

CO₂ Capture with Silylated Ethanolamines and Piperazines

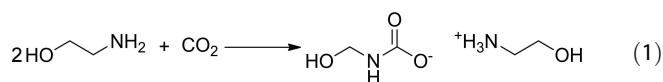
Marcus Herbig, Lia Gevorgyan, Moritz Pflug, Jörg Wagler, Sandra Schwarzer, and Edwin Kroke*^[a]

Amine treatment is commonly used to capture CO₂ from exhaust gases and from ambient air. The Si–N bond in aminosilanes is capable of reacting with CO₂ more readily than amines. In the current study we have synthesized trimethylsilylated ethanolamines, diethanolamines and piperazines and investigated their reaction toward CO₂. All products were characterized by ¹H, ¹³C, and ²⁹Si NMR, RAMAN spectroscopy as well as mass spectrometry. The product of a twofold CO₂-insertion into bis-trimethylsilylated piperazine was analysed by single-crystal X-ray diffraction. Furthermore, quantum chemical

calculations (DFT) were used to supplement the experimental results. Geometry optimizations and NBO calculations for each starting material were carried out at the B3LYP level with different basis sets. DFT calculations at the B3LYP, WB97XD and M062x level were conducted for geometry optimization and frequency calculations to examine the thermochemical data. The calculations were carried out both for the gas phase and in solvent environment. The calculated reaction enthalpies varied between –37 and –107 kJ mol^{–1}, while experimental values around –100 kJ mol^{–1} were determined.

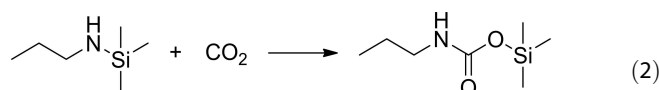
1. Introduction

Amines and carbon dioxide react to form ammonium carbamates (Equation 1). This reaction is successfully applied in amine gas treatment. According to Equation (1), one molecule of CO₂ can be absorbed by two molecules of amine.^[1]



For amine gas treatment a solution of ethanolamines in water is used in combination with accelerators (like piperazine) and other additives (like defoamers and corrosion inhibitors). In the absorber, the acidic gas stream is passed through a counter-stream of the washing solution. The acidic gases are absorbed and the saturated solution is pumped into a desorber to regenerate the washing solution and capture the liberated CO₂.^[1]

Similar to the reaction of N–H-bonds of amines the insertion reaction of CO₂ into the Si–N bond is also possible like in Equation (2). In this reaction, one Si–N bond can absorb one molecule of CO₂ yielding a carbamoyloxysilane.^[3] For the shown example, the reaction proceeds smoothly with quantitative yields.^[2,3]



In our previous investigations in the field of CO₂ absorption with aminosilanes, we have studied the silylation of various amines and other nitrogen containing organic compounds like lactams. Besides, we synthesised aminosilanes of the type R_xSi(NHR')_{4-x} with up to four Si–N bonds per molecule.^[2–7] Diaminosilanes R₂Si(NHR')₂ allow quantitative twofold CO₂ insertion, successive thermolysis of the insertion products leads to ureas and oligosiloxanes.^[4] Furthermore, we investigated the insertion reaction of other heteroallenes such as isocyanates and isothiocyanates into these aminosilanes.^[4,5]

The silylation of ethanolamines has been reported in older Russian literature,^[8–16] which reports primarily on vibrational and NMR spectroscopic data of the silanes. Studies on carbon dioxide insertion reaction into the title compounds have not been published so far.

In the present study, we report on reactions of CO₂ with trimethylsilylated ethanolamines and piperazines with a focus on the experimental determination of reaction enthalpies and corresponding quantum chemical calculations.

2. Results and Discussion

2.1. Synthesis of Silylated Starting Materials

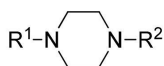
The silylation of the amines supported by a base, which was used in this study, proceeds in a straightforward manner and with good yields. Almost all silylations were successful using trimethylchlorosilane and triethylamine as silylating mixture. Figure 1 shows an overview of the aminosilanes synthesized in this work.

All compounds were purified by distillation and characterised by ¹H, ¹³C and ²⁹SiNMR spectroscopy and RAMAN

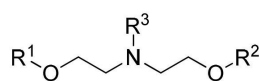
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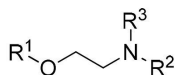
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Nr.	R ¹	R ²
1	H	H
2	CH ₃	H
3*	SiMe ₃	SiMe ₃
3a	SiMe ₃	C(O)OSiMe ₃
3b*	C(O)OSiMe ₃	C(O)OSiMe ₃
4	CH ₃	SiMe ₃
4a	CH ₃	C(O)OSiMe ₃



Nr.	R ¹	R ²	R ³	Russian lit.
5	H	H	H	
6*	SiMe ₃	H	H	[10]
7*	SiMe ₃	SiMe ₃	H	[8,9,10,13,15]
7a	SiMe ₃	H	SiMe ₃	
7b	SiMe ₃	H	C(O)OSiMe ₃	
8*	SiMe ₃	SiMe ₃	SiMe ₃	[9,10,13]
8a*	SiMe ₃	SiMe ₃	C(O)OSiMe ₃	[12]



Nr.	R ¹	R ²	R ³	Russian lit.
9	H	H	H	
10*	SiMe ₃	H	H	[8,9,10,13-16]
11*	SiMe ₃	SiMe ₃	H	[8-11,13,14,16]
11a*	SiMe ₃	C(O)OSiMe ₃	H	[11]
12*	SiMe ₃	SiMe ₃	SiMe ₃	[9,10,13,14,16]
12a	SiMe ₃	C(O)OSiMe ₃	SiMe ₃	
12b	SiMe ₃	C(O)OSiMe ₃	C(O)OSiMe ₃	

Figure 1. Compounds involved in this study. Substances marked with an * were synthesized and analyzed.

spectroscopy. The boiling points were determined by the method described in [19].

Surprisingly, the synthesis of **7** was not possible by reacting chlorotrimethylsilane with diethanolamine in a molar ratio of 2:1. Three different signals were detected in the ²⁹Si NMR

spectrum of the product mixture, one in the expected range for nitrogen bonded SiMe_3 moieties and the other two in the region of oxygen bonded SiMe_3 moieties. Therefore, in addition to one O-bound SiMe_3 group, the second SiMe_3 moiety is attached to either nitrogen or oxygen. Changing the solvent from diethyl ether to *n*-heptane altered the molar ratio but not the occurrence of the three signals. Storage for several days in deuterated chloroform (NMR sample) did not change the molar ratio of the compounds. Exclusive *O,O'*-bissilylation was achieved by using trimethylsilyl triflate as silylating agent. The *O,O'*-bissilylated product **7** did not convert into the product mixture, neither upon standing in deuterated chloroform for several days, nor by the addition of triethylammonium chloride as a catalyst. Further on, the threefold silylation of diethanolamine, to obtain **8**, could only be achieved with trimethylsilyl triflate, whereas reaction with trimethylchlorosilane failed. The synthesis of **12** is performed with trimethylsilyl triflate starting with **11** due to steric hindrance at the nitrogen atom and the reduced basicity/nucleophilicity of the nitrogen lone pair due to the Me_3Si substituent.

2.2. Carbon Dioxide Insertion Reactions

Following the syntheses of the set of aminosilanes, the insertion of CO_2 into the Si–N bonds of compounds **3**, **4**, **8**, **11** and **12** was studied. All insertion reactions with CO_2 were performed by passing the gas from a gas cylinder through conc. sulphuric acid and afterwards into the aminosilane solution in THF at 0°C . Among this set of aminosilanes under investigation, CO_2 only reacts with **3**, **4**, and **11**. No reaction was observed with **8** and **12**, most likely due to steric reasons. Repeating the experiment inside an autoclave with slightly higher pressure (4 to 8 bar) did not change the results. Interestingly, reaction in refluxing THF affords a product of CO_2 insertion into the Si–N bond of **8**.

From the twofold insertion product of **3** (i.e. **3b**, Figure 1) crystals suitable for X-ray diffraction analysis were obtained. This compound crystallizes in the monoclinic space group $C2/c$. Its piperazine ring is in chair conformation and situated around a crystallographically imposed inversion centre. Hence, the asymmetric unit comprises one half of the molecule. The carbamic moieties are planar as expected. Furthermore, the piperazine C–N bonds are situated almost in the same plane. The ^1H NMR signals of the piperazine protons are broadened (because of the hindered rotation about the C1–N1 bond, which in principle gives rise to two different conformers of the molecule). Additionally, two signals are obtained for the piperazine carbon atoms in the ^{13}C NMR spectrum (Figure 2).

The ability of the silylated piperazine to absorb CO_2 from dry ambient air was studied by passing air through a solution of **4** in THF. The exhaust gas was passed into an aqueous solution of barium hydroxide to visualize the breakthrough of CO_2 . The analysis of the reaction product shows that the starting material is converted into the carbamoyloxysilane. Additionally, some hydrolysis products and side products were found in the NMR spectra, like hexamethyldisiloxane (^{29}Si NMR: $\delta = 7.2$ ppm), most

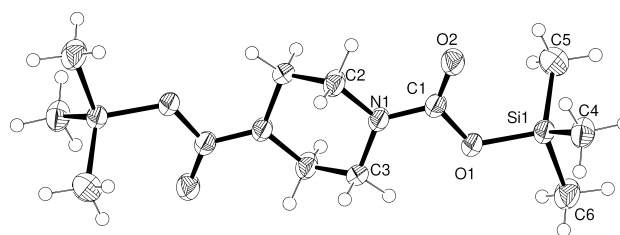
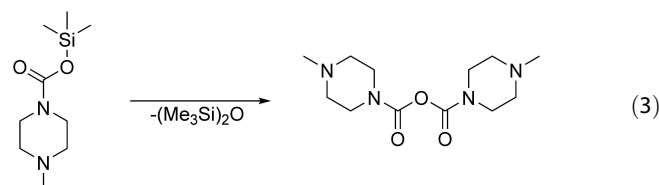


Figure 2. Molecular structure of **3b** with thermal displacement ellipsoids at 50% probability level. Atoms of the asymmetric unit are labelled. The positions of the corresponding symmetry equivalent atoms of the molecule are generated by a centre of inversion (1-x, 1-y, 1-z). Selected bond lengths (Å) and angles (deg): Si1–O1 1.6964(11), C1–O1 1.3495(17), C1–O2 1.2173(18), C1–N1 1.3514(18), Si1–O1–C1 122.64(9), O1–C1–O2 122.88(13), O1–C1–N1 112.94(12), O2–C1–N1 124.18(13).

likely caused by traces of water and/or by dicarbonic diamide formation according to Equation (3).



Another signal at 17.3 ppm could not be assigned. The low yield (33%) of carbamoyloxysilane **4a** (which is less volatile and should remain in the flask upon workup) indicates that the aminosilane has not been converted quantitatively, and leftover silane **4** is removed by the vacuum distillation applied for removal of the solvent. To reduce the reaction time, the experiment was repeated in a modified manner: the aminosilane is added dropwise onto a 20 cm column packed with glass tubings to increase the surface area, counter-streamed by CO_2 -containing air. Also, the passing ambient air was bubbled into the solution which already passed through the column before entering the column (see Supporting Information). The experiment was stopped when the barium hydroxide solution at the exhaust of the apparatus turned opaque. Thereafter, the reaction products were washed from the column using THF. According to NMR analysis, only small amounts of the expected insertion product are contained in the product mixture. A signal at 23.1 ppm in the ^{29}Si NMR spectrum is evidence for the insertion product, but the more intense signal at 5.6 ppm belongs to the starting material. Except for hydrolysis products no other side products can be found. Hence, under the conditions applied a noticeable amount of CO_2 from the ambient air can pass through the reaction solution without reacting with the aminosilane. Since the CO_2 insertion reactions are expected to be thermodynamically favourable in the cases studied, we suspect kinetic hindrance as the predominant obstacle. In order to prove our assumption (thermodynamic favorability of CO_2 insertion), and to investigate the effect of the different silanes, computational analyses were performed.

2.3. Quantum Chemical Calculations of $\Delta_r G$ and $\Delta_r H$

The quantum chemical calculations were performed at B3LYP/6-31G(d), B3LYP/6-31++G(d), M062X/6-311+G(d) and WB97XD/6-31G(d) levels of theory in the gas phase and in the solvent (THF by using polarizable continuum model, PCM). The M062X and WB97XD methods include dispersion correction, which includes both short-range as well as long-range interactions. Therefore, results obtained from these calculations usually show better agreement with experiment than those obtained at B3LYP theory level. The calculations were performed by using different basis sets as 6-31G(d), 6-31++G(d) and 6-311+G(d,p). After an optimization calculation a frequency calculation was performed for each molecule. All energy values and optimised structures were obtained from these frequency calculations. The results mostly confirm the experimental results (vide infra). Calculations at the M062X/6-31G(d) level in the gas phase already deliver data consistent with the experimental findings. Even better results were obtained at the same level of theory in the solvent phase. Therefore, only the values of this level of theory are discussed here.

The energies of the calculated structures show that **7** should be thermodynamically more stable than **7a**, which matches our expectations, but is in contrast with the obtained experimental results. It can be assumed that **7a** is a side product due to the nucleophilicity of the nitrogen atom towards the chlorosilane. Trimethylsilyl triflate is more ionic and does react more likely with the hydroxy moiety. Storing **7a** several days in chloroform with or without triethylammonium chloride does not change the product distribution showing the kinetic stability of **7a** in the mixture, i.e., hindered rearrangement to **7**.

To understand the thermodynamics of the insertion reaction, the Gibbs free energy of the reactions were calculated from the Gibbs energy values obtained from the frequency calculations. The results are listed in Table 1.

The Gibbs free energy of the insertion reaction of CO₂ into the Si–N bond is always negative, except for the reaction of CO₂ with **12a**. The reaction enthalpy is always negative. Regarding the influence of the solvent as PCM changes the values of the energies but exergonic reactions stay exergonic as well as all reactions stay exothermic. The enthalpies obtained from calculations at the above mentioned level of theory in the gas phase vary from –105 to –40 kJ mol^{–1} and in the solvent from –107 to –37 kJ mol^{–1} (see Table 1). This set of calculations does

Table 1. Gibbs free energies and enthalpies (in kJ/mol) of the insertion of CO₂ into the Si–N bond of different molecules. The calculations were performed at M062X/6-31G(d) level of theory in the gas phase (g) and in THF (solv).

Reaction	$\Delta_r G$ (g)	$\Delta_r G$ (solv)	$\Delta_r H$ (g)	$\Delta_r H$ (solv)
3 → 3a	–44.72	–49.31	–104.80	–106.74
3a → 3b	–66.09	–62.12	–91.67	–92.71
4 → 4a	–45.51	–50.36	–100.12	–102.12
8 → 8a	–47.46	–67.04	–103.93	–100.30
11 → 11a	–51.35	–55.98	–96.21	–100.50
12 → 12a	–57.56	–62.49	–100.20	–102.45
12a → 12b	20.56	17.48	–39.31	–36.71

not explain the insertion behaviour on a sufficient level. Thus, experimental data were determined via calorimetric measurements. For a comparison with experimental data it should be mentioned that reactions **3** to **3a** and **3a** to **3b** cannot be measured separately. Thus, the sum of both calculated values of –199.45 kJ mol^{–1} needs to be considered.

2.4. Calorimetric Measurements

In order to experimentally confirm the quantum chemical calculations, calorimetric measurements of the heat of reaction were performed. Details of the experimental setup and the applied procedures can be found in the experimental part. It is assumed that all hydrolysis due to residual traces of water inside the calorimetric chamber were finished before the CO₂ enters and the insertion reaction commences. All results and all correlations of the experimental findings with the theoretical calculations are summarized in Table 2.

Further reactions of the amines **1**, **2**, **5** and **9** with carbon dioxide were conducted in the calorimeter yielding enthalpies of –55.96, –49.22, –16.36 and –37.17 kJ mol^{–1}. These values should not be compared with the results found for the aminosilanes, because a 1:2 reaction as shown in Equation (1) takes place. However, the results of the calorimetric measurements show that the insertions into the aminosilanes are always more exothermic than the reaction of CO₂ and the free amine. Therefore, all values determined for the aminosilane should be seen as lower boundary. With these values, the quantum chemical calculations could be verified. In the Supporting Information more calculation results with other basis sets and methods can be found. The results of M062X/6-31G(d) show the best correlation with the measured values (Table 3).

Table 2. Yields, measured enthalpy of the reaction of CO₂ with the aminosilane and calculated values, respectively.

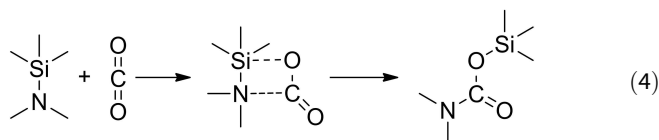
Reaction	Isolated yield in %	$\Delta_r H$ (exp) in kJ/mol	$\Delta_r H$ (solv) in kJ/mol (see table 1)
3 → 3b	85	–174.11	–199.45
4 → 4a	93	–79.89	–102.12
8 → 8a	61	–67.93	–100.3
11 → 11a	77	–76.15	–100.5

Table 3. Correlation of $\Delta_r H$ values obtained by quantum chemical calculations with measured values.

Method/basis set	Coefficient of correlation
b3lyp/6-31G(d)	0.9596
b3lyp/6-31G(d)/THF	0.9586
m062x/6-31G(d)	0.9774
m062x/6-31G(d) in THF	0.9924
wb97xd/6-31G(d)	0.9775
wb97xd/6-31G(d) in THF	0.9746
b3lyp/6-31++G(d)	0.9467
b3lyp/6-31++G(d) in THF	0.9675
m062x/611+G(d,p)	0.9761
m062x/611+G(d,p) in THF	0.9853

2.5. Mechanistic Considerations

As a further approach, NBO calculations at B3LYP/6-31G(d) level of theory were used to explain the insertion reaction behaviour. We assumed the mechanism with a cyclic four-centered transition state proposed by our group in 2012^[18] to be relevant (see Equation (4)).



Therefore, some values obtained from the NBO calculations (Natural Charges) were used in an attempt to explain the insertion behaviour. The mechanism includes a nucleophilic attack of the lone pair of the nitrogen atom towards the carbon atom of the CO₂ molecule. Therefore, a more negative charge of the nitrogen atom should be favourable and activate the reaction. Besides, a lone pair from an oxygen atom of the CO₂ must attack the silicon centre of the aminosilane. Therefore a positive charge of the silicon atom should be favourable. Contrarily, the Natural Charge on the silicon atoms do not differ significantly comparing all aminosilanes and carbamoyloxysilanes. The Natural Charge of the nitrogen atom strongly depends on its substitution pattern. Aminosilanes derived from secondary amines have similar charge, while for the monoethanolamine derivatives this charge becomes more negative with increasing number of Me₃Si substituents, but turns significantly less negative upon the first insertion of CO₂ into **12**.

In addition to charges, orbital interactions (nucleophilicity) must also be considered (Table 4). The lone pair energies decrease and the ratio p/s-orbital contributions to the lone pair as well as the sum of angles around the nitrogen atom increase with increasing degree of silylation. These effects lead to a deactivation of the system with respect to the insertion reaction. The silylation leads to more planar environment around the nitrogen atom. In fact, aminosilanes with a lower sum of angles around the nitrogen atom and with a lone pair composed with lower p/s-ratio, namely **3**, **4** and **11**, react with CO₂ under the given mild conditions. In agreement with this, **8** reacts only under harsher conditions. The reaction of **12** with CO₂ is most unlikely: the nitrogen atom is nearly planar and the lone pair is mostly a p-orbital. Additionally, the trimethylsilyl moieties lead to a highly sterically hindered nitrogen atom. So,

the kinetic hindrance of the exergonic reaction of **12** to **12a** can be explained consulting the NBO calculations. This explains why this thermodynamically favourable reaction has not been observed in the experiments.

In further work we investigated more details of the insertion mechanism. The kinetics and activation energies of the reaction, which are important for the reversibility, are going to be published soon elsewhere.

In order to study the dependence of CO₂ insertion on CO₂ pressure, we had to move to a system with rather inhibited reactivity in order to adjust to higher CO₂ pressure and monitor the reaction under quasi-constant CO₂ pressure (whereas in the current case lower CO₂ pressure would have to be used, and thus the molar amount of CO₂ consumed during reaction in an autoclave batch would have altered the system significantly). As the above mentioned system is less related to the herein studied aminosilanes, these data will be published separately in near future.

3. Conclusions

We have synthesized trimethylsilylated mono- and diethanolamine with up to three trimethylsilyl moieties as well as piperazine and 1-methylpiperazine with one or two trimethylsilyl moieties, respectively. Due to the steric hindrance of the trimethylsilyl groups, for the threefold silylation of monoethanolamine trimethylsilyl triflate had to be used. Bonding more than one TMS moiety onto diethanolamine using chlorotrimethylsilane as silylation agent leads to two different isomers (*O,O'* and *O,N* silylated), whereas silylation with trimethylsilyl triflate affords the (thermodynamically favoured) *O,O'*-(SiMe₃)₂ isomer.

The reaction of all silylated products containing a Si–N bond with CO₂ was studied. The reaction strongly depends on the silylation pattern. Despite the activation of the nitrogen atom due to silylation, not all products of the insertion of CO₂ into the Si–N bond could be observed. The absorption of CO₂ from dry ambient air is possible but not efficient so far.

The experimental results were compared with quantum chemical calculations. The insertion behaviour observed so far can be explained by considering a combination of thermodynamic aspects (derived from optimization and frequency calculations for all the starting materials and products at different levels of theory, including dispersion correction and solvent model, which afford enthalpy data well in accord with our calorimetric observations) and kinetic aspects (elucidated

Table 4. Calculation of Natural Charges (NCs), sum of angles ($\sigma < (N)$), lone pair (LP) energies and LP hybrid orbital composition of the reacting nitrogen atom.

Molecule	NC of N atom	$\sigma < (N)$ in °	LP energies in a.u.	LP p-orbital contribution (in %)
3	−0.94	347.43	−0.222	21.7
4	−0.94	347.09	−0.223	21.2
8	−0.95	357.82	−0.212	99.9
11	−1.14	349.26	−0.227	17.9
12	−1.36	359.82	−0.208	99.9
12a	−0.89	359.33	−0.235	99.9

by NBO calculations, which deliver hints at charges and orbital energies as kinetic driving forces). These analyses allowed to distinguish between thermodynamically unfavorable and kinetically hindered reactions for those cases where no CO₂ insertion was observed in the experiment.

As the thermodynamics of CO₂ insertion into Si–N bonds were shown to be favourable in most cases (for monosilylated primary and secondary amines) and superior to the reaction of CO₂ with the corresponding amine, kinetics of the reaction are now of crucial interest for the further applicability, e.g., in synthesis and reversible CO₂ storage. Therefore, detailed studies of the kinetics are currently performed.

Experimental Part

Materials and Methods

Monoethanolamine was purchased from ACROS and stored over molecular sieve 3 Å. Diethanolamine was purchased from Alfa Aesar (99%) and piperazine from ABCR (anhydrous, 99%), both were used without further purification. 1-Methylpiperazine was purchased from Sigma-Aldrich (99%) and was distilled from calcium hydride before use. Triethylamine was purchased from AppliChem (pure) and distilled from sodium/benzophenone before use. Chlorotrimethylsilane was purchased from Sigma-Aldrich (99%) and distilled through a 20 mm column filled with Raschig glass rings. Trimethylsilyl triflate was purchased from Corbolution Chemicals (98%) and used without further purification. Diethyl ether and tetrahydrofuran were purchased from VWR (Normapur) and purified by a MBRAUN SPS 800 solvent drying system. Pentane and hexane were ordered in technical grade and chemically purified by storing over molecular sieve 3 Å for several days. Deuterated chloroform was purchased from AMAR Chemicals (99,8% D) and distilled from calcium hydride. After distillation about 0.03 vol% tetramethylsilane (ABCR, 99%) was added. Carbon dioxide was purchased from Linde (purity grade 5.3) and used without further purification.

All experiments were performed with standard Schlenk technique using an atmosphere of dry argon (Praxair, 4.0), unless stated otherwise.

RAMAN data were measured with FT-Raman spectrometer RFS 100/S (Bruker). Boiling points were measured as described in [19]. NMR spectra were recorded in CDCl₃ solution if not stated otherwise using a 500 MHz spectrometer (Bruker AVANCE III).

All calculations were performed using the Gaussian 09 program package. For visualization of the structures Gaussview 5.0.9 was used. First optimization calculations were performed at B3LYP/6-31G(d), B3LYP/6-31++G(d), M062X/6-311+G(d), WB97XD/6-31G(d) levels of theory. Afterwards, frequency calculations at the same level of theory were performed. All calculations were applied both in the gas phase and in the solvent. The NBO calculations were carried out at B3LYP/6-31G(d) level in the gas phase.

Calorimetric measurements were performed on a Setaram C80 instrument with a 9.5 cm³ stainless steel vessel (vacuum to 5 bar). Measurements were performed isothermal at 30 °C. The vessel was evacuated for several hours before inserting a small amount (50 to 150 mg) of pure compound under ambient pressure argon atmosphere. The vessel was connected with a 2 l-round bottom flask filled with CO₂ (ambient pressure) but separated with a stop cock. After equilibration of the setup (upon inserting the vessel into the C80 instrument) the measurement was started and the stop

cock was opened. CO₂ entered the vessel by convection and diffusion, and the volume of the CO₂ reservoir used served as a buffer for almost constant CO₂ pressure throughout the experiment (only a small fraction of the CO₂ provided was used as starting material in the reaction).

Determination of the Molecular Structure of Compound 3b Using Single-Crystal X-ray Diffraction

Data collection was performed on a STOE IPDS-2T image plate diffractometer (STOE) at 200(2) K in ω scans using Mo–K α radiation ($\lambda=0.71073$ Å). For data collection and cell refinement the implemented software X-Area was used, for data reduction X-RED. The structure was solved with direct methods (ShelXS^[20]) and refined in full-matrix least-squares cycles against F^2 using ShelXL2014/7.^[21] Selected crystal data and parameters of unit cell determination and structure refinement for **3b**: Crystal dimensions 0.22·0.15·0.03 mm, C₁₂H₂₆N₂O₄Si₂, $M_r=318.53$, monoclinic, space group C2/c, $a=11.3654(9)$, $b=6.0171(3)$, $c=25.3198(19)$ Å, $\beta=96.531(6)^\circ$, $V=1720.3(2)$ Å³, $Z=4$, $\rho_{\text{calcd}}=1.230$ Mgm⁻³, $\mu(\text{Mo–K}\alpha)=0.219$ mm⁻¹, $F(000)=688$, $2\theta_{\text{max}}=54.0^\circ$, 9139 collected reflections, 1885 unique reflections ($R_{\text{int}}=0.0340$), 94 parameters, $S=1.027$, $R_1=0.0311$ [$I>2\sigma(I)$], $wR_2(\text{all data})=0.0794$, max./min. residual electron density +0.222/–0.207 eÅ⁻³.

CCDC 1917759 contains the complete 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.

General Procedure for Silylation with Chlorotrimethylsilane

To a stirred solution of 1-methylpiperazine (4.61 g, 46 mmol) and triethylamine (4.66 g, 46 mmol) in diethyl ether (60 mL) at 0 °C chlorotrimethylsilane (5.00 g, 46 mmol) was added dropwise. The reaction mixture was stirred overnight. The triethylamine hydrochloride precipitate was removed by filtration (using a G4-frit). From the filtrate the volatiles were removed under reduced pressure (condensation into a cold trap) to yield 7.46 g (91%) of *N*-methyl-*N'*-trimethylsilylpiperazine.

General Procedure for Silylation with Trimethylsilyl Triflate

To a stirred solution of *O,N*-bis(trimethylsilyl)ethanolamine (5.60 g, 27 mmol) and triethylamine (2.76 g, 27 mmol) in diethyl ether (80 mL) at 0 °C trimethylsilyl triflate (6.05 g, 27 mmol) was added dropwise. The reaction mixture was stirred at room temperature overnight and then cooled with an iso-propanol/dry ice bath. From the cold mixture the liquid solution was transferred into a new flask (by decantation). From this solution the volatiles were removed under reduced pressure (condensation into a cold trap). The residue was distilled in vacuo to yield 4.55 g (61%) of *O,N,N*-tris(trimethylsilyl)ethanolamine.

N,N'-Bis(trimethylsilyl)piperazine 3

Compound **3** was synthesized by general procedure for silylation with chlorotrimethylsilane using diethyl ether or pentane as solvent, 4.66 g (46 mmol) triethylamine, 5.00 g (46 mmol) trimethylchlorosilane and 1.98 g (23 mmol) piperazine. Yield: 4.63 g (87%) of **3** after filtration through syringe filter (0.2 μm , PTFE).

bp: 190.4 °C (977 mbar), 210–216 °C (1 bar),^[22] ¹H NMR: (500 MHz, CDCl₃, 25 °C, TMS) $\delta = -0.05$ (s, 18H, SiMe₃), 2.63 ppm (s, 8H, CH₂N); Lit.: ¹H NMR $\delta = 2.9$ ppm,^[17] ¹³C NMR: (125 MHz, CDCl₃, 25 °C, TMS)

$\delta = -1.0$ (N–SiMe₃), 46.8 ppm (CH₂N); ²⁹Si NMR: (99 MHz, CDCl₃, 25 °C, TMS) $\delta = 4.9$ ppm; Raman (neat) (cm^{-1}) = 2953 (s), 2897 (vs), 2814 (w), 2732 (vw), 2674 (vw), 1449 (vw), 1410 (vw), 1345 (vw), 1208 (vw), 1131 (vw), 1052 (vw), 682 (vw), 602 (s), 325 (vw), 259 (vw), 215 (vw), 174 (vw).

N-Methyl-N'-trimethylsilylpiperazine 4

Compound **4** was synthesized by general procedure for silylation with chlorotrimethylsilane using diethyl ether or pentane as solvent, 4.66 g (46 mmol) triethylamine 5.00 g (46 mmol) trimethylchlorosilane and 4.61 g (46 mmol) 1-methylpiperazin. Yield: 7.46 g (91 %) of **4** after filtration through syringe filter (0.2 μm , PTFE).

bp: 162 °C (977 mbar); ¹H NMR: (500 MHz, CDCl₃, 25 °C, TMS) $\delta = 0.00$ (s, 9H, SiMe₃), 2.38 (m, 4H, CH₂–N–Si), 2.20 (m, 7H, CH₂–N–CH₃); ¹³C NMR: (125 MHz, CDCl₃, 25 °C, TMS) $\delta = -1.2$ (SiMe₃), 45.0 (CH₂NSi), 46.6 (CH₃), 56.6 (CH₂NCH₃); ²⁹Si NMR: (99 MHz, CDCl₃, 25 °C, TMS) $\delta = 5.6$; Raman (neat) (cm^{-1}) = 2953 (s), 2897 (vs), 2834 (w), 2787 (m), 2735 (vw), 2693 (vw), 2656 (vw), 1459 (vw), 1418 (vw), 1285 (vw), 1202 (vw), 1144 (vw), 1069 (vw), 780 (vw), 682 (vw), 624 (m), 558 (vw), 493 (vw), 435 (vw), 338 (vw), 261 (vw), 207 (vw), 163 (vw).

O-Trimethylsilyldiethanolamine 6

Compound **6** was synthesized by general procedure for silylation with chlorotrimethylsilane using diethyl ether as solvent, 4.48 g (44 mmol) triethylamine, 4.93 g (47 mmol) diethanolamine and 5.02 g (46 mmol) trimethylchlorosilane. Yield: 5.41 g (97 %) of **6** after distillation in vacuo.

bp: 228 °C (984 mbar); ¹H NMR: (500 MHz, CDCl₃, 25 °C, TMS) $\delta = 0.00$ (s, 9H, SiMe₃), 2.62 (m, 2H, CH₂N), 3.58 (m, 2H, CH₂O); ¹³C NMR: (125 MHz, CDCl₃, 25 °C, TMS) $\delta = -0.3$ (SiMe₃), 51.8 (CH₂N), 62.1 (CH₂O); ²⁹Si NMR: (99 MHz, CDCl₃, 25 °C, TMS) $\delta = 17.8$; Raman (neat) (cm^{-1}) = 2959, 2900, 1464, 1409, 613.

O,O'-Bis(trimethylsilyl)diethanolamine 7

Compound **7** was synthesized by general procedure for silylation with trimethylsilyl triflate using diethyl ether as solvent, 4.68 g (46 mmol) triethylamine, 2.43 g (23 mmol) diethanolamine and 10.21 g (46 mmol) trimethylsilyl triflate. Yield: 2.40 g (42 %) of **7** after distillation in vacuo.

bp: 209 °C (967 mbar, 74 °C (2 torr)^[10]); ¹H NMR: (500 MHz, CDCl₃, 25 °C, TMS) $\delta = -0.05$ (s, 18H, SiMe₃), 2.57 (m, 4H, CH₂N), 3.53 (m, 4H, CH₂O); ¹³C NMR: (125 MHz, CDCl₃, 25 °C, TMS) $\delta = -0.6$ (SiMe₃), 51.5 (CH₂N), 61.8 (CH₂O); ²⁹Si NMR: (99 MHz, CDCl₃, 25 °C, TMS) $\delta = 17.8$ (16.2^[8]); Raman (neat) (cm^{-1}) = 2959, 2900, 1464, 1409, 613. Lit: ¹H NMR: $\delta = 0.08$, 2.63, 3.64, 1.97 (NH);^[9] ¹³C NMR: $\delta = -0.4$, 51.9, 62.2.^[8]

O,O',N-Tris(trimethylsilyl)diethanolamine 8

Compound **8** was synthesized by general procedure for silylation with trimethylsilyl triflate using diethyl ether as solvent, 4.66 g (46 mmol) triethylamine, 1.55 g (15 mmol) diethanolamine and 10.26 g (46 mmol) trimethylsilyl triflate; Yield: 3.50 g (73 %) of **8** after distillation in vacuo.

bp: 227 °C (960 mbar); ¹H NMR: (500 MHz, CDCl₃, 25 °C, TMS) $\delta = 0.01$ (s, 9H, N–SiMe₃), 0.07 (s, 18H, O–SiMe₃), 2.82 (m, 4H, CH₂N), 3.44 (m, 4H, CH₂O); ¹³C NMR: (125 MHz, CDCl₃, 25 °C, TMS) $\delta = -0.6$ (N–SiMe₃), 0.2 (O–SiMe₃), 50.2 (CH₂N), 62.4 (CH₂O); ²⁹Si NMR:

(99 MHz, CDCl₃, 25 °C, TMS) $\delta = 6.3$ (N–Si), 17.3 (O–Si); Raman (neat) (cm^{-1}) = 2958, 2899, 1460, 1409, 616. Lit: ¹H NMR: $\delta = 0.03$, 0.09, 2.80, 3.42.^[9]

O-Trimethylsilylmonoethanolamine 10

Compound **10** was synthesized by general procedure for silylation with chlorotrimethylsilane using diethyl ether or pentane as solvent, 9.33 g (92 mmol) triethylamine, 5.49 g (90 mmol) monoethanolamine and 10.46 g (96 mmol) trimethylchlorosilane. Yield: 4.61 g (35 %) of **10** after distillation in vacuo.

bp: 130 °C (961 mbar); ¹H NMR: (500 MHz, CDCl₃, 25 °C, TMS) $\delta = -0.12$ (s, 9H, SiMe₃), 0.93 (s, 2H, NH), 2.53 (m, 2H, CH₂N), 3.34 (m, 2H, CH₂O); ¹³C NMR: (125 MHz, CDCl₃, 25 °C, TMS) $\delta = -0.8$ (SiMe₃), 44.0 (CH₂N), 64.5 (CH₂O); ²⁹Si NMR: (99 MHz, CDCl₃, 25 °C, TMS) $\delta = 18.0$ (16.9^[8]); Raman (neat) (cm^{-1}) = 2959, 2900, 1463, 1410, 612; Lit: ²⁹Si NMR $\delta = 16.9$; ¹³C NMR $\delta = -0.6$, 44.6, 65.2;^[23] ¹³C NMR $\delta = 0.0$, 44.6, 65.0 and ¹H NMR $\delta = 0.12$, 0.87, 2.79, 3.60;^[24] ¹H NMR $\delta = 0.10$, 1.03, 2.67, 3.54;^[9] ¹H NMR $\delta = 0.10$, 2.66, 3.51;^[16] IR:^[10] ¹³C NMR: (125 MHz, CDCl₃, 25 °C, TMS) $\delta = -0.6$, 44.6, 65.2.^[8]

O,N-Bis(trimethylsilyl)monoethanolamine 11

Compound **11** was synthesized by general procedure for silylation with chlorotrimethylsilane using diethyl ether as solvent 4.66 g (46 mmol) triethylamine, 1.43 g (23 mmol) monoethanolamine and 5.04 g (46 mmol) trimethylchlorosilane; Yield: 3.04 g (64 %) of **11** after distillation in vacuo.

bp: 172 °C (985 mbar) (80 °C (4 torr)^[10]); ¹H NMR: (500 MHz, CDCl₃, 25 °C, TMS) $\delta = -0.03$ (s, 9H, O–SiMe₃), 0.05 (s, 9H, N–SiMe₃), 2.75 (s (br), 3H, CH₂N and NH), 3.44 (m, 2H, CH₂O); ¹³C NMR: (125 MHz, CDCl₃, 25 °C, TMS) $\delta = -0.5$ (N–SiMe₃), -0.0 (O–SiMe₃), 44.0 (CH₂N), 65.6 (CH₂O); ²⁹Si NMR: (99 MHz, CDCl₃, 25 °C, TMS) $\delta = 4.0$ (N–Si), 17.6 (O–Si) (:^[8] 2.9 (N–Si), 16.0(O–Si)); Raman (neat) (cm^{-1}) = 2958, 2899, 1461, 1409, 610. Lit: ¹H NMR: $\delta = 0.02$, 0.08, 2.76, 3.44;^[9] ¹H NMR: $\delta = 0.07$, 2.78, 3.42;^[16] ¹³C NMR: $\delta = -0.5$, 0.1, 44.0, 65.6.^[8]

O,N,N-Tris(trimethylsilyl)monoethanolamine 12

Compound **12** was synthesized by general procedure for silylation with trimethylsilyl triflate using diethyl ether as solvent, 2.76 g (27 mmol) triethylamine, 5.60 g (27 mmol) **12** and 6.05 g (27 mmol) trimethylsilyl triflate; Yield: 4.55 g (61 %) of **3** after distillation in vacuo.

bp: 213 °C (960 mbar); Lit.: bp: 101 °C (12 Torr);^[25] ¹H NMR: (500 MHz, CDCl₃, 25 °C, TMS) $\delta = 0.09$ (s, 27H, SiMe₃), 2.89 (s, 2H, CH₂N), 3.44 (t, 2H, CH₂O); ¹³C NMR: (125 MHz, CDCl₃, 25 °C, TMS) $\delta = -0.3$ (N–SiMe₃), 2.3 (O–SiMe₃), 47.1 (CH₂N), 65.1 (CH₂O); ²⁹Si NMR: (99 MHz, CDCl₃, 25 °C, TMS) $\delta = 6.3$ (N–Si), 17.0 (O–Si); Raman (neat) (cm^{-1}) = 2957, 2900, 1467, 1409, 616. Lit: ¹H NMR: $\delta = 0.09$, 0.10, 2.87, 3.40;^[9] ¹H NMR: $\delta = 0.07$, 2.84, 3.34.^[16]

General Procedure for CO₂ Insertion

CO₂ was passed through a solution of *N*-methyl-*N'*-trimethylsilylpiperazine (0.94 g, 5 mmol) in about 40 mL of THF for 20 minutes. Volatiles were removed in vacuo yielding 1.10 g (93 %) of pure **4a**.

Absorption of CO₂ from Ambient Air – Procedure 1

A gas stream of about 105 to 120 mL min⁻¹ passed through a rotameter, a column of activated molecular sieve 3 Å and conc. sulphuric acid before entering the reaction solution. Subsequent to the reaction solution (0.29 g of **4** in about 40 mL THF) the gas streams through anhydrous calcium chloride and finally into a solution of barium hydroxide. First the whole apparatus was filled with dry nitrogen until the barium hydroxide solution remained free of solid (about 30 minutes). Then the gas stream was changed to compressed ambient air (oil free with low water content) until the barium hydroxide solution became milky turbid (about 2 hours). Volatiles in the reaction solution were removed in vacuo yielding 0.15 g of a colourless solution identified as mixture of starting material and insertion products.

Absorption of CO₂ From Ambient Air – Procedure 2

A gas stream of about 105 to 120 mL min⁻¹ passed through a rotameter, a column of activated molecular sieve 3 Å and conc. sulphuric acid before entering THF and flowing upwards through a 20 cm column (diameter of 2 cm) filled with pieces of glass tubes. Subsequent to the reaction solution the gas streams were passed through anhydrous calcium chloride and finally into a solution of barium hydroxide. First the whole apparatus was filled with dry nitrogen until the barium hydroxide solution remained free of solid (about 30 minutes). Then the gas stream was changed to compressed ambient air (oil free with low water content). From the top of the column 0.45 g of **4** were added dropwise in counterstream to the flow of ambient air. The gas flow was maintained until the barium hydroxide solution became opaque (about 1 hour). Volatiles in the reaction solution were removed in vacuo yielding 0.44 g of a colourless solution.

Insertion into **3**, Product **3 b**

No mono-insertion product (insertion into one of the two Si–N bonds) is observed. The reaction was performed using the general procedure for CO₂ insertion and 0.95 g (4 mmol) of **3** and yielded 1.12 g (85%) of a white solid (**3 b**).

mp: 100 °C (subl.); ¹H NMR: (500 MHz, CDCl₃, 25 °C, TMS) δ = 0.20 (s, 18H, SiMe₃), 3.35 (br, 8H, piperazine); ¹³C NMR: (125 MHz, CDCl₃, 25 °C, TMS) δ = -0.1(CH₃–Si), 43.1, 44.1 (Si–NCH₂), 153.6 (CO); ²⁹Si NMR: (99 MHz, CDCl₃, 25 °C, TMS) δ = 23.9; Raman (neat) ν (cm⁻¹) = 3005 (s), 2953 (w), 2905 (vw), 2853 (w), 2793 (vw), 2691 (vw), 1445 (w), 1376 (vw), 1285 (vw), 1198 (vw), 1146 (w), 1060 (w), 980 (vw), 923 (vw), 849 (vw), 805 (m), 724 (vw), 683 (vw), 610 (w), 520 (w), 473 (w), 423 (w), 342 (w), 298 (w), 234 (w), 167 (w), 107 (w).

Insertion into **4**, Product **4 a**

Compound **4 a** was obtained using the general procedure for CO₂ insertion and 0.94 g (5 mmol) of **4** and yielded 1.10 g (93%) of a colourless liquid (**4 a**).

bp: 143 °C (967 mbar); ¹H NMR: (500 MHz, CDCl₃, 25 °C, TMS) δ = 0.00 (s, 9H, SiMe₃), 2.00 (s, 3H, CH₃–N), 2.06 (br, 4H, CH₃–NCH₂), 3.18 (br, 4H, Si–NCH₂); ¹³C NMR: (125 MHz, CDCl₃, 25 °C, TMS) δ = -0.5(CH₃–Si), 42.8, 44.1 (Si–NCH₂), 45.7 (CH₃–N), 54.2 and 54.5 (CH₃–NCH₂), 153.6 (CO); ²⁹Si NMR: (99 MHz, CDCl₃, 25 °C, TMS) δ = 22.9; Raman (neat) ν (cm⁻¹) = 2944 (m), 2903 (vs), 2795 (w), 2706 (vw), 1464 (vw), 1422 (vw), 1295 (vw), 1206 (vw), 1148 (vw), 1073 (vw), 1007 (vw), 913 (vw), 851 (vw), 780 (w), 697 (vw), 626 (s), 518 (w), 473 (w), 433 (w), 363 (w), 321 (w), 259 (w), 215 (w), 132 (w).

Insertion into **8**, Product **8 a**

No insertion could be observed using the general procedure for CO₂ insertion. Heating the reaction mixture to reflux before passing the CO₂ into the solution leads to the expected product. Starting from 0.97 g (30 mmol) of **8** the procedure yielded 0.59 g (61%) of the insertion product **8 a**.

¹H NMR: (500 MHz, CDCl₃, 25 °C, TMS) δ = -0.02 (s, 18 H, Me₃SiO), 0.16 (s, 9H, Me₃SiOC(O)), 3.27 (t, 2H, N–CH₂), 3.53 (m, 2H, CH₂), 3.59 (m, 2H, CH₂); ¹³C NMR: (125 MHz, CDCl₃, 25 °C, TMS) δ = -0.4 (Me₃SiO), -0.2 (Me₃SiOC(O)), 51.0 and 51.6 (N–CH₂), 60.9 (O–CH₂), 155.0 (CO); ²⁹Si NMR: (99 MHz, CDCl₃, 25 °C, TMS) δ = 18.2 (Si–O), 22.3 (Si–OC(O)); Raman (neat) ν (cm⁻¹) = 2960, 2902, 1468, 1412, 611; Lit: bp: 118–20 °C (2.5 torr).^[12]

Insertion into **11**, Product **11 a**

Compound **11 a** was obtained using the general procedure for CO₂ insertion and 1.1 g (53 mmol) of **11** and yielded 1.02 g (77%) of a colourless liquid **11 a**.

¹H NMR: (500 MHz, CDCl₃, 25 °C, TMS) δ = -0.02 (s, 9H, Me₃SiOC(O)), 0.13 (s, 9H, Me₃SiO), 2.66 (s, 1H, NH), 3.11 (m, 2H, N–CH₂), 3.50 (m, 2H, O–CH₂); ¹³C NMR: (125 MHz, CDCl₃, 25 °C, TMS) δ = -0.4 (Me₃SiOC(O)), 0.1 (Me₃SiO), 44.0 (N–CH₂), 61.8 (O–CH₂), 155.5 (CO); ²⁹Si NMR: (99 MHz, CDCl₃, 25 °C, TMS) δ = 18.9 (SiO), 22.4 (SiOC(O)); Raman (neat) ν (cm⁻¹) = 2960, 2902, 1412, 613.

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Conflict of Interest

The authors declare no conflict of interest.

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