Inorganica Chimica Acta 473 (2018) 20–28

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Research paper

# Insertion of $CO_2$ and related heteroallenes into the Si–N-bond of methyl (*N*-morpholino)silanes

Marcus Herbig, Uwe Böhme *, Edwin Kroke *

*Department of Inorganic Chemistry, TU Bergakademie Freiberg, Leipziger Str. 29, 09599 Freiberg, Germany*

A R T I C L E I N F O

*Article history:*
Received 4 September 2017
Received in revised form 8 December 2017
Accepted 11 December 2017
Available online 12 December 2017

*Keywords:*
Insertion reaction
$CO_2$
Heteroallenes
*N*-Aminosilanes
Morpholine

A B S T R A C T

Trimethyl(*N*-morpholino)silane ($Me_3SiMorph$) and dimethyl-di(*N*-morpholino)silane ($Me_2SiMorph_2$) were synthesised. The insertion reactions of both silanes with $CO_2$, *n*-butylisocyanate ($^nBuNCO$), phenylisocyanate (PhNCO), methylisothiocyanate (MeNCS), *n*-butylisothiocyanate ($^nBuNCS$) and phenylisothiocyanate (PhNCS) into the Si–N-bond were investigated. One $CO_2$ molecule inserts into each Si–N-bond forming carbamoylic moieties. The insertion reaction of isocyanates depends on the organic substituents bound to the heteroallene unit. PhNCO inserts twofold forming a biuret moiety, while $^nBuNCO$ yields urea units by insertion of just one molecule per Si–N-bond. The isothiocyanates are less reactive forming thiourea moieties. Aliphatic isothiocyanates furnish equilibria between the reactants and the insertion product at room temperature. All products have been characterized by spectroscopic methods. Single crystal X-ray diffraction analyses of five insertion products have been performed. The observed reactivity is discussed on the basis of NBO charges and calculated Gibbs free energies of the insertion reactions.

## 1. Introduction

Aminoorganosilanes are known for many years [1–3] and used as versatile reagents [4,5], substrates for further transformations [6], and precursors for the generation of silicon nitride [7]. The Si–N-bond offers possibilities for new syntheses routes, since the reactivity is higher than the typical reactivity of Si–O-bonds but lower than Si–Cl-bonds. Insertion reactions of heteroallenes can be used for the generation of diverse structural units [14] (Scheme 1).

The reaction of aminosilanes with $CO_2$ leads to carbamoyloxysilanes [e.g. 5] which is described to be reversible in case of trimethylsilylcarbamates [8]. For example, $CO_2$ also reacts with di (n-hexylamino)dimethylsilan to form di(carbamoyloxy)dimethylsilanes which can be decomposed by heating into polysiloxanes and *N,N′*-dihexylurea [9]. COS reacts in a similar manner e.g. with N-methyldisilylamine but the products are unstable at room temperature [10]. Breederveld described the reaction of diethylaminotrimethylsilan with carbon disulfide witch forms trimethylsilyl-diethylthiocarbamate [11]. In the reaction of isocyanates with silylated primary amines no insertion into the N–H-bond could be observed before all original Si–N-bonds have reacted [12], which is confirmed by the reaction of hexamethyldisilazan with phenylisocyanate in the same work. Isothiocyanates react in a similar way [13]. Nitriles can insert into Si–N-bonds of (3,5-dimethylpyrazol)methylsilanes [3].

The insertion products of isocyanates contain a Si–N-bond into which a second isocyanate molecule or an isothiocyanate can insert. For instance, phenylisocyanate yields a twofold insertion with trimethyl(diethylamino)silane [15]. This reaction was performed at 15 °C generating the product after a reaction time of 15 min in 80% yield (Scheme 2).

On the basis of these preliminary results from our group we studied the insertion reaction of different heteroallenes ($CO_2$, PhNCO, $^nBuNCO$, MeNCS, $^nBuNCS$, PhNCS) with the Si–N-bond of trimethyl(N-morpholino)silane (**1**) and dimethyl-di(*N*-morpholino)silane (**2**).

## 2. Experimental part

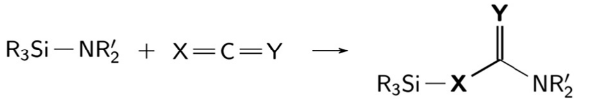
THF was purchased from VWR (AnalaR Normapuran) and purified by MBRAUN MB-SPS-800. *N*-pentane is used in technical grade (VWR TECHNICAL) dried by standing over activated molecular sieve (type 3 Å, purchased from Sigma-Aldrich) several days. Triethylamine (<98%) and morpholine (>98%) are both purchased from Acros and purified by distillation from Na/benzophenone.

---

* Corresponding authors.

*E-mail addresses:* uwe.boehme@chemie.tu-freiberg.de (U. Böhme), edwin.kroke@chemie.tu-freiberg.de (E. Kroke).

https://doi.org/10.1016/j.ica.2017.12.020



**Scheme 1.** General scheme for the insertion reaction of a heteroallene into Si–N-bonds (R, R′ = alkyl, aryl; X = O, N-aryl, N-alkyl; Y = O, S).

$^{n}$BuNCO, MeNCS, PhNCS and $^{n}$BuNCS are purchased from Sigma-Aldrich, $^{n}$BuNCO is purified by distillation, MeNCS is purified by recrystallization from *n*-pentane. PhNCS and $^{n}$BuNCS are used as purchased. $CO_2$ is used from a gas cylinder, grade 4.5.

All reactions were carried out under dry argon atmosphere using standard Schlenk-techniques.

NMR-spectra were measured with a BRUKER DPX 400 (frequencies: $^{1}$H: 400.13 MHz; $^{13}$C: 100.61 MHz; $^{29}$Si: 79.49 MHz) or BRUKER AVANCE III 500 MHz (frequencies: $^{1}$H: 500.13 MHz; $^{13}$C: 125.76 MHz; $^{29}$Si: 99.36 MHz) spectrometer in $CDCl_3$ (Amar chemicals, purified by distillation from $CaH_2$) with TMS as internal standard.

RAMAN-spectra were measured with Bruker FT-Raman spectrometer RFS 100/S. The device works with an air-cooled Nd: YAG-Laser with a wavelength of 1064 nm and a nitrogen-cooled detector. The samples were filled in glass tubes and sealed with PTFE-paste. The intensity is listed as follows: vs (very strong) 80–100% of the highest signal, s (strong), m (medium), w (weak), vw (very weak) next 20% respectively.

Boiling points of liquid samples were measured as described in [20].

Elemental analyses (C, H, N, S) were done with varioMICRO (company: Elementar). Samples were prepared in an argon filled glovebox using 2–2.5 mg substance in a tin capsule. Low values of carbon and higher values of hydrogen are due to formation of silicon carbide.

### 2.1. Synthesis of methylmorpholinosilanes

The morpholinosilanes were synthesized by the reaction of morpholine (about 10 mol% excess, 7.45 g/86 mmol) and chloromethylsilane (5.00 g/39 mmol $Me_2SiCl_2$) and trimethylamine (about 10 mol% excess, 8.60 g/85 mmol) in 150 ml of *n*-pentane. After filtration (G4-fritt), the solvent was removed in vacuo and the product was distilled slowly over a 10 cm Vigreux fractionating column at reduced pressure.

### 2.2. Insertion reactions

#### 2.2.1. General procedure of $CO_2$-insertion

$CO_2$ from a gas cylinder is bubbled through conc. $H_2SO_4$ and into a solution of *N*-aminosilane in THF in an ice bath. After 20 min the gas flow is stopped and the reaction mixture allowed to reach room temperature. Removing the solvent under reduced pressure leads to the pure product.

#### 2.2.2. General procedure of insertion reactions with PhNCO, $^{n}$BuNCO, PhNCS, $^{n}$BuNCS, acetone, and acetonitrile

To a solution of *N*-aminosilane in *n*-pentane at 0 °C $^{n}$BuNCO is added dropwise via syringe. The reaction mixture is allowed to reach room temperature and stand overnight. The solvent is removed in vacuo. The experiments with PhNCO are repeated at −78 °C (dry ice/*iso*-propanol) and slow warming up to room temperature over several hours and in boiling hexane. Experiments with **2** are repeated in boiling toluene as solvent.

#### 2.2.3. General procedure of MeNCS-insertion

To a solution of *N*-aminosilane in *n*-pentane at 0 °C a solution of MeNCS in *n*-pentane is added dropwise via syringe. The reaction mixture is allowed to reach room temperature and stand overnight. The solvent is removed in vacuo.

### 2.3. Reaction products

#### 2.3.1. Trimethyl(N-morpholino)silane (*1*)

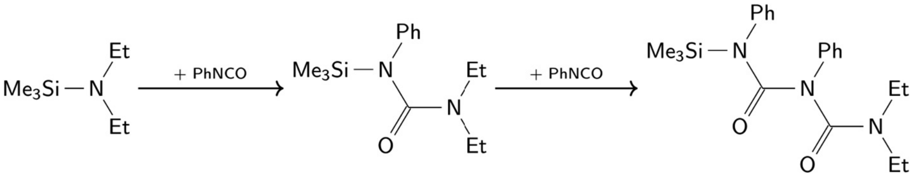
According to procedure 2.1 4.51 g (52 mmol) morpholine and 5 g (46 mmol) $Me_3SiCl$ were used yielding 3.65 g (50%) of a colourless liquid. $^{1}$H NMR: $\delta = 3.43$ (t, $^{3}J_{H,H} = 4.5$ Hz, 4H, O-$CH_2$); 2.71 (t, $^{3}J_{H,H} = 4.5$ Hz, N-$CH_2$); −0.07 (s, 9H, $SiMe_3$) ppm. $^{13}$C{$^{1}$H} NMR: $\delta = 68.5$ (O-$CH_2$); 45.4 (N-$CH_2$); −1.4 ($SiMe_3$) ppm. $^{29}$Si NMR: $\delta = 6.0$ ppm. RAMAN (298 K, neat in glass capillary): $\nu$ [$cm^{-1}$] = 2955 (vs), 2897 (vs), 2847 (m), 2828 (w), 2757 (vw), 2735 (vw), 2701 (vw): ($\nu$(CH)), 1441 (vw), 1410 (vw, $\delta_{as}$(Si-Me)), 1214 (vw), 840 (vw, ρ(Si-Me)), 683 (vw), 620 (w), 560 (w, $\nu$(Si-C)), 354 (vw), 228 (vw), 207 (vw), 194 (vw). Bp = 170 °C (760 torr); EA: C found 52.30%, calc. 52.78%; H found 11.77%, calc. 10.76%, N found 8,71%, calc. 8,79%. Identity confirmed by literature: NMR [18], bp: 170 °C (167 °C [24], 160 °C [21], 160 °C [22], 161–167 °C [23]).

#### 2.3.2. Dimethyl-di(N-morpholino)silane (*2*)

According to procedure 2.1 7.45 g (86 mmol) morpholine and 5,00 g (39 mmol) $Me_2SiCl_2$ were used yielding 5.56 g (62%) of a colourless liquid. $^{1}$H NMR: $\delta = 3.31$ (pseudo-t, 8H, O-$CH_2$-); 2.66 (pseudo-t, 8H, N-$CH_2$-); −0.16 (s, 6H, $SiMe_2$) ppm. $^{13}$C{$^{1}$H} NMR: $\delta = 68.2$ (O-$CH_2$-); 45.9 (N-$CH_2$-); −3.6 ($SiMe_2$) ppm. $^{29}$Si NMR: δ = −4.9 ppm. RAMAN (298 K, neat in glass capillary): $\nu$ [$cm^{-1}$] = 2955 (vs), 2899 (m), 2843 (m), 2828 (m), 2755 (vw), 2735 (vw), 2699 (vw), 2651 (vw): $\nu$(CH), 1455 (vw), 1441 (vw), 1408 (vw, $\delta_{as}$(Si-Me)), 1329 (vw), 1295 (vw), 1214 (vw), 1131 (vw), 1027 (vw), 844 (w, ρ(Si-Me)), 635 (vw), 554 (w, $\nu$(Si-C)), 483 (vw), 224 (vw), 184 (vw). bp = 273 °C (760 torr), EA: C found 51.26% calc. 52.13%, H found 10.84% calc. 9.63%, N found 11.82% calc. 12.16%.

#### 2.3.3. Trimethyl-(morpholine-4-carbonyloxy)silane (*3*)

This compound was obtained by the general procedure 2.2.1. 0.99 g (6.2 mmol) **1** were used yielding 1.27 g (62 mmol, 100%) of a white solid. $^{1}$H NMR: $\delta$ [ppm] = 0.21 (9H, s, $SiMe_3$), 3.37 (4H, m, N-$CH_2$), 3.57 (4H, m, O-$CH_2$); $^{13}$C NMR: $\delta$ [ppm] = 154.2 (C=O), 66.6 (O-$CH_2$), 44.9 and 43.6 (N-$CH_2$), −0.1 ($SiMe_3$); $^{29}$Si NMR: $\delta$ [ppm] = 23.7; RAMAN: $\nu$ [$cm^{-1}$] = 3005 (vw), 2982 (vs), 2926 (vw), 2905 (w), 2866 (m), 2828 (m), 2774 (vw), 2718 (vw), 2649



**Scheme 2.** Mono and twofold insertion of PhNCO into the Si–N-bond of trimethyl(diethylamino)silane [15].

(vw), 2514 (vw): $\nu$(CH), 1466 (vw), 1449 (w), 1418 (vw, $\delta_{as}$(Si-Me)), 1395 (vw), 1366 (vw), 1326 (vw), 1314 (vw), 1270 (vw), 1222 (vw), 1200 (vw), 1133 (vw), 1108 (vw), 1088 (vw), 1056 (vw), 1025 (vw), 996 (vw), 845 (vw, $\rho$(Si-Me)), 826 (w), 809 (w), 564 (vw), 479 (vw), 452 (vw), 429 (vw), 377 (vw), 190 (vw), 130 (vw), 109 (vw); mp = 42 °C; EA: C found 46.29% calc. 47.26%, H found 9.37% calc. 8.43%, N found 6.68% calc. 6.89%; Identity confirmed by literature: mp: 42 °C [8], 44–45 °C [25]; Standing at room temperature in *$CDCl_3$* for 24 h yielded colourless crystals suitable for single-crystal X-ray diffraction, which were solved as $C_8H_{17}NO_3Si$ (CCDC-1561279).

### 2.3.4. Dimethyl-di(morpholin-4-carbonyloxy)silane (4)

This compound was obtained by the general procedure 2.2.1. 0,86 g (4.8 mmol) **2** were used yielding 1.19 g (100%) of a white solid. $^{1}$H NMR: $\delta$ [ppm] = 0.43 (6H, s, $SiMe_2$), 3.37 (8H, m, N-$CH_2$), 3.56 (8H, m, O-$CH_2$); $^{13}$C NMR: $\delta$ [ppm] = 152.9 (C═O), 66.4 (morpholin ring), −1.2 ($SiMe_2$); $^{29}$Si NMR: $\delta$ [ppm] = 5.1; RAMAN: $\nu$ [$cm^{-1}$] = 2986 (vs), 2909 (vs), 2866 (vs), 2772 (vw), 2714 (vw): $\nu$(CH), 1675 (vw), 1663 (vw), 1457 (w), 1445 (w), 1420 (vw, $\delta_{as}$(Si-Me)), 1397 (vw), 1306 (vw), 1222 (vw), 1202 (vw), 1131 (vw), 1114 (vw), 1094 (vw), 1025 (vw), 1000 (vw), 851 (vw, $\rho$(Si-Me)), 815 (m), 790 (vw), 664 (w), 577 (vw), 485 (vw), 467 (vw), 342 (vw), 331 (vw), 277 (vw), 230 (vw), 176 (vw), 130 (vw), 105 (w); mp = 156 °C (decomp.); EA: C found 44.63% calc. 45.27%, H found 7.55% calc. 6.96%, N found 8.53% calc. 8.80%. Standing at room temperature in *$CDCl_3$* for 24 h yielded colourless crystals suitable for single-crystal X-ray diffraction, which were solved as $C_{12}H_{22}N2O_6Si$ (CCDC-1561278).

### 2.3.5. Trimethyl-(3-(morpholine-4-carbonyl)-1,3-diphenylureayl) silane (5)

This compound was obtained by the general procedure 2.2.2. 0.99 g (6.2 mmol) **1** and 1.45 g (12 mmol) PhNCO were used yielding 2.41 g (99%) of a colourless solid. $^{1}$H NMR: $\delta$ = 0.00 (s, 9H, $SiMe_3$), 2.60 (m, 2H, N-$CH_2$-), 2.87 (m, 2H, O-$CH_2$-) 6.71–7.07 (m, 10H, ArH) ppm. $^{13}$C{$^{1}$H} NMR: $\delta$ = 0.2 ($SiMe_3$), 44.7 (N-$CH_2$-), 65.5 (O-$CH_2$-), 124.7, 126.0, 126.7, 128.5, 129.3, 129.8, 140.6, 140.7, 155.7 (ArC), 161.0 and 155.7 (C═O) ppm. $^{29}$Si NMR: $\delta$ = 13.2 ppm. RAMAN (298 K, neat in glass capillary): $\nu$ [$cm^{-1}$] = 3067 (vs), 3034 (vw), 2990 (w), 2963 (s), 2899 (m), 2865 (w): $\nu$(CH), 1667 (vw, Amid I), 1596 (w, Amid II), 1449 (vw), 1434 (vw), 1304 (vw, Amid III), 1256 (w), 1229 (vw), 1177 (vw), 1158 (vw), 1036 (vw), 1021 (vw), 1006 (m, $\delta_{inplane}$(CH)), 994 (w), 965 (vw), 732 (vw), 695 (vw, $\nu$(Si-C)), 629 (vw), 616 (vw), 388 (vw), 340 (vw), 315 (vw), 257 (vw), 238 (vw), 219 (vw), 199 (w), 170 (vw), 157 (w), 109 (s). mp = 112 °C; EA: C found 62.83% calc. 63.45%, H found 7.22% calc. 6.85%, N found 10.44% calc. 10.57%. Standing at room temperature in *n*-pentane for 24 h yielded colourless crystals suitable for single-crystal X-ray diffraction, which were solved as $C_{21}H_{27}N_3O_3Si$ (CCDC-1561280). In the reaction pathway a twofold insertion of phenylisocyanate take place.

### 2.3.6. Trimethyl-N-butyl-morpholin-4-carboxamidosilane (6)

This compound was obtained by the general procedure 2.2.2. 1.05 g (6.6 mmol) **1** and 0.65 g (6.6 mmol) $^{n}$BuNCO were used yielding 1,70 g (100%) of a colourless liquid. $^{1}$H NMR: $\delta$ [ppm] = 0.0 (9H, s, $SiMe_2$), 0.68 (t, $^{3}J_{H,H}$ = 7.3 Hz, 3H, Bu: $CH_3$), 1.06 (m, 2H, Bu: $CH_2$), 1.21 (m, 2H, Bu-$CH_2$), 2.89 (t, $^{3}J_{H,H}$ = 7.2 Hz, 2H, Bu: N-$CH_2$), 3.12–3.05 (m, 4H, N-$CH_2$-), 3.47–3.39 (m, 4H, O-$CH_2$-); $^{13}$C NMR: $\delta$ [ppm] = 165.6 (C═O), 66.3 (O-$CH_2$-), 47.0 (N-$CH_2$-), 45.7 (Bu: $CH_2$), 33.3 (Bu: $CH_2$), 19.7 (Bu: $CH_2$), 13.5 (Bu: $CH_3$), −0.1 ($SiMe_3$); $^{29}$Si NMR: $\delta$ [ppm] = 9.1; RAMAN: $\nu$ [$cm^{-1}$] = 2961 (s), 2938 (m), 2901 (vs), 2876 (m), 2859 (m), 2766 (vw), 2735 (vw), 2708 (vw): $\nu$(CH), 1636 (vw), 1459 (vw), 1445 (vw), 1414 (vw, $\delta_{as}$(Si-Me)), 1385 (vw), 1301 (vw), 1114 (vw), 847 (vw, $\rho$(Si-Me)), 778 (vw), 689 (vw), 626 (w), 479 (vw), 327 (vw), 259 (vw), 221 (vw), 205 (vw), 182 (vw), 151 (vw), 105 (vw); bp = 198 °C (760 torr); EA: C found 55.13% calc. 55.77%, H found 9.63% calc. 10.14%, N found 10.99% calc. 10.84%.

### 2.3.7. Trimethyl-N-methyl-morpholin-4-carbothioylamidosilane (7)

To obtain higher yields excess of MeNCS must be used.

This compound was obtained by the general procedure 2.2.3. 0.99 g (6.2 mmol) **1** and 0.50 g (6.6 mmol) MeNCS were used yielding a pale yellow solid; $^{1}$H NMR: $\delta$ [ppm] = 0.2 ($SiMe_3$, 9H, s); 2.79 (N-Me, 3H, s); 3.53–3.60 (N-$CH_2$-$CH_2$-O, 8H, m); $^{13}$C NMR: $\delta$ [ppm] = 0.3 ($Me_3Si$); 38.5 (N-Me); 51.3 (-N$CH_2$); 66.2 (-O$CH_2$), 197.2 (C═S); $^{29}$Si NMR: $\delta$ [ppm] = 12.0; mp = 72 °C; yield = 96% (according to NMR, impurity is MeNCS). Standing at room temperature in *n*-pentane for several days yielded colourless crystals suitable for single-crystal X-ray diffraction, which were solved as $C_9H_{20}N_2OSSi$ (CCDC-1561276).

### 2.3.8. Trimethyl-N-phenyl-morpholin-4-carbothioylamidosilane (8)

This compound was obtained by the general procedure 2.2.2. 0.99 g (6.2 mmol) **1** and 0.85 g (6.3 mmol) PhNCS were used yielding 0.1 g (5%, 0.3 mmol) of pure yellow crystals; $^{1}$H NMR: $\delta$ [ppm] = 0.37 (Si,$Me_3$ 9H, s); 3,33 (N-$CH_2$, 4H, t, $^{3}J_{H,H}$=5.0 Hz); 3,65 (-$CH_2$-O, 4H, t, $^{3}J_{H,H}$ = 5.0 Hz); 7.01–7.28 (ArH, 5H, m); $^{13}$C NMR: $\delta$ [ppm] = 2.3 ($SiMe_3$); 51.2 (-N-$CH_2$); 65.9 (-O-$CH_2$); 125.3, 127.1, 129.2 and 146.0 (ArC), 193.5 (C═S); $^{29}$Si NMR: $\delta$ [ppm] = 9.3; RAMAN: $\nu$ [$cm^{-1}$] = 3081 (vw), 3057 (vs), 3036 (w), 2988 (w), 2967 (s), 2897 (vs), 2868 (w), 2853 (w): $\nu$(CH), 1594 (w), 1580 (vw), 1439 (vw), 1426 (vw, $\delta_{as}$(Si-Me)), 1303 (vw), 1212 (vw), 1196 (vw), 1177 (vw), 1156 (vw), 1021 (vw), 1002 (m), 982 (vw), 842 (vw, $\rho$(Si-Me)), 666 (vw), 622 (w), 608 (w), 533 (vw), 502 (vw), 408 (vw), 342 (m), 296 (vw), 280 (vw), 263 (vw), 242 (vw), 219 (vw), 205 (vw), 188 (vw), 132 (w), 116 (w), 103 (m); mp = 122 °C; EA: C found 56.10% calc. 57.10%, H found 8.28% calc. 7.53%, N found 9.25% calc. 9.51%. Standing at room temperature in $CHCl_3$ for several days yielded colourless crystals suitable for single-crystal X-ray diffraction, which were solved as $C_{14}H_{22}N_2OSSi$ (CCDC-1561277).

### 2.3.9. Trimethyl-N-n-butyl-morpholin-4-carbothioylamidosilane (9)

To obtain higher yields excess of $^{n}$BuNCS must be used.

This compound was obtained by the general procedure 2.2.2. 0.95 g (5.9 mmol) **1** and 0.71 g (6.2 mmol) $^{n}$BuNCS were used yielding 98% (according to $^{29}$Si NMR, impurity is $^{n}$BuNCS) of a pale yellow liquid; $^{1}$H NMR: $\delta$ [ppm] = 0.13 ($SiMe_3$, 9H, s); 0.78 (N-$CH_2CH_2CH_2$**C**$H_3$); 1.77 (N-$CH_2CH_2$**C**$H_2CH_3$); 1.34 (N-$CH_2$**C**$H_2CH_2CH_3$); 1.57 (N-**C**$H_2CH_2CH_2CH_3$); 3.57 (N-$CH_2$, 4H, t, $^{3}J_{H,H}$ = 4.7 Hz); 3.72 (O$CH_2$, 4H, t, $^{3}J_{H,H}$ = 4.7 Hz); $^{13}$C NMR: $\delta$ [ppm] = 0.1 ($SiMe_3$); 13.6 (N-$CH_2CH_2CH_2$**C**$H_3$); 20.1 (N-$CH_2CH_2$**C**$H_2CH_3$); 31.7 (N-$CH_2$**C**$H_2CH_2CH_3$); 50.5 (N-**C**$H_2CH_2CH_2CH_3$); 51.2 (-N$CH_2$); 66.3 (-O$CH_2$), 196.8 (C═S); $^{29}$Si NMR: $\delta$ [ppm] = 1.6. RAMAN: $\nu$ [$cm^{-1}$] = 2963 (vs), 2899 (vs), 2473 (vs), 1443 (m), 1299 (m), 1085 (m), 1011 (m), 901 (m), 822 (m), 687 (m), 637 (m), 564 (m), 512 (vw), 464 (vw), 331 (w), 255 (w), 213 (m), 142 (m), 97 (m). The bands of $^{n}$BuNSC have been omitted in the RAMAN spectrum, since the product contains traces of that educt.

### 2.3.10. Insertion of isocyanates and isothiocyanates into 2

These reactions were performed as described in the general procedures above yielding mixtures of unidentified products.

### 2.3.11. Attempted insertion of acetone and acetonitrile into 1

These reactions were performed as described in Section 2.2.2. No reactions were observed.

### 2.4. Determination of molecular structures

Data collections for the structures discussed here were performed on a STOE IPDS-2T image plate diffractometer equipped with a low-temperature device with Mo-Kα radiation ($\lambda = 0.71073$ Å) using ω and φ scans. Software for data collection: X-AREA, cell refinement: X-AREA and data reduction: X-RED [26]. Preliminary structure models were derived by direct methods [27] and the structures were refined by full-matrix least-squares calculations based on $F^2$ for all reflections using SHELXL [28]. Hydrogen atoms were included in the models in calculated positions and were refined as constrained to the bonded atoms. Crystal structures of **3** and **5** were refined as twins. Crystals of **9** had poor quality showing broad or multiple split reflections in the X-ray experiment. Therefore, the obtained data set has limited quality and is only good for qualitative discussion. Further crystallographic data are listed in Tables 1 and 2.

CCDC-1561276–1561280 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

### 2.5. Quantum chemical calculations

The quantum chemical calculations have been performed with GAUSSIAN 09 [29]. All calculated molecule geometries have been optimized with M062X/6-311+G(d,p) [30]. The calculation of Hessian-matrices verified the presence of local minima on the potential energy surface with zero imaginary frequencies. NBO analyses have been performed with NBO 6.0 [31].

## 3. Results and discussion

### 3.1. Reactions of silanes *1* and *2* with $CO_2$ and related heteroallenes

Trimethyl(*N*-morpholino)silane (**1**) and dimethyl-di(*N*-morpholino)silane (**2**) were synthesised from anhydrous morpholine and the corresponding methylchlorosilane in the presence of triethylamine using *n*-pentane as a solvent. Both silanes react with $CO_2$, $^{n}$BuNCO, PhNCO, MeNCS, $^{n}$BuNCS, and PhNCS in solution. The chemical shift of the C-atom of the heteroallene moiety in the $^{13}$C NMR spectra changes during the reaction to a typical chemical shift

**Table 1**
Crystal data and structure refinement for **3** and **4**.

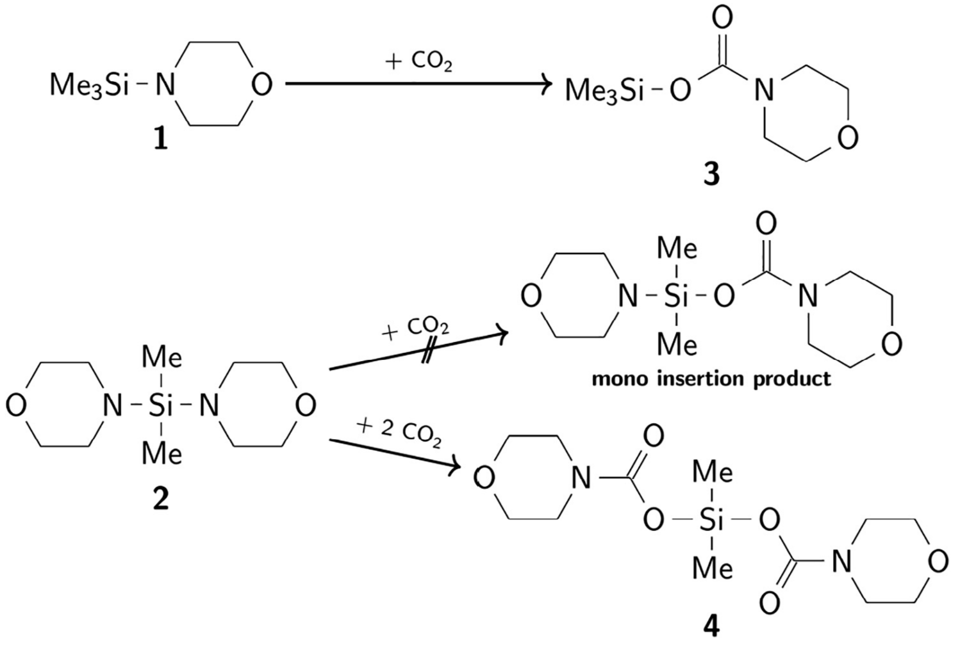
| | **3** | **4** |
|---|---|---|
| Empirical formula | $C_8H_{17}NO_3Si$ | $C_{12}H_{22}N_2O_6Si$ |
| Formula weight | 203.31 | 318.40 |
| Temperature/K | 173(2) | 203(2) |
| Crystal system, space group | Triclinic, P-1 | Monoclinic, I2/c |
| a/Å | 9.9310(7) | 19.9910(9) |
| b/Å | 10.1907(7) | 7.6922(2) |
| c/Å | 11.6645(7) | 21.1521(9) |
| α/° | 89.455(5) | 90 |
| β/° | 71.271(5) | 102.753(4) |
| γ/° | 88.170(5) | 90 |
| Volume/Å$^3$ | 1117.41(13) | 3172.4(2) |
| Z | 4 | 8 |
| $\rho_{calc}$ (g/cm$^3$) | 1.209 | 1.333 |
| Absorption coefficient/mm$^{-1}$ | 0.190 | 0.175 |
| F(0 0 0) | 440 | 1360 |
| Crystal size (mm) | 0.42 × 0.36 × 0.30 | 0.50 × 0.45 × 0.40 |
| Reflections collected/unique | 24,992/24,992 | 22,006/3608 [R(int) = 0.0373] |
| Data/restraints/parameters | 24,992/13/296 | 3608/44/247 |
| Final R indices [I > 2sigma(I)] | R1 = 0.0567, wR2 = 0.1689 | R1 = 0.0384, wR2 = 0.0969 |
| R indices (all data) | R1 = 0.0778, wR2 = 0.2206 | R1 = 0.0441, wR2 = 0.1009 |

**Table 2**
Crystal data and structure refinement for **5**, **7**, and **8**.

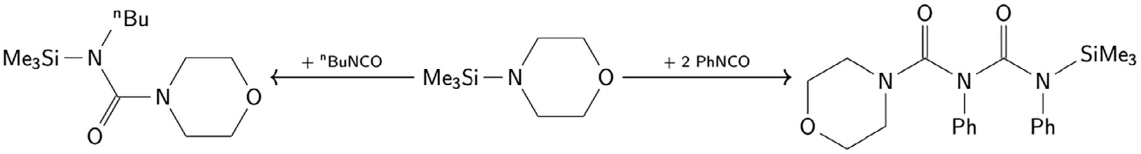
| | **5** | **7** | **8** |
|---|---|---|---|
| Empirical formula | $C_{21}H_{27}N_3O_3Si$ | $C_9H_{20}N_2OSSi$ | $C_{14}H_{22}N_2OSSi$ |
| Formula weight | 397.54 | 232.42 | 294.48 |
| Temperature/K | 153(2) | 213(2) | 153 |
| Crystal system, space group | Monoclinic, P2$_1$/c | Orthorhombic, Pbca | Triclinic, P-1 |
| a/Å | 6.3623(5) | 6.2174(4) | 6.4646(7) |
| b/Å | 16.1178(9) | 11.9172(8) | 9.9991(11) |
| c/Å | 21.0265(19) | 35.368(3) | 13.3502(15) |
| α/° | 90 | 90 | 71.601(9) |
| β/° | 101.611(7) | 90 | 88.904(9) |
| γ/° | 90 | 90 | 73.318(9) |
| Volume/Å$^3$ | 2112.1(3) | 2620.6(3) | 781.95(16) |
| Z | 4 | 8 | 2 |
| $\rho_{calc}$ (g/cm$^3$) | 1.250 | 1.178 | 1.251 |
| Absorption coefficient/mm$^{-1}$ | 0.137 mm^−1 | 0.314 | 0.278 |
| F(0 0 0) | 848 | 1008 | 316 |
| Crystal size | 0.33 × 0.18 × 0.15 | 0.40 × 0.30 × 0.11 | 0.48 × 0.35 × 0.35 |
| Reflections collected/unique | 44,892/44,892 | 2805/2805 | 12,239/3589 [R(int) = 0.0452] |
| Data/restraints/parameters | 44,892/36/256 | 2805/24/132 | 3589/0/175 |
| Final R indices [I > 2sigma(I)] | R1 = 0.0514, wR2 = 0.1245 | R1 = 0.1234, wR2 = 0.2567 | R1 = 0.0625, wR2 = 0.1536 |
| R indices (all data) | R1 = 0.0644, wR2 = 0.1387 | R1 = 0.1777, wR2 = 0.2852 | R1 = 0.0757, wR2 = 0.1666 |

**Table 3**
Chemical shift of the central C-atom of the heteroallene and the shift of the same carbon atom, the silicon atom in the products of the reaction with **1** (in ppm relative to TMS) and the yield of the insertion products.

| Heteroallene | Chemical shift of carbon atom of the heteroallene [18] | Insertion product | Chemical shift of carbonyl carbon atom | Chemical shift of silicon atom | Yield |
|---|---|---|---|---|---|
| $CO_2$ | 125.0 | **3** | 154.2 | 23.7 | 100% |
| $^{n}$BuNCO | 122.3 | **6** | 165.6 | 9.1 | 100% |
| PhNCO | 124.9 | **5** | 161.0, 155.7 | 13.2 | 99% (double insertion) |
| MeNCS | 128.9 | **7** | 197.2 | 12.0 | 96% |
| $^{n}$BuNCS | 129.6 | **9** | 196.5 | 11.6 | 96% |
| PhNCS | 135.4 | **8** | 193.5 | 9.3 | 5% (crystalline) |



**Scheme 3.** Reaction of **1** and **2** with $CO_2$. No mono-insertion product of **1** and $CO_2$ is found.



**Scheme 4.** Different insertion pattern of the reaction of **1** with isocyanates. Arylisocyanates insert twofold while alkyl isocyanate inserts onefold.

of the formed carbamic, urea or thiourea moieties, respectively (Table 3, Scheme 1). The chemical shift of the silicon atom in the $^{29}$Si NMR-spectra is also changed (Table 3), which can be used to indicate the completeness of the reaction.

Each Si–N-bond of the starting materials is transformed to a carbamic moiety during the reaction with $CO_2$ (Scheme 3). The products were obtained quantitatively as white solids showing the expected thermal behaviour: The trimethylsilyl derivative melts reversible and the dimethylsilyl derivative decomposes in the same way as the compounds in [5]. The mono-*O*-carbamic-silane (**3**) melts at 42 °C and the bis-*O*-carbamic-silane (**4**) decomposes at 156 °C. For both insertion products the molecular structure is determined by single crystal X-ray diffraction. An insertion in only one Si–N-bond of **2** is not observed. Equally, **4** in presence of **2** is not converted to the mono-insertion product by heating in THF or anisole under reflux for two hours. This is due to the fact, that the activation energy as well as the reaction energy for the insertion into the first Si–N-bond and the second insertion reaction into the remaining Si–N-bond of diaminosilanes $R_2Si(NR'_2)_2$ are very similar. These values have been calculated and were reported to be $E_a = 124.4$ kJ/mol (first insertion) and 123.1 kJ/mol (second insertion). The Gibbs free energy of the two insertions are $\Delta_RG = -24.7$ and $-16.7$ kJ/mol respectively [5].

Morpholinosilane **1** reacts also smoothly with isocyanates (Scheme 4). The NMR-spectra of the reaction of **1** with PhNCO having two signals in the range for carbonyl groups in $^{13}$C NMR and 10 arylic H-atoms per 9H-atoms of the $SiMe_3$ group in $^{1}$H NMR-spectrum hints to a double insertion product. With a stoichiometry of less than 2 mole PhNCO to one mole **1**, the signal of **1** remains in the $^{29}$Si NMR spectrum. A double insertion is preferred. With the aim to synthesize mono insertion products, the reaction was carried out at −78 °C and in another experiment in boiling *n*-hexane but no difference in the reaction behaviour is observed. To synthesize threefold insertion products, which would give a triuret, the stoichiometric corresponding amount of PhNCO is added to the morpholinosilanes at −78 °C, at room temperature, and in boiling *n*-hexane but the formation of triuret is not observed.

In contrast to PhNCO with the alkylisocyanate $^{n}$BuNCO only one molecule inserts per Si–N-bond under the same conditions.

Isothiocyanates form a thiourea moiety when inserting into Si–N-bonds. In the spectra of the reaction products of **1** with the aliphatic isothiocyanates with a 1:1 stoichiometry both, **1** and the corresponding isothiocyanate could be observed next to the expected product signal. With an excess of about 50 mol% the equilibrium can be shifted to yield the thiourea **7** and **9** respectively, mostly quantitatively in solution according to the $^{29}$Si NMR spectra. PhNCS inserts only onefold per Si–N-bond and nearly quantitatively at stoichiometric amounts.

All investigated reactions of dimorpholinosilane **2** with isocyanates or isothiocyanates lead to product mixtures, as indicated by the NMR-spectra of the obtained solutions.

### *3.2. Properties of the insertion products*

The NMR-shifts of the carbonyl carbon atoms change significantly during the reaction. The chemical shifts after the reaction of the heteroallene with **1** are summarized in Table 3. The $CO_2$ insertion products show the expected signal of the carbonyl atom in $^{13}$C NMR (154.2 ppm for **3** and 152.9 ppm for **4**). Equally, the isocyanate and isothiocyanate insertion products show a signal in $^{13}$C NMR spectra at about 160 ppm for the carbonyl and 195 ppm for the thiocarbonyl atom. The signals of the silicon atom are always shifted to higher values due to a newly formed carbamoic, urea or thiourea unit respectively. The signals for the carbonyl/thiocarbonyl atoms show the same tendency as the signals of the silicon atom in $^{29}$Si NMR spectra due to the influence of the N-bonded arylic or aliphatic moiety.

The insertion products of the reaction of **2** with isocyanates are obtained impure. There are several signals in all NMR spectra in the expected range for carbonyl atoms and the phenyl ring or butyl chain respectively. As well, there are at least four signals for the carbon atoms in the morpholine ring, which means that both morpholines are different with respect to NMR spectroscopy. These results show that there are different insertion patterns on both Si–N-bonds of the molecule or other side reactions, e.g. oligomerisation, took place.

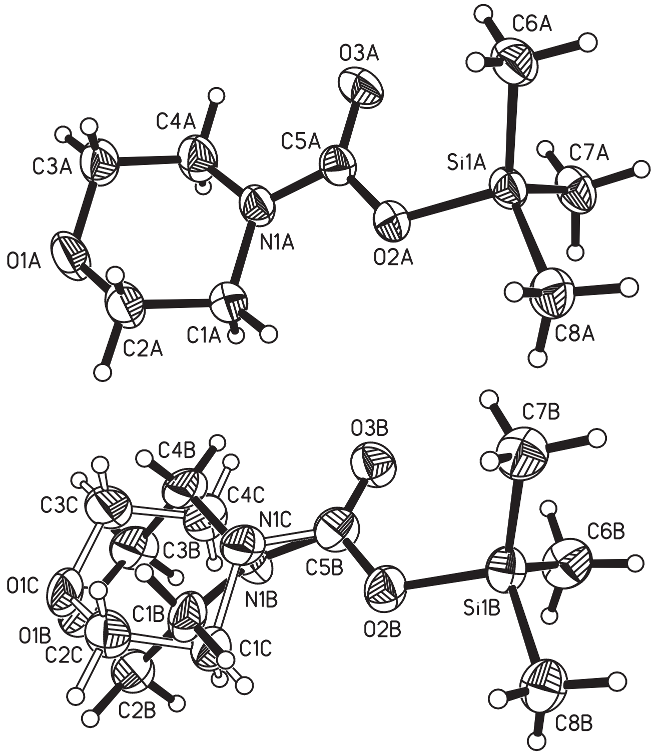


**Fig. 1.** Molecular structure of compound **3** with two crystallographically independent molecules including numbering scheme. The thermal displacement ellipsoids of the non-hydrogen atoms are drawn at the 50% probability level.

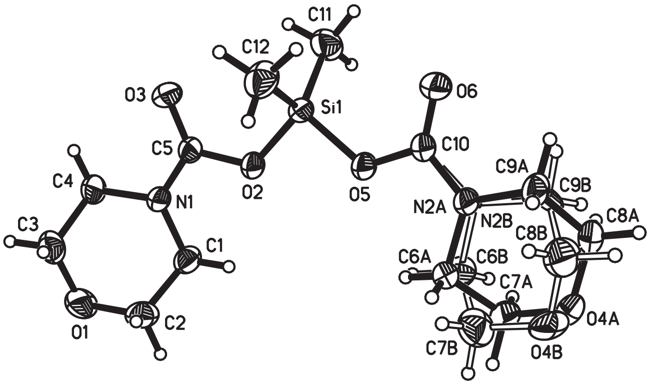


**Fig. 2.** Molecular structure of **4** including numbering scheme. The thermal displacement ellipsoids of the non-hydrogen atoms are drawn at the 50% probability level.

The isothiocyanate insertion products with **2** show the same phenomena as the isocyanates insertion products. As example, the product of the reaction of **2** with PhNCS is analysed by $^{1}$H-$^{1}$H-COSY-NMR-spectroscopy showing that the four different $^{1}$H signals for the morpholine ring are related as pairs of two.

### *3.3. Molecular structures*

Compound **3** crystallizes in the triclinic space group P-1 with two crystallographic independent molecules. One of these molecules is disordered at the morpholino ring with site occupation factors of 0.52/0.48 (see Fig. 1). Structural features are discussed below together with compound **4**.

Compound **4** crystallizes in the monoclinic space group I2/c with one crystallographically independent molecule in the

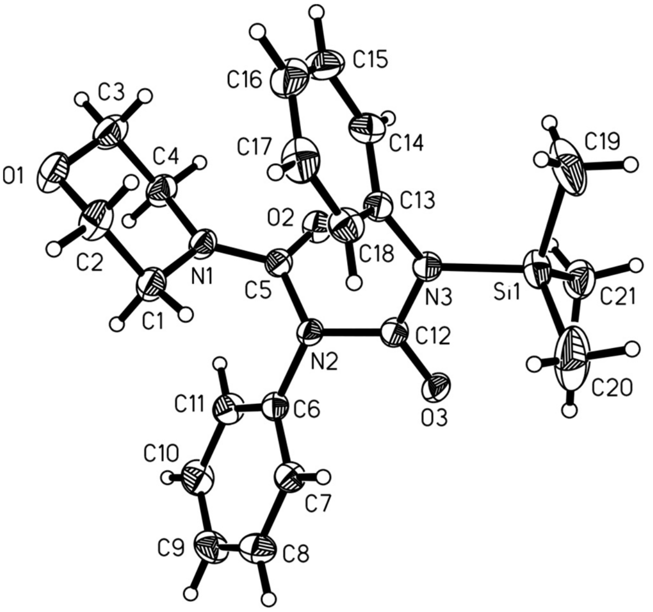


**Fig. 3.** Molecular structure of **5** including numbering scheme. The thermal displacement ellipsoids of the non-hydrogen atoms are drawn at the 50% probability level.

asymmetric unit. There is a disorder at one of the morpholino rings with site occupation factors 0.9/0.1 (see Fig. 2). The silicon atoms in both compounds are in distorted tetrahedral coordination. The sum of the bond angles around the nitrogen atoms is close to 360°. This means that the nitrogen atoms are nearly planar coordinated. The morpholino rings in compounds **3** and **4** are in chair conformation. This can be seen at the torsion angles which are between 50 and 61° with alternating signs (+/−). The carbamic units (N1-C5-O2/O3 and N2-C10-O5/O6) are planar.

Compound **5** crystallizes in the monoclinic space group $P2_1/c$ with one molecule in the asymmetric unit. Two molecules phenylisocyanate were inserted into the Si–N-bond of **1** (SiN1) leading to **5** (see Fig. 3). This twofold insertion yields a biuret unit (carbamylurea) given by the atoms N1—C5(═O2)—N2—C12(═O3)—N3. This unit is composed of two planar urea subunits with a dihedral angle between these subunits of 69.9(1)°. Both phenyl rings are rotated away from the planes of the urea subunits with dihedral angles of 57.1(1) and 82.6(1)° respectively. The morpholino unit is in chair conformation. The tip of the hexagon containing the oxygen atom O1 is more acute than the tip containing the nitrogen atom N1. This can be seen at the torsion angles C3-O1-C2-C1 (−61.4(3)°) and C2-O1-C3-C4 (62.5(3)°) in comparison with the smaller torsion angles C1-N1-C4-C3 (50.8(3)°) and C2-C1-N1-C4 (−49.4(3)°). The nitrogen atom N1 is planar with the sum of bond angles of 359.1° around this atom.

Compound **7** crystallizes in large very thin crystal plates. These show smeared or multiple splitted reflections in the X-ray experiment. Nevertheless one crystal plate with barely acceptable reflections was used for single crystal structure determination. The obtained data set has limited quality with R-values of 12.34 ($I > 2\sigma I$) and 17.77% (all data). Therefore the structure is only suitable for a qualitative discussion. The molecule structure is shown in Fig. 4 and features the expected topology for the insertion product. Me-SCN was inserted into trimethyl(N-morpholino)silane (**1**) under formation of a thiourea derivative. The morpholino group is in chair conformation as in the other derivatives discussed in this paper.

The compound **8** crystallizes in the triclinic space group P-1 with one molecule in the asymmetric unit (see Fig. 5). The silicon atom is in distorted tetrahedral coordination. The nitrogen atom N1 is planar with the sum of bond angles of 359.8° around this atom. The morpholino ring is in chair conformation. The urea subunit formed by the atoms N1, C5, S1, and N2 is planar. The phenyl group C6-C11 is orientated nearly perpendicular to the urea unit with an angle of 81.2° between both planes.

Common feature of all molecular structures is the presence of N-substituted morpholines in chair conformation with planar nitrogen atoms. The unsubstituted morpholine molecule crystallizes also in chair conformation but has the hydrogen atom bound to nitrogen in an equatorial position [16]. Planarization of amino nitrogen atoms was observed when the amine was substituted with phenyl groups and with silicon containing substituents [2,17]. In the structures discussed here planarization occurs due to the presence of the groups bound to the morpholino unit. These groups have π-electrons which resonate with the free electron pair at the morpholino nitrogen atom.

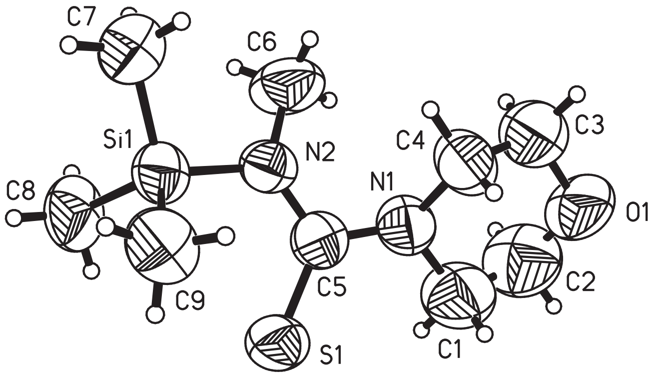


**Fig. 4.** Molecular structure of **7** including numbering scheme. The thermal displacement ellipsoids of the non-hydrogen atoms are drawn at the 50% probability level.

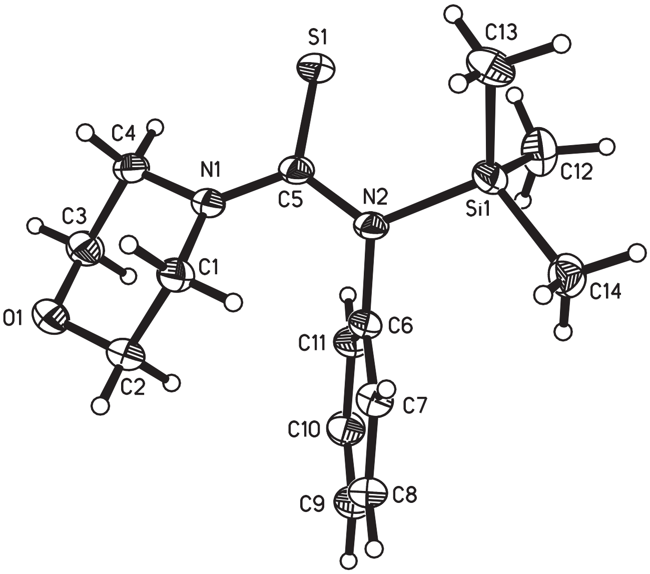


**Fig. 5.** Molecular structure of **8** including numbering scheme. The thermal displacement ellipsoids of the non-hydrogen atoms are drawn at the 50% probability level.

### 3.4. DFT calculations and comparative discussion

If one assumes a concerted insertion mechanism via a four-membered (cyclic) transition state as described and investigated in [5] the following steps are expected (Fig. 6):

The reaction is initiated by a nucleophilic attack of the lone pair of the silicon-bonded nitrogen atom to the carbon atom of the heteroallene moiety as well as a more or less simultaneous nucleophilic attack of the lone pair of the nitrogen atom of the heteroallene to the Si-atom. NBO-analysis is used to calculate the charges of the carbon atom in the isocyanates and isothiocyanates and the charges of the silicon-bonded nitrogen atom in **1** and some insertion products (Tables 4 and 5). A higher charge difference between the electropositive carbon atom and the electronegative Si-bonded N-atom leads to a faster reaction than a low charge difference. Therefore, the sum of absolute charges can be used as a comparative value for the reaction kinetics of the insertion. The calculations confirm that the isocyanates react faster than the isothiocyanates, which could be assumed because of the lower electronegativity of sulphur compared with oxygen. Moreover, the calculations show that the negative charge at the Si-bonded N-atom is only slightly influenced by the organic moiety while

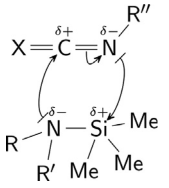


**Fig. 6.** Electron movement in the assumed mechanism of the insertion reaction of isocyanates and isothiocyanates.

**Table 4**
Calculated NBO-charges of the C-atom of the heteroallene moiety of some isocyanates and isothiocyanates.

| Molecule | NBO Charges of C |
|---|---|
| MeNCO | 0.867 |
| PhNCO | 0.892 |
| MeNCS | 0.261 |
| PhNCS | 0.267 |

**Table 5**
Calculated NBO-charges of the silicon-bonded N-atom of **1** and some insertion products.

| Molecule | NBO Charges of Si-bonded N |
|---|---|
| **1** | −0.968 |
| $\mathbf{5}^{*}$[a] | −0.936 |
| **8** | −0.936 |
| $\mathbf{6}^{*}$[b] | −0.922 |
| **7** | −0.906 |
| **5** | −0.894 |

[a] Theoretically calculated mono-insertion product.
[b] Theoretically calculated insertion product with Me instead of $^{n}$Bu.

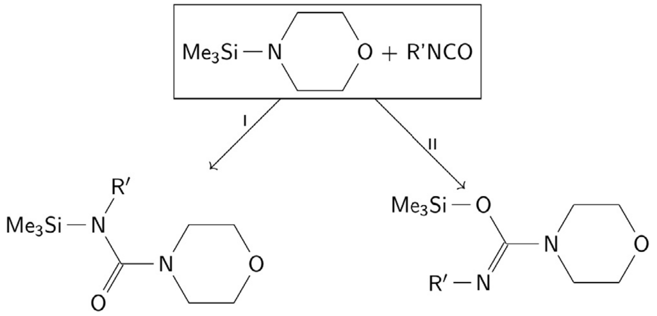
the charge of the carbon atom in the heteroallenes depends more on the organic substituents. The phenyl-ring is an electron withdrawing moiety while the aliphatic groups do not promote the negative charge of the nitrogen atom or the positive charge of the carbon atom, respectively. The calculations match the observed insertion behaviour, i.e. the double insertion of PhNCO is preferred and the sum of charge of the mono insertion product $\mathbf{5}^{*}$ and phenylisocyanate is slightly higher as the sum of charges of **1** and MeNCO. Besides the reaction of **1** and PhNCO is more exothermic than the reaction of PhNCS and **1**.

Quantum chemical calculations have been performed yielding the Gibbs free energies for the insertion reactions. The values for $\Delta G$ are summarized in Table 6. As can be seen from these data the first insertion of PhNCO into trimethyl(N-morpholino)silane (**1**) is strongly exergonic with −40.5 kJ/mol. The second insertion of PhNCO and the single insertion of PhNCS are both exergonic with similar values around −12 kJ/mol. The insertion of MeNCS has a small value of −7 kJ/mol. This hints to the presence of an equilibrium. Calculation of the equilibrium constant K with the thermodynamic relation $\Delta G = -RT \ln K$ gives a value of $K = 16.8$. That means the ratio of product to educt is 16.8 to 1 for the reaction in the gas phase. The insertion of $^{t}$BuNCO is endergonic. This explains the presence of **1**, aliphatic isothiocyanates and thioureas in the NMR spectra of **7** and **9**. All attempts to insert $^{t}$BuNCO into the Si–N-bond of **1** leads to decomposition of **1** and the isocyanate to unidentified products.

In accordance with the literature [5] and the postulated mechanism, only one product of the insertion of $CO_2$ into **1** was observed. The driving force of the insertion of $CO_2$ is the formation of a Si–O-bond. In case of the insertion of isocyanates or isothiocyanates, more insertion patterns can be assumed (Scheme 5). In contrast to the $CO_2$ insertion, no Si–O-bond is formed by the insertion of isocyanates and isothiocyanates into the Si–N-bond of **1**. The formation of a Si–O-bond might be expected to be favoured but the high reactivity of a C=N double bond drives the reaction into the more stable urea containing insertion product. The formation of a Si–C-bond is not expected due to its higher bond energy. Obviously the formation of an urea unit is thermodynamically favoured in these reactions.

**Table 6**
Calculated Gibbs free energies of the insertion reactions into trimethyl(N-morpholino)silane (**1**) at 298.15 K and 1 atm.

| Reaction | $\Delta_R G$ (kJ/mol) |
|---|---|
| first insertion of PhNCO | −40.5 |
| second insertion of PhNCO | −11.6 |
| insertion of PhNCS | −12.0 |
| insertion of MeNCS | −7.0 |
| first insertion of $^{t}$BuNCO | 6.9 |
| second insertion of $^{t}$BuNCO | 40.8 |



**Scheme 5.** Possible insertion patterns of an isocyanate into the Si–N-bond of a morpholinosilane according to the postulated mechanism.

While $CO_2$ reacts with both, **1** and **2**, quantitatively and without side products the insertion of isocyanates is more prone to unwanted reactions like the oligomerisation of the isocyanates. The oxygen atom of morpholine acts as Lewis base witch catalyses the oligomerisation [19]. Moreover, the first insertion into one of the Si–N-bonds of **2** changes the reactivity and other insertion patterns according to Scheme 5 may become possible. This is assumed because of two different signals for the morpholine ring in the $^{1}$H and $^{13}$C NMR-spectra of the insertion reaction product mixtures. Therefore, the insertion products of **2** with isocyanates are obtained as a mixture even if the experiments are performed at low temperatures.

## 4. Conclusion

We have studied the insertion reaction of different heteroallenes and acetone into the Si–N-bond of morpholinosilanes. $CO_2$ inserts readily to forming morpholine-*O*-carbamoylsilanes quantitatively. The insertion pattern of isocyanates and isothiocyanates is mostly influenced by the negative charge of the Si-bonded nitrogen atom and the positive charge of the carbon atom in the isocyanate or isothiocyanate. The reaction with PhNCO prefers the twofold insertion, i.e. biuret moieties are formed, while nBuNCO and PhNCS only insert once per Si–N-bond. Aliphatic isothiocyanates form equilibria in solution between the educts and the thiourea formed by the insertion reaction. The reaction with dimethyl-di(*N*-morpholino)silane (**2**) yielded only with $CO_2$ a pure product, all reactions with isocyanates or isothiocyanates result in product mixtures. The molecular structures of key products prove the different insertion patterns indicated by NMR-spectroscopic data.

## Acknowledgment

The authors thank TU Bergakademie Freiberg (Freiberg, Germany) and the German Research Foundation (Deutsche Forschungsgemeinschaft, DFG, Bonn) for financial support. U.B. thanks the computing centre of the TU Bergakademie Freiberg for computing time at the High Performance Compute Cluster. E. Brendler (Institute for Analytical Chemistry, TU Bergakademie Freiberg) is acknowledged for help with the NMR measurements. Part of this work was performed within the research group "Chemical utilization of carbon dioxide with aminosilanes ($CO_2$Sil)" that is financially supported by the European Union (European regional development fund), the Ministry of Science and Art of Saxony (SMWK) and the Sächsische Aufbaubank (SAB).

## References

[1] K. Tamao, A. Kawachi, Y. Ito, Organometallics 12 (1993) 580–582;
T. Schlosser, A. Sladek, W. Hiller, H. Schmidbaur, Z. Naturforsch. 49b (1994) 1247–1255;
K. Tamao, A. Kawachi, Y. Nakagawa, Y. Ito, J. Organomet. Chem. 473 (1994) 29–34;
G. Huber, N.W. Mitzel, A. Schier, H. Schmidbaur, Chem. Ber. 130 (1997) 1159–1166;
G. Huber, A. Schier, H. Schmidbaur, Chem. Ber. 130 (1997) 1167–1174;
G. Huber, N.W. Mitzel, A. Schier, H. Schmidbaur, Chem. Ber. 130 (1997) 1159–1166;
K. Trommer, U. Herzog, G. Roewer, J. Prakt. Chem. 339 (1997) 637–641;
U. Herzog, K. Trommer, G. Roewer, J. Organomet. Chem. 552 (1998) 99–108;
G. Huber, A. Schier, H. Schmidbaur, Z. Naturforsch. B 54 (1999) 18–20;
G. Huber, H. Schmidbaur, Monatsh. Chem. 130 (1999) 133–138;
U. Böhme, B. Günther, B. Rittmeister, Inorg. Chem. Comm. 3 (2000) 428;
U. Böhme, B. Günther, B. Rittmeister, Eur. J. Inorg. Chem. (2003) 751;
B. Meinel, B. Günther, U. Böhme, J. Mol. Struct. 1079 (2015) 363–369.

[2] B. Meinel, B. Günther, A. Schwarzer, U. Böhme, Z. Anorg. Allg. Chem. (2014) 1607–1613.

[3] F. Bitto, K. Kraushaar, U. Böhme, E. Brendler, J. Wagler, E. Kroke, Eur. J. Inorg. Chem. 16 (2013) 2954–2962.

[4] H. Juvaste, E.I. Iiskola, T.T. Pakkanen, J. Organomet. Chem. 587 (1999) 38–45;
J. Heinicke, S. Mantey, A. Oprea, M.K. Kindermann, P.G. Jones, Heteroat. Chem. 10 (1999) 605–613;
A. Kawachi, K. Tamao, J. Organomet. Chem. 601 (2000) 259–266;
C. Strohmann, O. Ulbrich, D. Auer, Eur. J. Inorg. Chem. (2001) 1013–1018.

[5] Kraushaar, Konstantin, Wiltzsch, Conny, Wagler, Joerg, Böhme, Uwe, Schwarzer, Anke, Roewer, Gerhard, Kroke, Edwin, Organometallics, 2012, 31, 13, 4779–4785.

[6] K. Tamao, G.R. Sun, A. Kawachi, S. Yamaguchi, Organometallics 16 (1997) 780–788;
K. Trommer, U. Herzog, N. Schulze, G. Roewer, Main Group Metal Chem. 20 (2001) 425–433.

[7] C. Ackerhans, B. Räke, P. Müller, H.W. Roesky, I. Uson, Eur. J. Inorg. Chem. (2000) 827–830;
S. Sysoev, L. Nikulina, M. Kosinova, V. Rakhlin, I. Tsirendorzhieva, A. Lis, M. Voronkov, Inorg. Mat. 47 (2011) 1324–1329;
E. Kroke, Y.-L. Li, C. Konetschny, E. Lecomte, C. Fasel, R. Riedel, Mater. Sci. Eng. R. 26 (2000) 97–199;
K.-H. Kim, J. Korean Phys. Soc. 67 (2015) 2115–2119;
H. Kato, K. Fukushima, M. Yonezawa, J. Hiraga, CVD method for forming silicon nitride film, Tokyo Electron Limited, WO 2004105115 A1 (http://www.freepatentsonline.com/WO2004105115.html).;
L. Du, C. Xu, W. Chu, Y. Ding, Polyhedron 117 (2016) 729–734.

[8] D. Knausz, A. Meszticzky, L. Szakacs, B. Csakvari, J. Organomet. Chem. 256 (1983) 11–21.

[9] C. Wiltzsch, K. Kraushaar, A. Schwarzer, E. Kroke, Z. Naturforsch. 66b (2011) 917–922.

[10] E.A.V. Ebsworth, G. Rocktäschel, J.C. Thompson, J. Chem. Soc. A: Inorg., Phys., Theor., 1967, 362–365.

[11] H. Breederveld, Rec. Trav. Chim. 81 (1962) 267.

[12] W. Fink, Chem. Ber. 97 (1964) 1433–1438.

[13] W. Walter, H. Kubel, H.-W. Lüke, Liebigs Ann. Chem. 1979 (1979) 263–277.

[14] Kraushaar, K., Schmidt, D., Schwarzer, A., Kroke, E. in $CO_2$ Chemistry, van Eldik, R. & Aresta, M. (Eds.), Elsevier, 2014, 66, 117–162.

[15] D. Schöne, D. Gerlach, C. Wiltzsch, E. Brendler, T. Heine, E. Kroke, J. Wagler, Eur. J. Inorg. Chem. 3 (2010) 461–467.

[16] A. Parkin, I.D.H. Oswald, S. Parsons, Acta Cryst. B 60 (2004) 219–227.

[17] N. Mitzel, A. Schier, H. Schmidbaur, Chem. Ber. 125 (1992) 2711–2712.

[18] National Insitute of Advanced Industrial Science, T. (Japan), AIST: Integrated Spectral Database System of Organic Compounds; accessible under http://sdbs.db.aist.go.jp.

[19] C. Kurt, D. Frisch, Klempner, Advances in Urethane: Science & Technology, vol. 12, CRC Press, 1992.

[20] Marcus Herbig, Edwin Kroke, Thermochim. Acta 654 (2017) 81–84.

[21] P.U. Gelest, Inc. of Morrisville, Metal-Organics Catalog.

[22] R.A. Pike, R.L. Schank, J. Org. Chem. 27 (1962) 2190–2192.

[23] K. Itoh, S. Sakai, Y. Ishii, J. Org. Chem. 31 (1966) 3948–3951.

[24] S.N. Goodman, E.N. Jacobsen, Angew. Chem., Int. Ed. 41 (2002) 4703–4705.

[25] D.S. Tarbell, Y. Yamamoto, J. Org. Chem. 36 (1971) 2954–2956.

[26] Stoe & Cie, X-RED and X-AREA, Stoe & Cie, Darmstadt, Germany, 2009.

[27] G.M. Sheldrick, Acta Crystallogr., Sect. A 64 (2008) 112–122.

[28] G.M. Sheldrick, Acta Cryst. C 71 (2015) 3–8.

[29] Gaussian 09, Revision E.01, M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery, Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K. N. Kudin, V.N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian Inc, Wallingford CT, 2013.

[30] Y. Zhao, D.G. Truhlar, Theor. Chem. Acc. 120 (2008) 215–241;
R. Krishnan, J.S. Binkley, R. Seeger, J.A. Pople, J. Chem. Phys. 72 (1980) 650;
A.D. McLean, G.S. Chandler, J. Chem. Phys. 72 (1980) 5639.

[31] NBO 6.0. E.D. Glendening, J.K. Badenhoop, A.E. Reed, J.E. Carpenter, J.A. Bohmann, C.M. Morales, C.R. Landis, F. Weinhold (Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, 2013); http://nbo6.chem.wisc.edu/.