

## Quantification of the $\beta$ -Stabilizing Effect of the Dicarboxyl( $\eta^5$ -cyclopentadienyl)iron Group

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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- $\eta$ )propene]iron(II) tetrafluoroborate (**9**·BF<sub>4</sub>) with  $\pi$ -nucleophiles have been performed to elucidate the magnitude of the  $\beta$ -effect of the [(CO)<sub>2</sub>FeCp] group (Fp group). Introduction of the Fp group into the allylic position of propene and 2-methylpropene increases the nucleophilicity of the  $\pi$ -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  $\pi$ -nucleophiles. Replacement of one  $\beta$ -H-atom in the isopropyl cation by the Fp group reduces the electrophilicity by more than 20 orders of magnitude, so that **9**<sup>+</sup> 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<sub>2</sub>=CH–CH<sub>2</sub>R towards C-electrophiles increases considerably in the series R = H < Pr < Me<sub>3</sub>Si < Bu<sub>3</sub>Sn, with relative reaction rates ( $k_{\text{rel}}$ ) toward [Ar<sub>2</sub>CH]<sup>+</sup> of 1.0 (H), 1.5 (Pr),  $1.6 \times 10^4$  (Me<sub>3</sub>Si), and  $7.4 \times 10^7$  (Bu<sub>3</sub>Sn) in CH<sub>2</sub>Cl<sub>2</sub> 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( $\eta^5$ -cyclopentadienyl)iron (Fp) moiety, and we will show that the  $\beta$ -activating effect of the Fp group even exceeds that of the Bu<sub>3</sub>Sn group by more than one order of magnitude.

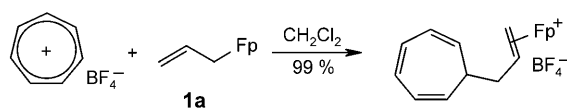
While the reactions of electrophiles with allyl silanes, stannanes, and other metalated compounds are usually accompanied by successive demetalation, the reactions of allyl-Fp complexes [4] with electrophiles have been reported to give persistent  $\eta^2$ -Fp cations [5–8], as shown for the reaction 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 methylenemalonate (**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],

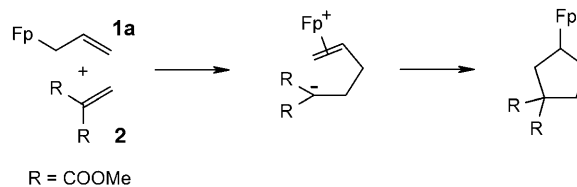
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Scheme 1



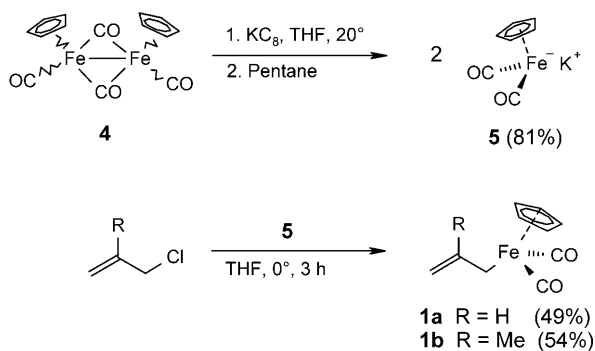
Scheme 2



which prompted us to employ the weak electrophiles **3**<sup>+</sup> listed in Table 1 for kinetic investigations.

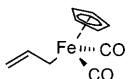
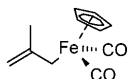
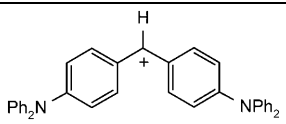
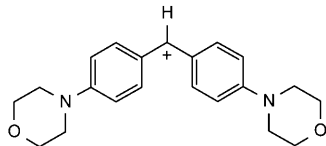
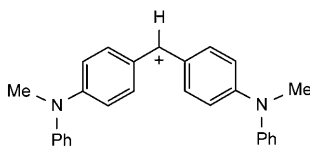
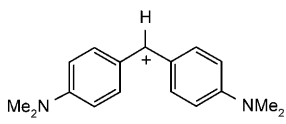
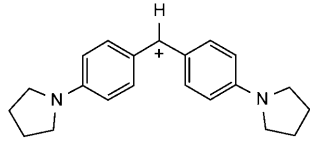
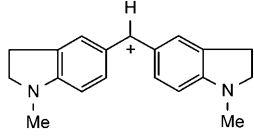
**2. Results and Discussion.** – 2.1. *Synthesis of Allyl-Fp Complexes.* The allyl-Fp complexes **1a** and **1b** were prepared by nucleophilic substitution of the corresponding allyl chlorides (Scheme 3) following literature procedures [16–18]. For the reduction of the commercially available bimetallic complex di- $\mu$ -carbonyldicarbonylbis( $\eta^5$ -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  $\text{K}[\text{FeCp}(\text{CO})_2]$  (**5**) by treatment of **4** with potassium-graphite laminate,  $\text{C}_8\text{K}$  [21], which was obtained according to the procedure described by Rabinovitz and co-workers [22].

Scheme 3



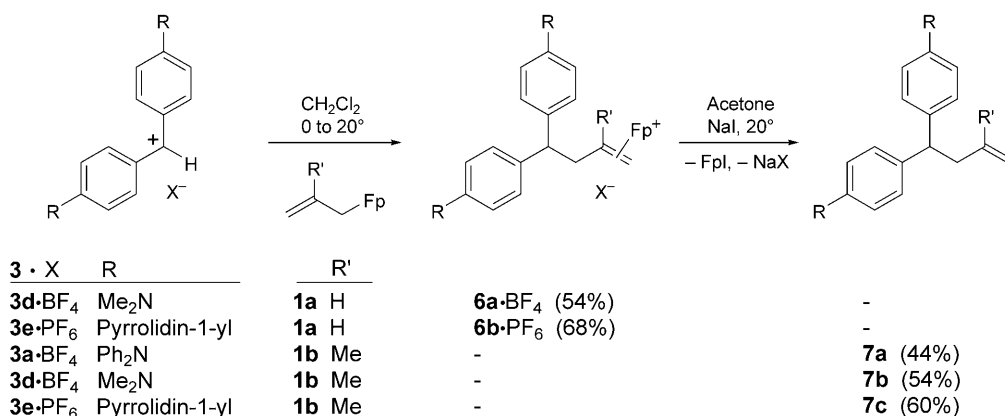
2.2. *Electrophilic Addition to Allyl-Fp Complexes.* Treatment of **1a** with the benzhydrylium salts **3d**· $\text{BF}_4$  and **3e**· $\text{PF}_6$  gave the  $\pi$ -complexes **6a**· $\text{BF}_4$  and **6b**· $\text{PF}_6$ , respectively, which were recrystallized from  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$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

| <div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;">  <p><b>1a</b></p> </div> <div style="text-align: center;">  <p><b>1b</b></p> </div> </div> |                                                                                     |        |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|--------|
| Compound                                                                                                                                                                                                                                                                                                                                                                        | Formula                                                                             | $E$    |
| <b>3a</b> <sup>+</sup>                                                                                                                                                                                                                                                                                                                                                          |    | – 4.72 |
| <b>3b</b> <sup>+</sup>                                                                                                                                                                                                                                                                                                                                                          |    | – 5.53 |
| <b>3c</b> <sup>+</sup>                                                                                                                                                                                                                                                                                                                                                          |    | – 5.89 |
| <b>3d</b> <sup>+</sup>                                                                                                                                                                                                                                                                                                                                                          |   | – 7.02 |
| <b>3e</b> <sup>+</sup>                                                                                                                                                                                                                                                                                                                                                          |  | – 7.69 |
| <b>3f</b> <sup>+</sup>                                                                                                                                                                                                                                                                                                                                                          |  | – 8.76 |

resonances at  $\delta(\text{H})$  4.54 and 4.81, the corresponding vinyl H-atoms of **6a** were more shielded, resonating at  $\delta(\text{H})$  3.42 and 3.81, respectively. The conversion of the  $\eta^1$ -complex **1a** into the cationic  $\eta^2$ -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  $\text{cm}^{-1}$  in **1a** [16] to 2035 and 2075  $\text{cm}^{-1}$  in **6a**· $\text{BF}_4$ .

Scheme 4



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  $\text{CH}_2\text{Cl}_2$  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  $k_{\text{obs}}$  were derived. Second-order rate constants ( $k_2$ ; Table 2) were derived from the relation  $k_{\text{obs}} = k_2 [\text{Nu}]$ .

Table 2. Second-Order Rate Constants ( $k_2$ ) for the Reaction of **1** with Benzhydrylium Ions **3**<sup>+</sup>. In  $\text{CH}_2\text{Cl}_2$  at  $20^\circ$ . The  $E$  values were taken from [3].

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

<sup>a</sup>) Extrapolated with the Eyring activation parameters  $\Delta H^\ddagger = 28.35 \pm 0.59 \text{ kJ mol}^{-1}$  and  $\Delta S^\ddagger = -109.9 \pm 2.5 \text{ J mol}^{-1} \text{ K}^{-1}$  obtained from measurements in the temp. range  $-50$  to  $-20^\circ$ .

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°.

$$\log k = s (N + E) \quad (1)$$

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.

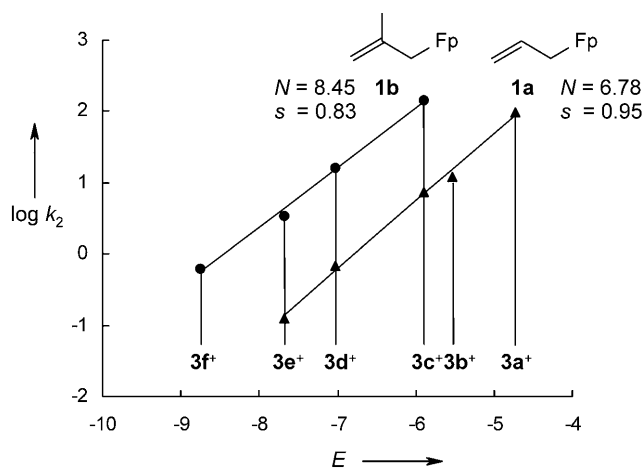


Fig. 1. Correlation between the Empirical Electrophilicity Parameter  $E$  and the Second-Order Rate Constants  $k_2$  (at 20° in  $\text{CH}_2\text{Cl}_2$ ) for the Reactions of the Fp Complexes **1a,b** with Different Benzhydrylium Ions  $3^+$

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  $\beta$ -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  $\pi$ -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  $\beta$ -effects is the comparison of the electrophilicities of the  $\beta$ -substituted carbocations  $8^+$ . Quantum-chemical calculations show that increasing hyperconjugative stabilization of the positive charge in  $8^+$  by the C–R  $\sigma$ -bond is associated with a decrease of the C<sup>+</sup>–C–R angle  $\alpha$  [25]. For R = Fp, bending of the hyperconjugating bond is so strong that the structure is generally represented by formula **9**<sup>+</sup>.

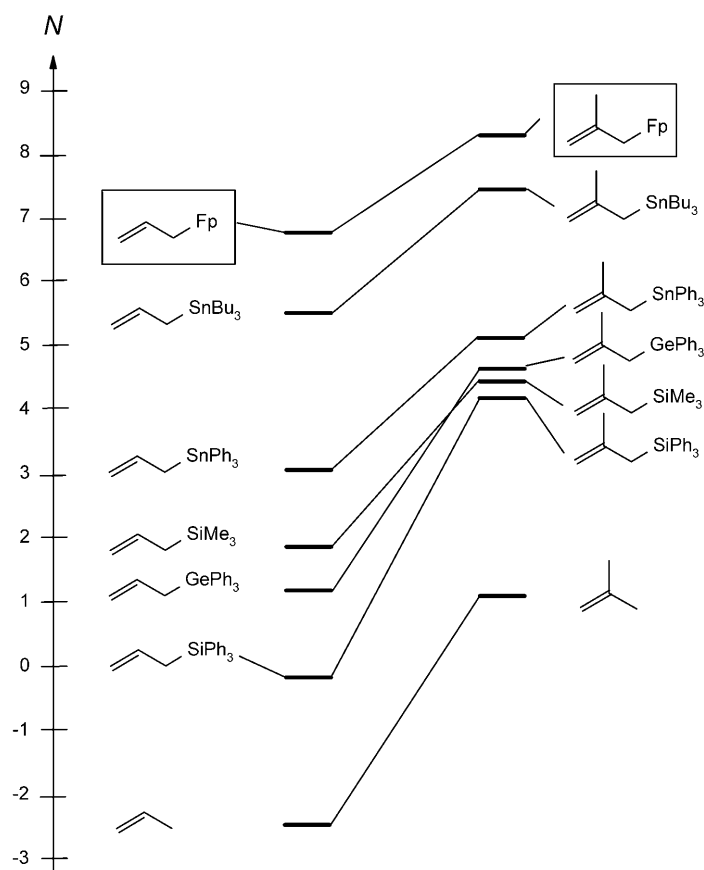
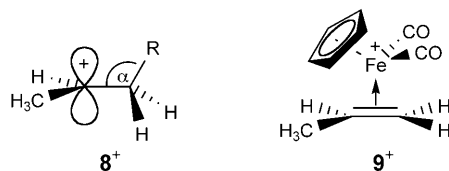
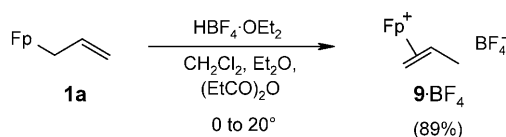


Fig. 2. Comparison of the Empirical Nucleophilicity Parameters  $N$  of the Fp Complexes **1a,b** with those of Analogous Allyl Stannanes, Silanes, and Germanes



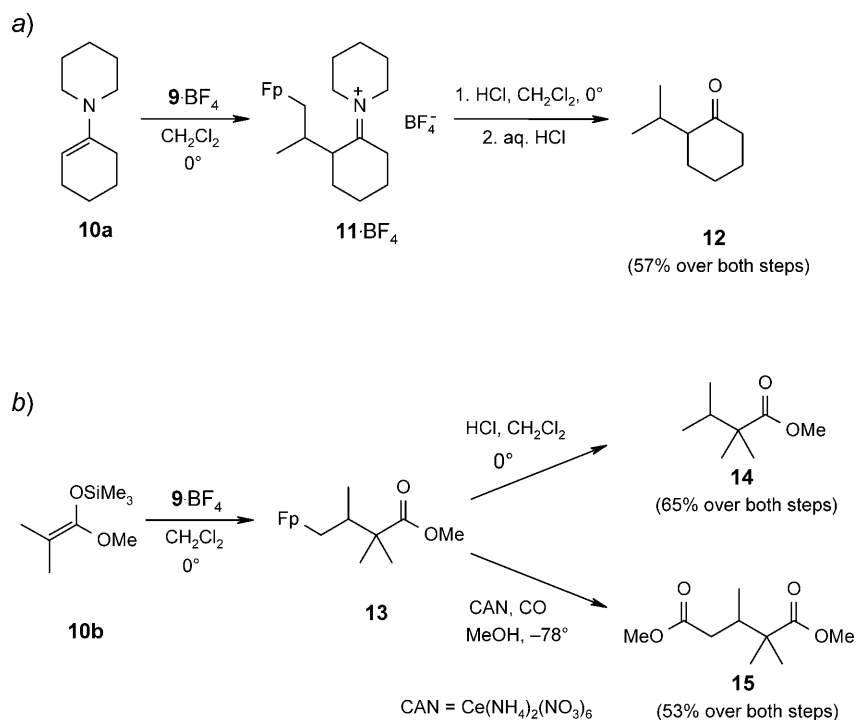
Several methods for the generation of the propene-Fp complex **9<sup>+</sup>** have been reported [10][16][26][27], including treatment of propene with FpBr/AlCl<sub>3</sub>, hydride abstraction from propyl-Fp with triphenylmethyl cation ('tritylium') ions, protonation of **1a**, exchange of the olefin 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<sub>4</sub> in a mixture of CH<sub>2</sub>Cl<sub>2</sub>, Et<sub>2</sub>O, and propanoic anhydride yielded a crystalline precipitate of pure **9**·BF<sub>4</sub> in almost quantitative yield.

Scheme 5



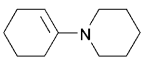
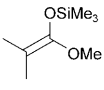
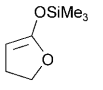
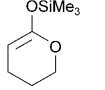
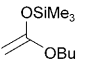
Whereas the reaction between  $9 \cdot \text{BF}_4$  and cyclohex-1-enylpyrrolidine was reported to afford a 1:1-mixture of two regioisomers [28],  $9 \cdot \text{BF}_4$  and the higher ring-homologue **10a** reacted in  $\text{CH}_2\text{Cl}_2$  at  $0^\circ$  regioselectively to **11**· $\text{BF}_4$ , 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  $\text{HCl}$  or  $\text{Ce}^{\text{IV}}$  in  $\text{CO}$ -saturated  $\text{MeOH}$  [29] to afford the mono or diesters **14** and **15**, respectively (Scheme 6, *b*).

Scheme 6



The rates of the reactions of  $9 \cdot \text{BF}_4$  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  $k_{\text{obs}} = k_2 [\text{Nu}]$  (for nucleophiles **10a–c**), or derived from plots of pseudo-first-order rate constants  $k_{\text{obs}}$  vs.  $[\text{Nu}]$  (for **10d,e**).

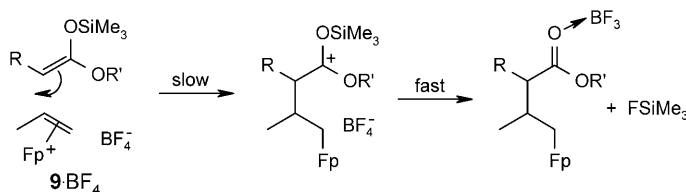
Table 3. *Second-Order Rate Constants and Eyring Activation Parameters* (see text) *for the Reactions of 9 · BF<sub>4</sub> with the Nucleophiles 10*. All reactions were performed in CH<sub>2</sub>Cl<sub>2</sub>. The *N* and *s* parameters were taken from [1][23].

| <div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;"> <br/> <b>10a</b> </div> <div style="text-align: center;"> <br/> <b>10b</b> </div> <div style="text-align: center;"> <br/> <b>10c</b> </div> <div style="text-align: center;"> <br/> <b>10d</b> </div> <div style="text-align: center;"> <br/> <b>10e</b> </div> </div> |          |          |                                                                                 |                                                    |                                                                   |                    |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------|----------|---------------------------------------------------------------------------------|----------------------------------------------------|-------------------------------------------------------------------|--------------------|
| Nucleophile                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       | <i>N</i> | <i>s</i> | <i>k</i> <sub>2</sub> (at <i>T</i> = 20°)<br>[M <sup>-1</sup> s <sup>-1</sup> ] | Δ <i>H</i> <sup>‡</sup><br>[kJ mol <sup>-1</sup> ] | Δ <i>S</i> <sup>‡</sup><br>[J mol <sup>-1</sup> K <sup>-1</sup> ] | Temp. range<br>[°] |
| <b>10a</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        | 13.36    | 0.81     | 4.50 <sup>a)</sup>                                                              | 41.20                                              | −91.74                                                            | −28 to +20         |
| <b>10b</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        | 9.00     | 0.98     | 0.0516 <sup>a)</sup>                                                            | 50.49                                              | −97.18                                                            | −32 to +25         |
| <b>10c</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        | 12.56    | 0.70     | 2.32 <sup>a)</sup>                                                              | 47.08                                              | −77.21                                                            | −48 to +1          |
| <b>10d</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        | 10.61    | 0.86     | 0.373                                                                           | —                                                  | —                                                                 | —                  |
| <b>10e</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        | 10.21    | 0.82     | 0.651                                                                           | —                                                  | —                                                                 | —                  |

<sup>a)</sup> 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** · BF<sub>4</sub> 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**<sup>+</sup>, amounts to  $-11.2 \pm 0.9$ , by minimizing the error  $\Delta^2 = \Sigma(\log k_2 - s(N + E))^2$ . The standard deviation of  $\pm 1$  unit of *E* is typical for non-benzhydryl type electrophiles [1].

*Scheme 7*



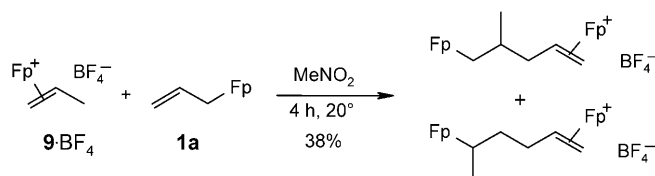
The kinetics of the addition reaction of **9**<sup>+</sup> with phosphanes has previously been reported by *Kane-Maguire* and co-workers [31], though it is not fully clear whether, under the conditions of these experiments, also partial olefin-phosphane ligand exchange occurs [32]. We can now use *Eqn. 1* to calculate the rates for the reactions of **9**<sup>+</sup> with phosphanes from the electrophilicity parameter *E*(**9**<sup>+</sup>) 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  $\mathbf{9} \cdot \text{BF}_4$  with Different Phosphanes

| Nucleophile           | $N^a)$ | $s^a)$ | $k_{\text{exp}} [\text{M}^{-1} \text{s}^{-1}]^b)$ | $k_{\text{calc}} [\text{M}^{-1} \text{s}^{-1}]^c)$ |
|-----------------------|--------|--------|---------------------------------------------------|----------------------------------------------------|
| $\text{Bu}_3\text{P}$ | 15.49  | 0.69   | 140                                               | 912                                                |
| $\text{Ph}_3\text{P}$ | 14.33  | 0.65   | 3.8                                               | 108                                                |

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

Because the half-life  $\tau$  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  $\mathbf{1a}$  in Eqn. 1, a second-order rate constant  $k_2$  of  $6.3 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$  (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  $\mathbf{9} \cdot \text{BF}_4$  (1M solution in  $\text{MeNO}_2$ ) with 1 equiv. of  $\mathbf{1a}$  yields 38% of a 1:1 mixture of regioisomers after 4 h at room temperature (Scheme 8).

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

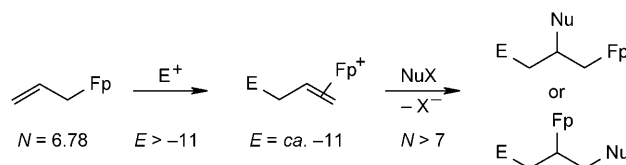
The electrophilicity parameter  $E$  for the isopropyl cation is not precisely known, but can be estimated to be *ca.* +11 [35], which is four orders of magnitude more electrophilic than tertiary alkyl cations [36]. One, therefore, can conclude that substitution of a  $\beta$ -H-atom in the isopropyl 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  $\mathbf{1a,b}$ , 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  $\mathbf{1a,b}$  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  $\text{cm}^{-1}$ .  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR Spectra: Bruker ARX-300 (300/75.5 MHz, resp.) and Varian VXR-400S (400/100 MHz, resp.) spectrometers; in  $\text{CDCl}_3$ ,  $\text{CD}_2\text{Cl}_2$ , or  $(\text{D}_6)\text{acetone}$  soln., referencing to residual solvent signals;  $\delta$  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 Dicarboxyl( $\eta^5$ -cyclopentadienyl)ferrate (5).** Potassium-graphite laminate ( $\text{C}_8\text{K}$ ), 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].

**( $\eta^1$ -Prop-2-enyl)dicarbonyl( $\eta^5$ -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  $\text{C}_8\text{K}$ , 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<sup>-3</sup> mbar) to yield **1a** (3.63 g, 49%). Brown oil. <sup>1</sup>H-NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ ): 2.11 (d, *J* = 8.2,  $\text{CH}_2(3)$ ); 4.54 (d, *J* = 8.6, 1 H of  $\text{CH}_2(1)$ ); 4.72 (s, Cp); 4.81 (d, *J* = 16.8, 1 H of  $\text{CH}_2(1)$ ); 6.04 (ddt, *J* = 16.8, 8.6, 8.2, H-C(2)). <sup>13</sup>C-NMR (75.5 MHz,  $\text{CD}_2\text{Cl}_2$ ): 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].

**( $\eta^1$ -2-Methylprop-2-enyl)dicarbonyl( $\eta^5$ -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<sup>-3</sup> mbar) to yield **1b** (4.2 g, 54%). Brown oil. <sup>1</sup>H-NMR (300 MHz, ( $\text{D}_6$ )acetone): 1.75 (s, 2-Me); 2.11 (s,  $\text{CH}_2(3)$ ); 4.42 (m, 1 H of  $\text{CH}_2(1)$ ); 4.61 (m, 1 H of  $\text{CH}_2(1)$ ); 4.82 (s, Cp). <sup>13</sup>C-NMR (75.5 MHz, ( $\text{D}_6$ )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 (GPA).** Under exclusion of  $\text{H}_2\text{O}$ ,  $\text{O}_2$ , and light, to a soln. of the appropriate salt **3** in  $\text{CH}_2\text{Cl}_2$  was slowly added a  $\text{CH}_2\text{Cl}_2$  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( $\eta^5$ -cyclopentadienyl)[(1,2- $\eta$ )-4,4-bis[4-(dimethylamino)phenyl]but-1-ene]iron(II) Tetrafluoroborate (6a · BF<sub>4</sub>).** Prepared according to GPA, from **3d** · BF<sub>4</sub> (330 mg, 0.970 mmol) and **1a** (235 mg, 1.08 mmol) in  $\text{CH}_2\text{Cl}_2$  (15 ml). After removal of the solvent in vacuum, the crude product was dissolved in  $\text{CH}_2\text{Cl}_2$  (7 ml), and cooled to -30°. During 10 min,  $\text{Et}_2\text{O}$  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. <sup>1</sup>H-NMR (300 MHz, ( $\text{D}_6$ )acetone): 2.15 (m, 1 H of  $\text{CH}_2(3)$ ); 2.91 (s, 2 Me<sub>2</sub>N); 3.26 (m, 1 H of  $\text{CH}_2(3)$ ); 3.42 (d, *J* = 14.6, 1 H of  $\text{CH}_2(1)$ ); 3.81 (d, *J* = 8.3, 1 H of  $\text{CH}_2(1)$ ); 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 (2d, AA'BB', *J* = 8.5 each, 2 × 2 arom. H). <sup>13</sup>C-NMR (75.5 MHz, ( $\text{D}_6$ )acetone): 41.8 (q, (Me<sub>2</sub>N)); 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( $\eta^5$ -cyclopentadienyl)[(1,2- $\eta$ )-4,4-bis(4-pyrrolidinophenyl)but-1-ene]iron(II) Hexafluorophosphate (6b · PF<sub>6</sub>).** Prepared according to GPA, from **3e** · PF<sub>6</sub> (1.25 g, 2.77 mmol) and **1a** (675 mg, 3.10 mmol) in  $\text{CH}_2\text{Cl}_2$  (20 ml). Workup as described for **6a** afforded **6b** · PF<sub>6</sub> (1.26 g, 68%). Green powder. IR: 3120, 2920,

2075, 2033, 1612, 1519, 1488, 1372, 844, 595, 557, 534. <sup>1</sup>H-NMR (300 MHz, (D<sub>6</sub>)acetone)<sup>3</sup>): 1.97 (br. s, 1 H of H–C(3), 4 CH<sub>2</sub>); 3.21 (br. s, 4 CH<sub>2</sub>); 3.42–4.05 (m, 5 H); 4.95 (m<sub>c</sub>, H–C(2)); 5.84 (s, Cp); 6.49 (br. s, 4 H); 7.08–7.15 (m, 4 H). <sup>13</sup>C-NMR (75.5 MHz, (D<sub>6</sub>)acetone)<sup>3</sup>): 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<sup>4</sup> (**7a**) [3]. Compound **3a** · BF<sub>4</sub> (500 mg, 0.850 mmol) was reacted with **1b** (260 mg, 1.12 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (12 ml) according to *GPA*. 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<sub>2</sub>O (8 ml) was added, the mixture was extracted with CHCl<sub>3</sub> (3 × 25 ml), the combined org. layers were dried (MgSO<sub>4</sub>), and evaporated in vacuum. The resulting crude product was purified by column chromatography (CC) (SiO<sub>2</sub>; 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. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): 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). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): 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*<sup>+</sup>, C<sub>41</sub>H<sub>36</sub>N<sub>2</sub><sup>+</sup>; calc. 556.2878).

4,4-Bis[4-(dimethylamino)phenyl]-2-methylbut-1-ene<sup>4</sup> (**7b**) [3]. Prepared in analogy to **7a**, from **3d** · BF<sub>4</sub> (805 mg, 2.37 mmol) and **1b** (638 mg, 2.75 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 ml), followed by treatment with NaI (1.50 g) in acetone (12 ml), extraction with CHCl<sub>3</sub>, and purification by CC (SiO<sub>2</sub>; hexane/AcOEt 15 : 1). Yield of **7b**: 380 mg, 54%. Colorless crystals. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): 1.71 (s, 2-Me); 2.73 (d, *J* = 7.7, CH<sub>2</sub>(3)); 2.90 (s, 2 Me<sub>2</sub>N); 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]. <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): 22.9 (q, 2-Me); 41.1 (q, Me<sub>2</sub>N); 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<sup>4</sup> (**7c**) [3]. Prepared in analogy to **7a**, from **3e** · BF<sub>4</sub> (600 mg, 1.33 mmol) and **1b** (410 mg, 1.76 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (12 ml), followed by treatment with NaI (750 mg) in acetone (10 ml), extraction with CH<sub>2</sub>Cl<sub>2</sub> (3 × 40 ml), and purification by CC (SiO<sub>2</sub>; hexane/Et<sub>2</sub>O 10 : 1). Yield of **7c**: 285 mg, 60%. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 1.68 (s, 2-Me); 1.96 (m<sub>c</sub>, 8 H); 2.69 (d, *J* = 7.9, CH<sub>2</sub>(3)); 3.23 (m<sub>c</sub>, 8 H); 4.00 (t, *J* = 7.9, H–C(4)); 4.62, 4.67 (2s, CH<sub>2</sub>(1)); 6.45–6.50 (m, 4 H); 7.02–7.05 (m, 4 H). <sup>13</sup>C-NMR (75.5 MHz, CDCl<sub>3</sub>): 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<sup>5</sup>-cyclopentadienyl)[(1,2-η)propene]iron(II) Tetrafluoroborate (**9** · BF<sub>4</sub>). A soln. of **1a** (600 mg, 2.75 mmol) in CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O/propanoic anhydride 5 : 10 : 2 (10 ml) was cooled to 0°. Addition of HBF<sub>4</sub> · OEt<sub>2</sub> (52% in Et<sub>2</sub>O; 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<sub>2</sub> atmosphere, washed with Et<sub>2</sub>O (3 × 5 ml), and dried in vacuum to afford **9** · BF<sub>4</sub> (750 mg, 89%). Yellow solid. <sup>1</sup>H-NMR (400 MHz, (D<sub>6</sub>)acetone): 1.90 (d, *J* = 6.1, Me); 3.65 (d, *J*<sub>trans</sub> = 14.6, 1 H of H–C(1)); 4.05 (d, *J*<sub>cis</sub> = 8.2, 1 H of H–C(1)); 5.34 (m, H–C(2)); 5.86 (s, Cp). <sup>13</sup>C-NMR (100 MHz, (D<sub>6</sub>)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<sub>4</sub> with Nucleophiles **10**. General Procedure B (*GP B*). In the dark, to a suspension of **9** · BF<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub> 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<sub>4</sub> (290 mg, 0.948 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (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<sub>2</sub>; CH<sub>2</sub>Cl<sub>2</sub>) and *Kugelrohr* distillation (75°/5 × 10<sup>–3</sup> mbar) to afford **12** (76 mg, 57%). Colorless oil. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 0.86, 0.88 (2d, *J* = 6.9 each, 2 Me); 1.56–2.41 (m, 10 H). <sup>13</sup>C-NMR (75.5 MHz, CDCl<sub>3</sub>): 19.1, 21.2 (2q, 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].

<sup>3</sup>) <sup>1</sup>H, <sup>1</sup>H- and <sup>1</sup>H, <sup>13</sup>C-COSY experiments were used to assign the NMR signals.

<sup>4</sup>) 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<sub>4</sub> (250 mg, 0.818 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (8 ml). The decomplexation was performed as described for **12**, the *Kugelrohr* distillation being performed at 60°/8 × 10<sup>−3</sup> mbar, to afford **14** (77 mg, 65 %). Colorless oil. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 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). <sup>13</sup>C-NMR (75.5 MHz, CDCl<sub>3</sub>): 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<sub>4</sub> (650 mg, 2.13 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (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<sub>4</sub>)<sub>2</sub>(NO<sub>3</sub>)<sub>6</sub> 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<sub>2</sub>; CH<sub>2</sub>Cl<sub>2</sub>) and *Kugelrohr* distillation (70°/6 × 10<sup>−4</sup> mbar) to afford **15** (201 mg, 53%). Colorless oil. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 0.81 (*d*, *J* = 6.9, 3-Me); 1.05, 1.06 (2*s*, 2 × 2-Me); 1.97, 2.29 (2*m*, H–C(3), CH<sub>2</sub>(4)); 3.59 (*s*, 2 MeO). <sup>13</sup>C-NMR (75.5 MHz, CDCl<sub>3</sub>): 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 Δ*H*‡ and Δ*S*‡ of the electrophile/nucleophile combinations (see *Table 3*) were calculated from second-order rate constants measured at different temperatures (Δ*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<sub>2</sub> atmosphere and exclusion of H<sub>2</sub>O and O<sub>2</sub>. 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<sub>4</sub> (*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  $tk_{\text{obs}} = \ln(A_t - A_{\text{end}}) - \ln(A_0 - A_{\text{end}})$ , the rate constants *k*<sub>obs</sub> were obtained from a plot of ln(*A*<sub>*t*</sub> − *A*<sub>end</sub>) vs. time (*t*). The second-order rate constants were then calculated from *k*<sub>obs</sub> = *k*<sub>2</sub> [Nu].

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

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Table 5. *Kinetics of the Reactions of the Fp Complex 1a with Benzhydrylium Ions 3<sup>+</sup>. In CH<sub>2</sub>Cl<sub>2</sub>; the electrophiles were analyzed spectrophotometrically. All concentrations expressed in mol/l.*

| <i>T</i> [°]                              | [ <b>3<sup>+</sup></b> ] <sub>0</sub> | [ <b>1a</b> ]           | [ <b>1a</b> ] <sub>0</sub> /[ <b>3<sup>+</sup></b> ] <sub>0</sub> | Conversion [%] | <i>k</i> [M <sup>-1</sup> s <sup>-1</sup> ] |
|-------------------------------------------|---------------------------------------|-------------------------|-------------------------------------------------------------------|----------------|---------------------------------------------|
| <b>3e</b> · BF <sub>4</sub> (λ = 630 nm): |                                       |                         |                                                                   |                |                                             |
| 20.0                                      | 1.94 × 10 <sup>-5</sup>               | 1.40 × 10 <sup>-3</sup> | 72                                                                | 45             | 1.05 × 10 <sup>-1</sup>                     |
| 20.0                                      | 1.64 × 10 <sup>-5</sup>               | 1.63 × 10 <sup>-3</sup> | 99                                                                | 53             | 1.19 × 10 <sup>-1</sup>                     |
| 20.0                                      | 1.55 × 10 <sup>-5</sup>               | 1.88 × 10 <sup>-3</sup> | 121                                                               | 64             | 1.23 × 10 <sup>-1</sup>                     |
| 20.0                                      | 1.68 × 10 <sup>-5</sup>               | 2.51 × 10 <sup>-3</sup> | 149                                                               | 55             | 1.63 × 10 <sup>-1</sup>                     |
| <b>3d</b> · BF <sub>4</sub> (λ = 600 nm): |                                       |                         |                                                                   |                |                                             |
| 20.0                                      | 2.05 × 10 <sup>-5</sup>               | 1.26 × 10 <sup>-3</sup> | 61                                                                | 86             | 5.95 × 10 <sup>-1</sup>                     |
| 20.0                                      | 1.82 × 10 <sup>-5</sup>               | 1.85 × 10 <sup>-3</sup> | 102                                                               | 68             | 6.71 × 10 <sup>-1</sup>                     |
| 20.0                                      | 1.91 × 10 <sup>-5</sup>               | 2.91 × 10 <sup>-3</sup> | 152                                                               | 54             | 8.15 × 10 <sup>-1</sup>                     |
| <b>3c</b> · BF <sub>4</sub> (λ = 630 nm): |                                       |                         |                                                                   |                |                                             |
| 20.0                                      | 1.40 × 10 <sup>-5</sup>               | 4.17 × 10 <sup>-4</sup> | 30                                                                | 80             | 6.48                                        |
| 20.0                                      | 1.52 × 10 <sup>-5</sup>               | 8.03 × 10 <sup>-4</sup> | 53                                                                | 74             | 7.94                                        |
| 20.0                                      | 1.69 × 10 <sup>-5</sup>               | 1.46 × 10 <sup>-3</sup> | 86                                                                | 69             | 7.82                                        |
| 20.0                                      | 1.46 × 10 <sup>-5</sup>               | 1.94 × 10 <sup>-3</sup> | 133                                                               | 53             | 6.80                                        |
| <b>3b</b> · BF <sub>4</sub> (λ = 630 nm): |                                       |                         |                                                                   |                |                                             |
| 20.0                                      | 1.91 × 10 <sup>-5</sup>               | 1.92 × 10 <sup>-4</sup> | 10                                                                | 92             | 1.20 × 10 <sup>1</sup>                      |
| 20.0                                      | 1.93 × 10 <sup>-5</sup>               | 5.82 × 10 <sup>-4</sup> | 30                                                                | 95             | 1.17 × 10 <sup>1</sup>                      |
| 20.0                                      | 1.78 × 10 <sup>-5</sup>               | 8.94 × 10 <sup>-4</sup> | 50                                                                | 89             | 1.19 × 10 <sup>1</sup>                      |
| 20.0                                      | 1.70 × 10 <sup>-5</sup>               | 1.11 × 10 <sup>-3</sup> | 65                                                                | 82             | 1.21 × 10 <sup>1</sup>                      |
| <b>3a</b> · BF <sub>4</sub> (λ = 640 nm): |                                       |                         |                                                                   |                |                                             |
| – 20.0                                    | 2.12 × 10 <sup>-5</sup>               | 4.55 × 10 <sup>-4</sup> | 21                                                                | 72             | 1.37 × 10 <sup>1</sup>                      |
| – 30.0                                    | 2.24 × 10 <sup>-5</sup>               | 7.71 × 10 <sup>-4</sup> | 34                                                                | 79             | 7.31                                        |
| – 40.0                                    | 2.37 × 10 <sup>-5</sup>               | 1.02 × 10 <sup>-3</sup> | 43                                                                | 82             | 4.05                                        |
| – 50.0                                    | 2.45 × 10 <sup>-5</sup>               | 2.37 × 10 <sup>-3</sup> | 97                                                                | 70             | 1.94                                        |

Table 6. *Kinetics of the Reactions of the Fp Complex 1b with Benzhydrylium Ions 3<sup>+</sup>. In CH<sub>2</sub>Cl<sub>2</sub>; the electrophiles were analyzed spectrophotometrically. All concentrations expressed in mol/l.*

| <i>T</i> [°]                             | [ <b>3<sup>+</sup></b> ] <sub>0</sub> | [ <b>1b</b> ] <sub>0</sub> | [ <b>1b</b> ] <sub>0</sub> /[ <b>3<sup>+</sup></b> ] <sub>0</sub> | Conversion [%] | <i>k</i> [M <sup>-1</sup> s <sup>-1</sup> ] |
|------------------------------------------|---------------------------------------|----------------------------|-------------------------------------------------------------------|----------------|---------------------------------------------|
| <b>3f</b> · BF <sub>4</sub> (λ = 630 nm) |                                       |                            |                                                                   |                |                                             |
| 20.0                                     | 1.45 × 10 <sup>-5</sup>               | 1.99 × 10 <sup>-3</sup>    | 137                                                               | 55             | 7.21 × 10 <sup>-1</sup>                     |
| 20.0                                     | 1.05 × 10 <sup>-5</sup>               | 1.26 × 10 <sup>-3</sup>    | 120                                                               | 75             | 5.71 × 10 <sup>-1</sup>                     |
| 20.0                                     | 1.54 × 10 <sup>-5</sup>               | 1.55 × 10 <sup>-3</sup>    | 101                                                               | 62             | 6.23 × 10 <sup>-1</sup>                     |
| 20.0                                     | 1.42 × 10 <sup>-5</sup>               | 7.33 × 10 <sup>-4</sup>    | 52                                                                | 59             | 6.10 × 10 <sup>-1</sup>                     |
| <b>3e</b> · BF <sub>4</sub> (λ = 630 nm) |                                       |                            |                                                                   |                |                                             |
| 20.0                                     | 1.66 × 10 <sup>-5</sup>               | 1.65 × 10 <sup>-3</sup>    | 99                                                                | 95             | 3.43                                        |
| <b>3d</b> · BF <sub>4</sub> (λ = 600 nm) |                                       |                            |                                                                   |                |                                             |
| 20.0                                     | 1.79 × 10 <sup>-5</sup>               | 2.97 × 10 <sup>-4</sup>    | 17                                                                | 75             | 1.57 × 10 <sup>1</sup>                      |
| 20.0                                     | 1.40 × 10 <sup>-5</sup>               | 4.63 × 10 <sup>-4</sup>    | 33                                                                | 94             | 1.57 × 10 <sup>1</sup>                      |
| 20.0                                     | 1.54 × 10 <sup>-5</sup>               | 8.15 × 10 <sup>-4</sup>    | 53                                                                | 84             | 1.67 × 10 <sup>1</sup>                      |
| 20.0                                     | 1.66 × 10 <sup>-5</sup>               | 8.76 × 10 <sup>-4</sup>    | 53                                                                | 88             | 1.52 × 10 <sup>1</sup>                      |
| 20.0                                     | 1.45 × 10 <sup>-5</sup>               | 9.58 × 10 <sup>-4</sup>    | 66                                                                | 86             | 1.54 × 10 <sup>1</sup>                      |
| <b>3c</b> · BF <sub>4</sub> (λ = 630 nm) |                                       |                            |                                                                   |                |                                             |
| 20.0                                     | 1.34 × 10 <sup>-5</sup>               | 1.47 × 10 <sup>-4</sup>    | 11                                                                | 85             | 1.54 × 10 <sup>2</sup>                      |
| 20.0                                     | 1.34 × 10 <sup>-5</sup>               | 2.75 × 10 <sup>-4</sup>    | 21                                                                | 83             | 1.46 × 10 <sup>2</sup>                      |
| 20.0                                     | 1.28 × 10 <sup>-5</sup>               | 4.03 × 10 <sup>-4</sup>    | 31                                                                | 81             | 1.43 × 10 <sup>2</sup>                      |
| 20.0                                     | 1.32 × 10 <sup>-5</sup>               | 5.42 × 10 <sup>-4</sup>    | 41                                                                | 82             | 1.45 × 10 <sup>2</sup>                      |
| 20.0                                     | 1.16 × 10 <sup>-5</sup>               | 6.06 × 10 <sup>-4</sup>    | 52                                                                | 80             | 1.45 × 10 <sup>2</sup>                      |

Table 7. *Kinetics of the Reactions of 9 · BF<sub>4</sub> with Nucleophiles 10*. In CH<sub>2</sub>Cl<sub>2</sub> 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 <sup>-1</sup> s <sup>-1</sup> ] |
|-------------|-----------------------|-----------------------|------------------|----------------|------------------------------------------|
| <b>10a:</b> |                       |                       |                  |                |                                          |
| 20.0        | $5.76 \times 10^{-4}$ | $2.20 \times 10^{-2}$ | 38               | 94             | 4.90                                     |
| 20.0        | $5.36 \times 10^{-4}$ | $8.37 \times 10^{-3}$ | 15               | 98             | 5.01                                     |
| 20.0        | $9.19 \times 10^{-4}$ | $2.19 \times 10^{-2}$ | 24               | 90             | 5.81                                     |
| 7.0         | $7.99 \times 10^{-4}$ | $1.87 \times 10^{-2}$ | 23               | 96             | 1.84                                     |
| − 0.4       | $1.03 \times 10^{-3}$ | $1.05 \times 10^{-2}$ | 10               | 98             | 1.16                                     |
| − 10.2      | $9.84 \times 10^{-4}$ | $1.47 \times 10^{-2}$ | 15               | 99             | $4.61 \times 10^{-1}$                    |
| − 27.5      | $7.93 \times 10^{-4}$ | $1.72 \times 10^{-2}$ | 22               | 95             | $1.68 \times 10^{-1}$                    |
| <b>10b:</b> |                       |                       |                  |                |                                          |
| 25.0        | $3.19 \times 10^{-4}$ | $1.35 \times 10^{-2}$ | 42               | 85             | $7.04 \times 10^{-2}$                    |
| 20.0        | $2.23 \times 10^{-4}$ | $9.88 \times 10^{-3}$ | 44               | 88             | $5.22 \times 10^{-2}$                    |
| 20.0        | $3.19 \times 10^{-4}$ | $1.88 \times 10^{-2}$ | 59               | 92             | $5.36 \times 10^{-2}$                    |
| 20.0        | $2.59 \times 10^{-4}$ | $7.55 \times 10^{-3}$ | 29               | 80             | $5.18 \times 10^{-2}$                    |
| − 12.0      | $3.08 \times 10^{-4}$ | $1.72 \times 10^{-2}$ | 56               | 69             | $3.90 \times 10^{-3}$                    |
| − 22.2      | $3.34 \times 10^{-4}$ | $2.11 \times 10^{-2}$ | 63               | 76             | $1.43 \times 10^{-3}$                    |
| − 31.7      | $3.83 \times 10^{-4}$ | $1.61 \times 10^{-2}$ | 42               | 27             | $4.62 \times 10^{-4}$                    |
| <b>10c:</b> |                       |                       |                  |                |                                          |
| 1.0         | $7.14 \times 10^{-4}$ | $2.76 \times 10^{-2}$ | 39               | 59             | $5.55 \times 10^{-1}$                    |
| − 9.0       | $8.97 \times 10^{-4}$ | $3.31 \times 10^{-2}$ | 37               | 58             | $2.63 \times 10^{-1}$                    |
| − 9.0       | $7.74 \times 10^{-4}$ | $4.75 \times 10^{-2}$ | 61               | 50             | $2.99 \times 10^{-1}$                    |
| − 18.8      | $8.76 \times 10^{-4}$ | $5.38 \times 10^{-2}$ | 61               | 50             | $9.48 \times 10^{-2}$                    |
| − 48.2      | $8.42 \times 10^{-4}$ | $5.78 \times 10^{-2}$ | 69               | 56             | $5.19 \times 10^{-3}$                    |
| <b>10d:</b> |                       |                       |                  |                |                                          |
| 20.0        | $8.03 \times 10^{-4}$ | $9.78 \times 10^{-3}$ | 12               | 74             | $2.40 \times 10^{-3}$ a)                 |
| 20.0        | $6.94 \times 10^{-4}$ | $1.55 \times 10^{-2}$ | 22               | 89             | $4.90 \times 10^{-3}$ a)                 |
| 20.0        | $7.36 \times 10^{-4}$ | $3.31 \times 10^{-2}$ | 45               | 84             | $1.19 \times 10^{-2}$ a)                 |
| 20.0        | $7.42 \times 10^{-4}$ | $7.23 \times 10^{-2}$ | 97               | 64             | $2.59 \times 10^{-2}$ a)                 |
| <b>10e:</b> |                       |                       |                  |                |                                          |
| 20.0        | $3.54 \times 10^{-4}$ | $3.39 \times 10^{-2}$ | 96               | 94             | $1.99 \times 10^{-2}$ a)                 |
| 20.0        | $3.37 \times 10^{-4}$ | $4.53 \times 10^{-2}$ | 134              | 76             | $2.58 \times 10^{-2}$ a)                 |
| 20.0        | $3.43 \times 10^{-4}$ | $2.76 \times 10^{-2}$ | 81               | 72             | $1.30 \times 10^{-2}$ a)                 |
| 20.0        | $3.34 \times 10^{-4}$ | $1.43 \times 10^{-2}$ | 43               | 76             | $6.90 \times 10^{-3}$ a)                 |
| 20.0        | $3.20 \times 10^{-4}$ | $2.06 \times 10^{-2}$ | 64               | 88             | $8.70 \times 10^{-3}$ a)                 |

a)  $k_{\text{obs}}$  [s<sup>-1</sup>];  $k_2$  was obtained from the slopes of plots of  $k_{\text{obs}}$  vs. [Nu].

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