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Aminolysis of the Si–Cl bond and ligand exchange reaction between silicon amido derivatives and $SiCl_4$: synthetic applications and kinetic investigations†

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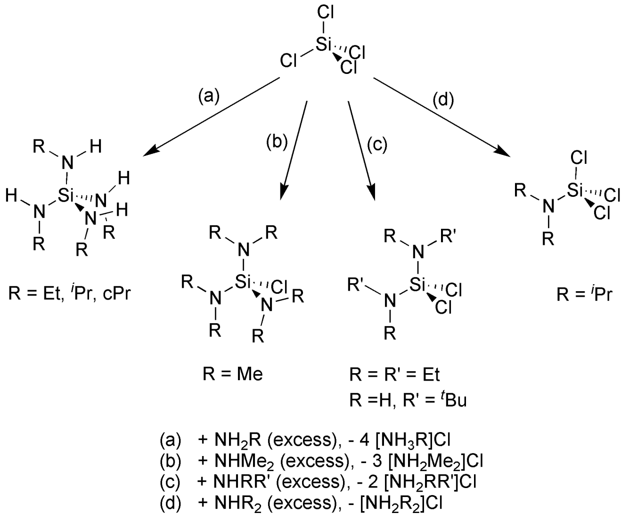
The aminolysis of the Si–Cl bond in $SiCl_n(NR_2)_{4-n}$ (n = 1, 2, 3, 4) has been employed for the synthesis of binary amido, chloro–amido or mixed amido derivatives, depending on the nature of the silicon derivative and of the amine. The kinetics of the reaction have been investigated in some representative cases, *i.e.* $SiCl_4$ + NH^iPr_2, $SiCl(NMe_2)_3$ + $NH_2{}^iPr$, $SiCl_2(NEt_2)_2$ + $NH_2{}^iPr$, showing that the rate law is first-order with respect to the silicon compound and does not depend on the concentration of the amine. Moreover, the activation parameters of the reaction of $SiCl_2(NEt_2)_2$ with $NH_2{}^iPr$ have been determined. The ligand exchange reaction between $SiCl_4$ and $SiCl_n(NR_2)_{4-n}$ yields a number of chloro–amido derivatives, whose composition is strictly determined by the molar ratio of the reactants. The kinetics of the reaction between $SiCl_4$ and $SiCl_n(NR_2)_{4-n}$ were investigated for n = 3, R = Me, and n = 2, R = Et. Moreover in the latter case the equilibrium and activation parameters have been determined.

Introduction

The synthesis of silicon amido derivatives (SADs) is an area of great interest due to the application of these compounds in the preparation of silicon nitride *via* CVD[1,2] or of polymeric high performance silicon–based ceramics.[3] Moreover, these derivatives have been used in the synthesis of adducts or cage–compounds containing elements of Groups 4,[4] 13[5,6] and 14.[5]

The synthesis of SADs is generally based on the halide substitution operated by lithium amides or amines, the halide being eliminated as the lithium or the ammonium salt, respectively. As a matter of fact, some examples are reported of compounds of general formula $SiR_n(amide)_{4-n}$ (R = H, alkyls, halides).[7–9]

In this connection, to the best of our knowledge, a systematic investigation of the interaction of primary or secondary amines with $SiCl_4$ is not available in the literature. Therefore, we undertook a study of the $SiCl_4$–amine (primary or secondary) system, in order to: (a) clarify the parameters affecting the course of the reaction and the nature of the final product(s); (b) investigate the kinetics of the aminolysis.



Scheme 1

Results and discussion

Reaction of $SiCl_4$ with amines

The reaction of $SiCl_4$ with an excess of primary or secondary amines (amine/Si molar ratio = 10) affords the amido-derivatives $SiCl_n(amide)_{4-n}$ reported in Scheme 1. Interestingly, the least hindered amines $NH_2{}^iPr$, NH_2cPr (cPr = cyclopropyl) and NH_2Et afford the tetraamido species $Si(NHR)_4$. On the other hand, $NHMe_2$ reacts with $SiCl_4$ affording the trisamido species $SiCl(NMe_2)_3$, even after prolonged reaction times, and only in the presence of a large excess of the amine. The diethyl and the *tert*-butyl amines react with $SiCl_4$ yielding the dichloro derivatives $SiCl_2(NR_2)_2$ (NR_2 = NEt_2, NH^tBu), thus showing that: (a) the increased steric hindrance of diethylamine with respect to $NHMe_2$ prevents the formation of the monochloro species $SiCl(NEt_2)_3$; (b) the formal substitution of the methyne hydrogen in $NH_2{}^iPr$ with a methyl group makes the primary amine so hindered that only the substitution of two chlorine atoms is observed.

The ^{1}H-NMR characteristic resonances of the amido groups in $SiCl_n(amide)_{4-n}$ are reported in Table 1. As far as the dialkylamido derivatives are concerned, expected ^{1}H-NMR spectral patterns are observed, *i.e.* the multiplicities due to the ^{1}H–^{1}H vicinal coupling ($^3J_{HH}$ in the range 5–10 Hz). On the other hand, the ^{1}H-NMR spectra of the monoalkylamido species show the ^{1}H–^{1}H coupling between the NH proton and the vicinal protons, *i.e.* the methylene and methyne protons of the NHEt and NH^iPr groups, respectively. As a matter of fact, the signal of the CH proton in $Si(NH^iPr)_4$ appears as a doublet of septets, due to the coupling to the methyl ($^3J_{HH}$ = 6.4 Hz) and to the NH ($^3J_{HH}$ = 9.8 Hz) protons. On the other hand, the signal of the methylene protons in $Si(NHEt)_4$ appears as a quintet, reasonably due to similar coupling to the methyl and to the NH protons ($^3J_{HH}$ = 7.1 Hz). As a confirmation, the proton COSY spectra of $Si(NHEt)_4$ and $Si(NH^iPr)_4$ show cross-peaks between the resonance of the NH proton and the resonances of the vicinal methylene or methyne protons, respectively.

It is of note that the signal of the NH proton appears as a doublet of two broad lines or eventually a single broad line, reasonably due to the quadrupolar effect of the ^{14}N nucleus.

The ^{13}C-NMR spectra of the compounds show the characteristic signals of the ^{13}C nuclei of the amido groups (Table 1);

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† Electronic supplementary information (ESI) available: details of the aminolysis and the ligand exchange reaction. See http://www.rsc.org/suppdata/dt/b2/b210282j/

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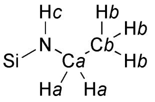
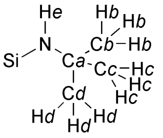
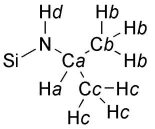
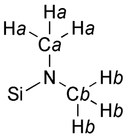
Table 1 Spectroscopic and analytical data for the compounds $SiX_n(NR_2)_{4-n}$ (X = Cl, NR'_2)

Compound	δ_H	δ_C	Analysis (%) C	H	N	Cl	Yield (%)	Ref.
$Si(NHEt)_4$	2.84, 1.05, 0.39	36.2, 20.7	47.2	11.4	27.0	—	76	[a]
$Si(NHcPr)_4$	2.23, 1.04, 0.39, 0.38, 0.36	23.8, 8.8	56.9	10.0	22.1	—	91	[a]
$Si(NH^iPr)_4$	3.22, 1.11, 0.35	42.6, 28.3	55.0	12.8	20.9	—	87	[a]
$SiCl(NH^iPr)_3$	3.23, 1.02, 0.82	—	45.5	10.5	17.5	14.7	92	[a]
$SiCl_2(NH^iPr)_2$	3.17, 1.11, 0.88	43.5, 26.5	33.2	7.4	12.8	32.5	89	[a]
$SiCl(NMe_2)_3$	2.43	37.1	36.9	8.9	22.0	18.0	89	9[a]
$SiCl_2(NMe_2)_2$	2.34	36.7	25.5	6.8	15.2	38.1	93	[a]
$SiCl_3(NMe_2)$	2.17	—	13.4	3.5	8.0	60.0	85	[a]
$SiCl_2(NEt_2)_2$	2.88, 0.94	39.5, 14.6	39.8	8.1	11.2	29.4	95	[a]
$SiCl_3(NEt_2)$	2.74, 0.80	—	23.0	5.2	6.8	51.9	82	[a]
$SiCl_2(NH^tBu)_2$	1.49, 1.11	50.6, 32.5	39.1	8.0	11.9	29.2	88	[a]
$SiCl_3(N^iPr_2)$	2.79, 1.05	40.3, 23.8	30.9	5.8	6.2	45.1	91	[a]
$Si(NMe_2)(NH^iPr)_3$	3.16, 2.62, 1.09, 0.35	42.5, 38.5, 28.1	53.2	12.0	23.0	—	95	[a]
$Si(NMe_2)_2(NH^iPr)_2$	3.07, 2.59, 1.06, 0.31	42.5, 38.1, 28.1	51.5	12.0	23.9	—	95	[a]
$Si(NMe_2)_3(NH^iPr)$	3.03, 2.55, 1.05, 0.33	42.6, 38.2, 28.1	49.8	12.2	26.0	—	87	[a]
$SiCl(NEt_2)_2(NH^iPr)$	3.19, 2.98, 1.11, 1.07, 0.37	42.5, 39.7, 28.1, 15.7	49.5	10.9	16.0	12.9	82	[a]

[a] This work.

Table 2 CH coupling constants (^1J, ^2J, ^3J) for $SiX_n(NR_2)_{4-n}$ (X = Cl, NR'_2) and the numbering scheme

$Si(NHEt)_4$		
C*a*–H*a*	133.2	
C*b*–H*b*	124.7	
C*a*–H*b*	4.4	
C*b*–H*a*	2.9	
$SiCl_2(NH^tBu)_2$		
C*a*–H*e*	1.5	
C*a*–H*b*,*c*,*d*	4.1	
C*b*–H*b*(C*c*–H*c*, C*d*–H*d*)	125.6	
C*b*–H*c*,*d*(C*c*–H*b*,*d*, C*d*–H*b*,*c*)	4.4	
C*b*,*c*,*d*–H*e*	3.2	
$Si(NH^iPr)_4$		
C*a*–H*a*	133.5	
C*a*–H*d*	1.8	
C*a*–H*b*,*c*	4.8	
C*b*–H*b* (C*c*–H*c*)	124.4	
$Si(NH^iPr)(NMe_2)_3$		
C*a*–H*a*	131.2	
C*b*–H*b* (C*c*–H*c*)	125.1	
C*c*–H*a* (C*b*–H*a*)	2.5	
C*c*–H*b* (C*b*–H*c*)	5.1	
$SiCl(NMe_2)_3$		
C*a*–H*a* (C*b*–H*b*)	134.1	
C*b*–H*a* (C*a*–H*b*)	5.0	
$Si(NH^iPr)(NMe_2)_3$		
C*a*–H*a* (C*b*–H*b*)	137.3	
C*b*–H*a* (C*a*–H*b*)	5.1	

moreover, for $Si(NH^iPr)_4$, $Si(NHEt)_4$, $SiCl_2(NH^tBu)_2$, $SiCl(NMe_2)_3$ the $^1J_{CH}$, $^2J_{CH}$ and eventually the $^3J_{CH}$ are observed, thus indicating the occurrence of long-range CH couplings (Table 2).

As far as $Si(NHcPr)_4$ is concerned, some additional remarks are in order. The ^{13}C-NMR spectrum shows two lines at 23.8 and 8.8 ppm, due to the methyne and methylene carbon atoms, respectively. On the other hand, five signals have been observed in the ^{1}H-NMR spectrum: the signal of the methyne proton is a multiplet at 2.23 ppm, due to the vicinal coupling to NH and methylene protons; the signal of the NH proton is a broad line at 1.04 ppm; three resonances are observed for the methylene protons at 0.39, 0.38, 0.36 ppm (integral ratio 1:1:2), thus indicating the occurrence of three different chemical environments for them.

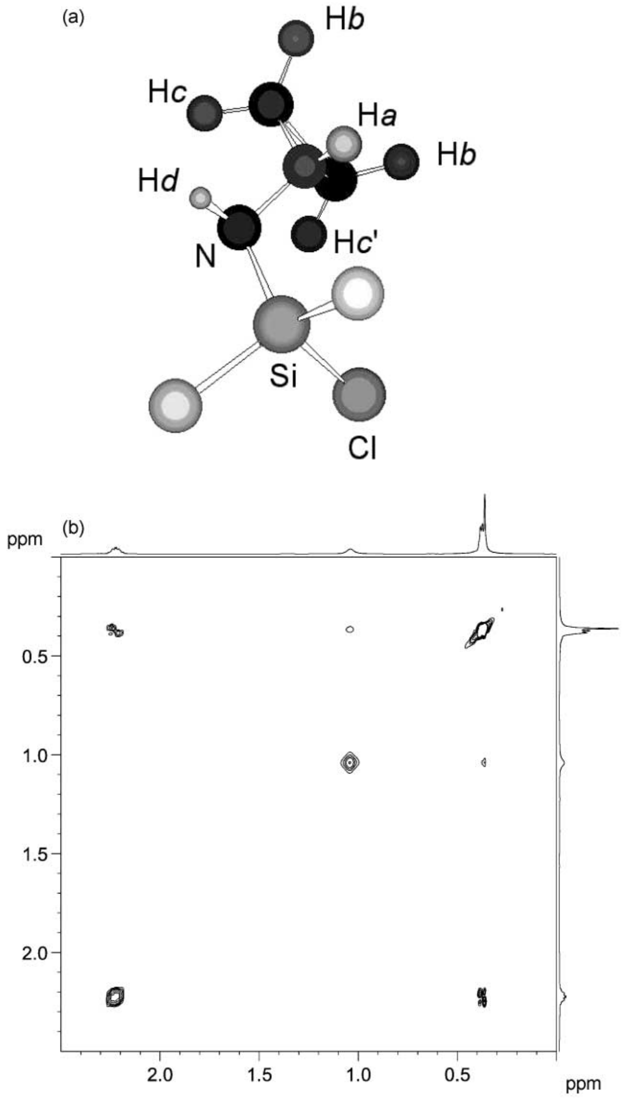


Fig. 1 (A) Optimised molecular[10] structure of $SiCl_3(NHcPr)$. (B) Proton NOESY spectrum of $Si(NHcPr)_4$.

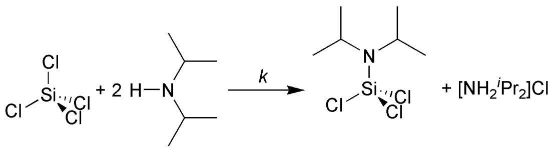
As a matter of fact, the optimised structure[10] of $SiCl_3(NHcPr)$ (Fig. 1A), chosen as representative for the arrangement of the amido ligand, shows that three different methylene protons can be recognised, *i.e.* the two H*b* protons (*syn* with respect to the methyne proton) and the H*c* and H*c*′ protons (*anti* with respect to the methyne proton) one "looking" at the NH proton, and the other facing the silicon. Therefore, the preliminary assignment of the resonances in the range 0.35–0.40 ppm is the following: 0.36 ppm (H*b*), 0.38 ppm (H*c* or H*c*′), 0.39 ppm (H*c*′ or H*c*).

The proton NOESY spectrum of Si(NHcPr)$_4$ (Fig. 1B) shows negative cross-peaks between the resonances at 0.36 (H*b*) and 2.23 ppm (CH), thus confirming the above-proposed assignment. On the other hand, negative crosspeaks are observed between the resonances at 0.38 and 1.04 ppm, and between those at 2.23 and 1.04 ppm, thus confirming the proposed mutual orientation of the NH and CH protons, and indicating that the resonance at 0.38 ppm is due to H*c*, and that, therefore, H*c*′ is responsible for the signal at 0.39 ppm.

Kinetics

Aminolysis. The kinetics of the aminolysis of the Si–Cl bond in $SiCl_4$, $SiCl_2(NEt_2)$ and $SiCl(NMe_2)_3$ were investigated by reacting these derivatives with primary or secondary amines (in C_6D_6), and monitoring the signals of the reactants and of the product(s) by sequential ^{1}H-NMR spectra (of note is the fact that the signals of [amineH]Cl have not been detected due to the low solubility of this salt in the reaction medium). In the case of $SiCl_2(NEt_2)_2$, the course of the reaction was monitored at three different temperatures, in order to estimate the activation parameters.

As anticipated, the reaction of $SiCl_4$ with NH^iPr_2 yields the trichloro derivative $SiCl_3(N^iPr_2)$ (Scheme 2). The plot of the conversion (297 K) *vs.* time of one of the experiments carried out ($[SiCl_4] = 0.223$ M; $[NH^iPr_2] = 0.964$ M) is reported in Fig. 2. The experimental data proves that the rate law is first-order with respect to $[SiCl_4]$ and does not depend on the concentration of the amine ‡ (Scheme 2), the calculated kinetic constant being reported in Table 3.



$$\frac{d[SiCl_3(N^iPr_2)]}{dt} = k\,[SiCl_4]$$

Scheme 2

As far as the aminolysis of $SiCl_2(NEt_2)_2$ operated by $NH_2{}^iPr$ is concerned, the reaction yields the chloro–amido derivative $SiCl(NH^iPr)(NEt_2)_2$ (Scheme 3). The conversion of the reactant *vs.* time is reported in Fig. 3, for three temperatures.

The experimental data indicate a first-order rate law with respect to $SiCl_2(NEt_2)_2$, the reaction rate not depending on the concentration of the amine ‡ (Scheme 3). The calculated kinetic constants are reported in Table 3. The activation parameters of the reaction have been derived from the Arrhenius plot: $\Delta H^{\#} = 93 \pm 5$ kJ mol^{-1}, $\Delta S^{\#} = 300 \pm 20$ J K^{-1} mol^{-1}. The positive value of $\Delta S^{\#}$ indicates that a dissociative pathway (*i.e.* S_N1) is operating and that the intermediate should be the tricoordinate derivative $[SiCl(NEt_2)_2]^+$.

Table 3 Kinetic constants (k/min^{-1}) for the aminolysis of the Si–Cl bond in $SiCl_n(NR_2)_{4-n}$

$SiCl_4 + 2NH^iPr_2$ (*cf.* Scheme 2)	
$T = 297$ K	$\ln k = -0.69 \pm 0.03$
$SiCl_2(NEt_2)_2 + 2NH_2{}^iPr$ (*cf.* Scheme 3)	
$T = 283$ K	$\ln k = -7.62 \pm 0.01$
$T = 297$ K	$\ln k = -5.53 \pm 0.02$
$T = 303$ K	$\ln k = -5.03 \pm 0.01$
$SiCl(NMe_2)_3 + 2NH_2{}^iPr$ (*cf.* Scheme 4)	
$T = 297$ K	$\ln k = -8.75 \pm 0.01$

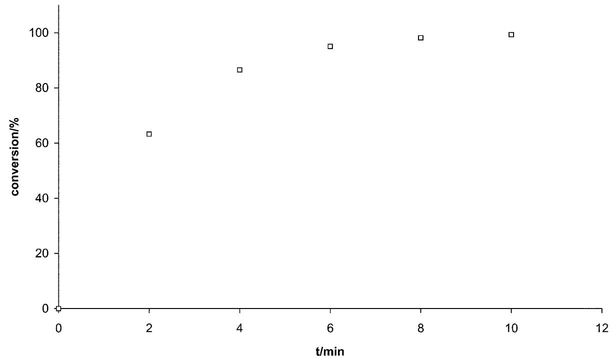


Fig. 2 Conversion *vs.* time for the reaction of $SiCl_4$ and NH^iPr_2 at 297 K.

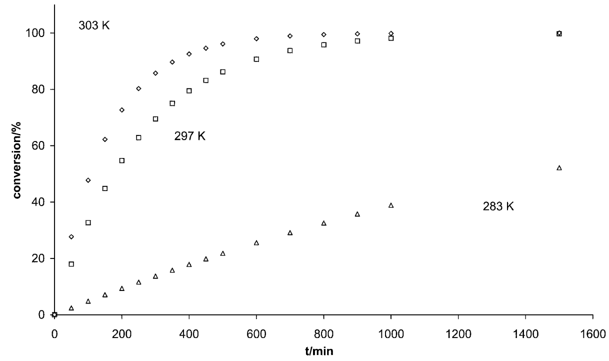
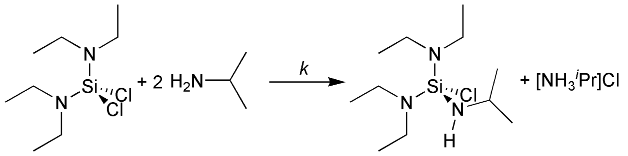


Fig. 3 Conversion *vs.* time for the reaction of $SiCl_2(NEt_2)_2$ with $NH_2{}^iPr$, yielding $SiCl(NH^iPr)(NEt_2)_2$ at 283 K ($[SiCl_4] = 0.306$ M; $[NH_2{}^iPr] = 1.42$ M), 297 K ($[SiCl_4] = 0.344$ M; $[NH_2{}^iPr] = 1.63$ M) and 303 K ($[SiCl_4] = 0.315$ M; $[NH_2{}^iPr] = 1.22$ M).



$$\frac{d[SiCl(NH^iPr)(NEt_2)_2]}{dt} = k\,[SiCl_2(NEt_2)_2]$$

Scheme 3

The aminolysis of the Si–Cl bond in $SiCl(NMe_2)_3$ was investigated with $NH_2{}^iPr$ (Scheme 4) and NH_2cPr (Scheme 5).

The reaction of $SiCl(NMe_2)_3$ with $NH_2{}^iPr$ affords the mixed-amido derivative $Si(NH^iPr)(NMe_2)_3$ (Scheme 4), the conversion being reported in Fig. 4 (after about 3.5 days the reaction was stopped, although not complete).

The experimental data indicate that the reaction rate is first-order with respect to $SiCl(NMe_2)_3$ and does not depend on the concentration of the incoming amine ‡ (Scheme 4), the kinetic constant being reported in Table 3.

At variance with $NH_2{}^iPr$, the reaction of $SiCl(NMe_2)_3$ with NH_2cPr yields the binary tetraamido derivative $Si(NHcPr)_4$, the

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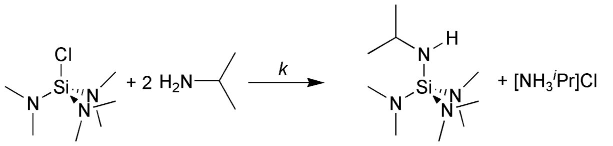
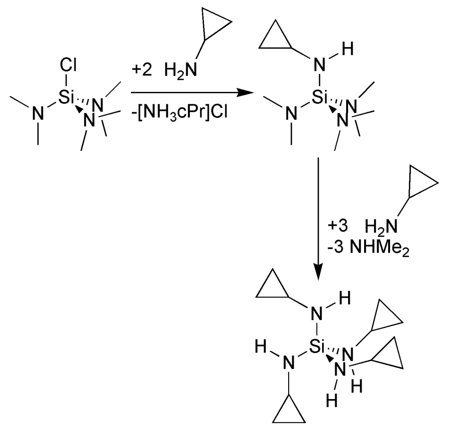
‡ The first-order dependence on the concentration of the silicon compound and the zero-order with respect to [amine] were unambiguously assessed by: (a) running the experiments with different starting amine/silicon molar ratios (*cf.* Experimental section, Table 4); (b) testing the integrated rate laws of the general differential equation $v = k[SiClX_3]^m[amine]^n$ ($m,n = 0,1,2$, X = Cl, NR_2) (*cf.* ESI †).



$$\frac{d[\mathrm{Si(NH^{\mathit{i}}Pr)(NMe_2)_3}]}{dt} = k\,[\mathrm{SiCl(NMe_2)_3}]$$

Scheme 4



$\mathrm{NHMe_2 + [NH_3cPr]Cl \longrightarrow [NH_2Me_2]Cl + NH_2cPr}$

Scheme 5

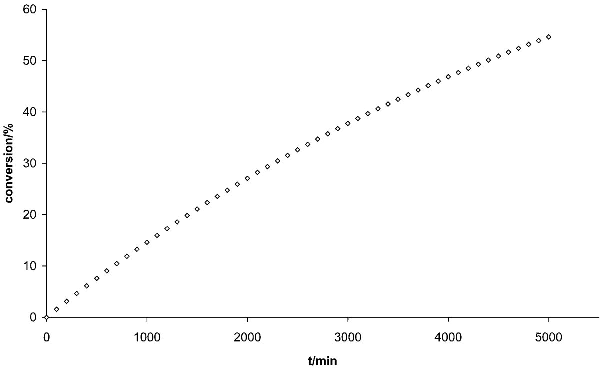


Fig. 4 Conversion *vs.* time for the reaction of $\mathrm{SiCl(NMe_2)_3}$ with $\mathrm{NH_2{}^{\mathit{i}}Pr}$, yielding $\mathrm{Si(NH^{\mathit{i}}Pr)(NMe_2)_3}$ at 297 K.

ammonium salt $\mathrm{[NH_2Me_2]Cl}$ being recovered as a substantially insoluble solid from the reaction mixture. Of note, $\mathrm{Si(NHcPr)(NMe_2)_3}$ is the only intermediate detected in the course of the reaction (*vide infra*). On these bases, Scheme 5 can be proposed, given the concentration of $\mathrm{[SiCl(NMe_2)_3]}$, $\mathrm{[Si(NHcPr)(NMe_2)_3]}$ and $\mathrm{[Si(NHcPr)_4]}$ *vs.* time reported in Fig. 5.

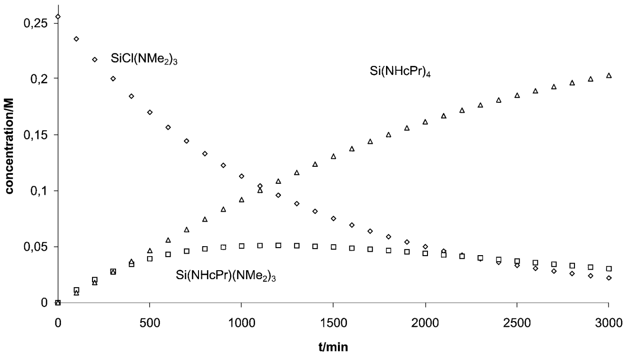


Fig. 5 Concentration *vs.* time of the species involved in the reaction of $\mathrm{SiCl(NMe_2)_3}$ with $\mathrm{NH_2cPr}$ at 297 K.

Reasonably, the chloro derivative reacts with NHcPr affording the mixed amido derivative $\mathrm{Si(NHcPr)(NMe_2)_3}$, which is still reactive towards $\mathrm{NH_2cPr}$, thus yielding the tetraamido species $\mathrm{Si(NHcPr)_4}$, no intermediate being detected.

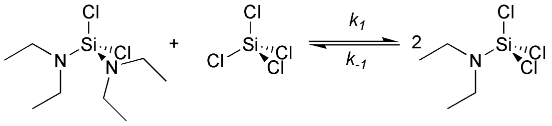
As far as the formation of $\mathrm{[NH_2Me_2]Cl}$ is concerned, we propose that once $\mathrm{[NH_3cPr]Cl}$ forms from the aminolysis of the Si–Cl bond, the $\mathrm{NHMe_2}$ [resulting from the reaction of $\mathrm{NH_2cPr}$ with the $\mathrm{Si(NMe_2)}$ functionality] reacts with it, affording $\mathrm{[NH_2Me_2]Cl}$ and $\mathrm{NH_2cPr}$. It is noteworthy that this is in agreement with the known higher basicity of secondary alkylamines with respect to the primary ones.[11]

In order to determine the rate laws and the kinetic constants, the fit of the experimental data was attempted but it was unsuccessful, reasonably due to the complexity of the reaction scheme. Nevertheless, it is noteworthy that the decay of $\mathrm{[SiCl(NMe_2)_3]}$ is exponential up to almost three half-lifetimes ($\tau_{1/2} = 800 \pm 50$ min).

As far as the different reactivity of $\mathrm{SiCl(NMe_2)_3}$ towards $\mathrm{NH_2{}^{\mathit{i}}Pr}$ with respect to $\mathrm{NH_2cPr}$ is concerned, some observations are in order. The reduced steric hindrance of $\mathrm{NH_2cPr}$ allows the reaction with both the Si–Cl bond and the $\mathrm{Si(NMe_2)}$ functionality. On the other hand, the more hindered alkyl group in $\mathrm{NH_2{}^{\mathit{i}}Pr}$ still allows the aminolysis of Si–Cl in $\mathrm{SiCl(NMe_2)_3}$ to occur, but prevents the reaction of the $\mathrm{Si(NMe_2)}$ functionality.

Ligand exchange reaction. Provided that little hindered amines yield exhaustive aminolysis of $\mathrm{SiCl_4}$, it appeared of interest to attempt the synthesis of mixed-amido derivatives using $\mathrm{SiCl}_n\mathrm{(amide)}_{4-n}$ as the starting material (*vide infra*). In this connection, the ligand exchange reaction between chloro–amido derivatives and $\mathrm{SiCl_4}$ seemed to be a valuable synthetic route affording $\mathrm{SiCl}_n\mathrm{(amide)}_{4-n}$. For this reason, the ligand exchange reaction was investigated, aiming at clarifying the nature of the products and its course. Two systems were chosen as representative, $\mathrm{SiCl_2(NEt_2)_2 + SiCl_4}$ and $\mathrm{SiCl(NMe_2)_3 + SiCl_4}$, and the reactions were monitored as a function of time by ^{1}H-NMR spectroscopy (in $\mathrm{C_6D_6}$). Moreover, in the case of $\mathrm{SiCl_2(NEt_2)_2}$, the experiments were carried out at three different temperatures.

The reaction of $\mathrm{SiCl_2(NEt_2)_2}$ with $\mathrm{SiCl_4}$ yielding $\mathrm{SiCl_3(NEt_2)}$ is reversible (Scheme 6), the conversion of $\mathrm{SiCl_2(NEt_2)_2}$ being reported in Fig. 6.



$$\frac{d[\mathrm{SiCl_3(NEt_2)}]}{dt} = k_1\,[\mathrm{SiCl_2(NEt_2)_2}] - k_{-1}\,[\mathrm{SiCl_3(NEt_2)}]$$

Scheme 6

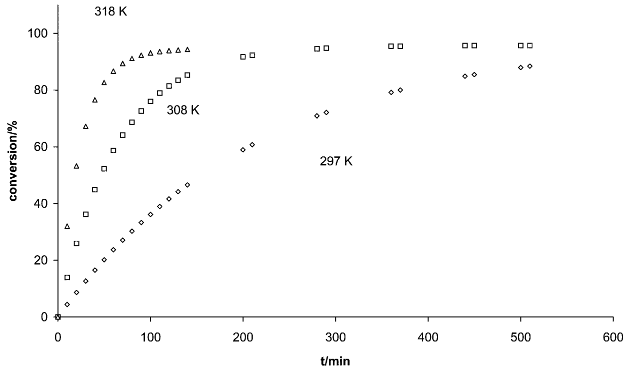


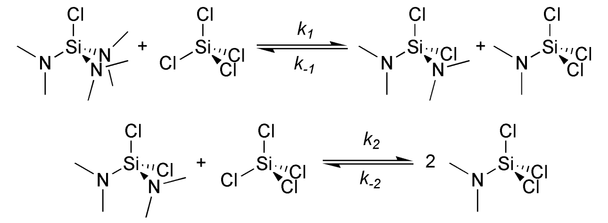
Fig. 6 Conversion *vs.* time for the reaction of $\mathrm{SiCl_2(NEt_2)_2}$ with $\mathrm{SiCl_4}$ yielding $\mathrm{SiCl_3(NEt_2)}$ at 297, 308 and 318 K.

The equilibrium constants have been calculated (*cf.* ESI †) at the three temperatures (297 K, $\ln K_{eq} = 8.1 \pm 0.2$; 308 K, $\ln K_{eq} = 6.3 \pm 0.2$; 318 K, $\ln K_{eq} = 5.7 \pm 0.2$), thus allowing to derive the enthalpy and entropy of the reaction: $\Delta H_r = -99 \pm 15$ kJ mol^{-1}, $\Delta S_r = -302 \pm 48$ J K^{-1} mol^{-1}.

As far as ΔH_r is concerned, the observed negative value is reasonably related to the steric hindrance release associated with the conversion of $SiCl_2(NEt_2)_2$ to $SiCl_3(NEt_2)$. On the other hand ΔS_r is unexpectedly negative; due to the transfer of one $[NEt_2]$ group from $SiCl_2(NEt_2)_2$ to $SiCl_4$ yielding $SiCl_3(NEt_2)$, one would expect that the entropy of the system should raise. Nevertheless, the number of conformers for $SiCl_2(NEt_2)_2$ is higher than for $SiCl_3(NEt_2)$ and, therefore, in our opinion, this could be the reason of the observed decrease of entropy.

As far as the kinetics are concerned, the forward reaction (Scheme 6) is first-order with respect to $[SiCl_2(NEt_2)_2]$, and the reverse reaction is first-order with respect to $[SiCl_3(NEt_2)_3]$ (*cf.* ESI †). This indicates that the limiting step involves only the species donating the amido group, *i.e.* $SiCl_2(NEt_2)_2$ in the forward reaction and $SiCl_3(NEt_2)_2$ in the reverse one. In addition, by measuring the kinetic constants (min^{-1}) at three different temperature (297 K, $\ln k_1 = -5.40 \pm 0.01$, $\ln k_{-1} = -9.76 \pm 0.01$; 308 K, $\ln k_1 = -4.19 \pm 0.01$, $\ln k_{-1} = -8.0 \pm 0.1$; 318 K, $\ln k_1 = -3.24 \pm 0.03$, $\ln k_{-1} = -6.8 \pm 0.5$) the activation parameters have been derived (direct reaction: $\Delta H^{\#} = 82.6 \pm 0.8$ kJ mol^{-1}, $\Delta S^{\#} = 267 \pm 3$ J K^{-1} mol^{-1}; reverse reaction: $\Delta H^{\#} = 120 \pm 8$ kJ mol^{-1}, $\Delta S^{\#} = 359 \pm 26$ J K^{-1} mol^{-1}), indicating a dissociative pathway for the reactions ($\Delta H^{\#}$ and $\Delta S^{\#}$ positive, for both the forward and reverse reaction), *i.e.* the rate limiting step should be the formation of the tricoordinate species $[SiCl_2(X)]^+$ ($X = NEt_2$, forward reaction; X = Cl, reverse reaction) through the dissociation of the amido group from the amido donating compounds.

The ligand exchange reaction between $SiCl_4$ and $SiCl(NMe_2)_3$ was monitored at 297 K (in C_6D_6), by recording sequential ^{1}H-NMR spectra. In the course of the reaction the formation of $SiCl_2(NMe_2)_2$ and $SiCl_3(NMe_2)$ was observed, thus suggesting the following reaction scheme (Scheme 7). The concentration *vs.* time is reported in Fig. 7, and the experimental rate laws are given in Scheme 7.



$$\frac{d[SiCl_3(NMe_2)]}{dt} = k_1\,[SiCl(NMe_2)_3]\cdot(k_{-1}+k_{-2})\,[SiCl_3(NMe_2)]+k_2\,[SiCl_2(NMe_2)_2]$$

$$\frac{d[SiCl_2(NMe_2)_2]}{dt} = k_1\,[SiCl(NMe_2)_3]-(k_{-1}-k_{-2})\,[SiCl_3(NMe_2)]-k_2\,[SiCl_2(NMe_2)_2]$$

Scheme 7

As observed in the ligand exchange reaction between $SiCl_2(NEt_2)_2$ and $SiCl_4$, the reactions are reversible and both the forward and reverse reactions are first order with respect to the species donating the amido group (*cf.* ESI †), *i.e.* $SiCl(NMe_2)_3$ and $SiCl_2(NMe_2)_2$ in the first and second forward reactions, respectively, and $SiCl_3(NMe_2)$ in both the first and second reverse reactions (k_i/min^{-1}; $\ln k_1 = -3.2 \pm 0.2$, $\ln k_{-1} = -6.0 \pm 0.3$; $\ln k_2 = -0.6 \pm 0.2$; $\ln k_{-2} = -5.0 \pm 0.3$).

The equilibrium constants of the two reactions have been determined (*cf.* ESI †) ($\ln K_{eq1} = 4.2 \pm 0.3$; $\ln K_{eq2} = 4.34 \pm 0.08$). Interestingly, as far as the ligand exchange between $SiCl_2(NR_2)_2$ and $SiCl_4$ is concerned, K_{eq} is higher for R = Et ($\ln K_{eq} = 8.1 \pm 0.2$) than for R = Me ($\ln K_{eq} = 4.34 \pm 0.08$), thus suggesting that the higher steric hindrance of the diethyl amido group makes the ligand exchange reaction more favourable, due to the higher steric release associated with the exchange.

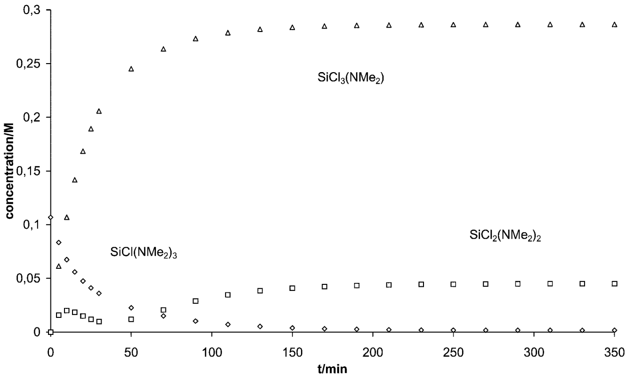
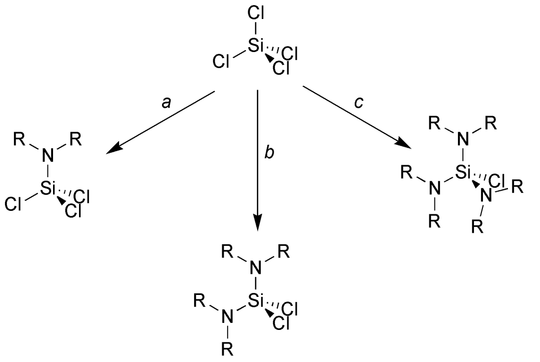


Fig. 7 Concentration (*vs.* time) of the products in the reaction of $SiCl(NMe_2)_3$ with $SiCl_4$. For clarity $[SiCl_2(NMe_2)_2]$ is scaled-up by 20.

Ligand exchange reactions

Due to the observed K_{eq} for the the ligand exchange reaction between $SiCl_n(amide)_{4-n}$ and $SiCl_4$ (amide = NEt_2, $n = 2$; amide = NMe_2, $n = 1$), it appeared that this reaction could be a valuable synthetic tool to mixed chloro–amido derivatives, containing a variable Cl/amide molar ratio.

As a matter of fact, as anticipated, the reaction between $SiCl_2(NEt_2)_2$ and $SiCl_4$ yields the trichloro derivative $SiCl_3(NEt_2)$, this compound being isolated as a pure material after 24 hours stirring at room temperature, after removing all the volatiles *in vacuo*. Moreover, this synthetic route has been fruitfully applied to the synthesis of a number of chloro–amido derivatives of general formula $SiCl_n(NR_2)_{4-n}$ (Scheme 8).



a + $SiCl_2(NEt_2)_2$; or +1/2 $SiCl(NMe_2)_3$
b + 2 $SiCl(NMe_2)_3$; or + $Si(NH^iPr)_4$
c + 3 $Si(NH^iPr)_4$

Scheme 8

The ^{1}H- and ^{13}C-NMR spectra of the compounds show the characteristic signals of the amido-groups (Table 1); in particular, the ^{1}H–^{1}H vicinal coupling is observed between the NH and the CH protons in $SiCl_n(NH^iPr)_{4-n}$ ($n = 1, 2$) ($^3J_{HH}$ about 10.0 Hz).

Synthesis of mixed amido derivatives

Once a number of chloro amido derivatives of general formula $SiCl_n(amide)_{4-n}$ were available (*vide supra*), the synthesis of mixed-amido derivatives was achieved by using these compounds as the starting materials. As a matter of fact, the reaction of chloro–amido derivatives with appropriate amines, such as dimethylamine or *iso*-propylamine, affords the expected mixed amido derivative (eqn. 1).

$$\mathrm{SiCl}_n(\mathrm{NR}_2)_{4-n} + 2m\ \mathrm{NHR}_2' \longrightarrow \mathrm{SiCl}_{n-m}(\mathrm{NR}_2')_m(\mathrm{NR}_2)_{4-n} + m\ [\mathrm{NH}_2\mathrm{R}_2']\mathrm{Cl} \qquad (1)$$

$$\begin{gathered}\mathrm{NR}_2 = \mathrm{NEt}_2,\ n = 2,\ \mathrm{NHR}_2' = \mathrm{NH}_2{}^i\mathrm{Pr},\ m = 1\\ \mathrm{NR}_2 = \mathrm{NMe}_2,\ n = 1, 2,\ \mathrm{NHR}_2' = \mathrm{NH}_2{}^i\mathrm{Pr},\ m = n\\ \mathrm{NR}_2 = \mathrm{NH}^i\mathrm{Pr},\ n = 1,\ \mathrm{NHR}_2' = \mathrm{NHMe}_2,\ m = 1\end{gathered}$$

The ^{1}H- and ^{13}C-NMR spectra show the characteristic signals of the amido groups (Table 1); moreover, similar to the other compounds above reported, (a) the ^{1}H–^{1}H vicinal coupling between the methyne and NH proton is observed in $\mathrm{Si(NH^iPr)}_n\mathrm{(NMe_2)}_{4-n}$ (n = 1, 2, 3), and (b) the $^1J_{\mathrm{CH}}$, $^2J_{\mathrm{CH}}$ and $^3J_{\mathrm{CH}}$ have been measured for $\mathrm{Si(NH^iPr)(NMe_2)_3}$ (Table 2), thus indicating the occurrence of long range CH couplings.

Conclusions

The aminolysis of the Si–Cl bond in $\mathrm{SiCl}_n\mathrm{(NR_2)}_{4-n}$ (n = 4; n = 3, $\mathrm{NR_2 = NMe_2}$; n = 2, $\mathrm{NR_2 = NEt_2}$) yielding the [Si(amide)] functionality is dramatically affected by the nature of the silicon reagent, *i.e.* the number of the Si–Cl involved in the reaction (Schemes 1–4) and the aminolysis' rate depend on the steric hindrance at the silicon centre. In addition, a dissociative pathway is postulable for the reaction, based on: (a) the positive values of $\Delta H^{\#}$ and $\Delta S^{\#}$ measured in the aminolysis of $\mathrm{SiCl_2(NEt_2)_2}$ with $\mathrm{NH_2{}^iPr}$; (b) the observed first-order rate law with respect to the derivatives bearing the Si–Cl bond (Schemes 2–4).

The ligand exchange reaction between $\mathrm{SiCl_4}$ and $\mathrm{SiCl}_n\mathrm{(NR_2)}_{4-n}$ is a general and valuable tool yielding chloro–amido derivatives with the desired Cl/$\mathrm{NR_2}$ ratio (Scheme 8), the composition of the chloro–amido product being strictly related to the molar ratio of the reactants. Moreover, the kinetic investigation of this reaction indicates that (a) the reaction is reversible; (b) the rate determining step involves only the amido-donor species [observed first-order rate law with respect to these species (Schemes 6, 7)]; and (c) the pathway is dissociative [positive $\Delta H^{\#}$ and $\Delta S^{\#}$ for both the forward and reverse reaction of $\mathrm{SiCl_2(NEt_2)_2}$ with $\mathrm{SiCl_4}$].

Experimental

All operations were carried out in a glove-box, under an atmosphere of dinitrogen. Elemental analyses (C, H, N) were performed using a Fisons Instruments analyser (Mod. EA 1108); the chlorine content of the samples was determined by potentiometric titration using a standard solution of silver nitrate (Aldrich). NMR spectra were recorded with a BRUKER AMX 300 spectrometer (300 MHz for ^{1}H). ^{1}H- and ^{13}C-NMR spectra are referred to TMS. The multiplicity is indicated as s (singlet), d (doublet), t (triplet), q (quartet), qn (quintet), sept (septet), tq (triplet of quartets), qt (quartet of triplets), qq (quartet of quartets), ds (doublet of septets), dsd (doublet of septets of doublets), qqd (quartet of quartets of doublets), qsd (quartet of septets of doublets), m (multiplet).

The following reagents were used as received: $\mathrm{SiCl_4}$ (silicon tetrachloride, Fluka), $\mathrm{NHMe_2}$ (dimethylamine, Fluka), $\mathrm{NH_2Et}$ (ethylamine, Fluka). The following amines were refluxed over BaO for 3 hours, distilled and stored under an atmosphere of dinitrogen; $\mathrm{NH_2{}^iPr}$ (isopropylamine, Fluka), $\mathrm{NH_2cPr}$ (cyclopropylamine, Fluka), $\mathrm{NHEt_2}$ (diethylamine, Fluka), $\mathrm{NH_2{}^tBu}$ (*tert*-butylamine, Fluka), $\mathrm{NH^iPr_2}$ (diisopropylamine, Fluka).

Reaction of $\mathrm{SiCl_4}$ with $\mathrm{NHR_2}$ ($\mathrm{NHR_2 = NHMe_2, NH_2Et, NH_2{}^iPr, NH_2cPr, NHEt_2, NH_2{}^tBu, NH^iPr_2}$

NHR_2 = $NHMe_2$, NH_2Et. Only the procedure for $\mathrm{NH_2Et}$ is reported in detail, the others being similar.

The gaseous amine $\mathrm{NH_2Et}$ was bubbled into a pentane solution (25 ml) of $\mathrm{SiCl_4}$ (1.20 g, 7.06 mmol) for 15 min, the mixture having been cooled to 263 K. The precipitation of a colourless solid was observed. Once at room temperature, the solid was filtered off, dried *in vacuo* and identified analytically (C, H, N, Cl) and spectroscopically (^{1}H-NMR) as $\mathrm{[NH_3Et]Cl}$ (2.1 g, 25.8 mmol of Cl). The pentane was removed *in vacuo* from the filtrate thus yielding a colourless liquid, which was identified as $\mathrm{Si(NHEt)_4}$ (1.10 g, 76% yield). Found: C, 47.2; H, 11.4; N, 27.0. $\mathrm{C_8H_{24}N_4Si}$ requires: C, 47.0; H, 11.8; N, 27.4%. δ_{H} ($\mathrm{C_6D_6}$, 293 K): 2.84 (qn, 2H, $\mathrm{CH_2}$, $^3J_{\mathrm{HH}}$ = 7.1 Hz), 1.05 (t, 3H, $\mathrm{CH_3}$, $^3J_{\mathrm{HH}}$ = 7.1 Hz), 0.39 (br, 1H, NH). δ_{C} ($\mathrm{C_6D_6}$, 293 K): 36.2 (tq, $\mathrm{CH_2}$, $^1J_{\mathrm{CH}}$ = 133.2, $^2J_{\mathrm{CH}}$ = 4.4 Hz), 20.7 (qt, $\mathrm{CH_3}$, $^1J_{\mathrm{CH}}$ = 124.7, $^2J_{\mathrm{CH}}$ = 2.9 Hz).

$\mathrm{SiCl(NMe_2)_3}$ (colourless liquid, 89% yield). Found: C, 36.9; H, 8.9; Cl, 18.0; N, 22.0. $\mathrm{C_6H_{18}ClN_3Si}$ requires: C, 36.8; H, 9.3; Cl, 18.1; N, 21.5%. δ_{H} ($\mathrm{C_6D_6}$, 293 K): 2.43 (s, $\mathrm{CH_3}$). δ_{C} ($\mathrm{C_6D_6}$, 293 K): 37.1 (qq, $\mathrm{CH_3}$, $^1J_{\mathrm{CH}}$ = 134.1, $^3J_{\mathrm{CH}}$ = 5.0 Hz).

NHR_2 = $NH_2{}^iPr$, NH_2cPr, $NHEt_2$, $NH_2{}^tBu$, NH^iPr_2. Only the procedure for $\mathrm{NH_2{}^iPr}$ is reported in detail, the others being similar.

A pentane solution (15 ml) of $\mathrm{NH_2{}^iPr}$ (2.70 mg, 45.7 mmol) was added dropwise to a pentane solution (15 ml) of $\mathrm{SiCl_4}$ (900 mg, 5.30 mmol). A colourless solid precipitated out. After 18 h stirring, the suspension was filtered: the solid was dried *in vacuo* and identified analytically (C, H, N, Cl) and spectroscopically (^{1}H-NMR) as $\mathrm{[NH_3{}^iPr]Cl}$ (1.90 g, 19.9 mmol of Cl). The filtrate was evaporated yielding a colourless solid, identified as $\mathrm{Si(NH^iPr)_4}$ (1.20 g, 87% yield). Found: C, 55.0; H, 12.8; N, 20.9. $\mathrm{C_{12}H_{32}N_4Si}$ requires: C, 55.3; H, 12.4; N, 21.5%. δ_{H} ($\mathrm{C_6D_6}$, 293 K): 3.22 (ds, 1H, CH, $^3J_{\mathrm{HH}}$ = 6.4, 9.8 Hz), 1.11 (d, 6H, $\mathrm{CH_3}$, $^3J_{\mathrm{HH}}$ = 6.4 Hz), 0.35 (d, 1H, NH, $^3J_{\mathrm{HH}}$ = 9.8 Hz). δ_{C} ($\mathrm{C_6D_6}$, 293 K): 42.6 (dsd, CH, $^1J_{\mathrm{CH}}$ = 133.5, $^2J_{\mathrm{CH}}$ = 1.8, 4.8 Hz), 28.3 (q, $\mathrm{CH_3}$, $^1J_{\mathrm{CH}}$ = 124.4 Hz).

$\mathrm{Si(NHcPr)_4}$ (colourless liquid, 91% yield). Found: C, 56.9; H, 10.0; N, 22.1. $\mathrm{C_{12}H_{24}N_4Si}$ requires: C, 57.1; H, 9.6; N, 22.2%. δ_{H} ($\mathrm{C_6D_6}$, 293 K): 2.23 (m, 1H, CH), 1.04 (br, 1H, NH), 0.39 (br, 1H), 0.38 (br, 1H), 0.36 (br, 2H). δ_{C} ($\mathrm{C_6D_6}$, 293 K): 23.8 (d, CH, $^1J_{\mathrm{CH}}$ = 172.2 Hz), 8.8 (t, $\mathrm{CH_2}$, $^1J_{\mathrm{CH}}$ = 160.5).

$\mathrm{SiCl_2(NH^tBu)_2}$ (colourless liquid, 88% yield). Found: C, 39.1; H, 8.0; Cl, 29.2; N, 11.9. $\mathrm{C_8H_{20}Cl_2N_2Si}$ requires: C, 39.5; H, 8.3; Cl, 29.1; N, 11.5%. δ_{H} ($\mathrm{C_6D_6}$, 293 K): 1.49 (br, 1H, NH), 1.11 (s, 9H, $\mathrm{CH_3}$). δ_{C} ($\mathrm{C_6D_6}$, 293 K): 50.6 (m, C, $^2J_{\mathrm{CH}}$ = 1.5; 4.1 Hz), 32.5 (qsd, $\mathrm{CH_3}$, $^1J_{\mathrm{CH}}$ = 125.6, $^3J_{\mathrm{CH}}$ = 4.4, 3.2 Hz).

$\mathrm{SiCl_2(NEt_2)_2}$ (colourless liquid, 95% yield). Found: C, 39.8; H, 8.1; Cl, 29.4; N, 11.2. $\mathrm{C_8H_{20}Cl_2N_2Si}$ requires: C, 39.5; H, 8.3; Cl, 29.1; N, 11.5%. δ_{H} ($\mathrm{C_6D_6}$, 293 K): 2.88 (q, 2H, $\mathrm{CH_2}$, $^3J_{\mathrm{HH}}$ = 7.1 Hz), 0.94 (t, 3H, $\mathrm{CH_3}$, $^3J_{\mathrm{HH}}$ = 7.1 Hz). δ_{C} ($\mathrm{C_6D_6}$, 293 K): 39.5 ($\mathrm{CH_2}$), 14.6 ($\mathrm{CH_3}$).

$\mathrm{SiCl_3(N^iPr_2)}$ (colourless liquid, 91% yield). Found: C, 30.9; H, 5.8; Cl, 45.1; N, 6.2. $\mathrm{C_6H_{14}Cl_3NSi}$ requires: C, 30.7; H, 6.0; Cl, 45.3; N, 6.0%. δ_{H} ($\mathrm{C_6D_6}$, 293 K): 2.79 (sept, 1H, CH, $^3J_{\mathrm{HH}}$ = 6.2 Hz), 1.05 (d, 6H, $\mathrm{CH_3}$, $^3J_{\mathrm{HH}}$ = 6.2 Hz). δ_{C} ($\mathrm{C_6D_6}$, 293 K): 40.3 (CH), 23.8 ($\mathrm{CH_3}$).

The ligand exchange reaction: synthesis of $\mathrm{SiCl}_x\mathrm{(NR_2)}_{4-x}$ ($\mathrm{NR_2 = NMe_2}$, x = 2, 3; $\mathrm{NR_2 = NEt_2}$, x = 3; $\mathrm{NR_2 = NH^iPr}$, x = 2, 3)

Only the procedure for $\mathrm{NR_2 = NMe_2}$ is reported in detail, the others being similar.

A pentane solution (15 ml) of $\mathrm{SiCl_4}$ (1.05 g, 6.18 mmol) was contacted with a pentane solution (15 ml) of $\mathrm{SiCl(NMe_2)_3}$ (2.40 g, 12.3 mmol). After 18 h stirring, the solvent was removed *in vacuo*, yielding a colourless liquid, which was identified as $\mathrm{SiCl_2(NMe_2)_2}$ (3.2 g, 93% yield). Found: C, 25.5; H, 6.8; Cl, 38.1; N, 15.2. $\mathrm{C_4H_{12}Cl_2N_2Si}$ requires: C, 25.7; H, 6.5; Cl, 37.9; N, 15.0%. δ_{H} ($\mathrm{C_6D_6}$, 293 K): 2.34 (s, $\mathrm{CH_3}$). δ_{C} ($\mathrm{C_6D_6}$, 293 K): 36.7 ($\mathrm{CH_3}$).

$\mathrm{SiCl_3(NMe_2)}$ (colourless liquid, 85% yield). Found: C, 13.4; H, 3.5; Cl, 60.0; N, 8.0. $\mathrm{C_2H_6Cl_3NSi}$ requires: C,13.5; H, 3.4; Cl, 59.6; N, 7.8%. δ_{H} ($\mathrm{C_6D_6}$, 293 K): 2.17 (s, $\mathrm{CH_3}$).

$\mathrm{SiCl(NH^iPr)_3}$ (colourless liquid, 92% yield). Found: C, 45.5; H, 10.5; Cl, 14.7, N, 17.5. $\mathrm{C_9H_{24}ClN_3Si}$ requires: C, 45.4; H, 10.2; Cl, 14.9; N, 17.7%. δ_H (C_6D_6, 293 K): 3.23 (m, 1H, CH), 1.02 (d, 6H, CH_3, ${}^3J_{HH}$ = 6.4 Hz), 0.82 (br, 1H, NH).

$SiCl_2(NH^iPr)_2$ (colourless liquid, 89% yield). Found: C, 33.2; H, 7.4; Cl, 32.5; N, 12.8. $C_6H_{16}Cl_2N_2Si$ requires: C, 33.5; H, 7.5; Cl, 32.9; N, 13.0%. δ_H (C_6D_6, 293 K): 3.17 (m, 1H, CH), 1.11 (br, 1H, NH), 0.88 (d, 6H, CH_3, ${}^3J_{HH}$ = 6.4 Hz). δ_C (C_6D_6, 293 K): 43.5 (d, CH, ${}^1J_{CH}$ = 135.3 Hz), 26.5 (t, CH_3, ${}^1J_{CH}$ = 125.7 Hz).

$SiCl_3(NEt_2)$ (colourless liquid, 82% yield). Found: C, 23.0; H, 5.2; Cl, 51.9; N = 6.8. $C_4H_{10}Cl_3SiN$ requires: C, 23.3; H, 4.9; Cl, 51.5, N, 6.8%. δ_H (C_6D_6, 293 K): 2.74 (q, 2H, CH_2, ${}^3J_{HH}$ = 7.1 Hz), 0.80 (t, 3H, CH_3, ${}^3J_{HH}$ = 7.1 Hz).

Synthesis of $SiCl_m(NR_2)_{x-m}(NR_2')_{4-x}$ ($NR_2 = NMe_2$, $NR_2' = NH^iPr$, $m = 0$, $x = 1, 2, 3$; $NR_2 = NEt_2$, $NR_2' = NH^iPr$, $m = 1$, $x = 3$)

Only the procedure for $NR_2 = NMe_2$, $NR_2' = NH^iPr$, $x = 3$, $m = 0$ is reported in detail, the others being similar.

A pentane solution (15 ml) of $SiCl(NMe_2)_3$ (920 mg, 4.70 mmol) was treated with a pentane solution (15 ml) of $NH_2{}^iPr$ (780 mg, 13.2 mmol). The prompt precipitation of a colourless solid was observed. After 12 h stirring, the solid was filtered off, dried *in vacuo* and identified analytically (C, H, N, Cl) and spectroscopically (^{1}H-NMR) as $[NH_3{}^iPr]Cl$ (402 mg, 4.21 mmol of Cl). The colourless filtrate was evaporated, yielding a liquid, identified as $Si(NH^iPr)(NMe_2)_3$ (890 mg, 87% yield). Found: C, 49.8; H, 12.2; N, 26.0. $C_9H_{26}N_4Si$ requires: C, 49.5; H, 12.0; N, 25.7%. δ_H (C_6D_6, 293 K): 3.03 (ds, 1H, CH), 2.55 (s, 18H, NCH_3), 1.05 (d, 6H, $CHCH_3$, ${}^3J_{HH}$ = 6.3 Hz), 0.33 (br, 1H, NH). δ_C (C_6D_6, 293 K): 42.6 (d, CH, ${}^1J_{CH}$ = 131.2 Hz), 38.2 (qq, NCH_3, ${}^1J_{CH}$ = 137.3 Hz, ${}^3J_{CH}$ = 5.1 Hz), 28.1 (qqd, $CHCH_3$, ${}^1J_{CH}$ = 125.1, ${}^2J_{CH}$ = 2.5, ${}^3J_{CH}$ = 5.1 Hz).

$Si(NH^iPr)_2(NMe_2)_2$ [from $SiCl_2(NMe_2)_2$ and $NH_2{}^iPr$; colourless liquid, 92% yield]. Found: C, 51.5; H, 12.0; N, 23.9. $C_{10}H_{28}N_4Si$ requires: C, 51.7; H, 12.1; N, 24.1%. δ_H (C_6D_6, 293 K): 3.07 (m, 2H, CH), 2.59 (s, 12H, NCH_3), 1.06 (d, 12H, $CHCH_3$, ${}^3J_{HH}$ = 6.4 Hz), 0.31 (br, 2H, NH). δ_C (C_6D_6, 293 K): 42.5 (CH), 38.2 (NCH_3), 28.1 ($CHCH_3$).

$Si(NH^iPr)_3(NMe_2)$ [from $SiCl(NH^iPr)_3$ and $NHMe_2$, colourless liquid, 95% yield]. Found: C, 53.2; H, 12.0; N, 23.0. $C_{11}H_{30}N_4Si$ requires: C, 53.6; H, 12.3; N, 22.7%. δ_H (C_6D_6, 293 K): 3.16 (m, 3H, CH), 2.62 (s, 6H, NCH_3) 1.09 (d, 18H, $CHCH_3$, ${}^3J_{HH}$ = 6.2 Hz), 0.35 (br, 3H, NH). δ_C (C_6D_6, 293 K): 42.5 (CH), 38.5 (NCH_3), 28.1 ($CHCH_3$).

$SiCl(NH^iPr)(NEt_2)_2$ [from $SiCl_2(NH^iPr)_2$ and $NH_2{}^iPr$, colourless liquid, 82% yield]. Found: C, 49.5; H, 10.9; Cl, 12.9; N, 16.0. $C_{11}H_{28}ClN_3Si$ requires: C, 49.7; H, 10.6; Cl, 13.3; N, 15.8%. δ_H (C_6D_6, 293 K): 3.19 (ds, 1H, CH, ${}^3J_{HH}$ = 9.9, 6.4 Hz), 2.98 (q, 8H, CH_2, ${}^3J_{HH}$ = 7.4 Hz), 1.11 (d, 6H, $CHCH_3$, ${}^3J_{HH}$ = 6.4 Hz), 1.07 (t, 12H, CH_2CH_3, ${}^3J_{HH}$ = 7.4 Hz), 0.37 (d, 1H, NH, ${}^3J_{HH}$ = 9.9 Hz). δ_C (C_6D_6, 293 K): 42.5 (CH), 39.7 (CH_2), 28.1 ($CHCH_3$), 15.7 (CH_2CH_3).

Kinetics

The reactions were carried out in 5 mm NMR tubes; the reactants and the solvent (C_6D_6) were introduced in the tube and the zero-time was taken at the addition of the second reagent. The evolution of the reaction was monitored by recording the ^{1}H-NMR spectra of the mixture at different times and measuring the integral ratios between representative peaks. The concentrations of the compounds and the temperature of the experiments are reported in Table 4.

Table 4 Selection of experimental conditions for the kinetic measurements

A + B	T/K	[A]/M	[B]/M
$SiCl_4 + NH_2{}^iPr$	297	0.223	0.964
	297	0.290	0.700
$SiCl_2(NEt_2)_2 + NH_2{}^iPr$	283	0.306	1.42
	297	0.344	1.63
	297	0.306	0.810
	297	0.153	0.483
	303	0.315	1.22
$SiCl(NMe_2)_3 + NH_2{}^iPr$	297	0.215	1.96
	297	0.362	1.78
$SiCl(NMe_2)_3 + NH_2cPr$	297	0.256	1.85
$SiCl_2(NEt_2)_2 + SiCl_4$	297	0.315	0.322
	308	0.280	0.310
	318	0.158	0.197
$SiCl(NMe_2)_3 + SiCl_4$	297	0.107	0.247

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