

THE SYNTHESIS OF BINUCLEAR IRON CARBONYL COMPLEXES WITH DIMETHYLAMINOALLYL LIGAND

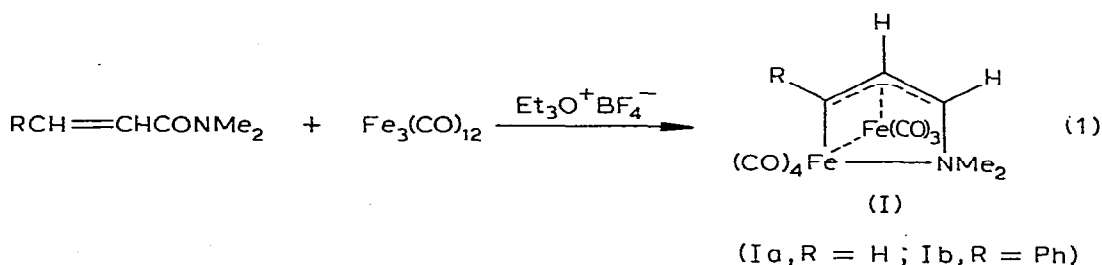
A.N. NESMEYANOV *, L.V. RYBIN, A.A. POGREBNIYAK and M.I. RYBINSKAYA
Institute of Organo-Element Compounds, Academy of Sciences, Moscow (U.S.S.R.)
 (Received March 10th, 1976)

Summary

Binuclear iron carbonyl complexes with a common aminoallyl ligand were obtained by reaction of iminoester salts $[RCH=CHC(OEt)NMe_2]^+BF_4^-$, or their tetracarbonyliron π -complexes $[\pi-RCH=CHC(OEt)NMe_2Fe(CO)_4]^+BF_4^-$, with $Fe_3(CO)_{12}$. Apart from these unsaturated amides, β -aminovinylketone ethylation products $[RC(OEt)CH=CHNMe_2]^+BF_4^-$ or a mixture of the β -aminovinylketone with an alkylating agent may also be used.

Introduction

In a previous paper we have shown [1] that dodecarbonyltriiron reacts with *N,N*-disubstituted α,β -unsaturated amides in the presence of strong alkylating agents giving the binuclear complexes I with both iron atoms bound to the common aminoallyl ligand (eq. 1). The structure of Ib has been established by X-ray



analysis [1].

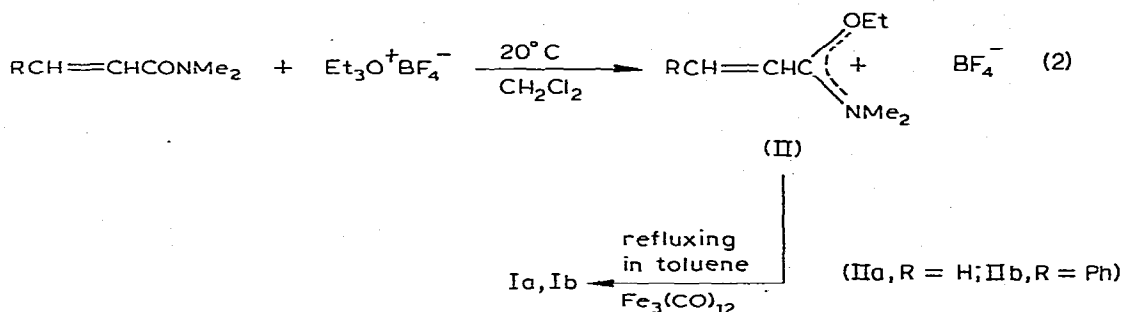
The present paper is concerned with elucidation of some possible intermediate products of this reaction. We have investigated the possibility of preparing complex I from iminoester salts of α,β -unsaturated acids or their tetracarbonyl-

* Author to whom correspondence should be addressed.

iron complexes and $\text{Fe}_3(\text{CO})_{12}$. We have also studied the reactions of $\text{Fe}_3(\text{CO})_{12}$ with β -aminovinylketones in the presence of $\text{Et}_3\text{O}^+\text{BF}_4^-$ and with *O*-ethylated β -aminovinylketone fluoroborates.

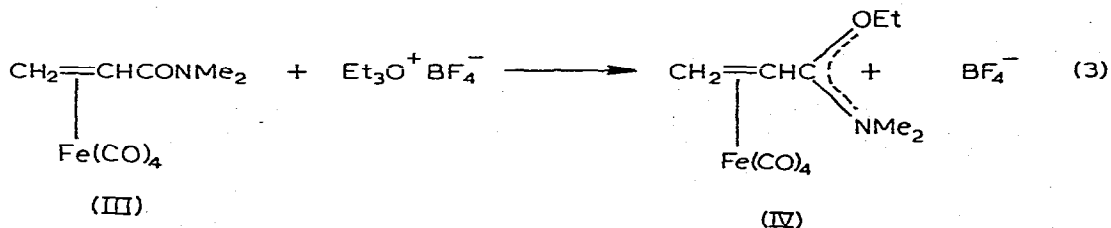
Results and discussion

We found that *N,N*-dimethyliminoesters of acrylic (IIa) and cinnamic acids (IIb), obtained by alkylation of the respective amides with $\text{Et}_3\text{O}^+\text{BF}_4^-$ using the Meerwein reaction [2], when heated with $\text{Fe}_3(\text{CO})_{12}$ in toluene produced complexes Ia and Ib respectively. Their yields were rather low, comparable to the yields obtained from reaction of the amides, $\text{Fe}_3(\text{CO})_{12}$ and $\text{Et}_3\text{O}^+\text{BF}_4^-$ as described in ref. 1 (eq. 2).



With the acryloiminoester salt, besides compound Ia we also obtained another iron carbonyl complex ($\nu(\text{C}=\text{O})$ 2065, 2060, 2017, 1984, 1980, 1962 cm^{-1}). Detailed investigation showed that this complex is also obtained from *N,N*-dimethylacrylamide, upon heating with $\text{Fe}_3(\text{CO})_{12}$ and $\text{Et}_3\text{O}^+\text{BF}_4^-$ (cf. eq. 1). The structure of this compound is under study.

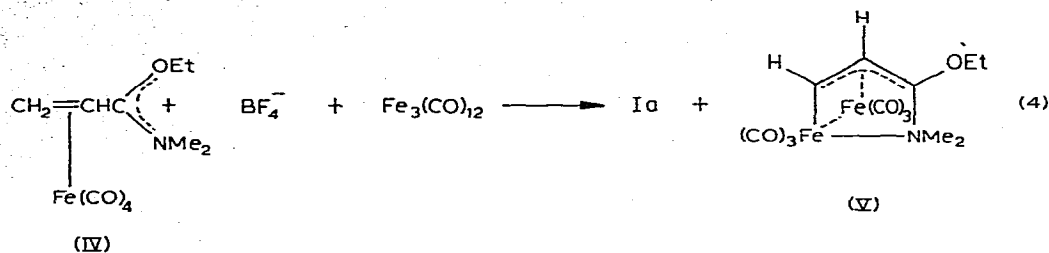
It was interesting to consider the alkylation of the tetracarbonyliron unsaturated amide complexes with provision for further use of the salts in reaction with $\text{Fe}_3(\text{CO})_{12}$. It was shown that the π -complex, $(\text{CH}_2=\text{CHCONMe}_2)\text{Fe}(\text{CO})_4$ (III) may be easily ethylated, under conditions identical to the alkylation of non-coordinated amides, giving the stable complex cation IV (eq. 3).



Cation IV may exist for a long time in aqueous solution, from which it can be isolated as the weakly soluble hexafluorophosphate and tetraphenylborate.

This reaction is an example of the ability of iron carbonyl groups to stabilize the cation center. The acetylation reaction, previously described by us [3], is another example of the ease of reaction of iron carbonyl complexes of α,β -unsaturated carbonyl compounds with electrophilic agents.

Refluxing complex IV with $\text{Fe}_3(\text{CO})_{12}$ in toluene gives the known complex Ia and the hexacarbonyl complex V (eq. 4). The proposed structure of complex



V was confirmed by elemental analysis and spectral data. The mass spectrum showed the respective molecular ion and consecutive cleavage of six CO groups. The IR spectrum of this compound is similar to that of complex Ia; the regions of C=O stretching being almost identical: 2066, 2014, 1991, 1987, 1941 cm^{-1} for V and 2063, 2016, 1985, 1976, 1967, 1946 cm^{-1} for Ia. The PMR spectrum of complex V in CCl_4 shows the signals of ethoxy groups ($\delta(\text{CH}_3)$ 1.24 and $\delta(\text{CH}_2)$ 3.70 ppm), two allyl proton doublets (δ 5.26 and 8.29 ppm, J 1 Hz) and two methyl hydrogen singlets (δ 2.27 and 2.62 ppm).

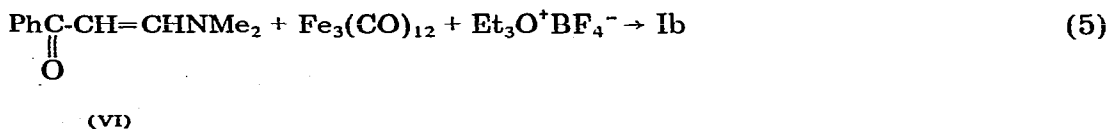
It is interesting to note that complex V is unlikely to be an intermediate in the synthesis of Ia from salt IV and $\text{Fe}_3(\text{CO})_{12}$, since refluxing V in toluene in the presence of $\text{Fe}_3(\text{CO})_{12}$ and $\text{Et}_3\text{O}^+\text{BF}_4^-$ does not produce any of complex Ia.

It should also be noted that we failed to detect complex V in reactions 1 and 2.

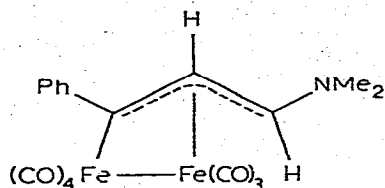
Thus, the composition of the products isolated in reactions 1–3 enable us to assume that the formation of complex I by heating unsaturated amide with $\text{Fe}_3(\text{CO})_{12}$ and $\text{Et}_3\text{O}^+\text{BF}_4^-$ (eq. 1) occurs predominantly via preliminary alkylation of the amide with subsequent reaction of iminoester fluoroborate with iron carbonyl (eq. 2).

The possibility of alkylating $\text{Fe}_3(\text{CO})_{12}$ during the course of the reaction is unlikely since we failed to reveal (IR spectroscopy) any novel iron carbonyl complexes by heating $\text{Fe}_3(\text{CO})_{12}$ with $\text{Et}_3\text{O}^+\text{BF}_4^-$.

The formation of complex I from unsaturated acid amides suggests the reduction of amide carbonyl and possible 1–3 hydrogen migration. Thus, it was reasonable to use β -aminovinylketones, being the isomers of α,β -unsaturated amides, in reaction with $\text{Fe}_3(\text{CO})_{12}$ and $\text{Et}_3\text{O}^+\text{BF}_4^-$. We found that refluxing phenyl- β - N,N -dimethylaminovinylketone (VI) with $\text{Fe}_3(\text{CO})_{12}$ and $\text{Et}_3\text{O}^+\text{BF}_4^-$ in toluene produced complex Ib, although in rather a low yield (eq. 5). The yield of Ib in-



creased when $\text{Fe}_3(\text{CO})_{12}$ was treated with $[\text{PhC}(\text{OEt})\text{CH}=\text{CHNMe}_2]^+\text{BF}_4^-$, prepared by action of $\text{Et}_3\text{O}^+\text{BF}_4^-$ on compound VI. Moreover, in this reaction another binuclear complex, $(\text{PhCHCHNMe}_2) \cdot \text{Fe}_2(\text{CO})_7$ was also obtained, which, on the basis of the data was assigned structure VII. The mass spectrum of complex VII showed the molecular ion with m/e 467 and the fragment ions gen-



(VII)

erated upon consecutive loss of seven CO groups. The IR spectrum showed no absorption in the amide carbonyl stretching region or in the bridged carbonyl region. Thus, we may suggest that fragment $\text{Fe}_2(\text{CO})_7$ contains $\text{Fe}(\text{CO})_3$ and $\text{Fe}(\text{CO})_4$ groups. The absence of bonds between the N and Fe atoms in complex VII may be explained by steric factors, due to the NMe_2 and $\text{Fe}(\text{CO})_4$ groups being in the *syn*- and *anti*-positions of the π -allyl ligand.

Experimental

Phenyl- β -(*N,N*-dimethylamino)vinylketone was prepared from phenyl- β -chlorovinylketone [4]. Triethyloxonium fluoroborate was obtained using the Meerwein approach [5]. $(\text{CH}_2=\text{CHCONMe}_2)\text{Fe}(\text{CO})_4$ was obtained from the respective amide and $\text{Fe}_2(\text{CO})_9$ [6].

IR spectra of the complexes used for identification were taken on a UR-10 spectrophotometer. The mass spectra were obtained on a MX-1303 spectrometer. The complexes were prepared and isolated under argon using absolute solvents.

Ethylation of $\text{CH}_2=\text{CHCONMe}_2$

7.0 g (70 mmol) of *N,N*-dimethylacrylamide was added dropwise to a solution of 13.3 g (70 mmol) of $\text{Et}_3\text{O}^+\text{BF}_4^-$ in 10 ml of dichloromethane. The solution was allowed to stand overnight. The upper layer was removed and the lower layer washed with absolute ether and reprecipitated from alcohol with absolute ether. 12.3 g (86%) of IIa were obtained and identified in the form of tetraphenylborate $[\text{CH}_2=\text{CHC}(\text{OEt})\text{NMe}_2]^+\text{BPh}_4^-$, m.p. 86–87°C (from acetone). Found: C, 82.42; H, 7.74. $\text{C}_{31}\text{H}_{34}\text{BNO}$ calcd.: C, 83.22; H, 7.66%.

Ethylation of $\text{PhCH}=\text{CHCONMe}_2$

3.5 g (20 mmol) of *N,N*-dimethylcinnamamide in 10 ml of dichloromethane was added to a solution of 3.8 g (20 mmol) of $\text{Et}_3\text{O}^+\text{BF}_4^-$ in 10 ml of the same solvent. After a day the solvent was evaporated under vacuo and the remaining oil dissolved in water. An excess of NaBPh_4 was added to the aqueous solution. 7.0 g (67%) of $[\text{PhCH}=\text{CHC}(\text{OEt})\text{NMe}_2]^+\text{BPh}_4^-$ were obtained, m.p. 138–139°C (reprecipitated from acetone/ether). Found: C, 85.24; H, 7.44. $\text{C}_{37}\text{H}_{38}\text{BNO}$ calcd.: C, 84.89; H, 7.32%.

Reaction of $[\text{CH}_2=\text{CHC}(\text{OEt})\text{NMe}_2]^+\text{BF}_4^-$ with $\text{Fe}_3(\text{CO})_{12}$

1.4 g (6 mmol) of the salt and 6.0 g (12 mmol) of $\text{Fe}_3(\text{CO})_{12}$, in 30 ml of toluene, were refluxed with vigorous stirring for 20 min. The toluene solution was separated and the residue extracted with toluene. The toluene solutions

were combined and filtered through a silica gel column. The yellow substance retained on the column was eluted with dichloromethane. After crystallizing from petroleum ether, 25 mg of the yellow crystals were obtained. IR: $\nu(\text{C}\equiv\text{O})$, 2065, 2060, 2017, 1984, 1980, 1962 cm^{-1} (heptane). The toluene filtrate was evaporated under vacuo and the residue chromatographed on a silica gel column. From the main yellow orange band, 0.45 g (19%) of complex Ia, identified by comparison of the IR spectrum with that of an authentic sample [1] were eluted with a mixture of petroleum ether and benzene.

Reaction of $[\text{PhCH}=\text{CHC}(\text{OEt})\text{NMe}_2]^+\text{BF}_4^-$ with $\text{Fe}_3(\text{CO})_{12}$

9.7 g (33 mmol) of the salt and 24.9 g (50 mmol) of $\text{Fe}_3(\text{CO})_{12}$ in 100 ml of toluene were refluxed for 1 h. The solvent was evaporated under vacuo and the residue extracted in benzene. The benzene extracts and the oil were chromatographed on an alumina column with petroleum ether. 3.0 g (20%) of complex Ib, identified by comparison of the IR spectra [1], were obtained.

Ethylation of complex $(\text{CH}_2=\text{CHCONMe}_2)\text{Fe}(\text{CO})_4$ (III)

A solution of 10.7 g (40 mmol) of $\text{CH}_2=\text{CHCONMe}_2\text{Fe}(\text{CO})_4$ and 7.6 g (40 mmol) of $\text{Et}_3\text{O}^+\text{BF}_4^-$ in 30 ml of dichloromethane was allowed to stand overnight at room temperature. The solvent was evaporated under vacuo. The yellow-brown viscous oil was precipitated from methanol with ether and recrystallized from methanol at -78°C . 10.7 g (70%) of the complex salt IV, identified in the form of the hexafluorophosphate, m.p. $101-103^\circ$ (decomp.), were obtained. Found: C, 30.10; H, 3.32; N, 3.49; Fe, 12.15. $\text{C}_{11}\text{H}_{14}\text{F}_6\text{FeNO}_5\text{P}$ calcd.: C, 29.95; H, 3.20; N, 3.17; Fe, 12.66%. IR: $\nu(\text{C}\equiv\text{O})$ 2109, 2038, 2011 cm^{-1} (chloroform).

Reaction of IV with $\text{Fe}_3(\text{CO})_{12}$

1.90 g (5 mmol) of $[\text{CH}_2=\text{CHC}(\text{OEt})\text{NMe}_2\text{Fe}(\text{CO})_4]^+\text{BF}_4^-$ and 2.52 g (5 mmol) of $\text{Fe}_3(\text{CO})_{12}$ in 30 ml of toluene were heated to 110°C for 35 min. The toluene solution was separated and the residue extracted with toluene. The toluene solutions were combined and the solvent was evaporated under vacuo. The residue, a dark oil, was dissolved in benzene and filtrated through an alumina column. Benzene was evaporated under vacuo and the residue separated by TLC on silica gel (petroleum ether/benzene 8 : 1). The following were isolated: (a) a rather small amount (<0.01 g) of dark oil (the upper brown band); (b) 0.05 g of complex Ia, total yield 3%, (c) 0.21 g of complex V in the form of a yellow-orange oil, which slowly crystallized in the refrigerator, yield 10% m.p. $52-53^\circ\text{C}$ (petroleum ether). Found: C, 38.49; H, 3.31; N, 3.42; Fe, 27.70. $\text{C}_{13}\text{H}_{13}\text{NO}_7\text{Fe}_2$ calcd.: C, 38.36; H, 3.22; N, 3.44; Fe, 27.44%. IR: $\nu(\text{C}\equiv\text{O})$ 2066, 2014, 1991, 1987, 1964, 1941 cm^{-1} (heptane).

Reaction of V with $\text{Fe}_3(\text{CO})_{12}$ and $\text{Et}_3\text{O}^+\text{BF}_4^-$

A mixture of 0.10 g (0.3 mmol) of complex V, 0.15 g (0.3 mmol) of $\text{Fe}_3(\text{CO})_{12}$ and 0.10 g (0.5 mmol) of $\text{Et}_3\text{O}^+\text{BF}_4^-$ in 20 ml of toluene were refluxed with stirring for 4 h. IR spectra (every 0.5 h) detected no complex Ia. The solvent was evaporated under vacuo, thin layer chromatography on silica gel (eluent petroleum ether/benzene 8 : 1) returned 0.07 g of the initial complex V.

Ethylation of phenyl-β-N,N-dimethylaminovinylketone (VI)

A solution of 12.2 g (70 mmol) of $\text{PhCOCH}=\text{CHNMe}_2$ and 13.3 g (70 mmol) of $\text{Et}_3\text{O}^+\text{BF}_4^-$ in 50 ml of dichloromethane was allowed to stand overnight at room temperature. The solution was evaporated under vacuo. The residue was washed with benzene and precipitated twice from alcohol with ether. 7.9 g (40%) of $[\text{PhC}(\text{OEt})\text{CH}=\text{CHNMe}_2]^+\text{BF}_4^-$, m.p. 123–124°C, were obtained. Found: C, 53.01; H, 6.06. $\text{C}_{13}\text{H}_{13}\text{BF}_4\text{NO}$ calcd.: C, 53.63; H, 6.23%.

Reaction of $[\text{PhC}(\text{OEt})\text{CH}=\text{CHNMe}_2]^+\text{BF}_4^-$ with $\text{Fe}_3(\text{CO})_{12}$

2.90 g of fluoroborate (10 mmol) and 12.5 g (25 mmol) of $\text{Fe}_3(\text{CO})_{12}$ in 30 ml of toluene were refluxed in vacuo. The residue was extracted with benzene. After removal of the solvent the residue was chromatographed on a silica gel column. The first band eluted with benzene gave 0.12 g (2.7%) of complex Ib, identified by comparison of IR spectra. The second band afforded 0.17 g (3.7%) of complex VII in the form of a yellow solid, which darkened at 80°C. Found: C, 46.70; H, 2.78; N, 2.85. $\text{C}_{18}\text{H}_{13}\text{Fe}_3\text{NO}_7$, calcd.: C, 46.29; H, 2.81; N, 2.99. Mass spectrum showed along with other peaks, the series m/e 467 – $n \times 28$ ($n = 0-7$).

The reaction of phenyl-β-N,N-dimethylaminovinylketone with $\text{Fe}_3(\text{CO})_{12}$ and $\text{Et}_3\text{O}^+\text{BF}_4^-$

A mixture of 1.75 g (10 mmol) of $\text{PhCOCH}=\text{CHNMe}_2$, 2.85 g (15 mmol) of $\text{Et}_3\text{O}^+\text{BF}_4^-$ and 10.06 g (20 mmol) of $\text{Fe}_3(\text{CO})_{12}$ in 50 ml of toluene was refluxed with stirring for 6 h. The solvent was removed under vacuo and the residue extracted with benzene. Chromatography on silica gel with a mixture of benzene and petroleum ether gave 0.02 g (<1%) of complex Ib.

References

- 1 A.N. Nesmeyanov, L.V. Rybin, A.A. Pogrebnyak, M.I. Rybinskaya, T.N. Sal'nikova, V.G. Andrianov and Yu.T. Struchkov, *Koordinatsionnaya Khimiya*, 1 (1975) 971.
- 2 H. Meerwein, W. Florian, N. Schön and G. Stopp, *Ann.* 641 (1961) 1.
- 3 A.N. Nesmeyanov, L.V. Rybin, N.T. Gubenko, M.I. Rybinskaya and P.V. Petrovskii, *J. Organometal. Chem.*, 71 (1974) 271.
- 4 N.K. Kochetkov, M.G. Ivanova and A.N. Nesmeyanov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1956, 676.
- 5 H. Meerwein, *Org. Synth.*, 46 (1966) 113.
- 6 H.E. Dessy, I.C. Charkondian, T.P. Abeles and A.L. Rheingold, *J. Amer. Chem. Soc.*, 92 (1970) 3947.