Propagation Rate of the Cationic Polymerization of 2,4,6-Trimethylstyrene: A Linear Free Energy Approach

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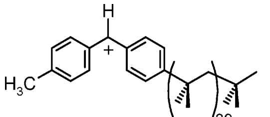
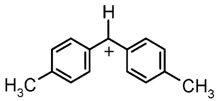
ABSTRACT: Kinetics of the reactions of benzhydryl cations with 2,4,6-trimethylstyrene have been performed to determine its nucleophilicity parameters $N = 0.68$ and $s = 1.09$, which are comparable to styrene and considerably less nucleophilic than 4-methylstyrene, indicating the retarding effect of the ortho methyl groups. Kinetic investigations of the reactions of the 2,4,6-trimethylstyryl cation $\mathbf{6}^+$ and the corresponding dimer $\mathbf{7}^+$ with the reference nucleophile 2-chloropropene allow us to calculate the closely similar electrophilicity parameters $E(\mathbf{6}^+) = 6.04$ and $E(\mathbf{7}^+) = 6.16$ which are considerably lower than that of the styryl cation ($E = 9.6$). As a consequence, the propagation rate constant of the cationic polymerization of 2,4,6-trimethylstyrene is considerably lower than that of styrene. Substituting these values into the correlation $\log k_{20\,°\mathrm{C}} = s(N + E)$ yields a propagation rate constant of 3×10^7 M^{-1} s^{-1}, which has to be considered an upper limit because extra steric strain generated in the reaction of $\mathbf{7}^+$ with 2,4,6-trimethylstyrene is not included in this correlation.

Introduction

Propagation rate constants for the carbocationic polymerization of vinyl derivatives have controversially been discussed for many years.[1,2] For the polymerization of isobutylene, propagation rate constants between 6×10^3 and 7×10^8 M^{-1} s^{-1} have been reported,[1−7] and for the polymerization of styrene, values between 10^3 and 10^9 M^{-1} s^{-1} can be found in the literature.[1,2,6−11] In all cases, rate constants determined with low-molecular weight model compounds were at the high end of the published reactivity range. To exclude that macromolecular carbocations differ considerably in reactivity from their low-molecular weight analogues, we have generated the carbocations $\mathbf{1a}^+$ ($M_n \approx 2400$ g mol^{-1}) and $\mathbf{1b}^+$ ($M = 195$ g mol^{-1}) in the presence of π-nucleophiles and found that the reactivity of $\mathbf{1a}^+$ was only 25% smaller than that of $\mathbf{1b}^+$.[12]



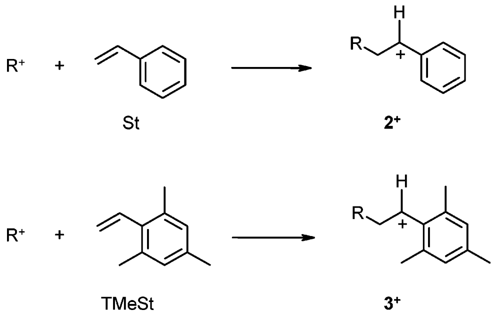
1a⁺



1b⁺

Since different kinetic behavior of high and low molecular weight compounds was thus excluded, the most likely origin for the deviating propagation rate constants is the uncertainty in the concentration of the active species.

Though the propagating species of carbocationic styrene (St) polymerization $\mathbf{2}^+$ can be detected by UV-spectrometry,[9] its ability to undergo indane cyclization with formation of carbocations with similar absorption maxima may cause problems in determining its concentration. Since the *o*-methyl groups in 2,4,6-trimethylstyrene (TMeSt) inhibit intramolecular cyclizations, determination of the concentration of the propagating carbocation $\mathbf{3}^+$ in its polymerization is less ambiguous.[13,14] The carbocationic polymerization of TMeSt[15] has, therefore, been used as a test system to compare the different methods for determining propagation rate constants in ionic polymerizations as described in this and the following paper.[16]



Rates of the reactions of carbocations with nucleophiles, including olefins, can be described by eq 1, where k represents the second-order rate constant in M^{-1} s^{-1}, E is the electrophilicity parameter of the carbocation, N is the nucleophilicity parameter of the olefin, and s is the corresponding nucleophile-specific slope parameter.[17−23]

$$\log k_{20\,°\mathrm{C}} = s(E + N) \qquad (1)$$

To employ this equation for calculating the propagation rate constant k_p of the carbocationic polymerization of 2,4,6-trimethylstyrene, the electrophilicity parameter E of the propagating carbocation $\mathbf{3}^+$ as well as the reactivity parameters N and s of 2,4,6-trimethylstyrene are needed.

Nucleophilic Reactivity of 2,4,6-Trimethylstyrene

In previous work, diarylcarbenium ions (benzhydryl cations) have been recommended as reference electrophiles for determining the reactivity parameters N and s of many types of nucleophiles.[23−28] We have now used

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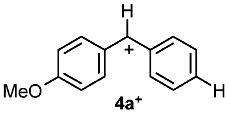
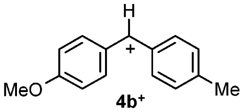
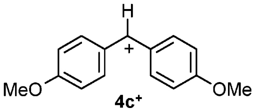
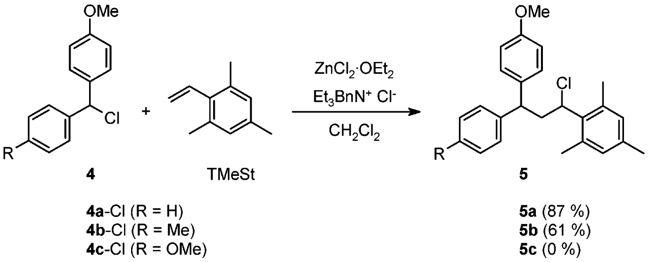
Table 1. Eyring Activation Parameters for the Reactions of 2,4,6-Trimethylstyrene with the Benzhydrylium Ions $4a^+$, $4b^+$, and $4c^+$ (in CH_2Cl_2)

electrophile	E[a]	$\Delta H^{\ddagger}$ / kJ mol^{-1}	$\Delta S^{\ddagger}$ / J mol^{-1} K^{-1}	k_2(20 °C) / M^{-1} s^{-1}	log k_2
 **4a⁺**	2.11	21.6 ± 0.2	–113.4 ± 0.9	(1.06 ± 0.03) × 10^3	3.02
 **4b⁺**	1.48	25.7 ± 0.2	–111.4 ± 0.9	(2.41 ± 0.06) × 10^2	2.38
 **4c⁺**	0.00	30.6 ± 1.0	–126.5 ± 4.1	5.38 ± 1.3	0.73

[a] From ref 23.

Scheme 1. Lewis Acid Induced Reactions of TMeSt with Benzhydryl Chlorides 4-Cl



this method for determining N and s of 2,4,6-trimethylstyrene (TMeSt).

Scheme 1 shows that the benzhydryl chlorides **4a**-Cl and **4b**-Cl combine with TMeSt in the presence of zinc chloride and benzyltriethylammonium chloride (to suppress polymerization) to give fair yields of the addition products **5a** and **5b**. These products are formed as mixtures of diastereoisomers which have not been separated. So far, we have not been able to isolate a 1:1-product from the reaction of **4c**-Cl with TMeSt.[29]

When TMeSt (>2 equiv) was added to solutions of the benzhydrylium tetrachloroborates (**4a**–**c**)-BCl_4 in dichloromethane, the absorbances of the benzhydrylium cations **4a**–**c**$^+$ disappeared, following the second-order rate law given in eq 2.

$$-\mathrm{d}[\mathbf{4}^+]/\mathrm{d}t = k_2[\mathbf{4}^+][\mathrm{TMeSt}] \qquad (2)$$

For the determination of the second-order rate constants k_2, the previously described methods were employed.[23,30,31] Because previous work has shown that free and paired carbocations exhibit almost the same reactivities,[30] the degree of ion-pairing is not taken into account.

From the temperature dependence of the second-order rate constants (Figure 1), the Eyring activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were obtained as listed in Table 1. As previously found for analogous reaction series,[23] variation of the para-substituents of the benzhydrylium ions affected $\Delta H^{\ddagger}$ whereas $\Delta S^{\ddagger}$ remained almost constant (-117 ± 7 J mol^{-1} K^{-1}).

A plot of log $k_{20\,°C}$ vs the electrophilicity parameters E of the benzhydrylium ions (Figure 2) yields the nucleophilicity parameter $N = 0.68$ and the slope parameter $s = 1.09$ for TMeSt. These parameters, as well as the underlying rate constants depicted in Figure 2 reveal that TMeSt and styrene show almost identical nucleophilic reactivities. The increase of nucleophilicity due to the electron donating effect of the three methyl groups is almost completely canceled by the distortion

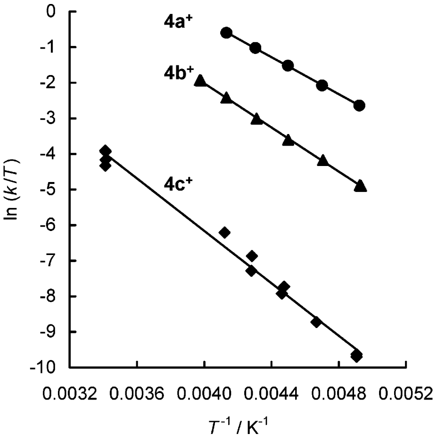


Figure 1. Eyring plots for the reactions of 2,4,6-trimethylstyrene with the benzhydrylium ions **4a**$^+$, **4b**$^+$, and **4c**$^+$ (in CH_2Cl_2).

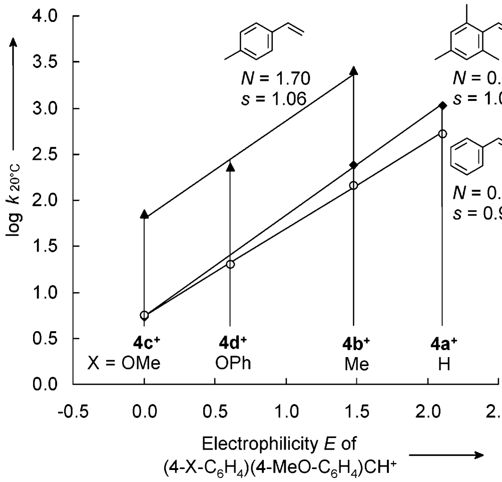
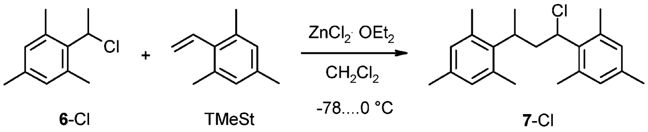


Figure 2. Linear free enthalpy relationships for the reactions of ring-substituted styrenes with benzhydrylium ions **4**$^+$ (in CH_2Cl_2). Rate constants are from Table 1 and ref 23.

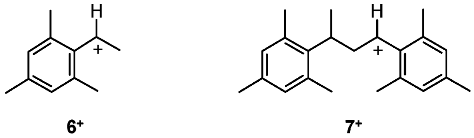
Scheme 2. Synthesis of 1-Chloro-1,3-dimesitylbutane (7-Cl)



from coplanarity between the vinylic double bond and the aromatic ring.

Electrophilic Reactivity of the 2,4,6-Trimethylstyryl Cation

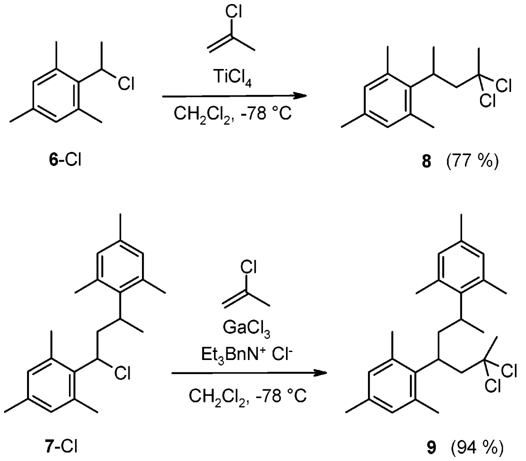
The 2,4,6-trimethylstyryl cation $\mathbf{6}^+$ and its addition product to 2,4,6-trimethylstyrene ($\mathbf{7}^+$) were considered as model systems for the propagating species in trimethylstyrene polymerization.



Compound **7**-Cl, the precursor of cation $\mathbf{7}^+$, was obtained by $ZnCl_2 \cdot OEt_2$-catalyzed addition of trimethylstyryl chloride **6**-Cl to TMeSt as shown in Scheme 2. Recrystallization of the initially produced mixture of diastereoisomers of **7**-Cl yielded a single diastereomer, the configuration of which was not determined.

Addition of **6**-Cl or **7**-Cl to solutions of excess $GaCl_3$ in dichloromethane at −70 °C gives rise to the formation of the carbocations $\mathbf{6}^+$ and $\mathbf{7}^+$, respectively, which show similar UV−vis spectra (Figure 3). Since the same UV−vis spectrum for $\mathbf{6}^+$ was observed when the corresponding bromo compound **6**-Br [= 1-bromo-1-(2,4,6-trimethylphenyl)ethane] was treated with $GaCl_3$, the species responsible for the UV−vis spectra depicted in Figure 3 must not contain halogen.

Scheme 3. Lewis Acid Induced Reactions of 6-Cl and 7-Cl with 2-Chloropropene (−78 °C, CH$_2$Cl$_2$)



To determine the electrophilic reactivities of $\mathbf{6}^+$ and $\mathbf{7}^+$, the rates of their reactions with 2-chloropropene, a reference nucleophile,[23] were determined. As shown in Scheme 3, good yields of the 1:1-addition products **8** and **9** were obtained, when mixtures of 2-chloropropene with either **6**-Cl or **7**-Cl were treated with Lewis acids in dichloromethane at −78 °C.

Addition of >3 equiv of 2-chloropropene to solutions of **6**−$GaCl_4$ or **7**−$GaCl_4$ (usually in the presence of Et_3BnN^+ $GaCl_4^-$ to avoid multiple addition) led to a decay of the carbocation absorbances. From the time dependence of the UV−vis absorptions, the second-order rate constants were derived following the procedure described in ref 31. Kinetic experiments at variable temperature gave rise to the Eyring plots shown in Figure 4. The unusually large scatter of the individual points around the correlation lines in Figure 4 is due to the low stability of the addition products **8** and **9** under the conditions of the kinetic experiments, as recognized by the slow development of an UV-absorption at $\lambda \approx 330$ nm after the completion of the addition reaction.

More important than the activation parameters given in Table 2, which have a high uncertainty, are the similar values of the rate constants observed for the reactions of both $\mathbf{6}^+$ and $\mathbf{7}^+$ with 2-chloropropene. At −67 °C, the cation $\mathbf{7}^+$ reacts only 2.4 times faster with 2-chloropropene than $\mathbf{6}^+$, which reduces to a factor of 1.4 at 20 °C (Table 2). Thus, the additional mesityl

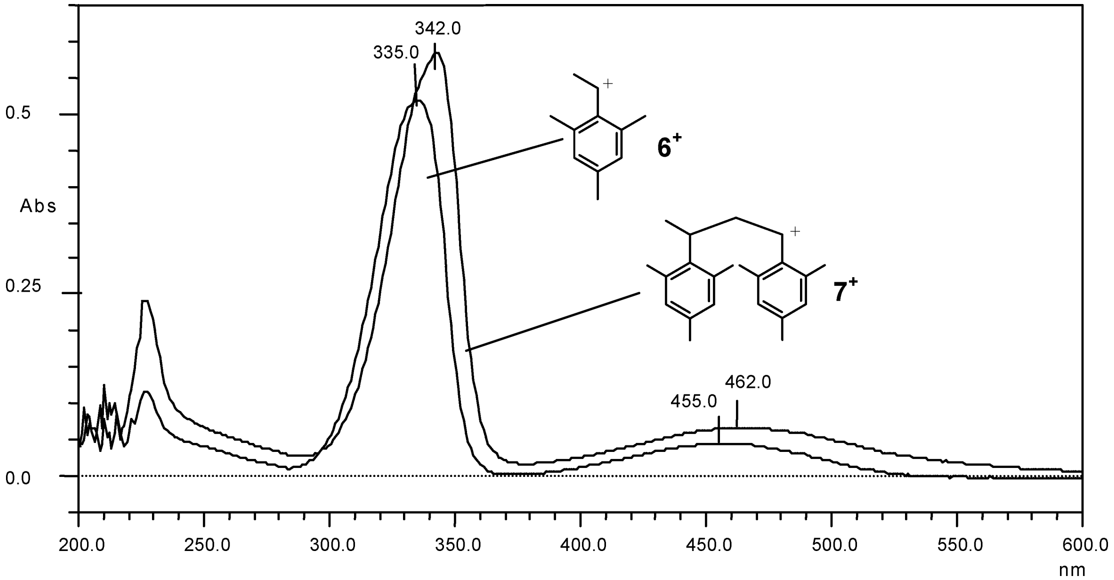


Figure 3. UV−vis spectra of the tetrachlorogallate salts of cations $\mathbf{6}^+$ and $\mathbf{7}^+$ (generated at −70 °C by adding **6**-Cl or **7**-Cl, respectively, to dichloromethane solutions of excess $GaCl_3$).

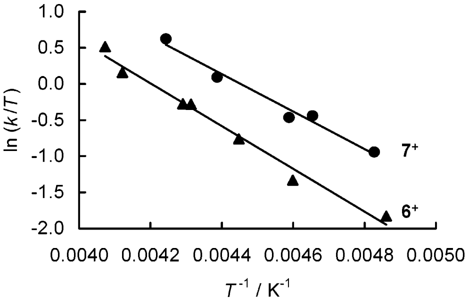


Figure 4. Eyring plots for the reactions of 2-chloropropene with the carbocations $\mathbf{6}^+$ and $\mathbf{7}^+$ (in CH_2Cl_2).

Table 2. Eyring Activation Parameters of the Reactions of 6-GaCl$_4$ and 7-GaCl$_4$ with 2-Chloropropene in Dichloromethane

electrophile	$\Delta H^‡$/kJ mol^{-1}	$\Delta S^‡$/J mol^{-1} K^{-1}	k_2(20 °C)/M^{-1} s^{-1}
$\mathbf{6}^+$	24.6 ± 1.4	−94.1 ± 6.2	$(3.05 \pm 0.51) \times 10^3$
$\mathbf{7}^+$	21.6 ± 1.9	−101 ± 8.6	$(4.37 \pm 1.14) \times 10^3$

group in $\mathbf{7}^+$ does not have a significant influence on the electrophilicity of the carbocation. Substitution of $N = -3.46$ and $s = 1.35$ for 2-chloropropene[23] and log $k_{20\,°C}$ for its reactions with the carbocations $\mathbf{6}^+$ and $\mathbf{7}^+$ into eq 1 yields the electrophilicity parameters $E(\mathbf{6}^+) = 6.04$ and $E(\mathbf{7}^+) = 6.16$ for the carbocations. The magnitude of the E parameters thus determined was confirmed by the competition experiment described in Scheme 4.

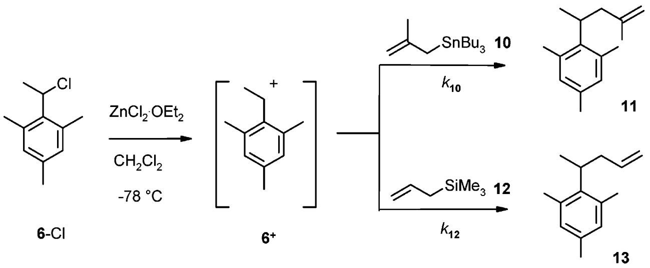
Treatment of **6**-Cl with $ZnCl_2 \cdot OEt_2$ in the presence of a mixture of tributyl(2-methylallyl)stannane (**10**) and allyltrimethylsilane (**12**) gave rise to the formation of the 4-mesityl-pent-1-enes **11** and **13**, respectively. From a series of experiments with variable concentrations of **10** and **12** (see Experimental Section) a competition constant $\kappa = k_{\mathbf{10}}/k_{\mathbf{12}} = 24.7 \pm 2.7$ was obtained.[32] Even if the E value for $\mathbf{6}^+$ determined above was wrong by 2 orders of magnitude, the high nucleophilicity of **10** ($N = 7.48$, $s = 0.89$)[23] implies that the reaction of $\mathbf{6}^+$ with **10** must be diffusion-controlled; that is, $k_{\mathbf{10}} \approx 3 \times 10^9$ M^{-1} s^{-1}. Combination with the competition constant $\kappa = 24.7$ yields a rate constant of $k_{\mathbf{12}} \approx 1.2 \times 10^8$ M^{-1} s^{-1} for the reaction of $\mathbf{6}^+$ with allyltrimethylsilane (**12**). Because reactions of such high rate do not have an activation enthalpy,[33] the value of $k_{\mathbf{12}}$ can be considered to be independent of temperature. Substitution of $k_{\mathbf{12}} = 1.2 \times 10^8$ M^{-1} s^{-1}, $N(\mathbf{12}) = 1.79$,[23] and $s(\mathbf{12}) = 0.94$[23] into eq 1 now gives an electrophilicity parameter $E(\mathbf{6}^+) = 6.79$, in fair agreement with that derived from direct rate measurements with 2-chloropropene, which confirms the reliability of E determined for the trimethylstyryl cation $\mathbf{6}^+$.

Propagation Rate Constant

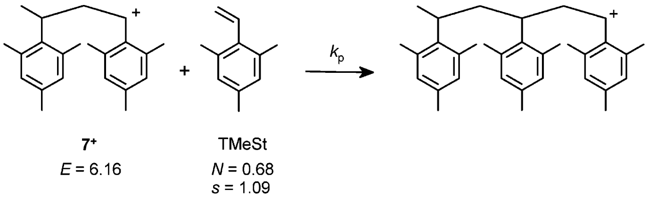
If carbocation $\mathbf{7}^+$ is accepted as a model for the propagating cation in trimethylstyrene polymerization, the propagation step can be approximated by the reaction in Scheme 5.

When the reactivity parameters for $\mathbf{7}^+$ and 2,4,6-trimethylstyrene, summarized in Scheme 5, are substituted into eq 1, a rate constant of $k_p(20\ °C) = 3 \times 10^7$ M^{-1} s^{-1} is calculated, which is considerably higher than that derived in the following paper.[16] It has to be regarded, however, that Scheme 5 describes the combination of a bulky electrophile with a sterically hindered nucleophile, and it has previously been demonstrated that rate constants of such reactions are overestimated by eq 1, which does not specifically treat steric effects.[17,19,22,24,27] The propagation rate constant k_p calculated by eq 1 should, therefore, be considered as an upper limit.

Scheme 4. Competition of the in Situ Generated Carbocation $\mathbf{6}^+$ with the Nucleophiles Tributyl(2-methylallyl)stannane (10) and Allyltrimethylsilane (12) in Dichloromethane at −78 °C



Scheme 5



The isolation of the 1:1 adducts **8** and **9** as described in Scheme 3 indicates that reionization of the 2-chloropropene adducts is difficult, even in the presence of strong Lewis acids. For that reason, 2-chloropropene may be used as a capping agent, particularly when the weaker Lewis acid BCl_3 is employed, as described in the following article.[16] Because carbocation $\mathbf{7}^+$ resembles the propagating species in trimethylstyrene polymerization, the rate constant for the reaction of $\mathbf{7}^+$ with 2-chloropropene determined in this work can be assumed to reflect the rate of the capping reaction. The following article[16] shows how these data can be used for the direct determination of k_p in Scheme 5.

Experimental Section

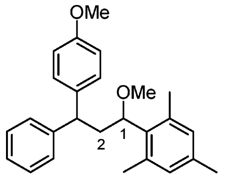
General Data. ^1H (300 MHz) and ^{13}C NMR (75.5 MHz) spectra of solutions in $CDCl_3$ were obtained on a Bruker ARX 300 instrument and calibrated to tetramethylsilane as internal standard (δ_H 0.00) or to the solvent signal (δ_C 77.0), respectively. DEPT-135 experiments were used to obtain information about the multiplicities of ^{13}C resonances. Mass spectra were obtained with a Finnigan MAT 95Q.

All reactions were performed in carefully dried glassware under an atmosphere of dry nitrogen.

TMeSt is commercially available but was obtained in this work from a synthetic sequence[15,34,35] which starts with a $AlCl_3$ promoted acylation of mesitylene by acetyl chloride (83%). Reduction of the resulting ketone with lithium aluminum hydride yielded alcohol **6**-OH (74%) which was subsequently converted into chloride **6**-Cl by reaction with thionyl chloride (98%). Potassium *tert*-butoxide induced HCl elimination gave access to TMeSt (77%).

Dichloromethane solutions of the $ZnCl_2 \cdot OEt_2$ complex were prepared according to ref. 36.

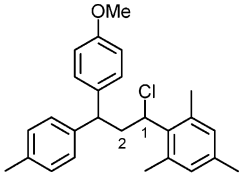
2-(1-Chloro-3-(4-methoxyphenyl)-3-phenylpropyl)-1,3,5-trimethylbenzene (5a). A mixture of the benzhydryl chloride **4a**-Cl (232 mg, 1.00 mmol) and benzyltriethylammonium chloride (455 mg, 2.00 mmol) in CH_2Cl_2 (50 mL) was cooled to 0 °C. The $ZnCl_2 \cdot OEt_2$ complex (1.0 mL of a 3.9 M solution in CH_2Cl_2) and TMeSt (146 mg, 1.00 mmol) were successively added to the stirred and cooled solution. After 45 min, the reaction mixture was hydrolyzed by the addition of a mixture of concentrated ammonia and water (1/1, 20 mL). After the separation of the phases, the aqueous layer was extracted with diethyl ether (2 × 20 mL). The combined organic layers were dried ($MgSO_4$), and the solvent was evaporated under reduced pressure. Purification of the crude product by column chromatography (silica gel, eluent: hexane/diethyl ether = 10:1) yielded **5a** (330 mg, 87%) as a colorless oil. MS (70 eV), *m/z* (%): 380 (7), 378 (M^+, 19), 342 (14), 198 (14), 197 (100). During the attempt to crystallize the chloride **5a** from methanol, **5a** was completely converted into the corresponding methyl ether **5a′**.



5a'

Because of hindered rotations and the formation of a mixture of diastereomers, we were not able to assign all NMR signals unambiguously. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.70, 1.72 (2 s, 3 H, CH_3), 2.20, 2.55 (2 s, 2 × 3 H, 2 × CH_3), 2.65−2.77, 2.99−3.10 (2 m, 2 × 1 H, 2-H), 3.67, 3.68, 3.69 (3 s, 6 H, OCH_3), 4.05−4.13 (m, 1 H, Ar_2CH), 5.15−5.24 (m, 1 H, 1-H), 6.77−7.36 (m, 11 H, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 19.7/19.8, 20.7, 21.1 (4 q, CH_3), 43.0/43.2 (2 t, C-2), 47.9 (q, 1-OCH_3), 55.1 (q, OCH_3), 57.9/58.0 (2 d, Ar_2CH), 79.4 (d, C-1), 113.7/113.8, 114.0/114.1 (4 s, Ar), 126.4, 126.5, 127.0, 127.1, 127.2, 127.3, 127.6, 127.8, 128.3, 128.5, 128.6, 128.7, 128.9, 129.1, 131.5 (d, Ar), 133.8, 134.3, 135.6, 137.6, 142.7, 144.0, 158.3, 159.0 (8 s, Ar).

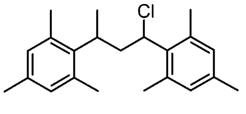
2-(1-Chloro-3-(4-methoxyphenyl)-3-(4-tolyl)propyl)-1,3,5-trimethylbenzene (5b). A mixture of the benzhydryl chloride **4b**-Cl (246 mg, 1.00 mmol) and benzyltriethylammonium chloride (455 mg, 2.00 mmol) in CH_2Cl_2 (50 mL) was cooled to 0 °C. The $ZnCl_2{\cdot}OEt_2$ complex (1.0 mL of a 3.9 M solution in CH_2Cl_2) and TMeSt (292 mg, 2.00 mmol) were successively added to the stirred and cooled solution. After 2.5 h, the reaction mixture was hydrolyzed by the addition of a mixture of concentrated ammonia and water (1/1, 20 mL). After the separation of the phases, the aqueous layer was extracted with diethyl ether (2 × 20 mL). The combined organic layers were dried ($MgSO_4$), and the solvent was evaporated under reduced pressure. Purification of the crude product by column chromatography (silica gel, eluent: hexane/diethyl ether = 10:1) yielded **5b** (240 mg, 61%) as a colorless oil.



5b

Because of hindered rotations and the formation of a mixture of diastereomers, we were not able to assign all NMR signals unambiguously. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.73, 1.74 (2 s, 3 H, CH_3), 2.13, 2.27, 2.55 (3 s, 3 × 3 H, 3 × CH_3), 2.67−2.73, 2.99−3.05 (2 m, 2 × 1 H, 2-H), 3.69 (s, 3 H, OCH_3), 4.03−4.10 (m, 1 H, Ar_2CH), 5.17−5.22 (m, 1 H, 1-H), 6.77−7.16 (m, 10 H, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 19.9, 20.7, 20.91, 20.94, 21.1 (5q, CH_3), 43.1 (t, C-2), 47.4 (d, Ar_2CH), 55.1 (q, OCH_3), 58.0 (d, C-1), 113.76, 113.80, 114.0, 114.1 (4 s, Ar), 127.5, 127.7, 128.4, 128.6, 128.7, 128.8, 129.0, 129.1, 129.2, 129.3, 129.7, 131.4 (d, Ar), 133.7/133.9, 135.8/135.9, 136.0, 137.6/137.8, 141.0/141.1, 158.1/158.2 (s, Ar). MS (EI, 70 eV), *m/z* (%): 392 (M^+, 16), 356 (11), 212 (21), 211 (100). Anal. Calcd for $C_{26}H_{29}ClO$ (392.97): C, 79.47; H, 7.44; Cl, 9.02. Found: C, 79.99; H, 7.68; Cl, 8.74.

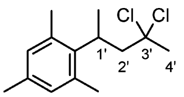
1-Chloro-1,3-bis(2,4,6-trimethylphenyl)butane (7-Cl). A solution of **6**-Cl (913 mg, 5.00 mmol) in CH_2Cl_2 (45 mL) was cooled to −78 °C. Then dichloromethane solutions of $ZnCl_2{\cdot}OEt_2$ (1.50 mL of a 3.9 M solution in CH_2Cl_2, 5.9 mmol) and TMeSt (731 mg, 5.00 mmol in 5 mL CH_2Cl_2) were slowly added and stirring was continued for 60 min at −78 °C. The reaction mixture was hydrolyzed by addition of a mixture of concentrated ammonia and saturated aqueous ammonium chloride (1/1, 20 mL). Then the aqueous layer was separated and extracted with diethyl ether (2 × 20 mL). The combined organic layers were dried ($MgSO_4$), and the solvent was removed under reduced pressure. The residue was purified by filtration through a short column of neutral alumina (activity I, eluent: hexane/diethyl ether = 20:1). Recrystallization from pentane yielded a single diastereomer of **7**-Cl (320 mg, 20%) as colorless crystals.



7-Cl

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.28 (d, J = 7.4 Hz, 3 H, 4-H), 1.77, 1.78, 2.22, 2.23, 2.39, 2.54 (6 s, 6 × 3 H, 6 × CH_3), 2.59−2.84 (m, 2 H, 2-H), 3.13−3.25 (m, 1 H, 3-H), 5.24 (t, J = 8.2 Hz, 1 H, 1-H), 6.71−6.82 (m, 4 H, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 18.8, 19.8, 20.6, 20.8, 21.1, 21.5 (6 q, CH_3), 32.6 (d, C-3), 42.2 (t, C-2), 58.5 (d, C-1), 129.2, 129.3, 131.0, 131.4 (4 d, Ar), 133.3, 135.3, 136.0, 136.8, 137.1, 137.7, 137.86, 137.94 (8 s, Ar). MS (EI, 70 eV), *m/z* (%): 330 (11), 328 (M^+, 34), 277 (12), 148 (12), 147 (100).

2-(3,3-Dichloro-1-methyl-butyl)-1,3,5-trimethylbenzene (8). A solution of titanium tetrachloride (1.50 mL of a 0.89 M solution in CH_2Cl_2, 1.33 mmol) in CH_2Cl_2 (20 mL) was cooled to −78 °C. After the dropwise addition of a solution of **6**-Cl (183 mg, 1.00 mmol) and 2-chloropropene (153 mg, 2.00 mmol) in CH_2Cl_2 (5 mL), stirring was continued for another 4 h at −78 °C. The reaction mixture was then hydrolyzed by the addition of a mixture of concentrated ammonia and saturated aqueous ammonium chloride (1/1, 50 mL). After the separation of the phases, the aqueous layer was extracted with diethyl ether (2 × 20 mL). The combined organic layers were dried ($MgSO_4$), and the solvent was evaporated under reduced pressure. Purification of the crude product by column chromatography (silica gel, eluent: hexane/diethyl ether = 10:1) yielded **8** (200 mg, 77%) as a yellowish oil.



8

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.41 (d, J = 7.2 Hz, 3 H, 1′-CH_3), 2.05, 2.21, 2.33, 2.40 (4 s, 4 × 3 H, 4 × CH_3), 2.61 (ABX system with $^2J_{AB}$ = 14.6 Hz, $^3J_{AX}$ = 5.6 Hz, 1 H, 2′−H), 2.77 (ABX system with $^2J_{AB}$ = 14.6 Hz, $^3J_{AX}$ = 4.6 Hz, 1 H, 2′−H), 3.62−3.72 (m, 1 H, 1′−H), 6.80 (s, 2 H, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 21.1, 21.6, 21.81, 21.84 (4 q, CH_3), 32.8 (d, C-1′), 38.1 (q, C-4′), 56.4 (t, C-2′), 91.4 (s, C-3′), 129.8, 131.6 (2 d, Ar), 135.3, 135.4, 135.6, 140.2 (4 s, Ar).

2,2-Dichloro-4,6-bis(2,4,6-trimethylphenyl)heptane (9). A solution of **7**-Cl (330 mg, 1.00 mmol), 2-chloropropene (153 mg, 2.00 mmol), and benzyltriethylammonium chloride (455 mg, 2.00 mmol) in CH_2Cl_2 (50 mL) was cooled to −78 °C. Then a solution of gallium trichloride (8.00 mL of a 0.29 M solution in CH_2Cl_2, 2.32 mmol) was added and stirring was continued for another 30 min at −78 °C. The reaction mixture was hydrolyzed by the addition of a mixture of concentrated ammonia and water (1/1, 20 mL). After the separation of the phases, the aqueous layer was extracted with diethyl ether (2 × 20 mL). The combined organic layers were dried ($MgSO_4$),

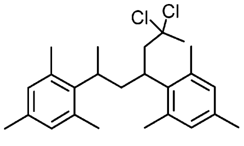
Table 3. Kinetics of the Reactions of 2,4,6-Trimethylstyrene (TMeSt) with $4a^+$ (in CH_2Cl_2)

T/°C	[**4a**-Cl]$_o$/M	[BCl_3]$_0$/M	[TMeSt]$_o$/M	convn/%	k_2/M^{-1} s^{-1}
−70.0	9.18×10^{-5}	3.68×10^{-2}	6.68×10^{-4}	88	1.45×10^{1}
−60.4	4.66×10^{-5}	3.74×10^{-2}	4.52×10^{-4}	63	2.68×10^{1}
−50.8	6.76×10^{-5}	3.61×10^{-2}	5.25×10^{-4}	76	4.87×10^{1}
−40.8	8.71×10^{-5}	3.97×10^{-2}	7.68×10^{-4}	89	8.34×10^{1}
−31.1	4.91×10^{-5}	3.28×10^{-2}	3.97×10^{-4}	83	1.33×10^{2}

Table 4. Kinetics of the Reactions of 2,4,6-Trimethylstyrene (TMeSt) with $4b^+$ (in CH_2Cl_2)

T/°C	[**4b**-Cl]$_o$/M	[BCl_3]$_0$/M	[TMeSt]$_o$/M	convn/%	k_2/M^{-1} s^{-1}
−70.4	2.05×10^{-4}	3.74×10^{-2}	6.33×10^{-4}	31	1.51
−70.1	1.55×10^{-4}	3.85×10^{-2}	9.76×10^{-4}	90	1.55
−60.7	2.13×10^{-4}	3.64×10^{-2}	4.93×10^{-4}	32	3.28
−50.9	1.50×10^{-4}	3.42×10^{-2}	5.79×10^{-4}	86	6.06
−41.2	1.40×10^{-4}	3.48×10^{-2}	2.94×10^{-4}	70	1.15×10^{1}
−31.1	1.25×10^{-4}	3.42×10^{-2}	4.05×10^{-4}	50	2.16×10^{1}
−21.9	1.05×10^{-4}	3.59×10^{-2}	6.06×10^{-4}	40	3.61×10^{1}
−21.5	9.71×10^{-5}	3.31×10^{-2}	2.81×10^{-4}	87	3.67×10^{1}

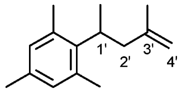
and the solvent was evaporated under reduced pressure to give **9** (380 mg, 94%) as a yellowish oil.



9

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.22 (d, J = 7.1 Hz, 3 H, 7-H), 1.63, 1.72, 1.94 (3 s, 3 × 3 H, 3 × CH_3), 2.20 (s, 6 H, 2 × CH_3), 2.38, 2.44 (2 s, 2 × 3 H, 2 × CH_3), 2.51−2.75 (m, 4 H, 2 × CH_2), 2.95−3.02 (m, 1 H, 6-H), 3.38−3.47 (m, 1 H, 4-H), 6.69−6.80 (m, 4 H, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 19.7, 20.1, 20.5, 20.9, 21.2, 21.6, 26.9 (7 q, 7 × CH_3), 32.8, 36.9 (2 d, C-4 and C-6), 38.0 (q, C-1), 40.7, 54.9 (2 t, C-3 and C-5), 90.9 (s, C-2), 129.3, 129.9, 130.8, 131.2 (4 d, Ar), 135.3, 135.6, 136.0, 136.2, 137.0, 137.6, 137.7, 138.8 (8 s, Ar).

2-(1,3-Dimethyl-but-3-enyl)-1,3,5-trimethylbenzene (11). A dichloromethane solution of $ZnCl_2 \cdot OEt_2$ (1.00 mL of a 3.9 M solution in CH_2Cl_2, 3.9 mmol) was further diluted with CH_2Cl_2 (50 mL) and cooled to −78 °C. Subsequently, a mixture of **6**-Cl (327 mg, 1.79 mmol) and **10** (1.38 g, 4.00 mmol) in CH_2Cl_2 (2 mL) was slowly added. After stirring at −78 °C for another 2 h, the reaction mixture was hydrolyzed by adding a mixture of concentrated ammonia and water (1/1). The organic layer was separated, dried ($MgSO_4$), and the solvent was removed under reduced pressure. The crude product was dissolved in a mixture of hexane and diethyl ether (4/1) and purified by filtration through a short column filled with silica gel which contained tetrabutylammonium fluoride. The solvent was removed under reduced pressure to give **11** (330 mg, 91%) as a colorless oil.



11

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.26 (d, J = 7.5 Hz, 3 H, 1′-CH_3), 1.69 (s, 3 H, 3′-CH_3), 2.21−2.49 (m, 11 H), 3.31−3.41 (m, 1 H, 1′−H), 4.70−4.72 (m, 2 H, 4′−H), 6.79 (s, 2 H, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 18.4, 20.6, 21.5, 22.3 (4 q, CH_3), 32.9 (d, C-1′), 43.8 (t, C-2′), 111.5 (t, C-4′), 129.2, 131.2 (2 br d, Ar), 134.8 (s, Ar), 136.0 (br s, Ar), 140.2 (s, Ar), 144.8 (s, C-3′). MS (EI, 70 eV), m/z (%): 202 (M^+, 5), 148 (11), 147 (100).

1,3,5-Trimethyl-2-(1-methyl-but-3-enyl)benzene (13). As described above for the preparation of **11**, $ZnCl_2 \cdot OEt_2$ (1.00

Table 5. Kinetics of the Reactions of 2,4,6-Trimethylstyrene (TMeSt) with $4c^+$ [Generated from 4c-Cl and Different Lewis Acids (LA), in CH_2Cl_2]

T/°C	[**4c**-Cl]$_o$/M	Lewis acid	[LA]$_0$/M	[TMeSt]$_o$/M	convn/%	k_2/M^{-1} s^{-1}
−69.3	1.24×10^{-4}	$ZnCl_2 \cdot OEt_2$	1.71×10^{-2}	2.72×10^{-2}	80	1.35×10^{-2}
−69.3	9.33×10^{-5}	BCl_3	3.70×10^{-2}	3.36×10^{-2}	31	1.25×10^{-2}
−58.9	6.75×10^{-5}	BCl_3	3.39×10^{-2}	3.84×10^{-2}	70	3.48×10^{-2}
−49.7	1.13×10^{-4}	$ZnCl_2 \cdot OEt_2$	1.56×10^{-2}	3.71×10^{-2}	73	9.83×10^{-2}
−49.0	5.62×10^{-5}	BCl_3	3.53×10^{-2}	4.00×10^{-2}	26	8.13×10^{-2}
−39.7	9.59×10^{-5}	$ZnCl_2 \cdot OEt_2$	8.25×10^{-3}	1.31×10^{-2}	53	2.42×10^{-1}
−39.5	8.44×10^{-5}	BCl_3	3.74×10^{-2}	2.83×10^{-2}	78	1.61×10^{-1}
−30.5	8.52×10^{-5}	BCl_3	3.21×10^{-2}	1.21×10^{-2}	42	4.89×10^{-1}
19.9	6.23×10^{-5}	TMSOTf	4.23×10^{-3}	1.06×10^{-3}	35	4.56
19.9	7.57×10^{-5}	$TiCl_4$	3.53×10^{-3}	4.55×10^{-4}	20	5.71
20.0	8.14×10^{-5}	TMSOTf	4.14×10^{-3}	1.39×10^{-2}	61	3.87
20.0	4.47×10^{-5}	TMSOTf	4.55×10^{-3}	1.27×10^{-2}	31	5.91

Table 6. Kinetics of the Reactions of 2-Chloropropene (Nuc) with 6^+ [Generated from 6-Cl and $GaCl_3$ in the Presence of Benzyltriethylammonium Chloride (TEBA), in CH_2Cl_2]

T/°C	[**6**-Cl]$_0$/M	[$GaCl_3$]$_0$/M	[TEBA]$_0$/M	[Nuc]$_0$/M	convn/%	k_2/M^{-1} s^{-1}
−67.4	1.41×10^{-4} [a]	6.76×10^{-3}		4.37×10^{-4}	32	33.1
−55.7	2.09×10^{-4}	6.42×10^{-3}	2.04×10^{-3}	7.86×10^{-4}	57	57.5
−48.3	1.06×10^{-4}	6.52×10^{-3}	2.07×10^{-3}	5.32×10^{-4}	31	105
−41.3	8.44×10^{-5}	6.49×10^{-3}	2.06×10^{-3}	5.30×10^{-4}	31	175
−40.1	6.02×10^{-5}	6.28×10^{-3}	1.99×10^{-3}	6.34×10^{-4}	35	177
−30.5	7.85×10^{-5}	5.85×10^{-3}	1.86×10^{-3}	5.91×10^{-4}	58	284
−27.6	4.85×10^{-5}	4.70×10^{-3}	1.66×10^{-3}	3.10×10^{-4}	53	411

[a] Compound **6**−Br was used as precursor of cation 6^+.

Table 7. Kinetics of the Reactions of 2-Chloropropene (Nuc) with 7^+ [Generated from 7-Cl and $GaCl_3$ in the Presence of Benzyltriethylammonium Chloride (TEBA), in CH_2Cl_2]

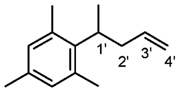
T/°C	[**7**−Cl]$_0$/M	[$GaCl_3$]$_0$/M	[TEBA]$_0$/M	[Nuc]$_0$/M	convn/%	k_2/M^{-1} s^{-1}
−66.0	9.69×10^{-5}	5.36×10^{-3}	1.90×10^{-3}	4.41×10^{-4}	24	80.7
−58.3	8.72×10^{-5}	5.79×10^{-3}	2.05×10^{-3}	3.24×10^{-4}	66	138
−55.2	1.06×10^{-4}	5.85×10^{-3}	2.07×10^{-3}	7.23×10^{-4}	58	137
−45.2	7.54×10^{-5}	5.01×10^{-3}	1.77×10^{-3}	4.12×10^{-4}	82	250
−37.5	6.30×10^{-5}	5.23×10^{-3}	1.85×10^{-3}	3.44×10^{-4}	82	440

Table 8. Relative Reactivities of Tributyl(2-methallyl)stannane (10) and Allyltrimethylsilane (12) toward $\mathbf{6}^+$ Generated from 6-Cl and $ZnCl_2{\cdot}OEt_2$ (CH_2Cl_2, − 78 °C)

n_0(**6**−Cl)/mmol	n_0(**10**)/mmol	n_0(**12**)/mmol	product ratio [**11**]/[**13**][a]	κ
0.22	0.50	2.50	3.50	21.2
0.22	0.50	5.00	2.39	28.4
0.22	0.50	3.00	3.22	23.3
0.22	0.50	1.50	6.37	23.8
0.22	0.50	8.00	1.61	29.9
0.22	0.50	2.00	4.85	23.9
0.22	0.25	2.50	1.69	24.2
0.22	0.50	4.00	2.41	22.9

[a] Determined from the ratio of the GC peak areas.

mL of a 3.9 M solution in CH_2Cl_2, 3.9 mmol), **6**-Cl (327 mg, 1.79 mmol), and **12** (457 mg, 4.00 mmol) reacted in CH_2Cl_2 (50 mL) at −78 °C to give a crude product which was dried in the high vacuum to yield **13** (280 mg, 83%) as a yellowish oil.



13

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.28 (d, J = 7.2 Hz, 3 H, 1′-CH_3), 2.21−2.54 (m, 11 H), 3.20−3.30 (m, 1 H, 1′−H), 4.89−5.04 (m, 2 H, 4′−H), 5.64−5.78 (m, 1 H, 3′−H), 6.78 (s, 2 H, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 18.6, 20.6, 21.6 (3 q, CH_3), 34.9 (d, C-1′), 39.8 (t, C-2′), 115.2 (t, C-4′), 129.1, 131.1 (2 br d, Ar), 134.8, 136.0 (2 s, Ar), 138.0 (d, C-3′), 139.5 (s, Ar). MS (EI, 70 eV), m/z (%): 188 (M^+, 1), 148 (11), 147 (100).

Kinetic Experiments. Because the reactions of the colored carbenium ions $\mathbf{4a}-\mathbf{c}^+$ with TMeSt (Tables 3−5) or of $\mathbf{6}^+$ and $\mathbf{7}^+$ with 2-chloropropene (Tables 6 and 7) gave rise to colorless products, the second-order rate constants k_2 (M^{-1} s^{-1}) could be determined photometrically. The reactions of the benzhydrylium ions $\mathbf{4a}-\mathbf{c}^+$ with TMeSt were followed with a Schölly KGS III UV/vis photometer with band-pass filters by Corion as described in ref 30. For the reactions of $\mathbf{6}^+$ and $\mathbf{7}^+$ with 2-chloropropene, UV−visible spectra in the range of 200−600 nm were collected as a function of time by the use of a J&M TIDAS diode array spectrophotometer that was linked to a Hellma 661.502-QX quartz Suprasil immersion probe (5 mm light path) via fiber optic cables with standard SMA connectors.[31] Calibration curves, i.e., the correlation between absorbance and concentration of the carbocations, were obtained by determination of the absorbance of solutions of $\mathbf{4a}-\mathbf{4c}^+$, $\mathbf{6}^+$, and $\mathbf{7}^+$ at different concentrations. The temperature of solutions during all kinetic studies was maintained (±0.2 °C) by using circulating bath cryostats (water−glycol bath for $T > -10$ °C, ethanol bath for $T < -10$ °C) and monitored with a thermocouple probe that was inserted into the reaction mixture.

Competition Experiments. Under an atmosphere of dry nitrogen, a mixture of **6**-Cl, **10**, and **12** was dissolved in dry CH_2Cl_2 (20 mL), a drop of 2,6-di-*tert*-butylpyridine was added, and the solution was cooled to −78 °C. Subsequently, the reaction was started by adding a 3.9 M solution of $ZnCl_2{\cdot}OEt_2$ (0.1 mL) in CH_2Cl_2. After being stirred at −78 °C for 60 min, the reaction mixture was hydrolyzed with concentrated NH_3/water (5 mL, 1/1). The organic layer was separated, dried over $MgSO_4$, filtered, and analyzed by GC (Fisons GC 8100 with FID, packed column SE 30, 2.5 m × 2 mm, temperature range of 50−300 °C, heating-up rate of 10 °C min^{-1}). Because of the similarities of the products **11** and **13**, the GC peak areas of **11** and **13** were directly taken as a measure for the product ratios, which were then used for the calculation of the competition constants[32] $\kappa = k_{10}/k_{12}$. Details of the individual experiments are summarized in Table 8.

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References and Notes

(1) (a) Plesch, P. H. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 2537−2544. (b) Plesch, P. H. *Macromolecules* **2001**, *34*, 1143−1147. (c) Plesch, P. H. *Prog. React. Kinet.* **1993**, *18*, 1−62.

(2) Sigwalt, P.; Moreau, M.; Polton, A. *Macromol. Symp.* **2002**, *183*, 35−42.

(3) Roth, M.; Mayr, H. *Macromolecules* **1996**, *29*, 6104−6109.

(4) Sipos, L.; De, P.; Faust, R. *Macromolecules* **2003**, *36*, 8282−8290.

(5) Puskas, J. E.; Peng, H. *Polym. React. Eng.* **1999**, *7*, 553−576.

(6) Schlaad, H.; Kwon, Y.; Sipos, L.; Faust, R.; Charleux, B. *Macromolecules* **2000**, *33*, 8225−8232.

(7) Storey, R. F.; Thomas, Q. A. *Macromolecules* **2003**, *36*, 5065−5071.

(8) Puskas, J. E.; Luo, W. *Macromolecules* **2003**, *36*, 6942−6944.

(9) Vairon, J.-P.; Rives, A.; Bunel, C. *Makromol. Chem., Macromol. Symp.* **1992**, *60*, 97−105.

(10) Puskas, J. E.; Lanzendörfer, M. G.; Pattern, W. E. *Polym. Bull. (Berlin)* **1998**, *40*, 55−61.

(11) De, P.; Faust, R.; Schimmel, H.; Ofial, A. R.; Mayr, H. *Macromolecules* **2004**, *37*, 4422−4433.

(12) Mayr, H.; Schimmel, H.; Kobayashi, S.; Kotani, M.; Prabakaran, T. R.; Sipos, L.; Faust, R. *Macromolecules* **2002**, *35*, 4611−4615.

(13) Vairon, J.-P.; Moreau, M.; Charleux, B.; Cretol, A.; Faust, R. *Macromol. Symp.* **2002**, *183*, 43−52.

(14) (a) Györ, M.; Kennedy, J. P.; Kelen, T.; Tudös, F. *J. Macromol. Sci.-Chem.* **1984**, *A21*, 1295−1309. (b) Faust, R.; Kennedy, J. P. *Polym. Bull. (Berlin)* **1988**, *19*, 35−41.

(15) Zwegers, J.; Maréchal, E. *Bull. Soc. Chim. Fr.* **1972**, 1157−1169.

(16) De, P.; Sipos, L.; Faust, R.; Moreau, M.; Charleux, B.; Vairon, J.-P. *Macromolecules* 2005, 38, 41−46.

(17) Mayr, H.; Patz, M. *Angew. Chem.* **1994**, *106*, 990−1010; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 938−957.

(18) Mayr, H. In *Cationic Polymerization: Mechanisms, Synthesis and Applications*; Matyjaszewski, K., Ed.; Marcel Dekker: New York, 1996; pp 51−136.

(19) Mayr, H.; Roth, M.; Lang, G. In *Cationic Polymerization, Fundamentals and Applications*; Faust, R., Shaffer, T. D., Eds.; ACS Symposium Series Vol. 665: Washington, DC, 1997; pp 25−40.

(20) Mayr, H.; Kuhn, O.; Gotta, M. F.; Patz, M. *J. Phys. Org. Chem.* **1998**, *11*, 642−654.

(21) Mayr, H.; Patz, M.; Gotta, M. F.; Ofial, A. R. *Pure Appl. Chem.* **1998**, *70*, 1993−2000.

(22) Mayr, H. In *Ionic Polymerizations and Related Processes*; Puskas, J. E., Michel, A., Barghi, S., Paulo, C., Eds.; NATO Science Series: E Applied Sciences 359; Kluwer Academic Publishers: Dordrecht, 1999; pp 99−115.

(23) Mayr, H.; Bug, T.; Gotta, M. F.; Hering, N.; Irrgang, B.; Janker, B.; Kempf, B.; Loos, R.; Ofial, A. R.; Remennikov, G.; Schimmel, H. *J. Am. Chem. Soc.* **2001**, *123*, 9500−9512.

(24) Mayr, H.; Kempf, B.; Ofial, A. R. *Acc. Chem. Res.* **2003**, *36*, 66−77.

(25) (a) Kempf, B.; Hampel, N.; Ofial, A. R.; Mayr, H. *Chem.—Eur. J.* **2003**, *9*, 2209−2218. (b) Bug, T.; Hartnagel, M.; Schlierf, C.; Mayr, H. *Chem.—Eur. J.* **2003**, *9*, 4068−4076. (c) Tokuyasu, T.; Mayr, H. *Eur. J. Org. Chem.* **2004**, 2791−2796.

(26) (a) Lucius, R.; Loos, R.; Mayr, H. *Angew. Chem.* **2002**, *114*, 97−102; *Angew. Chem., Int. Ed.* **2002**, *41*, 91−95. (b) Bug, T.; Mayr, H. *J. Am. Chem. Soc.* **2003**, *125*, 12980−12986. (c) Loos, R.; Kobayashi, S.; Mayr, H. *J. Am. Chem. Soc.* **2003**, *125*, 14126−14132.

(27) Minegishi, S.; Mayr, H. *J. Am. Chem. Soc.* **2003**, *125*, 286−295.

(28) Minegishi, S.; Kobayashi, S.; Mayr, H. *J. Am. Chem. Soc.* **2004**, *126*, 5174−5181.

(29) Under analogous conditions as described for the formation of **5a** and **5b**, hydrolyzed starting material (**4c**-OCH_3) was

isolated in almost quantitative yield after the addition of methanol to a mixture of **4c**-Cl, 2,4,6-trimethylstyrene (TMeSt), and $ZnCl_2 \cdot OEt_2$, possibly because the equilibrium is on the reactant side in the absence of a large excess of TMeSt.

(30) Mayr, H.; Schneider, R.; Schade, C.; Bartl, J.; Bederke, R. *J. Am. Chem. Soc.* **1990**, *112*, 4446−4454.

(31) Dilman, A. D.; Ioffe, S. L.; Mayr, H. *J. Org. Chem.* **2001**, *66*, 3196−3200.

(32) For the evaluation of the competition constant κ from the product ratios, see: Ingold, C. K.; Shaw, F. R. *J. Chem. Soc.* **1949**, 575−581.

(33) Patz, M.; Mayr, H.; Bartl, J.; Steenken, S. *Angew. Chem.* **1995**, *107*, 519−521; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 490−492.

(34) Charlton, J. C.; Hughes, E. D. *J. Chem. Soc.* **1954**, 2939−2942.

(35) Schimmel, H. Dissertation. Ludwig-Maximilians-Universität, München, Germany, 2000.

(36) Mayr, H.; Hagen-Bartl, G. In *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L. A., Ed.; Wiley: New York, 1995; Vol. 8, pp 5552−5554.

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