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REACTION OF PENTADIENYLIRON TRICARBONYL CATIONS WITH HYDRIDE DONORS

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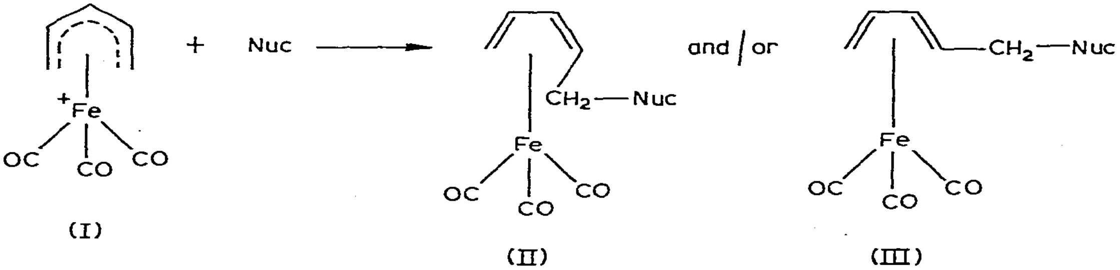
Summary

A series of pentadienyliron tricarbonyl cations has been prepared and reacted with the hydride ion donors sodium borohydride, sodium cyanoborohydride, and lithium triethylborohydride in order to determine steric and electronic effects in these reduction reactions. Sodium cyanoborohydride yields products of retained configuration whereas lithium triethylborohydride yields dieneiron tricarbonyl compounds of inverted configuration. Kinetic and thermodynamic considerations are used to account for these results.

Introduction

Even though acyclic pentadienyliron tricarbonyl cations are stable when exposed to light and air, they react readily with a variety of nucleophiles to generate compounds containing a butadieneiron tricarbonyl fragment. Nucleophilic attack on these cissoid cations (I) can produce *cis*-dieneiron tricarbonyl compounds II (retained configuration) or *trans*-dieneiron tricarbonyl compounds III (inverted configuration). The structure of the product obtained depends on the nature of the nucleophile. Thus reaction with water [1], alcohols [1,2], and polymethoxybenzenes [3] proceeds with total inversion of con-

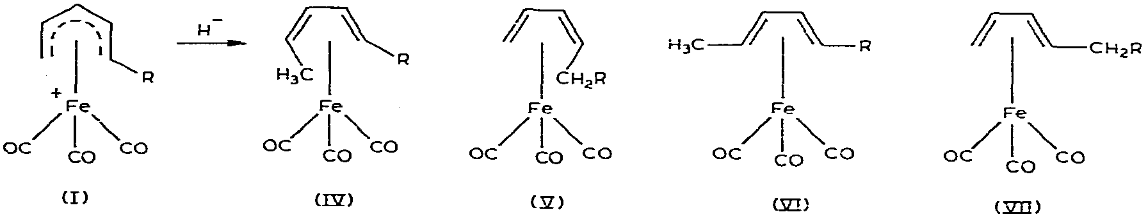


figuration. On the other hand, organocadmium reagents react to form products with retained configuration [4]. Reaction of I with various amines produces *cis* or *trans* compounds depending on the basicity of the amines [5,6]. Strongly basic amines produce *cis* compounds whereas weakly basic amines yield *trans* products. Amines of intermediate basicity yield mixtures. When unsymmetrically substituted pentadienyliron tricarbonyl cations react, the position of nucleophilic attack is also important. Their reactions with water [1,7], organocadmium reagents [4] and tertiary amines [8] indicate that both steric and electronic effects are important in determining the position of nucleophilic attack.

As part of our continuing study of factors that determine products formed during nucleophilic reactions with these cations, we have studied their reactions with various hydride donors. The hydride donors were chosen as nucleophiles since they span a wide range of reactivity while transferring the same atom to the cation. The comparison of product ratios obtained from each reaction thus becomes more meaningful.

Results

A series of pentadienyliron tricarbonyl fluoroborates (I) was prepared and reacted with various hydride donors in tetrahydrofuran solvent at —25° C. As shown below these reactions can yield four products (except when R = H). Products arising from attack at C(2), C(3), or C(4) of the pentadienyl ligand were not detected. Product composition was determined by two different methods. When R = H only two products (IV and VI) are formed and the ratio



(a) R = H
(b) R = CH_3
(c) R = CH_2CH_3
(d) R = $CH(CH_3)_2$

can be determined by NMR spectroscopy. The *syn* methyl groups of the *trans* complex possessed a doublet at 8.57 τ, and the *anti* methyl group of the *cis* complex shifts upfield to 8.91 τ making quantitative analysis simple. A second method of analysis involved oxidative degradation of the complexes followed by GLC analysis of the liberated dienes. Use of ceric ammonium nitrate in aqueous alcohol caused degradation of the complexes but also caused isomerization of the dienes. Studies with ferric chloride in aqueous alcohol revealed that no isomerization occurred upon decomplexation. In several trial systems, NMR and GLC analyses yielded identical results. In more complicated cases only GLC analyses were performed.

The first hydride donor studied was sodium borohydride. The results of

TABLE 1

REDUCTION OF CATIONS BY $NaBH_4$

Cation	Products (%)			
	IV	V	VI	VII
Ia	78	—	22	—
Ib	57	13	29	1
Ic	85	—	11	4
Id	84	—	9	7

these reductions are reported in Table 1. Reactions of cations Ia and Ib with $NaBH_4$ had been described previously by Pettit and coworkers [1,2]. They had obtained a ratio of IV/VI of 80/20. In the case of Ib they obtained four products but identified only the major product IV. Our results can be summarized as follows. Products of retained configuration (IV, V) are preferred (70—85% retained, 15—30% inverted). The products of retained configuration arise from preferential nucleophilic attack at the least hindered terminus of the cation. Selectivity is generally not as great in the inverted products. Stirring of tetrahydrofuran solutions of the individual products with $NaBH_4$ (or any of the other hydride donors used in this study) caused no isomerization; therefore the reported ratios represent actual product distribution produced by the initial reduction of the cations.

The next hydride donor chosen was sodium cyanoborohydride. This reagent is a milder, more selective reducing agent than sodium borohydride because of the electron withdrawing effect of the cyano group [9]. The results of the reductions are shown in Table 2. The most striking aspect of these reactions is the very strong preference for retention of configuration in the products. Only in the reaction with cation Ib was any inverted product formed and then only in trace amounts. Steric factors appear to have some importance in these reactions as well. When the substituent is small (Ib) there is some preference for attack at the substituted end, but this preference is easily overcome as the bulk of the substituent increases. Whitesides [12] has reported similarly that the reduction of the 1,5-diphenylpentadienyliron tricarbonyl cation with $NaBH_3CN$ produced a diene complex of retained configuration as the sole product. Another mild reducing agent, diborane, was studied, but the reaction rates were very slow. When reacted with cation Ia, IV was the exclusive product.

TABLE 2

REDUCTION OF CATIONS BY $NaBH_3CN$

Cation	Products (%)			
	IV	V	VI	VII
Ia	100	—	—	—
Ib	36	56	1	3
Ic	100	—	—	—
Id	100	—	—	—

TABLE 3

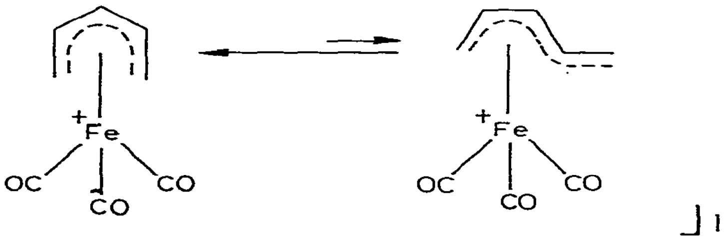
REDUCTIONS OF CATIONS WITH $Li(C_2H_5)_3BH$

Cation	Products (%)			
	IV	V	VI	VII
Ia	—	—	100	—
Ib	13	—	64	23
Ic	18	—	65	17
Id	17	—	65	18

Reactions with the extremely nucleophilic species lithium triethylborohydride were also studied. This reagent is 10,000 times more nucleophilic than lithium borohydride since the hydride ion is more easily transferred from the weaker Lewis acid, triethylborane, than from the stronger Lewis acid, borane [10]. Results are given in Table 3. When the very reactive hydride donor is utilized there is a great preference for products possessing inverted configuration. In the substituted cations a minor amount of the product of retained configuration is obtained regardless of the substituent. There is also a moderate preference for attack at the unsubstituted end of the cation. Attempted reactions with other potent donors such as lithium aluminum hydride led to total decomposition of the organometallic compound.

Discussion

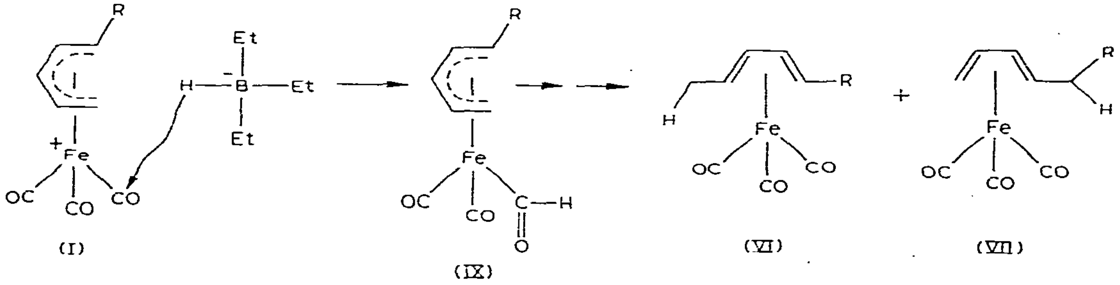
Reactions of pentadienyliron tricarbonyl cations with amines give products of retained or inverted configuration depending on the basicity of the amine. Maglio's explanation [5,6] of these results is based on a postulate that the cation exists as an equilibrium mixture of the *cissoid* (I) and *transsoid* (VIII) forms with I being the predominant species but with VIII being more reactive. The sparse evidence for such an equilibrium rests on NMR [13] and kinetic data [3,14]. Therefore, weakly basic amines react with VIII to form the thermodynamic product (*trans*-diene complex) while strongly basic amines capture the major cationic form I yielding the kinetic product (*cis*-diene complex).



(I) (VIII)

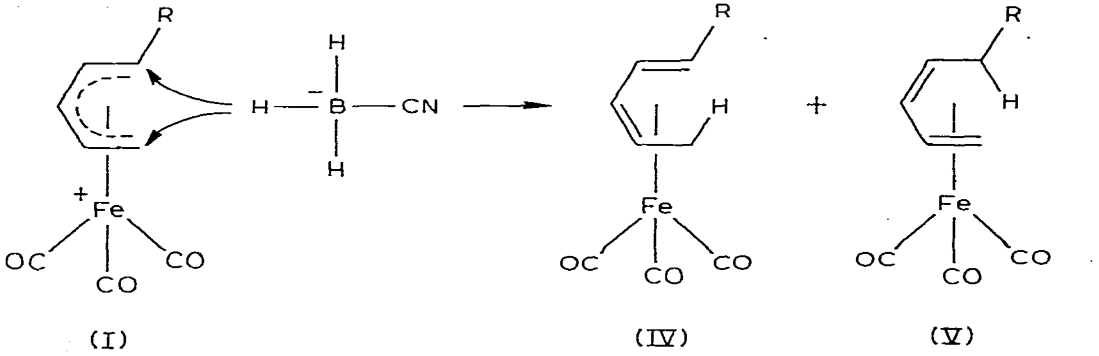
We feel that the course of our reduction reactions can be rationalized also on the basic of kinetic or thermodynamic control. Lithium triethylborohydride is a very reactive hydride donor; therefore, it is proposed that the hydride ion will be transferred rapidly to the electron-deficient carbon of the metal carbonyl group to form a neutral metal formyl complex IX such as that described by Casey [15]. The hydride is then transferred [16,17] inter- or intra-molecularly to the terminal carbon of the ligand producing VI or VII. A detailed mechanism for the inversion of the pentadienyl ligand cannot be presented at this time, but inversion must occur prior to formation of VI or VII. When *cis*-diene complexes such as IV or V are reacted with $LiBEt_3H$ under usual reaction conditions, there is no detectable reaction and no isomerization of the diene ligand. Products of retained configuration may arise from direct attack (by Et_3BH^-) on the terminal carbon in I or from internal transfer of hydride to the terminal carbon in IX prior to inversion [18].

SCHEME 1



The proposed mechanism for the reduction with sodium cyanoborohydride is shown in Scheme 2. Since this reagent is much less reactive and thus more selective than lithium triethylborohydride, it is proposed that the reaction is controlled by thermodynamic considerations. Since V is the major product when $R = CH_3$ and IV is the exclusive product when $R = C_2H_5$, steric factors also play an important role. Sodium borohydride is intermediate in reactivity between these two hydride donors and may react by both mechanisms with the one illustrated in Scheme 2 being predominant in the cases that we have studied.

SCHEME 2



Experimental

The cations used in this study were prepared according to literature procedure [1,2,7].

General procedure for reduction reactions: reaction of pentadienyliron tricarbonyl fluoroborate (Ia) with sodium cyanoborohydride

To a stirred suspension of cation Ia (1.00 g, 48 mmol) in 25 ml of dry tetrahydrofuran (freshly distilled under N_2 from $LiAlH_4$) was added 0.30 g (50 mmol) of sodium cyanoborohydride. The reaction mixture was stirred for 2 h under a N_2 atmosphere at —25° C. During this time a color change occurred and the reaction mixture became homogeneous. The mixture was warmed to room temperature, diluted with water, and extracted with pentane. Removal of the pentane yielded 0.29 g (41%) of the crude product. NMR analysis (CS_2 solvent) revealed the presence of *cis*-1,3-pentadieneiron tricarbonyl as the sole product.

Reactions with sodium borohydride were carried out according to the same procedure. Since lithium triethylborohydride is available as a tetrahydrofuran solution, the appropriate volume was added from an addition funnel to the stirred solutions. The hydride donor was always used in excess and isolated yields of dieneiron tricarbonyl complexes ranged from 35 to 75%.

General procedure for degradation of complexes and GLC analysis of dienes:

To 0.5 g of the dieneiron tricarbonyl complexes was added 4 g of ferric chloride hexahydrate in 10 ml of 80% aqueous ethanol at 0° C. After 1 h gas evolution ceased and the mixture was diluted with water and extracted with pentane. The pentane extract was washed with water and analyzed directly by GLC utilizing a silver nitrate column [11]. Identity of peaks was established through the use of authentic compounds.

Degradation of known dieneiron tricarbonyl complexes established that this procedure does not cause isomerization of the diene. Furthermore, NMR and GLC analyses gave identical results with mixtures of *cis*- and *trans*-1,3-pentadieneiron tricarbonyl compounds.

Acknowledgments

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