A Journal of the Gesellschaft Deutscher Chemiker

Angewandte International Edition GDCh Chemie

www.angewandte.org

Accepted Article

Title: Silicon-Mediated Coupling of Carbon Monoxide, Ammonia and Primary Amines to Form Acetamides

Authors: Matthias Driess, Marcel-Philip Luecke, Yuwen Wang, Arseni Kostenko, and Shenglai Yao

To be cited as: *Angew. Chem. Int. Ed.* 10.1002/anie.201904361
Angew. Chem. 10.1002/ange.201904361

Link to VoR: http://dx.doi.org/10.1002/anie.201904361
http://dx.doi.org/10.1002/ange.201904361

WILEY-VCH

10.1002/anie.201904361

WILEY-VCH

COMMUNICATION

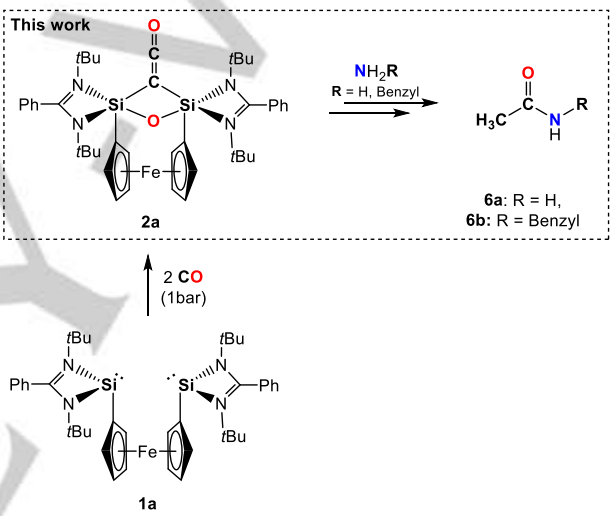
Silicon-Mediated Coupling of Carbon Monoxide, Ammonia and Primary Amines to Form Acetamides

Marcel-Philip Luecke, Arseni Kostenko, Yuwen Wang, Shenglai Yao and Matthias Driess*

Dedicated to Professor Hansjörg Grützmacher

Abstract: *For the first time, a direct transformation of CO, NH_3 and primary amines into acetamides, mediated by a main-group element (silicon), is reported. Starting point is the selective deoxygenative reductive homocoupling of two CO molecules by the Fc-bis(silylene)* ***1a*** *(Fc = ferrocendiyl) as reducing agent to form the corresponding ferrocendiyl-bridged disila(μ-O)(μ-CCO)ketene intermediate* ***2a****. Exposing* ***2a*** *to NH_3 (1 bar, 298 K) and benzylamine yield the corresponding Fc-disiloxanediamines [Fc(RHSi-O-SiNHR)]* ***5a****, (R = H) and* ***5b*** *(R = benzyl) under liberation of the acetamides $H_3CC(O)NHR$, respectively, as confirmed by ^{13}C-isotopic labelling experiments. IR and NMR studies of the reaction progress revealed a three-step reaction mechanism including an N-silylated carboxamide that could be isolated and fully characterized. The striking reaction mechanism for this unprecedented transformation, involving a facile Si-C bond cleavage and ammonolysis of a Si-O bond, has been uncovered experimentally and by quantum chemical calculations.*

The activation and coupling of small molecules offers very attractive pathways to a variety of functional organic compounds. The ultimate aim of this strategy is to synthesize more organic commodities (hydrocarbons, alcohols, ketones, carbonic acids etc.) and fine chemicals with far less or even without consumption of fossil resources. With respect to heteroatom-containing organic molecules, the bottom-up synthesis of basic C-N compounds such as amines, amides and cyanides from CO_x and ammonia as simple building blocks is of particular interest. The importance of CO serving as a versatile C_1-building block and NH_3 as a source of N atoms for C-N bond formation cannot be overestimated. Among the most important reactions in (bio)organic chemistry is the sequential CO-NH (amide) bond formation because of its widespread occurrence in nature and role for pharmaceuticals, agrochemicals and dyes.[1,2] The conventional approach to amides includes the reaction of carboxylic acids and halides (RCOX, X = OH, halogen) with *NH*-amines. A transition-metal(TM)-mediated formation of amides can be achieved as shown in the case of the palladium-catalyzed aminocarbonylation of aryl halides with NH_3 in the presence of CO.[3] Carbonyl TM complexes and ammonium salts as non-gaseous sources of CO and NH_3, respectively, have also been applied successfully in aminocarbonylations.[4] The energetically more demanding reductive cleavage of N_2 as a source of nitrogen and homologation of CO, two simple diatomic molecules with the strongest bonds in chemistry, could be achieved in a hafnocene-mediated coupling reaction to yield oxamide, $H_2N\text{-}CO\text{-}CO\text{-}NH_2$.[5] However, to the best of our knowledge, a main-group element-mediated direct coupling of CO and NH_3 or primary amines affording an organic molecule is currently unknown. Recently, our group reported the silicon-mediated deoxygenative reductive homocoupling of two CO molecules with the bis(silylene) **1a** at room temperature to give the respective disila(μ-O)(μ-CCO)ketene **2a** (Scheme 1).[6]



Scheme 1. Formation of acylamines **6a**, **b** via disilaketene **2a**. The latter results from deoxygenative reductive homocoupling of two CO molecules with the corresponding bis(silylene) **1a**.

With the disilaketene **2a** in hand, we now learned that its ketene moiety possesses an unprecedented reactivity towards ammonia and primary amines affording acetamides. This type of reactivity is currently unknown for diorganoketenes [7,8] and disilaketenes.[9] Herein, we report on the unexpected formation and striking mechanism of the acetamides **6a**, **b** through ammonolysis of the disilaketenes **2a**.

Treatment of **2a** with NH_3 under ambient conditions (1 bar, 298 K) furnished acetamide **6a** along with the corresponding Fc-disiloxanediamine **5a**, which could be crystallized from THF at – 30 °C. Similarly, the acetamide **6b** and disilyldiamine **5b** were obtained upon reaction of **2a** with *N*-benzylamine in toluene at room temperature (Scheme 2); **5b** could be isolated as yellow crystals in 64 % yields. Disiloxanediamine **5a** crystallizes in the monoclinic space group $P2_1/c$ with two THF molecules in the unit cell, while **5b** in the triclinic space group $P\,\bar{1}$. Both compounds feature a central structure motif of an disiloxanediamine $[O(SiNHR)_2]$ with typical Si-N bond distances (**5a**: 1.712(2) Å, **5b**: 1.703(2) Å) for silylamines (1.70-1.76 Å).[10b]

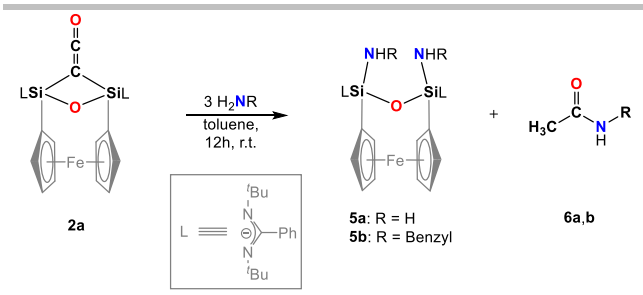
MSc. M.-P. Luecke, Dr. A. Kostenko, MSc. Y. Wang, Dr. S. Yao, Prof. Dr. M. Driess
Department of Chemistry: Metalorganics and Inorganic Materials
Technische Universität Berlin
Strasse des 17. Juni 115, Sekr. C2, D-10623 Berlin Germany;
E-mail: matthias.driess@tu-berlin.de

Supporting information for this article is given via a link at the end of the document.

10.1002/anie.201904361

WILEY-VCH

COMMUNICATION



Scheme 2. Reaction of **2a** with NH_3 and benzylamine to disiloxanediamines **5a**, **5b** and acetamides **6a**, **6b**, respectively.

The ^{29}Si NMR chemical shift of δ = - 57.7 (**5a**) and - 45.6 ppm (**5b**) in C_6D_6 are in accordance with the different coordination modes of the ligand L (L = [PhC(N^{t}Bu)$_2$], Scheme 2) at the Si1 atom in **5a** (chelating) and **5b** (monodentate), in line with the molecular structures in the solid state (Fig. 1).

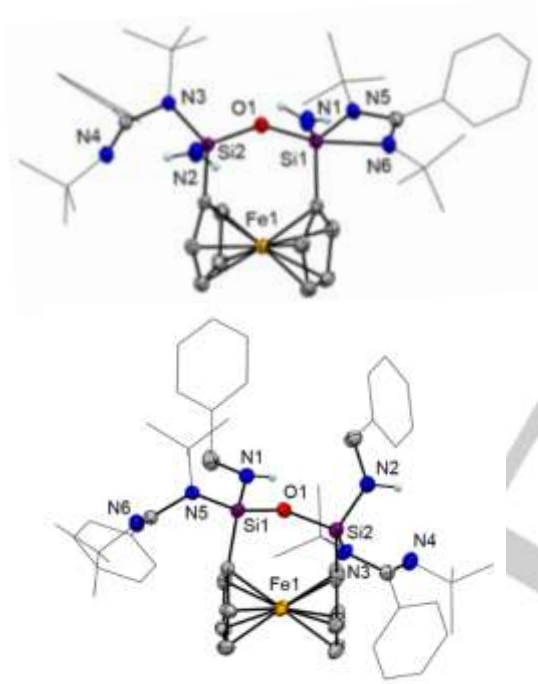


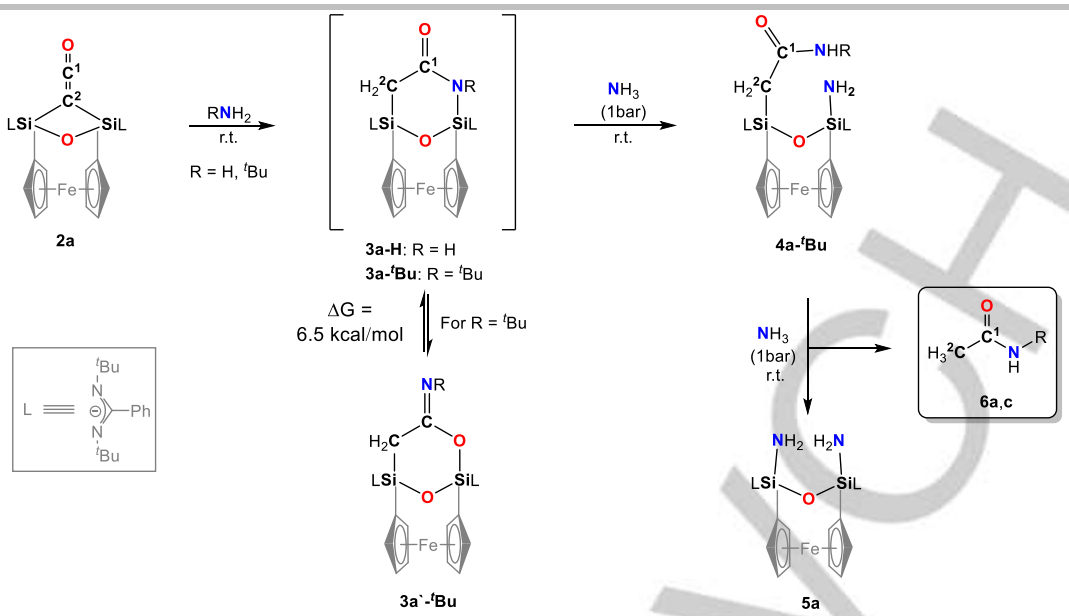
Figure 1. Molecular structures of **5a** (top) and **5b** (bottom) with thermal ellipsoids at 50 % probability level. Hydrogen atoms, except of those at N1 and N2, and solvent molecules are omitted for clarity. Selected distances [Å] and angles [°]: Compound **5a** Si1-O1 1.6214(16), Si1-N1 1.712(2); Si1-O1-Si2 135.53(10), O1-Si1-N1 109.49(10), O1-Si2-N2 94.80(10), ∑Si1 = 323.45°. Compound **5b** Si1-O1 1.6388(17), Si1-N1 1.703(2), Si2-N2 1.713(2); Si1-O1-Si2 142.08(12), O1-Si1-N1 102.56(10), O1-Si2-N2 106.14(10), ∑Si1 = 314.4°.

Silylamines are well known and generally prepared by ammonolysis or aminolysis of the Si-Cl bond in chlorosilanes.[10] The formation of the known acetamides **6a** and **6b** was confirmed by ESI mass spectrometry, NMR- and IR-spectroscopy with characteristically strong carbonyl stretching vibration modes.[11a,b] Isotopic labeling experiments using ^{13}C labeled **2a-^{13}C** confirmed the assignment. The FT-IR absorption spectra obtained from the reaction mixtures (**2a** + amine) after 24 h exhibit a strong absorption at 1644 and 1646 cm^{-1} assigned to the C=O stretching vibration of **6a** and **6b**, respectively. The ^{13}C NMR signals of the corresponding carbon nuclei were observed at δ = 172 ppm (**6a**) and δ = 168 ppm (**6b**).[11a,b] In-situ heteronuclear NMR spectroscopic analysis of the reaction mixture revealed a clean reaction progress to the corresponding acylation products **6a**,**b** and **5a**,**b** (*see Supporting Information*). Monitoring the reaction progress of ^{13}C-labeled disilaketene **2a-^{13}C** with NH_3 in C_6D_6 suggested the formation of cyclic *N*-silylated carboxamide **3a-H** (Scheme 3) as exemplified by the observation of two doublets at δ = 175.8 (^{13}C=O) and 31.5 ppm (Si^{13}CH$_2$) in the ^{13}C NMR spectrum with a characteristic value of the ^{13}C-^{13}C coupling constant of 47.0 Hz.[12] The ^{29}Si,^{1}H-HMQC NMR spectrum shows two cross peaks at δ = - 79.5 ppm (^{1}H: δ = 4.50 ppm) and - 24.5 ppm (^{1}H: δ = 2.98 ppm), suggesting the formation of the cyclic *N*-silylated carboxamide **3a-H** as the first observable intermediate. **3a-H** is not isolable and decomposes in solution within a few minutes in the absence of NH_3. To gain further mechanistic insights, a bulky *tert*-butyl group was introduced by treatment of disilaketene **2a** with ^{t}BuNH$_2$, which could increase the stability of the proposed intermediate through an equilibrium of a cyclic *O*-silylated carboximidate and its tautomer (*N*-silylated carboxamide, Scheme 4).[13] Reaction of **2a** with ^{t}BuNH$_2$ in deuterated benzene at room temperature led to the selective formation of *O*-silylated carboxamide **3a`-^{t}Bu** in accordance with the better shielding of the carbon nucleus of the CO moiety at δ = 154.2 ppm compared to that of **3a-H** (δ = 175.8 ppm) in the ^{13}C NMR spectrum, and a slight red shift of the C=N absorption band at ν = 1656 cm^{-1} in the IR spectrum.[13] The protons of the methylene moiety gave rise to a set of two doublets (^{1}H: δ = 2.95 and 3.42 ppm, $^2J_{H,H}$ = 14.0 Hz) as evidenced by the H,C-HSQC NMR spectrum (see *Supporting Information*). The proposed equilibrium shown in Scheme 3 is supported by Density Functional Theory (DFT) calculations revealing a rather small free energy difference of ΔG = 6.5 kcal mol^{-1} between the favored *O*-silylated carboxamide **3a`-$^t$Bu** tautomer and **3a-$^t$Bu** at room temperature. [14] However, the chemical shift of the $^{13}$C NMR resonance of the CO moiety in **3a`-^{t}Bu** remains unchanged over a wide temperature range from - 80 °C to + 40 °C in d_8-THF. Reaction of the ^{13}CO-labeled disilaketene **2a-^{13}C** with ^{t}BuNH$_2$ furnishes the expected ^{13}C labeled complex **3a`-^{t}Bu-^{13}C** in solutions, containing a [^{13}C-^{13}C(=N^{t}Bu)-O)] moiety in accordance with multinuclear NMR spectroscopic data and a bathochromic shifted C=N absorption band (ν = 1621 cm^{-1}, $\Delta\nu$ = 35 cm^{-1}) in the FT-IR spectrum. Further evidence is given by the ^{29}Si NMR spectrum of **3a`-$^t$Bu-$^{13}$C** with a singlet at $\delta$ = - 86.8 ppm and a doublet at $\delta$ = - 29.6 ppm ($^1J^{29}_{Si,}{}^{13}_{C}$ = 66 Hz), confirming the presence of a Si-O and Si-$^{13}$C bond, respectively. **3a`-^{t}Bu-^{13}C** is stable in solutions over a longer period of time and does not further react with ^{t}BuNH$_2$ upon prolonged heating (60 °C for 12 h). However, exposure of **3a`-^{t}Bu** to NH_3 (1 bar, 298 K) in C_6D_6 led to the formation of **5a** and *N-tert*-butylacetamide **6c** as confirmed by ESI mass spectrometry, NMR- and FT-IR spectroscopy (*Supporting Information*).[11b] Monitoring the reaction progress of **3a-^{t}Bu** with NH_3 (1 bar, 298 K) in C_6D_6 indicated the formation of the proposed silylamine [SiNH_2] (^{15}N: δ = 30.9 ppm) intermediate **4a-^{t}Bu** featuring a new singlet signal in the ^{1}H-NMR spectrum at δ = 2.46 ppm (Scheme 3). The second cross peak in the ^{1}H,^{15}N-HMQC NMR spectrum at lower field (^{15}N: δ = 133.4 ppm) corresponds to the CO-NH^{t}Bu amide proton, which exhibits a singlet at δ = 7.43 ppm in the ^{1}H NMR spectrum (see *Supporting Information*).

10.1002/anie.201904361

WILEY-VCH

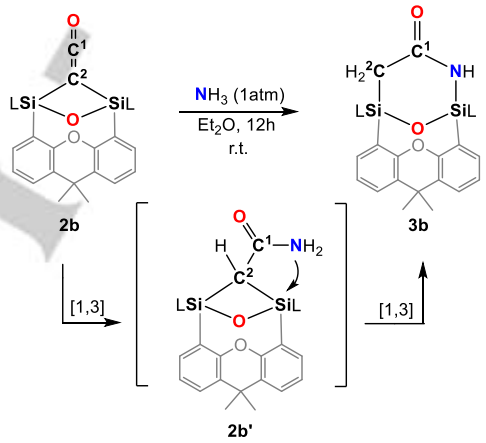
COMMUNICATION



Scheme 3. Proposed mechanism for the amination of **2a** with ^{t}BuNH$_2$ and NH$_3$.

The methylene protons (^{1}H: δ = 2.84 ppm, $^2J_{H,H}$ = 11.8 Hz) still remained in the ^{1}H NMR spectrum and gave rise to a cross peak in the ^{1}H,^{29}Si-HMQC NMR spectrum at δ = – 25.6 ppm [*Si*C^2*H*$_2$]. The second cross peak at δ = - 78.6 ppm (^{29}Si), coupling to the protons at δ = 2.46 ppm, attributed to the O-Si-NH$_2$ silylamine moiety. Further evidence stems from the low-field shift for the carbonyl ^{13}C nucleus in the ^{13}C-NMR spectrum at δ = 172.5 ppm (**3a`-$^{t}$Bu**, C=N: 154.2 ppm) and a red shifted strong IR absorption band at $\nu$ = 1644 cm$^{-1}$ (**3a`-^{t}Bu**: ν = 1656 cm^{-1}, C=N) assigned to the C=O stretching vibration mode of the alkylamide **4a-^{t}Bu**. Additional absorption bands at ν = 3331 and 3345 cm^{-1} stem from the N-H bonds. Based on the higher stability of the Si-O vs. Si-N bond we propose that the *N*-silylated carboxamide **3a-^{t}Bu** (Scheme 3) is more reactive towards ammonolysis of the Si-N bond to give **5a**. This is supported by the large σ*(Si-N) bond character of the [LUMO+3] frontier orbitals of **3a-^{t}Bu** (*Supporting Information*).

Notably, a derivative of the proposed cyclic *N*-silylated carboxamide **3a-H**, compound **3b**, could be isolated in 72 % yields as colorless crystals through reaction of the less flexible xanthene-linked disilaketene **2b** with NH$_3$ (Scheme 4, *Supporting Information*). **3b** crystallizes in the triclinic space group *P* $\bar{1}$ with a non-planar six membered Si$_2$C$_2$NO δ-lactam core as central structural motif (Fig. 2). The amination of disilaketene **2b** takes place at the carbonyl C^{1}atom via nucleophilic attack of NH$_3$ followed by a 1,3-H migration to the where a strained four-membered Si$_2$CO-ring is formed (Scheme 4). Upon formation of the Si-N bond a second 1,3-H migration occurs, leading to the final product **3b** with a six-membered δ-lactam structure (Fig. 3). C^2 atom upon **2b`** A possible two-step reaction involving an enol of an amide as intermediate was not observed, indicating a concerted mechanism involving addition across the C=C bond of the ketene.[15]



Scheme 4. Conversion of disilaketene **2b** with NH$_3$ yielding the cyclic *N*-silylated carboxamide **3b**.

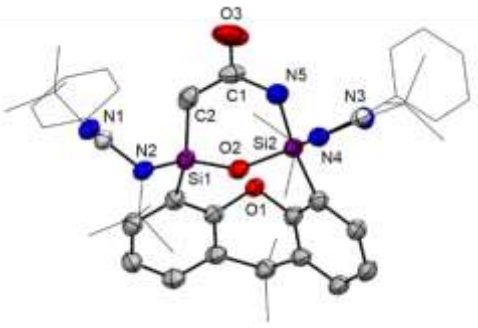


Fig. 3. Molecular structure of **3b** at 50 % probability level. Hydrogen and solvent atoms are omitted for clarity. Bond lengths [Å]: Si1-C2 1.797(1), C1-C2 1.450(9), Si2-N5 1.809(3), C1-N5 1.414(9). Bond angle [°]: Si1-C2-C1 123.01(3), C2-C1-O3 119.67(1), C2-C1-N5 122.30(5).

10.1002/anie.201904361

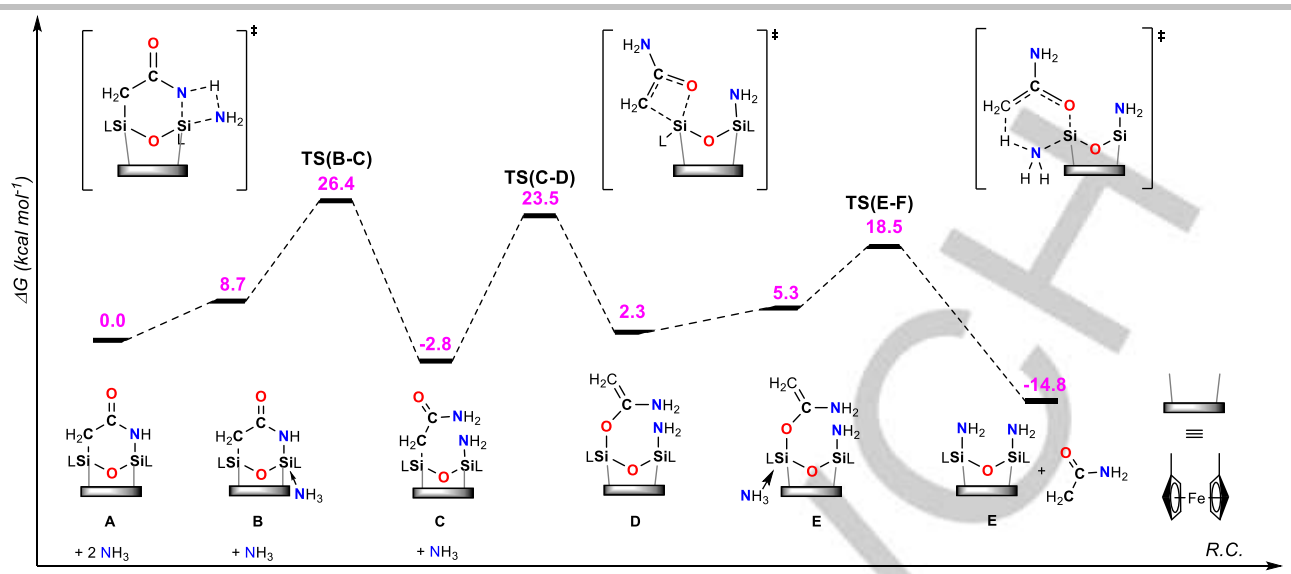


Fig. 4. DFT-Derived potential energy surface (PES) of the proposed mechanism. L = chelating PhC(N*t*Bu)$_2$ ligand in all intermediates.

The calculated potential energy surface for the proposed mechanism of transformation of carboxamide **3** to disiloxanediamine **5** is presented in Figure 4.[14] Coordination of ammonia to **A** results in formation of intermediate **B** at ΔG = 8.7 kcal mol^{-1}. **B** undergoes an ammonolysis of the Si-N bond via the four-membered **TS(B-C)** (ΔG = 26.4 kcal mol^{-1}) forming the α-silylated acetamide (**C**) at ΔG = 26.4 kcal mol^{-1}, that further rearranges to the silyl enolether **D** (at ΔG = 2.3 kcal mol^{-1}) via **TS(C-D)** at ΔG = **23.5** kcal mol^{-1}. This type of rearrangement was previously reported for a α-boryl(silyl) substituted *N,N*-dimethylacetamide leading to the isolation of silylethers.[16] Coordination of NH_3 to **D** forms intermediate **E** (at ΔG = 5.3 kcal mol^{-1}) allowing the transfer of an H atom from NH_3 to the vinyl moiety via the six-membered **TS(E-F)** at ΔG = 18.5 kcal mol^{-1} yielding the final disilyldiamine **F** and acetamide. The barrier for the xanthene-linked carboxamide for Si-N bond ammonolysis (**3b** + NH_3) is 4 kcal mol^{-1} higher in energy explaining the spacer depending reactivity thereof. Additional mechanisms for this transformation were also considered but could be excluded energetically (see *Supporting Information*).

In summary, the direct coupling of CO, NH_3 and primary amines into acetamides could be accomplished in a silicon-mediated reaction sequence. Exposure of disilaketene **2a** to NH_3 (1 bar, 298 K) and benzylamine yields the corresponding disiloxanediamines **5a** and **5b** under liberation of the acetamides $H_3CC(O)NHR$ (R = H, benzyl), respectively, as confirmed by ^{13}C-isotopic labelling experiments. Further studies revealed a three-step reaction mechanism including an *N*-silylated carboxamide **3b** which could be isolated and fully characterized. As a primary example, the strikingly facile Si-C bond cleavage is accomplished by an intramolecular rearrangement to give the silylated enolether **D**, resulting in an unprecedented Si-O bond ammonolysis under ambient conditions.

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft [Germany´s Excellence Strategy – EXC 2008/1– 390540038 (UniSysCat) and with a PhD fellowship by the Einstein Foundation Berlin (M.-P.L.). Y.W. gratefully acknowledges financial support by the China Scholarship Council. A.K. is grateful to the Alexander von Humboldt Foundation for a postdoctoral fellowship. We thank Paula Nixdorf (TU Berlin) for her assistance in the XRD measurements and Dr. Terrance J. Hadlington (TU Berlin) for helpful discussions.

Keywords: disilaketene • carbonylamination • ammonolysis • carbonylation • silylenes

[1] V. R. Pattabiraman, J. W. Bode, *Nature* **2011**, 480, 471.
[2] a) A. Brennführer, H. Neumann, M. Beller, *Angew. Chem., Int. Ed.* **2009**, 48, 4114; b) J. Magano, J. R. Dunetz, *Chem. Rev.* **2011**, 111, 2177.
[3] a) A. Schoenberg, R. F. Heck, *J. Org. Chem.* **1974**, 39, 3327; b) J. R. Martinelli, D. M. M. Freckmann, S. L. Buchwald, *Org. Lett.* **2006**, 8, 4843; c) J. R. Martinelli, T. P. Clark, D. A. Watson, R. H. Munday, S. L. Buchwald, *Angew. Chem., Int. Ed.* **2007**, 46, 8460; d) X.-F. Wu, H. Neumann, M. Beller, *Chem.-Eur. J.* **2010**, 16, 9750; e) R. J. Atkins, A. Banks, R. K. Bellingham, G. F. Breen, J. S. Carey, S. K. Etridge, J. F. Hayes, N. Hussain, D. O. Morgan, P. Oxley, S. C. Passey, T. C. Walsgrove, A. S. Wells, *Org. Process Red. Dev.* **2003**, 7, 663; f) C. Torborg, M. Beller, *Adv. Synth. Catal.* **2009**, 351, 3027; g) J. Y. Wang, A. E. Strom, J. F. Hartwig, *J. Am. Chem. Soc*. **2018**, 140, 7979.
[4] D. J. Knobloch, E. Lobkovsky, P. J. Chirik, *Nature* **2009**, 2, 30.
[5] W. Ren, M. Yamane, *J. Org. Chem.* **2010**, 75, 24. b) A. S. Suresh, P. Baburajan, M. Ahmed, *Tetrahedron Letters* **2015**, 56, 4864.
[6] Y. Wang, A. Kostenko, T. J. Hadlington, M.-P. Luecke, S. Yao, M. Driess, *J. Am. Chem. Soc.* **2019**, 141, 1, 626.
[7] First isolation of ketenes, see: a) H. Staudinger, *Chem. Ber.* **1905**, 38, 1735; b) H. Staudinger, *Chem. Ber.* **1906**, 39, 968; c) H. Staudinger, *Chem. Ber*. **1906**, 39, 3062.
[8] For a ketene reactivity and synthesis overview, see: a) A. D. Allen, T. T. Tidwell, *Structure and Mechanism in Ketene Chemistry*, Elsevier Ltd. **2014**; b) T. T. Tidwell, *Ketenes II*, John Wiley & Sons, Inc. **2006**; c) T. Tidwell, *J. Am. Chem. Soc.* **1990**, 112, 6396; d) T. T. Tidwell, *Eur. J. Org. Chem.* **2006**, 44, 563.
[9] For reactivity of disilaketenes see: a) M. Ito, E. Shirakawa, H. Takaya, *Synlett* **2002**, 8, 1329; b) M. Ito, E. Shirakawa, H. Takaya, *Synlett* **1996**, 635; c) Y. Kita, Y. Tsuzuki, S. Kitagaki, S. Akai, *Chem Pharm. Bull.* **1994**, 42,2, 233; d) M. Majumdar, I. Omlor, C. B. Yildiz, A.

10.1002/anie.201904361

Azizoglu, V. Huch, D. Scheschkewitz, *Angew. Chem. Int. Ed.* **2015**, 54, 8746.

[10] a) N. Wiberg, W. Uhlenbrock *Chem. Ber*. **1971**, 104, 2643; K. Rühlmann, K. Lehmann, *Liebigs. Ann. Chem.* **1962**, 657, 1; b) W. S. Sheldrick, *The Chemistry of Organic Silicon Compounds,* Wiley **1989**.

[11] a) Z. Li, L. Wang, X. Zhou, *Adv. Synth. Catal.* **2012**, 354, 584; b) E. Callens, A. J. Burtonb, A. G. M. Barretta, *Tetrahedron Lett.* **2006**, 47, 8699. M. Nasr-Esfahani, M. Montazerozohori, Z. Karami, *Org. Prep. Proced. Int.* **2016**, 48, 321.

[12] C.-J. Park, G.-C. Han, S.-G. Lee, *Bull. Korean. Chem. Soc.* **2000**, 21, 11, 1159.

[13] For example of tautomerization, see: a) N. F. Lazareva, A. Yu, N. N. Chipanina, L. P. Oznobikhina, I. V. Sterkhova, A. I. Albanov, *J. Organomet. Chem.* **2017**, 846, 88; b) *T. H. Lane, C. L. Frye, J. Org. Chem.* **1978**, 43, 25.

[14] The geometries were optimized at B3LYP-D3 level with s6-31g* basis for iron and def2-SVP basis set for all other atoms. The *t*Bu and Ph groups of the amidinato substituents were replaced by methyl groups. For details see *Supporting Information*.

[15] For discussion of the reactivity of a dialkylketene with amines including an amide of enol, see: a) M. Mishima, *J. Phys. Org. Chem.* **2013**, 26, 1071; b) K. Sung, T. T. Tidwell, *J. Am. Chem. Soc.* **1998**, 120, 3043; c) A. W. Acton, A. D. Allen, L. M. Antunes, A. V. Fedorov, K. Najafian, T. T. Tidwell, B. D. Wagner, *J. Am. Chem. Soc.* **2002**, 124, 1379.

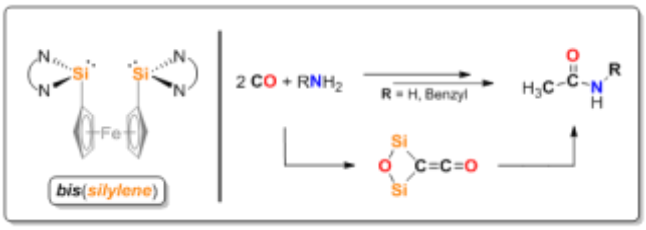
[16] D. E. Kaufmann, *Science of Synthesis*, 6, 664. Thieme Verlagsgruppe, **2005**.

10.1002/anie.201904361

WILEY-VCH

COMMUNICATION

Entry for the Table of Contents



*M.-P. Luecke, A. Kostenko, Y. Wang, S. Yao, M. Driess**

Page No. – Page No.

Silicon-Mediated Coupling of Carbon Monoxide, Ammonia and Primary Amines to Form Acetamides

What silicon can do: In the presence of a bis(silylene), CO, NH_3 and primary amines can be transformed into corresponding acetamides. Starting point is a silicon-based reaction sequence via the ferrocendiyl-bridged disila(μ-O)(μ-CCO)ketene intermediate, derived from a deoxygenative reductive homocoupling of two CO molecules. Spectroscopic results and theoretical calculations revealed a three-step reaction mechanism, including an N-silylated carboxamide that could even be isolated and characterized.