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CHELATE π-ALLYL-σ-CARBAMOYLIRON TRICARBONYL COMPLEXES. PREPARATION AND MOLECULAR STRUCTURE

A.N. NESMEYANOV, M.I. RYBINSKAYA *, L.V. RYBIN, N.T. GUBENKO, N.G. BOKII, A.S. BATSANOV and Yu.T. STRUCHKOV·

Institute of Organo-Element Compounds, Academy of Sciences of the U.S.S.R., Vavilova 28, Moscow B-312 (U.S.S.R.)

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Summary

The π-complex (chalcone)Fe(CO)$_4$ with boron fluoride gives an adduct, which by action of primary amines yields chelate π-allyl-σ-carbamoyl complexes. Their structure has been established by X-ray analysis.

Introduction

It is known that α,β-unsaturated ketones react with primary amines to give additional products on the double carbon—carbon bond. The imines of unsaturated ketones are not obtained. It was interesting therefore to find the conditions necessary to produce ketonic group derivatives from iron—carbonyl complexes of α,β-unsaturated ketones, the double bond of which is protected by coordination with the metal.

We have found previously that the electrophilic activity of the ketonic carbonyl group in these complexes strongly decreases [1]. Such a decrease is obviously due to the electron-releasing properties of the iron tetracarbonyl group and displays the inability of the ketonic group in the complex (π-PhCOCH=CHPh)Fe(CO)$_4$ (I) to react with the nitrogen base without breaking the metal—ligand π-bond.

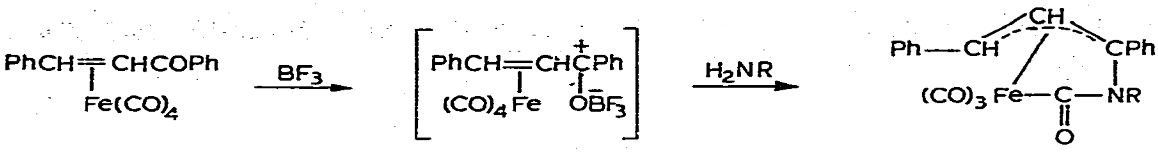
Since the reactions with amines, hydrazines and other nitrogen bases enabled us to obtain a number of the various derivatives, the activation of the carbonyl group in complexes of type I is still on ongoing project.

Results and discussion

In the present paper we have shown that activation of the ketonic group may be reached with Lewis acids. It is known that the attack of electrophiles is directed at the ketonic oxygen atom of the iron carbonyl complexes of α,β-

unsaturated ketones [2,3]. The cationoid species formed by addition of electrophile are stabilized by the presence of the electron-releasing iron carbonyl group.

It turned out that the adduct (II), obtained by the interaction of the chalcone iron tetracarbonyl complex I with boron fluoride is stable enough to be used as the intermediate in subsequent reactions with nucleophiles *. In the present paper the reactions of this adduct with primary amines are described.



(I) (II) (III)

a, R = Me;
b, R = C_6H_{11}

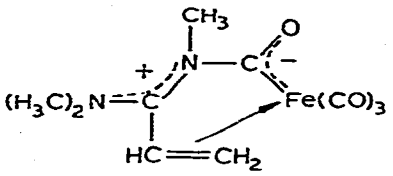
Treatment of adduct II by methyl- or cyclohexylamine gives the complexes III. Complexes III are yellow crystalline substances stable in air and light. The structure of these compounds as carbamoylallyl chelates of iron carbonyls was established by X-ray analysis of IIIb.

Molecular structure of the complex IIIb

Atomic coordinates, bond distances and angles are given in Tables 1, 2 and 3 respectively.

The molecule of complex IIIb consists of a $Fe(CO)_3$ group and an organic ligand, attached to the iron atom via a π-allyl moiety (C5—C6—C7) and an Fe—C4 σ-bond (Fig. 1). The coordination of the iron atom is distorted octahedral, and its outer electron shell is completed to 18 electrons.

The Fe—C4 bond length is 1.978(7) Å, i.e. it is shorter than the sum of the covalent radii (2.11 Å), but close to similar bond lengths in complex IV 1.98(1) Å [6] and acyl iron complexes $(C_6H_6CH{=}CHCO)Fe(CO)_2$ 1.979(5) Å [7], $[OCOMe{=}C(C{=}CMe)CO]Fe(CO)_2$ 2.012 and 2.035 Å [8] and $(OC)_3FeCO{-}C_6H_6{-}C_5H_4Fe(CO)_2$ 1.9596(30) Å [9]). Such shortening cannot be explained by sp^2 hybridization of the carbon atom only.



(IV)

Bonds of the iron atom with CO groups, which are in *cis* positions with respect to C4, are of usual lengths: Fe—C1 1.774(8), Fe—C2 1.768(7) Å. At the same time the Fe—C3 bond in the *trans* position to the σ-bond Fe—C4 is

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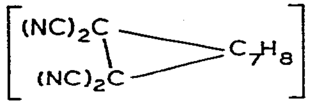
* Similar adducts of uncoordinated ketones are well known [4;5].

somewhat longer (1.846(7) Å). The similar lengthening was previously observed in the complexes IV (*cis* bond distances being 1.74(1) and 1.76(1) Å, *trans* bond 1.80(1) Å) [6] and  Fe(CO)$_3$ (*cis* 1.72(1) Å; *trans* 1.82(1) Å) [10].

The central carbon atom C6 of the π-allyl fragment is somewhat closer to iron (2.089(6) Å) than the terminal atoms C5 and C7 (2.235(7) and 2.180(7) Å respectively). In previously studied π-allyl iron complexes corresponding distances vary in the ranges of 2.05—2.08 and 2.09—2.20 Å respectively [10—14].

Atom C4 is displaced out of the π-allyl plane, C5, C6, C7 towards the Fe atom by 0.617(7) Å, whereas the nitrogen atom deviates from this plane in the opposite direction by 0.293(6) Å, increasing Fe...N separation to 2.62(1) Å. The latter value seems to be too long for any Fe...N bonding interaction.

The plane, defined by carbonyl carbons C1, C2 and C3 is inclined at 7.6° to the π-allyl plane.

The C4 atom has trigonal and the N atom almost trigonal bonding geometry (sums of bond angles are 360.0° and 355.8° respectively). However bond angles at these atoms differ significantly from the ideal value of 120° (Fe—C4—N 100.7(4)°, Fe—C4—O4 134.8(5)°, N—C4—O4 124.5(6)°, C4—N—C5 106.3(5)°,

TABLE 1

ATOMIC COORDINATES (X 10^4)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Fe	3978(1)	1825(1)	2061(1)	C22	2404(7)	5578(6)	3976(6)
O1	2099(5)	509(4)	1717(4)	C23	1173(7)	5585(6)	3834(6)
O2	5629(4)	737(4)	3557(4)	C24	740(6)	4553(7)	3946(6)
O3	4851(4)	1160(4)	258(4)	C25	1110(6)	3818(5)	3221(5)
O4	3556(3)	202(3)	4166(3)	H6	4020	3550	910
N	2744(4)	3044(4)	2811(4)	H7	4820	3070	3140
C1	2847(6)	1013(6)	1836(5)	H9	5580	3550	590
C2	4974(6)	1143(6)	2944(5)	H10	7380	3610	360
C3	4487(5)	1452(5)	916(6)	H11	8920	3360	1780
C4	3417(5)	2278(5)	3261(6)	H12	8590	3080	3490
C5	2911(5)	3162(5)	1750(5)	H13	6810	2980	3760
C6	3925(5)	3318(5)	1632(5)	H15	2630	4420	130
C7	4896(5)	3200(5)	2392(5)	H16	980	4740	—1260
C8	5990(5)	3251(5)	2204(5)	H17	—620	3830	—1200
C9	6182(5)	3436(5)	1213(5)	H18	—680	2610	140
C10	7213(6)	3483(5)	1085(6)	H19	930	2300	1480
C11	8109(6)	3342(6)	1898(7)	H20	2520	3670	4200
C12	7912(6)	3165(6)	2873(6)	H21	2450	5060	2500
C13	6890(6)	3124(6)	3014(5)	H21′	3560	4830	3370
C14	1910(5)	3337(5)	933(5)	H22	2650	6280	3880
C15	1935(5)	4038(5)	151(5)	H22′	2720	5390	4730
C16	1001(7)	4204(5)	—615(5)	H23	810	5830	3100
C17	74(6)	3706(6)	—628(6)	H23′	920	6060	4340
C18	28(5)	3003(5)	142(6)	H24	—80	4550	3850
C19	965(5)	2834(5)	904(5)	H24′	1050	4320	4700
C20	2324(6)	3807(5)	3426(5)	H25	750	4040	2480
C21	2768(6)	4833(5)	3253(6)	H25′	790	3140	3310

TABLE 2

BOND DISTANCES *d* (Å)

Atoms	*d*	Atoms	*d*	Atoms	*d*
Fe—C1	1.774(8)	N—C5	1.48(1)	C14—C15	1.41(1)
Fe—C2	1.768(7)	N—C20	1.48(1)	C15—C16	1.39(1)
Fe—C3	1.846(7)	C5—C6	1.35(1)	C16—C17	1.35(1)
Fe—C4	1.978(7)	C6—C7	1.41(1)	C17—C18	1.40(1)
Fe—C5	2.235(7)	C7—C8	1.47(1)	C18—C19	1.39(1)
Fe—C6	2.089(6)	C5—C14	1.49(1)	C14—C19	1.37(1)
Fe—C7	2.180(7)	C8—C9	1.41(1)	C20—C21	1.53(1)
C1—O1	1.15(1)	C9—C10	1.36(1)	C21—C22	1.53(1)
C2—O2	1.16(1)	C10—C11	1.39(1)	C22—C23	1.52(1)
C3—O3	1.15(1)	C11—C12	1.39(1)	C23—C24	1.52(1)
C4—O4	1.22(1)	C12—C13	1.35(1)	C24—C25	1.53(1)
N—C4	1.39(1)	C8—C13	1.39(1)	C20—C25	1.50(1)

TABLE 3

BOND ANGLES ω (°)

Atoms	ω	Atoms	ω
C1—Fe—C2	102.6(4)	Fe—C5—C6	66.1(4)
C1—Fe—C3	93.9(3)	Fe—C5—N	87.2(4)
C1—Fe—C4	84.3(3)	Fe—C5—C14	130.0(4)
C1—Fe—C5	92.0(3)	C5—C6—C7	127.0(6)
C1—Fe—C6	125.1(3)	Fe—C6—C5	77.9(4)
C1—Fe—C7	158.9(3)	Fe—C6—C7	74.3(4)
C2—Fe—C3	96.7(3)	C6—C7—C8	125.5(6)
C2—Fe—C4	88.0(3)	Fe—C7—C6	67.3(4)
C2—Fe—C5	148.4(3)	Fe—C7—C8	119.3(4)
C2—Fe—C6	130.9(3)	C7—C8—C9	122.6(6)
C2—Fe—C7	92.4(3)	C7—C8—C13	120.4(6)
C3—Fe—C4	177.7(3)	C9—C8—C13	117.0(6)
C3—Fe—C5	112.3(3)	C8—C9—C10	120.1(6)
C3—Fe—C6	92.0(3)	C9—C10—C11	122.6(7)
C3—Fe—C7	97.2(3)	C10—C11—C12	117.0(7)
C4—Fe—C5	65.5(3)	C11—C12—C13	121.1(7)
C4—Fe—C6	85.7(3)	C8—C13—C12	122.3(7)
C4—Fe—C7	81.4(3)	C5—C14—C15	118.8(6)
C5—Fe—C6	36.1(2)	C5—C14—C19	122.6(6)
C5—Fe—C7	67.9(2)	C15—C14—C19	118.7(6)
C6—Fe—C7	38.5(2)	C14—C15—C16	119.0(6)
Fe—C1—O1	177.3(7)	C15—C16—C17	121.6(7)
Fe—C2—O2	176.5(7)	C16—C17—C18	120.5(7)
Fe—C3—O3	174.3(6)	C17—C18—C19	117.8(7)
Fe—C4—O4	134.8(5)	C14—C19—C18	122.4(6)
Fe—C4—N	100.7(4)	N—C20—C21	110.8(5)
O4—C4—N	124.5(6)	N—C20—C25	112.9(5)
C4—N—C5	106.3(5)	C21—C20—C25	111.2(6)
C4—N—C20	123.1(5)	C20—C21—C22	109.1(6)
C5—N—C20	126.4(5)	C21—C22—C23	111.9(7)
N—C5—C6	118.4(5)	C22—C23—C24	111.4(7)
N—C5—C14	115.0(5)	C23—C24—C25	111.5(6)
C6—C5—C14	124.8(6)	C20—C25—C24	110.0(6)

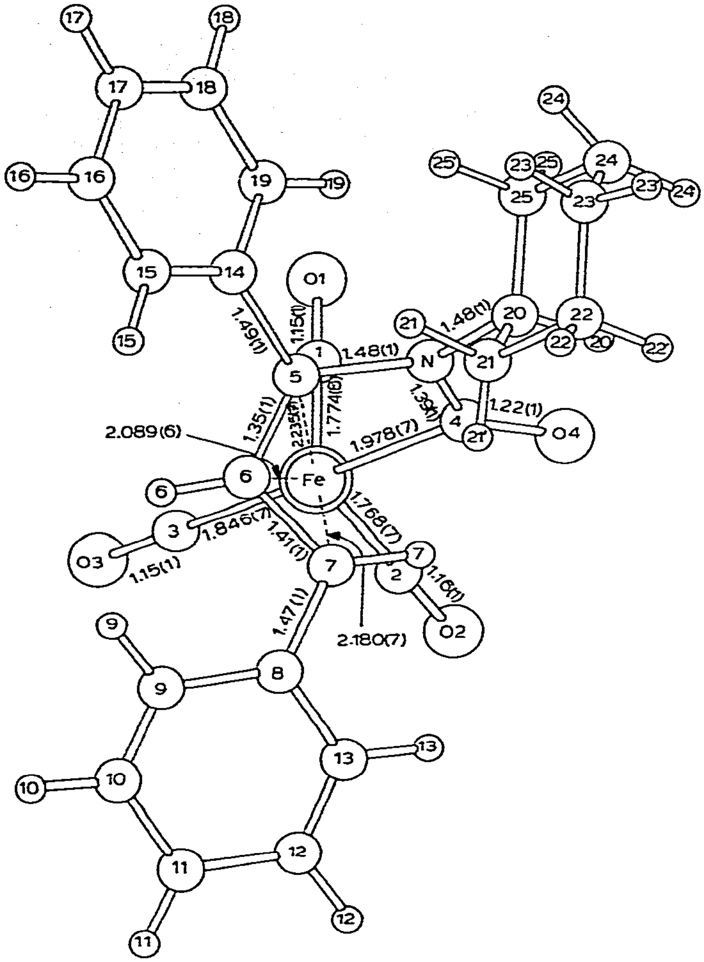


Fig. 1. Structure of molecule IIIb as viewed down the *b* axis.

C4—N—C20 123.1(5)°, C5—N—C20 126.4(5)°). Obviously these distortions reflect a strain of the C4—N—C5 group. Similar distortions were reported for IV [6].

The N—C5 and N—C20 bond distances (both 1.48(1) Å) correspond to single bonds, and the N—C4 distance (1.39(1) Å) to a bond order ~1.5.

The C4—O4 bond length 1.22(1) Å is close to the standard value for the double bond, 1.215 Å [15], and to values previously reported for IV (1.20(1) Å) and acyl iron complexes (1.201—1.208 Å) [6—9].

The phenyl ring at C5 is inclined at 27.6° to the π-allyl plane and the phenyl—allyl conjugation is weak (C5—C14 1.49(1) Å). For the other phenyl ring at C7 the corresponding dihedral angle is only 8.2°, and a significant shortening of the C7—C8 bond (1.46(1) Å) reveals a stronger conjugation.

The cyclohexyl ring adopts a chair conformation and has mean C—C bond length 1.52 Å and mean C—C—C angle 110.8°.

Conclusion

We have found essential structural differences in the case of complexes obtained from the chalcone (complex IIIb) and from *N,N*-dimethylacrylamide (complex IV). At present it is difficult to explain the reasons for such differences. It is possible that they are due to the different electron properties of phenyl and dimethylamine groups or to the different mode of synthesis [6].

Experimental

The IR spectra were recorded in KBr pellets or heptane solutions with a UR-10 spectrometer.

The ^{1}H NMR spectra of complexes IIIa,b were obtained with a Hitachi—Perkin—Elmer R-20 instrument in $CDCl_3$ using hexamethyldisiloxane as internal standard.

The X-ray experiments were made with a Syntex $P2_1$ four-circle computer-controlled diffractometer using the graphite-monocromated Cu-K_α radiation.

Crystal data: $C_{25}H_{23}FeNO_4$, M = 457.31, monoclinic, $a = 12.684(2)$, $b = 13.488(2)$, $c = 13.218(2)$ Å, $\beta = 103.23(1)°$, $V = 2200.4(2)$ Å^3, $D_m = 1.39$, $D_c = 1.38$ g/cm^3, $Z = 4$, space group $P2_1/c$.

Of the total 2669 independent reflections measured by means of θ—2θ scan technique for $2\theta_{max} = 108°$, those 1912 having $F^2 \geqslant 2\sigma(F^2)$, were considered as observed and used in the analysis.

The structure was solved by the heavy-atom technique and refined by full-matrix least squares to R 0.111 isotropically and then to R 0.093 anisotropically. Hydrogen atoms were introduced in calculated positions (with C—H distances of 1.00 Å and isotropic temperature factors of $B = 6.00$ Å^2), 270 weak reflections excluded from refinement and the weighting scheme $w = [\sigma(F^2) + (0.005\ F_0)^2]^{-1}$ $[F_0 \geqslant 4\sigma(F)]$ was used. Final least squares refinement (with non-hydrogen atoms treated anisotropically and hydrogen atoms having fixed coordinates and isotropic temperature factors) reduced R to 0.050 and improved an overall geometry of the molecule.

All computing was made with a "Nova-1200" computer and XTL programmes.

Synthesis of IIIa

BF_3 and argon were passed through 20 ml of dichloromethane solution of 2.35 g (6.2 mmol) of $(PhCH{=}CHCOPh)Fe(CO)_4$ at —78°C over a period of 10 min. Then $MeNH_2$ was passed (10 min) through the reaction mixture and the temperature was raised to 25°C.

The solvent was evaporated under vacuo. The residue was washed with water, and dissolved in chloroform. The solution was washed with water once again. The solvent was evaporated under vacuo. 1.7 g (70%) of complex IIIa was obtained, m.p. 135°C (dec.) (from methanol). Found: C, 61.62; H, 4.16; Fe, 15.45; N, 3.52. $C_{20}H_{15}FeNO_4$ calcd.: C, 61.72; H, 3.88; Fe, 14.35; N, 3.60%. IR: $\nu(C{\equiv}O)$ 2068, 2012, 1997 cm^{-1} (heptane); $\nu(C{=}O)$ 1650 cm^{-1} (KBr). ^{1}H NMR: δ 4.96 (H_α), δ 6.63 (H_β) ppm; $J_{\alpha,\beta} = 9.7$ Hz; δ 2.70 (Me) ppm, δ 7.0—8.0 (Ph) ppm.

Synthesis of IIIb

BF_3 and argon were passed through 20 ml of dichloromethane solution of

3.76 g (10 mmol) of (PhCH=CHCOPh)Fe(CO)$_4$ at −78°C over a period 10 min. The solvent was evaporated under vacuo at −30°C. 2.4 ml (20 mmol) of cyclohexylamine in 20 ml of dichloromethane was added to the residue at the same temperature. After 2 h at −30°C the reaction mixture was heated to room temperature for 30 min.

The solvent was evaporated under vacuo. The residue was washed with water, methanol and dried. 0.7 g of the initial (PhCH=CHCOPh)Fe(CO)$_4$ identified by its IR spectrum was isolated from the methanol solution. 2.20 g (50%) of complex IIIb was obtained, m.p. 95°C (dec.) (from methanol). Found: C, 64.91; H, 5.07; Fe, 12.14; N, 3.02. $C_{25}H_{23}FeNO_4$ calcd.: C, 65.66; H, 5.07; Fe, 12.21; N, 3.06%. IR: ν(C≡O) 2065, 2006, 1993 cm^{-1} (heptane); ν(C=O) 1650 cm^{-1} (KBr). ^{1}H NMR: δ 4.81 (H_α), δ 6.16 (H_β) ppm; $J_{\alpha,\beta}$ = 9.7 Hz; δ 7.0—8.0 (Ph) ppm.

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