How Electrophilic are Ferrocenylmethyl Cations? Kinetics of their Reactions with π Nucleophiles and Hydride Donors[☆]

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Second-order rate constants for the reactions of the ferrocenylmethylium ions 2a−e with silyl enol ethers, allylsilanes, allylstannanes, and hydride donors have been determined photometrically and conductometrically in dichloromethane. The ferrocenylmethylium ions 2a−d (fc-CHR+, R = H, Me, Ph, An) are slightly stronger electrophiles than the tropylium ion, and their electrophilic reactivities depend only slightly on the nature of R. The bis(ferrocenyl)methylium ion 2e is a considerably weaker electrophile, comparable to the tricarbonyl(cyclohexadienyl)iron cation.

Combinations of electrophiles with nucleophiles represent the most important reaction type in organic chemistry, and there have been numerous attempts to quantify the terms electrophilicity and nucleophilicity[1]. It is well-known that relative reactivities of electrophiles and nucleophiles are not generally independent of the nature of the reaction partner. In the case of the reactions of benzhydryl cations with π nucleophiles (alkenes[2,3], allylsilanes and -stannanes[4], arenes[5]) and hydride donors[6,7] the relative nucleophilicities depend only slightly on the nature of the reference carbenium ion. Taking into account the different slopes of the linear free energy relationships, nucleophilicity parameters have been derived[8] which have been reported to hold also for the corresponding reactions with tricarbonyl(cycloalkadienyl)iron cations[9]. Recently, we have linked our kinetic data with related rate constants determined by other groups, and thus have obtained the correlation equation (1), which has been demonstrated to be applicable to a large variety of electrophile-nucleophile combinations[8].

$$\lg k = s(E + N) \text{ (aprotic solvents, 20°C)} \tag{1}$$

In this equation, electrophiles are characterized by a single parameter (E), while nucleophiles are characterized by the nucleophilicity parameter N and the slope parameter s. The application of this scale is hampered by the fact, however, that in contrast to the large number of nucleophilicity parameters which are already available, there is only a relatively small number of electrophiles, the reactivity of which has been established quantitatively. We have, therefore, started a program to assign reactivity parameters to various classes of electrophiles.

Only few years after its discovery in 1951[10], the ability of ferrocene to stabilize positive charge has been recognized[11,12]. Ferrocenylmethylium ions have been isolated as stable salts, e.g. as tetrafluoroborates[13], and numerous spectroscopic, mechanistic, and crystal structural investigations on these ions have been published[14]. Several groups have studied the kinetics of their reactions with n nucleophiles and anionic hydride donors[11,13,15,16].

In this work, we have studied the kinetics of the reactions of ferrocenylmethylium ions with π nucleophiles and neutral hydride donors in order to quantify their electrophilicity and to characterize the electrophilic potential of these cations.

Reaction Products

Though ferrocenylmethylium ions are relatively stable entities, their handling requires some care. Some of the free cations are sensitive to moisture, and in the case of alkyl-substituted ferrocenylmethylium ions, deprotonation may occur to give alkenylferrocenes which may successively react with ferrocenylmethylium ions to yield undesired oligomeric byproducts[16]. In order to circumvent these problems, we have usually generated solutions of the ferrocenylmethylium ions from the corresponding acetoxy derivatives and a Lewis acid immediately before use (Scheme 1).

Scheme 1. [a] An = 4-MeOC₆H₄, [b] fc = Ferrocenyl, C₅H₅FeC₅H₄
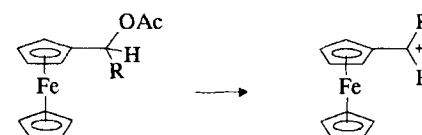
R		
H	1a	2a
Me	1b	2b
Ph	1c	2c
An[a]	1d	2d
fc[b]		2e

Successive treatment of the ferrocenyl derivatives 1a−d with ZnCl₂ · Et₂O[1.6] and the nucleophiles 3−9 gives the products listed in Scheme 2 as the only compounds detectable by NMR. The reactions of 2e with 6 and 8 have been performed with 2e · BF₄.

As indicated in Scheme 2, several of the reaction products have been described before, and since the NMR spectra confirm the expected and well-established course of the reactions of electrophiles with allylstannanes, allylsilanes[4,17], silylenol ethers[18,19], and hydride donors[7,20], further analytical data for the reaction products have not been collected.

Scheme 2. Reactions of ferrocenylmethylium ions with π nucleophiles and HSiMe₂Ph. – [a]–[d] Product previously described in [a] ref.[33], [b] ref.[34], [c] ref.[35], [d] ref.[31,36]

Nucleophile		Electrophile/R	Product	
⟋⟍SnPh₃	3	2c/Ph	fc ⟍⟋⟍ R	3c
⟋⟍SiMe₃	4	2b/Me 2c/Ph 2d/An	fc ⟍⟋⟍ R	4b 4c 4d
OSiMe₃ ⟋⟍	5	2c/Ph 2d/An	fc ⟍ R O	5c[a] 5d
OSiMe₃	6	2c/Ph 2d/An 2e/fc	fc R O	6c 6d 6e
OSiMe₃	7	2b/Me	fc R O	7b[b]
OSiMe₃ OMe	8	2e/fc	fc R O OMe	8e
HSiMe₂Ph	9	2a//H 2d/An	fc R	9a[c] 9d[d]

Kinetic Investigations

In previous kinetic investigations of the reactions of carbenium ions with allylstannanes, silylated enol ethers, and hydrosilanes problems have been encountered due to the reactions of these nucleophiles with some of the Lewis acids employed in excess for the generation of the carbenium ions. Since trimethylsilyl triflate has been observed not to react with any of the nucleophiles 3–11, the reaction of trimethylsilyl triflate with the ferrocenylmethyl acetates 1 has been employed to produce colored solutions of the ferrocenylmethylium triflates for the kinetic experiments. When the nucleophiles 3–11 are added successively, decolorization takes place. Its rate is followed photometrically and conductometrically as described previously[21]. In accord with studies of other carbocations[2,21], the reactions follow second-order kinetics, first order with respect to carbenium ion and first order with respect to nucleophile. Since related investigations show independence of the rate constants of the nature of the negative counterion[2,4,7,21], the k_2 values given in Table 1 can be considered to represent the rate constants of the attack of the ferrocenylmethylium ions at the nucleophiles.

Table 1. Rate constants for the reactions of ferrocenylmethyl cations fcCHR$^{+[a]}$ with nucleophiles (20°C, CH₂Cl₂)

R/ Electrophile	Nucleophile		k_2 [l mol⁻¹ s⁻¹]	$\Delta H^{\ddagger}$ [kJ mol⁻¹] ($\Delta S^{\ddagger}$ [J K⁻¹ mol⁻¹])	E
H/2a	HSiMe₂Ph	9	1.17x10¹	46.7 ± 0.4 (-65 ± 2)	-1.91
	HSiPh₃	10	1.04	52.9 ± 1.4 (-64 ± 5)	-1.89
Me/2b	⟋⟍SiMe₃	4	5.98x10¹	31.3 ± 1.4 (-104 ± 6)	-2.90
	HSiMe₂Ph	9	2.19	46.1 ± 1.7 (-81 ± 7)	-2.92
Ph/2c	⬠—OSiMe₃	6	3.31x10³	22.1 ± 0.1 (-102 ± 1)	-3.08
	⬡—OSiMe₃	7	3.70x10²	25.1 ± 0.4 (-110 ± 2)	-2.79
	OSiMe₃ ⟋⟍	5	3.49x10²	31.4 ± 2.9 (-89 ± 13)	-3.12
	⟋⟍SiMe₃	4	5.45x10¹	28.3 ± 2.8 (-115 ± 12)	-2.95
	⟋⟍SnPh₃	3	2.21	32.3 ± 2.6 (-128 ± 9)	-2.90
	HSiMe₂Ph	9	1.56	48.1 ± 0.9 (-77 ± 3)	-3.12
An[b]/2d	OSiMe₃ ⟋⟍	5	2.40x10²	32.9 ± 2.7 (-87 ± 12)	-3.31
	⟋⟍SiMe₃	4	2.37x10¹	27.4 ± 0.7 (-125 ± 3)	-3.36
	HSiMe₂Ph	9	8.99x10⁻¹	47.1 ± 1.2 (-85 ± 4)	-3.45
fc[a]/2e	⬡—OSiMe₃	7	1.21x10⁻³		-8.75
	⬠—OSiMe₃	6	3.05x10⁻²	36.0 ± 0.6 (-151 ± 2)	-8.49
	OSiMe₃ O Me	8	5.21x10⁻¹	28.2 ± 1.0 (-154 ± 4)	-9.79
	HSnBu₃	11	3.50	39.1 ± 0.6 (-101 ± 2)	-8.34

[a] fc = (C₅H₅)Fe(C₅H₄). – [b] An = 4-MeOC₆H₄.

Discussion

The activation parameters in Table 1 show that within one class of nucleophiles the reactivity differences are due to variable values of $\Delta H^{\ddagger}$ while $\Delta S^{\ddagger}$ remains almost constant. As in analogous reactions with benzhydryl cations, there are characteristic values of $\Delta S^{\ddagger}$ for the reactions of alkyl- and aryl-substituted ferrocenylmethylium ions with the different classes of nucleophiles. While most π nucleophiles used in this study possess activation entropies of (-105 ± 15) J mol⁻¹ K⁻¹, the corresponding values for the hydride donors HSiMe₂Ph and HSiPh₃ are noticeably less negative (-81 ± 5) J mol⁻¹ K⁻¹. Unusually large negative values of $\Delta S^{\ddagger}$ have only been found for the reactions of 2e with π nucleophiles and HSnBu₃, which may be due to the larger steric shielding of this cation. An X-ray analysis of 2e reveals the transoid conformation of the cation. The

cyclopentadienyl rings are almost eclipsed, and the ferrocenyl groups are bent toward the carbenium carbon[22]. Consequently, the π orbital of the carbenium center is shielded from both sides. An analogous increase of the negative value of $\Delta S^{\neq}$ due to steric effects has been reported in ref.[9].

Eq. (1) can now be used to calculate the E values for the electrophiles 2a−e from $\lg k_2$ (Table 1) and the nucleophilicity parameters N and s for 3−11 given in ref.[8]. The last column in Table 1 shows that the electrophilicity parameters E determined from the reactivities toward different nucleophiles are closely similar, indicating that ferrocenylmethylium ions match the linear free energy relationship (1). Only in the case of 2e steric effects play a noticeable role, and the bulky nucleophile 8 reacts more slowly than expected from the reactivities of the other nucleophiles. The graphical presentation of these reactivities in Figure 1 also shows that ferrocenylmethylium ions and benzhydryl cations follow the same linear free energy relationship.
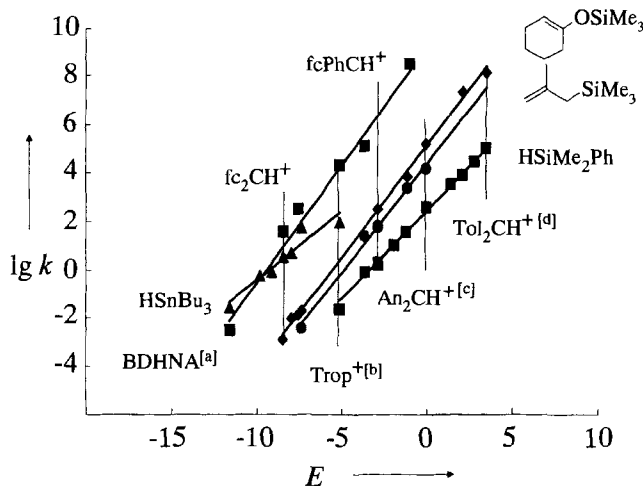

Figure 1. Correlation between the rate constants of the reactions of electrophiles with nucleophiles and the electrophilicity parameters given in Table 1 and ref.[8] – [a] BDHNA: N-Benzyl-1,4-dihydronicotinamide. – [b] Trop+: Tropylium ion. – [c] An2CH+: Bis(4-methoxyphenyl)carbenium ion. – [d] Tol2CH+: Bis(4-methylphenyl)carbenium ion.

The rate constants given in Table 1 were combined with the rate constants reported for the reactions of ferrocenylmethylium ions 2c, d with H_2O and N-benzyl-1,4-dihydronicotinamide (BDHNA)[11,13] to give the averaged E values compiled in Figure 3. The reactivity order of the cations 2a−d reveals that replacement of a hydrogen by a methyl, a phenyl, or a p-anisyl group in 2a reduces the reactivity by less than two orders of magnitude, indicating little electron demand of the formal carbenium center of 2a. Only when a second ferrocenyl group is introduced (cation 2e), a strong reduction of electrophilicity is observed. The relatively small differences of the electrophilic reactivities of the cations 2a−d can be rationalized by their structures. X-ray analysis of ferrocenyldiphenylcarbenium tetrafluoroborate[23] manifests an Fe−C_{exo} distance of 271.5 pm, and C_{exo} is bent to iron (angle 20.7°). The direct interaction of the cationic C_{exo} with the iron atom essentially stabilizes

the ferrocenylmethylium ions. Hence, the cation can also be described as an η^6 iron-fulvene complex with little charge at C_{exo}.
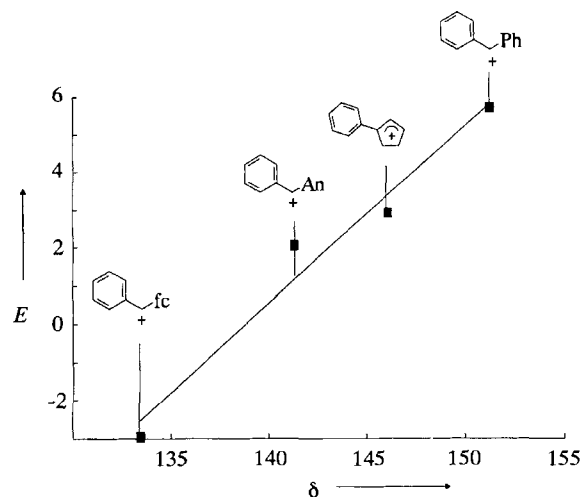

Figure 2. Correlation of the electrophilicity parameter E with the ¹³C-NMR chemical shift of C_{para} in phenyl-substituted carbenium ions
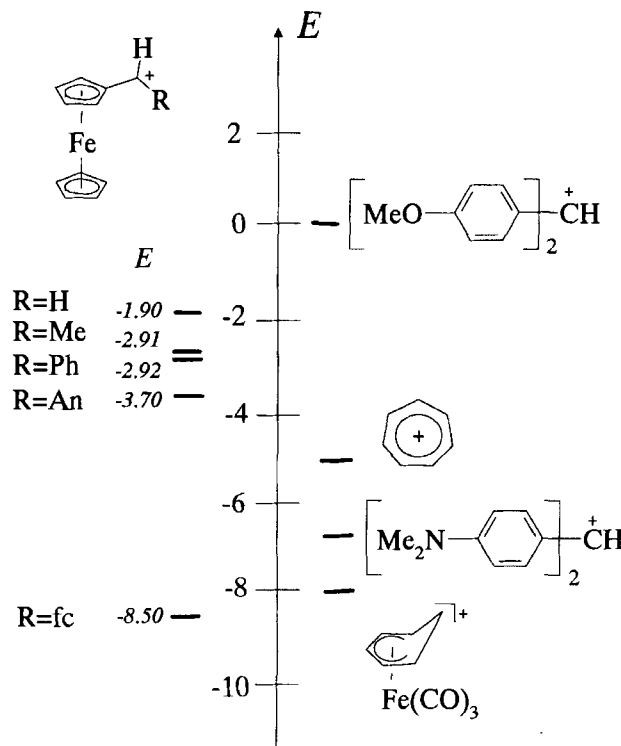

Figure 3. Comparison of the electrophilicity parameters E of ferrocenylmethylium ions with those of other carbenium ions

¹³C-NMR chemical shifts of the para-carbons in phenyl-substituted carbenium ions have been used as a probe for determining the positive charge at the carbenium center[24]. A comparison of δ (C_{para}) of 2c with the corresponding chemical shifts of other phenyl-substituted carbenium ions (Figure 2) also leads to the conclusion that the positive charge in ferrocenylmethylium ions is located only to a small extent on C_{exo}. Figure 2 furthermore shows that this

chemical shift shows a fair correlation with the electrophilicity parameter E of these compounds.

As indicated in Figure 3, the unsubstituted, methyl-, phenyl-, and anisyl-substituted ferrocenylmethylium ions are slightly stronger electrophiles than the tropylium ion. Their electrophilicity lies between the well-established bis[p-(dimethylamino)phenyl]- and bis(p-methoxyphenyl) carbenium ions[18,25], while the bis(ferrocenyl)methylium ion **2e** is a considerably weaker electrophile.

Experimental

NMR: Bruker WM 300. All NMR spectra (300 MHz) were recorded in $CDCl_3$. – Ferrocenecarbaldehyde (Aldrich) was reduced with $LiAlH_4$ to give ferrocenemethanol[26] (76%, ref.[26] 90%) which was treated with acetic anhydride/pyridine to give the acetate **1a** according to ref.[27] (87%). Reaction of ferrocene with acetic anhydride/BF_3[28], benzoyl chloride/$AlCl_3$[29] or p-anisoyl chloride/$AlCl_3$ according to ref.[29] gave ferrocenyl methyl ketone (72%, ref.[28] 67%), ferrocenyl phenyl ketone (72%, ref.[29] 70–75%), and ferrocenyl (p-anisyl) ketone (38%), respectively. Reduction with $LiAlH_4$ and subsequent acetylation with acetic anhydride/pyridine according to ref.[27] gave compounds **1b**[27] (82%), **1c** (87%), and **1d** (73%). For the preparation of the bis(ferrocenyl) compounds, bis(ferrocenyl)methyl ethyl ether (fc$_2$CHOEt) was prepared from ferrocene and triethyl orthoformate according to a procedure by Schaaf[30]. Treatment of fc$_2$CHOEt with HBF_4 or CF_3SO_3H according to ref.[31] gave a deep blue powder of fc$_2$CH$^+$BF$_4^-$ (88%) and fc$_2$CH$^+$CF$_3$-SO$_3^-$ (92%), respectively.

General Procedure for the Reactions of Ferrocenylmethylium Ions with Nucleophiles: Compounds **1a–d** ($\approx$1 mmol) were dissolved in dry CH_2Cl_2 (10 ml). The solutions were cooled at $-50°C$, and 0.5 ml of a 2 M solution of $ZnCl_2 \cdot (OEt_2)_{1.6}$[32] in CH_2Cl_2 was added to give deep-red solutions of the ferrocenylmethyl cations. After addition of 3 equiv. of **3–9** the solutions were allowed to warm up to 20°C (30 min). Decolorization took place, and the solutions were washed with water (20 ml). The aqueous layer was extracted with two 5-ml portions of CH_2Cl_2, and the combined organic fractions were then washed with $NaHCO_3$ (saturated aq. solution) and water and dried with $MgSO_4$. The solvent was evaporated in vacuo and the residue analyzed by ^1H and ^{13}C NMR. Compounds **6e** and **8e** were obtained by dissolving **2e-OTf** (1 mmol) in 30 ml of CH_2Cl_2, adding the nucleophiles **6** and **8**, respectively to the solution, and workup as described above.

(1-Phenyl-3-butenyl)ferrocene (**3c**): Orange powder, m.p. 46–46.5°C (ether/hexane, 1:1). – ^1H NMR: δ = 2.55–2.65, 2.80–2.88 (2 m, 2H, 2-H), 3.68 (dd, J = 4.7/10.4 Hz, 1H, 1-H), 3.94, 4.04, 4.09, 4.13 (4 br. s, 4H, C_5H_4), 4.06 (s, 5H, C_5H_5), 4.90–5.02 (m, 2H, 4-H), 5.62–5.75 (m, 1H, 3-H), 7.14–7.28 (m, 5H, aromatic H). – ^{13}C NMR: δ = 41.41 (t, C-2), 46.16 (d, C-1), 66.83, 66.90, 67.45, 67.56 (4 d, C_5H_4), 68.55 (d, C_5H_5), 93.68 (s, fc-C_i), 115.86 (t, C-4), 126.10, 127.89, 128.07 (3 d, aromatic C), 137.03 (d, C-3), 144.78 (s, C_i-aryl).

(1,3-Dimethyl-3-butenyl)ferrocene (**4b**): Orange oil. – ^1H NMR: δ = 1.09 (d, J = 6.8 Hz, 3H, 1-CH$_3$), 1.67 (t, J = 0.5 Hz, 3H, 3-CH$_3$), 1.95 (dd, J = 10/13.5 Hz, 1H, 2-H), 2.28 (dd, J = 4.4/13.5 Hz, 1H, 2-H), 2.56 (m$_c$, 1H, 1-H), 3.99 (m$_c$, 4H, C_5H_4), 4.06 (s, 5H, C_5H_5), 4.60, 4.69 (2 br. s, 2H, 4-H). – ^{13}C NMR: δ = 20.10,

22.28 (2 q, CH$_3$), 30.73 (d, C-1), 47.22 (t, C-2), 65.94, 66.76, 66.84, 66.88 (4 d, C_5H_4), 68.34 (d, C_5H_5), 95.96 (s, fc-C_i), 111.83 (t, C-4), 144.29 (s, C-3).

(3-Methyl-1-phenyl-3-butenyl)ferrocene (**4c**): Orange powder, m.p. 54°C (ether). – ^1H NMR: δ = 1.69 (s, 3H, 3-CH$_3$), 2.58 (dd, J = 11.1/13.6 Hz, 1H, 2-H), 2.83, (dd, J = 4.2/13.6 Hz, 1H, 2-H), 3.81 (dd, J = 4.3/11.1 Hz, 1H, 1-H), 3.96, 4.04, 4.09, 4.16 (4 br. s, 4H, C_5H_4), 4.07 (s, 5H, C_5H_5), 4.51, 4.64 (2 br. s, 2H, 4-H), 7.08–7.18 (m, 5H, aromatic H). – ^{13}C NMR: δ = 22.59 (q, CH$_3$), 44.30 (d, C-1), 45.29 (t, C-2), 66.70, 66.92, 67.48, 67.57 (4 d, C_5H_4), 68.56 (d, C_5H_5), 94.29 (s, fc-C_i), 112.52 (t, C-4), 126.04 (d, C_p), 127.83, 127.97 (2 d, C_o, C_m), 143.44, 144.87 (2 s, C_i-Aryl, C-3).

[1-(4-Methoxyphenyl)-3-methyl-3-butenyl]ferrocene (**4d**): Orange oil. – ^1H NMR: δ = 1.68 (s, 3H, 3-CH$_3$), 2.53 (dd, J = 11.2/13.6 Hz, 1H, 2-H), 2.80 (dd, J = 3.9/13.6 Hz, 1H, 2-H), 3.74 (s, 3H, OCH$_3$), 3.77 (dd, J = 4/11 Hz, 1H, 1-H, superimposed by the singlet at δ 3.74), 3.93, 4.03, 4.13 (3 br. s, 3H, C_5H_4), 4.06 (s, 6H, C_5H_5, C_5H_4), 4.52, 4.65 (2 br. s, 2H, 4-H), 6.79, 7.07 (AA'BB'-system, J_{AB} = 8.6 Hz, 4H, aromatic H). – ^{13}C NMR: δ = 22.56 (q, 3-CH$_3$), 43.37 (d, C-1), 45.32 (t, C-2), 55.05 (q, OCH$_3$), 66.60, 66.89, 67.41, 67.49 (4 d, C_5H_4), 68.53 (d, C_5H_5), 94.75 (s, fc-C_i), 112.42 (t, C-4), 113.29 (d, C_m), 128.64 (d, C_o), 137.02 (s, C_i-aryl), 143.53 (s, C-3), 157.70 (s, C-O).

4-Ferrocenyl-4-phenyl-2-butanone (**5c**)[33]: Yellow powder, m.p. 89°C (ether) (ref.[33] 96°C). – ^1H NMR: δ = 2.00 (s, 3H, 1-H), 3.05, 3.11 (AB part of an ABM system with J_{AB} = 16.2, J_{AM} = 9.6, J_{BM} = 4.7 Hz, 2H, 3-H), 3.95 (br. s, 2H, C_5H_4), 4.06 (s, 6H, C_5H_5, C_5H_4), 4.10 (br. s, 1H, C_5H_4), 4.27 (M part of an ABM system with J_{BM} = 4.7, J_{AM} = 9.6 Hz, 1H, 4-H), 7.13–7.28 (m, 5H, aromatic H). – ^{13}C NMR: δ = 30.95 (q, C-1), 40.90 (d, C-4), 51.04 (t, C-3), 66.66, 67.18, 67.67 (3 d, C_5H_4), 68.56 (d, C_5H_5), 92.97 (s, fc-C_i), 126.38, 127.61, 128.24 (3 d, aromatic C), 144.38 (s, C_i-aryl), 207.20 (s, CO).

4-Ferrocenyl-4-(4-methoxyphenyl)-2-butanone (**5d**): Yellow powder, m.p. 90–91°C (ether). – ^1H NMR: δ = 2.00 (s, 3H, 1-H), 3.02, 3.08 (AB part of an ABM system with J_{AB} = 16.0, J_{AM} = 9.9, J_{BM} = 4.6 Hz, 2H, 3-H), 3.74 (s, 3H, OCH$_3$), 4.04, 4.07 (2 m, 4H, C_5H_4), 4.06 (s, 5H, C_5H_5), 4.23 (M part of an ABM system with J_{AM} = 9.9, J_{BM} = 4.6 Hz, 1H, 4-H), 6.79, 7.12 (AA'BB' system, J_{AB} = 8.6 Hz, 4H, aromatic H). – ^{13}C NMR: δ = 30.89 (q, C-1), 40.21 (d, C-4), 51.20 (t, C-3), 55.10 (q, OCH$_3$), 66.56, 67.19, 67.61, 67.66 (4 d, C_5H_4), 68.52 (d, C_5H_5), 93.41 (s, fc-C_i), 113.61 (d, C_m), 128.54 (d, C_o), 136.56 (s, C_i-aryl), 158.01 (s, C-O), 207.26 (s, CO).

2-(Ferrocenylphenylmethyl)cyclopentanone (**6c**): Mixture of diastereomers ($\approx$ 3:1), orange powder. – ^1H NMR: δ = 1.35–1.83 (m, 4H, 2 CH$_2$), 2.04–2.22 (m, 2H, CH$_2$), 2.34–2.41, 2.88–2.95 (2 m, 1H, 2-H), 3.81, 4.05 (2 s, 5H, C_5H_5), 3.85, 3.93, 3.98, 4.07, 4.14 (5 m$_c$, 4H, C_5H_4), 4.33, 4.63 (2 d, J = 3.0/2.2 Hz, 1H, CH), 6.84–6.87, 7.03–7.11, 7.17–7.37 (3 m, 5H, aromatic H). – ^{13}C NMR: δ = 20.38, 20.66, 26.18, 38.44, 38.65 (5 t, CH$_2$), 44.16, 45.60, 54.48, 56.20 (4 d, CH, C-2), 66.87, 67.39, 67.51, 67.63, 68.00, 68.22, 68.45, 68.52, 68.66, 69.09 (10 d, C_5H_5, C_5H_4), 89.26, 91.98 (2 s, fc-C_i), 126.15, 126.41, 127.81, 128.10, 128.67 (5 d, aromatic C), 142.85, 143.49 (2 s, C_i-aryl), 219.60, 220.13 (2 s, CO).

2-[Ferrocenyl(4-methoxyphenyl)methyl]cyclopentanone (**6d**): Mixture of diastereomers ($\approx$ 1:4), orange oil. – ^1H NMR: δ = 1.45–1.80 (m, 4H, 2 CH$_2$), 2.05–2.30 (m, 2H, CH$_2$), 2.44, 2.95 (2 m$_c$, 1H, 2-H), 3.73, 3.83 (2 s, OCH$_3$), 3.93, 4.13 (2 s, C_5H_5), 3.98–4.21 (m, C_5H_4), 4.36, 4.65 (2 d, J = 2.8/1.4 Hz, 1H, fcArCH), 6.70, 6.86 (AA'BB' system, J_{AB} = 8.6 Hz, aromatic H), 6.90, 7.33

Table 2. Kinetics of the reactions of ferrocenylmethylium ions with nucleophiles[a]

Ferrocenylmethylium 2a [(8.72-14.5)x10^-5 mol l^-1] and Dimethylphenylsilane 9

T/°C	[9]/mol l^-1	Conversion/%[b]	k_2/ l mol^-1 s^-1
-0.5	3.09×10^{-3}	53	2.55
-9.5	1.78×10^{-3}	86	1.18
-11.3	3.20×10^{-3}	90	1.09
-30.7	3.25×10^{-3}	94	1.70×10^{-1}
-51.3	9.49×19^{-3}	33	1.87×10^{-2}

Ferrocenylmethylium 2a [(7.31-8.59)x10^-5 mol l^-1] and Triphenylsilane 10

T/°C	[10]/mol l^-1	Conversion/%[b]	k_2/ l mol^-1 s^-1
21.1	1.44×10^{-3}	46	1.17
5.1	2.01×10^{-3}	36	3.5×10^{-1}
0.0	2.99×10^{-3}	69	2.1×10^{-1}
-10.2	2.55×10^{-3}	43	8.0×10^{-2}

Ferrocenylethylium 2b [(1.45-1.88)x10^-3 mol l^-1] and Methallyltrimethylsilane 4

T/°C	[4]/mol l^-1	Conversion/%[b]	k_2/ l mol^-1 s^-1
-20.8	2.18×10^{-2}	67	6.77
-39.8	7.85×10^{-2}	64	1.73
-46.5	7.77×10^{-2}	97	8.7×10^{-1}
-47.2	2.45×10^{-2}	66	1.07
-57.3	1.89×10^{-2}	56	4.6×10^{-1}
-66.6	8.73×10^{-3}	72	2.0×10^{-1}

Ferrocenylethylium 2b [(1.50-1.75)x10^-3 mol l^-1] and Dimethylphenylsilane 9

T/°C	[9]/mol l^-1	Conversion/%[b]	k_2/ l mol^-1 s^-1
-0.4	2.27×10^{-2}	62	4.62×10^{-1}
-9.7	2.57×10^{-2}	49	2.13×10^{-1}
-20.5	2.21×10^{-2}	69	1.26×10^{-1}
-20.5	4.80×10^{-2}	72	9.32×10^{-2}
-40.3	2.67×19^{-2}	71	1.32×10^{-2}
-60.4	2.70×10^{-2}	61	1.22×10^{-3}

Ferrocenylphenylmethylium 2c [(1.74-2.00)x10^-4 mol l^-1] and Trimethylsiloxycyclopentene 6

T/°C	[6]/mol l^-1	Conversion/%[b]	k_2/ l mol^-1 s^-1
-51.8	2.05×10^{-3}	83	137.1
-61.8	2.36×10^{-3}	84	74.6
-71.7	2.20×10^{-3}	89	38.1

Ferrocenylphenylmethylium 2c [(3.57-5.04)x10^-4 mol l^-1] and Trimethylsiloxycyclohexene 7

T/°C	[7]/mol l^-1	Conversion/%[b]	k_2/ l mol^-1 s^-1
-40.0	6.48×10^{-3}	44	20.42
-50.8	4.87×10^{-3}	26	10.31
-68.5	5.02×10^{-3}	36	2.87
-69.1	7.47×10^{-3}	67	2.87

Ferrocenylphenylmethylium 2c [(2.07-2.53)x10^-4 mol l^-1] and Trimethylsiloxypropene 5

T/°C	[5]/mol l^-1	Conversion/%[b]	k_2/ l mol^-1 s^-1
-20.9	2.06×10^{-3}	67	44.0
-31.2	2.02×10^{-3}	76	16.2
-51.8	2.56×10^{-3}	49	3.04
-71.6	2.10×10^{-3}	79	0.77

Ferrocenylphenylmethylium 2c [(3.01-5.16)x10^-4 mol l^-1] and Methallyltrimethylsilane 4

T/°C	[4]/mol l^-1	Conversion/%[b]	k_2/ l mol^-1 s^-1
-9.8	1.78×10^{-3}	52	11.0
-29.3	4.17×10^{-3}	90	5.60
-41.2	5.72×10^{-3}	78	1.59
-49.6	8.23×10^{-3}	82	1.65
-62.0	6.06×10^{-3}	95	0.34
-69.1	6.10×10^{-3}	92	0.24

Ferrocenylphenylmethylium 2c [(2.33-2.80)x10^-4 mol l^-1] and Dimethylphenylsilane 9

T/°C	[9]/mol l^-1	Conversion/%[b]	k_2/ l mol^-1 s^-1
19.5	3.97×10^{-3}	80	1.59
-0.5	6.28×10^{-3}	82	0.33
-5.5	8.83×10^{-3}	32	0.23
-10.5	4.76×10^{-3}	62	0.15

Ferrocenylphenylmethylium 2c [(2.79-5.1)x10^-4 mol l^-1] and Allyltriphenylstannane 3

T/°C	[3]/mol l^-1	Conversion/%[b]	k_2/ l mol^-1 s^-1
23.1	4.63×10^{-3}	50	2.59
2.0	1.97×10^{-3}	63	0.81
-5.3	3.08×10^{-3}	88	0.60

Ferrocenyl-(p-anisyl)-methylium 2d [(1.67-3.73)x10^-4 mol l^-1] and Trimethylsiloxypropene 5

T/°C	[5]/mol l^-1	Conversion/%[b]	k_2/ l mol^-1 s^-1
-23.0	6.33×10^{-3}	78	18.4
-30.2	9.61×10^{-3}	74	15.4
-31.5	9.01×10^{-3}	32	13.1
-39.1	7.55×10^{-3}	93	5.04
-50.8	7.53×10^{-3}	95	3.81
-59.5	7.52×10^{-3}	92	0.97
-60.2	3.24×10^{-3}	75	1.03
-60.6	8.73×10^{-3}	72	1.26

Ferrocenyl-(p-anisyl)-methylium 2d [(2.55-3.96)x10^-4 mol l^-1] and Methallyltrimethylsilane 4

T/°C	[4]/mol l^-1	Conversion/%[b]	k_2/ l mol^-1 s^-1
-11.2	6.91×10^{-3}	51	5.57
-20.6	5.81×10^{-3}	43	3.56
-20.9	4.51×10^{-3}	18	3.26
-30.5	7.24×10^{-3}	49	1.83
-49.5	6.83×10^{-3}	60	0.56

Ferrocenyl-(p-anisyl)-methylium 2d [(3.11-3.82)x10^-4 mol l^-1] and Dimethylphenylsilane 9

T/°C	[9]/mol l^-1	Conversion/%[b]	k_2/ l mol^-1 s^-1
25.3	7.65×10^{-3}	57	1.21
-0.2	9.12×10^{-3}	69	0.20
-0.3	4.32×10^{-3}	89	0.24
-9.6	8.80×10^{-3}	53	8.98×10^{-2}
-20.5	9.36×10^{-3}	69	3.43×10^{-2}
-40.3	7.91×10^{-3}	85	4.79×10^{-3}

Diferrocenylmethylium 2e-BF4 (3.46x10^-4 mol l^-1) and Trimethylsiloxycyclohexene 7

T/°C	[7]/mol l^-1	Conversion/%[b]	k_2/ l mol^-1 s^-1
20.0	2.11×10^{-2}	74	1.31×10^{-3}
20.0	9.27×10^{-3}	41	1.11×10^{-3}

Diferrocenylmethylium 2e-BF4 [(3.05-3.51)x10^-4 mol l^-1] and Trimethylsiloxycyclopentene 6

T/°C	[6]/mol l^-1	Conversion/%[b]	k_2/ l mol^-1 s^-1
20.0	5.06×10^{-3}	88	3.05×10^{-2}
20.0	1.01×10^{-2}	81	2.94×10^{-2}
5.0	1.05×10^{-2}	83	1.36×10^{-2}
-14.4	1.03×10^{-2}	65	3.77×10^{-3}
-14.3	1.16×10^{-2}	93	3.72×10^{-3}

Diferrocenylmethylium 2e-BF4 [(2.96-3.82)x10^-4 mol l^-1] and Silylketeneacetal 8

T/°C	[8]/mol l^-1	Conversion/%[b]	k_2/ l mol^-1 s^-1
20.0	9.69×10^{-3}	93	5.46×10^{-1}
20.0	4.82×10^{-3}	53	4.90×10^{-1}
10.0	4.47×10^{-3}	94	3.36×10^{-1}
3.7	8.61×10^{-3}	88	2.83×10^{-1}
-18.1	9.59×10^{-3}	94	7.76×10^{-2}
-26.5	1.01×10^{-2}	93	5.13×10^{-2}

Diferrocenylmethylium 2e-OTf [(2.44-2.91)x10^-4 mol l^-1] and Tributylstannane 11

T/°C	[11]/mol l^-1	Conversion/%[b]	k_2/ mol^-1 s^-1
20.0	7.32×10^{-3}	98	3.54
20.0	3.11×10^{-3}	96	3.47
-4.8	3.70×10^{-3}	98	7.38×10^{-1}
-9.6	7.10×10^{-3}	96	4.87×10^{-1}
-29.2	7.02×10^{-3}	94	1.17×10^{-1}

[a] The reactions of 2a were followed conductometrically, the rate constants of 2b—e were determined photometrically. — [b] Range evaluated for the determination of k_2.

(AA'BB' system, J_{AB} = 8.6 Hz, aromatic H). – ^{13}C NMR: δ = 20.46, 20.74, 26.15, 26.23, 38.57, 38.79 (6 t, CH$_2$), 43.50, 44.84 (2 d, C-2), 54.60, 55.10, 55.22, 56.40 (2 q, OCH$_3$, 2 d, CH), 66.94, 67.46, 67.67, 68.06, 68.41, 68.78, 69.14 (7 d, C$_5$H$_5$, C$_5$H$_4$), 89.33, 92.47 (2 s, fc-C$_i$), 113.19, 113.44 (2 d, C$_m$), 129.69 (d, C$_o$), 135.07, 135.85 (2 s, C$_i$-aryl), 157.89, 158.05 (2 s, C–O), 219.91, 220.48 (2 s, CO).

2-[Bis(ferrocenyl)methyl]cyclopentanone (**6e**): Orange powder, m.p. 145.5°C (ether). – ^{1}H NMR: δ = 1.35–2.35 (m, 6H, CH$_2$), 3.02 (m$_c$, 1H, 2-H), 4.03, 4.15 (2 s, 10H, C$_5$H$_5$), 4.30 (d, J = 1.6 Hz, 1H, fc$_2$C*H*), 3.50, 3.79, 3.94, 3.98, 4.05, 4.20, 4.46 (7 m, 8H, C$_5$H$_4$). – ^{13}C NMR: δ = 20.68, 25.90, 38.63 (3 t, CH$_2$), 38.45 (d, fc$_2$C*H*), 56.54 (d, C-2), 68.36, 68.66 (2 d, C$_5$H$_5$), 66.27, 66.42, 66.60, 67.17, 67.35, 67.41, 69.90 (7 d, C$_5$H$_4$), 91.75, 92.18 (2 s, C$_i$), 220.9 (s, CO).

2-(1-Ferrocenylethyl)cyclohexanone (**7b**): Mixture of diastereomers (≈ 1:2.5), orange powder[34]. – ^{1}H NMR: δ = 1.20, 1.30 (2 d, J = 7 Hz, 3H, CH$_3$), 1.43–2.42 (m, 9H), 3.09, 3.29 (2 m$_c$, 1H), 4.04–4.23 (m, 9H, C$_5$H$_5$, C$_5$H$_4$).

Methyl 3,3-Bis(ferrocenyl)-2,2-dimethylpropionate (**8e**): Orange powder, m.p. 103–105°C (hexane). – ^{1}H NMR: δ = 1.19 (s, 6H, CH$_3$), 3.78 (s, 3H, OCH$_3$), 3.91 (s, 1H, 3-H), 4.00 (s, 10H, C$_5$H$_5$), 4.04 (m$_c$, 2H, C$_5$H$_4$), 4.11–4.13 (m, 6H, C$_5$H$_4$). – ^{13}C NMR: δ = 24.03 (q, CH$_3$), 43.99 (d, C-3), 47.92 (s, C-2), 51.84 (q, OCH$_3$), 67.30, 69.32, 70.42 (3 d, C$_5$H$_4$), 68.81 (d, C$_5$H$_5$), 91.83 (s, fc-C$_i$), 178.61 (s, CO).

Methylferrocene (**9a**): Orange oil[35]. – ^{1}H NMR: δ = 1.89 (s, 3H, CH$_3$), 3.94, 3.98 (2 m$_c$, 4H, C$_5$H$_4$), 4.01 (s, 5H, C$_5$H$_5$).

(4-Methoxybenzyl)ferrocene (**9d**)[31,36]: Orange needles from ether, m.p. 71.5°C (ref.[31] 72–75°C). – ^{1}H NMR: δ = 3.63 (s, 2H, CH$_2$), 3.77 (s, 3H, OCH$_3$), 4.07 (s, 4H, C$_5$H$_4$), 4.11 (s, 5H, C$_5$H$_5$), 6.80, 7.09 (AA'BB' system, J_{AB} = 8.6 Hz, 4H, aromatic H).

Kinetic Investigations (Table 2): The consumption of the ferrocenylmethylium ions was determined conductometrically (**2a**) or photometrically (**2b–e**) by using fiber optics and the working station described in ref.[21]. Calibration curves, i.e. the correlation between absorbance (or conductivity in the case of **2a**) and concentration of the ferrocenylmethylium ions **2a–d**, were obtained by adding the acetates **1a–d** in portions to a solution of Me$_3$SiOTf in CH$_2$Cl$_2$ and determination of the absorbance after completion of the ionization. In the case of **2e** the calibration curve was obtained by determination of the absorbance of solutions of **2e**-CF$_3$SO$_3^-$ or **2e**-BF$_4^-$ at different concentrations.

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