Quantification of the β-Stabilizing Effect of the Dicarbonyl(η^5-cyclopentadienyl)iron Group

by **Felix Dulich**[1], **Karl-Heinz Müller**[2], **Armin R. Ofial**, and **Herbert Mayr***

Department Chemie und Biochemie der Ludwig-Maximilians-Universität München,
Butenandtstraße 5–13 (Haus F), D-81377 München, Germany
(fax: +49-89-2180-77717; e-mail: herbert.mayr@cup.uni-muenchen.de)

Dedicated to Professor *Rolf Huisgen* on the occasion of his 85th birthday

Kinetic investigations of the reactions of (prop-2-enyl)dicarbonyl(cyclopentadienyl)iron complexes **1** with benzhydrylium ions **3**, and of dicarbonyl(cyclopentadienyl)[(1,2-η)propene]iron(II) tetrafluoroborate ($\mathbf{9} \cdot BF_4$) with π-nucleophiles have been performed to elucidate the magnitude of the β-effect of the $[(CO)_2FeCp]$ group (Fp group). Introduction of the Fp group into the allylic position of propene and 2-methylpropene increases the nucleophilicity of the π-bonds by nine and six orders of magnitude, respectively, with the result that the allyl-Fp complexes **1a** ($N = 6.78$) and **1b** ($N = 8.45$) are among the strongest neutral π-nucleophiles. Replacement of one β-H-atom in the isopropyl cation by the Fp group reduces the electrophilicity by more than 20 orders of magnitude, so that $\mathbf{9}^+$ ranks among the weakest cationic C-electrophiles ($E = -11.2$).

1. Introduction. – The nucleophilic reactivity of C=C bonds can be enhanced by electropositive elements in allylic position. In previous work [1] [2], we have shown that the reactivities of $CH_2=CH-CH_2R$ towards C-electrophiles increases considerably in the series $R = H < Pr < Me_3Si < Bu_3Sn$, with relative reaction rates (k_{rel}) toward $[Ar_2CH]^+$ of 1.0 (H), 1.5 (Pr), 1.6×10^4 (Me_3Si), and 7.4×10^7 (Bu_3Sn) in CH_2Cl_2 at 20°.

The comparison of compounds differing by eight orders of magnitude in reactivity was achieved by employing benzhydrylium ions of variable electrophilicity as reference electrophiles [1] [3]. We have now employed the same method for the characterization of the nucleophilic reactivities of allyl compounds that carry a dicarbonyl(η^5-cyclopentadienyl)iron (Fp) moiety, and we will show that the β-activating effect of the Fp group even exceeds that of the Bu_3Sn group by more than one order of magnitude.

While the reactions of electrophiles with allyl silanes, stannanes, and other metalated compounds are usually accompanied by successive demetalation, the reactions of allyl-Fp complexes [4] with electrophiles have been reported to give persistent η^2-Fp cations [5–8], as shown for the reaction of **1a** with tropylium tetrafluoroborate (*Scheme 1*) [9]. When **1a** is combined with a neutral, electron-deficient C=C bond, a 1,5-dipole is formed, which may cyclize to a five-membered ring, in which the Fp group has moved across the C=C bond, as exemplified by the reaction of **1a** with dimethyl methylidenemalonate (**2**; *Scheme 2*) [4].

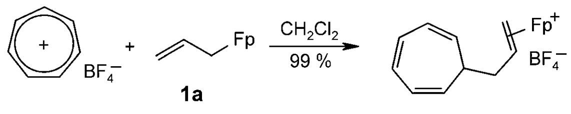
The literature on many analogous formations of carbocyclic and heterocyclic five-membered-ring compounds [10–13] has been reviewed [14] [15]. These reactions indicate a high nucleophilicity of allyl-Fp complexes such as **1a** [16] [17] and **1b** [18],

---

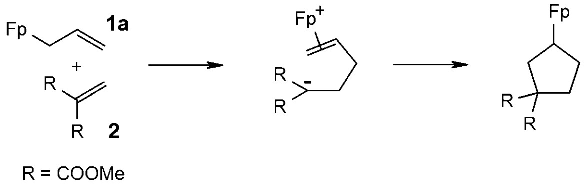
[1] Present address: GSF-Forschungszentrum für Umwelt und Gesundheit, Neuherberg, Germany.

[2] Present address: *CIBA Spezialitätenchemie*, Lampertheim, Germany

Scheme 1



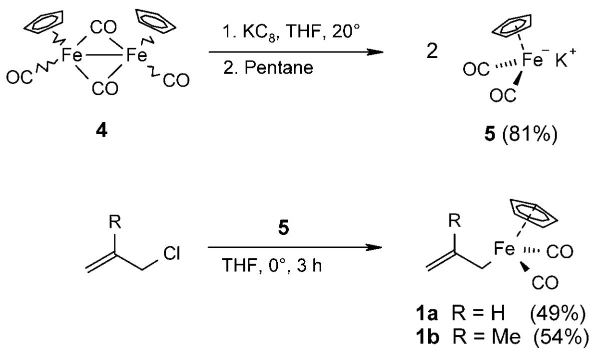
Scheme 2



which prompted us to employ the weak electrophiles **3**$^+$ listed in *Table 1* for kinetic investigations.

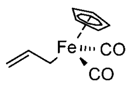
2. Results and Discussion. – 2.1. *Synthesis of Allyl-Fp Complexes.* The allyl-Fp complexes **1a** and **1b** were prepared by nucleophilic substitution of the corresponding allyl chlorides (*Scheme 3*) following literature procedures [16–18]. For the reduction of the commercially available bimetallic complex di-μ-carbonyldicarbonylbis(η^5-cyclopentadienyl)diiron (**4**), a variety of methods have been employed so far, as summarized by *Kühn* and *Rück-Braun* [19][20]. Because all of these procedures suffer from certain deficits, we synthesized K[FeCp(CO)$_2$] (**5**) by treatment of **4** with potassium-graphite laminate, C$_8$K [21], which was obtained according to the procedure described by *Rabinovitz* and co-workers [22].

Scheme 3

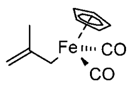


2.2. *Electrophilic Addition to Allyl-Fp Complexes.* Treatment of **1a** with the benzhydrylium salts **3d** · BF$_4$ and **3e** · PF$_6$ gave the π-complexes **6a** · BF$_4$ and **6b** · PF$_6$, respectively, which were recrystallized from CH$_2$Cl$_2$/Et$_2$O (*Scheme 4*). The difference in hybridization of the allyl fragments in **1a** and **6a** was reflected by their ^{1}H-NMR spectra. While the former indicated a typical vinyl group, with terminal H-atom

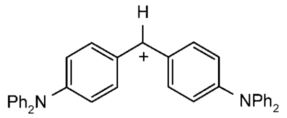
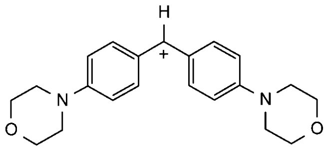
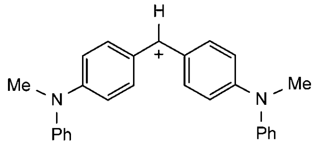
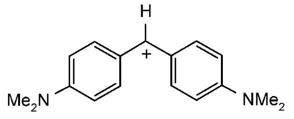
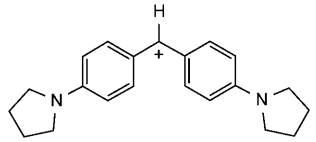
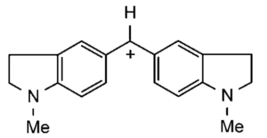
Table 1. *Structures and Electrophilicity Parameters* (*E*) *of Benzhydrylium Ions* **3**$^+$ *Used in Reactions with Compounds* **1a** *and* **1b**. The *E* values were taken from [3].



1a

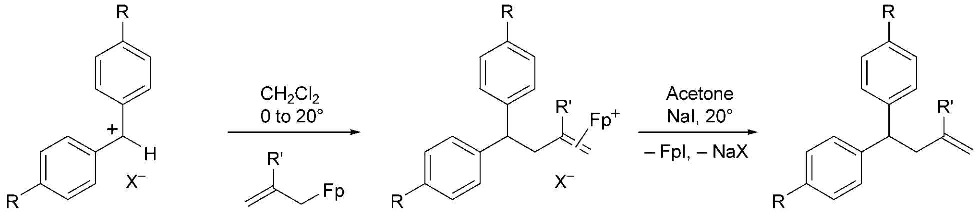


1b

Compound	Formula	*E*
3a$^+$		– 4.72
3b$^+$		– 5.53
3c$^+$		– 5.89
3d$^+$		– 7.02
3e$^+$		– 7.69
3f$^+$		– 8.76

resonances at δ(H) 4.54 and 4.81, the corresponding vinyl H-atoms of **6a** were more shielded, resonating at δ(H) 3.42 and 3.81, respectively. The conversion of the η^1-complex **1a** into the cationic η^2-complex **6a** is accompanied by a reduction in electron density at the Fe-atom, which results in a shift of the carbonyl IR frequencies from 1948 and 2010 cm^{-1} in **1a** [16] to 2035 and 2075 cm^{-1} in **6a** $\cdot$ BF$_4$.

Scheme 4



3 · X	R	R'		
3d·BF_4	Me_2N	**1a** H	**6a**·BF_4 (54%)	-
3e·PF_6	Pyrrolidin-1-yl	**1a** H	**6b**·PF_6 (68%)	-
3a·BF_4	Ph_2N	**1b** Me	-	**7a** (44%)
3d·BF_4	Me_2N	**1b** Me	-	**7b** (54%)
3e·PF_6	Pyrrolidin-1-yl	**1b** Me	-	**7c** (60%)

We were not able to purify the analogous addition products obtained from the 2-methylpropenyl complex **1b**. Therefore, the course of the reaction with the benzhydrylium salts was elucidated by treatment of the crude reaction mixtures with NaI in acetone, which resulted in the metal-free compounds **7a**–**c** (*Scheme 4*).

2.3. *Kinetics.* Kinetic experiments were performed in CH_2Cl_2 under pseudo-first-order conditions, with at least 10 mol-equiv. of the allyl-Fp complexes **1a**,**b** relative to the benzhydrylium salts **3**. Under these conditions, exponential decays of the UV/VIS absorption maxima of the benzhydrylium ions at 600–640 nm were observed, from which the pseudo-first-order rate constants k_{obs} were derived. Second-order rate constants (k_2; *Table 2*) were derived from the relation $k_{obs} = k_2$ [Nu].

Table 2. *Second-Order Rate Constants* (k_2) *for the Reaction of* **1** *with Benzhydrylium Ions* $\mathbf{3}^+$. In CH_2Cl_2 at 20°. The E values were taken from [3].

Nucleophile	Electrophile	E	k_2 [M^{-1} s^{-1}]
1a	$\mathbf{3a}^+$	– 4.72	98.9[a])
	$\mathbf{3b}^+$	– 5.53	11.9
	$\mathbf{3c}^+$	– 5.89	7.26
	$\mathbf{3d}^+$	– 7.02	0.694
	$\mathbf{3e}^+$	– 7.69	0.128
1b	$\mathbf{3c}^+$	– 5.89	145
	$\mathbf{3d}^+$	– 7.02	15.8
	$\mathbf{3e}^+$	– 7.69	3.43
	$\mathbf{3f}^+$	– 8.76	0.631

[a]) Extrapolated with the *Eyring* activation parameters $\Delta H^{\ddagger} = 28.35 \pm 0.59$ kJ mol^{-1} and $\Delta S^{\ddagger} = -109.9 \pm 2.5$ J mol^{-1} K^{-1} obtained from measurements in the temp. range – 50 to – 20°.

Plots of log k_2 for these reactions *vs.* the empirical electrophilicity parameters E showed linear correlations (*Fig. 1*), implying that these reactions follow *Eqn. 1*, where electrophiles are characterized by the electrophilicity parameter E, and nucleophiles are characterized by the nucleophilicity parameters N and s, the temperature being fixed at 20°.

$$\log k = s\,(N + E) \tag{1}$$

The similarity of the slope parameters s for compounds **1** and for other compounds with terminal C=C bonds [1] implies that the relative reactivities are almost independent of the electrophile. As a consequence, the comparison of nucleophilic reactivities can be based on the nucleophilicity parameters N, as illustrated in *Fig. 2*.

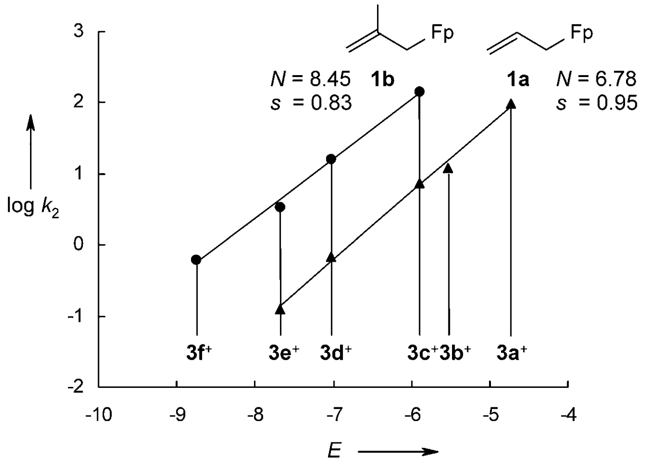


Fig. 1. *Correlation between the Empirical Electrophilicity Parameter* E *and the Second-Order Rate Constants* k_2 (at 20° in CH_2Cl_2) *for the Reactions of the Fp Complexes* **1a,b** *with Different Benzhydrylium Ions* $\mathbf{3}^+$

Obviously, the introduction of an Fp moiety into the allylic position of propene increases N by almost nine logarithmic units, while the reactivity of 2-methylpropene grows only by seven logarithmic units (see *Fig. 2*, bottom *vs.* top). The different behavior of both series can be rationalized by the reduced electron demand of the tertiary carbenium center arising from 2-methylpropene, compared with the secondary carbenium center arising from propene. In both series, the allyl compounds (*Fig. 2*, left row) and their 2-methyl analogues (right row), the β-activating effect of the Fp group exceeds that of the corresponding Sn compounds considerably, and is responsible for the fact that compounds **1a,b** rank among the strongest neutral π-nucleophiles, comparable to silylated 'ketene acetals' [1][23], only exceeded by enamines [24].

2.4. *The Electrophilicity of Alkene-Fp Cations.* An alternative approach to the quantification of β-effects is the comparison of the electrophilicities of the β-substituted carbocations $\mathbf{8}^+$. Quantum-chemical calculations show that increasing hyperconjugative stabilization of the positive charge in $\mathbf{8}^+$ by the C−R σ-bond is associated with a decrease of the C^+−C−R angle α [25]. For R = Fp, bending of the hyperconjugating bond is so strong that the structure is generally represented by formula $\mathbf{9}^+$.

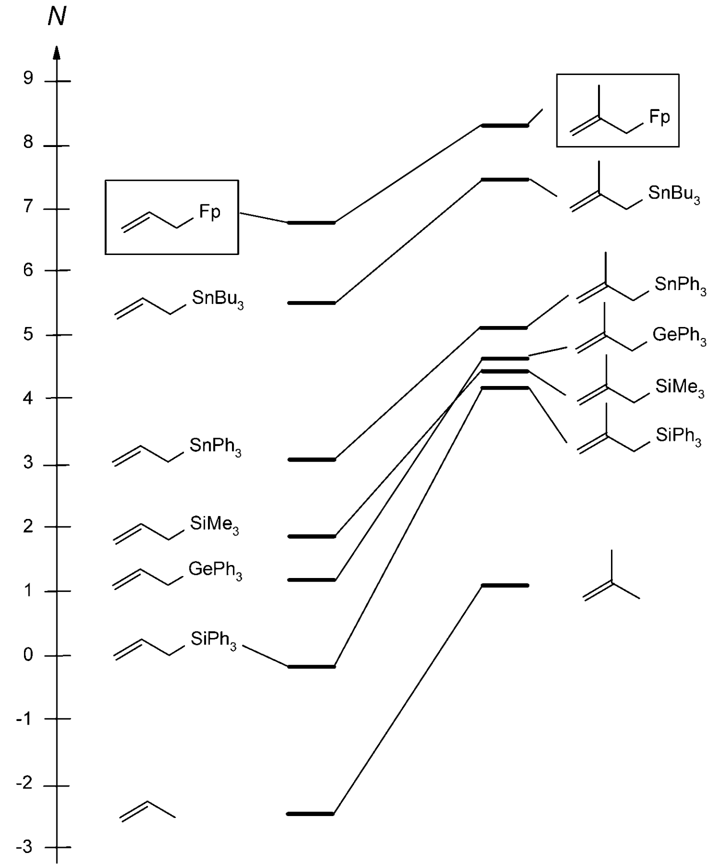
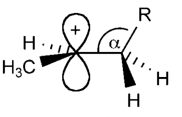
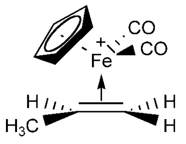


Fig. 2. *Comparison of the Empirical Nucleophilicity Parameters* N *of the Fp Complexes* **1a**,**b** *with those of Analogous Allyl Stannanes, Silanes, and Germanes*



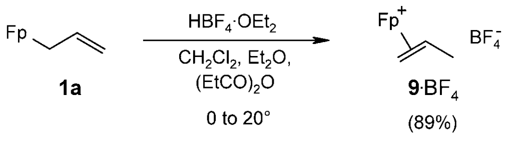
$\mathbf{8}^+$



$\mathbf{9}^+$

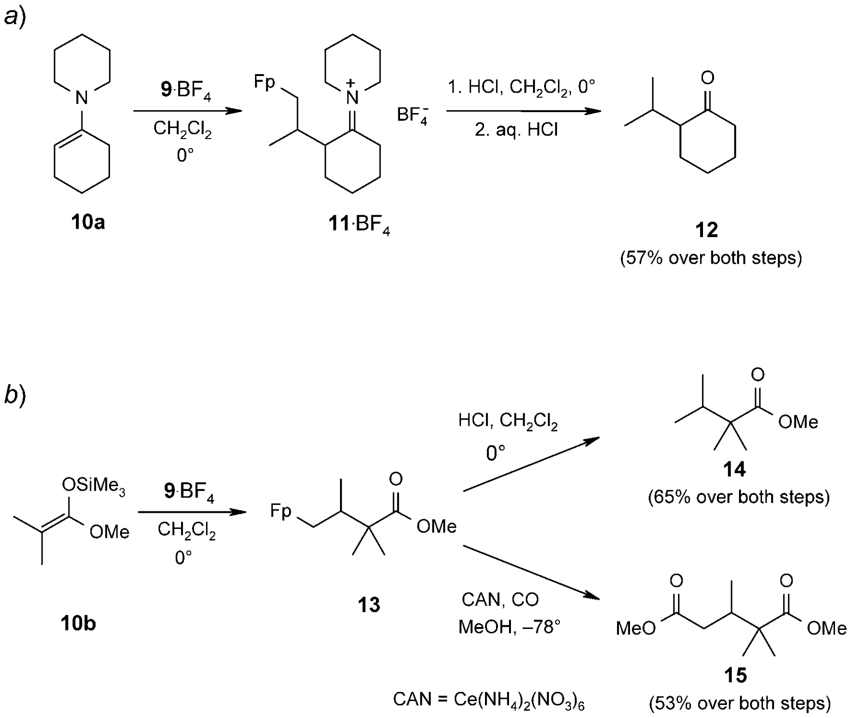
Several methods for the generation of the propene-Fp complex $\mathbf{9}^+$ have been reported [10][16][26][27], including treatment of propene with FpBr/$AlCl_3$, hydride abstraction from propyl-Fp with triphenylmethylium ('tritylium') ions, protonation of **1a**, exchange of the olefin ligand in the corresponding cationic 2-methylpropene-Fp complex, among others. In this work, the protonation of **1a** has been optimized (*Scheme 5*). Exposure to HBF_4 in a mixture of CH_2Cl_2, Et_2O, and propanoic anhydride yielded a crystalline precipitate of pure $\mathbf{9} \cdot BF_4$ in almost quantitative yield.

Scheme 5



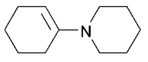
Whereas the reaction between **9** · BF$_4$ and cyclohex-1-enylpyrrolidine was reported to afford a 1 : 1-mixture of two regioisomers [28], **9** · BF$_4$ and the higher ring-homologue **10a** reacted in CH$_2$Cl$_2$ at 0° regioselectively to **11** · BF$_4$, which was not isolated, but demetalated and hydrolyzed to 2-(isopropyl)cyclohexanone (**12**; *Scheme 6, a*). The 'ketene acetal' **10b** reacted analogously. Again, the sensitive initial product **13** was not isolated, but demetalated either with HCl or Ce^{IV} in CO-saturated MeOH [29] to afford the mono or diesters **14** and **15**, respectively (*Scheme 6, b*).

Scheme 6

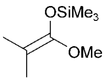


The rates of the reactions of **9** · BF$_4$ with the nucleophiles **10a – e** (*Table 3*) were studied under pseudo-first-order conditions (> 10 equiv. of Nu) by means of UV/VIS spectroscopy in the case of **10a** (signal increase at 305 – 340 nm), or by conductometry in the case of **10b – e**. Second-order rate constants k_2 were either calculated from $k_{obs} = k_2$ [Nu] (for nucleophiles **10a – c**), or derived from plots of pseudo-first-order rate constants k_{obs} *vs.* [Nu] (for **10d**,**e**).

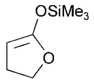
Table 3. *Second-Order Rate Constants and* Eyring *Activation Parameters* (see text) *for the Reactions of* **9** $\cdot$ *BF*$_4$ *with the Nucleophiles* **10**. All reactions were performed in CH_2Cl_2. The N and s parameters were taken from [1][23].



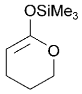
10a



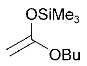
10b



10c



10d



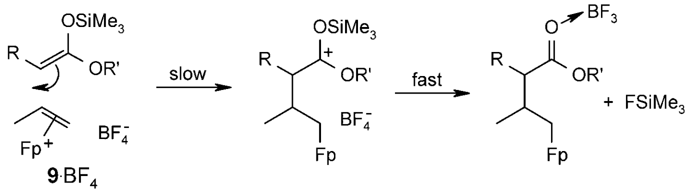
10e

Nucleophile	N	s	k_2 (at $T = 20°$) $[M^{-1} s^{-1}]$	$\Delta H^{\ddagger}$ $[kJ\ mol^{-1}]$	$\Delta S^{\ddagger}$ $[J\ mol^{-1}\ K^{-1}]$	Temp. range [°]
10a	13.36	0.81	4.50^a)	41.20	-91.74	-28 to $+20$
10b	9.00	0.98	0.0516^a)	50.49	-97.18	-32 to $+25$
10c	12.56	0.70	2.32^a)	47.08	-77.21	-48 to $+1$
10d	10.61	0.86	0.373	–	–	–
10e	10.21	0.82	0.651	–	–	–

^{a}) Calculated with the *Eyring* activation parameters.

The reactions of benzhydrylium tetrafluoroborates with silylated enol ethers or silylated 'ketene acetals' have been demonstrated to proceed with rate-determining C$-$C bond formation, followed by fast desilylation [23][30]. Hence, a similar course can be expected for the reactions of **9** $\cdot$ BF_4 with the nucleophiles **10b** – **e**, as shown in *Scheme 7*. All rate constants listed in *Table 3* can, therefore, be assumed to correspond to the C$-$C bond-forming step, and used for the calculation of the electrophilicity parameter E, which, for **9**$^+$, amounts to -11.2 ± 0.9, by minimizing the error $\Delta^2 = \Sigma(\log k_2 - s(N + E))^2$. The standard deviation of ± 1 unit of E is typical for non-benzhydryl type electrophiles [1].

Scheme 7



The kinetics of the addition reaction of **9**$^+$ with phosphanes has previously been reported by *Kane-Maguire* and co-workers [31], though it is not fully clear whether, under the conditions of these experiments, also partial olefin-phosphane ligand exchange occurs [32]. We can now use *Eqn. 1* to calculate the rates for the reactions of **9**$^+$ with phosphanes from the electrophilicity parameter E(**9**$^+$) and the previously published N and s parameters of phosphanes [33]. In *Table 4*, the calculated rate constants are compared with the experimental ones. The two sets of values 'match' within two orders of magnitude, which is remarkable in view of the large structural varieties of electrophiles and nucleophiles treated by *Eqn. 1*.

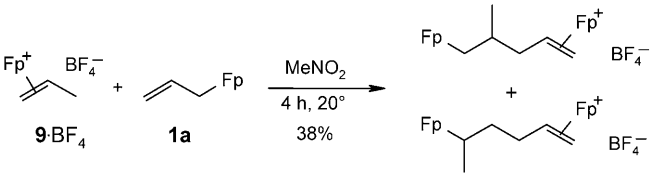
Table 4. *Comparison of Calculated* vs. *Experimental Rate Constants for the Reaction of* **9**$\cdot BF_4$ *with Different Phosphanes*

Nucleophile	N[a])	s[a])	k_{exp} [M^{-1} s^{-1}][b])	k_{calc} [M^{-1} s^{-1}][c])
Bu_3P	15.49	0.69	140	912
Ph_3P	14.33	0.65	3.8	108

[a]) From [33]. [b]) In acetone at 20°; data from [31]. [c]) Calculated according to *Eqn. 1*, with $E(\mathbf{9}^+) = -11.2$.

Because the half-life τ of bimolecular reactions with equal initial concentrations of reactants (c_0) is given by $\tau = 1/(kc_0)$, the reactivity parameters can also be employed to estimate reaction times of electrophile/nucleophile combinations [34]. For example, by substituting the parameters E of $\mathbf{9}^+$, and N and s of **1a** in *Eqn. 1*, a second-order rate constant k_2 of 6.3×10^{-5} M^{-1} s^{-1} (at 20°) is calculated, which corresponds to 50% conversion of 1M solutions of the reactants within *ca.* 4 h. In accord with this estimate, *Rosenblum* and co-workers [5b] reported that the reaction of **9**$\cdot BF_4$ (1M solution in $MeNO_2$) with 1 equiv. of **1a** yields 38% of a 1:1 mixture of regioisomers after 4 h at room temperature (*Scheme 8*).

Scheme 8. *Reaction of* **1a** *with* **9**$\cdot$*BF*$_4$*, as Reported by* Rosenblum *and Co-workers* [5b]



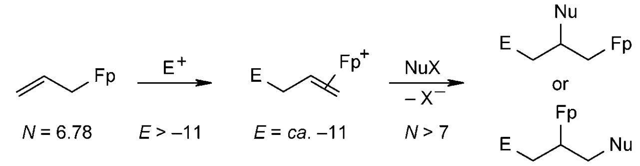
The electrophilicity parameter E for the isopropyl cation is not precisely known, but can be estimated to be *ca.* +11 [35], which is four orders of magnitude more electrophilic than tertiary alkyl cations [36]. One, therefore, can conclude that substitution of a β-H-atom in the isopropyl cation by the Fp group, which is associated with bridging, reduces the C-electrophilicity by more than 20 orders of magnitude. The propene-Fp cation $\mathbf{9}^+$, therefore, is among the weakest cationic C-electrophiles, and has been reported to react only with strong nucleophiles such as carbanions [28], enamines [28], amines, and phosphanes [32].

The nucleophilicity parameters N of **1a**,**b**, and the electrophilicity parameter E of $\mathbf{9}^+$ (determined in this work) can be used to estimate the feasibility of the reaction cascade described in *Scheme 9*. While strong and weak electrophiles ($E > -11$) can be expected to attack **1a**,**b** at a sufficient rate, only strong nucleophiles ($N > 7$) can be considered as potential reaction partners for the second step of *Scheme 9*.

Experimental Part

General. IR Spectra: *Perkin-Elmer Paragon-1000 PC* FT-IR spectrometer; in cm^{-1}. ^1H- and ^{13}C-NMR Spectra: *Bruker ARX-300* (300/75.5 MHz, resp.) and *Varian VXR-400S* (400/100 MHz, resp.) spectrometers; in $CDCl_3$, CD_2Cl_2, or (D_6)acetone soln., referencing to residual solvent signals; δ in ppm, J in Hz. MS: *Varian MAT-311*; in *m*/*z* (rel. %). HR-MS: *Jeol MStation JMS-700.*

Scheme 9



E = electrophile, Nu = nucleophile
E = electrophilicity parameter, *N* = nucleophilicity parameter

Potassium Dicarbonyl(η^5-cyclopentadienyl)ferrate (**5**). Potassium-graphite laminate (C_8K), prepared from graphite (6.00 g, 500 mmol) and K (2.00 g, 51.2 mmol) according to [21], was suspended in THF (180 ml) [22]. At r.t., the bimetallic complex **4** (6.00 g, 17.0 mmol) was added, and the mixture was stirred for 3 h. After dilution with pentane (180 ml), the graphite was separated by filtration under Ar atmosphere to leave an orange filtrate, which was evaporated under vacuum to yield **5** (5.94 g, 81%). Orange powder, identified by comparison of the spectral data with literature reports [20].

(η^1-Prop-2-enyl)dicarbonyl(η^5-cyclopentadienyl)iron(II) (**1a**). As described above, a soln. of **5** in THF (180 ml) was prepared from the bimetallic complex **4** (6.00 g, 17.0 mmol) and C_8K, obtained from K (2.00 g, 51.2 mmol) and graphite (6.00 g, 500 mmol). After removal of graphite by filtration, the orange filtrate was cooled to 0°. Then, a soln. of 3-chloropropene (4.20 ml, 52.0 mmol) in THF (30 ml) was added over a period of 20 min. The mixture was allowed to warm to r.t., stirred for another 2 h, diluted with hexane (200 ml), and filtered through *Celite*. After removal of the solvent in vacuum, the crude product was purified by *Kugelrohr* distillation (52°/1 × 10^{-3} mbar) to yield **1a** (3.63 g, 49%). Brown oil . ^{1}H-NMR (300 MHz, CD_2Cl_2): 2.11 (*d*, *J* = 8.2, $CH_2(3)$); 4.54 (*d*, *J* = 8.6, 1 H of $CH_2(1)$); 4.72 (*s*, Cp); 4.81 (*d*, *J* = 16.8, 1 H of $CH_2(1)$); 6.04 (*ddt*, *J* = 16.8, 8.6, 8.2, H–C(2)). ^{13}C-NMR (75.5 MHz, CD_2Cl_2): 4.7 (*t*, C(1)); 86.1 (*d*, Cp); 105.9 (*t*, C(3)); 148.7 (*d*, C(2)); 217.3 (*s*, CO). The chemical shifts were in accord with the NMR data reported earlier [37].

(η^1-2-Methylprop-2-enyl)dicarbonyl(η^5-cyclopentadienyl)iron(II) (**1b**) [18]. As described above for the formation of **1a**, a soln. of **5** (devoid of graphite) in THF (180 ml) was prepared, and treated with a soln. of 2-methylpropenyl chloride (5.00 ml, 51.0 mmol) in THF (30 ml). The crude product was purified by *Kugelrohr* distillation (61°/1 × 10^{-3} mbar) to yield **1b** (4.2 g, 54%). Brown oil . ^{1}H-NMR (300 MHz, (D_6)acetone): 1.75 (*s*, 2-Me); 2.11 (*s*, $CH_2(3)$); 4.42 (*m*, 1 H of $CH_2(1)$); 4.61 (*m*, 1 H of $CH_2(1)$); 4.82 (*s*, Cp). ^{13}C-NMR (75.5 MHz, (D_6)acetone): 8.1 (*t*, C(3)); 23.6 (*q*, 2-Me); 87.3 (*d*, Cp); 105.6 (*t*, C(1)); 155.6 (*s*, C(2)); 218.2 (*s*, CO). The chemical shifts were in accord with the NMR data reported in [37].

Reactions of Fp Complexes **1** *with Benzhydrylium Ions* **3**. *General Procedure A* (*GP A*). Under exclusion of H_2O, O_2, and light, to a soln. of the appropriate salt **3** in CH_2Cl_2 was slowly added a CH_2Cl_2 soln. of **1** at 0°. Stirring was continued at this temp. for 4 h. The mixture was then allowed to warm up to r.t., and stirring was continued for another 12 h. For workup, see below.

Dicarbonyl(η^5-cyclopentadienyl)[(1,2-η)-4,4-bis{4-(dimethylamino)phenyl}but-1-ene]iron(II) Tetrafluoroborate (**6a** · BF_4). Prepared according to *GP A*, from **3d** · BF_4 (330 mg, 0.970 mmol) and **1a** (235 mg, 1.08 mmol) in CH_2Cl_2 (15 ml). After removal of the solvent in vacuum, the crude product was dissolved in CH_2Cl_2 (7 ml), and cooled to – 30°. During 10 min, Et_2O was added to this soln. by condensation. Further cooling to – 32° led to precipitation of a solid, which was isolated by filtration, and dried in vacuum to afford **6a** (290 mg, 54%). Dark green powder. IR: 3120, 2931, 2889, 2856, 2804, 2075, 2035, 1612, 1521, 1481, 1449, 1431, 1352, 1082, 1057, 945, 875, 822, 595, 565, 536, 521. ^{1}H-NMR (300 MHz, (D_6)acetone): 2.15 (*m*, 1 H of $CH_2(3)$); 2.91 (*s*, 2 Me_2N); 3.26 (*m*, 1 H of $CH_2(3)$); 3.42 (*d*, *J* = 14.6, 1 H of $CH_2(1)$); 3.81 (*d*, *J* = 8.3, 1 H of $CH_2(1)$); 4.04 (*dd*, *J* = 8.0, 6.4, H–C(4)); 5.03 (*m*, H–C(2)); 5.81 (*s*, Cp); 6.76 (*m*, 4 arom. H); 7.15, 7.25 (2*d*, *AA'BB'*, *J* = 8.5 each, 2 × 2 arom. H). ^{13}C-NMR (75.5 MHz, (D_6)acetone): 41.8 (*q*, (Me_2N); 43.9 (*t*, C(3)); 53.8 (*d*, C(4)); 56.9 (*t*, C(1)); 87.5 (*d*, C(2)); 90.6 (*d*, Cp); 114.7 (*d*); 129.6 (*d*), 130.1 (*d*); 134.4 (*s*), 134.6 (*s*); 150.0 (*s*); 211.9 (*s*, CO), 212.0 (*s*, CO).

Dicarbonyl(η^5-cyclopentadienyl)[(1,2-η)-4,4-bis(4-pyrrolidinophenyl)but-1-ene]iron(II) Hexafluorophosphate (**6b** · PF_6). Prepared according to *GP A*, from **3e** · PF_6 (1.25 g, 2.77 mmol) and **1a** (675 mg, 3.10 mmol) in CH_2Cl_2 (20 ml). Workup as described for **6a** afforded **6b** · PF_6 (1.26 g, 68%). Green powder. IR: 3120, 2920, 2075, 2033, 1612, 1519, 1488, 1372, 844, 595, 557, 534. ^{1}H-NMR (300 MHz, (D_6)acetone)[3]): 1.97 (br. *s*, 1 H of H−C(3), 4 CH_2); 3.21 (br. *s*, 4 CH_2); 3.42–4.05 (*m*, 5 H); 4.95 (*m*$_c$, H−C(2)); 5.84 (*s*, Cp); 6.49 (br. *s*, 4 H); 7.08–7.15 (*m*, 4 H). ^{13}C-NMR (75.5 MHz, (D_6)-acetone)[3]): 25.9 (*t*); 43.8 (*t*, C(3)); 48.3 (*t*); 53.5 (*d*, C(4)); 56.1 (*t*, C(1)); 87.5 (*d*, C(2)); 90.1 (*d*, Cp); 112.5 (*d*); 112.6 (*d*); 129.0 (*d*); 129.4 (*d*); 131.6 (*s*); 131.7 (*s*); 147.2 (*s*); 147.5 (*s*); 209.1 (*s*, CO); 211.5 (*s*, CO).

4,4-Bis[4-(diphenylamino)phenyl]-2-methylbut-1-ene[4]) (**7a**) [3]. Compound **3a** · BF_4 (500 mg, 0.850 mmol) was reacted with **1b** (260 mg, 1.12 mmol) in CH_2Cl_2 (12 ml) according to *GP A*. Removal of the solvent in vacuum afforded the crude metal complex, which, however, could not be purified. For decomplexation, the compound was dissolved in acetone (6 ml), and treated with NaI (0.26 g, 1.7 mmol). After 13 h at r.t., H_2O (8 ml) was added, the mixture was extracted with $CHCl_3$ (3 × 25 ml), the combined org. layers were dried ($MgSO_4$), and evaporated in vacuum. The resulting crude product was purified by column chromatography (CC) (SiO_2; hexane/AcOEt 50 : 1) to afford **7a** (210 mg, 44 %). Colorless solid. IR: 3060, 3034, 2964, 2927, 1589, 1506, 1492, 1328, 1314, 1278, 1177, 1155, 1076, 1029, 1016, 892, 820, 754, 696, 622, 556, 536, 513, 499. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.62 (*s*, 3 H); 2.64 (*d*, *J* = 7.9, 2 H); 3.98 (*t*, *J* = 7.9, 1 H); 4.53 (*s*, 1 H); 4.64 (*s*, 1 H); 6.89–7.17 (*m*, 28 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 22.7 (*q*); 44.3 (*t*); 48.3 (*d*); 112.5 (*t*); 122.5 (*d*); 123.9 (*d*); 124.0 (*d*); 128.6 (*d*); 129.1 (*d*); 139.2 (*s*); 143.5 (*s*); 145.6 (*s*); 147.9 (*s*). The chemical shifts were in accord with the NMR data reported in [3]. HR-MS: 556.2876 (M^+, $C_{41}H_{36}N_2^+$; calc. 556.2878).

4,4-Bis[4-(dimethylamino)phenyl]-2-methyl-but-1-ene[4]) (**7b**) [3]. Prepared in analogy to **7a**, from **3d** · BF_4 (805 mg, 2.37 mmol) and **1b** (638 mg, 2.75 mmol) in CH_2Cl_2 (15 ml), followed by treatment with NaI (1.50 g) in acetone (12 ml), extraction with $CHCl_3$, and purification by CC (SiO_2; hexane/AcOEt 15 : 1). Yield of **7b**: 380 mg, 54%. Colorless crystals. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.71 (*s*, 2-Me); 2.73 (*d*, *J* = 7.7, CH_2(3)); 2.90 (*s*, 2 Me_2N); 4.04 (t, *J* = 7.7, H−C(4)); 4.65 (br. *s*, 1 H of H−C(1)); 4.71 (br. *s*, 1 H of H−C(1)); 6.68 (*d*, *J* = 8.4, 4 arom. H); 7.15 (*d*, *J* = 8.4, 4 arom. H); the chemical shifts were in accord with the NMR data reported in [3]. ^{13}C-NMR (100 MHz, $CDCl_3$): 22.9 (*q*, 2-Me); 41.1 (*q*, Me_2N); 44.6 (*t*, C(3)); 47.6 (*d*, C(4)); 112.5 (*t*, C(1)); 112.9 (*d*); 128.6 (*d*); 134.1 (*d*); 144.5 (*s*, C(2)); 149.1 (*s*).

4,4-Bis(4-pyrrolidinophenyl)-2-methylbut-1-ene[4]) (**7c**) [3]. Prepared in analogy to **7a**, from **3e** · BF_4 (600 mg, 1.33 mmol) and **1b** (410 mg, 1.76 mmol) in CH_2Cl_2 (12 ml), followed by treatment with NaI (750 mg) in acetone (10 ml), extraction with CH_2Cl_2 (3 × 40 ml), and purification by CC (SiO_2; hexane/Et_2O 10 : 1). Yield of **7c**: 285 mg, 60%. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.68 (*s*, 2-Me); 1.96 (*m*$_c$, 8 H); 2.69 (*d*, *J* = 7.9, CH_2(3)); 3.23 (*m*$_c$, 8 H); 4.00 (*t*, *J* = 7.9, H−C(4)); 4.62, 4.67 (2*s*, CH_2(1)); 6.45–6.50 (*m*, 4 H); 7.02–7.05 (*m*, 4 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 22.4 (*q*, 2-Me); 25.3 (*t*); 44.2 (*t*, C(3)); 47.0 (*d*, C(4)); 47.4 (*t*); 111.7 (*t*, C(1)); 112.4 (*d*); 128.2 (*d*); 132.3 (*s*); 144.1 (*s*); 149.9 (*s*). The chemical shifts were in accord with the NMR data reported in [3].

Dicarbonyl(η^5-cyclopentadienyl)[(1,2-η)propene]iron(II) Tetrafluoroborate (**9** · BF_4). A soln. of **1a** (600 mg, 2.75 mmol) in CH_2Cl_2/Et_2O/propanoic anhydride 5 : 10 : 2 (10 ml) was cooled to 0°. Addition of $HBF_4 \cdot OEt_2$ (52% in Et_2O; 2.7 g, 7.32 mmol) under vigorous stirring caused the precipitation of a yellow solid. Stirring at 0° was continued for 1 h. Then, the mixture was allowed to warm to r.t. The solid was collected by filtration under N_2 atmosphere, washed with Et_2O (3 × 5 ml), and dried in vacuum to afford **9** · BF_4 (750 mg, 89%). Yellow solid. ^{1}H-NMR (400 MHz, (D_6)acetone): 1.90 (*d*, *J* = 6.1, Me); 3.65 (*d*, J_{trans} = 14.6, 1 H of H−C(1)); 4.05 (*d*, J_{cis} = 8.2, 1 H of H−C(1)); 5.34 (*m*, H−C(2)); 5.86 (*s*, Cp). ^{13}C-NMR (100 MHz, (D_6)acetone): 21.8 (*q*, C(3)); 56.2 (*t*, C(1)); 86.1 (*d*, C(2)); 90.2 (*d*, Cp); 209.5 (*s*, CO); 211.4 (*s*, CO). The chemical shifts were in accord with the NMR data reported in [38].

Reactions of **9** · BF_4 *with Nucleophiles* **10**. *General Procedure B* (*GP B*). In the dark, to a suspension of **9** · BF_4 in CH_2Cl_2 was added the appropriate nucleophile (**10a** or **10b**) at 0°. The mixture was stirred at 0° for 4 h., and then at r.t. for 12 h. For workup, see below.

2-Isopropylcyclohexanone (**12**). Prepared according to *GP B*, from **10a** (230 mg, 1.39 mmol) and **9** · BF_4 (290 mg, 0.948 mmol) in CH_2Cl_2 (8 ml). For the decomplexation, the mixture was cooled to 0°, and saturated with HCl gas for 90 min. After removal of the solvent by distillation at 20°/15 mbar, the residue was dissolved in a small amount of acetone, and purified by CC (SiO_2; CH_2Cl_2) and *Kugelrohr* distillation (75°/5 × 10^{-3} mbar) to afford **12** (76 mg, 57%). Colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.86, 0.88 (2*d*, *J* = 6.9 each, 2 Me); 1.56–2.41 (*m*, 10 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 19.1, 21.2 (2*q*, 2 Me); 24.3 (*t*); 26.4 (*d*); 28.1 (*t*); 29.3 (*t*); 42.1 (*t*); 57.3 (*d*); 213.7 (*s*). The chemical shifts were in accord with the NMR data reported in [39].

---

[3]) ^{1}H,^{1}H- and ^{1}H,^{13}C-COSY experiments were used to assign the NMR signals.

[4]) Not fully systematic name to reflect the analogy to related compounds.

Methyl 2,2,3-Trimethylbutanoate (**14**). Prepared according to *GP B*, from **10b** (215 mg, 1.23 mmol) and **9** · BF_4 (250 mg, 0.818 mmol) in CH_2Cl_2 (8 ml). The decomplexation was performed as described for **12**, the *Kugelrohr* distillation being performed at 60°/8 × 10^{-3} mbar, to afford **14** (77 mg, 65 %). Colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.71 (*d*, $J = 6.9$, 2 × 3-Me); 0.97 (*s*, 2 × 2-Me); 1.84 (*sept.*, $J = 6.9$, H–C(3)); 3.53 (*s*, MeO). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 17.7 (*q*, 3-Me); 21.6 (*q*, 2-Me); 35.0 (*d*, C(3)); 45.8 (*s*, C(2)); 51.6 (*q*, MeO); 178.9 (*s*, C(1)). The chemical shifts were in accord with the NMR data reported in [40].

Dimethyl 2,2,3-Trimethylpentanedioate (**15**). Prepared according to *GP B*, from **10b** (430 mg, 2.47 mmol) and **9** · BF_4 (650 mg, 2.13 mmol) in CH_2Cl_2 (15 ml). The solvent was evaporated in vacuum to leave a solid residue, which was dissolved in MeOH (20 ml) and saturated with CO at – 78°. While the mixture was kept saturated by a permanent flow of CO, a soln. of $Ce(NH_4)_2(NO_3)_6$ in MeOH (15 ml) was added over a period of 60 min. Stirring under a CO atmosphere at – 78° was continued for 1 h. Then, the mixture was allowed to warm to r.t., the solvent was distilled off (30°C/15 mbar), the residue was dissolved in a small amount of acetone, and purified by CC (SiO_2; CH_2Cl_2) and *Kugelrohr* distillation (70°/6 × 10^{-4} mbar) to afford **15** (201 mg, 53%). Colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.81 (*d*, $J = 6.9$, 3-Me); 1.05, 1.06 (2*s*, 2 × 2-Me); 1.97, 2.29 (2m_c, H–C(3), CH_2(4)); 3.59 (*s*, 2 MeO). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 15.2 (*q*, 3-Me); 21.8, 22.0 (2*q*, 2-Me); 36.8 (*d*, C(3)), 36.9 (*t*, C(4)); 45.5 (*s*, C(2)); 51.7, 51.9 (2*q*, 2 MeO); 173.7 (*s*, C=O), 177.9 (*s*, C=O). The chemical shifts were in accord with the NMR data reported in [41].

Kinetics. The temp. of the solns. used for kinetic studies was maintained constant within ± 0.2° by means of a circulating-bath cryostat (water/glycol bath for $T > -10°$, EtOH bath for $T < -10°$), and monitored with a thermocouple probe inserted into the reaction mixture. *Eyring* activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ of the electrophile/nucleophile combinations (see *Table 3*) were calculated from second-order rate constants measured at different temperatures ($\Delta T > 30$ K).

As the reactions of the colored benzhydrylium ions **3** with allyl-Fp complexes **1a**,**b** gave rise to colorless products, the rates of the reactions were determined photometrically. The kinetic experiments were performed in *Schlenk* glassware under a N_2 atmosphere and exclusion of H_2O and O_2. UV/VIS Spectra in the range of 600–640 nm were collected as a function of time by use of a fiber-optics system (*Schölly KGS III*), described in [2a], that was combined with a *J&M TIDAS* diode-array spectrophotometer [42]. Typically, the nucleophile (Nu) concentrations (0.1–3 mM) were considerably higher than those of the cations [0.01–0.03 mM), which resulted in pseudo-first-order kinetics, with an exponential decay of the benzhydrylium ion concentration. The data are summarized in *Tables 5* and *6*.

The kinetics of the reaction of enamine **10a** with the Fp complex **9** · BF_4 (*Table 7*) were determined photometrically [2a] by following the product formation in the UV/VIS spectrum (*Zeiss MCS-220* diode-array spectrometer, resembling a similar experimental setup as reported in [42]). By using the increase of the signal integral in the range of 305–340 nm and the relation $tk_{obs} = \ln(A_t - A_{end}) - \ln(A_0 - A_{end})$, the rate constants k_{obs} were obtained from a plot of ln $(A_t - A_{end})$ *vs.* time (t). The second-order rate constants were then calculated from $k_{obs} = k_2$ [Nu].

Because of the formation of neutral products, the reactions of the cationic Fp complex $\mathbf{9}^+$ with the silylated 'ketene acetals' **10b**–**e** (*Table 7*) were followed by conductometry (*Tacussel CD810* conductometer, Pt plate electrodes *WTW LTA1*), as described in [2a]. At different temperatures, calibration curves for the correlation between conductivity and [$\mathbf{9}^+$] were determined by measuring the conductivity of solns. of $\mathbf{9}^+$ as a function of concentration. For the reactions of $\mathbf{9}^+$ with **10b**,**c**, the second-order rate constants were calculated from $k_{obs} = k_2$ [Nu]. However, for the reactions of $\mathbf{9}^+$ with **10d**,**e**, k_2 values (*Table 3*) were obtained from the slopes of plots of k_{obs} *vs.* [Nu].

We thank the *Deutsche Forschungsgemeinschaft* (Ma 673-19) for support of this work.

Table 5. *Kinetics of the Reactions of the Fp Complex* **1a** *with Benzhydrylium Ions* **3**$^+$. In CH_2Cl_2; the electrophiles were analyzed spectrophotometrically. All concentrations expressed in mol/l.

T [°]	[**3**$^+$]$_0$	[**1a**]	[**1a**]$_0$/[**3**$^+$]$_0$	Conversion [%]	*k* [M^{-1} s^{-1}]
3e · BF_4 ($\lambda = 630$ nm):					
20.0	1.94×10^{-5}	1.40×10^{-3}	72	45	1.05×10^{-1}
20.0	1.64×10^{-5}	1.63×10^{-3}	99	53	1.19×10^{-1}
20.0	1.55×10^{-5}	1.88×10^{-3}	121	64	1.23×10^{-1}
20.0	1.68×10^{-5}	2.51×10^{-3}	149	55	1.63×10^{-1}
3d · BF_4 ($\lambda = 600$ nm):					
20.0	2.05×10^{-5}	1.26×10^{-3}	61	86	5.95×10^{-1}
20.0	1.82×10^{-5}	1.85×10^{-3}	102	68	6.71×10^{-1}
20.0	1.91×10^{-5}	2.91×10^{-3}	152	54	8.15×10^{-1}
3c · BF_4 ($\lambda = 630$ nm):					
20.0	1.40×10^{-5}	4.17×10^{-4}	30	80	6.48
20.0	1.52×10^{-5}	8.03×10^{-4}	53	74	7.94
20.0	1.69×10^{-5}	1.46×10^{-3}	86	69	7.82
20.0	1.46×10^{-5}	1.94×10^{-3}	133	53	6.80
3b · BF_4 ($\lambda = 630$ nm):					
20.0	1.91×10^{-5}	1.92×10^{-4}	10	92	1.20×10^{1}
20.0	1.93×10^{-5}	5.82×10^{-4}	30	95	1.17×10^{1}
20.0	1.78×10^{-5}	8.94×10^{-4}	50	89	1.19×10^{1}
20.0	1.70×10^{-5}	1.11×10^{-3}	65	82	1.21×10^{1}
3a · BF_4 ($\lambda = 640$ nm):					
– 20.0	2.12×10^{-5}	4.55×10^{-4}	21	72	1.37×10^{1}
– 30.0	2.24×10^{-5}	7.71×10^{-4}	34	79	7.31
– 40.0	2.37×10^{-5}	1.02×10^{-3}	43	82	4.05
– 50.0	2.45×10^{-5}	2.37×10^{-3}	97	70	1.94

Table 6. *Kinetics of the Reactions of the Fp Complex* **1b** *with Benzhydrylium Ions* **3**$^+$. In CH_2Cl_2; the electrophiles were analyzed spectrophotometrically. All concentrations expressed in mol/l.

T [°]	[**3**$^+$]$_0$	[**1b**]$_0$	[**1b**]$_0$/[**3**$^+$]$_0$	Conversion [%]	*k* [M^{-1} s^{-1}]
3f · BF_4 ($\lambda = 630$ nm)					
20.0	1.45×10^{-5}	1.99×10^{-3}	137	55	7.21×10^{-1}
20.0	1.05×10^{-5}	1.26×10^{-3}	120	75	5.71×10^{-1}
20.0	1.54×10^{-5}	1.55×10^{-3}	101	62	6.23×10^{-1}
20.0	1.42×10^{-5}	7.33×10^{-4}	52	59	6.10×10^{-1}
3e · BF_4 ($\lambda = 630$ nm)					
20.0	1.66×10^{-5}	1.65×10^{-3}	99	95	3.43
3d · BF_4 ($\lambda = 600$ nm)					
20.0	1.79×10^{-5}	2.97×10^{-4}	17	75	1.57×10^{1}
20.0	1.40×10^{-5}	4.63×10^{-4}	33	94	1.57×10^{1}
20.0	1.54×10^{-5}	8.15×10^{-4}	53	84	1.67×10^{1}
20.0	1.66×10^{-5}	8.76×10^{-4}	53	88	1.52×10^{1}
20.0	1.45×10^{-5}	9.58×10^{-4}	66	86	1.54×10^{1}
3c · BF_4 ($\lambda = 630$ nm)					
20.0	1.34×10^{-5}	1.47×10^{-4}	11	85	1.54×10^{2}
20.0	1.34×10^{-5}	2.75×10^{-4}	21	83	1.46×10^{2}
20.0	1.28×10^{-5}	4.03×10^{-4}	31	81	1.43×10^{2}
20.0	1.32×10^{-5}	5.42×10^{-4}	41	82	1.45×10^{2}
20.0	1.16×10^{-5}	6.06×10^{-4}	52	80	1.45×10^{2}

Table 7. *Kinetics of the Reactions of* **9** $\cdot$ *BF*$_4$ *with Nucleophiles* **10**. In CH_2Cl_2 solution. All concentrations are expressed in mol/l. The kinetics were determined by conductometry, except for **10a**, where UV/VIS spectroscopy was used ($\lambda = 305-340$ nm).

T [°]	[**9**$^+$]$_0$	[**10**]$_0$	[**9**$^+$]$_0$/[**10**]$_0$	Conversion [%]	k_2 [M^{-1} s^{-1}]
10a:					
20.0	5.76×10^{-4}	2.20×10^{-2}	38	94	4.90
20.0	5.36×10^{-4}	8.37×10^{-3}	15	98	5.01
20.0	9.19×10^{-4}	2.19×10^{-2}	24	90	5.81
7.0	7.99×10^{-4}	1.87×10^{-2}	23	96	1.84
− 0.4	1.03×10^{-3}	1.05×10^{-2}	10	98	1.16
− 10.2	9.84×10^{-4}	1.47×10^{-2}	15	99	4.61×10^{-1}
− 27.5	7.93×10^{-4}	1.72×10^{-2}	22	95	1.68×10^{-1}
10b:					
25.0	3.19×10^{-4}	1.35×10^{-2}	42	85	7.04×10^{-2}
20.0	2.23×10^{-4}	9.88×10^{-3}	44	88	5.22×10^{-2}
20.0	3.19×10^{-4}	1.88×10^{-2}	59	92	5.36×10^{-2}
20.0	2.59×10^{-4}	7.55×10^{-3}	29	80	5.18×10^{-2}
− 12.0	3.08×10^{-4}	1.72×10^{-2}	56	69	3.90×10^{-3}
− 22.2	3.34×10^{-4}	2.11×10^{-2}	63	76	1.43×10^{-3}
− 31.7	$3.83 \times 10^{-\mathrm{v}4}$	1.61×10^{-2}	42	27	4.62×10^{-4}
10c:					
1.0	7.14×10^{-4}	2.76×10^{-2}	39	59	5.55×10^{-1}
− 9.0	8.97×10^{-4}	3.31×10^{-2}	37	58	2.63×10^{-1}
− 9.0	7.74×10^{-4}	4.75×10^{-2}	61	50	2.99×10^{-1}
− 18.8	8.76×10^{-4}	5.38×10^{-2}	61	50	9.48×10^{-2}
− 48.2	8.42×10^{-4}	5.78×10^{-2}	69	56	5.19×10^{-3}
10d:					
20.0	8.03×10^{-4}	9.78×10^{-3}	12	74	2.40×10^{-3} a)
20.0	6.94×10^{-4}	1.55×10^{-2}	22	89	4.90×10^{-3} a)
20.0	7.36×10^{-4}	3.31×10^{-2}	45	84	1.19×10^{-2} a)
20.0	7.42×10^{-4}	7.23×10^{-2}	97	64	2.59×10^{-2} a)
10e:					
20.0	3.54×10^{-4}	3.39×10^{-2}	96	94	1.99×10^{-2} a)
20.0	3.37×10^{-4}	4.53×10^{-2}	134	76	2.58×10^{-2} a)
20.0	3.43×10^{-4}	2.76×10^{-2}	81	72	1.30×10^{-2} a)
20.0	3.34×10^{-4}	1.43×10^{-2}	43	76	6.90×10^{-3} a)
20.0	3.20×10^{-4}	2.06×10^{-2}	64	88	8.70×10^{-3} a)

a) k_{obs} [s^{-1}]; k_2 was obtained from the slopes of plots of k_{obs} *vs.* [Nu].

REFERENCES

[1] H. Mayr, B. Kempf, A. R. Ofial, *Acc. Chem. Res.* **2003**, *36*, 66–77.

[2] a) H. Mayr, R. Schneider, C. Schade, J. Bartl, R. Bederke, *J. Am. Chem. Soc.* **1990**, *112*, 4446; b) H. Mayr, R. Schneider, B. Irrgang, C. Schade, *J. Am. Chem. Soc.* **1990**, *112*, 4454; c) H. Mayr, R. Schneider, U. Grabis, *J. Am. Chem. Soc.* **1990**, *112*, 4460; d) G. Hagen, H. Mayr, *J. Am. Chem. Soc.* **1991**, *113*, 4954.

[3] H. Mayr, T. Bug, M. F. Gotta, N. Hering, B. Irrgang, B. Janker, B. Kempf, R. Loos, A. R. Ofial, G. Remennikov, H. Schimmel, *J. Am. Chem. Soc.* **2001**, *123*, 9500.

[4] M. Rosenblum, *Acc. Chem. Res.* **1974**, *7*, 122.

[5] a) A. Rosan, M. Rosenblum, J. Tancrede, *J. Am. Chem. Soc.* **1973**, *95*, 3062; b) P. J. Lennon, A. Rosan, M. Rosenblum, J. Tancrede, P. Waterman, *J. Am. Chem. Soc.* **1980**, *102*, 7033.

[6] T. W. Bodnar, A. R. Cutler, *Organometallics* **1985**, *4*, 1558.

[7] S. R. Berryhill, J. G. Breitenbucher, *Tetrahedron Lett.* **1990**, *31*, 1671.

[8] G. E. Agoston, M. P. Cabal, E. Turos, *Tetrahedron Lett.* **1991**, *32*, 3001; S. Jiang, E. Turos, *Tetrahedron Lett.* **1991**, *32*, 4639.

[9] A. Cutler, D. Ehntholt, P. Lennon, K. Nicholas, D. F. Marten, M. Madhavarao, S. Raghu, A. Rosan, M. Rosenblum, *J. Am. Chem. Soc.* **1975**, *97*, 3149.

[10] A. Cutler, D. Ehntholt, W. P. Giering, P. Lennon, S. Raghu, A. Rosan, M. Rosenblum, J. Tancrede, D. Wells, *J. Am. Chem. Soc.* **1976**, *98*, 3495.

[11] T. S. Abram, R. Baker, C. M. Exon, V. B. Rao, *J. Chem. Soc.*, *Perkin Trans. 1* **1982**, 285; R. Baker, C. M. Exon, V. B. Rao, R. W. Turner, *J. Chem. Soc.*, *Perkin Trans. 1* **1982**, 295; T. S. Abram, R. Baker, C. M. Exon, V. B. Rao, R. W. Turner, *J. Chem. Soc., Perkin Trans. 1* **1982**, 301.

[12] W. Malisch, J. Zöller, M. Schwarz, V. Jäger, A. M. Arif, *Chem. Ber.* **1994**, *127*, 1243.

[13] S. Jiang, E. Turos, *Organometallics* **1993**, *12*, 4280.

[14] M. Rosenblum, *J. Organomet. Chem.* **1986**, *300*, 191.

[15] M. E. Welker, *Chem. Rev.* **1992**, *92*, 97.

[16] M. L. H. Green, P. L. I. Nagy, *J. Chem. Soc.* **1963**, 189.

[17] T. L. Underiner, in 'Encyclopedia of Reagents for Organic Synthesis', Ed. L. A. Paquette, J. Wiley & Sons, Chichester, 1995, Vol. 1, p. 100–101.

[18] W. P. Giering, M. Rosenblum, *J. Organomet. Chem.* **1970**, *25*, C71.

[19] J. Kühn, K. Rück-Braun, *J. Prakt. Chem.* **1997**, *339*, 675; G. R. Stephenson, M. Perseghini, A. Togni, in 'Science of Synthesis', Ed. M. Lautens, Thieme Verlag, Stuttgart, 2001, Vol. 1, Chapt. 1.7, p. 745–888

[20] T. Bodnar, E. Coman, K. Menard, A. Cutler, *Inorg. Chem.* **1982**, *21*, 1275; M. Brookhart, W. B. Studabaker, G. R. Husk, *Organometallics* **1987**, *6*, 1141.

[21] A. Fürstner, in 'Encyclopedia of Reagents for Organic Synthesis', Ed. L. A. Paquette, J. Wiley & Sons, Chichester, 1995, Vol. 6, p. 4226–4230.

[22] D. Tamarkin, Y. Cohen, M. Rabinovitz, *Synthesis* **1987**, 196.

[23] T. Tokuyasu, H. Mayr, *Eur. J. Org. Chem.* **2004**, 2791.

[24] B. Kempf, N. Hampel, A. R. Ofial, H. Mayr, *Chem.–Eur. J.* **2003**, *9*, 2209.

[25] Y. Apeloig, in 'The Chemistry of Silicon Compounds', Eds. S. Patai, Z. Rappoport, J. Wiley & Sons, New York, 1993, p. 57–226; S. G. Wierschke, J. Chandrasekhar, W. L. Jorgensen, *J. Am. Chem. Soc.* **1985**, *107*, 1496.

[26] W. P. Giering, M. Rosenblum, *J. Chem. Soc.*, *Chem. Commun.* **1971**, 441.

[27] D. E. Laycock, J. Hartgerink, M. C. Baird, *J. Org. Chem.* **1980**, *45*, 291.

[28] P. Lennon, A. M. Rosan, M. Rosenblum, *J. Am. Chem. Soc.* **1977**, *99*, 8426.

[29] S. Jiang, T. Chen, E. Turos, *Organometallics* **1995**, *14*, 4710.

[30] J. Burfeindt, M. Patz, M. Müller, H. Mayr, *J. Am. Chem. Soc.* **1998**, *120*, 3629.

[31] L. Cosslett, L. A. P. Kane-Maguire, *J. Organomet. Chem.* **1979**, *178*, C17; L. A. P. Kane-Maguire, E. D. Honig, D. A. Sweigart, *Chem. Rev.* **1984**, *84*, 525.

[32] P. Lennon, M. Madhavarao, A. M. Rosan, M. Rosenblum, *J. Organomet. Chem.* **1976**, *108*, 93.

[33] B. Kempf, H. Mayr, *Chem.–Eur. J.* **2005**, *11*, 917.

[34] H. Mayr, A. R. Ofial, in 'Carbocation Chemistry', Eds. G. A. Olah, G. K. S. Prakash, J. Wiley & Sons, Hoboken, N.J., 2004, Chapt. 13, p. 331.

[35] J. P. Pezacki, D. Shukla, J. Lusztyk, J. Warkentin, *J. Am. Chem. Soc.* **1999**, *121*, 6589.

[36] M. Roth, H. Mayr, *Angew. Chem.*, *Int. Ed.* **1995**, *34*, 2250.

[37] C. Siebert, in 'Gmelin Handbook of Inorganic Chemistry', 8th edn., 1990, B13, p. 100.

[38] U. Busch, P. Hübener, N. Kuhn, H. Schumann, C. Weber, in 'Gmelin Handbook of Inorganic Chemistry', 8th edn., 1990, B17, p. 6.

[39] M. Miyashita, S. Hara, A. Yoshikoshi, *J. Org. Chem.* **1987**, *52*, 2602; D. H. Marr, J. B. Stothers, *Can. J. Chem.* **1967**, *45*, 225.

[40] K. H. Ingold, D. C. Nonhebel, J. C. Walton, *J. Phys. Chem.* **1986**, *90*, 2859.

[41] M. Kawai, M. Onaka, Y. Isumi, *Bull. Chem. Soc. Jpn.* **1988**, *61*, 2157.

[42] A. D. Dilman, S. L. Ioffe, H. Mayr, *J. Org. Chem.* **2001**, *66*, 3196; H. Mayr, A. R. Ofial, *Einsichten – Forschung an der LMU München* **2001**, *20*(2), 30.

Received March 15, 2005