Journal of Organometallic Chemistry, 187 (1980) 253—265
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THE PREPARATION AND PROPERTIES OF CATIONIC DICARBONYLCYCLOPENTADIENYLIRON COMPLEXES OF ORGANIC CARBONYL COMPOUNDS: MOLECULAR STRUCTURE OF DICARBONYLCYCLOPENTADIENYLIRON(3-METHYLCYCLOHEXENONE) HEXAFLUOROPHOSPHATE *

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(Received February 22nd, 1979)

Summary

A number of complexes $CpFe(CO)_2(L)$ (L = aldehyde, ketone, ester, amide) have been prepared either by treatment of $[CpFe(CO)_2]_2$ or $CpFe(CO)_2Br$ with $AgPF_6$ in the presence of L or by a ligand exchange reaction employing $CpFe(CO)_2(isobutylene)BF_4$. NMR spectral data suggest that these complexes involve iron—oxygen σ-bonding rather than π-bonding to the carbonyl group. This is confirmed by an X-ray structure determination of the 3-methylcyclohexenone complex. The exchange stability of these complexes parallels their basicity.

Introduction

Although a considerable number of cations of the general form $[FpL]^+$ (Fp = $CpFe(CO)_2$; L = PR_3 [1—4,6,8], AsR_3 [1,6], SbR_3 [1,6], NR_3 [2—4,8], CO [1,4—6,8], RCN [2,3,8], NH_2NH_2 [2,3], olefin [7], CH_3NO_2 [7], are known, only one in which L is a ketone carbonyl has been reported [4,6]. In the course of another investigation concerned with enhancement of carbonyl group reactivity through metal complexation, we had occasion to prepare a number of $[CpFe(CO)_2L]^+$ cations in which L is either an aldehyde, ketone, ester or amide. The present paper describes the preparation and properties of these substances, and reports the results of an X-ray structure determination of the 3-methylcyclohexenone complex.

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* Taken in part from the Ph. D. thesis of Philip T. Klemarczyk, Brandeis University, February 1979.

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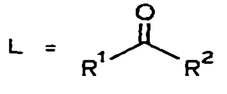
Results and discussion

The preparation of $\mathrm{CpFe(CO)_2(acetone)^+}$, by oxidation of $\mathrm{[CpFe(CO)_2]_2}$ in acetone solution with anhydrous ferric perchlorate, was first reported by Johnson, Meyer and Winterton [4], but they were unable to isolate the hexafluorophosphate salt. Williams and Lalor [6] subsequently prepared and isolated the hexafluorophosphate salt, employing $\mathrm{AgPF_6}$ as oxidizing reagent.

We found that the latter method (method A) worked well for the preparation of the cyclohexanone, cyclohexenone and 3-methylcyclohexenone complexes (Ia, IIa, IIb), but gave only low yields of product with ligands such as iso-butyraldehyde, methylisopropyl ketone, 7-norbornanone and methyl acetate. For these as well as the more hindered diisopropyl ketone, treatment with $\mathrm{CpFe(CO)_2Br}$ and $\mathrm{AgPF_6}$ (method B) is a convenient and more general route to carbonyl complexes Ib, Ic, Id, III as well as those above. The amount of bromonium salt $\mathrm{\{[CpFe(CO)_2]_2Br\}PF_6}$ [2], which forms competitively in these reactions, may be minimized by slow addition of $\mathrm{CpFe(CO)_2Br}$ to the methylene chloride solutions of $\mathrm{AgPF_6}$ and excess ligand. This procedure was used to prepare the dimethylformamide complex IVa, but proved inapplicable with *N*-methylacetamide or pivalamide. However, the high stability of amide complexes makes it possible to prepare these substances by the ligand exchange reaction [7] (method C):

$$\mathrm{CpFe(CO)_2(isobutylene)^+} + \mathrm{L} \xrightarrow{\mathrm{CH_2Cl_2}} \mathrm{CpFe(CO)_2L} + \qquad (1)$$

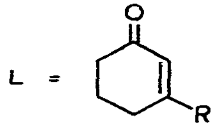
All complexes were isolated as deep red crystalline solids. Their methods of preparation, yields and spectral properties are recorded in Table 1.



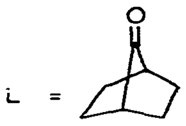
Ia. $R^1, R^2 = (CH_2)_5$
Ib. $R^1 = H$, $R^2 = CHMe_2$
Ic. $R^1 = Me$, $R^2 = CHMe_2$
Id. $R^1, R^2 = CHMe_2$

$\mathrm{[CpFe(CO)_2L]^+}$

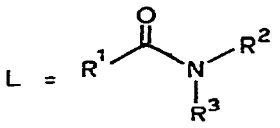
(I–IV)



IIa. R = H
IIb. R = Me

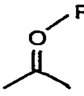


III

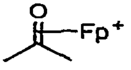


IVa. $R^1 = H$, $R^2 = R^3 = Me$
IVb. $R^1 = Me$, $R^2 = H$, $R^3 = Me$
IVc. $R^1 = t\text{-}Bu$, $R^2 = R^2 = R^3 = H$

Two forms of metal—carbonyl ligand bonding may be considered for these complexes. Of these σ-bonding to oxygen (Va) is well precedented in main group and transition metal β-diketone complexes [9,10]. Structures in which carbonyl groups are π-bonded as in Vb are less common but not unknown.



(Va)

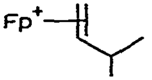


(Vb)

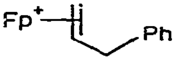
$Fp = CpFe(CO)_2$

In several complexes of Pd and Pt with dibenzylidene acetone, the metal has been suggested to be π-bonded to the carbonyl group alone, on the basis of spectral data [11]. Better authenticated, if formal, examples of this bonding mode are to be found in some recently reported Ru, W and Zr complexes [12] in which a carbonyl group acts as a σ,π 3-electron donor. Metals π-bonded to carbonyl groups are more commonly encountered in α,β unsaturated ketone and aldehyde complexes where the ligand functions as a 1-oxadiene system [13], in 1-oxapropenyl systems [14] and in 1-oxapentadienyl systems [15]. In closely related, but nonconjugated systems the carbonyl group may also function as a σ-donor through oxygen [16].

In the present circumstances, the NMR spectra of the isobutyraldehyde, methyl isopropyl and diisopropyl ketone complexes argue against their formulation as π-complexes (structure Vb). Such a structure would render the isopropyl methyl groups in these complexes diastereotopic, yet each exhibits only a single resonance doublet (Table 1). By contrast, the closely related olefin π-complex of a 3-methyl-butene (VI) exhibits two methyl doublet resonances separated by 0.35 ppm, while the two methylene protons in Fp(allylbenzene) (VII), which are more proximate to the center of chirality, exhibit a chemical shift difference of 1.06 ppm [17].



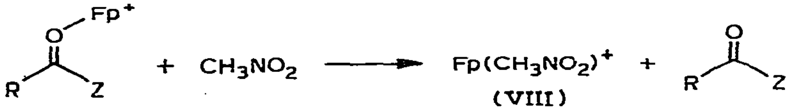
(VI)



(VII)

The spectral data are in accord with the σ-complex, but require that *syn—anti* interconversion be very fast on the NMR time scale since the single methyl and methine resonances in the diisopropyl ketone complex (Id) remain unchanged down to —95° C. The spectrum of the norbornanone complex III also remains substantially unchanged down to this temperature.

The stability of a series of Fp(carbonyl) cations, estimated from the half life of exchange with nitromethane at 37° C (eq. 2), parallels the increasing basicity of esters, aldehydes, ketones and amides [18]. These data are summarized in Table 2.



(VIII)

(2)

The complex of methyl acetate proved to be too unstable under these conditions to determine its half life. Its comparative instability is also shown by the fact that it undergoes exchange at room temperature with cyclohexene, a rela-

TABLE 1

PREPARATION, ANALYSIS AND SPECTRAL PROPERTIES OF $CpFe(CO)_2$-CARBONYL COMPLEXES

Ligand	Preparative method	Yield (%)	Analysis (Found (calcd.) (%))			$\nu(C\equiv O)$ (cm^{-1})	H^1 NMR absorptions, (δ, ppm)
			Formula	C	H		
Acetone	A	75				2090, 2040, 1660 [a]	5.40 (s, 5, Cp), 2.30 (s, 6, CH_3) [c]
Cyclohexenone	A	82	$C_{13}H_{13}FeO_3PF_6$	37.51 (37.36)	3.47 (3.13)	2060, 2020, 1610 [b]	7.50 (m, 1, =CH), 6.17 (m, 1, =CH) [a] 5.40 (s, 5, Cp), 1.80—2.70 (m, 6, CH_2)
Isobutyraldehyde	B	56				2080, 2040, 1660 [a]	9.58 (d, 1, J 2 Hz, CHO), 5.41 (s, 5, Cp) 2.60 (m, 1, CH), 1.05 (d, 6, J 7 Hz, CH_3) [c]
Methylisopropyl ketone	B	76				2070, 2030, 1650 [a]	5.41 (s, 5, Cp), 2.67 (m, 1, CH) [c], 2.25 (s, 3, $COCH_3$), 1.00 (d, 6, J 7 Hz, CH_3)
Diisopropyl ketone	B	71				2070, 2010, 1635 [b]	5.37 (s, 5, Cp), 2.50 (m, 2, CH) [c], 1.00 (d, 12, J 7 Hz, CH_3)
7-Norbornanone	B	40				2880, 2030, 1650 [a]	5.42 (s, 5, Cp), 1.40—2.20 (m, 10, CH, CH_2) [c]
Dimethylformamide	C	70	$C_{10}H_{12}FeO_3NPF_6$	30.12 (30.40)	2.83 (3.06)	2060, 2020, 1660 [b]	7.32 (s, 1, CHO), 5.29 (s, 5, Cp), [c] 3.02 (s, 3, NCH_3), 2.73 (s, 3, NCH_3)
N-Methylacetamide	C	60	$C_{10}H_{14}FeO_4NPF_6$	28.54 (29.07)	3.41 (2.92)	2070, 2080, 1610 [a]	5.45 (s, 5, Cp), 2.70 (s, 3, NCH_3), [c] 2.05 (s, 3, CH_3)
2,2-Dimethyl propanamide	C	44	$C_{12}H_{16}FeO_3NBF_4$	39.59 (39.49)	4.66 (4.42)	2090, 2040, 1640 [b]	7.18 (br, s, 1, NH), 6.67 (br, s, 1, NH), 5.35 (s, 5, Cp), 1.05 (s, 9, CH_3) [c]
N,*N*-Dimethyl benzamide	C	16	$C_{16}H_{16}FeO_3NPF_6$	40.12 (40.82)	3.38 (3.43)	2070, 2010, 1590 [a]	7.50 (,m, 5, Ph), 5.28 (s, 5, Cp), [d] 3.04 (s, 3, NCH_3), 2.91 (s, 3, NCH_3)
Cyclohexanone	A	78	$C_{13}H_{15}FeO_3PF_6$	37.66 (37.18)	3.69 (3.60)	2090, 2030, 1640 [b]	5.40 (s, 5, Cp), 1.50—1.60 (m, 10, CH_2) [c]
3-Methyl cyclohexenone	A	80	$C_{14}H_{15}FeO_3PF_6$	39.13 (38.92)	3.54 (3.50)	2060, 2020, 1575 [b]	6.00 (m, 1, =CH), 5.40 (s, 5, Cp) [c] 2.12 (s, 3, CH_3), 1.70—2.60 (m, 6, CH_2)
Methyl acetate	B	42				2090, 2040, 1640 [b]	5.40 (s, 5, Cp), 3.30 (s, 3, OCH_3) [c] 2.15 (s, 3, $COCH_3$)

[a] In CH_2Cl_2. [b] In KBr. [c] In CD_2Cl_2. [d] In CD_3NO_2.

TABLE 2

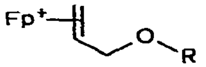
EXCHANGE RATES OF Fp(carbonyl)$^+$ CATIONS WITH CH_3NO_2 [a]

Ligand	Half life (min)
Isobutyraldehyde	2
Acetone	5
Cyclohexanone	8
Cyclohexenone	120
3-Methylcyclohexenone	>180
N,N-Dimethyl formamide	[b]
N-Methylacetamide	[b]

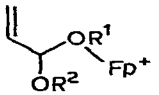
[a] In CD_2Cl_2 solution at 37°C. [b] No observable exchange after 1 h.

tively poor ligand, to give Fp(cyclohexene)$^+$ in 35% yield. Under the same conditions of exchange, Fp(acetone)$^+$ gave only a 14% yield of this cation.

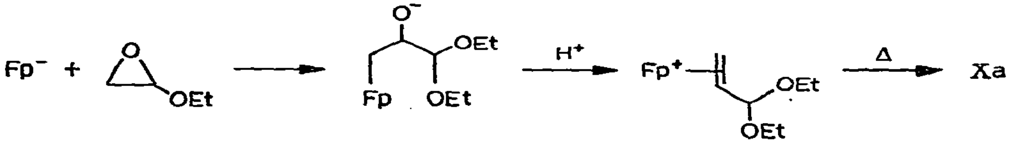
It is of interest to note that complexation of cyclohexenone and 3-methylcyclohexenone yield Fp(carbonyl)$^+$ rather than Fp(olefin)$^+$ complexes. While complexation of the relatively weak electron-donor olefin in these compounds would not be anticipated, the balance between oxygen and olefin coordination does not invariably favor oxygen. The exchange of methyl allyl ether [7] or of allyl acetate with Fp(isobutylene) (eq. 1), yields only the olefin complexes (IXa, IXb), but acrolein diethyl or ethylene acetals give only the relatively unstable oxygen coordinated complexes (Xa, Xb). The related olefin complex XI can be prepared indirectly from acrolein diethyl acetal epoxide by treatment with NaFp, followed by quenching of the intermediate alkoxide at −78° C with acid (eq. 3), but on heating in methylene chloride solution it is isomerized to the oxygen complex XIa. The enhanced stability of these latter oxygen complexes as well as the nitromethane complex VIII may be due to chelation but more definitive evidence on this point is lacking.



(IXa: R = Me;
IXb: R = Ac)



(Xa: $R^1 = R^2 = Et$;
Xb: $R^1, R^2 = C_2H_4$)



(XI)

(3)

In contrast to Fp(methylacetate)BF_4, which rapidly exchanges with nitromethane, the amide complexes are relatively inert. The high stability of these complexes makes it possible to prepare them from Fp(isobutylene)PF_6 by the exchange reaction (eq. 1). Like protonation of an amide [19], complexation by

Fp^+ produces a significant increase in the C—N rotational barrier. The NMR spectra of the pivalamide, *N,N*-dimethylbenzamide and *N,N*-dimethylformamide complexes in nitromethane or methylene chloride solutions show widely separated proton resonances at 37° C for the *N*-substituents, and the coalescence temperature of methyl proton resonances in the benzamide complex is above 85° C *. This corresponds to a calculated increase in C—N rotational barrier of at least 4 kcal/mol compared to the free amide [20]. Corresponding data for the protonated amide are not available, but protonation of dimethylformamide is observed to increase the C—N rotational barrier by 3 kcal/mol [21] **.

Molecular structure of Fp(3-methylcyclohexenone)PF_6

Crystals of Fp(3-methylcyclohexenone)PF_6 (IIb) were grown by diffusion; the salt was dissolved in a small volume of methylene chloride and placed in the freezer in a flask containing a much larger amount of ether. The crystals were then collected, washed in ether and dried in vacuo.

Preliminary examination of the thin, platelike crystals via Weissenberg ($h0l$, $h1l$) and precession ($0kl$) photography showed systematic absences for $0k0$ ($k \neq 2n$) and $h0l$ ($h \pm l \neq 2n$), which uniquely determine the space group to be $P2_1/n$. The crystal was then transferred to and optically centered on a Syntex $P2_1$ diffractometer. Most operations were carried out as described previously [22]; other operations are described below. Details of the structure analysis, in outline form, are presented in Table 3.

Analysis was carried out on a Syntex XTL Structure Determination System (24k Nova 1200 configuration) [23]. The analytical scattering factors of Cromer and Waber were used [24]; real and imaginary components of anomalous scattering were included in the calculations for the iron and phosphorous atoms [25].

The positions of the iron and phosphorus atoms were determined from a three-dimensional Patterson map. Subsequent structure factor and difference Fourier calculations revealed the positions of the other non-hydrogen atoms. At the conclusion of anisotropic refinement of all non-hydrogen atoms (R = 0.075), using a full matrix least squares procedure, a difference Fourier synthesis revealed the position of all hydrogen atoms except for two of the three methyl hydrogens attached to C(9).

The positions of the hydrogen atoms were not refined. Instead the program HPOSN [23] was used to calculate their position. For the methyl hydrogen atoms the program METHYL [26] was used to generate tetrahedral positions for the methyl hydrogen atoms at 10 degree intervals around the C(5)—C(9) bond axis. The other two hydrogen atom positions were fixed assuming local C_{3v} symmetry. All hydrogen atoms were included as fixed contributions to F_c (with C—H = 0.95 Å) in subsequent cycles of least squares refinement. At final

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* Above this temperature, decomposition occurs.

** The coalescence temperature for dimethylformide methyl protons lies above the decomposition temperature of its Fp complex and hence the C—N rotational barrier in this complex could not be determined by this technique.

TABLE 3

DATA FOR THE X-RAY DIFFRACTION STUDY OF $\{\pi\text{-}C_5H_5Fe(CO)_2(OC_7H_{10})\}PF_6$

(A) Crystal data at 21(1)°C

Crystal system: monoclinic
Space group: $P2_1/n$
a 7.170(2) Å
b 14.861(4) Å
c 17.005(5) Å
β 100.06(3)°

V 1776.6 Å^3
$Z = 4$
Crystal size: 0.25 × 0.33 × 0.05 mm
Formula wt. 432.1
ρ(calcd.) 1.615 g cm^{-3}
ρ(obsd) [a] 1.61(1) g cm^{-3}

Cell constant determination: 12 pairs of $\pm(hkl)$ and refined 2θ, ω, χ, (Φ fixed) values in the range $24° < |2\theta| < 35°$ (λ(Mo-K_α) 0.71069 Å)

(B) Measurement of intensity data

Radiation: Mo-K_α, graphite monochromator
Reflections measured: $-h$, $\pm k$, $\pm l$ (to 2θ 46°)
Scan type; speed: θ—2θ, variable, 1.95—4.51°/min
Scan range: Symmetrical, $[1.8 + \Delta(\alpha_1 - \alpha_2)]°$
Background measurement: stationary, for one-quarter of scan time at each of scan limits
No. of reflections measured: 3027; 2477 in unique set
Standard reflections: $0\bar{6}\bar{7}$, $40\bar{4}$, $2\bar{6}4$
Automatic recentering after every 700 reflections

(C) Treatment of intensity data [b]

Data reduction: intensities as before [22]; esd's of $|F_0|$ values calculated by method of finite differences, after Churchill et al. [30]
Statistical information: $R_s = 0.033$ ($I > 1.96\sigma(I)$); $R_{av} = 0.011$

(D) Refinement [c], with 1623 data for which $F > 3.92\sigma(F)$

Weighting of reflections: $w = [\sigma^2(|F_0|) + (p|F_0|)^2]^{-1}$; $p = 0.035$
Isotropic refinement, all hydrogen atoms: $R = 0.139$; $R_w = 0.185$
Anisotropic refinement, all nonhydrogen atoms: $R = 0.075$; $R_w = 0.096$
Anisotropic refinement as above, with 1839 data for which $F > 2.0\sigma(F)$, all hydrogen atoms included as fixed: $R = 0.074$; $R_w = 0.083$
Standard deviation of an observation of unit weight (SDU): 1.583
Final difference Fourier map: 10 peaks, 0.71 to 0.35 e Å^{-3} near fluorine atoms plus random peaks ≤ 0.35 e Å^{-3}

[a] Measured by flotation in methyl iodide and carbon tetrachloride. [b] $R_s = \Sigma\sigma(|F_0|)/\Sigma|F_0|$; $R_{av} = [(\Sigma||I| - |I_{av}||)/\Sigma|I|]$. [c] $R = \Sigma(|F_0| - |F_c|)/\Sigma|F_0|$; $R_w = \{\Sigma w[|F_0| - |F_c|]^2/\Sigma w|F_0|^2\}^{1/2}$. SDU = $\{\Sigma w[|F_0| - |F_c|]^2/(m - n)\}^{1/2}$ where $m = 1839$ is the number of observations and $n = 225$ is the number of parameters.

convergence, $(\Delta/\sigma_{max}) \leq 0.07$, $R = 0.074$ ($R = \Sigma||F_0| - |F_c||/|F_0|$) and $R_w = 0.083$ ($R_w = [\Sigma(|F_0| - |F_c|)^2]/\Sigma w|F_0|^2]$). A weighting scheme analysis revealed no systematic dependence of $w[|F_0| - |F_c|]^2$ on $|F_0|$, $\sin\theta/\lambda$, parity of indices or sequence number. Table 4 lists the positional and isotropic temperature factors for all atoms, while anisotropic temperature factors appear in Table 5.

The structure of the complex cation (Fig. 1) confirms that the iron atom is σ-bonded to the oxygen atom of the 3-methylcyclohexenone moiety. Pertinent bond lengths and angles are presented in Table 6. The salient features of the structure are:

(i) The Fe—O(3) bond length, 1.980(6) Å, is indicative of an Fe—O single

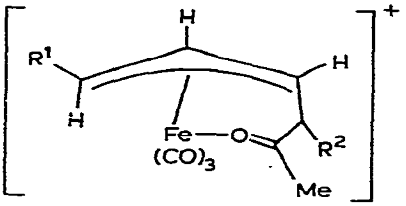
TABLE 4

POSITIONAL PARAMETERS FOR $[C_5H_5Fe(CO)_2OC_7H_{10}]PF_6$[a]

Atom	x	y	z
Fe	0.1587(2)	0.06675(7)	0.15851(7)
P	0.2179(3)	0.13041(15)	0.67868(16)
C(1)	−0.0889(14)	0.08090(54)	0.11620(53)
C(2)	0.1571(12)	−0.05346(62)	0.14116(55)
C(3)	0.2696(11)	0.15238(55)	0.01461(47)
C(4)	0.1750(12)	0.23512(58)	0.02529(46)
C(5)	0.1937(15)	0.30732(62)	−0.01944(52)
C(6)	0.3242(18)	0.30597(66)	−0.07953(61)
C(7)	0.4661(14)	0.23135(71)	−0.06867(56)
C(8)	0.3760(13)	0.14449(59)	−0.05330(50)
C(9)	0.0930(24)	0.39308(85)	−0.01118(77)
C(10)	0.1112(16)	0.10219(98)	0.26973(65)
C(11)	0.2513(20)	0.03943(66)	0.27776(55)
C(12)	0.4017(13)	0.07446(73)	0.24596(61)
C(13)	0.3527(17)	0.15971(76)	0.21888(61)
C(14)	0.1745(19)	0.17851(68)	0.23283(65)
O(1)	−0.2454(10)	0.08913(48)	0.09436(47)
O(2)	0.1517(10)	−0.12855(47)	0.13280(47)
O(3)	0.2615(8)	0.08537(35)	0.05886(33)
F(1)	0.4335(10)	0.12479(47)	0.69365(74)
F(2)	0.2352(12)	0.21812(61)	0.73036(62)
F(3)	0.2101(15)	0.07408(76)	0.75218(54)
F(4)	0.2071(14)	0.04276(62)	0.63640(71)
F(5)	−0.0013(9)	0.13757(49)	0.66413(60)
F(6)	0.2230(17)	0.19749(76)	0.61392(63)

[a] Standard deviations in the least significant digit appear in parentheses in this and subsequent tables.

bond, and is in good agreement with values obtained for substituted tricarbonylallyliron complexes of the type where Fe—O bond lengths of 1.999(5)



and 1.987(10) Å are found for the cases where R^1 = H, R^2 = H and R^1 = Me, R^2 = *endo*-Me, respectively [16].

(ii) The ketonic C—O bond length, 1.256(10) Å, is longer than that observed for the η^3-allyl-keto complex where R^1 = H and R^2 = H, 1.207(8) Å, but rather near to the range of values found in other transition-metal ketone complexes [10].

(iii) The C(1)—Fe—C(2) and C(1)—Fe—O(3) angles are distorted from 90° by as much as 7°. Presumably, the C(1)—Fe—O(3) angle "opens up" in order to minimize steric interaction between the cyclohexenone ring and the carbonyl group. This interaction also produces relatively large deviations from planarity in the O(3)—C(3)—C(4)—C(5)—C(6) plane (Table 5). Other bond lengths and

TABLE 5

ANISOTROPIC THERMAL PARAMETERS FOR NONHYDROGEN ATOMS IN $[C_5H_5Fe(CO)_2OC_7H_{10}]PF_6$ [a]

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe	0.0459(7)	0.0410(6)	0.0556(7)	0.0014(6)	0.0138(5)	0.0033(6)
P	0.067(2)	0.052(1)	0.079(2)	0.009(1)	0.025(1)	0.008(1)
C(1)	0.068(6)	0.052(5)	0.066(6)	−0.000(5)	0.006(5)	−0.007(4)
C(2)	0.069(6)	0.052(6)	0.085(7)	−0.002(5)	0.025(5)	−0.003(5)
C(3)	0.059(5)	0.051(5)	0.049(5)	0.000(4)	0.009(4)	0.008(4)
C(4)	0.079(6)	0.062(6)	0.045(5)	0.012(5)	0.020(4)	0.006(4)
C(5)	0.119(8)	0.065(6)	0.053(5)	0.028(6)	0.034(6)	0.013(5)
C(6)	0.150(10)	0.065(7)	0.078(7)	0.007(7)	0.055(7)	0.023(5)
C(7)	0.083(7)	0.092(8)	0.071(6)	−0.002(6)	0.026(5)	0.007(6)
C(8)	0.081(6)	0.062(6)	0.057(5)	0.007(5)	0.025(5)	−0.004(4)
C(9)	0.250(17)	0.093(8)	0.115(10)	0.076(10)	0.116(11)	0.052(8)
C(10)	0.081(7)	0.118(10)	0.073(7)	−0.016(7)	0.037(6)	−0.032(7)
C(11)	0.134(10)	0.063(6)	0.057(6)	−0.010(7)	0.013(7)	0.014(5)
C(12)	0.055(6)	0.084(7)	0.086(7)	0.004(5)	−0.017(5)	0.003(6)
C(13)	0.091(8)	0.080(8)	0.074(7)	−0.038(7)	−0.001(6)	0.003(6)
C(14)	0.111(9)	0.060(7)	0.080(7)	0.029(6)	−0.023(7)	−0.024(6)
O(1)	0.052(4)	0.101(6)	0.130(7)	0.008(4)	−0.011(4)	−0.006(5)
O(2)	0.116(6)	0.048(4)	0.136(6)	0.003(4)	0.033(5)	−0.004(4)
O(3)	0.067(4)	0.053(4)	0.070(4)	0.003(3)	0.026(3)	0.008(3)
F(1)	0.077(5)	0.086(5)	0.425(15)	0.012(4)	0.056(7)	0.037(7)
F(2)	0.144(7)	0.152(8)	0.236(10)	0.007(6)	0.019(7)	−0.095(7)
F(3)	0.223(10)	0.252(12)	0.120(6)	−0.033(8)	0.042(6)	0.081(7)
F(4)	0.202(9)	0.147(7)	0.279(12)	0.014(6)	0.038(9)	−0.139(8)
F(5)	0.074(5)	0.110(6)	0.294(11)	0.008(4)	−0.001(5)	0.005(8)
F(6)	0.298(13)	0.207(10)	0.180(9)	−0.021(9)	0.022(9)	0.142(8)

[a] The form of the thermal ellipsoid in this table is $\exp[-2\pi^2(a^*U_{11}h^2 + \ldots + 2b^*c^*U_{23}kl)]$.

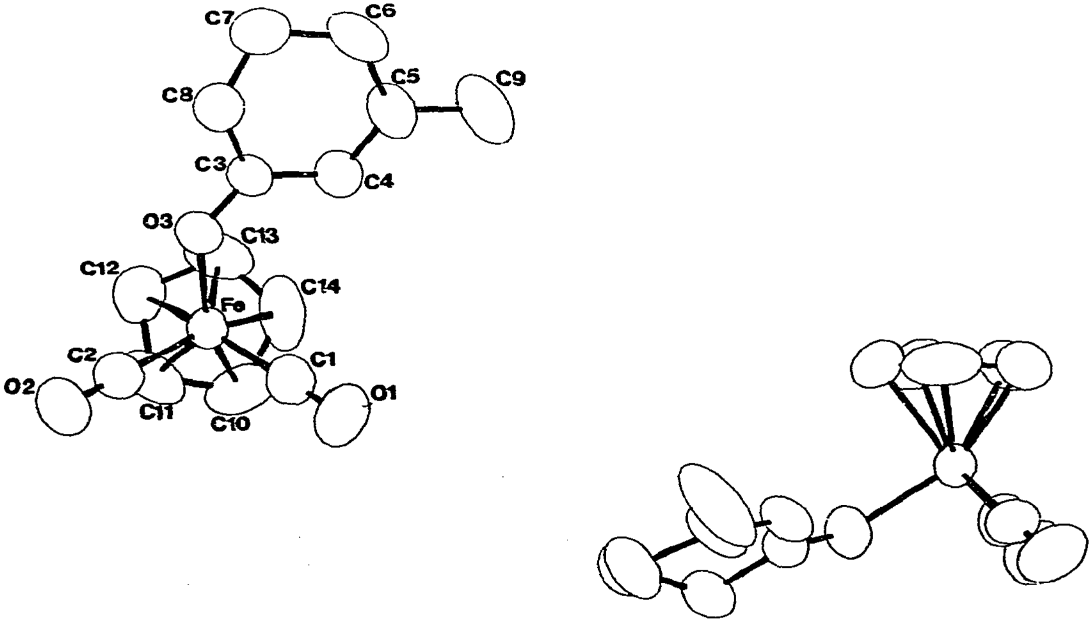


Fig. 1.

TABLE 6

SELECTED BOND LENGTHS (A) AND ANGLES (deg)

Fe—C(1)	1.801(10)	P—F(1)	1.518(8)		
Fe—C(2)	1.810(9)	P—F(2)	1.565(10)		
Fe—O(3)	1.980(6)	P—F(3)	1.513(10)		
C(1)—O(1)	1.121(12)	P—F(4)	1.483(10)	C(10)—C(11)	1.357(18)
C(2)—O(2)	1.125(12)	P—F(5)	1.545(7)	C(11)—C(12)	1.385(16)
O(3)—C(3)	1.256(10)	P—F(6)	1.491(11)	C(12)—C(13)	1.372(16)
C(3)—C(4)	1.430(12)	Fe—C(10)	2.048(11)	C(13)—C(14)	1.364(18)
C(4)—C(5)	1.335(12)	Fe—C(11)	2.061(9)	C(14)—C(10)	1.408(17)
C(5)—C(6)	1.499(15)	Fe—C(12)	2.081(10)		
C(6)—C(7)	1.491(15)	Fe—C(13)	2.094(11)		
C(7)—C(8)	1.486(14)	Fe—C(14)	2.078(11)		
C(8)—C(3)	1.493(12)				
C(5)—C(9)	1.482(17)				
Fe—O(3)—C(3)	133.4(5)	O(3)—Fe—C(1)	97.3(3)		
O(3)—C(3)—C(4)	122.3(7)	O(3)—Fe—C(2)	89.5(3)		
C(3)—C(4)—C(5)	121.5(8)	C(1)—Fe—C(2)	94.1(4)		
C(4)—C(5)—C(6)	120.9(9)	Fe—C(1)—O(1)	175.8(8)		
C(5)—C(6)—C(7)	114.5(9)	Fe—C(2)—O(2)	177.1(9)		
C(6)—C(7)—C(8)	111.2(8)	C(10)—C(11)—C(12)	108.1(10)		
C(7)—C(8)—C(3)	111.2(8)	C(11)—C(12)—C(13)	108.0(10)		
C(8)—C(3)—C(4)	118.8(7)	C(12)—C(13)—C(14)	108.8(10)		
C(4)—C(5)—C(9)	122.6(10)	C(13)—C(14)—C(10)	107.1(10)		
C(6)—C(5)—C(9)	116.5(9)	C(14)—C(10)—C(11)	108.1(11)		

TABLE 7

LEAST SQUARES PLANE FOR CYCLOHEXENONE RING

Equation: $(-0.6553)X + (-0.3167)Y - (-0.6858)Z - (-2.1696) = 0$
Atoms in plane: O(3), C(3), C(4), C(5), C(6)
Distances from plane:

O(3)	−0.017(6)	C(7)	−0.445(10)
C(3)	0.052(8)	C(8)	0.239(9)
C(4)	0.003(8)		
C(5)	0.002(10)		
C(6)	−0.029(11)		
C(9)	−0.009(15)		

Orthogonal coordinates X, Y, Z used in these calculations were obtained from fractional coordinates using the transformation

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} a & b\cos\gamma & c\cos\beta \\ 0 & b\sin\gamma & -c\sin\beta\cos\alpha^* \\ 0 & 0 & 1/c^* \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

angles, as well as intermolecular contacts, are within normal ranges. Final observed and calculated structure factors and positions of the hydrogen atoms were deposited with NAPS *.

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* The table of structure factors and hydrogen atom positions has been deposited as NAPS Document No. 03549 (10 pages). Order from ASIS/NAPS, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. A copy may be secured by citing document number, remitting $ 5.00 for photocopies or $ 3.00 for microfiche. Advance payment is required. Make checks payable to Microfiche Publications.

Experimental

Solvents were routinely dried by standard procedures and stored under nitrogen. All organometallic reactions and subsequent manipulations including reagent additions, filtrations, extractions, recrystallizations and chromatographic purification, as well as preparation of NMR samples and solution IR samples were conducted under a nitrogen atmosphere.

Infrared spectra were recorded on Perkin—Elmer spectrophotometers, model 137, 457 and 567. ^{1}H nuclear magnetic resonance spectra were recorded on the following spectrometers: Varian A-60 (NIH GM-13183) and Perkin—Elmer R-32 (NSF GU-3852).

Melting points were determined under a nitrogen atmosphere on a Kofler hot stage and are uncorrected.

Elemental analyses were determined by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Standard syntheses of carbonyl complexes

Method A. Fp(cyclohexenone)PF$_6$. [CpFe(CO)$_2$]$_2$ (1.0 g, 2.8 mmol) and cyclohexenone (1.15 g, 28 mmol) were dissolved in 20 ml of methylene chloride. The solution was cooled to 0°C, and AgPF$_6$ (1.4 g, 5.6 mmol) was added as rapidly as possible. The solution immediately turned dark red, with the precipitation of Ag^0. Silver was filtered off and 200 ml of ether was added to the methylene chloride solution. A red solid precipitated, which was collected in a Schlenk tube, recrystallized from methylene chloride/diethyl ether, and dried in vacuo. Yield 2.2 g (85%).

Method B. Fp(methylisopropyl ketone)PF$_6$. Fp bromide (1.0 g, 3.9 mmol) and methyl isopropyl ketone (0.68 g, 7.8 mmol) were dissolved in 20 ml of methylene chloride. The solution was then treated with AgPF$_6$ (0.99 g, 3.9 mmol) and worked up as in method A. Yield 1.2 g (76%).

Method C. Fp(2,2-dimethylpropanamide). Fp(isobutylene)BF$_4$ (1.0 g, 3 mmol) and 2,2-dimethylpropanamide (0.31 g, 3 mmol) were dissolved in 20 ml of methylene chloride. The solution was brought to reflux. The course of the reaction was monitored by IR, and was complete in 3.5 h. The reaction mixture was filtered to remove decomposition materials, and 250 ml of ether was added to the methylene chloride solution. A red solid precipitated, which was collected in a Schlenk tube, recrystallized from methylene chloride/diethyl ether, and dried in vacuo. Yield 0.5 g (44%).

7-Norbornanone

Norbornadiene was converted to 7-t-butoxynorbornadiene following the method of Story [27] and this was reduced and hydrolyzed with trifluoroacetic acid to give 7-norbornanol. Oxidation with CrO$_3$ in pyridine gave 7-norbornanone [28].

Fp(allyl acetate)BF$_4$

Fp(isobutylene)BF$_4$ (0.5 g, 1.6 mmol) was dissolved in 30 ml of methylene chloride; the solution was heated to reflux and allyl acetate (0.78 g, 7.8 mmol) was added. After 3 h the solution was cooled to room temperature, filtered and

200 ml of ether was added. The product separated as an orange oil (0.284 g, 50%); IR (CH_2Cl_2) 2080, 2050, 1745 cm^{-1}; NMR (CD_3NO_2) δ 4.75 (s, 5, Cp), 5.15 (m, 1, CH=), 4.60 (t, 2, CH_2, J 4 Hz) 4.15 (d, 1, CH_2=, J 7 Hz), 3.81 (d, 1, CH_2, J 15 Hz), 2.08 (s, 3, CH_3) ppm.

Exchange of Fp(isobutylene)BF$_4$ with acrolein diethyl acetal (Xa)

Fp(isobutylene)BF_4 (6.5 g, 1.6 mmol) was dissolved in 15 ml of methylene chloride and the solution was heated to reflux while acrolein diethyl acetal (0.61 g, 4.8 mmol) was added. After heating for 5 h, the solution was cooled to room temperature, filtered and 300 ml of diethyl ether was added. The product formed as a red precipitate, but oiled out on attempted collection in a Schlenk tube, yield 0.30 g (50%); IR (CH_2Cl_2) 2080, 2030 cm^{-1}; NMR (CD_2Cl_2) δ 5.20—5.90 (m, 4, CH=, $(RO)_2CH$), 5.35 (s, 5, Cp), 3.10 (m, 4, CH_2), 1.08 (t, 6, CH_3, J 7 Hz) ppm. The product is slowly converted to $[Fp(CH_3NO_2)]^+BF_4$ in nitromethane solution at room temperature.

Fp(acrolein diethyl acetal)BF$_4$. Complex XI

Acrolein diethyl acetal epoxide [29] (0.5 g, 3.4 mmol) was dissolved in 10 ml of THF and 6 ml of a 0.5 *M* THF solution of NaFp was added. The solution was stirred for 2 h at room temperature at the end of which time it had a green cast. It was then cooled to —78°C and 48% HBF_4 (0.55 g, 3.0 mmol) was added by syringe. The solution was then diluted with 200 ml of ether, allowed to warm to room temperature and the yellow precipitate was collected in a Schlenk tube. Recrystallization from methylene chloride/diethyl ether gave the product as yellow crystals (6.66 g, 55%); IR (CH_2Cl_2); IR (CH_2Cl_2) 2090, 2050 cm^{-1}; NMR (CD_3NO_2) δ 5.70 (s, 5, Cp), 5.00 (m, 2, CH=, $(RO)_2CH$), 4.12 (d, 1, CH_2=, J 8 Hz), 3.5—4.0 (m, 5, CH_2=, OCH_2), 1.20 (t, 6, CH_3, J 8 Hz). Anal. Found: C, 42.30; H, 5.21. $C_{14}H_{19}FeO_4BF_4$ calcd.: C, 42.69; H, 4.86%.

The corresponding ethylene acetal complex was prepared from the epoxide following the above procedure. NMR (CD_3NO_2) δ 5.75 (s, 5, Cp), 5.00 (m, 2, CH=, $(RO)_2CH$), 4.00 (m, 6, CH_2=, CH_2CH_2) ppm. Anal. Found: C, 39.29; H, 3.90. $C_{12}H_{13}FeO_4BF_4$ calcd.: C, 39.61; H, 3.60%.

Isomerization of complex XI to X

The olefin complex XI (0.2 g) was dissolved in 10 ml of methylene chloride and the solution was heated to reflux for 5 h, then cooled to room temperature and 200 ml of ether was added. The oil which separated was collected. An NMR spectrum of this product indicated the presence of $(FpCO)^+$, X and XI in the mixture, the latter two components in approximately equal amounts.

Acknowledgements

This work was supported by grants from the National Institutes of Health (GM-16395) and the National Science Foundation (CHE 75-09590) and through a National Science Foundation Instrumentation Grant (CHE 76-05582). R.E.L. acknowledges support from a US-PHS trainee grant (T 32 GM 07596).

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