Journal of Organometallic Chemistry, 117 (1976) C16—C20

Preliminary communication

THE SYNTHESIS AND STRUCTURE OF THE CHELATE OLEFINCARBAMYLATE COMPLEXES OF IRON CARBONYLS

A.N. NESMEYANOV, T.N. SAL'NIKOVA, YU.T. STRUCHKOV, V.G. ANDRIANOV, A.A. POGREBNYAK, L.V. RYBIN and M.I. RYBINSKAYA*

Institute of Organo-Element Compounds, Academy of Sciences, Moscow (U.S.S.R.)

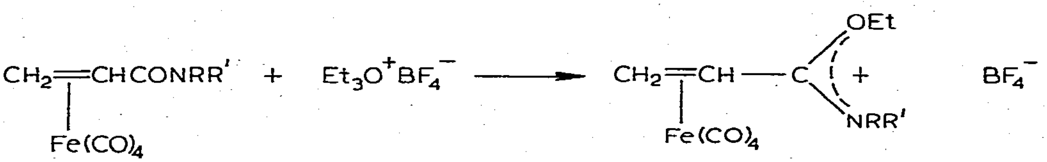
(Received June 15th, 1976)

Summary

The complexes $(CH_2{=}CHCONRR')Fe(CO)_4$ are alkylated by $Et_3O^+BF_4^-$ to give cationic derivatives I, which are used for the synthesis of olefincarbamylate complexes II and olefincarbene complexes III. The structure of II is established by X-ray analysis.

We found that the acrylamide ironcarbonyl π-complexes $(CH_2{=}CHONRR')$-$Fe(CO)_4$, analogous to carboxylic acid amides, may react at normal temperature with triethyloxonium tetrafluoroborate in dichloromethane giving O-ethyl cationic complexes of acrylimidates I (Table 1) in about 70% yield. Tetrafluoroborates (I) are crystalline yellow solids stable in air and to moisture. They were readily precipitated from the reaction mixture with absolute ether and purified by precipitation from methanol and absolute ether*.

The higher stability of the complex cations I with respect to the noncoordinated amidates may be the result of stabilization of the positive charge by electron transfer from the metalcarbonyl group.



(I)

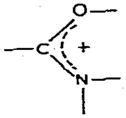
Ia, R = R′ = Me , Ib, R = Me, R′ = H, Ic R = R′ = H

---

*Satisfactory analyses were obtained for all complexes presented in the paper.

TABLE 1

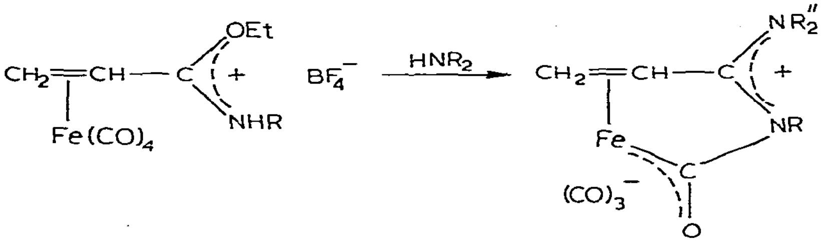
THE IR SPECTRA OF COMPLEXES I, ν (cm^{-1})

Compound	m.p. (°)	C≡O (CHCl$_3$)	 (KBr)
Ia[a]	60—61	2109, 2038, 2011	1628
Ib	69—71	2109, 2047, 2017	1632
Ic	109—110	2110, 2044(sh), 2032, 2009	1684

[a] PMR((CD$_3$)$_2$CO): δ (CH$_2$=) 3.02, 3.18 ppm; δ (CH=) 3.78 ppm; δ (—N(CH$_3$)$_2$) 3.50, 3.70 ppm; δ (—OCH$_2$CH$_3$) 1.48, 4.78 ppm; J_{AM} 3.5 Hz, J_{MX} 9 Hz, J_{AX} 11 Hz.

We have previously shown that the cationic complex Ia may be used for the synthesis of diironhexacarbonyl complexes with a common σ,π-*N,N*-dimethylaminoallyl ligand [1]. The structure of such complexes has been established by X-ray analysis [2].

In this paper we show that the cationic complexes I can be used for the synthesis of the earlier unknown olefincarbamylate chelates II*, which are formed by reaction of I (R′ = H) with the secondary amines HNR$''_2$ in methanol (~ 80% yield).



IIa, R = R″ = Me;
IIb, R = H, R″ = Me;
IIc, R = Me, R$''_2$ = (CH$_2$)$_5$;
IId, R = H, R$''_2$ = (CH$_2$)$_5$

(II)

The complexes IIa—IId are diamagnetic yellow solids (Table 2). The structure of IIa has been established by X-ray analysis. The intensities of 1250 independent reflections were measured with the four-cycle automatic Hilger—Watts diffractometer (ω-scan, MoK_α radiation, graphite monochromator).

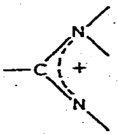
The crystals of IIa are monoclinic: a = 45.401(8), b = 15.246(3), c = 7.4071(5)Å, γ = 102.08(1), V = 5013(2)Å^3, mol.wt. = 280.06, D_{meas} = 1.46, $D_{calc.}$ = 1.49 g cm^{-3}, Z = 16 (two independent molecules), space group $B2/b$. The structure was solved using 1163 reflections with $F^2 \geqslant 2\sigma$ by the direct method and refined by the least squares procedure in isotropic approxima-

---

*We call $-\underset{O^-}{C}-N\textless$ in the complexes II a carbamylate group, analogous to the acylate group $-\underset{O^-}{C}-R$ in LFe(CO)$_3$$-\underset{O^-}{C}-R$ complexes [3,4].

TABLE 2

THE IR SPECTRA OF COMPLEXES II, ν (cm^{-1})

Compound	m.p. (°)	C=O (CHCl$_3$)	 (KBr)	—C(O)— (KBr)
IIa[a]	111—112	2039, 1964, 1947	1640	1585
IIb	128, dec.	2034, 1958, 1940	1640	1605
IIc	52—53	2040, 1964, 1943	1640	1568
IId	144—145, dec.	3031, 1954, 1937	1620	1590

[a] PMR ((CD$_3$)$_2$CO): δ (CH$_2$=) 1.83, 2.13 ppm, δ (—CH=) 3.23 ppm; δ (—N(CH$_3$)$_2$) 3.29, 3.59 ppm; δ (NCH$_3$) 2.81 ppm; J_{AM} 3 Hz, J_{MX} 7.5 Hz, J_{AX} 8.5 Hz.

tion to $R = 0.095$, then in an anisotropic one to $R = 0.065$ (all hydrogen atoms were located by difference synthesis).

The stereochemistry of IIa is shown in Fig. 1 with the mean bond lengths for two independent molecules. The iron atom has a somewhat distorted trigonal-bipyramidal coordination with two CO groups and the ethylene bond in the equatorial plane and one CO and the carbamylate groups in axial positions. The length of the coordinated double bond C(5)—C(6) (1.41(4)Å) and the distance from the Fe atom to its C(5) and C(6) atoms (2.05(3) and (2.02(3)Å) have the usual values. The C(O)—N (Me)—C(NMe$_2$) fragment can be looked upon as a bridge between the ethylene bond and the Fe(CO)$_3$ group causing some strain in the molecule. Thus the ethylene bond is bent out of the Fe(CO)$_2$ equatorial plane towards the carbamylate group: the C(1)FeC(5) and C(1)FeC(6) bond angles decrease to 84(1) and 82(1)° respectively and the angles C(1)FeC(2) and C(1)FeC(3) are close to 90° (87(1) and 90(1)°). The C(O)—N(Me)—C(NMe$_2$) bridge is practically planar (deviations of atoms from the plane are Fe 0.002, C(1) −0.004, N(1) 0.004, C(7) −0.002, O(1) −0.018, C(8) −0.245, N(2) 0.474Å) but somewhat strained (all internal angles at C(1), N(1) and C(7) are less than 120°).

The complex studied is a zwitter-ion with a positive charge distributed between the two nitrogen atoms and one carbon atom of the amidinium group and with a negative charge distributed mainly within the Fe—C(1)—O(1) fragment. Accordingly the bond lengths Fe—C(1) 1.97(2)Å and C(1)—O(1) 1.29(4)Å are greater than those in Fe(CO)$_3$ group (the mean Fe—C and C—O lengths are 1.80(3) and 1.16(4)Å) and are close to the distances in the acylate the distances in the acylate complexes (C$_6$H$_6$CH=CHCO)Fe(CO)$_2$ [5] (Fe—C 1.979 and C—O 1.208Å) and [OCCMe=C(C≡CMe)CO] Fe(CO)$_4$ [6] (Fe—C 2.012, 2.035 and C—O 1.201 and 1.206Å). The positive charge distribution between the two nitrogen atoms and the carbon atom of the amidinium group is confirmed by the planar trigonal geometry of both nitrogen atoms and the C(7) atom, by a considerable decrease of the C(7)—N(1) bond length (1.40 (3)Å) in comparison with the ordinary C—N bond length (1.47Å) and by an increase of the C(7)—N(2) bond length (1.32(3)Å with respect to the double bond C=N (1.26Å).

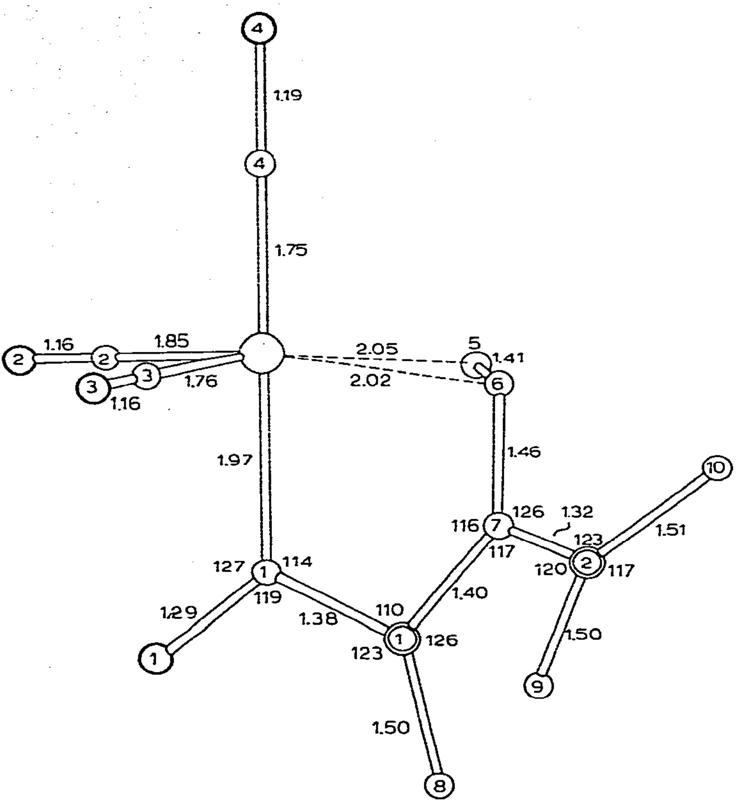
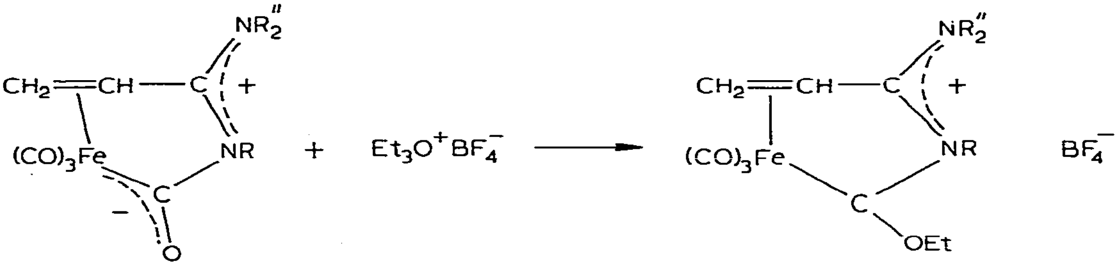


Fig. 1. Stereochemistry of molecule I with main bond lengths and angles. Standard deviations are for bonds: Fe—light atom 0.03 Å between light atoms 0.03—0.04 Å; for angles: 1—2°.

Thus the formation of chelate complexes II may proceed by internal attack of the nitrogen-containing group at the metalcarbonyl group. It should be noted that in [7] nucleophilic attack at the CO ligand has been assumed as the first reaction step of amines and iron pentacarbonyl. Unlike this example, however, where the substances generated are rather unstable the complexes II are quite stable. It may be explained by charge delocalization in the molecule and by the chelate effect.

Similarly to acylate complexes, compounds II and triethyloxonium tetrafluoroborate, at room temperature in dichloromethane, easily give the cationic olefin—carbene iron carbonyl complexes (III)



(II) (III)

The detailed characteristics of complexes III will be presented in our next communication.

References

1 A.N. Nesmeyanov, L.V. Rybin, A.A. Pogrebnyak and M.I. Rybinskaya, J. Organometal. Chem., 108 (1976) 89.
2 A.N. Nesmeyanov, L.V. Rybin, A.A. Pogrebnyak, M.I. Rybinskaya, T.N. Sal'nikova, V.G. Andrianov and Yu.T. Struchkov, Koordinatsion naya Khimiya, 2 (1976) 603.
3 E.O. Fischer and V. Kiener, J. Organometal. Chem., 23 (1970) 215.
4 H.L. Conder and M.Y. Darensbuorg, Inorg. Chem., 13 (1974) 506.
5 P.J. Van Vuuren, R.J. Fletterick, J. Meinwald and R.E. Hughes, J. Amer. Chem. Soc., 93 (1971) 4394.
6 R.C. Pettersen, J.L. Cihonski, F.R. Young and R.A. Levenson, J. Chem. Soc. Chem. Commun., (1975) 370.
7 W.F. Edgell, M.T. Yang, B.J. Bulkin, R. Bayer and N. Koizumi, J. Amer. Chem. Soc., 87 (1965) 3080.