Hz), 4.70 (d, 1, H, $J = 3$ Hz), 5.43 (s, 5, Cp), 6.28 (s, 3, CH_3), 6.60 (br, s, 1, H), 8.94 (br, s, 1, H). (Found: Fe, 21.28. $\text{C}_{12}\text{H}_{12}\text{FeO}_3$ calcd.: Fe, 21.54%.)

The third band crystallized as dark greenish-yellow plates A (0.95 g, 9%). IR (hexachlorobutadiene) 1929, 1973, 1732, 1705 cm^{-1} ; PMR (CS_2) τ 4.05 (d, 1, H, $J = 18$ Hz), 4.90 (d, 1, H), 5.66 (s, 5, Cp), 5.68 (s, 5, Cp), 6.23 (s, 3, CH_3), 6.39 (s, 3, CH_3), 7.46 (d, 1, H, $J = 3.0$ Hz), 11.07 (d, 1, H). (Found: Fe, 23.73. $\text{C}_{20}\text{H}_{20}\text{Fe}_2\text{O}_6$ calcd.: Fe, 23.86%.)

The fourth band contained approximately equal amounts of XIVa and B (0.39 g, 6% total yield). An analytical sample of B could be obtained by rechromatographing carefully on activity III alumina. M.p.: 158–159°C IR (hexachlorobutadiene) 1931, 1777, 1718, 1696 cm^{-1} ; PMR (CS_2) τ 4.11 (d, 1, H, $J = 16$ Hz), 5.01 (d, 1, H), 5.28 (s, 5, Cp), 5.62 (s, 5, Cp), 6.32 (s, 3, CH_3), 6.38 (s, 3, CH_3), 7.63 (d, 1, H, $J = 3.0$ Hz), 11.57 (d, 1, H). (Found: Fe, 23.81. $\text{C}_{20}\text{H}_{20}\text{Fe}_2\text{O}_6$ calcd.: Fe, 23.86%.)

The reaction of IV with ethanolic sodium ethoxide

To a solution of sodium ethoxide (made by the addition of 0.1 g of sodium to 20 ml of ethanol) was added IV (2.2 g, 3.1 mmol). The mixture was stirred 3 h. Methylene chloride was added and the mixture was filtered through Celite. The filtrate was concentrated by rotary evaporation and chromatographed on neutral activity III alumina. Elution with 1 : 1 methylene chloride and petroleum ether afforded 1,2,3- η^3 -(2-carboethoxy-1,3-butadienyl)- η^5 -cyclopentadienylcarbonyliron, XVb (0.47 g, 56%): IR (KBr) 1960 cm^{-1} (C≡O), 1700 cm^{-1} (C=O); PMR (CS_2) τ 4.16 (d, 1, H, $J = 3$ Hz), 4.82 (d, 1, H), 5.52 (q, 2, OCH_2 , $J = 7.5$ Hz), 6.68 (br, s, 1, H), 8.76 (t, 3, CH_3 , $J = 7.5$ Hz), 8.97 (br, s, 1, H). (Found: Fe, 20.14. $\text{C}_{13}\text{H}_{14}\text{FeO}_3$ calcd.: Fe, 20.44%.)

The PMR spectrum of the reaction mixture also exhibited absorption for the ethyl homologs of the A and B isomers. Yields for these compounds are estimated to be 10% and 3% respectively.

The reaction of IV with sodium isopropoxide in isopropanol

To a solution of sodium isopropoxide in isopropanol (made by the addition of 0.1 g of sodium to 20 ml of isopropanol) was added IV (2 g, 2.9 mmol). The mixture was stirred 0.5 h, filtered through Celite, and the solvent removed. The residue was extracted with methylene chloride and chromatographed on neutral activity III alumina (4 × 30 cm). Elution with 1 : 1 methylene chloride and petroleum ether afforded after rotary evaporation of the solvent, 1,2,3- η^3 -(2-carboisopropoxy-1,3-butadienyl)- η^5 -cyclopentadienylcarbonyliron XVc (0.345 g, 42%). This substance was characterized by its spectroscopic properties only. IR (KBr) 1960 cm^{-1} (C \equiv O) 1700 cm^{-1} (C=O); PMR (CS₂) τ 4.18 (d, 1, H, J = 3.0 Hz), 4.85 (d, 1, H), 5.05–5.30 (m, 1, H, J = 6Hz), 5.54 (s, 5, Cp), 6.70 (br, s, 1, H), 8.78 (d, 6, CH₃), 9.00 (br, s, 1, H).

The reaction between IV and sodium t-butoxide in t-butanol

IV (2.0 g, 9 mmol) was added to a solution of sodium t-butoxide in t-butanol. The mixture was stirred 30 min and the solvent was removed by rotary evaporation. The residue was extracted with methylene chloride, filtered through Celite and concentrated to about 4 ml. This was chromatographed on activity III alumina (4 × 30 cm) eluting with a 1 : 1 mixture of methylene chloride and petroleum ether. The first red band was identified by its PMR spectrum as η^5 -cyclopentadienyldicarbonyliron dimer (0.64 g, 50%). A second band was collected (0.06 g), but could not be characterized.

The attempted reaction of XIVa with methoxide

To a solution of sodium methoxide in methanol (10 ml) was added IX (0.3 g) dissolved in 10 ml of methylene chloride. The mixture was stirred 2 h, then was filtered through neutral activity III alumina (2 × 4 cm). The solvent was removed by rotary evaporation to yield 0.27 g of XIVa (90% recovery).

The attempted reaction of isomer A with sodium methoxide in methanol

To a solution of sodium methoxide in methanol was added 0.0746 g of A. This mixture was stirred 1 h, heated briefly to reflux and filtered through 1 cm of activity III alumina. The solvent was removed by rotary evaporation and the residue extracted with methylene chloride. The extract was filtered through 1 cm of alumina and the solvent removed to afford 0.0562 g (87%) of A unchanged.

The attempted reaction of isomer B with sodium methoxide in methanol

A solution of B (4.6 mg) in 5 ml of methanolic sodium methoxide was stirred 20 min and heated briefly to reflux. The mixture was then filtered through activ-

ity III alumina and the solvent removed. The residue was extracted with methylene chloride and filtered through 1 cm of alumina again. Removal of the solvent afforded 3.5 mg (80%) of B. PMR spectroscopy showed no other characterizable products in the material recovered.

The reaction between IV and aqueous sodium bicarbonate

Saturated aqueous sodium bicarbonate (3 ml) was added to a suspension of IV (1.0 g, 1.4 mmol) in 20 ml of methylene chloride. The mixture was stirred 3 days, then dried with anhydrous magnesium sulfate and filtered. The filtrate was concentrated by rotary evaporation and chromatographed on activity III alumina (2 × 30 cm). Elution with 1 : 1 methylene chloride and petroleum ether afforded, after evaporation of the solvent, η^5 -cyclopentadienyldicarbonyliron dimer IX, (55 mg, 15%) and 1,3-bis(η^5 -cyclopentadienyldicarbonyliron)-but-3-en-2-one (VIII) (177 mg, 30%): IR (KBr) 2016, 1967 cm^{-1} ($\text{C}\equiv\text{O}$), 1590 cm^{-1} ($\text{C}=\text{O}$); PMR (CS_2) τ 3.85 (br, s, 1, H), 4.43 (br, s, 1, H), 5.19 (s, 10, Cp), 8.04 (br, s, 2, CH_2Fp). (C_6D_6) τ 3.54 (s, 1, H), 4.18 (s, 1, H), 5.60 (s, 5, Cp), 5.62 (s, 5, Cp), 7.68 (s, 2, CH_2Fp). (Found: Fe, 25.99. $\text{C}_{18}\text{H}_{14}\text{Fe}_2\text{O}_5$ calcd.: Fe, 26.47%.)

The reaction between IV and aqueous sodium hydroxide

To a suspension of III (2.02 g, 2.8 mmol) in 20 ml of methylene chloride was added 10 ml of saturated aqueous sodium hydroxide. The mixture was stirred 14 h, dried with anhydrous magnesium sulfate and filtered. The filtrate was concentrated by rotary evaporation and chromatographed on neutral activity III alumina (2 × 30 cm). Elution with 1 : 1 methylene chloride and petroleum ether afforded, after evaporation of the solvent, η^5 -cyclopentadienyldicarbonyliron dimer (0.248 g, 24% based on IV) and an oil, 3-(η^5 -cyclopentadienyldicarbonyliron)-but-3-en-2-one (IX) (0.160 g, 21%): IR (neat) 2008, 1960 cm^{-1} ($\text{C}\equiv\text{O}$), 1654 cm^{-1} ($\text{C}=\text{O}$); PMR (CS_2) τ 3.83 (s, 1, H), 4.25 (s, 1, H), 5.10 (s, 5, Cp), 7.80 (s, 3, CH_3). (Found: Fe, 22.67. $\text{C}_{11}\text{H}_{10}\text{FeO}_3$ calcd.: Fe, 22.70%.)

The reaction of VIII with aqueous sodium hydroxide

To a solution of VIII (0.0523 g, 0.124 mmol) in 20 ml of methylene chloride was added 3 ml of saturated aqueous sodium hydroxide. The mixture was stirred 25 h, then dried with anhydrous magnesium sulfate. Removal of the solvent afforded 0.0395 g of material which was shown by PMR spectroscopy to be a 1 : 1 mixture of VIII and IX.

The reaction of VIII with triethyloxonium hexafluorophosphate

VIII (0.24 g, 0.6 mmol) was dissolved in 10 ml of methylene chloride and triethyloxonium hexafluorophosphate (0.134 g, 0.55 mmol) was added. This mixture was stirred for 20 min and diethyl ether was added to precipitate X as a golden salt (0.26 g, 80%): IR (KBr) 2040, 1960 cm^{-1} ($\text{C}\equiv\text{O}$), 1320 cm^{-1} ($\text{C}-\text{O}$); PMR (CD_3NO_2) τ 3.98 (s, 1, CH), 4.38 (s, 1, CH), 4.73 (s, 5, Cp), 4.90 (s, 5, Cp), 5.89 (q, 2, CH_2CH_3 , $J = 7$ Hz), 7.52 (s, 2, CH_2Fp), 8.56 (t, 3, CH_3). (Found: Fe, 18.64. $\text{C}_{20}\text{H}_{19}\text{F}_6\text{Fe}_2\text{O}_5\text{P}$ calcd.: Fe, 18.79%.)

The reaction between VIa and sodium methoxide in methanol

To a solution of sodium methoxide in methanol was added VIa (0.4185 g 0.69 mmol). The solution was stirred 1 min. Methylene chloride (30 ml) was added and the mixture was filtered through Celite. The solvent was removed by rotary evaporation. A methylene chloride extract of the residue was filtered through 1 cm of activity III alumina and the solvent removed to yield XIVA (0.2334 g, 73% yield).

The reaction between VIb and sodium methoxide in methanol

To a solution of sodium methoxide in methanol (20 ml) was added VIb (0.0592 g, 0.092 mmol). The solution was stirred 1 min and then filtered through Celite. The filtrate was evaporated. The residue was extracted with methylene chloride and filtered through 1 cm of alumina. Evaporation of the solvent afforded IX (0.0406 g, 96%). The same reaction between VIb and methanolic sodium bicarbonate afforded XIVA in 64% yield.

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