

**DETERMINATION OF THE NUCLEOPHILICITY OF TRICARBONYLIRON COORDINATED CYCLOHEPTA-1,3,5-TRIENE**Herbert MAYR<sup>1,\*</sup> and Karl-Heinz MÜLLER<sup>2</sup>

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*Dedicated to Professor Otto Exner on the occasion of his 75th birthday.*

The kinetics of the electrophilic additions of four diarylcarbenium ions (**4a–4d**) to tricarbonyl( $\eta^4$ -cyclohepta-1,3,5-triene)iron (**1**) have been studied photometrically. The second-order rate constants match the linear Gibbs energy relationship  $\log k_{20\text{ }^\circ\text{C}} = s(E + N)$  and yield the nucleophilicity parameter  $N(\mathbf{1}) = 3.69$ . It is concluded that electrophiles with  $E \geq -9$  will react with complex **1** at ambient temperature.

**Key words:** Carbocations; Carbocycles; Iron; Kinetics; Linear free energy relationships; Electrophilicity.

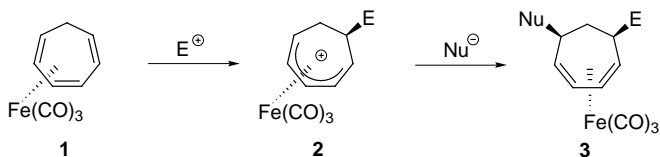
*Any regularity found in nature raises some kind of satisfaction. What is more important, it provokes further questions and encourages new experiments. The most significant of these questions is probably whether we are dealing with a rare phenomenon or with a general natural law.*

*Otto Exner, 1988 (in ref.<sup>1</sup>)*

Electrophiles usually act as hydride abstractors when combined with cyclohepta-1,3,5-triene to yield tropylium salts. In contrast, **1**, the tricarbonyliron complex of cycloheptatriene is attacked at the non-coordinated double bond in reactions with tritylium<sup>2</sup> or tropylium<sup>3</sup> tetrafluoroborate and in Friedel–Crafts acylations<sup>4</sup> to yield compounds **2**, which have been treated with  $\text{MeO}^-$  giving *cis*-5,7-disubstituted cyclohepta-1,3-dienes **3** ( $E = \text{acyl}$ ,  $\text{Nu} = \text{OMe}$ )<sup>4,5</sup>.

It was the goal of this work to determine the scope of the reaction sequence depicted in Scheme 1 for synthesizing *cis*-5,7-disubstituted cyclohepta-1,3-dienes.

In previous work, we have shown that cycloheptadienyl complexes of type **2** are rather weak electrophiles ( $E \approx -9.9$ ) which only react with strong nucleophiles ( $N > 5$ ). We now set out to determine the nucleophilicity of **1** in order to predict the types of electrophiles which are able to attack **1** in the first step of this reaction sequence (Scheme 1).



SCHEME 1

Extensive kinetic studies<sup>7</sup> on the reactions of carbocations with uncharged nucleophiles have shown that the corresponding rate constants can be derived from Eq. (1), where  $E$  represents the electrophilicities of the carbocations while nucleophiles are characterized by the nucleophilicity parameter  $N$  and the slope parameter  $s$ . The latter two parameters can be derived from the plot of  $\log k$  for the reactions of the corresponding nucleophile with various electrophiles against the  $E$  parameters.

$$\log k_{20^\circ\text{C}} = s(E + N) \quad (1)$$

## EXPERIMENTAL

### General

All reactions were performed with protection from light and in an atmosphere of dry argon or nitrogen. Dichloromethane was freshly distilled from  $\text{CaH}_2$  prior to use. Cycloheptatriene (Fluka) and  $\text{Fe(CO)}_5$  (Aldrich and BASF) are commercially available. Trimethylsilyl triflate (Fluka) was distilled from Na-Pb alloy prior to use. Compounds **4a**-Cl (ref.<sup>8</sup>), **4b**-OMe (ref.<sup>9</sup>), **4c**-OAc (ref.<sup>10</sup>), and **4d**- $\text{BF}_4$  (ref.<sup>11</sup>) were obtained according to literature procedures. NMR spectra were recorded on a Bruker ARX 300 spectrometer, and the solvents acetonitrile- $d_3$  and acetone- $d_6$  were carefully degassed before use. For  $^1\text{H}$  NMR measurements tetramethylsilane ( $\delta$  0.00) was used as internal standard,  $^{13}\text{C}$  NMR data were referenced either to  $\text{CDCl}_3$  ( $\delta$  77.0), acetonitrile- $d_3$  ( $\delta$  117.7), or acetone- $d_6$  ( $\delta$  29.8). Coupling constants  $J$  are given in Hz. Signal assignments are based on  $^1\text{H}$ ,  $^1\text{H}$ - and  $^1\text{H}$ ,  $^{13}\text{C}$ -COSY experiments. Mass spectra were obtained from a Varian MAT 311. For the kinetic investigations a Schöolly KGS III photometer with band-pass filters by Corion was employed<sup>12</sup>.

### Tricarbonyl-( $\eta^4$ -cyclohepta-1,3,5-triene)iron<sup>13a</sup> (1)

Under an argon atmosphere a mixture of  $\text{Fe(CO)}_5$  (35.8 g, 183 mmol) and cycloheptatriene (11.2 g, 122 mmol) was heated to reflux for 21 h. Then the unreacted starting materials

were recovered by distillation (1 Pa/40 °C) into a nitrogen-cooled trap. The recovered materials were refluxed again for 21 h. This procedure was repeated three times and the respective residues were dissolved in hexane, filtered through Celite, and combined. After the evaporation of the solvent *in vacuo* the crude product was purified by kugelrohr distillation (0.08 Pa/60 °C) to give **1** (20.4 g, 72%) which was stored under argon. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 2.25 dq, *J* = 22, *J* = 3.3, 1 H (7-*exo*-H); 2.42 dtd, *J* = 22, *J* = 4.5, *J* = 1.8, 1 H (7-*endo*-H); 3.06 m<sub>c</sub>, 1 H (4-H); 3.33 m<sub>c</sub>, 1 H (1-H); 5.14–5.20 m, 1 H and 5.24–5.30 m, 2 H (2-H, 3-H, 6-H); 5.80 m<sub>c</sub>, 1 H (5-H). <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>): 30.6 t (C-7); 55.9 d and 60.3 d (C-1, C-4); 88.3 d and 93.4 d (C-2, C-3); 125.4 d (C-6); 128.3 d (C-5); 211.3 s (CO). Analogous NMR spectra have been reported in ref.<sup>14</sup>.

#### Reaction of **1** with Bis(4-methoxyphenyl)methylm Triflate (**4a**-OTf)

At -78 °C trimethylsilyl triflate (250 mg, 1.13 mmol) was added to a solution of bis(4-methoxyphenyl)methyl chloride (**4a**-Cl, 285 mg, 1.09 mmol) which was dissolved in dichloromethane (8 ml). After the injection of **1** (260 mg, 1.12 mmol, dissolved in 2 ml CH<sub>2</sub>Cl<sub>2</sub>) the reaction mixture was stirred for 4 h without cooling before the solvent was removed *in vacuo*. Further evaporation of volatile compounds in high vacuum yielded a crude product which was purified by crystallization from a water-acetonitrile mixture (20 : 1, v/v) to give **5a**-OTf (407 mg, 61%) as orange microcrystals. For C<sub>26</sub>H<sub>23</sub>F<sub>3</sub>FeO<sub>8</sub>S (608.4) calculated: 51.33% C, 3.81% H; found: 51.67% C, 3.75% H. <sup>1</sup>H NMR (300 MHz, acetonitrile-*d*<sub>3</sub>): see Table II, additional signals: 3.22 d, *J*(8,6) = 11.1, 1 H (8-H); 3.68 s and 3.71 s, 2 × 3 H (OMe); 6.77 d and 6.86 d, both a part of an AA'BB' system *J*(AB) = 8.6, 2 × 2 H (arom. CH); 7.02 m<sub>c</sub>, 1 H (3-H); 7.14 d and 7.25 d, both a part of an AA'BB' system *J*(AB) = 8.5, 2 × 2 H (arom. CH). <sup>13</sup>C NMR (75.5 MHz, acetonitrile-*d*<sub>3</sub>): 32.5 t (C-7); 54.5 d (C-6); 55.57 q and 55.62 q (OMe); 59.8 d (C-8); 89.4 d (C-1); 94.4 d (C-5); 101.5 d (C-3); 103.2 d (C-4); 103.3 d (C-2); 114.6 d and 114.9 d (arom. C); 128.9 d and 129.6 d (arom. C); 135.3 s and 136.8 s (arom. C); 159.09 s and 159.14 s (arom. C); 202.7 s (CO). IR (KBr): 3 070 (=C-H), 3 000–2 840 (C-H), 2 120, 2 090, 2 060, 1 975 br (C=O), 1 615, 1 587, 1 510, 1 465 (C=C), 1 305, 1 255, 1 183, 1 070–1 035, 825, 590, 560. MS (FD, *m/z*, %): 459 (100) [M<sup>+</sup> - OTf].

#### Reaction of **1** with Bis(2,3-dihydrobenzofuran-5-yl)methylm Triflate (**4b**-OTf)

At -78 °C trimethylsilyl triflate (120 mg, 0.540 mmol) was added to a solution of bis(2,3-dihydrobenzo[*b*]furan-5-yl)methyl methyl ether (**4b**-OMe, 140 mg, 0.496 mmol) in dichloromethane (10 ml). After the injection of **1** (125 mg, 0.538 mmol, dissolved in CH<sub>2</sub>Cl<sub>2</sub>) the reaction mixture was stirred for 6 h at -78 °C and for further 10 h without cooling before the solvent was removed *in vacuo*. Further evaporation of volatile compounds in high vacuum yielded a crude product which was purified by recrystallization from water-acetonitrile (20 : 1, v/v) to yield **5b**-OTf (260 mg, 83%). <sup>1</sup>H NMR (300 MHz, acetonitrile-*d*<sub>3</sub>): see Table II, additional signals: 3.08–3.20 m, 5 H (8-H, OCH<sub>2</sub>CH<sub>2</sub>); 4.43–4.56 m, 5 H (5-H, OCH<sub>2</sub>CH<sub>2</sub>); 6.59 d and 6.68 d, each *J* = 8.2, 2 × 1 H (arom. CH); 6.94 dd, *J* = 8.2, *J* = 1.7, 1 H (arom. CH); 7.00–7.06 m, 2 H (3-H, arom. CH); 7.11 br s and 7.20 br s, 2 × 1 H (arom. CH). <sup>13</sup>C NMR (75.5 MHz, acetonitrile-*d*<sub>3</sub>): 30.0 t and 30.1 t (OCH<sub>2</sub>CH<sub>2</sub>); 32.7 t (C-7); 54.9 d (C-6); 60.6 d (C-8); 72.0 t (OCH<sub>2</sub>CH<sub>2</sub>); 89.5 d (C-1); 94.8 d (C-5); 101.5 d (C-3); 103.2 d (C-4); 103.4 d (C-2); 109.5 d and 109.7 d (arom. C); 124.6 d and 125.3 d (arom. C); 127.4 d and 128.2 d (arom. C); 128.8 s and 129.1 s (arom. C); 135.5 s and 137.0 s (arom. C); 159.7 s

(arom. C). IR (KBr): 3 065 (=C-H), 3 010–2 900 (C-H), 2 110, 2 070, 2 000–1 950 (C=O), 1 620, 1 585, 1 515 (C=C), 1 315, 1 255, 1 110, 1 050–1 030, 820, 580, 560, 510.

#### Reaction of **1** with Ferrocenylphenylmethylm Triflate (**4c**-OTf)

At  $-78\text{ }^{\circ}\text{C}$  trimethylsilyl triflate (157 mg, 0.706 mmol) was added to a solution of ferrocenyl(phenyl)methyl acetate (**4c**-OAc, 230 mg, 0.688 mmol) in dichloromethane (8 ml). After the injection of **1** (168 mg, 0.724 mmol, dissolved in 2 ml  $\text{CH}_2\text{Cl}_2$ ) the reaction mixture was stirred for 19 h without cooling before the solvent was evaporated *in vacuo*. Further evaporation of volatile compounds in high vacuum yielded a crude product (470 mg) that was analyzed by  $^1\text{H}$  NMR to be a 19 : 1 mixture of **5c**-OTf (84%) and **6**-OTf. The 56 : 44 ratio of diastereomeric products of **5c**-OTf was determined on the basis of the 7-*exo*-H integrals. Analytical properties were obtained from a sample with 80% d.e. which was obtained after dissolving the crude product in dichloromethane and allowing slow diffusion of pentane. For  $\text{C}_{28}\text{H}_{23}\text{F}_3\text{Fe}_2\text{O}_6\text{S}$  (656.2) calculated: 51.24% C, 3.53% H; found: 51.88% C, 3.79% H.  $^1\text{H}$  NMR (300 MHz, acetone- $d_6$ ): see Table II, additional signals: 3.32 d,  $J(8,6) = 8.4$ , 1 H (8-H); 3.93 br s, 6 H (6-H,  $\text{C}_5\text{H}_5$ ); 4.26–4.47 m, 4 H ( $\text{C}_5\text{H}_4$ ); 7.20–7.40 m, 6 H (3-H, arom. H).  $^{13}\text{C}$  NMR (75.5 MHz, acetone- $d_6$ ): 31.2 t (C-7); 55.0 d (C-8); 58.9 d (C-6); 68.6 d; 70.4 d; 71.7 d ( $\text{C}_5\text{H}_5$ ,  $\text{C}_5\text{H}_4$ ); 88.8 d and 94.8 d (C-1, C-5); 101.5 d (C-3); 103.5 d and 104.1 d (C-2, C-4); 127.6 d; 128.9 d; 129.0 d (arom. C); 144.0 s (arom. C). The signal of CO was not detected due to slow relaxation, while the substituted carbon of the cyclopentadienyl moiety is probably covered by other signals of ferrocenyl. IR (KBr): 3 092 (=C-H), 2 980–2 960 (C-H), 2 113, 2 052, 1 968 (C=O), 1 647, 1 494, 1 451 (C=C), 1 272, 1 156, 1 029, 823, 758, 710, 638, 592, 513. MS (FD,  $m/z$ , %): 656 (100) [ $\text{M}^+$ ], 507 (32) [ $\text{M}^+ - \text{OTf}$ ].

#### Kinetic Investigations

The consumption of the cations **4a–4d** was followed photometrically (**4a** at 520 or 540 nm; **4b** at 490 or 510 nm; **4c** at 450 or 510 nm; **4d** at 640 nm) by using fiber optics and the workstation described in ref.<sup>12</sup>. In order to prevent photoinduced side reactions the band-pass filters were placed between the light source and the glass fibers.

Calibration curves, *i.e.* the correlation between absorbance and concentration of the triflates of **4a–4c**, were obtained by adding **4a**-Cl, **4b**-OMe, or **4c**-OAc in portions to a solution of excess trimethylsilyl triflate (TMSOTf) in  $\text{CH}_2\text{Cl}_2$  and determination of the absorbance after completion of the ionization. Calibration curves of **4c**- $\text{BF}_4$  and **4d**- $\text{BF}_4$  were obtained by determination of the absorbance after the addition of different amounts of concentrated  $\text{CH}_2\text{Cl}_2$  solutions of **4c**- $\text{BF}_4$  and **4d**- $\text{BF}_4$  to  $\text{CH}_2\text{Cl}_2$ . In the case of the reactions of **1** with **4c** and **4d**, the absorbance at the monitored wavelength did not disappear completely, and for that reason, the measured absorbances  $A_t$  have been replaced by ( $A_t - A_{\text{end}}$ ) as described in ref.<sup>15</sup>.

For initial concentrations of the reactants ( $c_0$ ) and results of the kinetic measurements at different temperatures see Table I.

## RESULTS AND DISCUSSION

Several procedures for synthesis of **1** have been reported, all of which employ cycloheptatriene, which was combined with different  $\text{Fe}(\text{CO})_3$  precur-

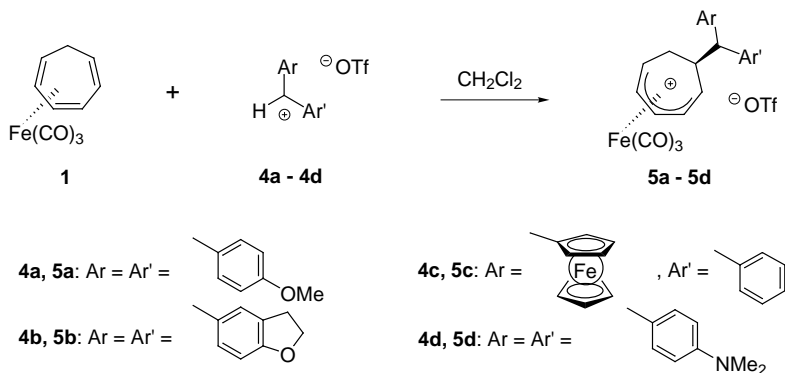
TABLE I  
Kinetics of the reactions of tricarbonyl( $\eta^4$ -cyclohepta-1,3,5-triene)iron (1) with the carbocations **4a–4d** (in  $\text{CH}_2\text{Cl}_2$ )<sup>a</sup>

Electrophile	<i>T</i> , °C	<i>c</i> <sub>0</sub> ( <b>4</b> ) mol l <sup>-1</sup>	<i>c</i> <sub>0</sub> ( <b>1</b> ) mol l <sup>-1</sup>	<i>c</i> <sub>0</sub> (TMSOTf) mol l <sup>-1</sup>	Conversion %	<i>k</i> l mol <sup>-1</sup> s <sup>-1</sup>
<b>4a<sup>b</sup></b>	-20.0	6.14 · 10 <sup>-5</sup>	6.32 · 10 <sup>-4</sup>	1.85 · 10 <sup>-3</sup>	24	350
	-20.0	4.86 · 10 <sup>-5</sup>	3.08 · 10 <sup>-3</sup>	7.52 · 10 <sup>-4</sup>	76	366
	-20.0	3.86 · 10 <sup>-5</sup>	2.20 · 10 <sup>-3</sup>	2.40 · 10 <sup>-3</sup>	70	332
	-20.1	2.05 · 10 <sup>-5</sup>	3.41 · 10 <sup>-4</sup>	1.79 · 10 <sup>-3</sup>	49	355
	-30.0	2.69 · 10 <sup>-5</sup>	4.62 · 10 <sup>-4</sup>	1.19 · 10 <sup>-3</sup>	55	295
	-40.0	6.07 · 10 <sup>-5</sup>	8.26 · 10 <sup>-4</sup>	9.97 · 10 <sup>-4</sup>	76	191
	-50.0	2.47 · 10 <sup>-5</sup>	2.60 · 10 <sup>-4</sup>	2.25 · 10 <sup>-3</sup>	37	116
	-50.2	4.02 · 10 <sup>-5</sup>	6.69 · 10 <sup>-4</sup>	1.26 · 10 <sup>-3</sup>	80	111
	-50.2	2.85 · 10 <sup>-5</sup>	1.08 · 10 <sup>-3</sup>	2.36 · 10 <sup>-3</sup>	81	114
	-60.0	1.60 · 10 <sup>-5</sup>	1.34 · 10 <sup>-3</sup>	2.27 · 10 <sup>-3</sup>	79	65.3
	-70.0	8.48 · 10 <sup>-5</sup>	3.76 · 10 <sup>-3</sup>	1.14 · 10 <sup>-3</sup>	71	44.2
	-70.0	5.26 · 10 <sup>-5</sup>	5.60 · 10 <sup>-3</sup>	1.28 · 10 <sup>-3</sup>	79	43.4
	-70.0	3.96 · 10 <sup>-4</sup>	1.03 · 10 <sup>-2</sup>	5.38 · 10 <sup>-3</sup>	76	46.0
	-70.2	1.84 · 10 <sup>-5</sup>	7.46 · 10 <sup>-4</sup>	2.32 · 10 <sup>-3</sup>	79	41.3
	-70.2	5.89 · 10 <sup>-4</sup>	6.14 · 10 <sup>-3</sup>	5.55 · 10 <sup>-3</sup>	87	39.3
-70.5	1.05 · 10 <sup>-5</sup>	5.71 · 10 <sup>-4</sup>	2.01 · 10 <sup>-3</sup>	92	40.0	
<b>4b<sup>b</sup></b>	-10.0	3.50 · 10 <sup>-4</sup>	7.74 · 10 <sup>-3</sup>	3.89 · 10 <sup>-3</sup>	42	26.6
	-30.0	4.69 · 10 <sup>-4</sup>	1.11 · 10 <sup>-2</sup>	5.61 · 10 <sup>-3</sup>	94	6.88
	-49.5	1.04 · 10 <sup>-4</sup>	1.25 · 10 <sup>-2</sup>	3.93 · 10 <sup>-3</sup>	84	2.45
	-50.0	5.61 · 10 <sup>-4</sup>	8.21 · 10 <sup>-3</sup>	5.81 · 10 <sup>-3</sup>	90	1.99
	-50.0	3.67 · 10 <sup>-4</sup>	1.89 · 10 <sup>-2</sup>	4.75 · 10 <sup>-3</sup>	95	2.17
	-50.0	3.39 · 10 <sup>-4</sup>	9.51 · 10 <sup>-3</sup>	3.71 · 10 <sup>-3</sup>	64	1.89
	-70.0	4.22 · 10 <sup>-4</sup>	8.70 · 10 <sup>-3</sup>	4.37 · 10 <sup>-3</sup>	98	0.459
<b>4c<sup>c</sup></b>	20.0	1.24 · 10 <sup>-3</sup>	1.58 · 10 <sup>-2</sup>	–	94	6.11
	0.0	1.23 · 10 <sup>-3</sup>	1.96 · 10 <sup>-2</sup>	–	88	2.09
	-20.0	7.55 · 10 <sup>-4</sup>	1.80 · 10 <sup>-2</sup>	–	94	0.698
	-39.7	3.21 · 10 <sup>-4</sup>	1.27 · 10 <sup>-2</sup>	2.19 · 10 <sup>-3b</sup>	82	0.165
	-39.8	1.52 · 10 <sup>-3</sup>	2.43 · 10 <sup>-2</sup>	–	89	0.131
	-60.0	1.31 · 10 <sup>-3</sup>	1.67 · 10 <sup>-2</sup>	–	40	2.30 · 10 <sup>-2</sup>
<b>4d<sup>c</sup></b>	20.0	3.43 · 10 <sup>-4</sup>	5.43 · 10 <sup>-2</sup>	–	76	3.93 · 10 <sup>-4</sup>
	20.0	2.22 · 10 <sup>-4</sup>	2.29 · 10 <sup>-2</sup>	–	48	3.82 · 10 <sup>-4</sup>

<sup>a</sup> As shown by multiple measurements at the same temperature, standard deviations of the rate constants of 4–7% can be assumed. <sup>b</sup> The electrophiles were generated by addition of TMSOTf to the respective BF<sub>4</sub><sup>-</sup> solutions of **4a-Cl**, **4b-OMe**, and **4c-OAc**. <sup>c</sup> The BF<sub>4</sub><sup>-</sup> salts of **4c** and **4d** were employed.

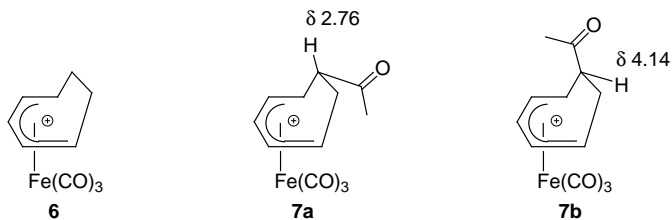
sors<sup>13</sup>. In this work, **1** was obtained by heating cycloheptatriene and  $\text{Fe}(\text{CO})_5$  without a solvent, and by a slight modification of the published procedure<sup>13a</sup>, the yield was improved from 52 to 72%. The concomitant production of (tricarbonyliron)cycloheptadiene as reported in ref.<sup>13b</sup> was not observed.

Treatment of **1** with the diarylcarbenium triflates **4a–4d** yielded the tricarbonyl( $\eta^5$ -cycloheptadienylum)iron triflates **5a–5d** (Scheme 2), contaminated by some **6-OTf** which could be removed by recrystallization of (**5a–5c**)-OTf. A pure sample of **5d-OTf** could not be obtained. Pearson *et al.* also reported the formation of **6** in related reactions due to traces of moisture in the reagents<sup>5b</sup>. The reaction with the prochiral carbocation **4c** yielded the adduct **5c** as a 56 : 44 mixture of two diastereoisomers.



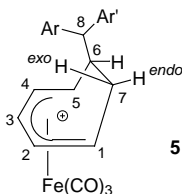
SCHEME 2

Investigations of Lewis *et al.*<sup>4</sup> and Pearson *et al.*<sup>5b</sup> have shown that electrophiles attack **1** *anti* to the  $\text{Fe}(\text{CO})_3$  group and yield 6-*exo*-substituted products. Lewis reported a large difference of  $\delta(6\text{-H})$  in the stereoisomeric 6-acetyl substituted tricarbonyliron coordinated cycloheptadienyl ions **7a** and **7b** (ref.<sup>4</sup>). The <sup>1</sup>H NMR absorbance of 6-H in compounds **5** ( $\delta$  3.93–4.09) can, therefore, be considered as evidence for the indicated *anti*-substitution of these complexes (Table II).



In all compounds **5**, 7-*exo*-H is shielded by 1 ppm compared to 7-*endo*-H. While 7-*endo*-H shows  $^3J$  couplings of 8.5 Hz to both vicinal protons (1-H and 6-H), 7-*exo*-H shows considerably smaller couplings which were only resolved in the case of **5a**.

TABLE II  
Selected  $^1\text{H}$  NMR data (300 MHz) of the tricarbonyl( $\eta^5$ -cycloheptadienylium)iron triflates **5a**-OTf, **5b**-OTf, and **5c**-OTf



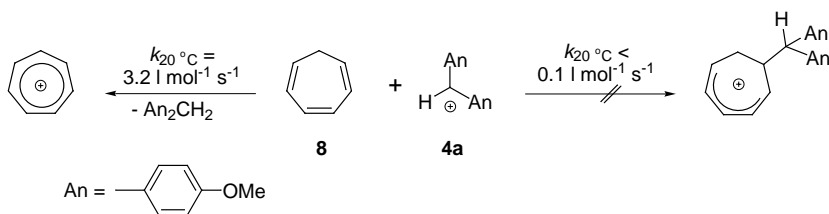
Hydrogen	<b>5a</b> -OTf <sup>a</sup>	<b>5b</b> -OTf <sup>a</sup>	<b>5c</b> -OTf <sup>b</sup>
7- <i>exo</i> -H	1.06 ddd $J(7,7) = 14.4$ $J(7,6) = 6.7$ $J(7,1) = 2.4$	1.09–1.14 m	1.07–1.15 m
7- <i>endo</i> -H	2.29 dt $J(7,7) = 14.5$ $J(7,1 \approx 7,6) \approx 8.5$	2.35 dt $J(7,7) = 14.5$ $J(7,1 \approx 7,6) \approx 8.4$	2.21 m <sub>c</sub>
6-H	4.01 m <sub>c</sub>	4.00–4.09 m	3.93 m <sub>c</sub>
5-H	4.49 dd $J(5,4) = 9.7$ $J(5,6) = 4.7$	(4.43–4.56) <sup>c</sup> m	5.04 m <sub>c</sub>
4-H	5.68 dd $J(4,5) = 9.7$ $J(4,3) = 6.7$	5.71 dd $J(4,5) = 9.7$ $J(4,3) = 6.8$	6.26 m $J(4,5) = 9.6$ $J(4,3) = 6.9$
2-H	6.05 br t $J(2,1) + J(2,3) = 14.6$	6.07 br t $J(2,1) + J(2,3) = 14.6$	6.38 br t $J(2,1) + J(2,3) = 14.6$
1-H	4.65 td $J(1,2 \approx 1,7\text{-endo}) \approx 8.2$ $J(1,7\text{-exo}) = 2.5$	4.67 tdd $J(1,2 \approx 1,7\text{-endo}) \approx 8.4$ $J(1,7\text{-exo}) = 3.3$ $J = 1.4$	4.93 tdd $J(1,2 \approx 1,7\text{-endo}) \approx 8.5$ $J(1,7\text{-exo}) = 3.4$ $J = 1.6$

<sup>a</sup> CD<sub>3</sub>CN. <sup>b</sup> (CD<sub>3</sub>)<sub>2</sub>CO. <sup>c</sup> Resonances of 5-H are superimposed by other signals.

## Kinetics

The rates of the reactions of **1** with **4a–4d** were measured by monitoring the visible absorption bands of the cations **4a–4d** (see Experimental). Evaluation of the data as reported previously<sup>12</sup> and specified in the Experimental showed that all reactions followed second-order kinetics, first-order with respect to **1** and first-order with respect to carbenium ions. In one case (**1** + **4c**), the independence of the rate constant of the counterion ( $\text{OTf}^-$  or  $\text{BF}_4^-$ ) has been demonstrated, as previously observed for the reactions of carbocation salts with other  $\pi$ -systems<sup>7,16</sup>.

From the fact that **4a**, like other carbocations, reacts with cycloheptatriene (**8**) with exclusive hydride transfer (Scheme 3), one can conclude that the rate constant for the addition of **4a** to the  $\pi$ -system of **8** is smaller than



SCHEME 3

$0.1 \text{ l mol}^{-1} \text{ s}^{-1}$  (assuming an NMR detection limit of 3%). Comparison of this value with the corresponding number in Table III (**1** + **4a**:  $k_{20 \text{ °C}} = 1\,246 \text{ l mol}^{-1} \text{ s}^{-1}$ ) shows that the tricarbonyliron coordination of cycloheptatriene increases its  $\pi$ -nucleophilicity by more than four orders of magnitude.

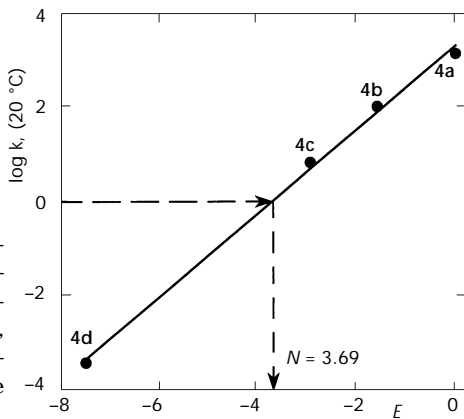


FIG. 1  
Determination of the nucleophilicity parameters  $N$  and  $s$  for tricarbonyl( $\eta^4$ -cyclohepta-1,3,5-triene)iron (**1**) (linear correlation: slope  $s = 0.89 \pm 0.03$ ,  $b = 3.27 \pm 0.13$ ,  $r = 0.9986$ ; the actual errors are larger because of the uncertainty of the  $E$  values, see ref.<sup>7</sup>)



Figure 1 shows a linear correlation between the logarithms of the rate constants listed in Table III and the electrophilicity parameters  $E$  of the corresponding carbocations, indicating that these reactions also follow the linear Gibbs energy relationship (1). The slope  $s = 0.89$  resembles that found for other  $\pi$ -systems<sup>7</sup>, and from the intercept with the abscissa at  $\log k = 0$  one derives  $N(\mathbf{1}) = 3.69$ , showing that the nucleophilicity of  $\mathbf{1}$  is comparable to that of 1,3,5-trimethoxybenzene<sup>7a</sup>, 2-methylfuran<sup>17</sup>, or (2-methylallyl)triphenylsilane<sup>7a</sup>. Since the rates of the reactions of cationic electrophiles with neutral nucleophiles are only slightly affected by solvents<sup>7a,12</sup>, one can conclude that at typical preparative concentrations (1 mol l<sup>-1</sup>) half reaction times of less than ten hours at 20 °C can be expected for reactions of  $\mathbf{1}$  with electrophiles  $E \geq -9$ .

TABLE III

Rate constants (20 °C) and activation parameters for the reactions of tricarbonyl-( $\eta^4$ -cyclohepta-1,3,5-triene)iron  $\mathbf{1}$  with the carbenium ions  $\mathbf{4a}$ – $\mathbf{4d}$  (CH<sub>2</sub>Cl<sub>2</sub>)

Electrophile	$k$ , l mol <sup>-1</sup> s <sup>-1</sup>	$\Delta H^\ddagger$ , kJ mol <sup>-1</sup>	$\Delta S^\ddagger$ , J K <sup>-1</sup> mol <sup>-1</sup>	$T$ -range, °C
<b>4a</b>	1 246	16.51 ± 0.36	-129.3 ± 1.6	-20 to -70
<b>4b</b>	98	27.76 ± 1.04	-112.0 ± 4.6	-10 to -70
<b>4c</b>	6.47	34.07 ± 0.91	-113.1 ± 3.7	20 to -60
<b>4d</b>	3.88 · 10 <sup>-4</sup>	-	-	20

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