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REACTION OF DICARBONYL (*pentahapto*-CYCLOPENTADIENYL)-(OLEFIN)IRON CATIONS WITH SODIUM AZIDE

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Summary

Reaction of the $(h^5\text{-}C_5H_5)Fe(CO)_2(C_2H_4)$ cation with sodium azide yields the azido complex $(h^5\text{-}C_5H_5)Fe(CO)_2N_3$ by ligand displacement, rather than the isocyanate complex $(h^5\text{-}C_5H_5)Fe(CO)(C_2H_4)(NCO)$ as had previously been reported. The azido complex may also be obtained from other $(h^5\text{-}C_5H_5)Fe(CO)_2$-(olefin) cations or in low yield from $(h^5\text{-}C_5H_5)Fe(CO)_2Cl$. The azido complex is converted to the isocyanate complex $(h^5\text{-}C_5H_5)Fe(CO)_2(NCO)$ in low yield by photolysis, and to a triazole complex on treatment with dimethyl acetylenedicarboxylate.

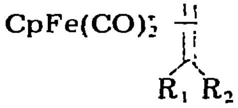
The reaction of the ethylene complex Ia with sodium azide in aqueous acetone has been reported to give a single product, m.p. 123—124°, in 65% yield, which was formulated as the isocyanato complex III [1] on the basis of its infrared spectrum. No NMR spectral data were given.

These results appeared anomalous to us in view of the reactions of cationic olefin complexes $(h^5\text{-}C_5H_5)Fe(CO)_2$(olefin) (I) with enolates, enamines and organometallic nucleophiles of general structure $(h^5\text{-}C_5H_5)Fe(CO)_2(h^1\text{-allyl})$ [2]. More extensive investigations with organolithium and Grignard reagents as well as with phosphines, phosphites, phosphoranes, alkoxides, thiols and amines [3] have shown that in general reaction products are derived either from addition of the nucleophile to the coordinated olefin or from attack at the metal center.

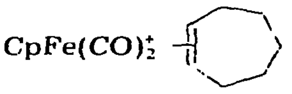
Nucleophilic addition to a carbonyl ligand, in related cationic complexes, occurs only when an effective alternative acceptor center is not available. The reactions of $(h^5\text{-}C_5H_5)Fe(CO)_3^+$ and $(h^5\text{-}C_5H_5)Fe(CO)_2PPh_3^+$ with azide [4], hydrazines [5], amines [6], and aryllithium reagents [7] exemplify such a process. However, even here, incursion of competitive addition to the cyclopentadienyl ring is observed with benzyllithium [7b], and this course of reaction becomes the exclusive one when attack on the carbonyl ligands by aryllithium reagents is impeded by replacement of a carbonyl ligand with PPh_3 [7a]. Preferential addition to the cyclopentadienyl ring of $(h^5\text{-}C_5H_5)Fe(CO)_2PPh_3^+$ is also observed with borohydride [8]. The reactions of $(h^5\text{-}C_5H_5)Fe(CO)_2CS^+$ with azide, hydrazine, amines and alkoxides likewise yield products derived from nucleophilic addition to coordinated CS [9], while the reactions of C_6F_5Li with $(h^5\text{-}C_5H_5)$-$Fe(CO)_2(CNCH_3)^+$ [10] further exemplify the comparatively low reactivity of coordinated carbon monoxide toward nucleophiles.

We have therefore repeated the reactions of sodium azide with Ia, but were unable to obtain the product reported earlier [1]. Instead, a red crystalline substance, m.p. 72—73° (dec.), corresponding to a formula $C_7H_5FeN_3O_2$, was consistently obtained. The same product is also formed in the reaction of sodium azide with the corresponding propylene, isobutylene, butadiene and cycloheptene complexes (Ib—Id and II), although the best yields are obtained with the latter complex.

A comparison of this substance with the azido complex IV, prepared from $(h^5\text{-}C_5H_5)Fe(CO)_2(H_2O)^+$ and sodium azide, following the procedure recently reported by Dombek and Angelici [11], show them to be identical. The complex is also obtained in low yield by the reaction of sodium azide with $(h^5\text{-}C_5H_5)Fe$-$(CO)_2Cl$.

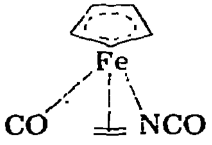


(I)

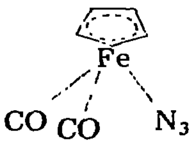


(II)

[Ia, $R_1 = R_2 = H$;
Ib, $R_1 = H$, $R_2 = Me$;
Ic, $R_1 = R_2 = Me$;
Id, $R_1 = H$, $R_2 = (CH{=}CH_2)$]



(III)



(IV)

The azido complex is very resistant to both photochemical and thermal decomposition. No reaction was evidenced when IV was refluxed in acetone solution for 1 h in the presence of ethylene, while decomposition at 100° in toluene solution saturated with carbon monoxide gave only the dimer $[h^5\text{-}C_5H_5Fe(CO)_2]_2$. Photolysis of benzene solutions of IV in the presence of carbon monoxide, employing a 3500 Å light source led, after four hours, to the recovery of 39% of starting material. No $(h^5\text{-}C_5H_5)Fe(CO)_2NCO$ complex could be detected in these reactions. Only when photolysis of benzene solutions of IV is conducted in a quartz apparatus with 2537 Å light does conversion to $(h^5\text{-}C_5H_5)Fe(CO)_2NCO$ occur, and then in very low yield.

The mass spectrum of IV provides some evidence for the formation of a nitrene in the fragmentation of the parent ion. This fragmentation takes two

TABLE 1

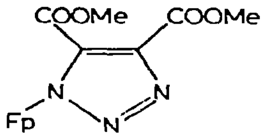
MASS SPECTRUM OF $(h^5\text{-}C_5H_5)Fe(CO)_2N_3$[a]

m/e	I(% of base peak)	Metastable transitions	Found	Calcd
219	47			
191	20	219 → 191+28	165 5	(165.6)
187	22	191 → 163+28	139.1	(139.1)
186	99	163 → 135+28	111 8	(111 8)
177	29			
163	80	219 → 177+42	143 0	(143 0)
149	45	177 → 149+28	125.6	(125.4)
135	54	149 → 121+28	98 4	(98.4)
122	28			
121	100	186 → 121+65	78.7	(78.8)
95	41			
94	33			
81	33			
56	100			

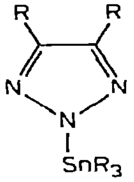
[a] At 100°C and 70 eV

independent paths, one involving the initial loss of 42 mass units (N_3), followed by the successive loss of two fragments of mass 28, and a second path proceeding through successive loss of three fragments of mass 28. These data are summarized in Table 1.

The azido complex IV reacts with dimethyl acetylenedicarboxylate in refluxing benzene to give the metallated triazole V. Similar dipolar cycloaddition reactions have been reported for triphenyllead azide [12] and for trialkyltin azides [13] with acetylenes.



(V)



(VI)

The triazoles derived from the corresponding azido tin complexes have been shown to be 2-substituted triazoles VI, formed by rearrangement of the initial cycloaddition product [14]. It is not possible, on the basis of present evidence, to exclude such a rearrangement in the reaction of IV, but the presence of two carbonyl absorptions in the infrared spectrum of the triazole is more in accord with V than with the isomeric 2-substituted triazole structure.

Experimental

All manipulations were conducted under nitrogen in flame dried apparatus. Solvents were dried, stored over molecular sieves and degassed before use. IR spectra were recorded on a Perkin–Elmer Model 457 spectrophotometer and NMR spectra on a Varian A-60 spectrometer (NIH GM-13183). Mass spectra were obtained on an A.E.I. MS-12 direct inlet spectrometer (NSF GP-3644).

Melting points were determined in sealed capillaries and are uncorrected. Analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Preparation of h^5-cyclopentadienyldicarbonylazidoiron (IV)

A solution of Ib (0.612 g, 2.0 mmol) in degassed acetone (30 ml) was treated with a solution of NaN_3 (0.130 g, 2.0 mmol) in degassed distilled H_2O (2 ml) at 0°. The solution was stirred at 0° for 1 hour, and was then filtered, and evaporated under reduced pressure. The residue was dissolved in 1/1 H_2O/CH_2Cl_2, extracted with 3 × 25 ml CH_2Cl_2, and the organic layers were combined, dried over $MgSO_4$, filtered and evaporated to leave an oily red residue. Chromatography on 65 g of activity III neutral alumina, with CH_2Cl_2 gave a dark green band which yielded the dimer $[(C_5H_5)Fe(CO)_2]_2$ (0.037 g). A slower moving red band yielded red crystalline IV. It was recrystallized from CH_2Cl_2/hexane to give 162 mg (37%), m.p. 72.5—73° (dec). IR (KBr): $\nu(CO)$ 2055, 1985 cm^{-1}, $\nu_{as}(N_3)$ 2000 cm^{-1}, $\nu_s(N_3)$ 1276 cm^{-1}; ($CHCl_3$) $\nu(CO)$ 2060, 2005 cm^{-1}, $\nu_{as}(N_3)$ 2010 cm^{-1}; (CS_2) $\nu(CO)$ 2050, 1995 cm^{-1}, $\nu_{as}(N_3)$ 2010 cm^{-1}. NMR(acetone-d_6): τ 4.70 ppm (s, Cp). Similar reactions with Ia, Ic, and Id gave the same product. The best yield (82%) was obtained with II.

Analysis found: C, 38.43; H, 2.52; N, 18.97. $C_7H_5FeN_3O_2$ calcd.: C, 38.39; H, 2.30; N, 19.19%.

Reaction of $C_5H_5Fe(CO)_2Cl$ with NaN_3

A deep red solution of $C_5H_5Fe(CO)_2Cl$ (0.425 g, 2.0 mmol) and NaN_3 (0.143 g, 2.2 mmol) in 10% aqueous acetone (11 ml) was refluxed at 56° for 3 h. The mixture was cooled, and 15 ml of CH_2Cl_2 was added followed by drying over $MgSO_4$. The mixture was filtered, evaporated and the product was chromatographed on activity III neutral alumina. Elution with CH_2Cl_2 gave the dimer $[C_5H_5Fe(CO)_2]_2$ followed by a red band yielding the azido complex (0.080 g, 18%). The same product was obtained following the procedure of Dombek and Angelici [11].

Preparation of 1-[(h^5-cyclopentadienyl)dicarbonyliron]-1,2,3-triazole-4,5-dicarboxylate (V)

A solution of IV (0.217 g, 1.0 mmol) and dimethylacetylene dicarboxylate (0.142 g, 0.07 ml, 1.0 mmol) in 10 ml of benzene was heated under reflux at 89—90° for 3 h. After cooling, filtration and evaporation of the residue afforded a yellow-orange solid. Recrystallization from benzene/hexane under nitrogen gave 137 mg (37%), m.p. 155.5—156.5° (gas evol.). IR (KBr): $\nu(CO)$ 2075, 2015 cm^{-1}, $\nu(CO_2Me)$ 1750, 1730 cm^{-1}. NMR ($CDCl_3$): τ 4.76 (s, 5H, Cp), 6.12 (s, 6H, CO_2Me).

Analysis found: C, 42.93; H, 2.99; N, 11.39. $C_{13}H_{11}FeN_3O_6$ calcd.: C, 43.22, H, 3.07; N, 11.67%.

Irradiation of IV

Complex IV (0.219 g, 1.0 mmol), dissolved in CO-purged benzene (15 ml) was photolyzed at 3500 Å and at 15° for 4 h under CO. Continuous monitoring of the reaction solution by IR showed no formation of $(C_5H_5)Fe(CO)_2NCO$. After 4 h 37% of unchanged azido complex was recovered.

Complex IV (0.033 g, 0.15 mmol) in CO-purged benzene (2.0 ml) was photolyzed at 2537 Å in a quartz fluorescence cell under CO at ambient temperature for 5 h. The solution was filtered and chromatographed on 10 g activity III neutral alumina. Elution with CH_2Cl_2 gave three bands. The first gave 5 mg of a mixture (3/1) of h^5-$C_5H_5Fe(CO)_2(h^1$-$C_5H_5)$ and ferrocene, identified by NMR. The second band gave 13 mg of recovered IV (37.5%). The last band gave 6 mg (30%) of $(C_5H_5)Fe(CO)_2NCO$, m.p. 98–99°.

Pyrolysis of h^5-cyclopentadienyldicarbonylazidoiron (IV)

Complex IV (0.110 g, 0.50 mmole) in acetone (10 ml) was refluxed at 56° with continuous introduction of ethylene for one hour. No change was observed spectroscopically.

The complex IV (0.022 g, 0.10 mmol) in CO-purged toluene (1.5 ml) was pyrolyzed at 100° under CO for 4 h. The reaction mixture was then cooled, filtered and the filtrate evaporated to give a dark red solid identified as the dimer, $[CpFe(CO)_2]_2$. No isocyanate complex was observed in the filtrates.

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