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π-ALLYL-σ-CARBAMOYLCARBONYLIRON COMPLEXES FROM BENZYLIDENEACETONE. SYNTHESIS AND π—σ REARRANGEMENT

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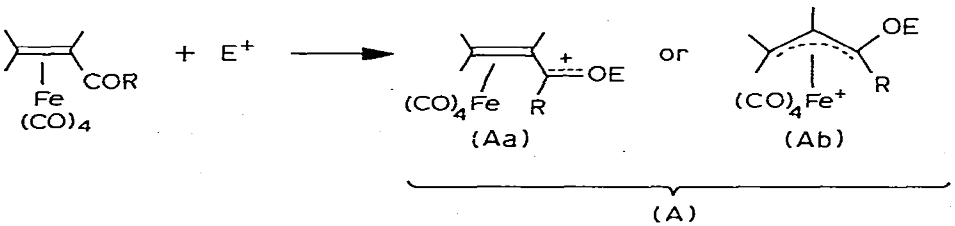
Summary

Chelate π-allyl-σ-carbamoyl carbonyliron compounds (VIII) are formed in the reaction of the BF_3 adduct of $(\pi\text{-PhCH=CHCOMe})Fe(CO)_4$ with primary amines. The presence of a ring—chain tautomeric equilibrium of these compounds with the opened complexes $(\pi\text{-PhCH=CHCMe=NR'})Fe(CO)_4$ (X) is confirmed by IR spectroscopy. In polar solvents the equilibrium is strongly displaced in the direction of chelate compounds VIII.

In the case of the *N*-methyl derivative the ring-chain tautomerism is complicated by a previously unknown $\pi \rightarrow \sigma(N)$ rearrangement with results in the formation of a tetracarbonyliron complex of benzylideneacetone *N*-methylimine with σ-coordination of the metal at the nitrogen atom. The mechanism of this rearrangement is discussed.

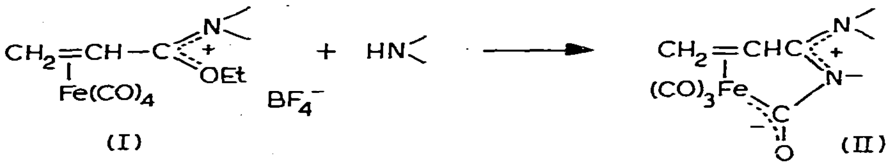
Introduction

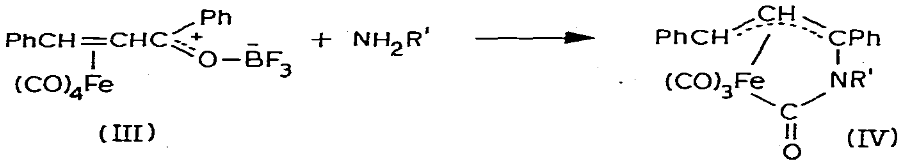
Carbonyliron complexes of α,β-unsaturated carbonyl compounds are readily subjected to electrophilic attack at the oxygen atom [1—3]:



In the above equation the product (A) is depicted in its two possible forms, the olefinic (Aa) and allylic (Ab). These adducts are convenient starting compounds for the synthesis of various organometallic derivatives and for studying the mechanism of carbenium center stabilization by organometallic fragments. The latter problem is directly related to the widely discussed stabilization of carbenium centers with ferrocenyl, cymantrenyl and other similar π-complex systems [4,5]. We shall consider this topic in a separate paper specially devoted to elucidation of the conditions under which structures Aa and Ab are realized [7].

We have previously shown that the compounds I, obtained by ethylation of acrylamide carbonyliron complexes, interact with amines, yielding olefincarbamylate complexes (II) [2]. At the same time, reaction of amines with the adduct III, obtained by treating chalcone tetracarbonyliron complex with boron trifluoride, gives carbamoyl complexes IV [3]. The structure of complexes II and IV was established by X-ray analysis [2,3].



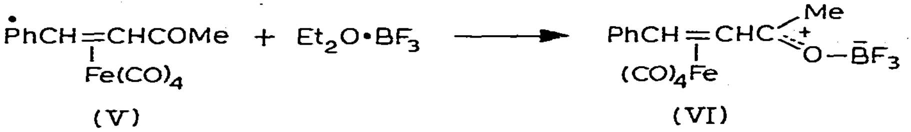


Thus, in both cases the nucleophile attacks the electron-deficient carbon atom, and chelate complexes are formed in which the olefinic form predominates in the first case and the allylic form in the second case.

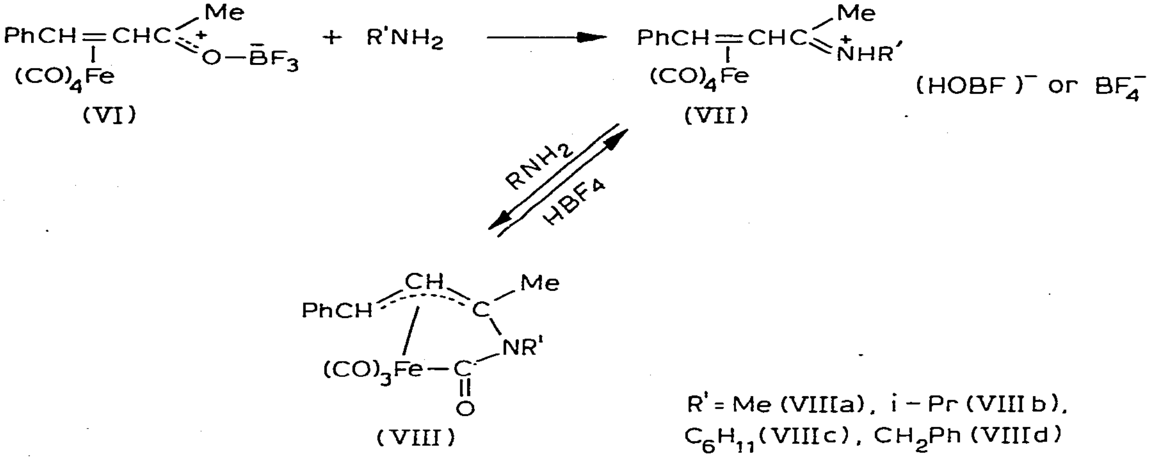
It seemed probable that realization of the olefinic or allylic form depends on the substituent at C_α. Therefore we undertook a similar study of the benzylideneacetone tetracarbonyliron complex V, assuming a proiri that in the case of a methyl substituent, which is even less capable of stabilizing the carbenium center than the phenyl substituent, the allylic structure should be realized.

Result and discussion

Adduct VI was formed by treatment of (π-benzylideneacetone)tetracarbonyliron (V) with boron trifluoride etherate in dichloromethane or toluene. The usual stretching mode of the ketonic group (in the 1600—1750 cm^{-1} region) is absent in the IR spectrum of the adduct. The appearance of a positive charge on the olefin ligand enhances donor-acceptor interaction between the metal and CO ligands and increases the order of the carbon—oxygen bond. As a result the CO stretching vibrations are shifted towards higher frequencies ($\Delta\nu(C{\equiv}O)(A_1) = \sim 25\ cm^{-1}$).



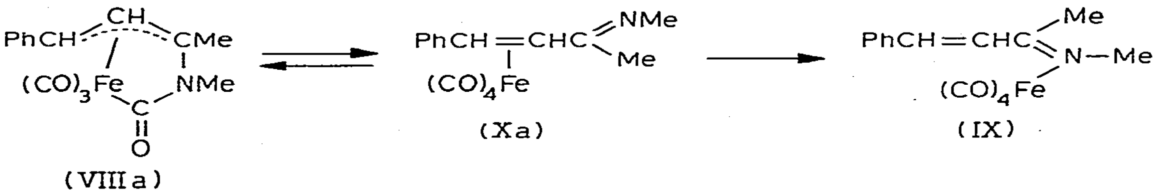
The adduct obtained (VI) is, unlike the initial complex V, very reactive towards amines. Interaction with one equivalent of amine leads to formation of products (VII) which we were unable to isolate in an analytically pure state and which, when treated with a second equivalent of amine, convert into allylcarbamoyl complexes (VIII).



R' = Me (VIIIa), i – Pr (VIII b), C_6H_{11}(VIIIc), CH_2Ph (VIIId)

This conversion is reversible; VIII is protonated by aqueous HBF_4 with formation of VII. On the basis of IR spectral data, the olefintetracarbonyliron structure was assigned to intermediate complexes VII. The end products (VIII) have allylcarbamoyl structures in the solid state. This was confirmed by the similarity of the spectral characteristics of VIII and of the allylcarbamoyl complexes IV (Table 1), the structure of which was established by X-ray analysis [3].

Hence, the methyl substituent at C_α indeed facilitates realization of the allylic form. At the same time, we unexpectedly discovered a pecularity in the behaviour of VIII as compared with IV. The complex VIIIa converts in hydrocarbon solvents into an isomeric complex (IX).

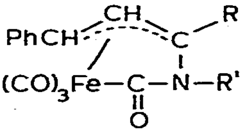


A σ-*N* structure was assigned to IX on the basis of IR and ^{13}C NMR data (see Experimental) and from the similarity of these data with the spectral characteristics of PhCH=CHCH=N(R')Fe(CO)$_4$ compounds, the structure of which was determined by X-ray analysis [7].

It was established by IR spectroscopy (in the 2000 cm^{-1} region) that this conversion proceeds through the intermediate complex Xa (ν(C≡O) 2084, 2018, 1981 cm^{-1}). Examination of VIIIb–d, containing isopropyl, cyclohexyl and benzyl substituents at the nitrogen atom, did not reveal transition into σ-*N*-complexes for these compounds. However, IR spectra of VIIIb–d in non-polar solvents exhibit, in addition to the three bands belonging to the initial

TABLE 1

IR AND NMR SPECTRAL DATA FOR THE COMPLEXES

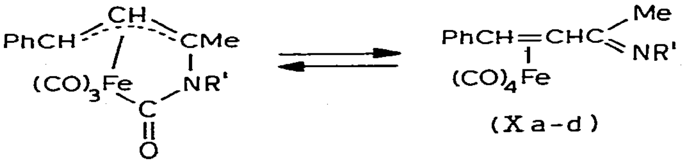


R	R'	ν (cm^{-1})		δ (ppm)(CH_2Cl_2)				
		C=O (hexane)	NC=O (KBr)	C_1	C_2	C_3	NCO [a]	C=O [a]
Me	Me	2068, 2009, 1991	1650	61.62	87.74	100.02	184.69	201.91, 209.98, 210.16
Me	iso-Pr	2068, 2008, 1993	1650	63.05	90.34	95.15	184.00	201.91, 210.29, 210.42
Me	C_6H_{11}	2068, 2008, 1992	1650	63.31	90.34	94.83	184.49	201.97, 210.09, 210.35
Ph	Me	2068, 2012, 1997 [b]	1650	64.48	85.27	114.8	—	—
Ph	C_6H_{11}	2065, 2006, 1993 [b]	1650	65.52	87.03	99.24		

[a] At −70°. [b] Ref. 3.

carbamoyl complexes (~2065, 2010 and 1990 cm^{-1}), three bands at ~2085, 2015 and 1980 cm^{-1} which we assigned to the intermediate compound Xa in the conversion VIIIa → IX.

Thus reversible isomerization of all complexes studied (VIIIa—d) occurs in nonpolar solvents.



(VIII a-d)

(X a-d)

R' = Me (a), i-Pr (b), C_6H_{11} (c), $PhCH_2$ (d)

The relative amount of X in the solution depends first of all on the polarity of the solvent. Its concentration is highest in hydrocarbon solvents. In a heptane/chloroform mixture its quantity decreases with increase of chloroform content. It is impossible to obtain X in a pure state since in solution it exists in equilibrium with VIII while on evaporation or freezing of solutions only the allylcarbamoyl form is isolated. This makes it difficult to establish precisely the structure of X. From the position and character of stretching modes of CO ligands it may be supposed that the complexes X are (π-olefin)tetracarbonyliron complexes * which only for R' = Me (Xa) undergo further conversion into σ-*N*-complexes (IX).

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* For (π-olefin)$Fe(CO)_4$complexes four ν(C≡O) bands are usually observed in accordance with the local C_{2v} symmetry of the $Fe(CO)_4$ group. The band at ~2010 cm^{-1} in the spectra of X possibly overlaps with absorption of VIII.

It should be noted that transition of Xa into IX proceeds relatively slowly while the equilibrium VIII $\rightleftharpoons$ X is established practically immediately. The fact that in polar solvent the equilibrium is shifted towards VIII is not surprising since compounds VIII should be more polar due to the presence of an carbamoyl moiety. If the suggested structure of complexes X is correct we are probably dealing with a new type of ring—chain tautomerism. Unfortunately, the data available at present are not sufficient to reliably establish the mechanism of the conversion VIII → IX. Formation of IX from the intermediate Xa (σ—π rearrangement) by intramolecular attack of the metal at the nitrogen atom with simultaneous cleavage of the olefin—iron π-bond cannot be excluded.

Experimental

$(PhCH{=}CHCOMe)Fe(CO)_4$ was synthesized as given in ref. 6. ^{13}C NMR spectra were recorded with a Bruker-90 instrument (working frequency 22.635 MHz). IR spectra were obtained on a UR-20 spectrophotometer. Synthesis and isolation of complexes was carried out under argon atmosphere.

Preparation of complexes VIII

0.7 cm^3 (5.5 mmol) of $Et_2O \cdot BF_3$ was added to 1.57 g (5 mmol) of $(PhCH{=}CHCOMe)Fe(CO)_4$ (V) in 20 cm^3 of CH_2Cl_2 at —78°C. 0.5 cm^3 of CH_3NH_2 in 7 cm^3 of CH_2Cl_2 was added at —78°C to the precipitated BF_3 adduct. The reaction mixture was then evaporated under vacuum, the residues washed with pentane. Recrystallization from methanol gave 0.5 g of VIIIa.

Under the same conditions 0.6 g of VIIIb was obtained from 1.57 g of V and 0.91 cm^3 (11 mmol) of isopropylamine.

Similarly from 1.57 g of V in 15 cm^3 of toluene treated with 0.7 cm^3 (5.5 mmol) of $Et_2O \cdot BF_3$ and then with 1.4 cm^3 (11 mmol) of $C_6H_{11}NH_2$ we obtained 0.6 g of VIIIc.

0.5 g of VIIId were obtained in the same conditions from 0.93 g (3 mmol) of V in 20 cm^3 of toluene and 0.66 cm^3 (6 mmol) of $C_6H_5CH_2NH_2$.

Yields, melting points and analyses for VIII are listed in Table 2.

TABLE 2

YIELDS, MELTING POINTS AND ELEMENTAL ANALYSES FOR COMPLEXES VIII

Complexes	Yield (%)	M.p. (decomp.) [a] (°C)	Found (calcd.) (%)				Molecular formula
			C	H	Fe	N	
VIIIa	30	79—80	55.07 (55.10)	4.11 (4.10)	16.95 (17.05)	4.25 (4.29)	$C_{15}H_{13}FeNO_4$
VIIIb	33	81—82	57.49 (57.45)	4.90 (4.82)	15.65 (15.68)	3.86 (3.95)	$C_{17}H_{17}FeNO_4$
VIIIc	30	88—89	60.72 (60.77)	5.45 (5.35)	14.02 (14.13)	3.88 (3.54)	$C_{20}H_{21}FeNO_4$
VIIId	40	94—95	62.68 (62.81)	4.32 (4.26)	13.95 (13.88)	3.67 (3.48)	$C_{21}H_{17}FeNO_4$

[a] Complexes recrystallized from methanol.

Preparation of IX

1 g of VIIIa in 100 cm^3 of pentane was agitated by argon flow at 10—15°C. After 30 min the dark-red solution was separated. Another 100 cm^3 portion of pentane was added to the solid residue. This operation was repeated 15 times. The pentane solutions were evaporated and the residue recrystallized from pentane. 0.25 g (25%) of IX as dark-red crystals were obtained, m.p. (dec.) 80°C. Found: C, 54.96; H, 3.95; Fe, 17.04; N, 4.34. $C_{15}H_{13}FeNO_4$ calcd.: C, 55.10; H, 4.10; Fe, 17.05; N, 4.29%. IR (cm^{-1}): ν(C≡O) 2048, 1969, 1962, 1938 (heptane); ν(C=N) 1620 (KBr); ν(C=C) 1580 (KBr). ^{13}C NMR (CH_2Cl_2, —70°C, ppm): δ 216.00 (C≡O); δ 176.11 (C=N); δ 138.42, 134.58, 130.63, 129.52, 128.55, 127.18 (Ph, C=C); δ 55.06 (CH_3N); δ 17.57 (CH_3).

Preparation of VIIb, c

a) 2 cm^3 of 5 *N* HBF_4 was added to 0.15 g of VIIIb in 10 cm^3 of CH_2Cl_2. The mixture was stirred for 15 min and the light-yellow organic layer separated. The solvent was evaporated under vacuum. Reprecipitation of the residue from CH_2Cl_2 with hexane gave 0.10 g of (VIIb), m.p. 90°C (dec.). Found: C, 47.55; H, 4.68; N, 3.35; Fe, 12.34. $C_{17}H_{18}BF_4FeNO_4$ calcd.: C, 46.10; H, 4.10; N, 3.16; Fe, 12.61%. IR (cm^{-1}): ν(C≡O), 2107, 2055, 2040(sh), 2010 ($CHCl_3$); ν(C=N), 1620 (KBr); ν(N—H), 3280 (KBr).

b) 0.7 cm^3 (5.5 mmol) of $Et_2O \cdot BF_3$ was added to 1.57 g (5 mmol) of $(PhCH{=}CHCOMe)Fe(CO)_4$ (V) in 20 cm^3 of CH_2Cl_2 at —78°C. 0.65 cm^3 (5.5 mmol) of $C_6H_{11}NH_2$ in 2 cm^3 of CH_2Cl_2 was then added to the precipitated BF_3 adduct, the reaction mixture evaporated and the residue washed with hexane and water. Drying and reprecipitation from CH_2Cl_2 with abs. ether gave 0.8 g of VIIc as a yellow solid. IR (cm^{-1}): ν(C≡O) 2105, 2053, 2038(sh), 2015 ($CHCl_3$); ν(C=N) 1620 (KBr); ν(C=C) 1455 (KBr); ν(N—H) 3270 (KBr).

Treatment of 80 mg of VIIc obtained above with 0.1 cm^3 of Et_3N in 3 cm^3 of CH_2Cl_2, evaporation of the solvent and excess of Et_3N in vacuo, washing with water and drying yielded 30 mg of VIIIc, identified by its IR spectrum.

Acknowledgement

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