Journal of Organometallic Chemistry, 220 (1981) 181—186
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

THE THERMOLYSIS AND PHOTOLYSIS OF η^6-AZIDOBENZENE-η^5-CYCLOPENTADIENYLIRON HEXAFLUOROPHOSPHATE

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(Received May 25th, 1981)

Summary

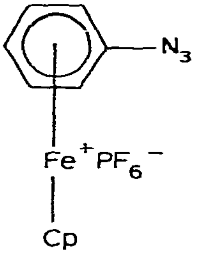
η^6-Azidobenzene-η^5-cyclopentadienyliron hexafluorophosphate (I) was synthesized and its thermolysis and photolysis under different experimental conditions were studied. Both reactions gave rise to various amounts of a ring contraction product, cyanoferrocene, and in most cases some η^6-aniline-η^5-cyclopentadienyliron hexafluorophosphate. The formation of these products may be explained as arising from the phenylnitrene complex as a reaction intermediate. The contrast in behaviors of the uncomplexed phenylnitrene and the complexed nitrene from I is also discussed.

Introduction

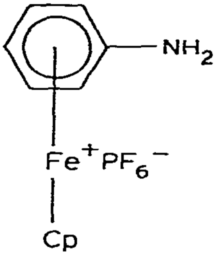
It is known that the thermolysis or photolysis of organic azides may give rise to nitrenes which can give a variety of products under different experimental conditions [1,2]. As an extension of our studies on η^6-arene-η^5-cyclopentadienyliron cations obtained from ligand exchange reactions between ferrocene and various arenes [3—5], we have investigated the thermally and photochemically induced decompositions of η^6-azidobenzene-η^5-cyclopentadienyliron hexafluorophosphate (I) in an attempt to ascertain the behavior of the nitrene generated from such an azido-substituted arenecyclopentadienyliron complex.

Results and discussion

The azido complex I was prepared from the treatment of η^6-chlorobenzene-η^5-cyclopentadienyliron hexafluorophosphate with NaN_3 in dimethylformamide. Pyrolysis of a pure sample of I without any solvent at 165°C in a vacuum sublimator (about 1 Torr) resulted in an explosive decomposition of the substrate. Work-up of the resulting material gave η^6-aniline-η^5-cyclopentadienyliron hexafluorophosphate (II) and cyanoferrocene (III) in yields of 44% and 18%, respectively. The same products, II and III, were also obtained when the thermolysis of I was carried out in cyclohexane solution. After such a solution was heated under pressure at 120°C for 36 h, the yields of II and III were 59% and 17%, respectively. Even under the relative mild conditions of refluxing a cyclohexane solution of I for 60 h, 23% and 6% yields, respectively, of II and III were obtained.



(I)



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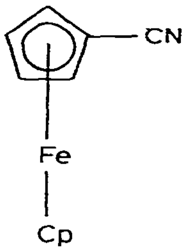
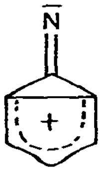


(III)

The photolysis of I was carried out in a Rayonet photochemical reactor equipped with 3000 Å lamps. Irradiation of a dilute solution of I in cyclohexane at ambient temperature for 3 h gave a 17% yield of cyanoferrocene (III) and about 11% of an impure product containing probably both unchanged reactant I and the aniline complex II. In addition, 43% of the unchanged reactant I was recovered. A similar irradiation of I in CH_2Cl_2 gave only a 10% yield of III and a 19% recovery of unreacted I. There was no detectable formation of II. A 7.8% yield of ferrocene was also obtained, while in the photolysis of I in cyclohexane, no ferrocene was detected.

From the above results, it is seen that the thermolysis of I, either without any solvent or in cyclohexane solution, gave the aniline complex II, and some ring contraction product, the cyanoferrocene III. The photolysis of I in cyclohexane gave similar results. In CH_2Cl_2, however, apparently some further photolytic decomposition could occur, leading to lower yields and the recovery of some ferrocene which possibly might be derived from cleavage of the cyanoferrocene. The formation of II likely resulted from H abstraction reactions, a well known process presumably involving triplet nitrenes [2]. The ring contraction reaction of the azido-complex I to III is of considerable interest. Such a transformation in the free ligand was first reported in 1967 by Crow and Wentrup [6], and soon after in 1968 by Hedaya and coworkers [7], in the gas phase pyrolysis of phenyl azide at temperatures of 600°C or higher to give 1-cyano-1,3-cyclopentadiene. More recently, Munro and Pauson [8] have reported the formation of the cyanocyclopentadienyltricarbonylmanganese complex when azidobenzenetricarbonylmanganese hexafluorophosphate was heated to above 130°C. The presently observed ring contraction reaction of I is quite similar to the findings of Munro and Pauson.

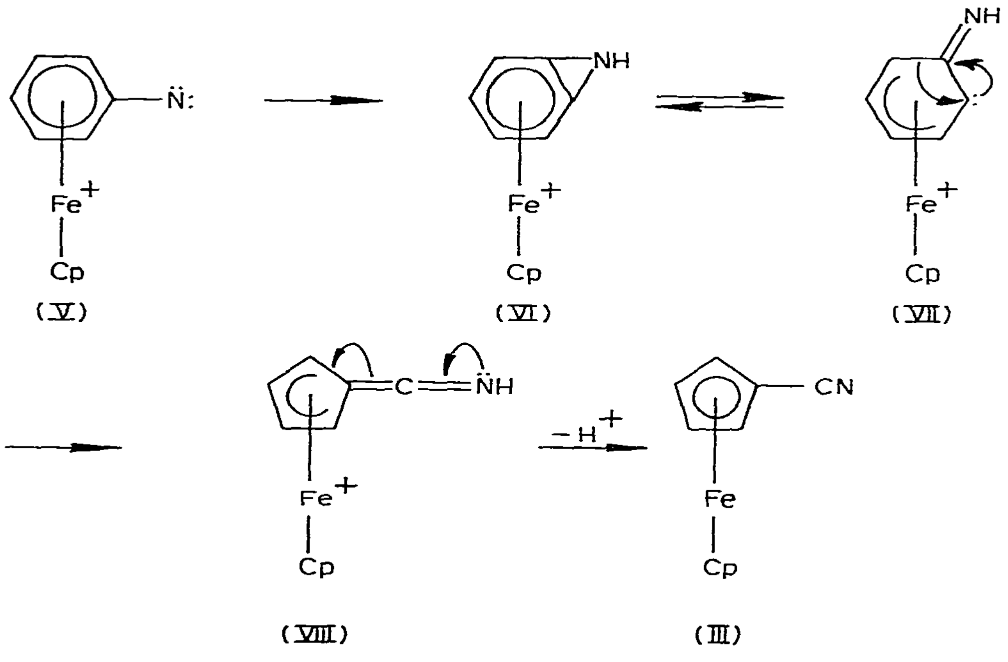
The mechanism of the ring contraction in the free ligand has been the subject of a number of investigations. Because of the high temperature required, it was originally suggested that a vibrationally excited or "hot" singlet nitrene may be involved in an intramolecular insertion leading to cyanocyclopentadiene [6]. The early suggestion that a species such as IV may be an intermediate [7,9] was later eliminated by some of the same workers [10]. The more recent work



(IV)

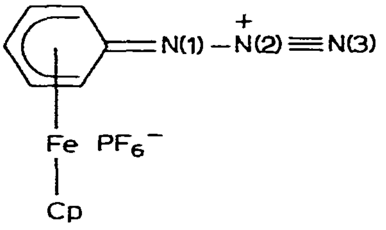
of Wentrup and his coworkers [11—13] has established the most probable mechanism as involving the interconversion of phenylnitrene to an iminocarbene followed by a Wolff-type of rearrangement to give the ring contraction. In accordance with the mechanism of Wentrup, the formation of III may be depicted as shown in Scheme 1. An intramolecular insertion by nitrene V gives

SCHEME 1.

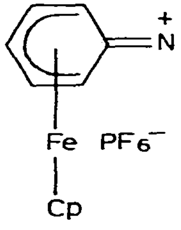


rise to the 1*H*-benzazirine complex VI which isomerizes to an iminocarbene, the iminocyclohexadienylidene complex VII. A Wolff-type rearrangement of the iminocarbene gives the ring contraction product VIII which readily loses a proton to give cyanoferrocene III, the overall ring contraction reaction being I → III + N_2 + HPF_6.

A marked difference in the ring contraction reaction for the azido-complex I and for the free ligand, phenyl azide, is that relatively low temperatures are sufficient to cause the reaction in the organometallic systems studied in the present work and by Munro and Pauson [8], while a very high temperature is required to bring about the same reaction in the phenyl azide [6,7]. As was pointed out by Munro and Pauson [8], an additional resonance structure IX can be written for the azido-complex I, while for the free ligand there is no counterpart to give an equivalent resonance contribution. It was suggested [8] that this implies a lowering of the N(1)—N(2) bond order, thus allowing for the loss of N_2 to give the nitrene at lower temperatures.



(IX)



(X)

Another factor may also play a part in enhancing the ease of the ring contraction reaction. As shown in Scheme 1, a key step initiating the ring contraction is an intramolecular insertion (V → VI) which likely involves singlet nitrene acting as an electrophile in the insertion [2]. The complexation of the nitrene to the electron-withdrawing $CpFe^+$ moiety should increase the electrophilic character of the nitrene. Moreover, a resonance contribution from structure X, which has no counterpart in the uncomplexed phenylnitrene, should also increase the electrophilic character. Hence both inductive and resonance effects should enhance the ease of the electrophilic insertion, giving rise to a more facile ring contraction reaction in the organometallic system. Thus the present work suggests that in both the thermolysis and photolysis of the azido-complex I, the nitrene initially formed is in the excited singlet state, part of which may undergo electrophilic insertion leading eventually to cyanoferrocene III. The remainder of the excited nitrene decays to the triplet state and then undergoes H abstraction to give the aniline complex II.

Experimental

η^6-Azidobenzene-η^5-cyclopentadienyliron hexafluorophosphate (I)

The η^6-chlorobenzene-η^5-cyclopentadienyliron cation was prepared from ligand exchange between ferrocene and chlorobenzene, effected in the presence of $AlCl_3$-Al and isolated as the hexafluorophosphate [14,15]. To a solution of 2.00 g (5.3 mmol) of the above hexafluorophosphate salt of the chlorobenzene complex in 25 ml of dry DMF, 2.50 g (38.5 mmol) of NaN_3 was introduced. After stirring in the dark and at room temperature for 24 h, the reaction mixture was filtered. The brown filtrate was diluted with twice its volume of CH_2Cl_2 and an excess of ether was added. On cooling with stirring in an ice bath, a yellow precipitate was obtained. This precipitate was dissolved in a minimum of acetone and then chromatographed through an alumina column (25 cm × 2.5 cm dia.). Elution of the yellow band with 1/1 mixture of CH_2Cl_2/acetone gave a yellow solution which, after removal of the solvent and recrystallization from CH_2Cl_2/acetone/ether gave 1.70 g (83%) of η^6-azidobenzene-η^5-cyclopentadienyliron hexafluorophosphate (I). The product darkened in color when heated to above 130°C but did not melt at temperatures of up to 230°C. ^1H NMR:

δ(acetone-d_6) 5.33(s, 5H, Cp), 6.57(m, 5H, arom.). Anal. Found: C, 34.52; H, 2.74; N, 10.91. $C_{11}H_{10}N_3F_6PFe$ calcd: C, 31.31; H, 2.62; N, 10.95%.

Vacuum pyrolysis of I

The azido-complex I (1.00 g, 2.6 mmol) was pyrolyzed in a vacuum sublimator at 165°C and about 1 Torr for less than 10 min. There was an explosive decomposition and the apparatus was filled with dark particles. These particles were taken up in acetone and mixed with above 1.0 g of alumina. After evaporation of the acetone under reduced pressure, the residual alumina with its absorbed products was introduced onto the top of an alumina column. On washing with Skelly B, a yellow band developed on the column. The elution of this band with Skelly B led to the recovery of 0.10 g (18%) of golden yellow crystals which proved to be cyanoferrocene (III). It melted at 105—106°C (lit. [16] m.p. 103—104°C); its IR spectrum was as reported [17] for cyanoferrocene with a characteristic C≡N absorption at 2230 cm^{-1}. ^1H NMR: δ(acetone-d_6) 4.40(s, 5H, Cp), 4.50(m, 2H, H's α to CN), 4.75(m, 2H, H's β to CN).

After the elution of III, the eluting solvent was changed to a 3/1 mixture of CH_2Cl_2/CH_3OH. A brownish orange band developed on the column. Elution of this band followed by removal of the solvent and trituration with ether gave 0.41 g (44%) of a brownish orange powder which was identical to a sample of η^6-aniline-η^5-cyclopentadienyliron hexafluorophosphate (II) prepared from the $LiAlH_4$ reduction of I. The product also showed essentially the same IR and NMR spectra of the aniline complex II as reported by Helling and Hendrickson [18].

Thermolysis of I in cyclohexane solution

A solution of 1.00 g (2.6 mmol) of I in 70 ml of cyclohexane was placed in a pressure flask with a tight-fitting ground glass stopper. The flask was put into a cast iron bomb equipped with a screw-on lid. The bomb was then filled with cyclohexane to provide an equalizing pressure outside of the flask when the system is heated. The bomb, with its lid in place, was then immersed in an oil bath maintained at 120°C for 36 h. After cooling, the content in the reaction flask was washed into a round bottom flask with acetone. The solvent was then removed under reduced pressure. The residue was taken up in acetone and chromatographed through an alumina column. As described in the preceding section, elution with Skelly B followed by elution with CH_2Cl_2/CH_3OH gave, respectively, 93 mg (17%) of cyanoferrocene III and 548 mg (59%) of the aniline complex II.

In another experiment, a solution of 1.50 g (4.0 mmol) of I in 30 ml of cyclohexane was refluxed under N_2 for 60 h. The solvent was then removed under reduced pressure and the residue was taken up in acetone and chromatographed through an alumina column. Elutions with Skelly B, with a 1/1 mixture of Skelly B/CH_2Cl_2 and with a 3/1 mixture of CH_2Cl_2/CH_3OH gave, respectively, 40 mg (6% based on the non-recovered I) of cyanoferrocene III, 314 mg (21%) of recovered azido-complex I, and 252 mg (23% based on the nonrecovered I) of the aniline complex II.

Photolysis of I

A solution of 515.5 mg (1.34 mmol) of I in 400 ml of CH_2Cl_2 in a Pyrex reaction vessel was photolyzed in a Rayonet photochemical reactor equipped with 3000 Å lamps for 3 h. The solvent was then removed under reduced pressure. The dark brown residue was extracted with ether in order to separate the non-ionic materials. After the ether was removed, yellowish orange crystals were obtained. These crystals were redissolved in ether, 2.0 g of alumina was added and after the ether was evaporated off, the alumina with its absorbed products was placed on top of an alumina column for chromatography. The first band was eluted with Skelly B to give 19.5 mg (7.8%) of yellowish orange crystals, the IR and NMR spectra of which were identical with those of an authentic sample of ferrocene. Further elution with a 3/1 mixture of Skelly B/CH_2Cl_2 gave 28.3 mg (10%) of cyanoferrocene III.

The ionic residue from the photolysis reaction mixture that remained after the ether extraction was dissolved in a minimum of CH_3NO_2 and chromatographed through another alumina column. Elution with CH_3NO_2 gave 95.9 mg (19%) of recovered unreacted azido-complex I.

In a similar experiment, a solution of 518.2 mg (1.35 mmol) of I in 400 ml of cyclohexane was photolyzed in the Rayonet reactor for 3 h and then worked up as described above. From the ether extracted non-ionic materials, elution with Skelly B failed to give any ferrocene; but elution with a 3/1 mixture of Skelly B/CH_2Cl_2 gave 48.5 mg (17%) of cyanoferrocene III. From the ionic residue remaining after the ether extraction, the first fraction eluted with a 1/4 mixture of CH_3NO_2/CH_2Cl_2 gave 223.8 mg (43%) of recovered I. A second fraction, eluted with CH_3NO_2, weighed 57.9 mg (about 11%); the IR and NMR spectra of which suggested that it was probably a mixture of unreacted I and the aniline complex II.

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