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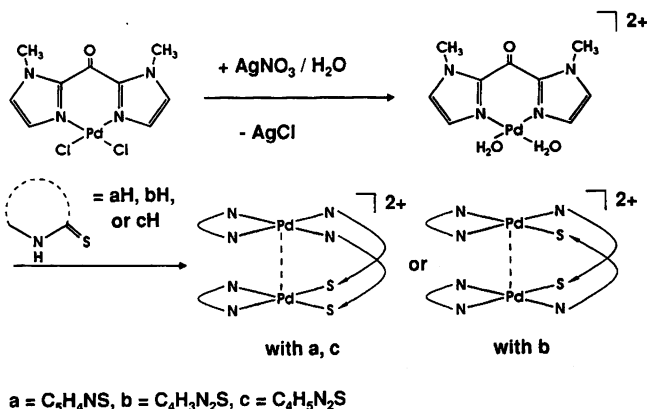
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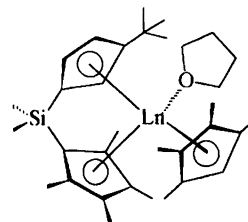


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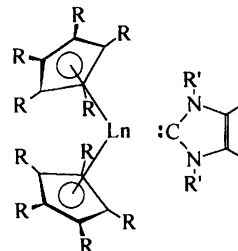


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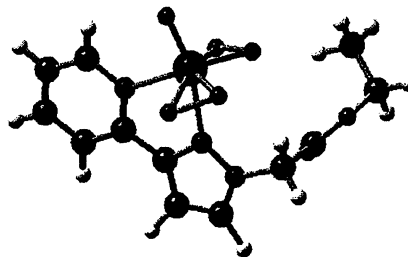


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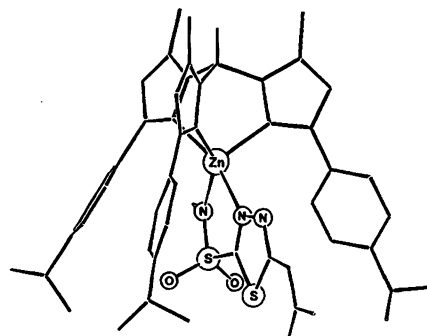


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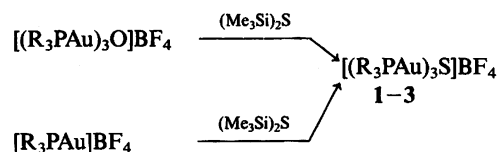
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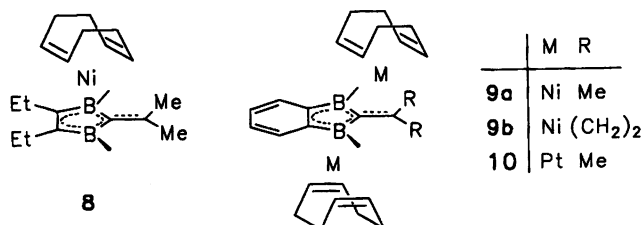
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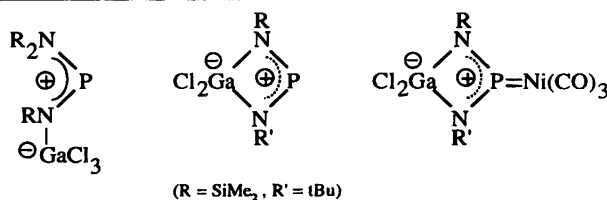
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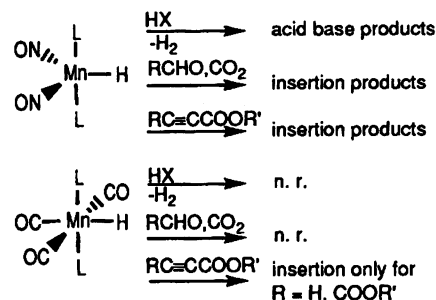
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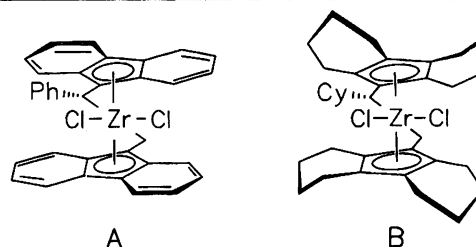
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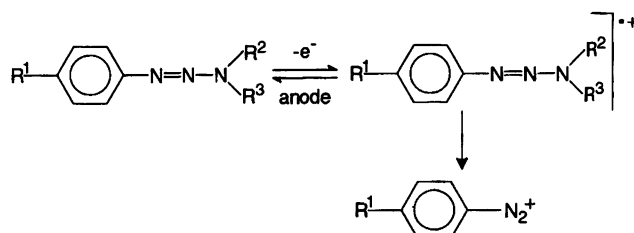
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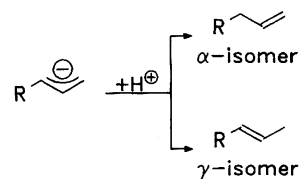
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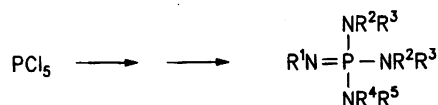
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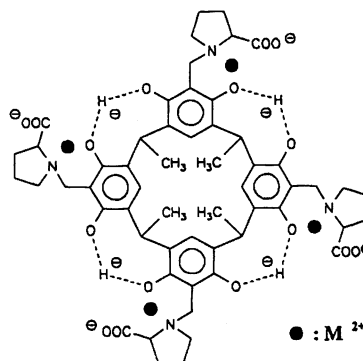
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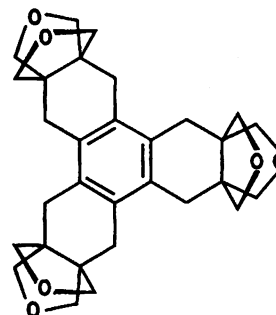
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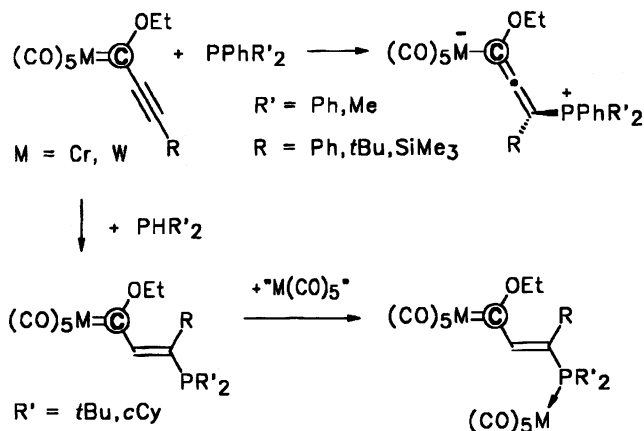
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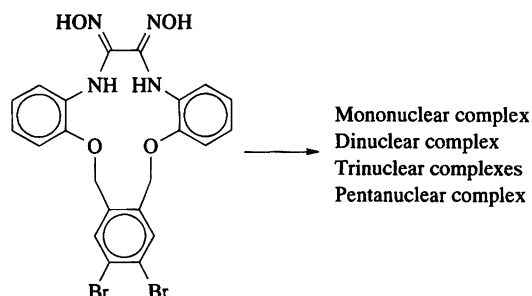


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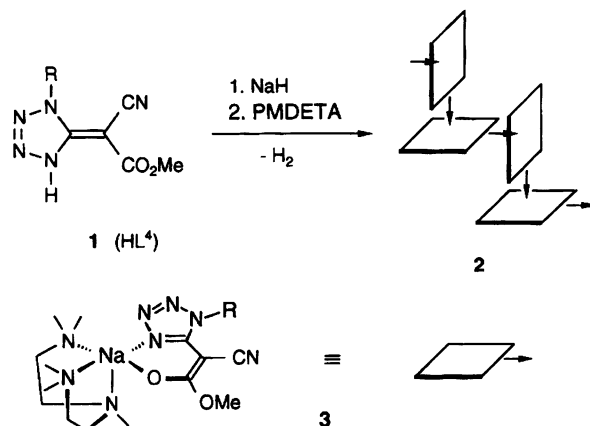


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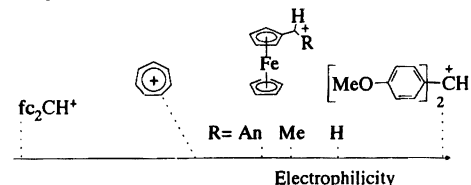
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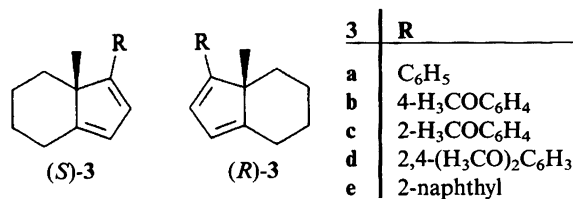


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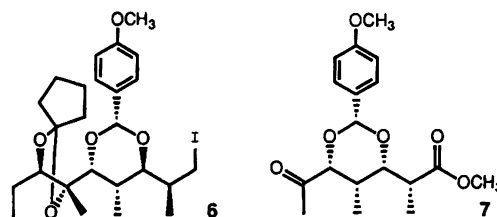


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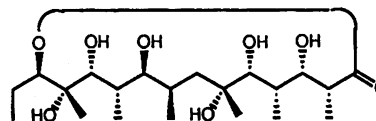
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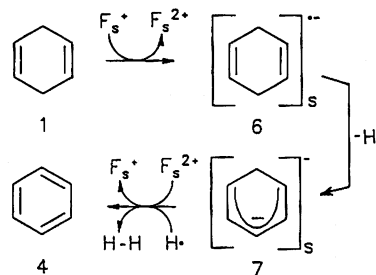
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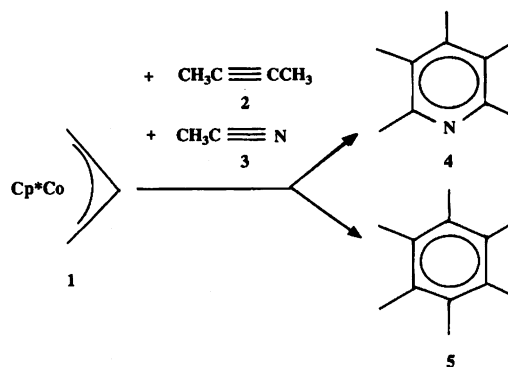
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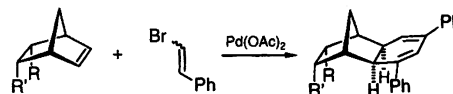
(η^3 -Allyl)(η^5 -pentamethylcyclopentadienyl)cobalt –
ein selektiver Katalysator für die Pyridinsynthese
(η^3 -Allyl)(η^5 -pentamethylcyclopentadienyl)cobalt – a
Selective Catalyst for the Pyridine Synthesis



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K. Albrecht, A. de Meijere*

Palladium-katalysierte Mehrfach-Kupplungs-Reaktio-
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dien
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diene



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

Herbert Mayr* and Doris Rau

Institut für Organische Chemie der Technischen Hochschule Darmstadt,
Petersenstraße 22, D-64287 Darmstadt, Germany

Received June 30, 1994

Key Words: Electrophilicity / Ferrocenylmethylium ions / Kinetics

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 tricarboxyl(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 tricarboxyl(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].

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

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

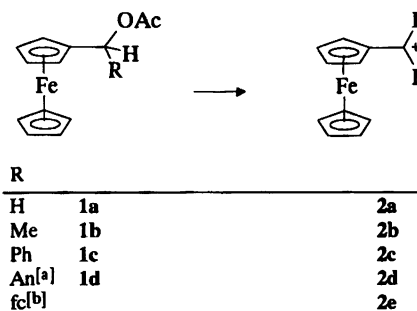
groups have studied the kinetics of their reactions with π nucleophiles and anionic hydride donors^[11,13,15,16].

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).



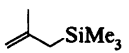






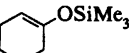



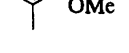





Scheme 1. [a] An = 4-MeOC₆H₄, [b] fc = Ferrocenyl, C₅H₅FeC₅H₄



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.

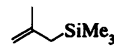
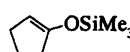
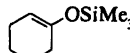
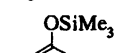
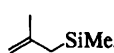
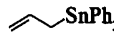
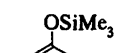
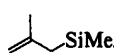
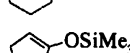
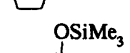
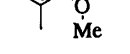
Scheme 2. Reactions of ferrocenylmethyl cations with π nucleophiles and HSiMe_2Ph . — [a]–[d] Product previously described in [a] ref.^[33], [b] ref.^[34], [c] ref.^[35], [d] ref.^[31,36]

Nucleophile	Electrophile/R	Product
 3	2c/Ph	 3c
 4	2b/Me	 4b
	2c/Ph	 4c
	2d/An	 4d
 5	2c/Ph	 5c ^[a]
	2d/An	 5d
 6	2c/Ph	 6c
	2d/An	 6d
	2e/fc	 6e
 7	2b/Me	 7b ^[b]
 8	2e/fc	 8e
HSiMe₂Ph 9	2a/H	 9a ^[c]
	2d/An	 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 ferrocenylmethyl 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 ferrocenylmethyl cations at the nucleophiles.

Table 1. Rate constants for the reactions of ferrocenylmethyl cations $\text{fcCHR}^+[\text{a}]$ with nucleophiles (20°C, CH_2Cl_2)

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

[a] $\text{fc} = (\text{C}_5\text{H}_5)\text{Fe}(\text{C}_3\text{H}_4)$. — [b] $\text{An} = 4\text{-MeOC}_6\text{H}_4$.

Discussion

The activation parameters in Table 1 show that within one class of nucleophiles the reactivity differences are due to variable values of ΔH^\ddagger while ΔS^\ddagger remains almost constant. As in analogous reactions with benzhydryl cations, there are characteristic values of ΔS^\ddagger for the reactions of alkyl- and aryl-substituted ferrocenylmethyl cations with the different classes of nucleophiles. While most π nucleophiles used in this study possess activation entropies of $(-105 \pm 15) \text{ J mol}^{-1} \text{ K}^{-1}$, the corresponding values for the hydride donors HSiMe_2Ph and HSiPh_3 are noticeably less negative $(-81 \pm 5) \text{ J mol}^{-1} \text{ K}^{-1}$. Unusually large negative values of ΔS^\ddagger have only been found for the reactions of **2e** with π nucleophiles and HSnBu_3 , 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 ΔS^\ddagger 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 ferrocenylmethyl cations 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 ferrocenylmethyl cations and benzhydryl cations follow the same linear free energy relationship.

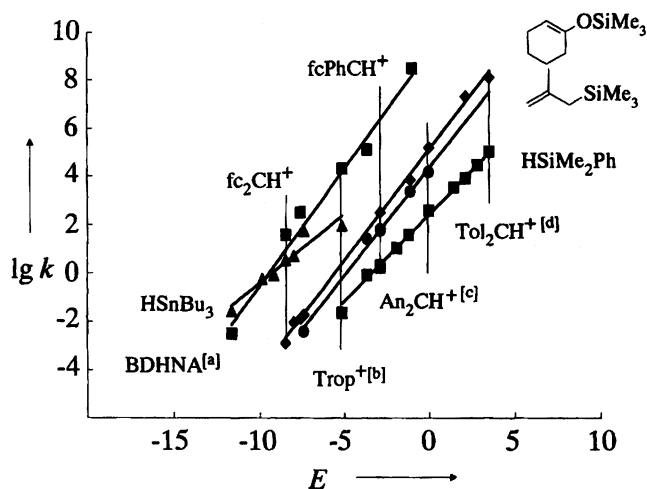


Figure 1. Correlation between the rate constants of the reactions of electrophiles with nucleophiles and the electrophilicity parameters given in Table 1 and ref.^[8]

[a] BDHNA: *N*-Benzyl-1,4-dihydronicotinamide. – [b] Trop⁺: Tropylum 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 ferrocenylmethyl cations **2c, d** with H₂O 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 ferrocenylmethyl cations. Hence, the cation can also be described as an η^6 iron-fulvene complex with little charge at C_{exo}.

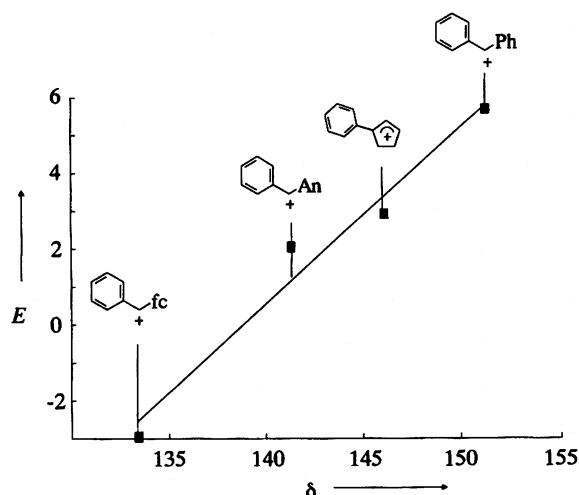


Figure 2. Correlation of the electrophilicity parameter E with the ¹³C-NMR chemical shift of C_{para} in phenyl-substituted carbenium ions

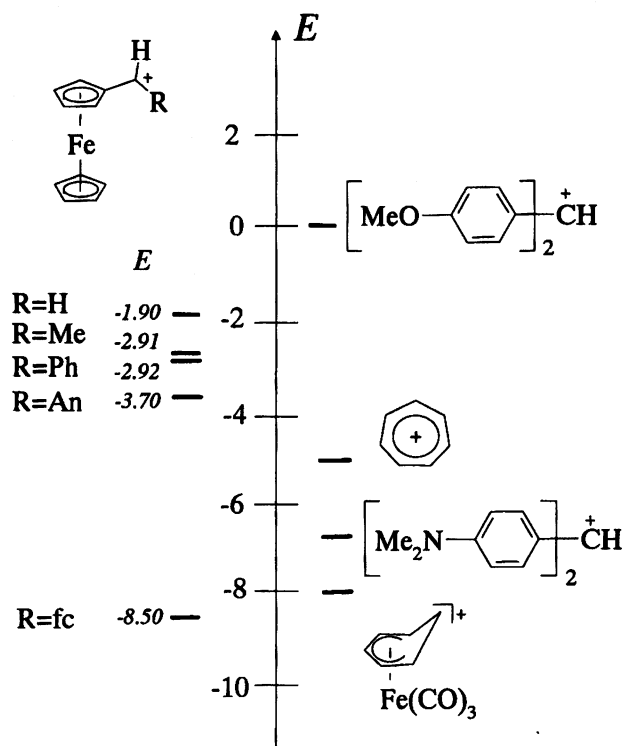


Figure 3. Comparison of the electrophilicity parameters E of ferrocenylmethyl cations with those of other carbenium ions

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 ferrocenylmethyl cations 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 ferrocenylmethyl cations 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)methyl cation **2e** is a considerably weaker electrophile.

Financial support by the Volkswagen-Stiftung and the Fonds der Chemischen Industrie is gratefully acknowledged. We thank Mr. O. Kuhn for experimental collaboration and Dr. M. Patz for discussions.

Experimental

NMR: Bruker WM 300. All NMR spectra (300 MHz) were recorded in CDCl₃. – Ferrocenecarbaldehyde (Aldrich) was reduced with LiAlH₄ 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/BF₃^[28], benzoyl chloride/AlCl₃^[29] or *p*-anisoyl chloride/AlCl₃ 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 LiAlH₄ 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 (fc₂CHOEt) was prepared from ferrocene and triethyl orthoformate according to a procedure by Schaaff^[30]. Treatment of fc₂CHOEt with HBF₄ or CF₃SO₃H according to ref.^[31] gave a deep blue powder of fc₂CH⁺BF₄[–] (88%) and fc₂CH⁺CF₃SO₃[–] (92%), respectively.

General Procedure for the Reactions of Ferrocenylmethyl cations with Nucleophiles: Compounds **1a–d** (≈ 1 mmol) were dissolved in dry CH₂Cl₂ (10 ml). The solutions were cooled at –50°C, and 0.5 ml of a 2 M solution of ZnCl₂ · (OEt)₂^[32] in CH₂Cl₂ 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 CH₂Cl₂, and the combined organic fractions were then washed with NaHCO₃ (saturated aq. solution) and water and dried with MgSO₄. The solvent was evaporated in vacuo and the residue analyzed by ¹H and ¹³C NMR. Compounds **6e** and **8e** were obtained by dissolving **2e**-OTf (1 mmol) in 30 ml of CH₂Cl₂, 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, C₅H₄), 4.06 (s, 5H, C₅H₅), 4.90–5.02 (m, 2H, 4-H), 5.62–5.75 (m, 1H, 3-H), 7.14–7.28 (m, 5H, aromatic H). – ¹³C NMR: δ = 41.41 (t, C-2), 46.16 (d, C-1), 66.83, 66.90, 67.45, 67.56 (4 d, C₅H₄), 68.55 (d, C₅H₅), 93.68 (s, fc-C), 115.86 (t, C-4), 126.10, 127.89, 128.07 (3 d, aromatic C), 137.03 (d, C-3), 144.78 (s, C₇-aryl).

(1,3-Dimethyl-3-butenyl)ferrocene (4b): Orange oil. – ¹H NMR: δ = 1.09 (d, $J = 6.8$ Hz, 3H, 1-CH₃), 1.67 (t, $J = 0.5$ Hz, 3H, 3-CH₃), 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, C₅H₄), 4.06 (s, 5H, C₅H₅), 4.60, 4.69 (2 br. s, 2H, 4-H). – ¹³C NMR: δ = 20.10,

22.28 (2 q, CH₃), 30.73 (d, C-1), 47.22 (t, C-2), 65.94, 66.76, 66.84, 66.88 (4 d, C₅H₄), 68.34 (d, C₅H₅), 95.96 (s, fc-C), 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-CH₃), 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, C₅H₄), 4.07 (s, 5H, C₅H₅), 4.51, 4.64 (2 br. s, 2H, 4-H), 7.08–7.18 (m, 5H, aromatic H). – ¹³C NMR: δ = 22.59 (q, CH₃), 44.30 (d, C-1), 45.29 (t, C-2), 66.70, 66.92, 67.48, 67.57 (4 d, C₅H₄), 68.56 (d, C₅H₅), 94.29 (s, fc-C), 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, C₇-Aryl, C-3).

[1-(4-Methoxyphenyl)-3-methyl-3-butenyl]ferrocene (4d): Orange oil. – ¹H NMR: δ = 1.68 (s, 3H, 3-CH₃), 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, OCH₃), 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, C₅H₄), 4.06 (s, 6H, C₅H₅, C₅H₄), 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). – ¹³C NMR: δ = 22.56 (q, 3-CH₃), 43.37 (d, C-1), 45.32 (t, C-2), 55.05 (q, OCH₃), 66.60, 66.89, 67.41, 67.49 (4 d, C₅H₄), 68.53 (d, C₅H₅), 94.75 (s, fc-C), 112.42 (t, C-4), 113.29 (d, C_m), 128.64 (d, C_o), 137.02 (s, C₇-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, C₅H₄), 4.06 (s, 6H, C₅H₅, C₅H₄), 4.10 (br. s, 1H, C₅H₄), 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). – ¹³C 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, C₅H₄), 68.56 (d, C₅H₅), 92.97 (s, fc-C), 126.38, 127.61, 128.24 (3 d, aromatic C), 144.38 (s, C₇-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, OCH₃), 4.04, 4.07 (2 m, 4H, C₅H₄), 4.06 (s, 5H, C₅H₅), 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). – ¹³C NMR: δ = 30.89 (q, C-1), 40.21 (d, C-4), 51.20 (t, C-3), 55.10 (q, OCH₃), 66.56, 67.19, 67.61, 67.66 (4 d, C₅H₄), 68.52 (d, C₅H₅), 93.41 (s, fc-C), 113.61 (d, C_m), 128.54 (d, C_o), 136.56 (s, C₇-aryl), 158.01 (s, C-O), 207.26 (s, CO).

2-(Ferrocenylphenylmethyl)cyclopentanone (6c): Mixture of diastereomers (≈ 3:1), orange powder. – ¹H NMR: δ = 1.35–1.83 (m, 4H, 2 CH₂), 2.04–2.22 (m, 2H, CH₂), 2.34–2.41, 2.88–2.95 (2 m, 1H, 2-H), 3.81, 4.05 (2 s, 5H, C₅H₅), 3.85, 3.93, 3.98, 4.07, 4.14 (5 m_c, 4H, C₅H₄), 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). – ¹³C NMR: δ = 20.38, 20.66, 26.18, 38.44, 38.65 (5 t, CH₂), 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, C₅H₅, C₅H₄), 89.26, 91.98 (2 s, fc-C), 126.15, 126.41, 127.81, 128.10, 128.67 (5 d, aromatic C), 142.85, 143.49 (2 s, C₇-aryl), 219.60, 220.13 (2 s, CO).

2-[Ferrocenyl(4-methoxyphenyl)methyl]cyclopentanone (6d): Mixture of diastereomers (≈ 1:4), orange oil. – ¹H NMR: δ = 1.45–1.80 (m, 4H, 2 CH₂), 2.05–2.30 (m, 2H, CH₂), 2.44, 2.95 (2 m_c, 1H, 2-H), 3.73, 3.83 (2 s, OCH₃), 3.93, 4.13 (2 s, C₅H₅), 3.98–4.21 (m, C₅H₄), 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 ferrocenylmethyl cations with nucleophiles^[a]

Ferrocenylmethyl cation 2a [(8.72-14.5)x10 ⁻⁵ mol l ⁻¹] and Dimethylphenylsilane 9				Ferrocenylmethyl cation 2a [(7.31-8.59)x10 ⁻⁵ mol l ⁻¹] and Triphenylsilane 10				Ferrocenylethyl cation 2b [(1.45-1.88)x10 ⁻³ mol l ⁻¹] and Methyltrimethylsilane 4			
T/°C	[9]/mol l ⁻¹	Conversion/% ^[b]	k ₂ /l mol ⁻¹ s ⁻¹	T/°C	[10]/mol l ⁻¹	Conversion/% ^[b]	k ₂ /l mol ⁻¹ s ⁻¹	T/°C	[4]/mol l ⁻¹	Conversion/% ^[b]	k ₂ /l mol ⁻¹ s ⁻¹
-0.5	3.09x10 ⁻³	53	2.55	21.1	1.44x10 ⁻³	46	1.17	-20.8	2.18x10 ⁻²	67	6.77
-9.5	1.78x10 ⁻³	86	1.18	5.1	2.01x10 ⁻³	36	3.5x10 ⁻¹	-39.8	7.85x10 ⁻²	64	1.73
-11.3	3.20x10 ⁻³	90	1.09	0.0	2.99x10 ⁻³	69	2.1x10 ⁻¹	-46.5	7.77x10 ⁻²	97	8.7x10 ⁻¹
-30.7	3.25x10 ⁻³	94	1.70x10 ⁻¹	-10.2	2.55x10 ⁻³	43	8.0x10 ⁻²	-47.2	2.45x10 ⁻²	66	1.07
-51.3	9.49x10 ⁻³	33	1.87x10 ⁻²					-57.3	1.89x10 ⁻²	56	4.6x10 ⁻¹
								-66.6	8.73x10 ⁻³	72	2.0x10 ⁻¹
Ferrocenylethyl cation 2b [(1.50-1.75)x10 ⁻³ mol l ⁻¹] and Dimethylphenylsilane 9				Ferrocenylphenylmethyl cation 2c [(1.74-2.00)x10 ⁻⁴ mol l ⁻¹] and Trimethylsiloxypropene 6				Ferrocenylphenylmethyl cation 2c [(3.57-5.04)x10 ⁻⁴ mol l ⁻¹] and Trimethylsiloxypropene 7			
T/°C	[9]/mol l ⁻¹	Conversion/% ^[b]	k ₂ /l mol ⁻¹ s ⁻¹	T/°C	[6]/mol l ⁻¹	Conversion/% ^[b]	k ₂ /l mol ⁻¹ s ⁻¹	T/°C	[7]/mol l ⁻¹	Conversion/% ^[b]	k ₂ /l mol ⁻¹ s ⁻¹
-0.4	2.27x10 ⁻²	62	4.62x10 ⁻¹	-51.8	2.05x10 ⁻³	83	137.1	-40.0	6.48x10 ⁻³	44	20.42
-9.7	2.57x10 ⁻²	49	2.13x10 ⁻¹	-61.8	2.36x10 ⁻³	84	74.6	-50.8	4.87x10 ⁻³	26	10.31
-20.5	2.21x10 ⁻²	69	1.26x10 ⁻¹	-71.7	2.20x10 ⁻³	89	38.1	-68.5	5.02x10 ⁻³	36	2.87
-20.5	4.80x10 ⁻²	72	9.32x10 ⁻²					-69.1	7.47x10 ⁻³	67	2.87
-40.3	2.67x10 ⁻²	71	1.32x10 ⁻²								
-60.4	2.70x10 ⁻²	61	1.22x10 ⁻³								
Ferrocenylphenylmethyl cation 2c [(2.07-2.53)x10 ⁻⁴ mol l ⁻¹] and Trimethylsiloxypropene 5				Ferrocenylphenylmethyl cation 2c [(3.01-5.16)x10 ⁻⁴ mol l ⁻¹] and Methyltrimethylsilane 4				Ferrocenylphenylmethyl cation 2c [(2.33-2.80)x10 ⁻⁴ mol l ⁻¹] and Dimethylphenylsilane 9			
T/°C	[5]/mol l ⁻¹	Conversion/% ^[b]	k ₂ /l mol ⁻¹ s ⁻¹	T/°C	[4]/mol l ⁻¹	Conversion/% ^[b]	k ₂ /l mol ⁻¹ s ⁻¹	T/°C	[9]/mol l ⁻¹	Conversion/% ^[b]	k ₂ /l mol ⁻¹ s ⁻¹
-20.9	2.06x10 ⁻³	67	44.0	-9.8	1.78x10 ⁻³	52	11.0	19.5	3.97x10 ⁻³	80	1.59
-31.2	2.02x10 ⁻³	76	16.2	-29.3	4.17x10 ⁻³	90	5.60	-0.5	6.28x10 ⁻³	82	0.33
-51.8	2.56x10 ⁻³	49	3.04	-41.2	5.72x10 ⁻³	78	1.59	-5.5	8.83x10 ⁻³	32	0.23
-71.6	2.10x10 ⁻³	79	0.77	-49.6	8.23x10 ⁻³	82	1.65	-10.5	4.76x10 ⁻³	62	0.15
				-62.0	6.06x10 ⁻³	95	0.34				
				-69.1	6.10x10 ⁻³	92	0.24				
Ferrocenylphenylmethyl cation 2c [(2.79-5.1x10 ⁻⁴ mol l ⁻¹)] and Allyltriphenylstannane 3				Ferrocenyl-(p-anisyl)-methyl cation 2d [(1.67-3.73)x10 ⁻⁴ mol l ⁻¹)] and Trimethylsiloxypropene 5				Ferrocenyl-(p-anisyl)-methyl cation 2d [(2.55-3.96)x10 ⁻⁴ mol l ⁻¹)] and Methyltrimethylsilane 4			
T/°C	[3]/mol l ⁻¹	Conversion/% ^[b]	k ₂ /l mol ⁻¹ s ⁻¹	T/°C	[5]/mol l ⁻¹	Conversion/% ^[b]	k ₂ /l mol ⁻¹ s ⁻¹	T/°C	[4]/mol l ⁻¹	Conversion/% ^[b]	k ₂ /l mol ⁻¹ s ⁻¹
23.1	4.63x10 ⁻³	50	2.59	-23.0	6.33x10 ⁻³	78	18.4	-11.2	6.91x10 ⁻³	51	5.57
2.0	1.97x10 ⁻³	63	0.81	-30.2	9.61x10 ⁻³	74	15.4	-20.6	5.81x10 ⁻³	43	3.56
-5.3	3.08x10 ⁻³	88	0.60	-31.5	9.01x10 ⁻³	32	13.1	-20.9	4.51x10 ⁻³	18	3.26
				-39.1	7.55x10 ⁻³	93	5.04	-30.5	7.24x10 ⁻³	49	1.83
				-50.8	7.53x10 ⁻³	95	3.81	-49.5	6.83x10 ⁻³	60	0.56
				-59.5	7.52x10 ⁻³	92	0.97				
				-60.2	3.24x10 ⁻³	75	1.03				
				-60.6	8.73x10 ⁻³	72	1.26				
Ferrocenyl-(p-anisyl)-methyl cation 2d [(3.11-3.82)x10 ⁻⁴ mol l ⁻¹)] and Dimethylphenylsilane 9				Diferrocenylmethyl cation 2e-BF ₄ (3.46x10 ⁻⁴ mol l ⁻¹) and Trimethylsiloxypropene 7				Diferrocenylmethyl cation 2e-BF ₄ [(3.05-3.51)x10 ⁻⁴ mol l ⁻¹)] and Trimethylsiloxypropene 6			
T/°C	[9]/mol l ⁻¹	Conversion/% ^[b]	k ₂ /l mol ⁻¹ s ⁻¹	T/°C	[7]/mol l ⁻¹	Conversion/% ^[b]	k ₂ /l mol ⁻¹ s ⁻¹	T/°C	[6]/mol l ⁻¹	Conversion/% ^[b]	k ₂ /l mol ⁻¹ s ⁻¹
25.3	7.65x10 ⁻³	57	1.21	20.0	2.11x10 ⁻²	74	1.31x10 ⁻³	20.0	5.06x10 ⁻³	88	3.05x10 ⁻²
-0.2	9.12x10 ⁻³	69	0.20	20.0	9.27x10 ⁻³	41	1.11x10 ⁻³	20.0	1.01x10 ⁻²	81	2.94x10 ⁻²
-0.3	4.32x10 ⁻³	89	0.24					5.0	1.05x10 ⁻²	83	1.36x10 ⁻²
-9.6	8.80x10 ⁻³	53	8.98x10 ⁻²					-14.4	1.03x10 ⁻²	65	3.77x10 ⁻³
-20.5	9.36x10 ⁻³	69	3.43x10 ⁻²					-14.3	1.16x10 ⁻²	93	3.72x10 ⁻³
-40.3	7.91x10 ⁻³	85	4.79x10 ⁻³								
Diferrocenylmethyl cation 2e-BF ₄ [(2.96-3.82)x10 ⁻⁴ mol l ⁻¹)] and Silylketeneacetal 8				Diferrocenylmethyl cation 2e-OTf [(2.44-2.91)x10 ⁻⁴ mol l ⁻¹)] and Tributylstannane 11							
T/°C	[8]/mol l ⁻¹	Conversion/% ^[b]	k ₂ /l mol ⁻¹ s ⁻¹	T/°C	[11]/mol l ⁻¹	Conversion/% ^[b]	k ₂ /l mol ⁻¹ s ⁻¹				
20.0	9.69x10 ⁻³	93	5.46x10 ⁻¹	20.0	7.32x10 ⁻³	98	3.54				
20.0	4.82x10 ⁻³	53	4.90x10 ⁻¹	20.0	3.11x10 ⁻³	96	3.47				
10.0	4.47x10 ⁻³	94	3.36x10 ⁻¹	-4.8	3.70x10 ⁻³	98	7.38x10 ⁻¹				
3.7	8.61x10 ⁻³	88	2.83x10 ⁻¹	-9.6	7.10x10 ⁻³	96	4.87x10 ⁻¹				
-18.1	9.59x10 ⁻³	94	7.76x10 ⁻²	-29.2	7.02x10 ⁻³	94	1.17x10 ⁻¹				
-26.5	1.01x10 ⁻²	93	5.13x10 ⁻²								

^[a] The reactions of 2a were followed conductometrically, the rate constants of 2b-e were determined photometrically. - ^[b] Range evaluated for the determination of k₂.

(AA'BB' system, $J_{AB} = 8.6$ Hz, aromatic H). — ^{13}C NMR: $\delta = 20.46, 20.74, 26.15, 26.23, 38.57, 38.79$ (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_5H_5 , C_5H_4), 89.33, 92.47 (2 s, fc-C), 113.19, 113.44 (2 d, C_m), 129.69 (d, C_o), 135.07, 135.85 (2 s, C-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). — ^1H NMR: $\delta = 1.35\text{--}2.35$ (m, 6H, CH_2), 3.02 (m, 1H, 2-H), 4.03, 4.15 (2 s, 10H, C_5H_5), 4.30 (d, $J = 1.6$ Hz, 1H, fc $_2\text{CH}$), 3.50, 3.79, 3.94, 3.98, 4.05, 4.20, 4.46 (7 m, 8H, C_5H_4). — ^{13}C NMR: $\delta = 20.68, 25.90, 38.63$ (3 t, CH_2), 38.45 (d, fc $_2\text{CH}$), 56.54 (d, C-2), 68.36, 68.66 (2 d, C_5H_5), 66.27, 66.42, 66.60, 67.17, 67.35, 67.41, 69.90 (7 d, C_5H_4), 91.75, 92.18 (2 s, C), 220.9 (s, CO).

2-(1-Ferrocenylethyl)cyclohexanone (**7b**): Mixture of diastereomers ($\approx 1:2.5$), orange powder^[34]. — ^1H NMR: $\delta = 1.20, 1.30$ (2 d, $J = 7$ Hz, 3H, CH_3), 1.43–2.42 (m, 9H), 3.09, 3.29 (2 m, 1H), 4.04–4.23 (m, 9H, C_5H_5 , C_5H_4).

Methyl 3,3-Bis(ferrocenyl)-2,2-dimethylpropionate (**8e**): Orange powder, m.p. 103–105°C (hexane). — ^1H NMR: $\delta = 1.19$ (s, 6H, CH_3), 3.78 (s, 3H, OCH_3), 3.91 (s, 1H, 3-H), 4.00 (s, 10H, C_5H_5), 4.04 (m, 2H, C_5H_4), 4.11–4.13 (m, 6H, C_5H_4). — ^{13}C NMR: $\delta = 24.03$ (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_5H_4), 68.81 (d, C_5H_5), 91.83 (s, fc-C), 178.61 (s, CO).

Methylferrocene (**9a**): Orange oil^[35]. — ^1H NMR: $\delta = 1.89$ (s, 3H, CH_3), 3.94, 3.98 (2 m, 4H, C_5H_4), 4.01 (s, 5H, C_5H_5).

(4-Methoxybenzyl)ferrocene (**9d**)^[31,36]: Orange needles from ether, m.p. 71.5°C (ref.^[31] 72–75°C). — ^1H NMR: $\delta = 3.63$ (s, 2H, CH_2), 3.77 (s, 3H, OCH_3), 4.07 (s, 4H, C_5H_4), 4.11 (s, 5H, C_5H_5), 6.80, 7.09 (AA'BB' system, $J_{AB} = 8.6$ Hz, 4H, aromatic H).

Kinetic Investigations (Table 2): The consumption of the ferrocenylmethyl cations 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 ferrocenylmethyl cations **2a–d**, were obtained by adding the acetates **1a–d** in portions to a solution of Me_3SiOTf in CH_2Cl_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_3SO_3^- or **2e**- BF_4^- at different concentrations.

* Dedicated to Professor Dr. W. Tochtermann on the occasion of his 60th birthday.

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