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Preliminary communication

THE STEREOCHEMISTRY OF THE HYDROGENATION DURING LIGAND EXCHANGE REACTIONS BETWEEN FERROCENE AND 9,10-DIMETHYLANTHRACENE

R.G. SUTHERLAND, W.J. PANNEKOEK AND C.C. LEE*

Department of Chemistry and Chemical Engineering, University of Saskatchewan,

Saskatoon, Saskatchewan S7N 0W0 (Canada)

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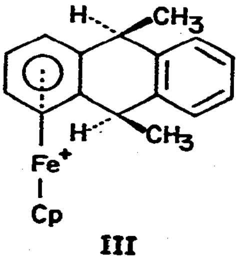
Summary

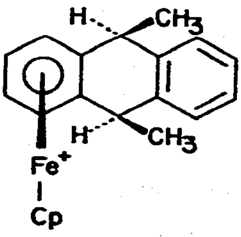
The reaction of 9,10-dimethylanthracene with FcH-$AlCl_3$-Al in decalin at 130°C gave stereospecifically the η^6-cis-(endo-9,10-dihydro)-9,10-dimethylanthracene-η^5-cyclopentadienyliron cation (III), the H atoms at C-9,10 being introduced from the same side of the ring system as the CpFe group. When cis-9,10-dihydro-9,10-dimethylanthracene was used as the arene in the ligand exchange reaction, the CpFe moiety could complex from either direction and gave a mixture of the cis-(endo-9,10-dihydro) cation III and the cis-(exo-9,10-dihydro) cation IV. The stereochemical results suggested a direct role for the Fe atom in the hydrogenations observed in such ligand exchange reactions.

Ligand exchanges between ferrocene (FcH) and arenes, effected in the presence of $AlCl_3$ and Al powder, to give η^6-arene-η^5-cyclopentadienyliron cations were first reported by Nesmeyanov et al in 1963 [1]. η^6-Arene-bis-η^5-cyclopentadienyliron dications were successfully prepared in this laboratory with arenes such as biphenyl and fluorene [2]. Subsequently, Hendrickson et al [3] reported the synthesis of a number of such dications from a variety of polynuclear aromatic hydrocarbons. However, we found that such reactions with polynuclear aromatic hydrocarbons resulted in a novel hydrogenation process. For example, reaction of naphthalene with FcH-$AlCl_3$-Al gave rise to both the η^6-naphthalene-η^5-cyclopentadienyliron cation (I) and the η^6-tetralin-η^5-cyclopentadienyliron cation (II), while anthracene gave only the hydrogenated η^6-9,10-dihydroanthracene-η^5-cyclopentadienylirion cation and the corresponding bis-dication [4]. A similar reaction with 1-bromonaphthalene gave a mixture of the expected η^6-1-bromonaphthalene-η^5-cyclopentadienyliron cation, the debrominated ion I and the hydrogenated ion II. With added radical scavengers such as I_2 or diphenylpicrylhydrazyl (DPPH), the formation of II was suppressed, thus implicating radical ions in the hydrogenation process [5].

In this communication, we wish to report that the reaction of 9,10-dimethylanthracene with FcH-$AlCl_3$-Al in decalin at 130°C gave stereospecifically the η^6-cis-(endo-9,10-dihydro)-9,10-dimethylanthracene-η^5-cyclopentadienyliron catio (III).* The reaction was carried out with an arene: FcH:$AlCl_3$:Al molar ratio of 1:1:2:1 using the procedure that has been described previously [4]. In contrast to the reaction with anthracene, which gave the hydrogenated complex at 80°C [4], a higher reaction temperature of at least 130°C was required to effect the reaction with 9,10-dimethylanthracene to give III. Upon removal of CpFe from III, either by photolysis or by pyrolytic sublimation, the hydrocarbon obtained was identical with an authentic sample of cis-9,10-dihydro-9,10-dimethylanthracene. When cis-9,10-dihydro-9,10-dimethylanthracene was used as the arene in the ligand exchange reaction, there was no hydrogenation and the CpFe group could complex from either side of the ring system, giving rise to a mixture of the cis-(endo-9,10-dihydro) cation III and the cis-(exo-9,10-dihydro) cation IV.



III



IV

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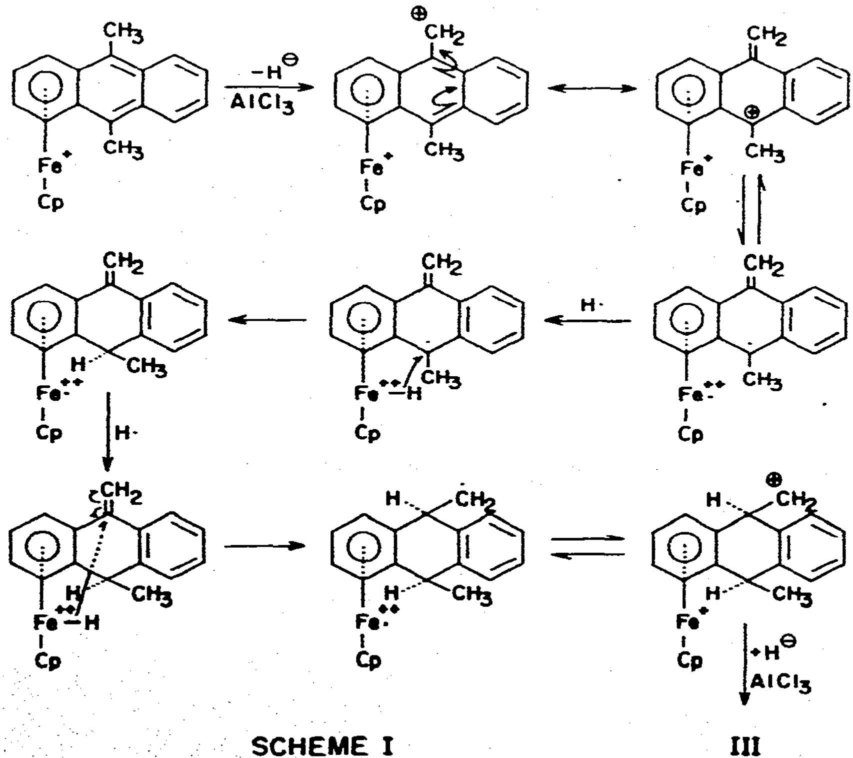
* The endo designation is used to indicate that the H atoms at C-9,10 and the CpFe group are on the same side of the ring system.

The chemical shifts from the ^{13}C and ^{1}H NMR spectra of ions III and IV are given in Table 1. Consider, for example, the CH_3 absorptions. In ion IV, the CH_3 groups are endo and their proton absorption at 1.97 p.p.m. showed a steric downfield shift [6] relative to the CH_3 proton absorption for III at 1.59 p.p.m. Similarly, in the ^{13}C NMR spectra, the same steric effect that caused a loss of electron density for the CH_3 hydrogens gave rise to more shielding for the CH_3 carbons, resulting in an upfield shift [7] for the CH_3 carbons of IV at 11.9 p.p.m. relative to the CH_3 carbons of III at 27.2 p.p.m. Such results definitely established the cis-(endo-9,10-dihydro) and cis-(exo-9,10-dihydro) structures for ions III and IV, respectively.

The finding that hydrogenation took place stereospecifically from the endo direction or the same side as the CpFe group is of mechanistic significance, indicating that the Fe atom must play an important part in bringing about the hydrogenation. The previously suggested ion-radical mechanism, proposed as a



SCHEME I

TABLE 1. ^{13}C AND ^{1}H CHEMICAL SHIFTS FOR η-CIS-(ENDO-9,10-DIHYDRO)-9,10-DIMETHYLANTHRACENE-η-CYCLOPENTADIENYLIRON CATION (III) AND η-CIS-(EXO-9,10-DIHYDRO)-9,10-DIMETHYLANTHRACENE-η-CYCLOPENTADIENYLIRON CATION (IV)

	δ, p.p.m. from TMS[a]									
	CH_3		CH		Cp		Complexed Aromatic		Uncomplexed Aromatic	
Ion	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H
III	27.2	1.59 (d)	39.2	4.13 (q)	76.4	4.59 (s)	86.2	6.27 (s)	127.2	7.42 (s)
		J=7.4 Hz		J=7.4 Hz			86.4		127.8	
							105.8[b]		137.4[b]	
IV	11.9	1.97 (d)	34.4	3.66 (q)	75.0	4.21 (s)	83.4	6.37 (m)	123.1	7.52 (bs)
		J=6.8 Hz		J=6.8 Hz			84.4		126.7	
							108.9[b]		140.5[b]	

[a] The ^{13}C and ^{1}H n.m.r. spectra were obtained in CD_3CN and CD_2Cl_2, respectively.

[b] Quaternary carbons.

working hypothesis [5], may, therefore, be modified to include a direct role for the Fe atom as shown in Scheme 1. A direct role for the Fe atom is quite reasonable since such hydrogenation of arenes apparently occurs only after the arene is complexed to the CpFe group. Among the key steps in Scheme 1 is the intramolecular oxidation-reduction [5] in which an electron is transferred from Fe(II) to give Fe(III), while at the same time a carbonium ion center is reduced to a free radical. Such a process has a very recent analogy in the work of Cais et al [8] who found that a tertiary amine could transfer an electron to an α-ferrocenylcarbonium ion to give an α-ferrocenylcarbinyl radical, which subsequently could abstract H to form product.

It may also be of interest to point out that a number of reductive methods to give 9,10-dihydro-9,10-dimethylanthracene generally resulted in a mixture of the cis and trans isomers [9-11], while the synthesis of the pure cis isomer required a sequence of stereospecific reactions [12,13]. In the present work, cis-9,10-dihydro-9,10-dimethylanthracene was obtained in about 80% yield from the pyrolysis of III under vacuum, whereby the hydrogenated hydrocarbon ligand sublimed. This finding thus points to the possible usefulness of the hydrogenation process in the ligand exchange reaction as a good synthetic approach to stereospecifically hydrogenated aromatic hydrocarbons.

Acknowledgment

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lish translations of the preface, the table of contents and the chapter and section headings are provided. Indexes are not included in this volume.

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139 (USA)

Dietmar Seyferth