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Synthesis of Metastable $Si^{II}X_2$ Solutions (X = F, Cl). A Novel Binary Halide for Synthesis

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Keywords: Thermochemical calculations; Silicon; Subhalides; Thermodynamics

Abstract. Thermodynamic data for gaseous SiF_2 and $SiCl_2$ known from literature show that these binary subhalides are formed nearly quantitatively at 1376 °C and 1076 °C, respectively, as products of the reaction of elemental silicon with SiF_4 or $SiCl_4$ at 1×10^{-2} mbar. Applying the co-condensation technique SiF_2 as well as $SiCl_2$ can be trapped at –196 °C and prepared in synthetic scale. Herein, first analysis of metastable SiF_2 and $SiCl_2$ solutions are presented, showing that SiF_2 is more reactive than $SiCl_2$ leading to compounds of low boiling point of so far unknown composition. The metastable $SiCl_2$ solution can be used as a $SiCl_2$ source, which is shown by the trapping reaction with Idipp [Idipp = 1,3-bis(2,6-iPr$_2$-C$_6$H$_3$)imidazol-2-ylidene] leading to Idipp-$SiCl_2$. The reactivity of the solution might be fine-tuned by changing the donor opening the door for further applications.

Introduction

Subvalent halides of silicon in oxidation state +2 with the general formulae SiX_2 (X = F, Cl, Br, I) exhibit a lone pair of electrons at the silicon atom and possess a $^1\Sigma^+{}_g$ electronic ground state. Such silylenes are key intermediates in a variety of thermal and reduction reactions of silicon halides.[1] Hence such silylenes have first been analyzed spectroscopically in the gas phase during high temperature gas phase reactions.[2] First reactions applying these high temperature molecules were reported by *Timms* et al. in 1968, where they co-condensed $SiCl_2$ as well as SiF_2 with various reagents like acetylene, benzene, PCl_3, etc.,[3] showing that the expected high reactivity of the silicon(II) halide can be used even to attack benzene to yield a bicyclic product, where *cyclo*-butadiene is bridged by a $(SiF_2)_n$ group (n = 2,3), indicating that pure SiF_2 is even able to react with aromatic compounds.[4] Without a reagent SiX_2 polymerizes to $(SiX_2)_n$ or oligomerizes to $(SiX_2)_n$ rings (n = 4–6) or it disproportionates to Si and SiX_4.[5]

In 1998 it was shown by *West* et al. that the cyclic perchlorosilane Si_4Cl_8 can be transferred into the perchlorpolysilane $(SiCl_2)_x$, which could be structurally characterized, showing a Si–Si bound backbone.[6] Recently, *Roesky* et al.[7] and *Filippou* et al.[8] showed that N-heterocyclic carbenes (NHC's) like Idipp [Idipp = 1,3-bis(2,6-iPr$_2$-C$_6$H$_3$)imidazol-2-ylidene] can be used for the synthesis of Idipp-SiX_2 (X = Cl, Br, I), which might be described as a stabilized form of the silicon(II) halide. However the stabilization strongly reduces the reactivity of the halide so that it can be e.g. dissolved in tetrahydrofurane (thf) without decomposition. Nevertheless starting from the formal silicon(II) compound Idipp-$SiCl_2$ or Idipp-$SiBr_2$ a variety of further reactions were possible leading e.g. to the trisilaallene $Si_3(SitBu_2Me)_4$,[9] the silaisonitrile dimer $(SiNAr)_2$ (Ar = 2,6-iPr$_2$-C$_6$H$_4$),[10] or the NHC-stabilized halosilyliden complex $(C_5R_5)(CO)_2Cr{=}SiBr$-Idipp (R = H,[11] Me[12]) indicating the synthetic potential of the Idipp-SiX_2 compounds.[13] As the reactivity of the silicon(II) chloride is strongly reduced by the NHC we asked ourselves if it is possible to obtain silicon(II) halides with weaker donors exhibiting a fine-tuned reactivity. Thereby starting from the prototype high temperature gas phase molecule seems most appropriate as this compound already exhibits the correct anticipated oxidation state of the silicon atom.

Results and Discussion

For the synthesis of metastable silicon(II) halide solutions the preparative co-condensation technique seems most suitable as one can start directly from the high temperature molecule in the gas phase. This procedure has already been shown to work for other high temperature molecules like the group 13 monohalides Al^IX / Ga^IX (X = Cl, Br, I)[14] or the group 14 monohalides Ge^IX and Sn^IX (X = Cl, Br).[15] Thereby, the temperature as well as the pressure dependence of the central high temperature reaction $SiX_4(g) + Si(f) \rightarrow 2SiX_2(g)$ is calculated using tabulated thermodynamic data (see below). The gas phase molecules can afterwards be condensed with a variety of different mixtures of solvents as well as donor molecules so that a large spectrum of donor as well as solvent properties can

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Table 1. Enthalpy and entropy changes of the independent reactions in the systems SiX_4/Si (X = F, Cl). The standard values[16] $\Delta_fH°_{298}$ and $_fS°_{298}$ taken for the calculations are given in the legend [a].

	X = F $\Delta_rH°_{298}$ /kJ·mol^{-1}	$\Delta_rS°_{298}$ /J·mol^{-1}·K^{-1}	X = Cl $\Delta_rH°_{298}$ /kJ·mol^{-1}	$\Delta_rS°_{298}$ /J·mol^{-1}·K^{-1}
Si(s) + 2X(g) = SiX_2(g)	–746.7	–79.8	–411.2	–67.9
Si(s) + X(g) = SiX(g)	–99.5	48.2	77	53.8
$SiCl_2$(g) + 2X(g) = SiX_4(g)	–1185.8	–291.4	–736.7	–280.8
X_2(g) = 2X(g)	158.8	114.8	242.6	107.3

a) $\Delta_fH°_{298}$ ($_fS°_{298}$) values in kJ·mol^{-1} (J·mol^{-1}·K^{-1}) taken for the calculations: SiF: –20.1 (225.8); SiCl: 198.3 (237.8); SiF_2: –578.9 (256.6); $SiCl_2$: –168.6 (281.3); SiF_4: –1614.9 (282.8); $SiCl_4$: –662 (330.9); F_2: 0 (202.8); Cl_2: 0 (223.1); Si(f): 0 (18.8); F: 79.4 (158.8); Cl: 121.3 (165.2).

be introduced into silicon(II) halide chemistry maybe gradually lowering the reactivity of the silicon(II) halide.

Composition of the Gas Phase, Thermochemical Calculations

By means of matrix isolation spectroscopy as well as by co-condensation techniques we proved that metastable solutions of subvalent group 13 monohalides are produced by high temperature reaction of the condensed phase (aluminum or gallium) with a gaseous component in a completely thermodynamic controlled manner.[14] Therefore it is possible to determine the composition of the gas phase over such a solid or liquid by thermochemical calculations. Accurately determined experimental standard values of enthalpy and entropy are known for all the possible components of the present problem.[16] In the chemical equilibrium of SiX_4 (X = F, Cl) over solid or liquid silicon we assume the gaseous molecules X, X_2, SiX, SiX_2, and SiX_4 to appear depending on the temperature and the pressure. The four independent reactions, their heats of reaction $\Delta_rH°_{298}$ and their entropy changes $\Delta_rS°_{298}$ together with the applied standard values $\Delta_fH°_{298}$ and $_fS°_{298}$ are given in Table 1. The temperature dependence of $\Delta_fH°$ and $_fS°$ was not taken into account – the error resulting from this approximation is negligible.

The partial pressures of the five gaseous components are then determined iteratively according to the four expressions of the equilibrium constants and the conditional equation (i.e., the given constant total pressure).[17] In Figure 1 the partial pressure diagrams of the fluorine and chlorine systems are presented for a total pressure of 10^{-2} mbar, which is the typical pressure for the high temperature reaction performed in a reactor used for the preparative co-condensation technique.

Under these pressure conditions at a temperature between 1600 und 1700 K (X = F) as well as 1150 and 1700 K (X = Cl) the vapor over silicon consists of more than 95 % of the divalent species SiX_2. At 2000 K the equilibrium mixture of the system SiF_4/Si contains 52 % SiF_2 and 48 % SiF, whereas in the case of $SiCl_4$/Si 62 % $SiCl_2$, 30 % SiCl, and 8 % Cl atoms are formed. In Figure 2 the relative amount $p(SiX_2)/p_{total}$ with respect to the temperature and the total pressure of the system is presented. We found that – going from a total pressure of 10^{-5}, 10^{-2}, to 10 mbar – the temperature of the highest amount of SiX_2 increases from 1350, 1650, to 2050 K for the fluorine and from 1100, 1350, to 1700 K for the chlorine system.

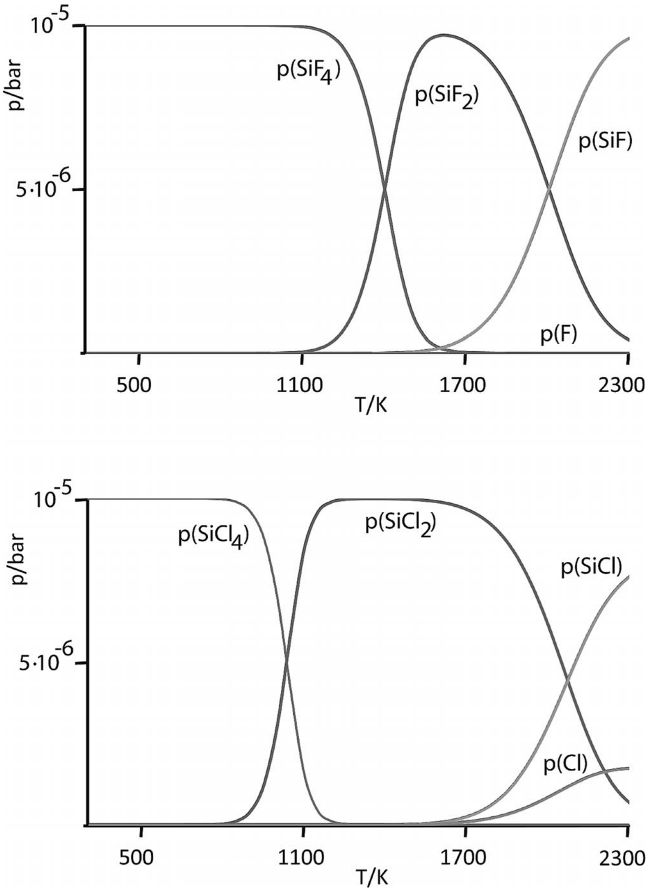


Figure 1. Diagram of the partial pressures of the components of the SiX_4/silicon system at a total pressure of 10^{-2} mbar; top: X = F; bottom: X = Cl.

In the case of the fluorine system the calculations thus show that a temperature of ca. 1700 K is needed to obtain a nearly quantitative amount of SiF_2 in the gas phase. This temperature is close to the melting point of silicon (1687 K). Hence for the synthesis an oven material is needed that can be used in combination with liquid silicon. Consequently the normally used pyrolytic graphite, which works well in the case of germanium and tin[15] cannot be used as it reacts with liquid silicon at this temperature to give SiC.[18] Additionally liquid silicon penetrates the normally used graphite.[19] Nevertheless glassy graphite can be used as crucible at this temperature as liquid silicon is not penetrating the glassy graphite and only

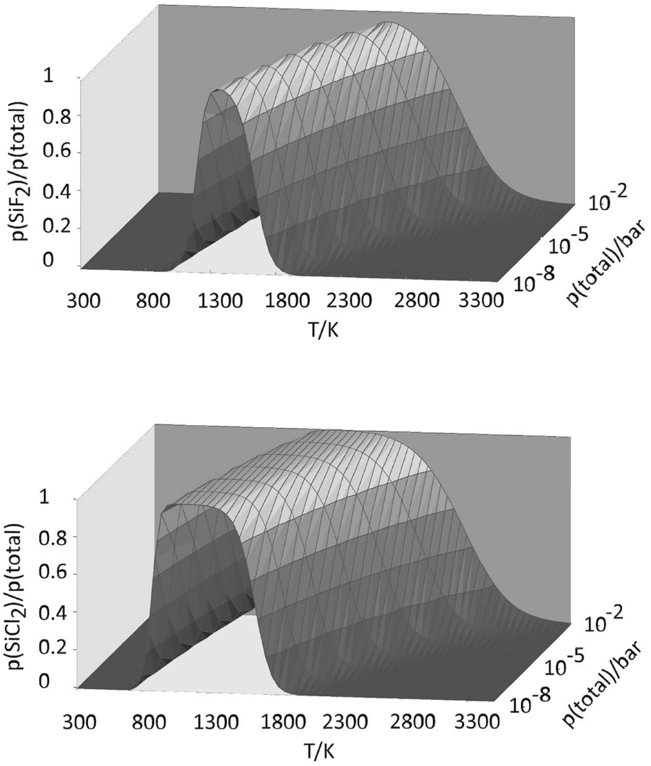
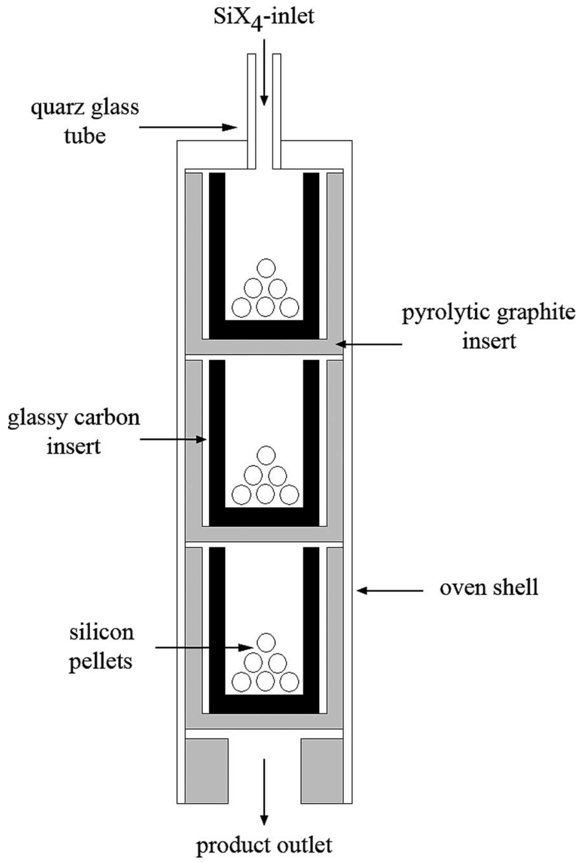


Figure 2. Diagram of the relative amounts $p(SiX_2)/p_{total}$ with respect to temperature and total pressure (top: X = F, bottom: X = Cl).



Scheme 1. Schematic presentation of the oven construction for the synthesis of silicon(II) halides by the high temperature reaction Si + $SiX_4 \rightarrow 2SiX_2$ (X = F, Cl). A photo of the new inlets is given in the Supporting Information.

reacting slowly with the surface to give SiC.[20] Thus we used a modified oven construction, where silicon is placed within glassy carbon inlets (Scheme 1).

Metastable SiF_2 Solutions

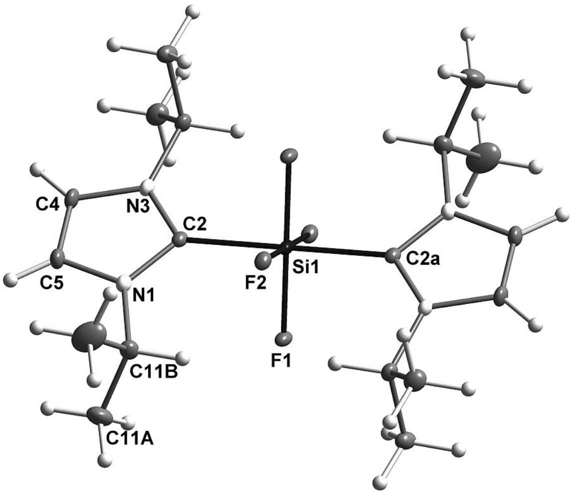


Figure 3. Molecular structure of $SiF_4[C(NiPrCH)_2]_2$ (**1**), thermal ellipsoids with 25 % probability. Selected bond lengths /pm and angles /°: Si1–F1:168.38(6); Si1–F2: 168.90(6); Si1–C2: 199.96(9); N1-C2: 135.8(1); C2–N3: 135.7(1); N3–C4: 138.4(1); C4–C5: 134.1(1); C5–N1: 138.6(1); N1–C11B: 147.9(1); C11B–C11A: 152.1(2); C2–Si1–C2a: 180.00(3); F1–Si1–F2: 90.48(3); N1–C2–N3: 104.71(8).

In a first experiment SiF_4 was reacted with elemental silicon slightly below the melting point at 1365 °C.[21] Thereby 20 mmol SiF_4 are applied and 7.5 mmol Si are consumed during the reaction, leading to an amount of SiF_2 in the gas phase of only 38 %. The gas phase molecules are condensed together with a solvent mixture of toluene and $P(n\text{Bu})_3$ as a donor component at –196 °C. After the co-condensation reaction is finished the solid matrix is heated to –78 °C with dry ice and after melting a pale yellow solution is obtained. On heating this solution to room temperature the color intensifies leading to a yellow-orange precipitate at the end that cannot be dissolved again. To get a first idea about the halide species present in solution we took 15 % of the –78 °C cold solution (ca. 4 mmol of silicon) and added the same amount of the carbene $C(N\textit{i}PrCH)_2$ as a trapping reagent. From this reaction solution we were able to obtain colorless crystals of the carbene adduct $SiF_4[C(N\textit{i}PrCH)_2]_2$ (**1**) (1 mmol; ca. 25 %), whose molecular structure is shown in Figure 3. Thus with the aid of the carbene we were able to trap the unreacted SiF_4 to give the hypercoordinated silicon compound $SiF_4[C(N\textit{i}PrCH)_2]_2$ (**1**), which crystallizes in the hexagonal crystal system with space group $R\bar{3}$, where the silicon atom is positioned on the inversion center leading to a stretched octahedral arrangement of the four fluorine and the two carbene ligands around the silicon atom.

The Si–F (168 pm) as well as the Si–C (200 pm) distances in **1** are thereby similar to a lately described isostructural adduct $SiF_4[Idipp]_2$ (**2**) [Idipp = 1,3-bis(2,6-$i$$Pr_2$-$C_6H_3$)imidazol-2-ylidene], which was synthesized by *Roesky* et al. by the reaction of SiF_4 with the bulkier carbene Idipp.[22] The main difference between both compounds in the solid state is as follows: in the case of **1** both carbenes are oriented parallel, whereas in the case of **2** the carbenes are oriented perpendicular to each other. However in the case of **1** this is only a packing effect as we were able to isolate a second sort (**1b**) of crystals of **1**, where toluene is incorporated in the crystal[23] and where the carbenes are now oriented perpendicular to each other (Figure 4).[24]

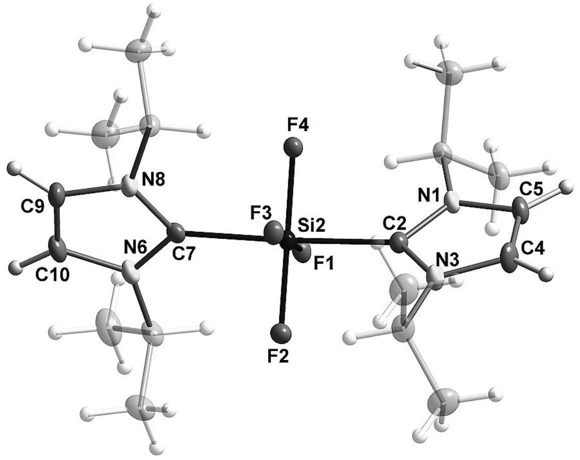


Figure 4. Molecular structure of $SiF_4[C(N\textit{i}PrCH)_2]_2$ (**1b**), thermal ellipsoids with 25 % probability. Selected bond lengths /pm and angles /°: Si2–F1:167.8(2); Si2–F2: 168.4(2); Si2–F3:168.4(2); Si2–F4: 167.7(2); Si2–C2: 203.1(3); Si2–C7: 202.3(3); C2–N1: 135.5(3); N1–C5: 138.0(4); C7–N6: 136.2(3); N6–C10: 138.2(4); C4–C5: 134.0(4); C10–C9: 133.0(4); C2–Si2–C7: 176.8(1); F1–Si2–F3: 178.68(10); F2–Si2–F4: 179.65(9); N1–C2–N3: 104.3(2); N6–C7–N8: 104.3(2).

In the case of **1b** the adduct **1** crystallizes in the monoclinic crystal system in space group $P2_1/c$ with two independent molecules in the asymmetric unit together with one toluene molecule. As the silicon atom is not placed on a symmetry center the fluorine atoms and the carbene carbon atoms are independent from each other, however again a nearly perfect stretched octahedral arrangement of the six substituents is realized as it was the case for **1**.

The orientation of the carbene ligands to each other thus seems to have no significant influence on the bonding to the central silicon atom as the Si–F (168 pm) as well as the Si–C (203 pm) bond lengths in **1b** are similar to the one in **1** within standard deviation.

Additionally in solution both arrangements gave the same NMR spectroscopic signals, indicating that the different arrangement of the carbene ligands in **1** and **1b** is only a result of packing effects. The ^{29}Si NMR signal appears thereby at –182 ppm, consistent with five or six coordinated silicon compounds[25] and the ^{19}F NMR signal appears at –102.5 ppm. ^{29}Si and ^{13}C satellites are detected with $^1J(^{19}F–^{29}Si)$ = 187.4 Hz and $^2J(^{19}F–^{13}C)$ = 61.5 Hz, showing that **1** stays intact in solution.

Nevertheless beside the SiF_4 adduct we were not able to isolate any further compound from the reaction mixture. Hence the excess of unreacted SiF_4 completely dominates the chemistry of the solution. To overcome this problem we increased the oven temperature during the co-condensation reaction in small steps from 1365 °C to 1510 °C (Table 2). Thereby the amount of silicon consumed during the reaction increases from 7.48 mmol to 19.97 mmol.

Table 2. Maximum oven temperature /°C applied and amount of silicon /mg (mmol) consumed during the high temperature reaction. In every reaction 20 mmol of SiF_4 are used.

T	1365	1430	1470	1490	1510
Si consumed	210 (7.48)	305 (10.86)	464 (16.52)	515 (18.33)	561 (19.97)

Consequently in the case of the oven temperature of 1510 °C only SiF_2 is present as a gas phase species. SiF_2 is condensed together with a solvent mixture of toluene and $P(\textit{n}Bu)_3$ or NEt_3 as a donor component at –196 °C. After the co-condensation reaction is finished the solid matrix is heated to –78 °C with dry ice and after melting a nearly colorless solution is obtained, which is quite reactive against moisture and air leading to smoke generation. However at –78 °C it can be stored without any obvious change. Heating this solution to room temperature the formation of a polymeric membrane on the surface is observed, indicating that a reaction takes place. However attempts to collect any solid product out of this subsequent reaction failed so far. Also the addition of the carbene $C(N\textit{i}PrCH)_2$ as a trapping reagent did not give any conclusive result and in the proton NMR spectrum only the free carbene is observed and re-isolated in high yield indicating that no reaction with a silicon species takes place. As it has already been shown by *Timms* et al. SiF_2 reacts with aromatic compounds to give solid products, where cyclohexadiene is bridged by Si_2F_4 or Si_3F_6 groups.[4] However when we evaporate the solvent in vacuo only a small amount of a pale yellow residue (ca. 60 mg) is obtained. Thus the subhalide must have reacted to volatile products, which we were not able to isolate and identify so far. As the reactivity of $SiCl_2$ should be lower than that of SiF_2 we tried to synthesize a metastable $SiCl_2$ solution, where the subhalide is available for further reactions.

Metastable $SiCl_2$ Solution

When elemental silicon is reacted with 20 mmol of $SiCl_4$ at an oven temperature of ca. 1440 °C 557 mg (19.8 mmol) silicon are consumed leading thus to a quantitative yield of $SiCl_2$ in the gas phase. The gaseous $SiCl_2$ is condensed together with a solvent mixture of toluene and $P(\textit{n}Bu)_3$ at –196 °C. After the co-condensation reaction is finished the solid matrix is heated to –78 °C with dry ice and after melting a pale yellow solution is obtained, which is less reactive than the corresponding SiF_2 solution as the exposition to normal atmosphere did not lead to smoke generation. However when this solution is heated to room temperature the yellow color intensifies leading after a couple of days to an orange precipitate of unknown composition.

When a cold sample of the solution (ca. 4 mmol of silicon) is reacted with the bulky carbene Idipp [Idipp = 1,3-bis(2,6-$i\mathrm{Pr}_2$-C_6H_3)imidazol-2-ylidene] we observe the formation of $SiCl_2$-Idipp (**3**), which can be identified by its proton NMR signals. Hence the proton NMR spectrum of the reaction mixture is in line with a 1:1 mixture of free carbene and **3**. Thus only 50 % of the $SiCl_2$ seems to be available for adduct formation. We were also able to crystallize Idipp-$SiCl_2$ (**3**), which is obtained as a second polymorph, i.e. it crystallizes in the monoclinic crystal system in space group $P2_1/n$ with one molecule in the asymmetric unit. However no differences concerning Si–Cl and Si–C bond lengths are present with respect to the previously published structure.[26]

Summary and Outlook

With respect to thermodynamic calculations SiF_2 and $SiCl_2$ should be obtained in maximum yield by the reaction of SiX_4 (X = F, Cl) with elemental silicon at a reaction temperature of 1377 °C and 1077 °C, respectively, by a reaction pressure of 0.01 mbar. The synthesis of SiF_2 and $SiCl_2$ is done via a preparative co-condensation reaction, where the high temperature reaction is performed at 1510 °C for SiF_2 and 1440 °C for $SiCl_2$ leading to quantitative yield of the silicon(II) halide in the gas phase. The gaseous compounds are then condensed together with a mixture of an inert solvent and a donor component, e.g. toluene/$P(n\mathrm{Bu})_3$ at –196 °C to give a solid matrix. After melting of the matrix a metastable solution of the subhalide is obtained. In the case of the reaction system SiF_4 / Si we could show that at lower reaction temperatures a high amount of SiF_4 remains, which can be isolated from the solution after reaction with the N-heterocyclic carbene $C(Ni\mathrm{Pr}CH)_2$ as the bis-carbene adduct $SiF_4[C(Ni\mathrm{Pr}CH)_2]_2$, which crystallizes in two different polymorphs (**1** and **1b**), where the carbene ligands are oriented planar or perpendicular to each other. SiF_2 seems to be too reactive to be trapped by stabilizing ligands and further experiments applying different solvents and donor molecules during the co-condensation reaction are necessary to transfer this subhalide from the gas phase to a useable reagent.

However in the case of $SiCl_2$ the solvent mixture toluene/$P(n\mathrm{Bu})_3$ seems useful to obtain a metastable solution of the subhalide $SiCl_2$. Thereby the reaction with the bulky carbene Idipp gives Idipp-$SiCl_2$ (**3**), which is also available by a different route using standard synthetic procedures as it has been lately shown by *Roesky* et al.[7] However before trapping with the carbene the subhalide solution shows a high intrinsic reactivity,[27] which might be used in further applications, which has to be shown in future experiments.

Experimental Section

Procedure of the Co-Condensation: The co-condensation reaction was performed within a homemade co-condensation apparatus which has been described elsewhere.[28] The apparatus was evacuated with an oil diffusion pump (Balzers Diff 900) to a pressure of 5×10^{-6} mbar. In a modified graphite reactor (Scheme 1) elemental silicon was placed. For bake-out the graphite reactor was first heated inductively for 30 min to ca. 1300 °C. Afterwards the reactor was further heated to the working temperature e.g. 1440 °C in the case of $SiCl_2$. Afterwards, SiX_4 gas was passed through the reactor and the resulting gaseous compounds were condensed together with a solvent mixture at a –196 °C cold surface. The amount of SiX_4 was measured by a flow controller; thereby 20 mmol of SiX_4 were used over the period of ca. 2 h, where additionally ca. 150 mL of solvent were condensed. Subsequently heating was switched off and after the removal of the liquid nitrogen cooling the whole apparatus was flushed with nitrogen gas 4.8. The reaction chamber was heated with dry ice to –78 °C. After the matrix melted the resulting solution was transferred by a steel cannula with nitrogen overpressure into a dry ice cooled Schlenk vessel.

Synthesis of $SiF_4[C(Ni\mathrm{Pr}CH)_2]_2$ (1, 1a): 1,3-Diisopropylimidazo-2-ylidene (600 mg, 1 equiv., 4 mmol) was dissolved in toluene (20 mL) at –78 °C and stirred for 10 min. To this solution the –78 °C cold SiF_2 solution [20 mL, 40 % SiF_2, toluene/$P(n\mathrm{Bu})_3$, 4 mmol Si] were added rapidly. The reaction mixture was warmed within 2 h to room temperature. After removal of all volatiles the remaining solid was washed 3 times with pentane (20 mL) and dried in vacuo to obtain 350 mg (0.857 mmol, 21.4 %) of pale beige solid. Crystallization of the solid from thf gave colorless hexagonal plates of **1**, while crystallization from toluene gave rhombic plates of **1a**. When the hexagonal crystals were filtered off and dried in vacuo they got turbid, leading to a pale yellow powder indicating that the crystal thf was evaporated. NMR spectra of the powder indicated that only half a thf molecule per **1** was left in the solid (NMR spectra are shown in the Supporting Information) which is in line with results of the elemental analysis of this solid. **^{1}H NMR** (C_6D_6, 250 MHz, TMS ext.): δ = 1.25 (d, 24 H, ^3J = 6.8 Hz, $CHMe_2$), 6.37 [s, 4 H, $^4J(^1H^{29}Si)$ = 190 Hz, C*H*], 6.40 (sept, 4 H, $CHMe_2$) ppm. **^{13}C NMR** (C_6D_6, 62.9 MHz, TMS ext.): δ = 24.1 ($CHMe_2$), 49.9 [$^4J(^{13}C^{19}F)$ = 4.3 Hz, $CHMe_2$], 115.7 (*C*H), 171.1 [$^2J(^{13}C^{19}F)$ = 61.6 Hz, N*C*N] ppm. **^{19}F NMR** (C_6D_6, 376.48 MHz, $CFCl_3$ ext.): δ = –102.5 [$^1J(^{19}F^{29}Si)$ = 187.4, $^2J(^{19}F^{13}C)$ = 61.5 Hz] ppm. **^{29}Si NMR** (C_6D_6, 99.36 MHz, TMS ext.): δ = –182.3 [$^1J(^{29}Si^{19}F)$ = 186.3 Hz] ppm. $C_{18}H_{32}F_4N_2Si{\cdot}0.5THF$: calcd.: C 54.03, H 8.16, N 12.60 %; found: C 53.93, H 8.03, N 12.28 %.

Synthesis of $SiCl_2$-Idipp (3): *Bis*(2,6-Diisopropylphenyl)imidazo-2-ylidene (1.55 g, 1 equiv., 4 mmol) was dissolved in toluene (40 mL) at –78 °C and stirred for 10 min. To this solution the –78 °C cold $SiCl_2$ solution (20 mL, 100 % $SiCl_2$ in toluene/$P(n\mathrm{Bu})_3$, 4 mmol) was added rapidly. The reaction mixture was warmed within 2 h to room temperature. After removal of all volatiles the yellowish solid was washed 3 times with pentane (20 mL) and dried in vacuo (940 mg). Slightly yellow crystals of **3** were formed in a concentrated toluene solution at –30 °C. **^{1}H NMR** (C_6D_6, 400 MHz, TMS ext.): δ = 1.01 (d, 12 H, ^3J = 7.0 Hz, $CHMe_2$), 1.43 (d, 12 H, ^3J = 6.7 Hz, $CHMe_2$), 2.79 (sept, 4 H, ^3J = 6.8 Hz, $CHMe_2$), 6.36 (s, 2 H, C*H*), 7.07 (d, 4 H, ^3J = 7.9 Hz, *m-H*Ph), 7.22 (t, 2 H, ^3J = 7.7 Hz, *p-H*Ph) ppm.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-991359 (**1**), CCDC-991360 (**1b**), and CCDC-991358 (**3**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Crystallographic data and structure refinement results are summarized in Table 3.

Supporting Information (see footnote on the first page of this article): Pictures of the thermal behavior of different $SiCl_2$ solutions and of the

Table 3. Crystallographic data and details for structure solution of $SiF_4[C(N\textit{i}PrCH)_2]_2$ (**1**), $SiF_4[C(N\textit{i}PrCH)_2]_2$ (**1b**), and $SiCl_2$-Idipp (**3**) [Idipp = 1,3-bis(2,6-$\textit{i}Pr_2$-C_6H_3)imidazol-2-ylidene].

Formula	$SiF_4[C(N\textit{i}PrCH)_2]_2$ (**1**)	$SiF_4[C(N\textit{i}PrCH)_2]_2 \cdot C_7H_8$ (**1b**)	Idipp-$SiCl_2$ (**3**)
Crystal system	hexagonal	monoclinic	monoclinic
Space group	$R\bar{3}$	$P2_1/c$	$P2_1/n$
Unit cell dimensions			
a /Å	24.5788(6)	26.995(3)	9.4284(7)
b /Å	25.5788(6)	10.643(2)	14.4275(10)
c /Å	11.1308(7)	17.784(2)	19.9208(12)
β /°		104.057(4)	100.804(2)
Volume /$Å^3$	5823.4(4)	4934.2(13)	2661.8(3)
Z	9	4	4
Density (calculated) /$g \cdot cm^{-3}$	1.049	1.224	1.217
Absorption coefficient μ /mm^{-1}	0.127	0.14	0.306
$F(000)$	1962	1944	1040
Crystal size /mm	$0.08 \times 0.08 \times 0.05$	$0.1 \times 0.1 \times 0.02$	$0.4 \times 0.3 \times 0.3$
Diffractometer	BRUKER APEX II	BRUKER APEX II	BRUKER APEX II
Temperature /K	150	200	150
Wavelength /Å	0.71073	0.71073	0.71073
Theta range for data collection /°	1.66-31.66	1.56–25.00	1.75–27.33
Index ranges	$-36 \le h \le 36$ $-36 \le k \le 36$, $-16 \le l \le 15$	$-32 \le h \le 30$ $-8 \le k \le 12$, $-21 \le l \le 21$	$-12 \le h \le 11$, $-13 \le k \le 18$, $-23 \le l \le 25$
Reflections collected	27663	27535	14758
Independent reflections	4372	8651	5946
Reflections $F^2 > 2\sigma$	3379	5890	4456
Used programs	SHELXL / SHELXS, PLATON	SHELXL / SHELXS	SHELXL / SHELXS
Used parameters	124	550	289
Final R indices [$I > 2\sigma(I)$]	0.0395	0.0485	0.0456
R indices (all data)	0.1085	0.1213	0.1094
Largest diff. peak and hole	0.353 and –0.284	0.288 and –0.388	0.704 and –0.678

oven design as well as the molecular structure and solid-state arrangement of **3** are given together with NMR spectra of **1** and **3** and of the reaction mixture: $SiCl_2[P(\textit{n}Bu)_3]$ solution with Idipp.

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Synthesis of Metastable $Si^{II}X_2$ Solutions (X = F, Cl). A Novel Binary Halide for Synthesis