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Grignard Reaction with Chlorosilanes in THF: A Kinetic Study

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Kinetics of the reactions of phenylmagnesium chloride and bromide and diphenylmagnesium with chlorosilanes were investigated in tetrahydrofurane (THF) and in THF−hydrocarbon mixtures. The reaction in THF is much faster than that in diethyl ether. Assuming coordination of magnesium halides with three molecules of THF, concentrations of all the species involved in Schlenk equilibrium were calculated. In the Grignard reaction, species R_2Mg and RMgX react competitively accompanied by additional reaction paths involving electrophilic catalysis by magnesium halide. This conclusion also proved to be valid for the Grignard reaction with a ketone and probably can be expanded to any Grignard reaction. When Schlenk equilibrium is shifted far to the RMgX species, the catalytic pathways are insignificant. Substituents at the silicon center control the rate of the reaction through their inductive and steric effects.

Introduction

Although the production of organosilanes by direct methods is greater than that with Grignard processes, the latter remain essential for many of the specialty silanes. The versatility of the Grignard process allows the introduction of a broader range of functionalities than alternative technologies.[1] Despite the viability of the Grignard process in organosilane production the quantitative aspects of the reaction have been little investigated. Only a small number of kinetic studies of the Grignard reaction with silanes, carried out mainly in diethyl ether solutions, have been published.[2]

Of the two most common solvents for Grignard reagents, tetrahydrofurane (THF) reveals advantages over diethyl ether. Apart from lower fire-hazard risks owing to the higher boiling point, THF allows the reaction to run at more elevated temperatures. One of the most significant differences between THF and diethyl ether arises from the occurrence of Schlenk equilibrium (eq 1) in solutions of Grignard reagents.[3]

$$2RMgX \rightleftharpoons R_2Mg + MgX_2 \qquad (1)$$

While the equilibrium is shifted far left in diethyl ether, all three species are present in appreciable concentration in THF. Although the importance of the Schlenk equilibrium in Grignard reactions with various substances has been stressed,[3b,c] no quantitative analysis of the contribution of Schlenk equilibrium in reaction kinetics is available.

In this paper we report the results of a kinetic investigation of the Grignard reaction with chlorosilanes in THF and in some THF−hydrocarbon mixtures. Also, an analysis of kinetic data involving the data for the Schlenk equilibrium will be presented. In the kinetic investigation, phenylmagnesium chloride and bromide served as model Grignard reagents.

Results and Discussion

Pure THF. As found in our previous work,[2e] kinetics of the Grignard reaction with chlorosilanes obeys the second order law, therefore, the pseudo-first-order rate constants determined with a great excess of the Grignard reagent should depend linearly upon the concentration of the reagent. However, this is not the case in THF, as seen in Figure 1. The upward curvature of the plot in Figure 1 may indicate a higher kinetic order in the Grignard reagent for the reaction. A similar kinetic feature has been found for the reaction of *n*-propylmagnesium bromide with pinacolone in THF.[4] According to the reaction mechanism deduced from our previous results for the reaction with silanes,[2d,e] inclusion of two Grignard reagent molecules in the transition state is not

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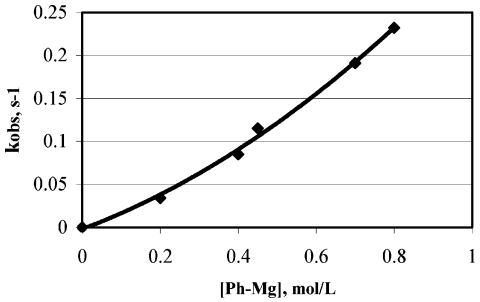

FIGURE 1. Dependence of pseudo-first-order rate constants on Grignard reagent concentration for the reaction of phenylmagnesium chloride with methyltrichlorosilane in THF at 20 °C.

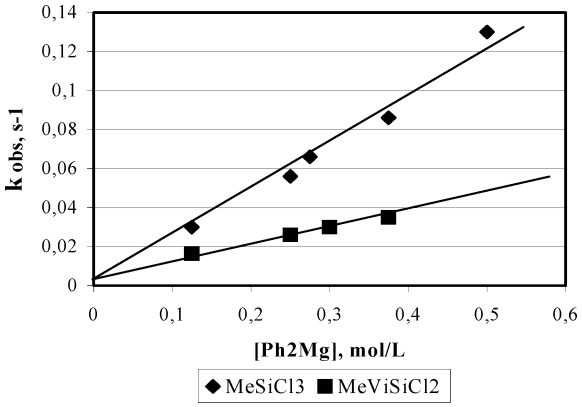

FIGURE 2. Dependence of pseudo-first-order rate constants on the concentration of diphenylmagnesium for the reaction with methyltrichlorosilane and methylvinyldichlorosilane in THF at 20 °C.

very plausible. The same is believed to be valid for the reaction with carbonyl compounds.[3c,5] Since such a kinetic feature has not been found for the reactions in diethyl ether, it should be assigned to a peculiarity of Grignard reagents in THF solutions.

To start unraveling the enigma we determined pseudo-first-order rate constants k_I for reactions of chlorosilanes with a great excess of diphenylmagnesium in THF. The plots of k_I vs diphenylmagnesium concentration in Figure 2 can be approximated to straight lines yielding second-order rate constants $k_{II} = 0.26 \pm 0.01$ L mol^{-1} s^{-1} for methyltrichlorosilane and $k_{II} = 0.101 \pm 0.006$ L mol^{-1} s^{-1} for methylvinyldichlorosilane.

THF−Hydrocarbon Mixtures. The next step of the study was an investigation of the reaction in THF−toluene mixtures. Replacement of THF by additions of nondonating toluene does not change the solvation of the Grignard species in equilibrium 1; however, this can lead to shifts in the equilibrium as will be subsequently shown.

Addition of nondonating species to Grignard reagents has been used in our previous works to alter the polarity and polarizability of the reaction medium.[6] Additions of toluene to the Grignard reagent prepared in THF should lower considerably the polarity of the solution and increase slightly the polarizability. Figure 3 indicates a

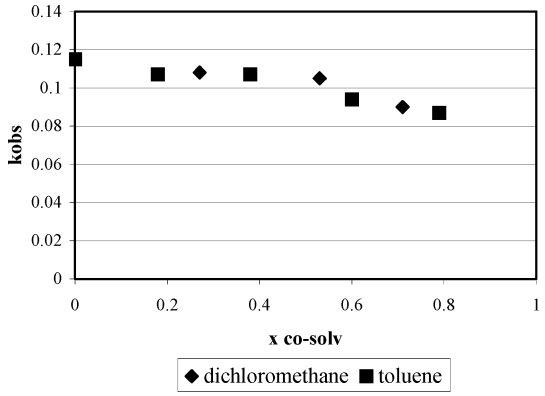

FIGURE 3. Dependence of pseudo-first-order rate constants for the reaction of 0.5 M PhMgCl with $MeSiCl_3$ in THF at 20 °C upon the molar fraction of cosolvents (X co-solv).

gradual decrease of the reaction rate with increasing content of toluene in the Grignard reagent solution. Although we were able to show the absence of nonspecific solvent effects for the Grignard reaction with silanes in diethyl ether,[2e] this could not be expanded directly to the reaction in THF. In a check experiment dichloromethane was used instead of toluene. Additions of dichloromethane to THF raise the medium polarity and do not change the polarizability. In Figure 3, points for dichloromethane additions fall on the curve for toluene−THF mixtures. Consequently, no nonspecific solvent effects are present in this case and both cosolvents act as indifferent diluting agents. Thus, the observed decrease of the reaction rate should be related to the changes in the Grignard reagent structure.

Schlenk Equilibrium. Consideration of the structure of Grignard reagents in THF is largely facilitated by the absence of association of the species involved in Schlenk equilibrium 1.[7,8] However, in contrast to diethyl ether, the Schlenk equilibrium in THF is concentration dependent, the dominant effect being associated with the solvation of magnesium halides.[3b] The alternative equilibriums 2 and 3 emphasize the dependency of the Schlenk equilibrium on solvent concentration.

$$R_2Mg{\cdot}2THF + MgX_2{\cdot}4THF \rightleftarrows RMgX{\cdot}2THF + 2THF \quad (2)$$

$$R_2Mg{\cdot}2THF + MgX_2{\cdot}3THF \rightleftarrows RMgX{\cdot}2THF + THF \quad (3)$$

As THF is sterically less demanding than diethyl ether, magnesium halide can probably coordinate up to four THF molecules, e.g. $MgBr_2{\cdot}4THF$, based on crystallographic data.[9] However, the crystal structure of $MgBr_2{\cdot}2THF$ also has been described.[10] It must be realized that the crystals do not necessarily reflect the

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components in solution. Our density functional theory calculations[11a] indicate that *trans*-dihalotetrakis(tetrahydrofurano)magnesiums are only by 3 kcal per mol or less stabilized over the tris(tetrahydrofurano) complexes while *cis*-tetrakis complexes are much more unstable.[12] The tris(tetrahydrofurano) complexes in their turn are by 4 to 5 kcal per mol more favored than the MgX_2·2THF complexes.[11] However, the calculations were performed for the gas phase. In the liquid phase, small differences can be detracted due to the presence of the second solvation sphere. Inferences from our DFT calculations encouraged us to adopt equilibrium 3, in particular, after the calculations described below failed when tetrasolvated magnesium chloride was assumed.

According to equilibrium 3, the Schlenk equilibrium constant can be expressed as

$$K_S = \frac{[RMgX]^2[THF]}{[R_2Mg][MgX_2]} \quad (4)$$

In experiment, e.g. from the NMR spectra, the Schlenk equilibrium constant is usually determined as[3b]

$$K_{S,exp} = \left(\frac{[RMgX]}{[R_2Mg]}\right)^2$$

assuming that $[R_2Mg] = [MgX_2]$.

Thus, in calculations for various Grignard reagent concentrations, the true equilibrium constant, $K_S = K_{S,exp}[THF]$, should be used provided $K_{S,exp}$ is determined in a dilute solution, and [THF] is the concentration of free THF in the solution.

The Schlenk equilibrium constant for phenylmagnesium chloride has been determined[13] as 1.66 in dilute THF solutions (0.1−0.15 M). Taking the free THF concentration approximately equal to the pure THF concentration (12.3 M) we further used in calculations $K_S = 20$ mol/L.

For calculations, experimentally determined concentrations of the basic magnesium, [RMg], and of halide ion, $[X^-]$ (or [Mg-X]), are available. The ratio $W = [MgX]/[MgR]$, incidentally expressing the contribution of the Wurtz reaction during the preparation of the Grignard reagent, was convenient to use in the derivation of eqs 5 and 6.

$$[RMgX] + 2[R_2Mg] = [RMg] \quad (5)$$

$$[RMgX] + 2[MgX_2] = [MgX] = W[RMg] \quad (6)$$

Eventually, from eqs 4, 5, and 6, values of [RMgX], $[R_2Mg]$, and $[MgX_2]$ can be calculated for any [RMg] and W. Equation 4 involves the concentration of free THF in the solution, $[THF]_F$, which was found as

$$[THF]_F = 12.3 - [THF]_S$$

where $[THF]_S$ is the molar amount of THF per liter of the reagent consumed for solvation of the species according to equilibrium 3. In the first approximation, $[THF]_S$ was calculated as

$$[THF]_S = [RMg] + [MgX] + (W - 1)[RMg] = 2W[RMg]$$

slightly underestimating the value. Then provisional concentrations of RMgX, R_2Mg, and MgX_2 were calculated, the corrected value for $[THF]_S$ was found, and ultimately the final values of the species were calculated. Actually, the corrections done by iteration were relatively small, ranging a few percent.

Somewhat problematic is the estimation of $[THF]_F$. For correct calculations, densities of Grignard reagent solutions are necessary. However, we have observed that an increase in the specific gravity of a Grignard reagent up to 1 M concentration usually does not exceed 10% of that of the pure solvent. Tentative calculations indicated that the probable error is small.[14]

Principally the same approach was used in the calculation of concentrations of the species in THF−toluene binary solvents. Because no appreciable volume effects were observed by mixing the solvents, the final volume of the mixture was considered as additive in the components.

Calculated concentrations of the species in equilibrium 3 for phenylmagnesium chloride in THF and THF−toluene mixtures are presented in Tables 1 and 2, respectively.

Treatment of Kinetic Data. In general, competitive reactions of PhMgCl and Ph_2Mg species with the silane can be expected:

TABLE 1. Composition of Phenylmagnesium Chloride (mol/L) in THF Solutions[a]

PhMg[b]	PhMgCl	Ph_2Mg	$MgCl_2$
0.2	0.084	0.058	0.073
0.4	0.171	0.115	0.144
0.5	0.215	0.142	0.185
0.7	0.304	0.200	0.250
0.8	0.350	0.225	0.285

[a] For $W = 1.15$. [b] Concentration of the Grignard reagent.

TABLE 2. Composition of 0.5 M Phenylmagnesium Chloride in THF−Toluene Mixtures[a]

toluene vol %	X_{tol}[b]	PhMgCl[c]	Ph_2Mg[c]	$MgCl_2$[c]
0	0	0.215	0.142	0.185
20	0.18	0.235	0.132	0.182
40	0.38	0.258	0.120	0.170
60	0.60	0.291	0.105	0.155
75	0.79	0.337	0.080	0.130

[a] For $W = 1.15$. [b] Molar fraction of toluene. [c] Mol/L.

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(11) (a) Tammiku-Taul, J.; Burk, P.; Tuulmets, A. *J. Phys. Chem. A* **2004**, *108*, 133−139. (b) For example, the calculated solvation enthalpies in kcal mol^{-1} are for $MgCl_2$·2THF −43.7, PhMgCl·2THF −35.1, and Ph_2Mg·2THF −27.8.

(12) Calculations were performed for chlorides and bromides.[11a] The cis-form is a deformed octahedron where two THF ligands are equatorial and the other two are axial. The trans-form is also an octahedron where equatorial and axial positions are indistinguishable.

(13) Smith, M. B.; Becker, W. E. *Tetrahedron* **1967**, *23*, 4215−4219.

(14) For example, if the density of 0.5 M PhMgCl is by 6% greater than that of pure THF, the error in $[THF]_F$ is +2%, and if it is greater by 10%, the error is −3%.

$$k_{obs} = k_1[Ph_2Mg] + k_2[PhMgCl]$$

From independent experiment, k_1 was obtained as 0.26 L mol^{-1} s^{-1} (see the section Pure THF). Thus, k_2 should be calculated as

$$k_2 = (k_{obs} - k_1[Ph_2Mg])/[PhMgCl]$$

However, k_2 calculated in this way was not a constant, obtaining values ranging from 0.23 L mol^{-1} s^{-1} for 0.2 M Grignard reagent up to 0.49 L mol^{-1} s^{-1} for 0.8 M Grignard reagent. Moreover, the difference $k' = k_{obs} - k_1[Ph_2Mg]$ revealed a trend similar to that of the concentrations of Ph_2Mg and $MgCl_2$, increasing with an increase in Grignard reagent concentration in pure THF, and decreasing with an increase in the cosolvent molar fraction in THF−toluene mixtures, respectively. Consequently, an additional term was to be included in the expression for k_{obs},

$$k_{obs} = k_1[Ph_2Mg] + k_2[PhMgCl] + k_3[Ph_2Mg][MgCl_2] \quad (7)$$

In Figure 2, extrapolation of the curve to molar fraction of toluene 1.0, corresponding to a solution of the complex PhMgCl·2THF in toluene, yields $k_{obs} = 0.07$ s^{-1}, and respectively $k_2 = 0.14$ L mol^{-1} s^{-1}. The residual rate constant, $k'' = k_{obs} - k_1[Ph_2Mg] - k_2[PhMgCl]$, correlates with the product $[Ph_2Mg][MgCl_2]$ as seen in Figure 4, yielding $k_3 = 1.8$ L^2 mol^{-2} s^{-2}.

Application of estimated rate constants to the kinetic data for pure THF led to a good fit between k_{obs} and k_{calc} within 4% or better.

Primarily we avoided using a formal statistical treatment of the data, because imperfect orthogonality between the columns for concentrations in Tables 1 and 2 could bring about irrelevant results. However, correlation of the rate data with concentrations of the species in pure THF according to eq 8, where k' was calculated as $k' = k_{obs} - k_1[Ph_2Mg]$,

$$k' = k_2[PhMgCl] + k_3[Ph_2Mg][MgCl_2] + k_4[PhMgCl][MgCl_2] \quad (8)$$

indicated the insignificance of the last term in the equation and gave for rate constants the values $k_2 = 0.124 \pm 0.003$ and $k_3 = 2.02 \pm 0.02$ ($R = 0.999$, $s = 0.0003$). From similar treatment of the data for the THF−toluene mixtures we obtained $k_2 = 0.137 \pm 0.013$ and $k_3 = 1.83 \pm 0.18$ ($R = 0.838$, $s = 0.003$), the last term in eq 8 being insignificant. Thus, the rate constants from two sets of experiments were not statistically different.

Mechanism of the Reaction. It appeared in the previous section that our kinetic data were well fitted by eq 7. While participation of species Ph_2Mg and PhMgCl in the reaction could be anticipated, the unignorable contribution of the last term in eq 7 was somewhat unexpected on the background of the mechanism suggested for chlorosilanes in our previous paper[2e] (Chart 1).

However, the Lewis acidities of the species vary largely ranging in the order $MgCl_2$ > PhMgCl > Ph_2Mg.[11b] Therefore, complexation of $MgCl_2$ with the chlorine center of the silane is even more favored than that for PhMgCl

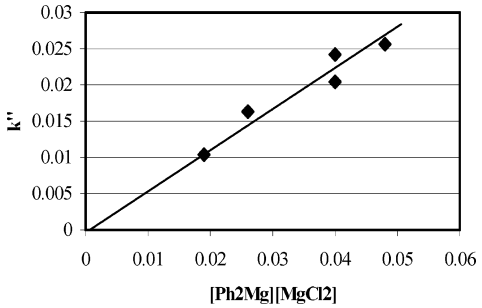


FIGURE 4. Plot of the residual rate constant k'' versus the product of concentrations $[Ph_2Mg][MgCl_2]$ for the THF−toluene system.

CHART 1

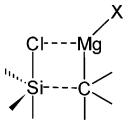
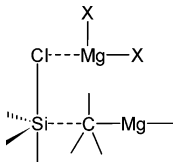


CHART 2



or Ph_2Mg molecules.[15] It appears that electrophilic assistance provided by the magnesium center in Chart 1 can be replaced by true electrophilic catalysis as depicted in Chart 2.

Whether the magnesium halide is bound to the organomagnesium species through a halide bridge forming a six-center transition state is not yet clear.

In this context, participation of PhMgCl species in the catalytic pathway cannot be excluded. Higher reactivity of Ph_2Mg and considerable concentrations of symmetrical species in the solution make the term with k_3 in eq 8 significant while the last term probably remains shaded by experimental uncertainties. Consequently, the general eq 9 for the kinetics of the Grignard reaction can be inferred:

$$k_{obs} = k_1[R_2Mg] + k_2[RMgX] + k_3[R_2Mg][MgX_2] + k_4[RMgX][MgX_2] \quad (9)$$

In common ethers, where the Schlenk equilibrium (equation 1) is shifted far left, only the noncatalytic pathway through RMgX species is significant provided the reactivity of diorganomagnesiums does not much exceed that of RMgX compounds. At least for the reactions with silanes, this seems to be the case.[2d]

Reaction with a Ketone. Consequences from the discussion above challenged us to expand the approach to an entirely different Grignard reaction in THF, viz. to the reaction between *n*-propylmagnesium bromide and pinacolone. The same trend in the pseudo-first-order rate constants as in Figure 1 was found for that reaction.[4] An explanation, similar to the mechanism suggested for the

(15) For that reason we preferred the term $k_3[Ph_2Mg][MgCl_2]$ in eq 8, although $[Ph_2Mg][MgCl_2]$ is roughly proportional to $[PhMgCl]^2$.

TABLE 3. Composition of *n*-propylmagnesium Bromide (mol L^{-1}) in THF Solutions[a]

n-PrMg[b]	n-PrMgBr	n-Pr_2Mg	$MgBr_2$
0.2	0.118	0.041	0.056
0.3	0.178	0.061	0.084
0.4	0.238	0.081	0.111
0.5	0.299	0.100	0.123
0.6	0.361	0.120	0.165
0.7	0.423	0.139	0.191
0.8	0.489	0.155	0.216

[a] For $W = 1.16$. [b] Concentration of the Grignard reagent.

reaction with chlorosilanes in the present work, was proposed, however, without quantitative verification.[4]

The Schlenk equilibrium constant for *n*-propylmagnesium bromide in THF is not available. Smith and Becker determined $K_{S,exp} = 5.09$ in 0.1 M ethylmagnesium bromide in THF[13] and Holm estimated $K_{S,exp} \approx 9$ in about 2 M THF solution of *n*-butylmagnesium bromide.[16] Recalculation of the latter for a dilute solution gave $K_{S,exp} \approx 6$, so $K_{S,exp} = 5.6$ was taken for *n*-propylmagnesium bromide in THF. Concentrations of the species in equilibrium 3 were calculated as described above. The results are presented in Table 3.

From an independent experiment[17] the second-order rate constant for dipropylmagnesium of 0.156 ± 0.019 L mol^{-1} s^{-1} was found. Similarly to the calculations for the silane reaction a statistical analysis of the rate data from ref 4 was performed for the concentration range of the Grignard reagent 0.2 to 0.8 M. Rate constants in eq 9 were found to be $k_2 = 0.704 \pm 0.017$ L mol^{-1} s^{-1} and $k_4 = 2.04 \pm 0.09$ L^2 mol^{-2} s^{-2} ($R = 0.999$, $s = 0.0003$), the term with k_3 being statistically insignificant.

Some differences in comparison with the reaction of silanes occasionally do not appear. Preponderant reactivity of n-PrMgBr over dipropylmagnesium, reverse to phenylmagnesium compounds, can be rationalized regarding the steric requirements of the species in relation to the sterically encumbered ketone, pinacolone. As a consequence of the reactivities, together with higher proportion of RMgX species in the reagent (cf. Tables 1 and 3), the last term in eq 9 becomes significant at the expense of that with k_3.

The most important conclusion ensuing from the reasonings above is the general validity of the mechanism expressed by eq 9. It is remarkable that the electrophilic catalysis by magnesium halides was not considered before, particularly in the case of carbonyl compounds. While transition states for the Grignard addition reaction incorporating two organomagnesium species were discarded for numerous reasons long ago,[3,5] it appears that similar six-member transition states including a magnesium halide molecule (Chart 3) can occur, being important in the case of Grignard reagents with the Schlenk equilibrium shifted toward symmetrical species.

Reactivity of Chlorosilanes. As this work was the first comprehensive kinetic study of the Grignard reaction with silanes in THF, it was of interest to involve some other chlorosilanes in addition to methyltrichlorosilane exploited as the model compound in the investigation. While with methyltrichlorosilane formation of methylphenyldichlorosilane was investigated, with methylphenyldichlorosilane and methylvinyldichlorosilane rate constants for formation reactions of methyldiphenylchlorosilane and methylphenylvinylchlorosilane respectively were determined. The pseudo-first-order rate constants in Table 4 provide a comparison of the reactivities of the chlorosilanes.

CHART 3

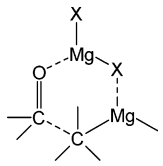


TABLE 4. Pseudo-First-Order Rate Constants, $k \times 10^3$ s^{-1}, for the Reactions of Chlorosilanes with 0.5 M Phenylmagnesium Halides in THF at 20 °C

silane	PhMgCl	PhMgBr
$MeSiCl_3$	115	44.7
$MePhSiCl_2$	1.28	0.86
$MeViSiCl_2$	32	23.4

The reaction in THF is much faster than that in diethyl ether, e.g. the corresponding rate constant for the reaction of PhMgBr with $MeSiCl_3$ in diethyl ether is as small as 1.62×10^{-3} s^{-1}.[2e] Also, higher reactivity of phenylmagnesium chloride is evident. In chlorosilanes, both polar and steric effects of substituents seem to be efficient. Indeed, in Charton terms,[18a] the phenyl group and a chlorine substituent exhibit close steric demands; however, substitution of a chlorine atom for the phenyl group reduces the reactivity of methylchlorosilanes by two powers of 10 in accordance with their inductive effects.[18b] Similarly, close inductive effects of vinyl and phenyl groups allow their different steric effects to become evident, although a contribution from the resonance effect cannot be excluded. A considerable contribution from the steric effect has been observed also for the Grignard reaction with alkoxysilanes.[2c]

Conclusions

We have carried out the first comprehensive kinetic investigation of the Grignard reaction with chlorosilanes in THF. The reaction in THF is much faster than that in diethyl ether.

The Schlenk equilibrium is concentration dependent in THF. Assuming coordination of magnesium halides with three molecules of THF, concentrations of all the species involved in the Schlenk equilibrium can be calculated for any Grignard reagent concentration. In the Grignard reaction, species R_2Mg and RMgX react competitively accompanied by additional reaction paths involving electrophilic catalysis by magnesium halide. This conclusion is also valid for the Grignard reaction with ketones and probably can be expanded to any Grignard reaction. However, when the Schlenk equilibrium is shifted far to the RMgX species, e.g. in diethyl

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ether, the other pathways, particularly the catalytic ones, are insignificant and hardly observable in experiment.

We were able to show that substituents at the silicon center control the rate of the reaction through their inductive and steric effects.

Experimental Section

The reagents and solutions were handled under dry argon and transferred by use of cannulas or syringes. Grignard reagents were obtained by conventional methods.[19]

To obtain diphenylmagnesium in THF, phenylmagnesium bromide was prepared in diethyl ether, magnesium bromide was precipitated with dioxane, diethyl ether was removed from the supernatant solution under reduced pressure, and the solid residue was dissolved in tetrahydrofurane.

Grignard reagents in THF−hydrocarbon mixtures were prepared by dilution of concentrated stock solutions in THF with appropriate amounts of THF and/or hydrocarbon (toluene or dichloromethane).

Kinetic Measurements. The reaction was carried out in a glass vessel mantled with foam plastic and placed in a thermostated housing. The equipment was sealed with a thermostated lid. The reaction cell was provided with a magnetic stirrer and a thermistor, which was connected through a bridge circuit to a recording potentiometer.

All parts of the equipment and the reagents were thermostated. The reaction vessel was purged thoroughly with pure argon, 15 mL of the Grignard reagent was cannulated into the cell, and the stirring was started. After the thermal equilibrium was set, 0.05 mL of silane was added providing a (20−40)-fold excess of Grignard reagent, and the temperature change of the reaction solution (usually up to 1 °C) was recorded as a plot of temperature versus time. Because the system was nearly adiabatic, the heat exchange with the internal part of the calorimeter caused only a little heat loss to an extent of a few percent.

First-order rate constants were usually calculated from the first two or three half-periods of the reaction (30 to 300 s). Use of a differential method[20] for calculation of rate constants practically eliminated the contribution of heat exchange with the reaction vessel.

The essence of the method consists of replacement of differentials by intervals in the equation for a first-order rate constant

$$k = -\frac{\mathrm{d}}{\mathrm{d}t}\ln\frac{\mathrm{d}T}{\mathrm{d}t}$$

where T denotes temperature. Thus the rate constant can be found from the linear plot of $\ln(\Delta T/\Delta t)$ vs t_m, where $\Delta T = T_{i+1} - T_i$, $\Delta t = t_{i+1} - t_i$, and $t_m = t_i + (t_{i+1} - t_i)/2$.

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