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STEREOCHEMISTRY OF THE REACTION BETWEEN AMINES AND THE PENTADIENYLIRON TRICARBONYL CATION

GIOVANNI MAGLIO and ROSARIO PALUMBO

Laboratorio di Ricerche su Tecnologia dei Polimeri e Reologia del C.N.R., 80072 Arco Felice, Napoli (Italy)

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Summary

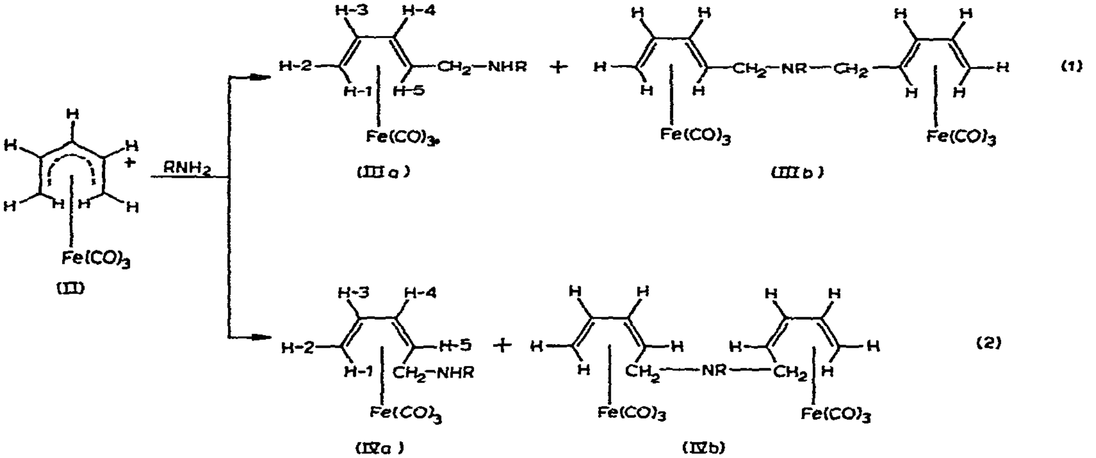
The addition of amines to the pentadienyliron tricarbonyl cation gives rise to (*cis, trans- or trans, trans*-dienylamine)iron tricarbonyl depending on their basicity. The complexes thus obtained can give binuclear species by further reaction with the cation. The stereochemistry of the reaction has been investigated by PMR spectroscopy.

Introduction

We previously described a study of the stereochemistry of the addition of amines to the (*syn, syn*-1,5-dimethylpentadienyl)iron tricarbonyl cation (I) [1, 2]. The reaction was found to be stereospecific, involving *exo* attack of the nucleophile on the carbon atom adjacent to the methyl group. It was also shown that the reaction could give either (*cis,trans-* or *trans,trans*-dienylamine)iron tricarbonyl complexes depending on the basicity of the amine and on the reaction conditions for a fixed amine. In order to determine whether the methyl groups were influencing the stereochemistry of the reaction we have now investigated the additions of amines of varying basicities to the unsubstituted pentadienyliron tricarbonyl cation (II).

Results and discussion

The reactions were performed by adding a solution of the amine in nitromethane to pentadienyliron tricarbonyl tetrafluoroborate dissolved in the same solvent (molar ratio 2/1). Four different dienylamineiron tricarbonyl species were formed, corresponding with two different reaction pathways shown in eqns. 1 and 2.



The reaction products were separated by column chromatography or fractional crystallization and were identified by elemental analysis and by infrared and PMR spectroscopy. All the complexes prepared are listed in Table 1 together with analyses and melting points. The relevant PMR data are shown in Table 2. The most significant differences between the two series of complexes (III and IV) are found in the chemical shifts of the H-5 and $-CH_2-N$ protons, and arise from the differing shielding effects of the iron on these protons associated with the *cis* or *trans* stereochemistry of the complexes. The results are in agreement

TABLE 1

ANALYTICAL DATA [a,b]

Compound			Analysis found (calcd.) (%)			M.p. (°C)
No	Type	R	C	H	N	
1	IVA	$CH_2C_6H_5$ [c]	51.58 (49.39)	4.58 (4.85)	4.01 (3.89)	124 (dec.)
2	IVB	$CH_2C_6H_5$	53.60 (53.18)	4.17 (4.05)	3.51 (3.69)	66
3	IVA	$CH(CH_3)C_6H_5$ [c,d]	52.60 (52.66)	4.95 (5.18)	3.85 (3.80)	104 (dec.)
4	IVB	$CH(CH_3)C_6H_5$ [c,d]	50.16 (50.63)	4.44 (4.21)	2.47 (2.46)	102 (dec.)
5	IVB	C_6H_5	52.34 (52.30)	3.95 (3.78)	2.58 (2.75)	126
6	IVB	C_6H_4Br-*p*	45.40 (45.20)	3.45 (3.10)	2.57 (2.40)	150
7	IVB	$C_6H_4CH_3$-*p*	52.78 (52.93)	4.09 (4.39)	2.96 (2.83)	145—146
8	IIIA	$C_6H_4NO_2$-*o*	48.19 (48.84)	3.51 (3.49)	7.65 (8.11)	75
9	IIIA	$C_6H_4NO_2$-*m*	48.76 (48.84)	3.58 (3.49)	8.16 (8.11)	95
10	IIIB	$C_6H_4NO_2$-*m*	47.80 (48.02)	3.47 (3.46)	5.10 (5.09)	110
11	IIIA	$C_6H_4NO_2$-*p*	48.39 (48.84)	3.59 (3.49)	7.71 (8.11)	138
12	IIIB	$C_6H_4NO_2$-*p*	47.87 (48.02)	3.42 (3.46)	5.14 (5.09)	148

[a] The IR spectra (n-hexane) showed two broad $\nu(C\equiv O)$ bands at 2052—2056 and 1983—1991 cm^{-1}. [b] Complexes 1—6 are yellow, 7—12 are orange. [c] Hydrochloride. [d] Complexes 3 and 4, derived from (*S*)-(—)-methylbenzylamine, have $[\alpha]_{589}$ —57.4 and —9.0, respectively (*c* 0.4, methanol).

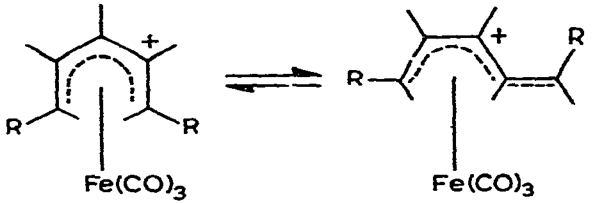
TABLE 2

PMR DATA FOR (DIENYLAMINE)IRON TRICARBONYL COMPLEXES [a]

R	Type	Chemical shifts (τ ppm)					
		H-3	H-4	H-5	H-1	H-2	CH_2 [b]
$CH_2CH_6H_5$	IVA [c,d]	≃ 4.1	≃ 4.1	≃ 6.5	8.48	8.02	≃ 7.5
C_6H_5	IVB [e]	≃ 4.4	≃ 4.4	≃ 6.5	8.55	8.24	≃ 7.6
C_6H_4Br-*p*	IVB [e]	≃ 4.5	≃ 4.5	≃ 6.4	8.54	8.18	≃ 7.5
$C_6H_4CH_3$-*p*	IVB [e]	≃ 4.6	≃ 4.6	≃ 6.5	8.46	8.16	≃ 7.5
$C_6H_4NO_2$-*o*	IIIA [f]	≃ 4.8	≃ 4.8	8.91	9.60	8.22	6.61
$C_6H_4NO_2$-*m*	IIIA [d,f]	≃ 4.7	≃ 4.7	8.92	9.64	8.24	6.68
$C_6H_4NO_2$-*p*	IIIA [d,f]	≃ 4.8	≃ 4.8	8.96	9.63	8.19	6.63

[a] TMS as internal standard. Solvent was chloroform-*d*, except for the hydrochlorides, which were dissolved in methanol-d_4. [b] These protons give rise to an ABX pattern. [c] Hydrochloride. [d] The chemical shifts found for the corresponding B type complex are almost coincident with those reported here, but the spectrum is somewhat more complex. [e] The corresponding A type complex was not isolated. [f] First order splittings: $J_{1,2}$ 3.0; $J_{1,3}$ 8.5; $J_{4,5}$ 8.0 Hz. Comparable values were found for the other complexes.

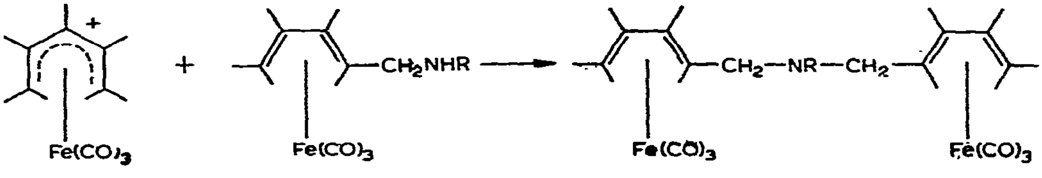
with those previously reported by us in the case of the cation I [1, 2], and by others [3] for dieneiron tricarbonyl compounds. The attack of the amine on the dienyl moiety probably follows an *exo* mechanism. The reported PMR data show that only with the very weakly basic nitroanilines does the reaction proceed with geometrical inversion (eqn. 1), stronger amines yielding the (*cis*-dienylamine)-iron tricarbonyl complex (eqn. 2). This finding agrees well with that reported for the cation I and shows that with cation II also, the basicity of the amine is the factor which determines the stereochemistry of the product. One difference was found, however, between the two cations. This is that the addition of aniline or *p*-toluidine to cation I may proceed following either eqn. 1 or eqn. 2 according to the molar ratio of the reagents [2], whereas in the case of cation II even with a large excess of these nucleophiles the *cis*-dienylamine complex III is not formed. If we assume that the stereochemistry of the addition products is related to the equilibrium 3 [4, 5] the different behaviour indicates that cation II is more available for nucleophilic attack in the *cisoid* arrangement than cation I, probably because of steric hindrance by the methyl groups of I.



(3)

(I : R = CH_3 ; II : R = H)

An interesting feature of the addition is as revealed in eqns. 1 and 2, that the A type complexes may further react with the cation II to give the B type complexes (eqn. 4).



(4)

All the amines except *o*-nitroaniline, yield B complexes, but generally in smaller amounts than the corresponding A complexes, as shown by PMR analysis of the reaction mixture. A requirement for the formation of B type compounds is that the (dienylamine)iron tricarbonyls must be nucleophiles of a strength comparable with that of the original amines. In the case of the cation I, the B type compounds were isolated only when ammonia was used as the nucleophile. Again steric hindrance by the methyl groups of I readily accounts for the difference between the two cations in this respect.

Finally it is noteworthy that two diastereoisomers, a racemate and a *meso* form, are expected in the case of B complexes. We were not able to separate such isomers, but the PMR spectra (in $CDCl_3$) of the pure B type complex obtained from benzylamine showed two different resonances for the methylene group bonded to the phenyl group, a singlet centered at τ 6.56 attributable to the racemate and an AB quartet, J(A, B) 13.0 Hz, centered at τ 6.58 ppm attributable to the *meso*-form. Integration of the signals showed that, at least in this case, the two diastereoisomers are present in equal amounts.

Experimental

NMR spectra were recorded with Varian Associates HA-100 or T-60 Spectrometers. Melting points are uncorrected. Elemental analyses were performed by A. Bernhardt Mikroanalytisches Lab., Helbach, W. Germany. Solvents were reagent grade, and were dehydrated by conventional techniques before use.

All compounds were prepared by the following general procedure: nitromethane solutions of the pentadienyliron tricarbonyl fluoroborate [6] were added to the amine dissolved in the minimum amount of the same solvent (molar ratio cation/amine 1/2). The mixture was stirred at room temperature for 10 min The solvent was removed and the residue extracted with ether, and the solvent re-evaporated. The yellow residue, containing both A and B type complexes (yield 90—95% based on the cation), was purified by the appropriate procedure as outlined in Table 3.

In most cases separation was accomplished quantitatively by column chromatography on silica gel with the eluants as listed in Table 3. Type B complexes were eluted first in all the cases. The purity of individual fractions was checked by TLC examination.

TABLE 3

SEPARATION OF A AND B TYPE COMPLEXES

Amine	Separation method [a]	Molar Ratio A/B
$NO_2C_6H_4NH_2$-*p*	E, $CHCl_3$/n-Hexane/Ether (2/2/1)	40
$NO_2C_6H_4NH_2$-*o* [b]	E, $CHCl_3$	
$NO_2C_6H_4NH_2$-*m*	E, $CHCl_3$	3.7
$C_6H_5CH_2NH_2$	E, Ether	0.54
(*S*)(−)-$C_6H_5CH(CH_3)NH_2$	E, Ether	2.5
$C_6H_5NH_2$ [c]	C, Ethanol/Ether	1
$CH_3C_6H_4NH_2$-*p* [c]	C, Ethanol/Ether	[d]
$BrC_6H_4NH_2$-*p* [c]	E, Ether/n-Hexane (2/1)	1—2

[a] Symbols E and C referred to silica gel column chromatography and fractional crystallization respectively. [b] Type A complex only was found in this case. [c] See text for details. [d] Not determined.

When the amine used was aniline, *p*-bromoaniline, or *p*-toluidine, chromatography was not effective in the separation in spite of use of several eluants. Fractional crystallization was therefore used after a preliminary filtration over silica gel to remove traces of unchanged amine or cation. Pure type B complexes were thus obtained in moderate yield by collecting the first precipitate. Attempts to recover pure samples of type A complexes from the mother liquor were unsuccessful. When gaseous ammonia was used as the nucleophile, much decomposition occurred, and the reaction was not further investigated.

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