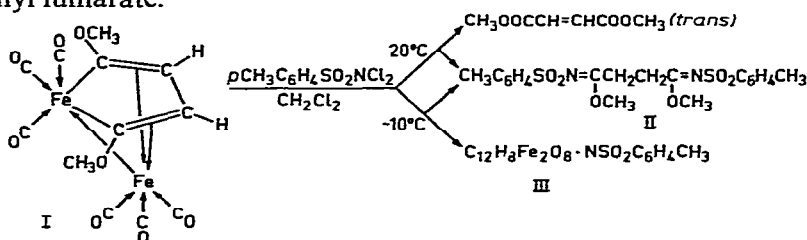


SHORT COMMUNICATION

Organometallic complexes

XVII*. A new type of iron carbonyl complex: the 1-aza-2-ferracyclohexadiene ring

The reaction between (1,1,1-tricarbonyl-2,5-dimethoxyferracyclopentadiene)- π -tricarbonyliron, $C_{12}H_8Fe_2O_8$ (I), and *N,N*-dichloro-*p*-toluenesulphonamide (dichloramine T) was investigated as part of a study of the formation of heterocyclic systems from "acetylene ironcarbonyl" complexes² (e.g. thiophenes^{3,4}, selenophenes^{4,5}, pyrroles^{4,5}, phospholes⁴⁻⁶, γ -pyrones^{4,5}, γ -thiapyrones^{4,5}, γ -selenapyrones^{4,5}). No pyrrole derivative could be isolated but dimethyl *N,N'*-bis(*p*-toluenesulphonyl)succinimide (II) and a new type of complex (III) were found beside some dimethyl fumarate.



At room temperature, only dimethyl fumarate and (II) were isolated (beside toluenesulphonamide and undefined products) whereas at -10° (III) was also obtained in 14% yield.

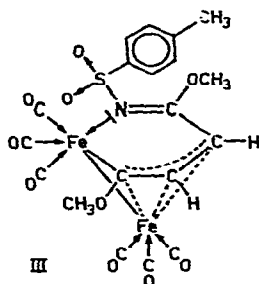
The structure of (II) is based on elemental analysis and the IR spectrum (KBr disc). The strong band at 1595 cm^{-1} is attributed to the $\text{C}=\text{N}$ stretching vibration; imidates have been shown to have high absorption coefficients for this group⁷. The strong bands at 1305 and 1157 cm^{-1} correspond to the absorption by the sulphone group; furthermore, the absence of NH bands rules out the alternative structure, $\text{Tos}-\text{NH}-\text{C}(\text{OCH}_3)=\text{CH}-\text{CH}=\text{C}(\text{OCH}_3)-\text{NHTos}^{**}$ ($\text{Tos} = p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2$).

The elemental analysis of complex(III) shows that it is formally obtained by the addition of a $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{N}$ residue to (I). Its IR spectrum, which shows three peaks for terminal carbonyl groups (at 2088 , 2037 with two shoulders, and 1972 cm^{-1} in CH_2Cl_2) was too complicated to suggest a structure. Reaction of (III) with bromine, FeCl_3 or PPh_3 gave only unidentifiable products. A structure with *N*-tosyl-2,5-dimethoxypyrrole as a ligand coordinating two $\text{Fe}(\text{CO})_3$ groups, one to *N* and one to the two double bonds, a structure similar to pentaphenylphosphole- $\text{Fe}_2(\text{CO})_6$ ⁸, can be excluded on the ground that under the fairly mild degradation conditions used, one would expect to isolate a pyrrole derivative.

In order to elucidate the structure of (III), a single crystal X-ray analysis has been carried out by Rodrique *et al.*⁹, revealing a new type of structure (III).

* For Part XVI see ref. 1.

** The latter type of compound was obtained when a solution of $(\text{PhC}\equiv\text{CPh})_2\text{Fe}_2(\text{CO})_6$ ³ and dichloramine T was irradiated with UV light, yielding $\text{TosNHC}(\text{Ph})=\text{CPh}-\text{CPh}=\text{C}(\text{Ph})-\text{NHTos}$ ⁵.



The net result of the reaction is the insertion of the N-tosyl group between the ring iron atom and the adjacent carbon atom. It is impossible to decide whether this insertion occurs via a nitrene intermediate, which could possibly be formed by reduction of dichloramine T by the zerovalent iron present in complex (I), or via a stepwise ionic mechanism. It is notable that the insertion takes place at the weakest covalent bond. One tricarbonyliron group is coordinated to the six-membered ring via a π -allylic system, involving the donation of three electrons. In order to satisfy the rare gas rule, a Fe-Fe covalent bond is required, in contrast to the Fe-Fe dative bond found in complexes of type (I)^{10,3}. The closely related alternative structure (fig. 1)

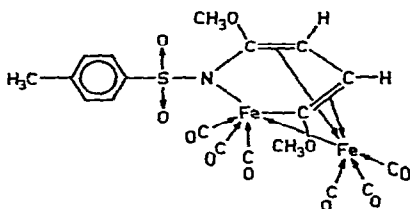


Fig. 1.

which was originally also contemplated, is ruled out from the interatomic distances measured in the "Fe- π -allyl" system.

It is assumed that the formation of dimethyl N,N'-bis(*p*-toluenesulfonyl)succinimide (II) proceeds through insertion of a second N-tosyl residue in the remaining Fe-C covalent bond of (III) forming an unstable intermediate complex which would be hydrolyzed very rapidly to (III) during work up. [Complex (III) is partially decomposed by short contact with 2 *N* HCl and completely with 3-4 *N* HCl].

Experimental*

(1,1,1-Tricarbonyl-2,5-dimethoxyferracyclopentadieneiron)- π -tricarbonyliron (I) was prepared according to Sternberg *et al.*¹¹.

Reaction of (I) with dichloramine T: compounds (II) and (III)

At room temperature. Dichloramine T (13 g; 54.6 mmoles) was added in small portions to a solution of 6 g (14 mmoles) of (I) in 100 ml of methylene chloride; each

* With the technical assistance of Mr. E. WITTOUCK. The elemental analyses were carried out by Miss D. GRAF, Messrs. F. GOES and R. HOUQUET.

addition provoked a gas evolution. After standing overnight, FeCl_2 was filtered off and the filtrate shaken rapidly with 2 N HCl. The dried organic layer was evaporated and the residue, taken up in benzene, was chromatographed on silica gel. Elution with CH_2Cl_2 gave 0.07 g of dimethyl fumarate (identified by m.p. 103–105° and IR spectrum). With diethyl ether, 0.2 g of (II) was eluted as colourless needles of m.p. 220–221° (from $\text{CH}_2\text{Cl}_2/\text{EtOH}$). (Found: C, 53.28; H, 5.02; N, 6.41; O, 21.38; S, 14.16. $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_6\text{S}_2$ calcd.: C, 53.08; H, 5.35; N, 6.19; O, 21.21; S, 14.17%.) The mother liquors of (II) yielded *p*-toluenesulphonamide.

At -10° . To a solution of 6 g of (I) in 100 ml of CH_2Cl_2 cooled to -10° , a cold solution of 13 g of dichloramine T in 100 ml of CH_2Cl_2 was added dropwise. After standing overnight in a refrigerator, the filtered reaction mixture was washed twice with 2 N Na_2CO_3 , the dried (CaCl_2) organic layer evaporated and the residue, dissolved in benzene, chromatographed on silica gel. Elution with benzene gave 0.07 g of dimethyl fumarate. With methylene chloride, 1.22 g [14.3% calcd. on (I)] of (III) was eluted. Crystallization from methylene chloride/petroleum ether gave red crystals which decomposed at 150–165° without melting. (Found: C, 40.92; H, 2.80; Fe, 20.10; N, 2.97; O, 28.38. $\text{C}_{19}\text{H}_{15}\text{Fe}_2\text{NO}_{10}\text{S}$ calcd.: C, 40.67; H, 2.70; Fe, 19.91; N, 2.50; O, 28.50%.) Further elution with methylene chloride/ether yielded 0.12 g of $[\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{N}=\text{C}(\text{OCH}_3)\text{CH}_2^-]_2$ (II); *p*-toluenesulphonamide was obtained from the last fractions.

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