Journal of Organometallic Chemistry, 182 (1979) 399—408

THE REACTION WITH AMINES OF THE ADDUCT FORMED BETWEEN (CINNAMALDEHYDE)TETRACARBONYLIRON π-COMPLEX AND BF_3. MOLECULAR STRUCTURE OF THE FORMED σ-*N*-TETRACARBONYLIRON COMPLEXES OF CINNAMALDEHYDE IMINES

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(Received June 5th 1979)

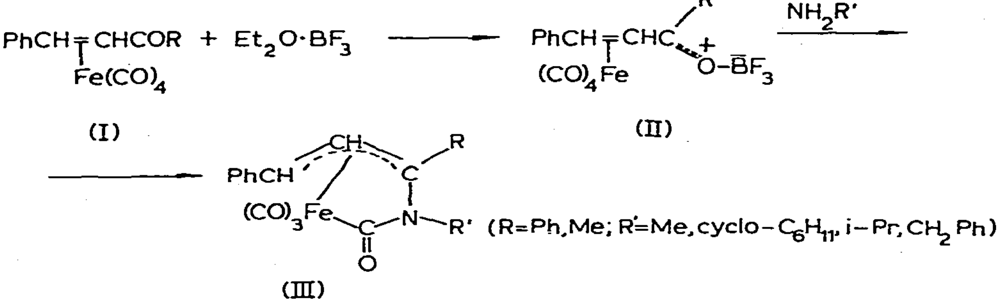
Summary

The adduct formed on reaction of boron trifluoride etherate with (π-PhCH=CHCHO)Fe(CO)$_4$ by addition of BF_3 to the oxygen atom of the aldehyde group, reacts with primary amines to give σ-*N*-tetracarbonyliron derivatives of cinnamaldehyde imines via (enimonium)tetracarbonyliron π-complexes. The structure of the former complexes is established by X-ray analysis and the effect of steric factors on $\pi \rightarrow \sigma(N)$ rearrangement is discussed.

Introduction

We have previously established that tetracarbonyliron complexes of α,β-unsaturated ketones (I) form stable adducts (II) with boron trifluoride by addition to the ketonic oxygen atom [1]. Adducts II were successfully reacted with amines to form chelate allylic complexes III (Scheme 1).

SCHEME 1.

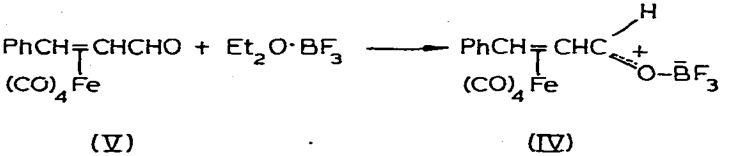


(R=Ph,Me; R'=Me, cyclo-C$_6$H$_{11}$, i-Pr, CH$_2$Ph)

In the present study we investigated the reaction of amines with the adduct formed the between the (cinnamaldehyde)tetracarbonyliron complex (IV) and BF_3, in order to determine how the course of the reaction changes for complexes of unsaturated aldehydes.

Results and discussion

The reaction of (cinnamaldehyde)tetracarbonyliron complex (V) with boron trifluoride etherate in dichloromethane or dichloroethane gives adduct IV in a quantitative yield. The product is poorly soluble in halohydrocarbons and forms a yellow precipitate on addition of $Et_2O \cdot BF_3$ to a solution of V in these solvents (eq. 1). Adduct IV is sufficiently stable to be stored for several weeks



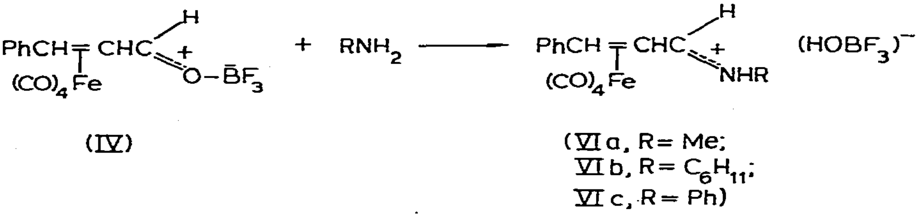
$$\underset{(CO)_4Fe}{PhCH{=}CHCHO} + Et_2O\cdot BF_3 \longrightarrow \underset{(CO)_4Fe}{PhCH{=}CH}\overset{H}{C}{\overset{+}{=}}O{-}\bar{B}F_3 \qquad (1)$$

(V) (IV)

at room temperature. However, donor solvents (water, methanol) rapidly decompose it to the initial complex V.

Coordination of BF_3 to the aldehyde oxygen atom in IV is confirmed by IR spectroscopy. The usual stretching mode of the aldehyde group (1600—1750 cm^{-1}) is absent in the IR spectrum of IV, whereas a new band appears at 1565 cm^{-1} which can be assigned to vibrations of the BF_3-coordinated aldehyde group. Therefore, the shift of the C=O stretching mode on formation of adduct IV is ~100 cm^{-1}, in accordance with literature data for BF_3 adducts of aldehydes and ketones [2]. Electron deficiency at the C_α atom of IV affects the position of absorption bands due to carbonylmetal groups. The increase in electron-withdrawing ability of the ligand results in a shift of these bands to higher frequencies. Thus, the band of totally symmetric in-phase A_1 vibration is displaced by ~20 cm^{-1}.

The reaction of adduct IV with one equivalent of primary amine yields an (olefin)tetracarbonyliron complex VI (eq. 2). Unfortunately, we were unable



$$\underset{(CO)_4Fe}{PhCH{=}CH}\overset{H}{C}{\overset{+}{=}}O{-}\bar{B}F_3 + RNH_2 \longrightarrow \underset{(CO)_4Fe}{PhCH{=}CH}\overset{H}{C}{\overset{+}{=}}NHR \quad (HOBF_3)^- \qquad (2)$$

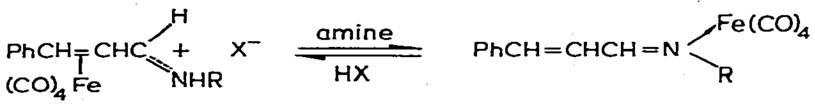
(IV)

(VIa, R = Me;
VIb, R = C_6H_{11};
VIc, R = Ph)

to isolate VI in an analytically pure state due to admixtures of salt-like products, presumably $(PhCH{=}CHCH{=}\overset{+}{N}HR)X^-$ and $R\overset{+}{N}H_3X^-$. Compounds VI were characterized by IR spectroscopy (see Experimental).

The structure of VI as tetracarbonyliron π-complexes is confirmed by their reaction with water which results in (π-cinnamaldehyde)tetracarbonyliron (V).

Treatment of VI with aliphatic amines leads to deprotonation and rearrangement into the σ-*N*-derivatives (VII) (eq. 3). Compounds of this type were



$$\underset{(CO)_4Fe}{PhCH{=}CHC}\overset{H}{\underset{NHR}{\ }}{}^{+}\ X^- \underset{HX}{\xrightarrow{amine}} PhCH{=}CHCH{=}N\overset{Fe(CO)_4}{\underset{R}{\ }} \qquad (3)$$

(VI)

(VIIa, R = Me;
VIIb, R = C_6H_{11};
VIIc, R = Ph)

obtained recently by reaction of $Fe_2(CO)_9$ with cinnamaldehyde anyls [3].

Direct synthesis of VII from BF_3-adducts IV is convenient using two equivalents of primary amine. However, under these conditions VII are formed as end products only when aliphatic amines are used. The reaction of IV with an excess of aniline terminates at the stage of formation of the immonium form VIc, which can be converted into the σ-*N*-complex VIIc by using a stronger base, for instance, triethylamine. The $\pi \rightarrow \sigma$(N) rearrangement (VI) → (VII) is reversible. Thus, protonation of complexes VII with aqueous HBF_4 leads to complexes VI.

Spectral methods did not provide an unambiguous determination of the structure of VII. The positions of CO stretching modes in IR spectra (Table 1) did not differ enough from the positions in chelate π-olefin-σ-carbamylate complexes [4] and the ^1H NMR spectrum is not very informative due to superimposition of signals. A spectral investigation is also complicated by rapid conversion of VII into (azabutadiene)tricarbonyliron complexes (see below). The mass spectra of VII exhibit the appropriate molecular ions and $M - n$CO ions ($n = 1, 2, 3, 4$).

The structure of the complexes formed was solved by X-ray analysis of VIIa. The structure found is shown in Fig. 1, the bond lengths and angles are given in Table 1.

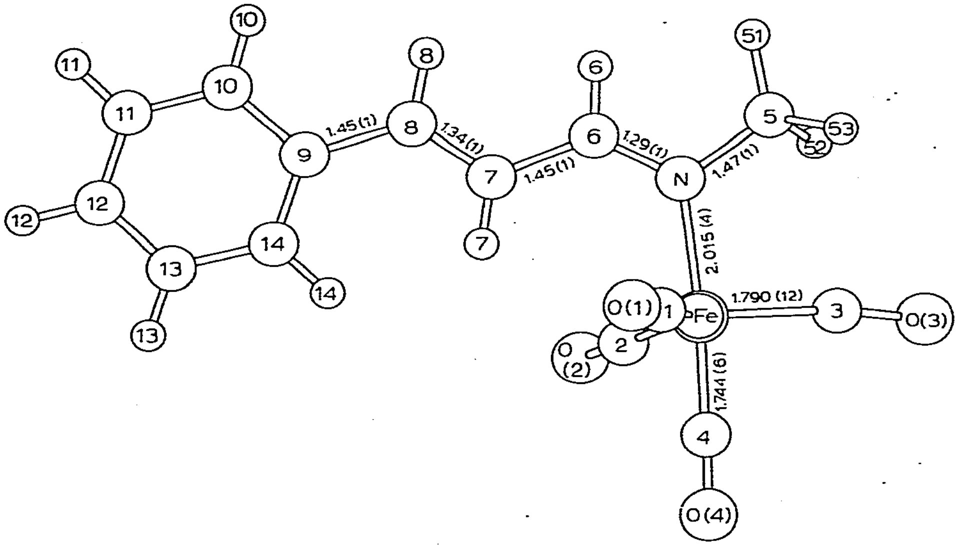


Fig. 1. Molecular structure of complex VIIa.

TABLE 1

BOND LENGTHS (Å) AND ANGLES (°) IN MOLECULE VIIa

Bond	d	Bond	d	Bond	d
Fe—C(1)	1.773(7)	C(4)—O(4)	1.16(1)	C(10)—C(11)	1.38(1)
Fe—C(2)	1.795(6)	N—C(5)	1.47(1)	C(11)—C(12)	1.37(1)
Fe—C(3)	1.803(6)	N—C(6)	1.29(1)	C(12)—C(13)	1.36(1)
Fe—C(4)	1.744(6)	C(6)—C(7)	1.45(1)	C(13)—C(14)	1.38(1)
Fe—N	2.015(4)	C(7)—C(8)	1.34(1)	C(5)—H(51)	1.19
C(1)—O(1)	1.17(1)	C(8)—C(9)	1.45(1)	C(5)—H(52)	1.12
C(2)—O(2)	1.13(1)	C(9)—C(10)	1.39(1)	C(5)—H(53)	1.08
C(3)—O(3)	1.14(1)	C(9)—C(14)	1.38(1)		

Angle	ω	Angle	ω
C(1)—Fe—N	88.7(2)	N—C(6)—C(7)	127.0(5)
C(2)—Fe—N	90.0(2)	C(6)—C(7)—C(8)	120.7(4)
C(3)—Fe—N	94.7(2)	C(7)—C(8)—C(9)	127.7(4)
C(4)—Fe—N	174.5(2)	C(8)—C(9)—C(10)	118.2(4)
C(1)—Fe—C(4)	88.7(3)	C(8)—C(9)—C(14)	124.0(5)
C(2)—Fe—C(4)	87.8(3)	C(10)—C(9)—C(14)	117.9(5)
C(3)—Fe—C(4)	90.9(3)	C(9)—C(10)—C(11)	120.5(5)
C(1)—Fe—C(2)	129.1(3)	C(10)—C(11)—C(12)	120.7(6)
C(1)—Fe—C(3)	116.8(3)	C(11)—C(12)—C(13)	119.2(6)
C(2)—Fe—C(3)	114.1(3)	C(12)—C(13)—C(14)	120.9(6)
Fe—C(1)—O(1)	178.4(6)	C(9)—C(14)—C(13)	120.8(5)
Fe—C(2)—O(2)	177.3(5)	N—C(5)—H(51)	115
Fe—C(3)—O(3)	171.0(6)	N—C(5)—H(52)	104
Fe—C(4)—O(4)	179.4(6)	N—C(5)—H(53)	115
Fe—N—C(5)	120.1(3)	H(51)—C(5)—H(52)	111
Fe—N—C(6)	126.3(3)	H(51)—C(5)—H(53)	118
C(5)—N—C(6)	113.6(4)	H(52)—C(5)—H(53)	90

The Fe atom has a trigonal-bipyramid environment consisting of 4 CO groups and an axial N atom of the imine ligand. The Fe—N distance (2.015(4) Å) is close to the same distance in Fe(CO)$_4$L complexes, where L is pyridine (2.046 Å) or pyrazine (2.031 Å) [5] and is slightly longer than in the 3,3-bis-(methoxycarbonyl)-4-phenyl-1-pyrazoline complex (1.979 Å) [6]. As in the complexes mentioned, the axial Fe—CO bond (1.744(6) Å) is shorter than the equatorial bonds(average 1.790(12) Å). Atoms Fe, C(1), C(2) and C(3) are coplanar within 0.02 Å.

The FeNC(6)C(7)C(8) moiety has *cis* and *trans* configuration with respect to C(6)—N and C(7)—C(8) double bonds, respectively. Atoms N, C(5), C(6), C(7), C(8) lie in one plane (A) (within 0.03 Å), atoms Fe and C(9) are displaced out of this plane by 0.11 and 0.06 Å, respectively. The dihedral angle formed by plane A and the benzene ring plane is only 3.7°. This planarity and shortening of C(6)—C(7) and C(8)—C(9) bonds to 1.45(1) Å suggests considerable conjugation between the C(7)—C(8) and N—C(6) double bonds and the aromatic nucleus.

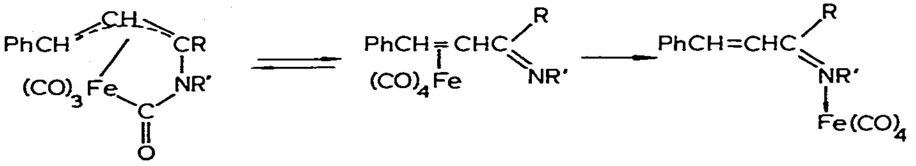
Plane A practically coincides with the plane passing through atoms Fe, C(4) and C(3) (dihedral angle 10.2°). Similar orientation of the ligand is observed in the pyridine complex [5].

The short intramolecular contacts between CH_3 and carbonyl C(3)—O(3) groups (the shortest C(3)···C(5) and C(3)···H(52) distances are 2.96 and 2.65 Å, respectively) results in an increase of the C(3)—Fe—N angle to 94.7(2)° and in distortion of carbonyl group linearity (the Fe—C(3)—O(3) angle is 171.0(6)°). On the other hand, an increase of the angle C(1)—Fe—C(2) to 129.1(3)° may be caused by steric hidrances between carbonyl groups C(1)—O(1) and C(2)—O(2) and atoms C(6) and C(7) (the shortest contacts are C(1)···C(6), 3.25; C(1)···C(7), 3.43; C(2)···C(6), 3.17; C(2)···C(7), 3.16; C(2)···H(7), 2.69 Å).

Molecules in the crystal are arranges at usual van der Waals distances, except for short contacts C(3)···H(53) (2.61) and H(51)···H(53) (1,94 Å) between molecules connected by the glide plane $n(x\frac{1}{4}z)$.

The difference between end products III and VII, formed in the reactions of BF_3-adducts of tetracarbonyliron complexes of unsaturated ketones and aldehydes with primary amines, does not seem surprising if one takes into account the previously established capacity of the allylic complex III to undergo a $\pi \rightarrow \sigma(N)$ rearrangement into VIII, when R = R′= Me (Scheme 2).

SCHEME 2.



(III) (IX) (VIII, R=R′=Me)

In a previous paper [9] we assumed that the σ-*N*-complex VIII is formed as a result of intramolecular reaction of iminic nitrogen with metal in the intermediate eniminic complex IX. If this assumption is correct, the $Fe(CO)_4$ and PhCH=CH moieties in the σ-*N*-complexes VII obtained in the present work should be arranged *cis* in relation to the C=N bond. An X-ray structural study of VIIa confirmed the *cis* arrangement of these groups. This, however, does not completely exclude the possibility of the rearrangement proceeding according to a dissociative mechanism.

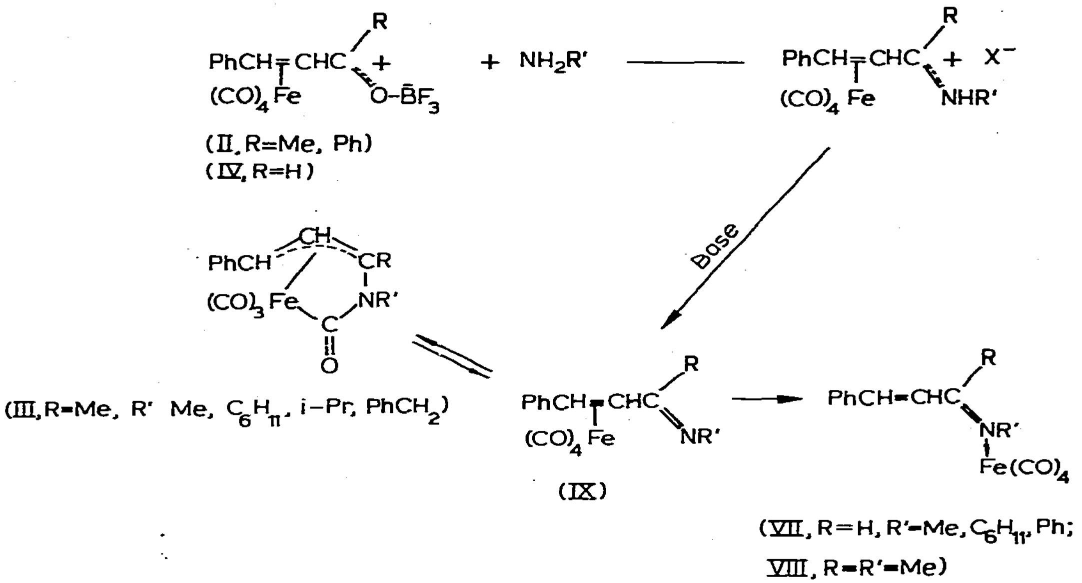
Results obtained in the study of the reactions of BF_3 adducts of (cinnamaldehyde)- and (benzylideneacetone)-tetracarbonyliron complexes with primary amines can be represented by the general Scheme 3.

This scheme shows the important role of steric effects in $\pi \rightarrow \sigma(N)$ rearrangement. Thus, the rearrangement is only possible when *cis* substituents R and R′at the C=N bond are methyl groups or when one of them (R) is a hydrogen atom. In the case of more bulky substituents (R = Ph, Me; R′= iso-C_3H_7, cyclo-C_6H_{11}, $PhCH_2$) the rearrangement does not occur.

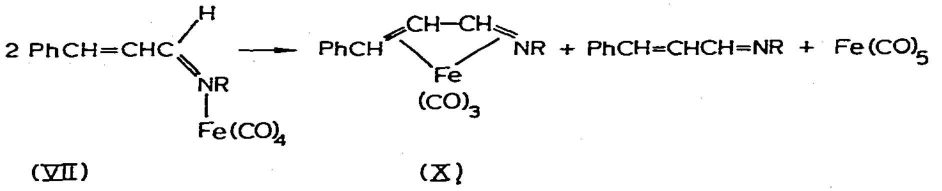
A specific feature of σ-*N*-tetracarbonyliron complexes (VII) is their capacity, solution, to convert into (azadiene)tricarbonyliron complexes (X) at room temperature. The readiness of such conversions seriously complicates the study of VII (eq. 4).

A similar conversion, at a slower rate, is observed for π-allyl-σ-carbamoyl complexes (III), obtained from benzylideneacetone (R = Me). In solution these

SCHEME 3.



complexes readily and reversibly convert (partially) into enimine complexes IX. However, complexes III (with R = Ph), which exist in the solid state and in solution only in the chelate form, do not form (azadiene)tricarbonyliron complexes under the same conditions. These results indicate that conversion into (azadiene)tricarbonyliron complexes X is connected with acyclic π-σ-N-(olefin) or tetracarbonyliron compounds are probably follows a dissociative mechanism.

 (4)

The latter assumption agrees with literature data about the mechanism of formation of tricarbonyliron complexes in the oxadiene series [7].

Experimental

The (PhCH=CHCHO)Fe(CO)$_4$ complex was synthesized according to the literature [8]. IR spectra were recorded with a UR-20 spectrophotometer. Syntheses and isolations of the complexes studied were carried out under an argon atmosphere.

The X-ray analyses were carried out with a "Syntex P-2$_1$" four-circle automatic diffractometer using graphite-monochromated Mo-K_α radiation. Crystals of VIIa are monoclinic, $a = 7.192(4)$, $b = 17.71(1)$, $c = 11.355(8)$ Å, $\beta = 90.39(5)^\circ$, $V = 1446(2)$ Å^3, $M = 313.1$, $d_{exp} = 1.41$, $d_{cal} = 1.44$ g cm^{-3}, $Z = 4$, space group $P2_1/n$. Of the total 2462 independent reflections measured by means of $\theta/2\theta$ - scan technique ($2\theta \leqslant 50°$), 1297 having $F^2 \geqslant 2\sigma$ were used in the analysis.

The structure was solved by the heavy-atom technique and refined by the least squares method to R 0.102 isotropically and then to R 0.069 anisotropically using weighting scheme $W^{-1} = \sigma^2(F) + (0.01\,F_o)^2$. At this stage all hydrogen atoms except H(14) were located in the difference synthesis. Coordinates of H(51), H(52) and H(53) were taken from the difference synthesis, all other hydrogen atoms were placed in calculated positions (with C—H distances of 1.00 Å and isotropic temperature factors with B = 5.00 Å^2). Final refinement (with hydrogen atoms having fixed coordinates and isotropic temperature factors) reduced R to 0.054 and the nearness of fit to 2.23.

TABLE 2

ATOMIC COORDINATES (X 10^4) AND TEMPERATURE FACTORS [a]

Atom	x	y	z	Atom	x	y	z
Fe	1728(1)	—25(1)	2232(1)	C(11)	—5287(9)	3293(4)	158(6)
O(1)	2669(6)	189(3)	—260(4)	C(12)	—6285(7)	2716(5)	—333(5)
O(2)	—1812(6)	183(2)	3436(5)	C(13)	—5608(8)	1999(4)	—263(5)
O(3)	4539(6)	—744(3)	3741(5)	C(14)	—3942(7)	1851(3)	298(5)
O(4)	430(7)	—1529(3)	1624(4)	H(51)	4510	1890	3260
N	2431(5)	1059(2)	2543(4)	H(52)	4010	960	4040
C(1)	2290(8)	115(4)	730(6)	H(53)	320	4140	7960
C(2)	—448(8)	120(3)	2963(5)	H(6)	2030	2170	2440
C(3)	3529(7)	—413(3)	3164(6)	H(7)	—810	1170	1260
C(4)	951(8)	—929(4)	1872(5)	H(8)	—450	2790	1720
C(5)	4180(7)	1237(3)	3159(5)	H(10)	—2850	3620	1070
C(6)	1509(7)	1649(3)	2214(5)	H(11)	—5840	3830	130
C(7)	—243(6)	1664(3)	1571(4)	H(12)	—7540	2820	—740
C(8)	—1138(6)	2316(3)	1382(4)	H(13)	—6390	1560	—640
C(9)	—2899(7)	2427(3)	781(4)	H(14)	—3430	1300	300
C(10)	—3599(7)	3157(3)	703(5)				

Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Fe	3.86(3)	4.25(3)	6.32(4)	0.47(4)	—0.81(2)	0.08(5)
O(1)	9.9(3)	7.3(3)	7.2(3)	—1.0(2)	—0.2(2)	—0.5(3)
O(2)	5.0(2)	7.4(3)	14.9(4)	—0.1(2)	2.2(2)	—1.1(2)
O(3)	6.8(2)	8.4(3)	17.3(4)	0.3(2)	—4.2(3)	4.8(3)
O(4)	11.2(3)	5.1(2)	9.9(3)	—1.2(2)	1.6(3)	—0.9(3)
N	3.5(2)	4.8(2)	5.4(2)	0.2(2)	—1.1(2)	0.1(2)
C(1)	6.1(3)	4.3(3)	7.5(4)	0.3(3)	—0.9(3)	—0.9(4)
C(2)	4.6(3)	5.0(3)	8.5(4)	0.5(3)	—0.9(3)	—0.9(3)
C(3)	4.5(3)	6.2(3)	10.4(5)	0.2(3)	—1.1(3)	2.4(3)
C(4)	6.5(3)	5.8(4)	5.7(3)	0.4(3)	—0.2(3)	0.8(3)
C(5)	4.1(2)	5.2(3)	8.8(4)	—0.3(2)	—2.5(3)	—0.2(3)
C(6)	4.6(3)	4.5(3)	5.1(3)	—0.3(2)	—0.3(2)	—0.5(3)
C(7)	4.4(3)	4.4(3)	5.2(3)	0.0(2)	—0.8(2)	—0.5(2)
C(8)	4.8(2)	3.7(3)	5.5(3)	0.3(2)	—0.2(2)	—0.1(2)
C(9)	4.5(2)	3.8(3)	4.5(3)	0.6(2)	0.2(2)	0.5(2)
C(10)	6.3(3)	4.5(3)	6.3(4)	1.0(3)	—0.3(3)	0.4(3)
C(11)	7.0(4)	6.8(4)	7.6(4)	3.7(3)	—0.4(3)	1.1(3)
C(12)	4.5(3)	9.7(5)	6.9(4)	1.8(3)	—0.9(3)	1.5(4)
C(13)	5.2(3)	6.7(4)	7.2(4)	—0.5(3)	—1.4(3)	1.0(3)
C(14)	5.2(3)	4.3(3)	7.1(4)	1.0(2)	—0.8(3)	0.8(3)

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[a] Anisotropic temperature factors are in the form: $T = \exp -\frac{1}{4}(b_{11}h^2a^{\star2} + b_{22}k^2b^{\star2} + b_{33}l^2c^{\star2} + 2b_{12}hka^{\star}b^{\star} + 1b_{13}hla^{\star}c^{\star} + 2b_{23}klb^{\star}c^{\star})$.

Final coordinates and temperature factors of atoms are given in Table 2.

All calculations were made with a "Eclipse" computer using EXTL programmes.

Preparation of adduct IV

1.5 g of $(PhCH{=}CHCHO)Fe(CO)_4$ (5 mmol) was dissolved in 10 ml of dichloroethane. 1.3 ml (10 mmol) of $BF_3 \cdot Et_2O$ was added to the solution. The yellow precipitate formed was filtered under an argon atmosphere, washed with CH_2Cl_2 and dried in vacuo, yielding 1.6 g of IV. IR: $\nu(C{\equiv}O)$ 2130, 2050 cm^{-1}; $\nu(C{=}O \cdot BF_3)$ 1565 cm^{-1} (Nujol mulls).

Preparation of VIIa

6 g (20 mmol of $(PhCH{=}CHCHO)Fe(CO)_4$ (V) was dissolved in 50 ml of CH_2Cl_2 and 2.8 ml (22 mmol) of $BF_3 \cdot Et_2O$ was added to the solution at —78° C. The BF_3 adduct precipitated. A flow of CH_3NH_2 was then passed through the reaction mixture until the color changed to dark red. The solvent was removed under vacuum and the residue was extracted with petroleum ether. Crystallization from petroleum ether gave 1.75 g of VIIa (Table 3). Mass spectrum (m/e): 313.026 (M), 285.018 (M — CO), 257.03 (M — 2CO), 229.01 (M — 3CO), 201.018 (M — 4CO).

Preparation of VIIb

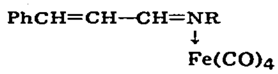
0.7 ml (5.5 mmol) of $BF_3 \cdot Et_2O$ was added to a 1.5 g (5 mmol) of V in 10 ml of CH_2Cl_2 at —78° C. The BF_3 adduct precipitated. 1.4 ml (11 mmol) of $C_6H_{11}NH_2$ in 2 ml of CH_2Cl_2 was then added to the reaction mixture at —78° C. After removal of the solvent under vacuum the residue was treated with a mixture of methanol and acetic acid, filtered, washed with methanol and recrystallized to give 0.6 g of VIIb (Table 1).

Preparation of VIIc

To a solution of 3 g (10 mmol) of $(PhCH{=}CHCHO)Fe(CO_4)$ (V) in 30 ml of CH_2Cl_2 was added 1.4 ml (11 mmol) of $BF_3 \cdot Et_2O$ at —78° C and then 1.42 ml (15 mmol) of $PhNH_2$ in 3 ml of CH_2Cl_2. A fine precipitate of VIc was formed.

TABLE 3

YIELDS, MELTING POINTS AND ELEMENTAL ANALYSES FOR COMPLEXES $PhCH{=}CH{-}CH{=}\underset{\displaystyle Fe(CO)_4}{\underset{\downarrow}{NR}}$ (VII)



R	Yield (%)	M.p. (°C)	Found (calcd.) (%)				Molecular formula	IR (ν, cm^{-1})	
			C	H	Fe	N		$C{\equiv}O$ (heptane)	$C{=}N$ (KBr)
Me 29	29	87—89	53.23 (53.70)	3.69 (3.54)	18.13 (17.84)	— (4.47)	$C_{14}H_{11}FeNO_4$	2049, 1965, 1942	1630
Ph	27	85—86	60.73 (60.83)	3.74 (3.49)	14.73 (14.89)	3.83 (3.73)	$C_{19}H_{13}FeNO_4$	2048, 1968, 1950, 1938	1630
C_6H_{11}	31	78—79	59.56 (59.86)	5.15 (5.02)	14.46 (14.65)	— (3.67)	$C_{19}H_{19}FeNO_4$	2048, 1972, 1962, 1938	1630

The reaction mixture was then treated with 1.65 ml (12 mmol) of triethylamine. The solvent was removed under vacuum and the residue extracted with petroleum ether. Recrystallization from hexane yielded 1 g of VIIc (Table 1).

Preparation of VIa

0.62 g of VIIa was dissolved in 12 ml of CH_2Cl_2 and 6 ml of 5 *N* HBF_4 was added to the solution. After mixing for 30 min at room temperature the color of the reaction mixture changed from dark red to yellow. The organic layer was separated and the solvent evaporated under vacuum. Triple reprecipitation with hexane from CH_2Cl_2 rendered 0.5 g of VIa as a yellow solid. IR (cm^{-1}): $\nu(C\equiv O)$ 2109, 2038, 2022 ($CHCl_3$); $\nu(C=N)$ 1660 (KBr).

Preparation of VIb

(*a*) 1.5 g of $(PhCH=CHCHO)Fe(CO)_4$ was dissolved in 20 ml of CH_2Cl_2 and 0.7 ml (5.5 mmol) of $BF_3 \cdot Et_2O$ was added to the solution. After precipitation of BF_3-adduct VI, 0.7 ml (5.5 mmol) of cyclohexylamine in 5 ml of CH_2Cl_2 was poured into the reaction mixture. The fine precipitate formed was filtered, washed with water, dried and washed with hexane. 1.8 g of a yellow substance was obtained. IR (cm^{-1}): $\nu(C\equiv O)$ 2106, 2053, 2046, 2017 ($CHCl_3$); $\nu(C=N)$ 1650 (KBr); $\nu(N-H)$ 3220 (KBr); $\nu(C=C$ coord.) 1460 (KBr).

(*b*) 3 ml of 5 *N* HBF_4 was added to a solution of 0.2 g (0.5 mmol) of VIIb in 5 ml of CH_2Cl_2. After stirring for 20—30 min the color of the mixture changed from dark red to yellow. The organic layer was separated and the solvent evaporated under vacuum. Double reprecipitation with hexane from CH_2Cl_2 rendered 0.15 g of a yellow solid. IR (cm^{-1}): $\nu(C\equiv O)$ 2107, 2055, 2045, 2020 ($CHCl_3$).

Preparation of VIc

(*a*) 1.4 ml (11 mmol) of $Et_2O \cdot BF_3$ and then 1.42 ml (15 mmol) of aniline in 3 ml of CH_2Cl_2 were added at —78°C to a solution of 3 g (10 mmol) of $(PhCH=CHCHO)Fe(CO)_4$ in 50 ml of CH_2Cl_2. The residue formed was filtered and washed with hexane. 3.5 g of a yellow solid was obtained. IR (cm^{-1}): $\nu(C\equiv O)$ 2112, 2059, 2024 ($CHCl_3$); $\nu(C=N)$ 1650 (KBr); $\nu(C=C$ coord.) 1490 (KBr); $\nu(N-H)$ 3220 (KBR). To a solution of 0.2 g of the substance obtained above in 5 ml of CH_2Cl_2 was added an equal volume of water. After stirring for 30 min the organic layer was separated and evaporated. According to the IR spectrum a mixture of complexes $(PhCH=CHCHO)Fe(CO)_4$ [$\nu(CO)$ 2096, 2093, 2035, 2023, 2018, 1998 cm^{-1}] and $PhCH=CHCH=N(Ph)Fe(CO)_4$ (VIIc) [$\nu(CO)$ 2048, 1968, 1950, 1938 cm^{-1}] was obtained.

(*b*) 0.2 g (0.5 mmol) of VIIc was dissolved in 3 ml CH_2Cl_2 and 3 ml of 5 *N* HBF_4 was added. After 30 min of stirring the color of the reaction mixture changed from dark red to yellow. The organic layer was separated and the solvent evaporated. Triple reprecipitation with hexane from CH_2Cl_2 gave 0.1 g of a yellow solid. IR (cm^{-1}): $\nu(C\equiv O)$ 2110, 2058, 2023 ($CHCl_3$).

Preparation of complexes X

0.1 g of VIIa, b, c was dissolved in 50 ml of hexane at room temperature and the solution was then stored in the dark. After 19 h, according to the IR spectrum, a mixture of (PhCH=CHCH=NR)Fe(CO)$_3$ [ν(C≡O) 2054, 1994, 1976 cm^{-1} (heptane)] and Fe(CO)$_5$ [ν(C≡O) 2023, 2001 cm^{-1} (heptane)] was obtained.

Acknowledgement

The authors are grateful to G.G. Aleksandrov for assistance in carrying out the X-ray experiments and for valuable discussions.

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