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Silagermylenation of C=O bonds and radical fragmentation of CO_2-expanded bis(germylene) by a cyclic (alkyl)(amino)carbene†

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The transformation of the greenhouse gas CO_2 into value-added products represents a major contemporary challenge. Low-valent p-block compounds typically react at the oxygen termini of CO_2 due to the oxophilicity of the metal centers. We now report on the selective activation of CO_2 and ethyl isocyanate at the central carbon atom by an N-heterocyclic carbene (NHC)-stabilized *para*-silylenephenylene-bridged bis(germylene). During the net silagermylenation, the C=X (X = O, NEt) bonds are inserted into the Ge–Si bonds through cooperativity of the low-valent metal center and the electrophilic silyl backbone. The germanium(II) centers are retained in the products, as is confirmed by multinuclear NMR data, IR spectroscopy and X-ray analysis and supported by DFT calculations. Attempts to substitute the NHCs by cyclic (alkyl)(amino)carbenes (CAACs) resulted in a germylene-CAAC radical by homolytic cleavage of the Si–O bonds as evidenced by single crystal X-ray diffraction and continuous-wave EPR spectroscopy.

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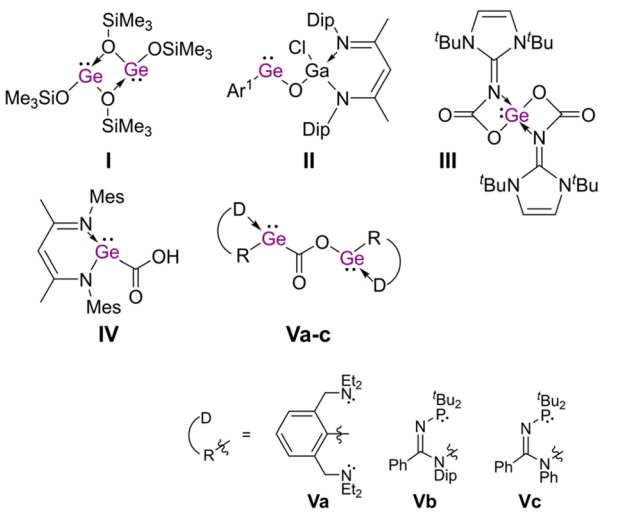
Introduction

Small molecules are elementary, easily accessible and inexpensive potential chemical feedstocks, and as such their transformation into value-added products is extensively investigated, particularly in the case of the greenhouse gas CO_2. In recent years, heavier p-block compounds have been demonstrated to activate small molecules without the support of the typically applied transition metals.[1] In low-valent Group 14 chemistry, heavier alkene and alkyne analogues have been applied to CO_2 activation[2,3] as well as various silylenes and even bis(silylene)s.[4] Whereas silylenes exclusively react under participation of the lone-pair and the vacant p orbital at the low-valent silicon in these reactions, the few reports on CO_2 reactivity of the heavier congeners[5,6] suggest a pronounced dependency on the nature of the substituents.

Despite the plethora of stable germylenes,[7] reports on their reactivity towards CO_2 are surprisingly scarce. Sita *et al.* have reported the metathesis of a homoleptic amino-substituted germylene and CO_2 to provide bis(siloxy)germylene dimer **I** (Scheme 1).[5a] Only very recently, a gallyl-substituted germylene has been shown to reduce CO_2 to CO through insertion of an oxygen atom into the Ge–Ga bond to give galloxy derivative



Scheme 1 Selected products of reactions of germylenes and digermynes with CO_2 (Ar^1 = 2,6-(2,6-$^iPr_2C_6H_3)_2C_6H_3$, Dip = 2,6-$^iPr_2C_6H_3$, Mes = 2,4,6-$Me_3C_6H_2$).

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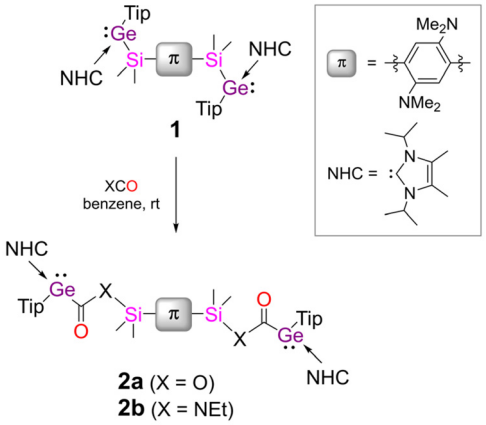
II.[5b] In contrast, in the reaction of an N-heterocyclic imino (NHI) di-substituted germylene, the carbonyl group adds in a [2 + 2]-cycloaddition across the Ge–N bonds to provide four-coordinate germylene **III**.[5c] The only known examples for reactions of the germanium center at the CO_2 carbon atom are hydrogermylenation reactions with heteroleptic hydrido germylenes, in which carboxy germylenes with Ge–C bonds, such as **IV**, are obtained instead.[5d,e] Such germylenes afford methanol and formic acid derivatives in stoichiometric reactions with suitable reactions[5e,f] and have also been proposed as intermediates of the rare examples of catalytic CO_2 derivatization by main-group systems.[5g] Certain digermynes undergo related insertion reactions of the C=O bond, forming germylenyl esters **Va–c**.[3]

Bis(tetrylene)s with linking units, spatially separating the two tetrylene centers, are of particular interest, for instance, as bidentate ligands or for the activation of small molecules.[1d,8] In our heavier acyclic diene metathesis (HADMET) polymerization, bis(germylene)s even constitute transient intermediates to σ,π-conjugated Ge=Ge-containing polymers.[9] A corresponding stabilized NHC-adduct has been isolated and employed as alternative precursor to poly(digermene)s.[10] Hence, we became interested in the derivatization of this NHC-bis(germylene). While simple substitution of the NHC occurs with a nucleophilic and sterically demanding CAAC,[10] we anticipated a fundamentally different reactivity with small electrophiles. Here we report on the activation of carbon dioxide and ethyl isocyanate through selective insertion reactions into the Ge–Si bonds of the silylenearylene-bridged NHC-bis(germylene) under retention of the germanium(II) functionalities. The CO_2 insertion product is shown to undergo CAAC-induced radical fragmentation.

Results and discussion

Exposure of a benzene suspension of yellow NHC-bis(germylene) **1** to CO_2 at room temperature results in immediate dissolution and decolorization. Multinuclear NMR spectroscopy of the crude reaction mixture confirms quantitative conversion to a new product to which we tentatively assign the constitution of silyl ester **2a** (Scheme 2), where the carboxy groups have been inserted into the Ge–Si bonds, based on NMR spectroscopic analysis. Notably, the silagermylenation of CS_2 has very recently been reported to result in the corresponding silyl dithioester.[11] Silyl ester **2a** is isolated as an off-white powder by removing the solvent under vacuum.

A characteristic $^{13}C\{^1H\}$ NMR low-field resonance at 173.2 ppm due to the carbenic carbon atoms as well as a broad septet in the ^1H NMR spectrum at 5.69 ppm arising from the N-bonded isopropyl groups suggest NHC-coordination to the Ge(II) centers.[10,12,13] In comparison to organic esters (158 to 177 ppm),[14] the carbonyl carbon resonance at 204.9 ppm of **2a** is similarly downfield-shifted as oxycarbonyl germylenes **Va–c** (206 to 209 ppm).[3] Furthermore, the considerable deviation from the corresponding shifts of organic



Scheme 2 Reactions of NHC-bis(germylene) **1** with CO_2 and ethyl isocyanate, respectively, to carboxy- and amide-functionalized NHC-bis(germylene)s **2a,b** (Tip = 2,4,6-triisopropylphenyl).

germylenyl esters (~177 ppm)[15] and oxycarbonyl silanes (184 to 192 ppm)[16] speaks against the formation of the corresponding product with reversed regioselectivity, *i.e.* with Ge–O and Si–C bonds (Scheme S1, ESI†), and corroborates the suggested constitution of **2a**.

In line with a more electronegative environment, the $^{29}Si\{^1H\}$ NMR peaks at 2.09 and 2.05 ppm are considerably downfield shifted compared to the germylenyl substituted silicon atoms of the starting material **1** (−11.07, −11.19 ppm).[10] Such low-field shifts are indeed characteristic for silanoles, silyl ethers and silyl esters with Si–O bonds (−3 to 34 ppm)[17] in contrast to the corresponding alkyl silanes (−11 to −3 ppm)[18] and in particular to acyl silanes, including esters (−30 to −7 ppm).[16a,19] The two $^{29}Si\{^1H\}$ NMR peaks with equal intensities in addition to two sets of signals for the phenylene, the NMe_2 and $SiMe_2$ groups in the $^{13}C\{^1H\}$ and ^1H NMR spectra suggest the presence of a 1 : 1 diastereomeric mixture of the racemate and the *meso*-form. Similar results have been obtained for NHC-bis(germylene) **1**[10] and corroborate NHC-coordination to the germylene centers in a pyramidal manner, thus giving rise to Ge-centered chirality. The peak separations are slightly smaller in the case of **2a**, in line with the larger spatial separation of the respective nuclei from the germanium stereocenters. Further evidence for the presence of the ester functionality is provided by a characteristic band in the IR spectrum at 1613 cm^{-1}, just between the C=O stretching vibrations in germylenyl esters **Vb,c** (1581, 1593 cm^{-1})[3b] and acyl digermenes (1649 to 1653 cm^{-1}).[20]

The formation of silyl ester **2a** *vs.* the alternative germylenyl ester (Scheme S1, ESI†) is rationalized by the formation of Si–O bonds (BDE ~ 191 kcal mol^{-1}),[21] which are substantially stronger than Ge–O bonds (BDE ~ 158 kcal mol^{-1}).[21] Accordingly, DFT-calculations for both isomers confirm the silyl ester **2a** to be favored by ΔG = 11.4 kcal mol^{-1} (see ESI†).

Unfortunately, crystallization attempts from pentane, hexane, benzene and thf remained unsuccessful, in part presumably due to the limited stability of **2a** in solution. In par-

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ticular in thf, precipitation of NHC–CO_2 [22] concomitant with the formation of a mixture of unidentified products is already observed after a few hours. We therefore turned our attention to ethyl isocyanate as an isolobal imine analogue of CO_2 in the anticipation that the additional organic substituent could facilitate crystallization without compromising the reactivity.

The reaction of NHC-bis(germylene) **1** with two equivalents of EtNCO in benzene at room temperature (Scheme 2) indeed gives rise to very similar NMR spectroscopic data, in line with the formation of the corresponding bis(amide) **2b**. The characteristic $^{13}C\{^1H\}$ and ^1H NMR peaks of the coordinated NHCs are observed at 172.6 ppm and 5.73 ppm, and the carbonyl carbon resonances at 212.2 and 211.9 ppm. The latter peaks are slightly downfield-shifted with respect to **2a** (204.9 ppm), as is typically observed for amides and imides in comparison to the corresponding esters.[14b,23] The low-field shift of the $^{29}Si\{^1H\}$ NMR resonances at −6.3 and −6.4 ppm in comparison to germylenyl silane **1** (−11.07, −11.19 ppm)[10] is considerably less pronounced than in the case of **2a** (2.09, 2.05 ppm). This is in perfect agreement with the substitution of the O- for an *N*-substituent at silicon as previously observed for silylamines ($PhMe_2SiNR_2$: −5 to −1 ppm)[17e] in comparison to the corresponding silanole ($PhMe_2SiOH$: 7 ppm), for instance.[17d]

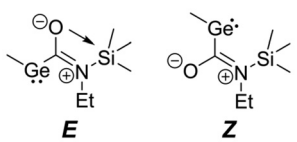
The appearance of two $^{13}C\{^1H\}$ carbonyl carbon resonances for **2b** in addition to the somewhat larger separation of the two $^{29}Si\{^1H\}$ NMR peaks in comparison to **2a** hints towards the presence of rotational isomers due to the newly introduced amide moieties. Hindered rotation about the C–N bond is further corroborated by low-temperature NMR spectra: the $^{29}Si\{^1H\}$ peak ratio changes from 1.5 : 1 at room temperature to 2.4 : 1 at −60 °C, suggesting one of the conformations of the zwitterionic form of the amide functionalities in **2b** (Scheme 3) to be thermodynamically favored.

Most probably, the interaction of the $SiMe_2$ group with the formally negatively charged oxygen center in the *E*-conformer is favorable compared to the germylene lone-pair in the *Z*-conformer, also on steric grounds. Equally characteristic for the presence of rotamers is the distinct increase of the peak separation at low temperature (40 Hz at −60 °C, 9.3 Hz at rt), corresponding to an estimated rotational barrier of $\Delta G^{\ddagger} \sim 60$ kJ mol^{-1} (see ESI†). Similar to dimethylbenzamide (62 kJ mol^{-1}),[24a] the rotation in **2b** is slightly less hindered than in *N*,*N*-dialkyl formamides and acetamides (68 to 88 kJ mol^{-1}),[24] which suggests competing interactions of the lone-pairs at the nitrogen and the germanium centers with the carbonyl group. Even the $SiMe_2$, the aryl protons of the Tip groups and the NHCs' isopropyl methine groups give rise to peak splitting in the ^1H NMR spectrum at −60 °C, despite a larger spatial separation from the C–N bonds (see ESI†).

In stark contrast to this and as expected for a diastereomeric mixture, **2a** does not show coalescence behavior. Notably, in the ^1H NMR spectrum of **2a** accidental isochrony of the diastereomers' peaks is exhibited in thf-d_8 as opposed to C_6D_6. It is therefore not surprising, that the thf-d_8 spectra of **2b** show no additional peak splitting either. Given the structural similarities and the common synthetic origin, however, the presence of different diastereomers is assumed for **2b** as well. Corresponding investigations in C_6D_6 are nonetheless prohibited by its poor solubility.

As in the case of organic amides,[25] the diminished C=O bond strength due to the interaction with the nitrogen lone-pair is reflected in the IR spectrum: the C=O stretching frequency of **2b** (1548 cm^{-1}) is considerably red-shifted compared to ester **2a** (1613 cm^{-1}).

The molecular structure of the *meso*-form of **2b**, obtained by X-ray diffraction on a single crystal (Fig. 1), indeed confirms coordination of the carbene to the germylene center with a characteristically elongated Ge–C single bond (2.078(2) Å). While this is in line with silyl–aryl and diaryl NHC-germylenes (2.067 to 2.078 Å; $\Sigma^{\circ}_{Ge} = 308.4°$ to 317.7°),[10,12] the pyramidalization in **2b** ($\Sigma^{\circ}_{Ge1} = 296.0(2)°$) is slightly increased in comparison. In contrast, the angles are considerably less acute than in intramolecularly stabilized oxycarbonyl germylenes **Va,b** and the related CS_2 insertion product of a silyl germylene ($\Sigma^{\circ}_{Ge1} = 253.4°$ to 282.8°).[3,11] With the smaller pyramidalization, enhanced interaction of the germanium lone-pair with the carbonyl moiety is possible, thus diminishing the donation of the nitrogen lone-pairs to the carbonyl groups: the N2–C10 bond (1.382(3) Å) lies at the upper end of the range constituted by considerably conjugated amides and anilines (1.31 to 1.38 Å).[26] The partial zwitterionic character in amides as opposed to esters results in an elongated C=O double bond length of 1.239(2) Å compared to germylenyl oxycarbonyl germylenes **Va,b** (1.19, 1.20 Å).[3] Notably, the coordination



Scheme 3 Schematic representation of the *E*- and *Z*-conformations of the zwitterionic form of the amide moieties in **2b**.

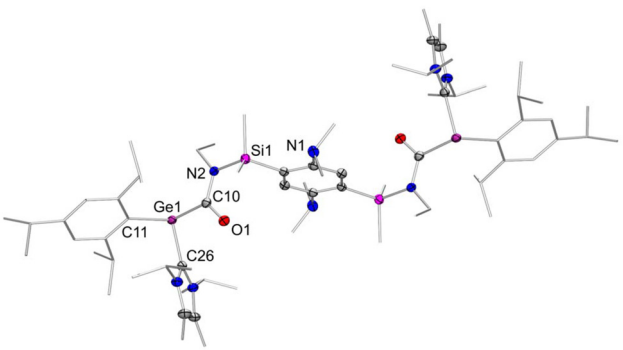


Fig. 1 Molecular structure of amide-functionalized NHC-bis(germylene) **2b** in the solid state (co-crystallized solvent molecules and hydrogen atoms omitted for clarity, thermal ellipsoids at 50%). Selected bond lengths [Å] and angles [°]: Ge1–C26 2.078(2), Ge1–C10 2.066(2), N2–C10 1.382(3), C10–O1 1.239(2), Σ°(Ge1) 296.0(2), Σ°(N2) 360.0(5), Si1–N2–C10–O1 9.1(2).

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environment of the nitrogen centers are perfectly planar (Σ°_{N2} = 360.0(5)°) and the carbonyl group only slightly deviates (Si1–N2–C10–O1 9.1(2)°) from the presumably favored *E*-conformation (*vide supra*).

According to DFT calculations for **2b** at the BP86-D3(BJ)/def2-TZVPP//BP86-D3(BJ)/def2-SVP level of theory, the HOMO and HOMO−1 (Fig. 2) are best represented by lone-pairs at the germanium atoms with π-contributions from the amide functionalities. In line with pronounced interaction between the germylene lone-pairs and the carbonyl groups, HOMO−4 and HOMO−5 exhibit contributions from the carbonyl groups as well as from the germanium and the nitrogen atoms (see ESI†). The LUMO is located at the arylene linker with little admixture from the adjacent silylene moieties. The unoccupied π orbitals at higher energy (LUMO+1 and LUMO+2) are predominantly located at the NHC ligands, suggesting σ,π-interaction only between the π-system of the linker and the $SiMe_2$ groups. In fact, the in-phase and out-of-phase combinations of the pairwise occurring orbitals at both sides of the bridging unit are degenerate, confirming the absence of extended conjugation between the germylene centers.

The activation of the C=X (X = N, O) bonds is presumably achieved through cooperativity of the nucleophilic germylene lone-pair and the electrophilic silyl backbone in bis(germylene) **1**, driven by the formation of strong Si–X bonds. This has been confirmed theoretically by Gonnade and Sen *et al*. for the silagermylenation of CS_2.[11] Notably, neither the CAAC-stabilized bis(germene) analogue of **1** with Ge=C bonds[10] nor the corresponding bis(digermene) with Ge=Ge bonds[9a] react similarly with CO_2, corroborating the importance of the nucleophilicity-enhancing NHC-donor.

Since the reaction of NHC-bis(germylene) **1** with $CAAC^{Me}$, as the stronger σ-donor and π-acceptor, yields the corresponding bis(germene),[10] we attempted the generation of Ge=C double bonds in the corresponding reaction of bis(carboxygermylene) **2a** as well. Surprisingly, however, treatment of **2a** with two equivalents of $CAAC^{Me}$ affords NHC-germylene **3** comprising a tethered radical center, albeit in a very low yield

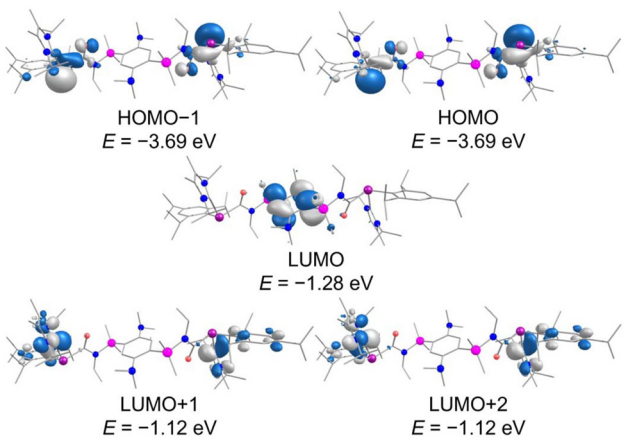
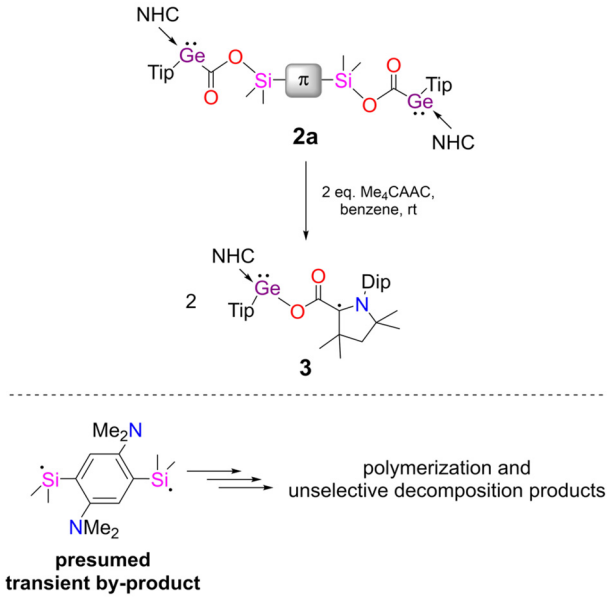


Fig. 2 Selected frontier orbitals of amide-functionalized NHC-bis(germylene) **2b** (contour value 0.036). Hydrogen atoms omitted for clarity.



Scheme 4 Synthesis of paramagnetic NHC-germylene **3** (NHC = 1,3-diisopropylimidazol-4,5-dimethyl-2-ylidene, $CAAC^{Me}$ = 1-(2,6-diisopropylphenyl)-3,3,5,5-tetramethyl-pyrrolidin-2-ylidene).

of 11% (Scheme 4). The constitution of **3** is confirmed by single crystal X-ray crystallography and continuous-wave EPR spectroscopy (Fig. 3). The obtained *g*-factor (2.0035) is slightly

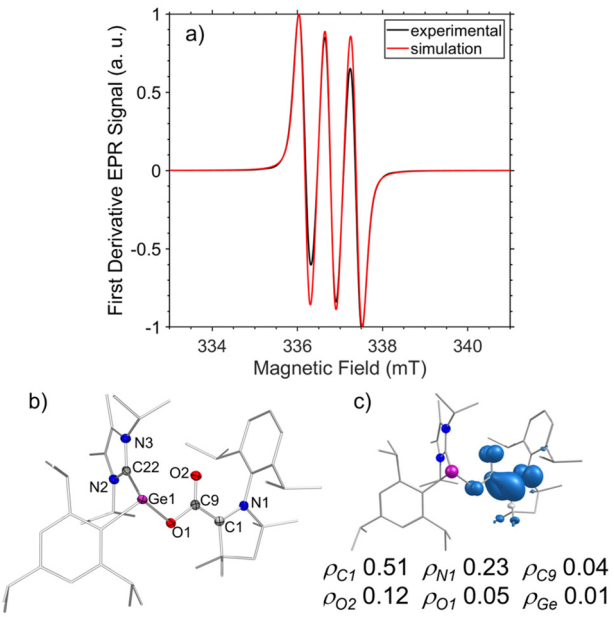


Fig. 3 (a) Experimental and simulated continuous-wave EPR spectra of a C_6D_6 solution of **3** (simulation parameters: g = 2.0035, $A(^{14}N)$ = 6.0 G). (b) Molecular structure of NHC-germylene radical **3** in the solid state (co-crystallized solvent molecules and hydrogen atoms omitted for clarity, thermal ellipsoids at 50%). Selected bond lengths [Å] and angles [°]: Ge1–O1 1.9528(7), C9–O1 1.339(1), C9–O2 1.238(1), C1–N1 1.376(1), C1–C9 1.441(1), Σ°(Ge1) 288.2(1). (c) Calculated Mulliken spin densities and spin density plot (contour value 0.0038).

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smaller than in germylenyl substituted CAAC-radicals (2.0070, 2.0075; $A(^{14}N)$ = 5.0, 5.3 G),[27] in line with a larger distance of the unpaired electron from the germanium. Furthermore, no ^{73}Ge coupling is observed and the ^{14}N coupling ($A(^{14}N)$ = 6.0 G), manifest in a triplet splitting, is only slightly increased, hence suggesting the spin-density to be predominantly located on the substituent.

Accordingly, the molecular structure of **3** (Fig. 3) exhibits an elongated C═O bond (1.238(1) Å) compared to oxycarbonyl germylenes **Va,b** (1.19, 1.20 Å)[3] and even similar to amide **2b** (1.239(2) Å). The short C1–C9 bond length of 1.441(1) Å confirms partial double bond character, in stark contrast to $CAAC^{Me}$–CO_2 (1.52 Å),[28] but in agreement with the delocalization of the unpaired electron across the carbonyl group and the CAAC substituent. The C1–N1 distance (1.376(1) Å) is similar to reported germylenyl substituted CAAC-radicals (1.37 Å).[27] Considerable pyramidalization ($\Sigma^{\circ}_{Ge1} = 288.2(1)^{\circ}$), comparable to a reported siloxy aryl NHC-germylene ($\varepsilon^{\circ}_{Ge1} = 283.7^{\circ}$),[29] suggests the presence of a lone-pair at germanium and no significant contribution from the unpaired electron. This is further confirmed by the Ge1–O1 (1.9528(7) Å) and C9–O1 distances (1.339(1) Å), which are comparable to germylenyl oxycarbonyl germylenes **Va,b** (Ge–O: 1.96 Å, C–O: 1.33 to 1.34 Å).[3]

In line with the experimental data, the Mulliken spin densities obtained at the UB3LYP-D3(BJ)/def2-TZVPP//UB3LYP-D3(BJ)/def2-SVP level of theory are highest at the carbene fragment (Fig. 3). The computed *g*-value of 2.0033 and the ^{14}N coupling constant of $A(^{14}N)$ = 4.2 G validate the accuracy of the computational model.

Apparently, germylene **3** is formed *via* CAAC-induced homolytic cleavage of the Si–O bonds in **2a**. Hence, most likely, a highly reactive silicon centered diradical by-product is formed, whose unselective decomposition and/or polymerization prevent its identification (Scheme 4). While CAACs are known to stabilize main group radicals,[30] they are, however, typically obtained through reduction or hydrogen abstraction. Substitution induced synthesis has only been reported in two cases for silicon and diborane centered diradicals.[31] With the carboxy group as an additional spacer separating the radical center from the Ge(II) moiety in **3**, as opposed to the directly connected CAAC-germylenes,[27] analogous diradicals could be envisaged. We are currently investigating more economic pathways towards such (poly-)radical germylenes, avoiding the use of the relatively complicated linking unit of **2a**.

Conclusions

In conclusion, the silagermylenation reactions of CO_2 and EtNCO with a *para*-silylenephenylene-bridged NHC-bis(germylene) are reported. These highly atom-economic transformations constitute a convenient strategy for the selective backbone functionalization with acyl groups under retention of the low-valent germylenes' integrity. In particular, this may facilitate the synthesis and characterization of structurally derived functionalized poly(digermene)s. In a reaction of the obtained carboxy germylene with $CAAC^{Me}$, structural evidence for an unprecedented germylene with a tethered radical is provided, which may serve as a prototype for related (poly-)radicals in future investigations.

Author contributions

A.-L. T. and D. S. conceptualized the project. D. S. held the project administration and supervision. A.-L. T. (lead) and R. V. (supporting) synthesized and isolated the compounds and collected the NMR, IR, and EPR spectroscopic data. A.-L. T. performed the quantum chemical calculations and carried out the visualization and analysis of the data. B. M. performed the single crystal X-ray analyses and the refinement of the structures. M. Z. performed the VT-NMR spectroscopic measurements. D. S., D. M. and A.-L. T. acquired funding for the project. A.-L. T. (original draft + review and editing) and D. S. (review and editing) wrote the manuscript. C. W. M. K. and D. M. validated the spectroscopic data and the quantum chemical calculations and contributed to the revision and editing of the manuscript.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

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