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THE PREPARATION AND PROPERTIES OF DICARBONYL-h^5-CYCLOPENTADIENYLIRON h^2-VINYL ETHER AND h^2-KETENE ACETAL COMPLEXES

A. CUTLER, S. RAGHU and M. ROSENBLUM*
Department of Chemistry, Brandeis University, Waltham, Ma. 02154 (U.S.A.)

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Summary

Metallation of β-haloacetals with sodium dicarbonyl-h^5-cyclopentadienylferrate (Fp^-) provides a convenient point of departure for the synthesis of aldehyde—iron complexes (FpCHRCHO) and of h^2-vinyl alcohol and vinyl ether cations $[Fp(CH_2{=}CHOR)]^+$. These latter complexes are shown to be best described as distorted *dihapto* cations. Treatment of $FpCOCH_2OMe$ with strong acid leads to the ketene hemiacetal cation $[Fp(CH_2{=}C(OH)OMe)]^+$ rather than to the expected ketene complex. This substance, as well as the acetal cation $[Fp(CH_2{=}C(OMe)OEt)]^+$ prepared by alkylation of $FpCH_2COOMe$, may possess the structure of an h^1-metal complex incorporating a carboxonium ion. A correlation is shown to exist between the chemical shift of cyclopentadienyl protons and the average infrared carbonyl stretching frequency in a variety of $Fp(olefin)^+$ and Fp—R complexes.

Introduction

A number of transition metal complexes of vinyl alcohol and of vinyl ethers are known. Several of these, among them the uncharged complexes I [1], II** [2], III [3], and IV [4], have been isolated and characterized, while V [5] has been postulated as an intermediate in the B_{12} dependent dioldehydrase reaction and a palladium analog of II (R = H) is believed to be a critical intermediate in the conversion of ethylene to acetaldehyde [6]. The preparation of a number of cationic platinum complexes of vinyl ethers either by addition of alchohol to platinum—acetylene complexes or by an exchange reaction has recently been reported [7].

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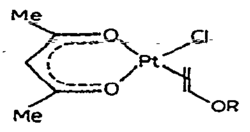
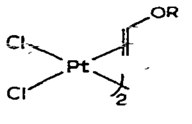
[*] To whom correspondence should be addressed.

[**] The authenticity of II has been questioned [3].



(I) R = H, SiMe$_3$



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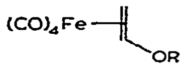
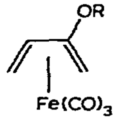
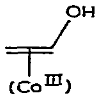


(III) R = H, Et



(IV) R = H, Ac, COPh



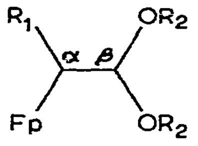
(V)

Our interest in the chemistry of h^5-$C_5H_5(CO)_2Fe$(olefin) cations [Fp(ol)$^+$], and in particular their use as substrates in nucleophilic addition reactions [8], prompted us to examine methods for the convenient preparation of the related vinyl ether and ketene acetal complexes. Ariyaratne and Green [9] had previously reported the preparation of the vinyl alcohol complexes IXa and IXb, by protonation of the related acetaldehyde and acetone complexes VIIIa and VIIIb. However these latter substances were obtained only in very low yield from the metallation of chloroacetaldehyde and chloroacetone with dicarbonyl-h^5-cyclopentadienyliron anion (Fp$^-$). An alternative synthesis of such vinyl alcohol and ether complexes was therefore sought.

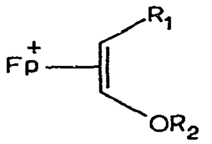
Results and discussion

Preparation of complexes

We have found that a simple and more general entry into this system of complexes can be made through the reactions of the readily available β-haloacetals and ketals [10]. Metallation of chloroacetaldehyde-dimethyl- or -diethyl-acetal with dicarbonyl-h^5-cyclopentadienyliron anion (Fp$^-$) led to the formation of the 2,2′-dialkoxyethyl complexes VIa and VIb in 85—90% yield*, while reaction of α-bromopropionaldehyde diethyl acetal gave VIc in 50% yield.



(VIa) R_1 = H, R_2 = Me
(VIb) R_1 = H, R_2 = Et
(VIc) R_1 = Me, R_2 = Et



(VIIa) R_1 = H, R_2 = Me
(VIIb) R_1 = H, R_2 = Et
(VIIc) R_1 = Me, R_2 = Et

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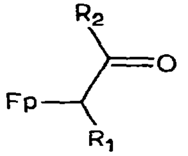
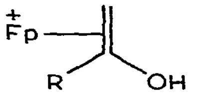
[*] Similar reactions have recently been reported for the preparation of 2,2-diethoxyethyl cobalamine and cobaloxime complexes [5].

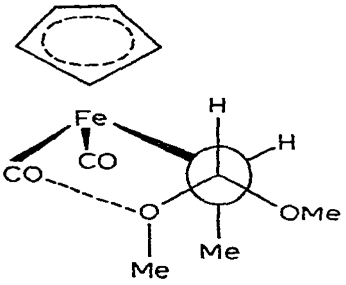


(VIIIa) R_1 , R_2=H
(VIIIb) R_1 = H, R_2=Me

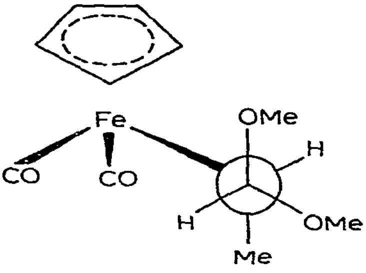


(IXa) R = H
(IXb) R = Me

The acetals VIa and VIb are very susceptible to hydrolysis; chromatography on neutral alimina suffices to convert then in over 90% yield to the aldehyde complex VIIIa. The vinyl ether complexes VIIa-c were obtained either from the aldehyde by treatment with triethyloxonium hexafluorophosphate or directly from VI by reaction of these with trityl cation. Significantly, the propionaldehyde acetal complex VIc is converted by triethyloxonium cation to the *cis*-vinyl ether complex VIIc exclusively. Conformation VIc-i, which would give the *cis*-propene complex VIIc by *trans* elimination of methoxyl [11], may be favored over VIc-ii since steric interactions between the cyclopentadienyl protons and substituents at the β-carbon atom are minimized. Moreover this conformation allows for stabilizing interaction between a methoxyl group and a terminal metal carbonyl group*.



(VIc-i)



(VIc-ii)

Protonation of VIIIa may be effected in high yield with either trifluoromethanesulfonic acid or hexafluorophosphoric acid etherate. Both the vinyl alcohol complex and the vinyl ether complex (IXa and VII) are relatively stable and show little decomposition in air after several days at room temperature

IXa is rapidly converted to the corresponding ether complex VIIb in high yield by dissolution in absolute ethanol and reprecipitation with ether.

During the course of this research we were led to explore the preparation of an Fp(ketene) complex, XI. Such complexes are unknown, although the related cationic allene complexes are well characterized and available either by proponation of propargyl—Fp complexes [13] (eqn. 1) or by an exchange

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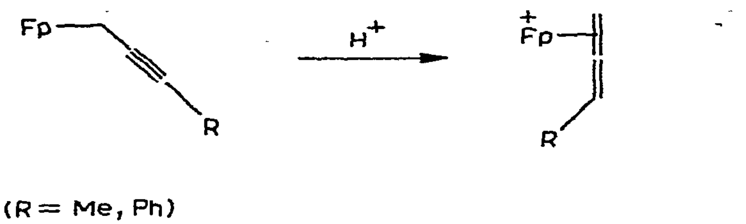
[*] Similar stereospecificity is observed in the deprotonation reactions of the bromomethyl and methoxymethyl substituted Fp(ethylene) cation which yields only the *cis*-1-bromo- and *cis*-1-methyloxyallyl Fp complexes [12].

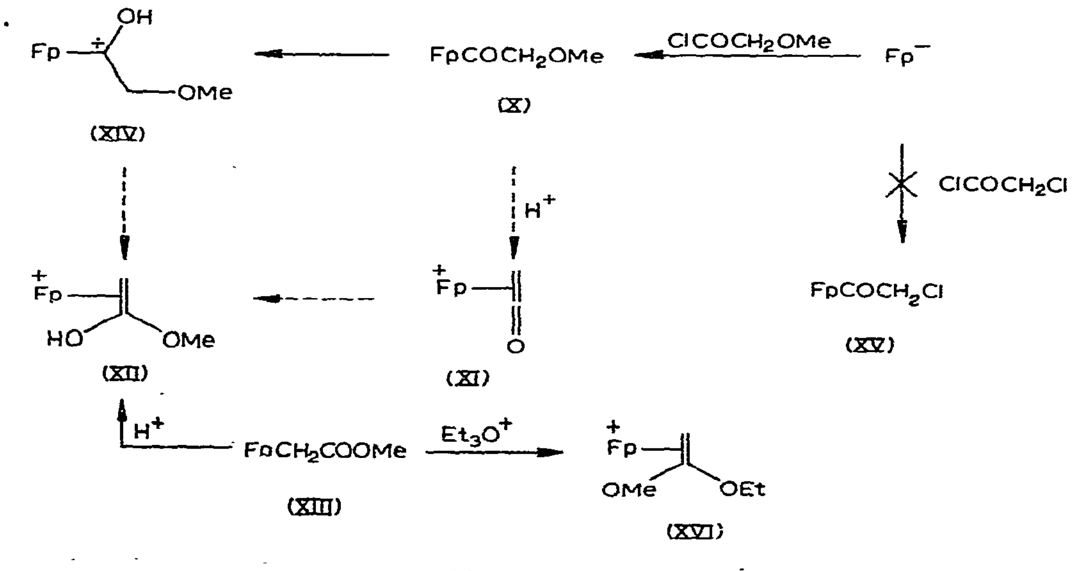


(1)

(2)

reaction with Fp(isobutylene) [14] (eqn. 2). The high reactivity of ketene precluded preparation of such a complex by the latter process. The alternative electrophilic reaction based on acid catalyzed elimination from β-substituted Fp—alkyl complexes, (for example VI → VII) seemed more promising. Accordingly, the 2-methoxyacetyl complex X was prepared by metallation of methoxyacetyl chloride. Treatment of this complex with hexafluorophosphoric acid etherate in methylene chloride failed to give XI, the expected ketene complex. Instead, the cation formed in this reaction was found to be identical with the ketene hemiacetal complex XII, prepared unambiguously by protonation of ester XIII [15] (Scheme 1). The corresponding methyl ethyl acetal XVI was readily prepared from XIII by treatment with triethyloxonium hexafluorophosphate.

SCHEME 1

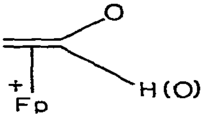


In view of the reactivity of ketenes toward nucleophiles and an anticipated heightening of this reactivity in cationic complex XI, conversion of such an intermediate to hemiketal complex XII seems plausible, even in strong acid solution. Nevertheless, a ketene complex is by no means required. The results do not exclude a process involving protonation of X and intramolecular conversion of the resulting carboxonium ion XIV directly to XII.

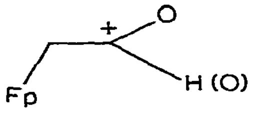
Attempts to prepare the related haloketone complex XV, from which halide ion might be abstracted with silver ion, were unsuccessful. No characterizable product could be obtained from the reaction of Fp$^-$ and chloroacetyl chloride. Neither could a ketene complex be obtained by the reaction of X with trityl cation in liquid SO_2. The only product isolated from this reaction was the tricarbonyl cation $CpFe(CO)_3^+$.

Structure of complexes

The structure of these cationic oxy- and dioxy-ethylene complexes is of interest insofar as the substituents might be expected to either induce unsymmetrical π-complexation of the double bond (A) or, in the extreme, to stabilize the cation in the form of a metal σ-complex incorporating a carboxonium ion (B).



(A)

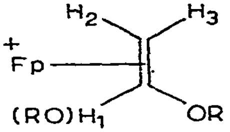


(B)

The presence of metal carbonyl absorption typical of a π-complexed cationic species in the IR spectram of IXa and IXb led Ariyaratne and Green to favor such a structure for these substances. However, the appearance of "vinyl" protons in IXa as an A_2X set could not be accounted for in terms of structure A, but was clearly more in accord with structure B. Moreover, the chemical shift of methylene protons in IXa and IXb is anomalously high and falls between those in the σ-complex (VIIIa, τ 8.38) and a π-olefin cation such as Fp(isobutylene)$^+$ where they appear at τ 6.05. Table 1 summarizes the PMR data for the complex cations prepared here, and those reported by Ariyaratne and Green [9].

TABLE 1

PMR DATA FOR OXY- AND 1,1'-DIOXY-ETHYLENE IRON COMPLEXES



Complex		Chemical shifts (τ)					Coupling constants (Hz)		
		Cp	H_1	H_2	H_3	OH	1,2	1,3	2,3
VIIa^a	(PF_6)	4.48	2.23	7.27	6.94		4.5	12.0	3.0
VIIb^a	(PF_6)	4.51	2.11	7.31	6.95		4.5	12.0	3.0
VIIc^a	(PF_6)	4.49	2.28	6.43			4.5		
IXa^a	(PF_6)	4.57	1.92	7.08	7.08	2.67	8.0	8.0	
IXa^a	(CF_3SO_3)	4.56	1.78	7.20	7.20	−0.38			
IXa^b	(Br)	4.62	1.83	7.15	7.15	1.43	8.0	8.0	
IXb^c	(CF_3COO)	4.75		7.38	7.38				
XII^a	(PF_6)	4.80		8.08	8.08	−2.25			
XVI^a	(PF_6)	4.80		8.00	8.00				

^{a} in CD_3NO_2 solution. ^{b} in liq SO_2, ref. 9. ^{c} in CF_3COOH, ref. 9.

The structural problem is resolved by an examination of the NMR spectrum of the corresponding ethers (VIIa or b) which clearly show an ABX proton absorption pattern characteristic of a π-olefin complex. The low field position of H_1 in VIIa and VIIb and IXa [compare with Fp(propene)$^+$, τ 4.67] suggests significant distortions towards the unsymmetrical mode of complexation illustrated by structure A and found to prevail in the neutral vinyl alcohol complex I (R = H) in the solid state [1b]. The absence of vinylic coupling in XIa is to be attributed to rapid equilibrium between IXa and VIIIa through proton exchange involving the solvent. A similar proton exchange has been invoked to account for the A_2X pattern observed for the protons in I (R = H) [1a]. The marked broadening of the hydroxyl proton signals in IXa in nitromethane solution ($\nu_{1/2}$ 4—6 Hz) and its chemical shift dependence on concentration suggest a rapid exchange process. From a comparison of the cyclopentadienyl proton chemical shifts for VIIa and VIIIa with IXa it may be estimated that in 5% CD_3NO_2 at 37° the salt is approximately 10% ionized. The implication that the cation IXa is a strong acid is confirmed by spectrophotometric measurements in aqueous sulfuric acid which give a pK_a value of —0.75 for the complex. This is to be contrasted with an approximate pK_a of 8.5 for IV (R = H) [4] and of 3.5 for I (R = H) [1a] in aqueous-acetone.

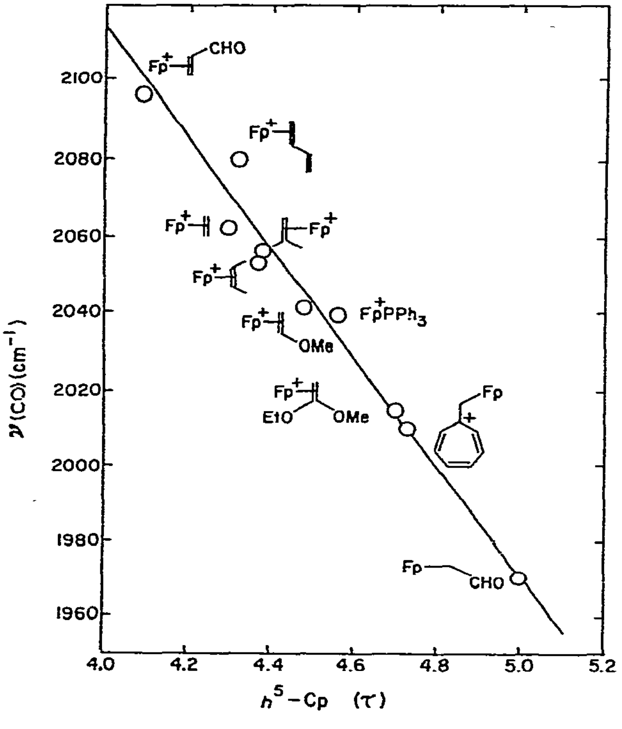
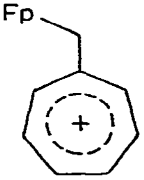


Fig. 1. Relationship between cyclopentadienyl proton resonance chemical shift (CD_3NO_3 solvent) and average carbonyl stretching frequency (KBr disks) in dicarbonyl-h^5-cyclopentadienyl iron complexes.

The structure of the ketene hemiacetal complex XII and acetal complex XVI cannot be adduced from the spectral evidence. It may be that stabilization afforded by an additional alkoxyl substituent leads to a balance in favor of the σ-bonded structure B. We have observed that a good monotonic relationship exists between the chemical shift of cyclopentadienyl protons in a large variety of dicarbonylcyclopentadienyliron complexes and the average of the two carbonyl stretching frequencies for these substances. The latter parameter has generally been accepted as providing a measure of effective charge on the metal [16]. Figure 1 illustrates this correlation for a number of cationic and neutral complexes in which the effective charge on the metal would be expected to differ markedly. The proximity of the parameters for XVI and the heptafulvene iron complex [17], shown to have a σ-bonded structure (XVII) [18] suggests that XVI may also possess such a structure.



(XVII)

Experimental section

All manipulations were carried out under nitrogen. Solvents were dried and generally stored over molecular sieves. These were degassed before use. IR spectra were recorded on a Perkin—Elmer Model 457 spectrophotometer and NMR spectra on a Varian A-60 spectrometer. Analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Preparation of dicarbonyl(h^5-cyclopentadienyl)(h^1-2,2'-dimethoxyethyl)iron (VIa)

A solution of dicarbonyl(h^5-cyclopentadienyl)iron dimer (4.424 g, 12.5 mmol) in 100 ml of tetrahydrofuran was reductively cleaved with an excess of 3% sodium amalgam [19]. Chloroacetaldehyde dimethyl acetal (3.125 g, 25.0 mmol) was added to the resulting solution, and the reddish-brown reaction mixture was then maintained at 45° for 2½ h. Solvent was removed in vacuo and the residue was extracted exhaustively with petroleum ether. The solution was filtered through sand in a Schlenk filter and concentrated to 50 ml in vacuo. On further reduction in volume with a stream of nitrogen, a yellow crystalline solid was deposited. This was collected and washed with small portions of precooled (—20°) petroleum ether to give 5.453 g of VIa as a waxy yellow solid, m.p. 29—30, (85%); (Found: C, 49.48; H, 5.32; Fe, 21.02. $C_{11}H_{14}O_4Fe$ calcd.: C, 49.66; H, 5.30; Fe, 20.99%). IR(KBr) 1998, 1944 cm^{-1} (C≡O). NMR (CS_2) τ 5.30 (s, 5, π-Cp), 5.76 (t, J 5.5 Hz, C—H), 6.85 (s, OCH_3), 8.60 (d, J 5.5 Hz, CH_2).

Preparation of dicarbonyl(h^5-cyclopentadienyl)(h^1-1,1-diethoxy-2-propyl)-iron (VIc)

α-Bromopropionaldehyde diethyl acetal, b.p. 94—96, was prepared by brominating the acetal [20]. The bromoacetal (1.72 g, 8.2 mmol) was added dropwise to a tetrahydrofuran solution of sodium dicarbonyl-h^5-cyclopentadienylferrate (8.2 mmol) at room temperature. After 3.5 h, solvent was removed and the residue was extracted with petroleum ether. The extract was filtered and solvent was removed leaving 1.26 g of product (50%) as a red brown oil. IR (neat) 2005, 1945 cm^{-1} (C≡O).

Preparation of dicarbonyl(h^5-cyclopentadienyl)(h^1-2-oxoethyl)iron (VIIIa)

The acetal complex VIa (2.07 g, 7.8 mmol) was chromatographed on 150 g of activity III alumina. Ether slowly eluted a dark yellow band which afforded 1.670 g of a yellow crystalline solid. This was identified as the aldehyde complex VIIIa (97% yield); IR (KBr) 2005, 1968 cm^{-1} (C≡O), 1645 cm^{-1} (C=O); NMR (CS_2) τ —0.88 (t, J 5.5 Hz, O=C—H), 5.22 (s, Cp), 8.38 (d, J 5.5 Hz, CH_2).

Preparation of dicarbonyl(h^5-cyclopentadienyl)(h^2-methoxyethylene)iron hexafluorophosphate (VIIa)

The acetal complex VIa (0.798 g, 3.0 mmol) was added to a solution of trityl hexafluorophosphate (1.165 g, 3.0 mmol) in 25 ml of methylene chloride. After 20 minutes at room temperature, a yellowish-orange solid had crystallized from solution. This was collected and washed with methylene chloride and ether. Recrystallization from acetone—ether gave an analytical sample of VIIa, 1.051 g, (93%); dec 129°. Found: C, 31.53; H, 2.97; Fe, 14.69. $C_{10}H_{11}O_3FePF_6$ calcd.: C, 31.61; H, 2.92; Fe, 14.70%. IR(KBr) 2050, 2005 cm^{-1} (C≡O); NMR(CD_3NO_2) τ 2.23 (dd, J 4.5, 12.0 Hz, =CH geminal to OMe), 4.48 (s, Cp), 5.97 (s, OCH_3), 6.94 (dd, J 3.0, 12.0 Hz, =CH *cis* to OMe), 7.27 (dd, J 3.0, 4.5 Hz, =CH *trans* to OMe).

Preparation of dicarbonyl(h^5-cyclopentadienyl)(h^2-ethoxyethylene)iron hexafluorophosphate (VIIb)

A solution of aldehyde complex VIII (0.440 g, 2.0 mmol) in 30 ml of methylene chloride was treated with triethyloxonium hexafluorophosphate (0.496 g, 2.0 mmol). After 0.5 h the volume was reduced to 10 ml, and yellow-orange crystals were obtained by dropwise addition of ether. This was collected, washed with ether and recrystallized from methylene chloride—ether to give 0.687 g (85%) of VIIb, dec. 123—124°. Found: C, 33.32; H, 3.33; Fe, 14.20. $C_{11}H_{13}O_3FePF_6$ calcd.: C, 33.53; H, 3.32; Fe, 14.17%. IR(KBr) 2055, 2008 cm^{-1} (C≡O); NMR(CD_3NO_2) τ 2.11 (dd, J 4.5, 12.0 Hz, =CH geminal to OEt), 4.51 (s, Cp), 5.64 (q, J 7.0 Hz, CH_2), 6.95 (dd, J 3.0, 12.0 Hz, =CH *cis* to OEt), 7.31 (dd, J 3.0, 4.5 Hz, =CH *trans* to OEt), 8.61 (t, J 7.0 Hz, CH_3).

Protonation of dicarbonyl(h^5-cyclopentadienyl)(h^1-2-oxoethyl)iron

(1). Trifluoromethanesulfonic acid (0.300 g, 3.6 mmol) was added dropwise to a cold (5°) solution of the aldehyde complex (0.66 g, 3.0 mmol) in 20 ml of methylene chloride. Addition of excess ether after 5 min gave a yellow crystalline solid that was collected and washed with ether. Recrystallization from acetone—ether yielded 0.965 g (90%) of dicarbonyl(h^5-cyclopentadienyl)(h^2-hydroxyethylene)iron trifluoromethanesulfonate (IX), dec. 103—110°. Found: C, 32.87; H, 2.45; Fe, 15.05. $C_{10}H_9O_6FeF_3S$ calcd.: C, 32.43; H, 2.45; Fe, 15.09%. IR(KBr) 2060, 2010 cm^{-1} ($C\equiv O$); NMR(CD_3NO_2) τ —0.55 (s, OH), 1.78 (t, J 8.0 Hz, =CH), 4.56 (s, Cp), 7.20 (d, J 8.0 Hz, $=CH_2$).

(2). Similar treatment of 0.660 g (3.0 mmol) of the aldehyde complex in methylene chloride with 0.670 g (3.0 mmol) of hexafluorophosphoric acid diethyletherate afforded 1.017 g of a yellow crystalline solid. This was identified spectroscopically as dicarbonyl(h^5-cyclopentadienyl) (h^2-hydroxyethylene)iron hexafluorophosphate (IX) (93% yield). IR(KBr) 2058, 2005 cm^{-1} ($C\equiv O$); NMR(CD_3NO_2) τ 1.95 (t, J 8.0 Hz, =CH), 2.61 (s, OH), 4.58 (s, Cp), 7.16 (d, J 8.0 Hz, $=CH_2$).

Conversion of IXa to VIIb. The vinyl alcohol PF_6 salt (366 mg, 1 mmol) was dissolved in ether 10 ml of absolute ethanol or an ethanol—acetone mixture (10 ml 50/50 v/v) and allowed to stand for 5 min at room temperature. Addition of 100 ml of ether precipitated vinyl ether complex VIIb. This was recrystallized from acetone—ether to give 360 mg (92%) of pure VIIb, identical to the product obtained by alkylation of VIIIa.

Preparation of dicarbonyl-h^5-cyclopentadienyl(cis-1-ethoxypropene)iron (VII)

Acetal VIc (0.41 mmol) was taken up in 40 ml of methylene chloride and treated with an equivalent of triethyloxonium hexafluorophosphate in the same solvent. After 3.5 h, removal of solvent left a yellow-orange gum which was taken up in 5 ml of methylene chloride, filtered and added dropwise to ether. The yellow precipitate was filtered off and recrystallized from methylene chloride—ether to give 6.96 g of propene salt VIIc, m.p. 112—113°. IR(CH_2Cl_2) 2058, 2020 cm^{-1} ($C\equiv O$). NMR (CD_3NO_2) τ 2.28 (d, J 4.5 Hz, O—CH=), 4.49 (s, Cp), 5.54 (q, J 7.0 Hz, CH_2), 6.43 (dq, J 6.0, 4.5 Hz, CH=), 8.35 (d, J 6.0 Hz, $CH_3C=$), 8.60 (t, J 7.0 Hz, CH_3). Found: C, 35.48; H, 3.83; Fe, 13.53. $C_{12}H_{15}FeO_3PF_6$ calcd.: C, 35.32; H, 3.71; Fe, 13.69%.

Preparation of dicarbonyl(h^5-cyclopentadienyl)(h^1-2-methoxyacetyl)iron (X)

A solution of sodium dicarbonyl h^5-cyclopentadienylferrate, prepared from 7.08 g (40 mmol) of the dimer in THF solution was added slowly to 5.42 g (50 mmol) of methoxyacetyl chloride in THF cooled to —78°. The solution was allowed to come to room temperature and solvent was removed in vacuo. The residue was extracted with ether, and the ether extracts were washed with degassed water and then dried. Removal of solvent left the product as an amber oil, 10 g (100%). Found: C, 48.30; H, 4.11. $C_{10}H_{10}FeO_4$ calcd.: C, 48.00; H, 4.00%. IR (KBr) 2040, 1960, 1660 cm^{-1}. NMR ($CDCl_3$) τ 5.09 (s, Cp), 6.0 (s, CH_2), 6.62 (s, CH_3).

Rearrangement of X by protonation. A solution of 500 mg of X (2 mmol) in dry degassed methylene chloride was treated with 1 ml of hexafluorophosphoric acid etherate. A yellow crystalline material was precipitated from solution within 5 min. This was filtered and washed under nitrogen with methylene chloride in a Schlenck apparatus to give 750 mg (95%) of XII, identical with the material obtained below by protonation of ester XIII.

Preparation of dicarbonyl(h^5-cyclopentadienyl)(h^1-carbomethoxymethyl)-iron (XIII)

A solution of sodium dicarbonyl h^5-cyclopentadienylferrate, prepared from 8.85 g (25 mmol) of dimer in 250 ml of dry degassed THF was added slowly to methyl chloroacetate (6.58 g, 60 mmol) in THF cooled to −78°. After allowing the solution to warm to room temperature, solvent was removed in vacuo and the residue was extracted with ether—petroluem ether. The extracts were concentrated and chromatographed twice on alumina to give 1.2 g (10%). IR (Neat film) 2030, 1980, 1680, 1240, 1090 cm^{-1} (lit. [10] 2034, 1983, 1677 cm^{-1}). NMR (CS_2) τ 5.20 (s, Cp), 6.55 (s, CH_3) 8.60 (s, CH_2).

Protonation of dicarbonyl(h^5-cyclopentadienyl)(h^1-carbomethoxymethyl)-iron

The ester above (1.0 g, 4 mmol) was taken up in 30 ml of dry degassed methylene chloride, and 1.5 ml of hexafluorophosphoric acid etherate was added under nitrogen. The mixture was stirred at room temperature for 30 min. The yellow precipitate was filtered and washed under nitrogen with methylene chloride in a Schlenck apparatus to give 1.0 g of XII (63%). Found: C, 30.48; H, 2.84. $C_{10}H_{11}FeO_4PF_6$ calcd.: C, 30.31; H, 2.78%. IR (KBr) 2040, 2000 cm^{-1} NMR (CH_3NO_2) τ −1.77 (s, OH), 4.80 (s, Cp), 5.81 (s, CH_3) 8.08 (s, CH_2).

Preparation of dicarbonyl(h^5-cyclopentadienyl)(h^2-ketene methyl ethyl acetal)-iron hexafluorophosphate (XVI)

Organometallic ester XIII (2.0 g, 8 mmol) in 30 ml of methylene chloride was added to 1.98 g (8 mmol) of triethyl oxonium hexafluorophosphate in 20 ml of methylene chloride. After stirring the solution for 18 h under N_2, 2 ml of ethanol was added and the solution was added dropwise to 300 ml of ether. The reddish brown solid was filtered and recrystallized from methylene chloride—ether to afford the product as orange-yellow crystals, 2.2 g (65%), m.p. 79—80.5°. Found: C, 33.79; H, 3.38. $C_{12}H_{15}FeO_4PF_6$ calcd.: C, 33.96; H, 3.54%. IR (KBr) 2060, 2000 cm^{-1} ($C\equiv O$). NMR (CD_3NO_2) τ 4.70 (s, Cp), 5.45 (q, J 7 Hz, OCH_2), 5.81 (s, OCH_3), 8.0 (s, $CH_2=$), 8.51 (t, J 7 Hz, CH_3).

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References

1 (a) M. Tsutsui, M. Ori and J. Francis, J. Amer. Chem. Soc., 94 (1972) 1414;
(b) F.A. Cotton, J.N. Francis, B.A. Frenz and M. Tsutsui, ibid., 95 (1973) 7907;
(c) J. Hillis and M. Tsutsui, ibid., 95 (1973) 7907.
2 Y. Wakatsuki, S. Nozakura and S. Murahaski, Bull. Chem. Soc. Japan, 42 (1969) 273.
3 H. Thyret, Angew. Chem. Int. Ed. Engl., 11 (1972) 520;
E. Koerner von Gustorf, M.C. Henry and C. DiPietro, Z. Naturforsch. B, 21 (1966) 42.
4 C.H. DePuy, R.N. Greene and T.E. Schroer, Chem. Commun., (1968) 1225.
5 R.B. Silverman and D. Dolphin, J. Amer. Chem. Soc., 95 (1973) 1686.
6 P.M. Maitlis, The Organic Chemistry of Palladium, Vol. II, Academic Press, New York, 1971, p. 141.
7 M.H. Chisholm and H.C. Clark, J. Amer. Chem. Soc., 94 (1972) 1532;
M.H. Chisholm and H.C. Clark, Inorg. Chem., 12 (1973) 991.

8 A. Rosan, M. Rosenblum and J. Tancrede, J. Amer. Chem. Soc., 95 (1973) 3062.
9 J.K.P. Ariyaratne and M.L.H. Green, J. Chem. Soc., (1964) 1.
10 P.E. Eaton, J. Amer. Chem. Soc., 84 (1962) 2344;
A. Roedig, in Houben-Weyl Methoden der Organischem Chemie, Vol. 5—4, G. Thieme Verlag, Stuttgart, 1960, p. 168;
A. Marquet, M. Drolaitzky, H.B. Kagan, L. Mamlok, C. Ouannes and J. Jacques, Bull. Soc. Chim. Fr., (1961) 1822.
11 W.P. Giering, M. Rosenblum and J. Tancrede, J. Amer. Chem. Soc., 94 (1972) 7170.
12 Unpublished observations with K. Nicholas and A. Rosan.
13 S. Raghu and M. Rosenblum, J. Amer. Chem. Soc., 95 (1973) 3060;
D.W. Lichtenberg and A. Wojcicki, ibid., 94 (1972) 8271;
J. Benaim, J. Merocu and J. Roustan, C.R. Acad. Sci. Paris, Ser. C, 272 (1971) 789.
14 M. Rosenblum and S. Raghu, unpublished observations.
15 M.L.H. Green, J.K.P. Ariyaratne, A.M. Bierrum, M. Ishag and C.K. Prout, Chem. Commun., (1967) 430.
16 E.W. Abel and F.G.A. Stone, Quart. Rev. (London), 23 (1969) 325.
17 D.J. Ehntholt, G.F. Emerson and R.C. Kerber, J. Amer. Chem. Soc., 91 (1969) 7547.
18 M.R. Churchill and J.P. Fennessey, Chem. Commun., (1970) 1056.
19 E.O. Fischer and R. Bottcher, Z. Naturforsch., 106 (1955) 600.
20 S. Sandler and W. Karo, in Organic Functional Group Preparations, Academic Press, New York, 1972, Vol. 3.