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η-C_5H_5(CO)LFe-SUBSTITUTED IMIDATES OF ACRYLIC ACID. SYNTHESIS AND STRUCTURE

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Summary

Ethylation of $Cp(CO)_2FeCH{=}CHCONR_2$ (I) yields the imidates $[Cp(CO)_2$-$FeCH{=}CHC(\overset{-}{=}OEt)\overset{-}{=}NR_2]^+X^-$ (II). A photochemical reaction between I and PPh_3 yields $Cp(CO)(PPh_3)FeCH{=}CHCONR_2$ (III) from which the corresponding imidates (IV) can be obtained.

Spectral data suggest that the positive charge in II and IV is localized mainly at the imidate group and that the participation of the Cp(CO)LFe substituent in the stabilization of the positive charge is insignificant, particularly in the case of cations II.

This conclusion is confirmed by X-ray analysis of IIb. Determination of the exact structure of IIb also reveals the absence of a direct interaction between the metal and the cationic center even though the complex has *cis* geometry. A reaction between Ic and $Fe_2(CO)_9$ yields a binuclear complex (IV). The initial complexes I were obtained by substitution of the anion $[CpFe(CO)_2]^-$ for chlorine in $ClCH{=}CHCONR_2$. These reactions are stereospecific.

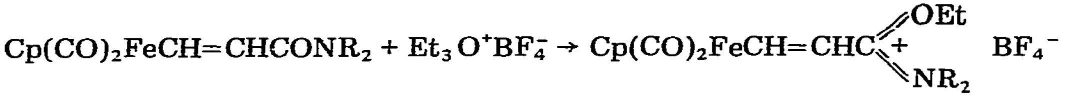
Introduction

Ethylation of η^1-vinyl derivatives of $Cp(CO)LFeCH{=}CHCOX$ yields the cations$[Cp(CO)LFe{-}CH{=}C(X)OEt]^+$. Formally, these can be regarded as allyl cations in which one of the substituents is the σ-bonded Cp(CO)LFe group. The contribution of this group to the positive charge distribution depends, on the one hand, on its own electron-donating ability, which becomes more pronounced as one goes from complexes with L = CO to those with L = PPh_3 and, on the other, on the capacity of the other terminal substituent X to interact with the electron-deficient carbon atom.

As was shown in the previous paper [1], for X = alkyl or aryl groups, the effect of the $Cp(CO)(PPh_3)Fe$ group on the positive charge distribution is rather strong. In the present work, cationic complexes with X = NR_2 (imidates) were synthesized and their structure examined.

Results and discussion

The ethylation of amides I according to the method of Meerwein [2] yields imidates (II):



$$\mathrm{Cp(CO)_2FeCH{=}CHCONR_2 + Et_3O^+BF_4^- \rightarrow Cp(CO)_2FeCH{=}CHC}\begin{smallmatrix}\mathrm{OEt}\\ +\\ \mathrm{NR_2}\end{smallmatrix}\ \mathrm{BF_4^-}$$

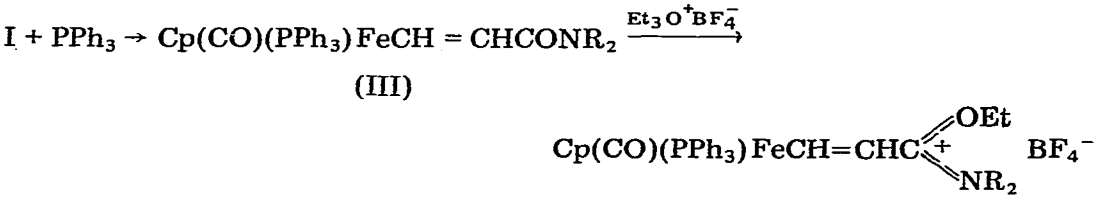
(Ia, R = H, *trans*;
IIb, R = H, *cis;* IIc, $R_2 = (CH_2)_5$, *trans*)

The amides I were, in turn, synthesized through the interaction of $[Cp(CO)_2Fe]^-$ with the amides of *trans*- and *cis*-β-chloroacrylic acids:

$ClCH{=}CHCONR_2 + [Cp(CO)_2Fe]^- \rightarrow$ Ia—Ic

These reactions, in which nucleophilic substitution of the $CpFe(CO)_2$ group for chlorine takes place, proceed without any change in the configuration at the vinyl carbon atom.

The CO ligand in complexes I can be photochemically replaced by triphenylphosphine. The phosphine derivatives (III) are also readily ethylated to imidates (IV):

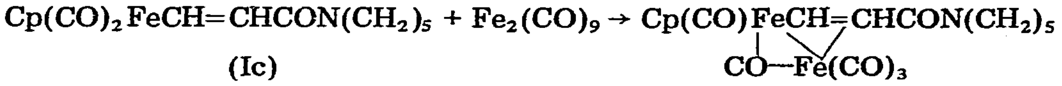


$$\mathrm{I + PPh_3 \rightarrow \underset{(III)}{Cp(CO)(PPh_3)FeCH = CHCONR_2} \xrightarrow{Et_3O^+BF_4^-} Cp(CO)(PPh_3)FeCH{=}CHC}\begin{smallmatrix}\mathrm{OEt}\\ +\\ \mathrm{NR_2}\end{smallmatrix}\ \mathrm{BF_4^-}$$

(IVa, R = H;
IVb, $R_2 = (CH_2)_5$)

Complexes I—IV are yellow (I and II) or orange (III and IV) solids, stable in air. Tables 1 and 2 give the spectral characteristics of these compounds, which are consistent with the structure assigned to them.

The ethylene bond in I is capable of π-complexing with iron carbonyls. When Ic is heated together with $Fe_2(CO)_9$, a binuclear complex (V) is formed, analogous to the complexes yielded earlier by the interaction between σ-vinyl derivatives of cyclopentadienyl iron dicarbonyl and $Fe_2(CO)_9$ [3]:



$$\mathrm{\underset{(Ic)}{Cp(CO)_2FeCH{=}CHCON(CH_2)_5} + Fe_2(CO)_9 \rightarrow \underset{(V)}{\underset{CO—Fe(CO)_3}{Cp(CO)FeCH{=}CHCON(CH_2)_5}}}$$

TABLE 1

IR SPECTRA OF COMPLEXES I—V (cm^{-1})

Complex	ν(C=C)	ν(NONR$_2$) [a]	$\nu\mathrm{C}\genfrac{}{}{0pt}{}{\diagup\mathrm{OEt}}{\diagdown\mathrm{NR_2}}+$ [a]	δ(NH) [a]	ν(C≡O) [b]
Ia	1550	1650	—	1600	2025 1970
Ib	1535	1665		1620	2030 1980
Ic	1540	1615	—	—	2025 1965
IIa	1510		1670	1580	2035 1980
IIb [c]	1505		1670	1580	2040 1990
IIc	1550		1625		2030 1980
IIIa	1545	1670		1620	1930
IIIb	1535	1615			1940
IVa	1500		1680	1570	
IVb	1500		1650		
V	1440	1610			1790

[a] KBr pellet. [b] In CHCl$_3$. [c] Hexafluorophosphate salt.

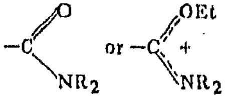
Imidates II and IV are very stable towards hydrolysis. They can be precipitated from aqueous or water/alcohol solutions in the form of hexafluorophosphates. When an aqueous solution of IIb is heated only *cis—trans* isomerization, rather than hydrolysis of the imidate group, takes place.

Comparison of the IR and NMR spectra of cations II and IV with those of their neutral precursors I and III, as well as the σ-ketovinyl derivatives $\mathrm{Cp(CO)(PPh_3)FeCH{=}CHCOR}$ (VI) and their ethylation products $[\mathrm{Cp(CO)(PPh_3)FeCH{=}CH{=}C(R){=}OEt}]^+X^-$ (VII) [1], enables some conclusions to be drawn concerning the role of the Cp(CO)LFe group in the electron density distribution in allyl cations of the $[\mathrm{Cp(CO)LFeCH{=}CH{=}CX{=}OEt}]^+$ type. The effect of this group is particularly pronounced in cases where the other terminal substituent X exhibits a slight electron-donating effect. We have previously studied such a situation for the salts VII. In the ^{13}C NMR spectra of complexes VII the signal due to the carbon atom bonded to the metal (C_α) is shifted to weak field ($\delta \sim 300$ ppm) and is found in a region of carbocations [4] or carbene complexes [5].

A different picture is observed in the case of acrylimidate complexes II and IV. In these compounds the positive charge is localized mainly within the imidate group. Therefore, the Cp(CO)LFe substituent plays only an insignificant role in the stabilization of the charge at the allyl cation. This conclusion agrees with the slight towards higher frequency of the stretching vibrations of the C≡O ligand ($\Delta\nu \sim 10$—15 cm^{-1}) and with that to the low field of the signals of the cyclopentadienyl protons ($\Delta\delta \sim 0.3$ ppm) when going from I to II or from III to IV. Note, for comparison, that the corresponding values in going from VI to VII are 35 to 40 cm^{-1} and 0.6 ppm [1].

TABLE 2

NMR DATA

Complex	Solvent	^1H NMR spectra (δ, ppm)				^{13}C NMR spectra (δ, ppm)				
		C_5H_5	H_α	H_β	$J_{\alpha\beta}$(Hz)	C_5H_5	C_α	C_β		C≡O
Ia	$(CD_3)_2SO$	5.27	8.77	6.24	16.0	86.67	158.85	138.00	164.31	215.64
Ib	$(CD_3)_2SO$	5.06	8.46	6.53	10.0	86.14	150.76	134.29	168.5	214.96
IIa	$(CD_3)_2SO$	5.38	10.06	6.51	17.5	76.02	180.32	116.36	151.19	202.64
IIb [a]	$(CD_3)_2SO$	5.40	10.20	7.04	12.0	88.1	191.86	128.33	170.72	214.4
IIIa [b]	$(Me_2N)_3PO$					85.24 85.51	171.31	138.98	164.13	221.28
IIIb	CH_2Cl_2					85.40	178.48	137.12	162.79	221.31
IVa [b]	$(CD_3)_2SO$					83.94 82.90	215.35	123.18	157.95	217.43
IVb	CH_2Cl_2					86.38	218.83	123.48	164.54	219.65

[a] Hexafluorophosphate salt. [b] Probably a mixture of isomers.

In the ^{13}C NMR spectra of cations II and IV the signals of C_α are shifted to weak field compared to the initial neutral amides I and III, but this shift is insignificant.

As expected, the greater electron-donating ability of the metal-containing group, exhibited in the case of substitution of triphenylphosphine for the CO ligand (i.e. in going from II to IV), results in a more active participation of this group in the stabilization of the allyl cation, which manifests itself in the increased low-field shift of the C_α signal.

For a more accurate determination of the nature of the bonding in cations II, the hexafluophosphate (IIb) was subjected to X-ray analysis. This *cis* isomer was selected for X-ray analysis because determination of its structure would also provide an answer to the question of whether the cationic center interacts directly with the metal. The *cis* geometry of the molecule must presumably promote such an interaction.

Molecular structure of complex IIb

The crystal structure of IIb comprises discrete $[(\eta^5\text{-}C_5H_5)(CO)_2FeCH{=}CHC(NH_2)OEt]^+$ and PF_6^- ions (Fig. 1) whose most important bond lengths and valence angles are summarized in Table 3.

The iron atom is coordinated by the η^5-cyclopentadienyl Cp ring, being located at 1.74 Å from its mean plane (the average Fe...C(Cp) distance is 2.098(8) Å), by two CO groups, and by the C(3) atom of the σ-vinyl ligand. The Fe—C(3) bond is somewhat shorter (1.943(5) Å) than in *trans*-$[Cp(CO)_2FeCH{=}CH—]_2$ (VIII) (1.987(5) Å) [6], but is practically the same (1.93—1.94 Å) as in the σ-vinyl ligands containing strong electron-accepting substituents (F, CF_3) [7]. In IIb such a substituent is the cationic center.

The C(3) atom is in eclipsed conformation with the C(9) atom of the Cp ring, whereas the carbonyl C(1) and C(2) atoms are above the C(10)—C(11) and C(8)—C(12) bonds, respectively, so that the immediate environment of the Fe atom has an approximate *m* local symmetry plane passing through the Fe, C(3),

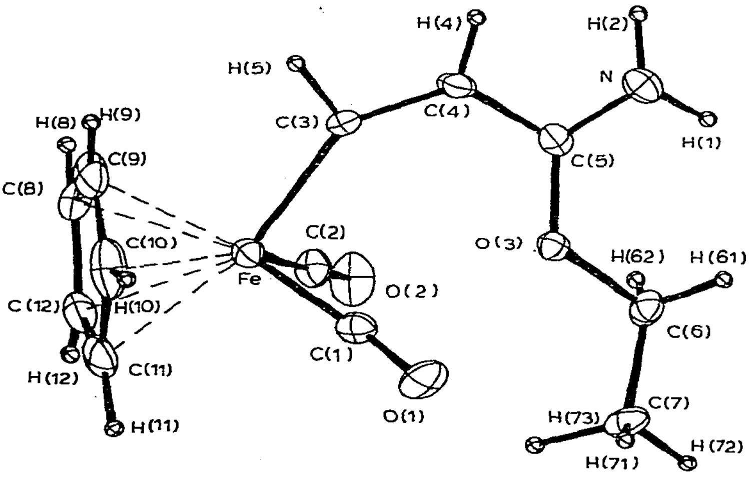


Fig. 1. The structure of complex IIb.

TABLE 3

BOND LENGTHS d(Å) AND ANGLES ω(°)

Bond	d	Bond	d	Bond	d
Fe—C(1)	1.755(5)	C(2)—O(2)	1.143(6)	C(8)—C(9)	1.39(1)
Fe—C(2)	1.754(5)	C(3)—C(4)	1.343(7)	C(8)—C(12)	1.38(1)
Fe—C(3)	1.943(5)	C(4)—C(5)	1.444(7)	C(9)—C(10)	1.38(2)
Fe—C(8)	2.103(7)	C(5)—O(3)	1.303(5)	C(10)—C(11)	1.41(1)
Fe—C(9)	2.10(1)	C(5)—N	1.305(7)	C(11)—C(12)	1.38(1)
Fe—C(10)	2.092(7)	N—H(1)	0.92(6)	*Averages*	
Fe—C(11)	2.112(7)	N—H(2)	0.88(7)	P—F	1.52(3)
Fe—C(12)	2.088(6)	O(3)—C(6)	1.462(6)	C(sp^2)—H	0.92(14)
C(1)—O(1)	1.133(6)	C(6)—C(7)	1.48(1)	C(sp^3)—H	1.02(7)

Angle	ω	Angle	ω	Angle	ω
C(1)FeC(2)	96.3(2)	C(4)C(5)O(3)	118.2(4)	H(1)NH(2)	118(6)
C(1)FeC(3)	90.3(2)	C(4)C(5)N	120.2(5)	C(9)C(8)C(12)	105.8(7)
C(2)FeC(3)	90.3(2)	O(3)C(5)N	121.7(4)	C(8)C(9)C(10)	109.7(9)
FeC(1)O(1)	177.1(5)	C(5)O(3)C(6)	121.4(4)	C(9)C(10)C(11)	107.3(8)
FeC(2)O(2)	178.4(5)	O(3)C(6)C(7)	107.3(5)	C(10)C(11)C(12)	106.2(7)
FeC(3)C(4)	138.4(4)	C(5)NH(1)	121(4)	C(8)C(12)C(11)	111.1(6)
C(3)C(4)C(5)	128.4(5)	C(5)NH(2)	121(5)		

C(9) atoms and the midpoint of the C(11)—C(12) bond. A similar conformation also occurs in VIII.

The vinyl moiety has a *cis* configuration with respect to the double C(3)—C(4) bond, and is planar, forming a dihedral angle of 99.5° with the Cp ring. The C(5)—O(3) (1.303(5) Å) and C(5)—N (1.305(7) Å) bonds are shorter than the normal C—O bonds in esters (1.358 Å) and C—N bonds in amides (1.333 Å), respectively [8]. The C(5) and N atoms have a planar-trigonal (sp^2) geometry (their coordination planes coinciding within experimental error), the C(5)O(3)-C(6) angle of 121.4(4)° also corresponding to the sp^2-hybridization of the O(3) atom. Hence, the delocalization of the positive charge occurs along the NC(5)O(3) moiety and does not extend over the FeC(3)C(4)C(5) moiety inclined to it at 23.3°, since the C(4)—C(5) bond length of 1.444(7) Å approaches the standard length of the normal bond between sp^2-hybridized carbon atoms, which is equal to 1.465 Å [8].

No direct interaction exists between the cationic center and Fe, as indicated by large Fe...C(5) (3.695(5) Å) and Fe...O(3) (3.419(3) Å) distances and the large FeC(3)C(4) and C(3)C(4)C(5) angles (138.4(4)° and 128.4(5)°, respectively, as compared to the ideal value of 120°) typical of non-chelate σ-vinyl complexes of iron [6,7,9], as well as by the absence of perceptible distortions of the bond angles at the Fe atom. Only the C(1)FeC(2) angle of 96.3(2)° is markedly different from the ideal 90° for the octahedral geometry of the metal, but this can also be explained by the steric repulsion due to short intramolecular O(3)...C(1) (2.846(6) Å) and O(3)...C(2) (2.797(6) Å) distances.

The octahedral PF_6^- anion is disordered and distributed with equal occupancies between two orientations differing from each other by rotation about the F(1)PF(2) axis by ca. 45°. The F(3), F(4), F(5) and F(6) atoms thus occupy two positions denoted F(31) and F(32), and so on. The ellipsoids of thermal

TABLE 4

HYDROGEN BONDS

D—H...A	Distances (Å)		Angle D—H—A (°)
	D...A	H...A	
N—H(1)...F(1) [a]	2.98(1)	2.11(6)	158(5)
N—H(2)...F(41) [b]	3.19(1)	2.35(7)	160(6)
N—H(2)...F(42) [b]	3.09(1)	2.26(7)	159(7)

Atoms, obtained from the basic by symmetry operations: [a] $1 - x, y + 1/2, 1/2 - z$. [b] $x, 1/2 - y, z - 1/2$.

vibrations of the F atoms, strongly elongated in a tangential direction, suggest the possibility of a more complex disordering or intense libration-induced vibrations of the anion, which accounts for the poor accuracy of its determined geometric parameters.

The H(2) atom of the amino group forms a hydrogen bond with the F(4) atom at both of its positions (Table 4), whereas H(1) forms a bond with the F(1) atom of another anion generated from the first one by the symmetry center 1/2, 1/2, 0. As a result, cycles are formed in the structure around this center, including two anions and two cations each.

Experimental

The starting materials were prepared by literature procedures: *trans*-3-chloroacrylic acid [10], its chloride and amide [11], *cis*-3-chloroacrylic acid, its chloride and amide [12]. The complexes were synthesized and purified in an argon atmosphere.

The IR spectra were recorded with a UR-20 spectrometer in KBr pellets or $CHCl_3$ solution; the ^1H NMR spectra were obtained with a Hitachi-Perkin Elmer R-20 spectrometer (60 MHz); and the ^{13}C NMR spectra were obtained with a Bruker HX-90 spectrometer (22.63 MHz).

X-ray experiments were carried out using a Syntex $P2_1$ 4-circle automatic diffractometer, graphite monochromated Mo-K_α radiation, and the computations were made with an Eclipse computer using EXTL software.

The crystals of IIb are monoclinic, at 20°C $a = 6.580(1)$, $b = 9.652(1)$, $c = 26.111(4)$ Å, $\beta = 92.50(2)°$, $V = 1656.8(5)$ Å^3, $M = 421.1$, $d_{calc} = 1.69$ g/cm^3, $Z = 4$, space group $P2_1/c$.

The intensities of 3201 reflections were measured by the $\theta/2\theta$ scan technique ($1 \leqslant \theta \leqslant 25°$), and 2116 reflections with $I \geqslant 2\sigma$ were used in the calculations. The structure was determined by the heavy atom technique and refined by the least squares method in an isotropic approximation to $R = 0.131$. A more accurate definition of the population factors for different positions of disordered F atoms did not reveal any perceptible deviations from 0.5, therefore in further refinement they were ascribed fixed values of 0.5. Refinement of all non-hydrogen atoms in an anisotropic approximation reduced R to 0.067. All H atoms were determined objectively by difference synthesis of the electron density and refined in an isotropic approximation. The final values $R = 0.052$ and $R_w =$

TABLE 5

ATOMIC COORDINATES (X 10^4, FOR Fe AND P X 10^5) AND ANISOTROPIC TEMPERATURE FACTORS IN THE FORM $T = \exp[-1/4(B_{11}a^{*2}h^2 + \ldots + 2B_{23}b^*c^*kl)]$

Atom	X	Y	Z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe	17405(10)	102368(7)	18497(2)	3.85(3)	3.50(3)	2.81(3)	0.08(3)	0.11(2)	−0.03(3)
P	72727(23)	11544(16)	58959(6)	6.08(8)	4.87(8)	−0.97(6)	0.96(7)	0.96(7)	−0.13(6)
O(1)	−2323(6)	9103(5)	1775(2)	3.6(2)	9.2(3)	6.8(2)	−0.6(2)	1.1(2)	−0.2(2)
O(2)	2243(7)	10694(5)	766(1)	10.5(3)	7.7(3)	3.3(2)	−2.2(2)	1.0(2)	−0.2(2)
O(3)	159(4)	8004(3)	897(1)	4.0(1)	4.2(2)	3.4(1)	0.7(1)	1.0(2)	1.0(2)
N	2372(9)	6374(5)	626(2)	5.3(3)	5.6(3)	5.4(3)	1.0(2)	−0.4(1)	−0.5(1)
C(1)	−719(8)	9534(5)	1793(2)	4.0(2)	5.0(3)	3.6(2)	0.9(2)	0.5(2)	−2.0(2)
C(2)	2024(8)	10501(5)	1192(2)	5.3(3)	4.0(3)	4.1(3)	−0.5(2)	0.9(2)	0.2(2)
C(3)	2903(7)	8395(5)	1797(2)	3.0(2)	4.4(3)	3.8(2)	0.3(2)	0.1(2)	0.0(2)
C(4)	2880(8)	7339(5)	1462(2)	4.3(2)	3.9(2)	4.4(3)	1.6(2)	−0.3(2)	0.2(2)
C(5)	1764(7)	7228(5)	975(2)	3.9(2)	3.2(2)	4.0(2)	−0.2(2)	−0.1(2)	−0.1(2)
C(6)	−993(9)	8001(6)	406(2)	5.3(3)	5.1(3)	3.1(2)	−0.3(2)	0.7(2)	−0.3(2)
C(7)	−2847(9)	8847(9)	470(3)	4.7(3)	8.7(5)	3.9(3)	1.5(3)	−0.7(2)	−0.2(2)
C(8)	4132(10)	11531(7)	2116(3)	5.5(3)	5.8(4)	7.4(4)	−0.8(3)	−0.1(2)	0.3(3)
C(9)	3590(19)	10647(9)	2507(4)	14.2(8)	5.1(4)	6.5(5)	1.6(5)	−1.3(3)	−2.3(3)
C(10)	1576(18)	10861(10)	2614(3)	14.1(7)	7.7(5)	3.1(3)	−4.2(5)	−6.6(6)	−1.6(3)
C(11)	838(11)	11943(7)	2293(3)	6.7(4)	5.8(4)	6.2(4)	0.0(3)	2.0(4)	−1.4(3)
C(12)	2426(11)	12315(7)	1996(3)	8.3(4)	3.5(3)	5.5(4)	−0.4(3)	1.2(3)	−2.9(3)
F(1)	8810(9)	978(8)	5481(2)	14.0(4)	23.0(7)	11.1(4)	7.8(4)	−0.4(3)	−1.0(3)
F(2)	5502(11)	1043(8)	6247(4)	15.6(5)	18.0(6)	21.8(7)	1.6(5)	7.1(3)	8.7(4)
F(31)	9188(24)	1023(20)	6228(6)	11.8(9)	15(1)	13(1)	−4(1)	11.7(5)	1.6(6)
F(32)	8515(36)	39(25)	6184(5)	20(2)	19(2)	5.8(6)	15(1)	−7.7(8)	−0.6(9)
F(41)	6848(19)	−398(9)	5981(6)	10.3(6)	4.5(4)	14(1)	−1.2(5)	4.8(8)	6.7(8)
F(42)	6407(22)	177(15)	5465(5)	15(1)	10.8(8)	9.6(7)	−3.5(7)	3.2(6)	2.1(5)
F(51)	5389(14)	1395(21)	5553(5)	6.2(5)	14(1)	13.1(9)	1.7(6)	0.8(7)	−5.2(7)
F(52)	6504(34)	2433(16)	5597(7)	18(2)	7.0(8)	15(1)	4.8(9)	−4.0(5)	1.4(9)
F(61)	7892(32)	2604(13)	5883(11)	21(2)	4.6(5)	25(2)	−5.1(8)	−0.5(10)	4.0(8)
F(62)	7657(26)	2072(20)	6356(6)	16(1)	13(1)	11.1(8)	0.5(10)	−7(2)	3.1(9)
								−2.4(8)	−8.5(8)

0.050 were obtained with the use of weighting scheme $W^{-1} = \sigma^2(F) + (0.01F_0)^2$. For atomic coordinates see Tables 5 and 6.

Preparation of trans-$ClCH{=}CHCON(CH_2)_5$

A solution of 17 g (0.2 mol) of piperidine in 50 ml of absolute ether was added dropwise to a solution of 12.65 g (0.1 mol) of the chloride of *trans*-3-chloroacrylic acid in 50 ml of absolute ether with stirring and cooling with ice. 2.5 hours later the reaction mixture was allowed to warm to room temperature and the precipitate was filtered off. Ether was removed from the filtrate and the residue was distilled in vacuum. 5.2 g (ca. 30%) of the piperidide of *trans*-3-chloroacrylic acid were obtained, b.p. 142° C/14 mmHg. Found: C, 55.80; H, 7.15; Cl, 19.87; N, 8.14. $C_8H_{12}ClNO$, calcd.: C, 55.33; H, 6.97; Cl, 20.42; N, 8.06%.

Preparation of trans-$CpFe(CO)_2CH{=}CHCONH_2$ (Ia)

A solution of $NaFe(CO)_2Cp$ obtained from 13.6 g (0.04 mol) of $[CpFe(CO)_2]_2$ in 200 ml of THF was added dropwise with stirring at —78° C for one hour to a solution of 7.75 g (0.075 mol) of $ClCH{=}CHCONH_2$ in 50 ml of THF. The reaction mixture was allowed to warm to room temperature, and the solvent was removed in vacuum. The residue was chromatographed twice on a column with Al_2O_3 (eluent CH_2Cl_2). Yield: 12.2 g (ca. 70%) of a complex Ia, m.p. 147—149° C (dec.) (toluene). Found: C, 48.57; H, 3.82; Fe, 22.65; N, 5.63. $C_{10}H_9FeNO_3$, calcd.: C, 48.62; H, 3.67; Fe, 22.61; N, 5.67%.

Preparation of cis-$CpFe(CO)_2CH{=}CHCONH_2$ (Ib)

A solution of $NaFe(CO)_2Cp$ obtained from 5.5 g (0.015 mol) of $[CpFe(CO)_2]_2$ in 50 ml of THF was added dropwise with stirring at —78° C for one hour to a solution of 3.25 g (0.03 mol) of *cis*-$ClCH{=}CHCONH_2$ in 50 ml of THF. The reaction mixture was allowed to warm to room temperature, and the solvent was removed in vacuum. The residue was chromatographed twice on a column with Al_2O_3 (eluent CH_2Cl_2). Yield: 4.85 g (64%) of Ib, m.p. 135—137°C (dec.)

TABLE 6

COORDINATES (X 10^3) AND B_{iso} ($Å^2$) OF H ATOMS

Atom	X	Y	Z	B
H(1)	166(9)	627(6)	32(2)	8(2)
H(2)	354(10)	594(8)	67(3)	10(2)
H(3)	388(6)	816(4)	210(2)	4(1)
H(4)	368(6)	663(4)	151(2)	3(1)
H(61)	—127(7)	705(5)	33(2)	5(1)
H(62)	—10(7)	842(5)	10(2)	6(1)
H(71)	—375(7)	855(5)	78(2)	6(1)
H(72)	—371(9)	881(6)	19(2)	8(2)
H(73)	—241(10)	987(7)	60(3)	10(2)
H(8)	562(11)	1158(8)	189(3)	12(2)
H(9)	426(10)	1017(7)	261(3)	8(2)
H(10)	72(10)	1041(7)	284(3)	9(2)
H(11)	—58(9)	1221(7)	231(2)	9(2)
H(12)	225(8)	1296(6)	179(2)	6(2)

(toluene). Found: C, 48.66; H, 3.64; Fe, 22.70; N, 5.68. $C_{10}H_9FeNO_3$, calcd.: C, 48.62; H, 3.67; Fe, 22.61; N, 5.67%.

Preparation of trans-CpFe(CO)₂CH=CHCON(CH₂)₅ (Ic)

A solution of $NaFe(CO)_2Cp$ obtained from 5.35 g (0.015 mol) of $[CpFe(CO)_2]_2$ in 50 ml of THF was added dropwise with stirring at —78°C for one hour to a solution of 5.22 g (0.03 mol) of $ClCH{=}CHCON(CH_2)_5$. The reaction mixture was allowed to warm to room temperature and the solvent was removed in vacuum. The residue was chromatographed on a column with Al_2O_3 (eluent CH_2Cl_2). Yield: 4.9 g (52%) of complex Ic, m.p. 132—134°C (dec.) (petroleum ether). Found: C, 57.80; H, 5.40; Fe, 18.09; N, 3.98. $C_{15}H_{17}FeNO_3$, calcd.: C, 57.16; H, 5.44; Fe, 17.72; N, 4.44%.

Preparation of trans-CpFe(CO)(PPh₃)CH=CHCONH₂ (IIIa) and CpFe(CO)(PPh₃)CH=CHCON(CH₂)₅ (IIIb)

A mixture of 5 mmol of Ia and 6 mmol of PPh_3 in 50 ml of THF was exposed to ultraviolet light for 20 hours at 20°C. The precipitate was filtered off. Yield: 1.95 g (80%) of IIIa, m.p. 195—197°C (dec.) (methanol). Found: C, 67.01; H, 4.96; Fe, 11.90; N, 2.71. $C_{27}H_{24}FeNO_2P$, calcd.: C, 67.37; H, 5.03; Fe, 11.60; N, 2.91%.

In a similar manner IIIb was synthesized from Ic; yield: 80%, m.p. 197—199°C (dec.) (methanol). Found: C, 69.97; H, 5.96; Fe, 9.99; N, 2.33. $C_{32}H_{32}FeNO_2P$, calcd.: C, 69.95; H, 5.87; Fe, 10.16; N, 2.55%.

Preparation of complex V

A mixture of 3.15 g (0.01 mol) of $CpFe(CO)_2CH{=}CHCON(CH_2)_5$ (Ic) and 3.64 g (0.01 mol) of $Fe_2(CO)_9$ in 50 ml of absolute benzene was stirred for two hours at 36—38°C. The solvent was removed in vacuum. The precipitate was washed with methanol. The yield was 1.6 g of complex V. Methanol was removed in vacuum, and 1.3 g of complex V were additionally separated from the residue by means of thin-layer chromatography (Al_2O_3, eluent $CHCl_3$). Total yield: 64%, m.p. 127—129°C (dec.). Found: C, 47.46; H, 3.98; Fe, 24.93; N, 3.10. $C_{18}H_{17}Fe_2NO_6$, calcd.: C, 47.51; H, 3.77; Fe, 24.55; N, 3.08%.

Ethylation of complexes I and III. Preparation of II and IV

1.23 g (5 mmol) of Ia and 0.95 g (5 mmol) of $Et_3O^+BF_4^-$ were stirred at room temperature for 30 minutes and the solvent was removed in vacuum. The residue was reprecipitated from CH_2Cl_2 with petroleum ether. Yield: 1.5 g (80%) of IIa, m.p. 153—155°C (dec.). Found: C, 39.49; H, 3.97; Fe, 14.95; N, 3.71. $C_{12}H_{14}BF_4FeNO_3$, calcd.: C, 39.71; H, 3.89; Fe, 15.39; N, 3.86%.

Similarly, ethylation of Ib, Ic, IIIa and IIIb yielded 80% of IIb, IIc, IVa and IVb, respectively.

Complex IIb. Hexafluorophosphate, m.p. 158—160°C (dec.). Found: C, 34.34; H, 3.30; Fe, 13.97; N, 3.39. $C_{12}H_{14}FeF_6NO_3P$, calcd.: C, 34.23; H, 3.35; Fe, 13.26; N, 3.33%.

Complex IIc. Hexafluorophosphate, m.p. 110°C (dec.) Found: C, 41.63; H, 4.56; Fe, 11.52; N, 3.89. $C_{17}H_{22}FeF_6NO_3P$, calcd.: C, 41.74; H, 4.53; Fe, 11.42; N, 2.86%.

Complex IVa. Fluoroboride, m.p. 109—113°C (dec.). Found: C, 59.74; H, 5.38; Fe, 8.99. $C_{17}H_{22}BF_4FeNO_2P$, calcd.: C, 58.32; H, 4.89; Fe, 9.35%.

Complex IVb. Hexafluorophosphate, m.p. 136—138°C (dec.). Found: C, 56.28; H, 5.49; Fe, 8.06. $C_{34}H_{37}FeNO_2P_2F_6$, calcd.: C, 56.44; H, 5.15; Fe, 7.72%.

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