

RESEARCH ARTICLE

View Article Online

View Journal | View Issue

Cite this: *Inorg. Chem. Front.*, 2025, 12, 4835Silagermylenation of C=O bonds and radical fragmentation of CO₂-expanded bis(germylene) by a cyclic (alkyl)(amino)carbene†Anna-Lena Thömmes,^a Robin Völker,^a Bernd Morgenstern,^b Michael Zimmer,^a Dominik Munz,^c Christopher W. M. Kay^{d,e} and David Scheschkewitz^{d,*a}

The transformation of the greenhouse gas CO₂ into value-added products represents a major contemporary challenge. Low-valent p-block compounds typically react at the oxygen termini of CO₂ due to the oxophilicity of the metal centers. We now report on the selective activation of CO₂ and ethyl isocyanate at the central carbon atom by an N-heterocyclic carbene (NHC)-stabilized *para*-silylenephénylene-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.

Received 7th March 2025,
Accepted 13th April 2025

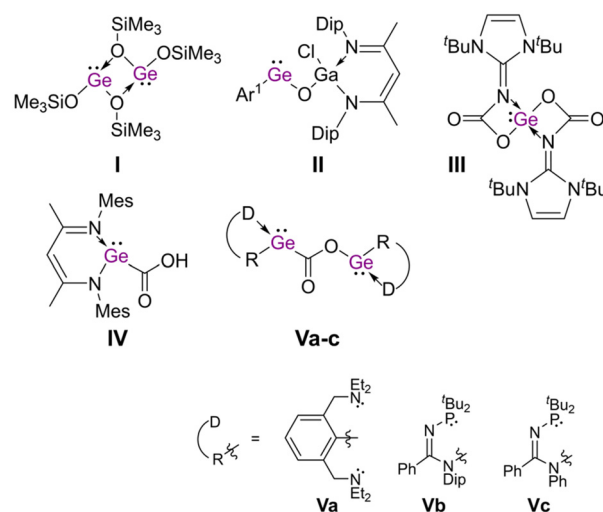
DOI: 10.1039/d5qi00678c

rsc.li/frontiers-inorganic

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 CO₂. 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 CO₂ 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 CO₂ 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 CO₂ are surprisingly scarce. Sita *et al.* have reported the metathesis of a homoleptic amino-substituted germylene and CO₂ to provide bis(siloxy)germylene dimer **I** (Scheme 1).^{5a} Only very recently, a gallyl-substituted germylene has been shown to reduce CO₂ 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 CO₂ (Ar¹ = 2,6-(2,6-ⁱPr₂C₆H₃)₂C₆H₃, Dip = 2,6-ⁱPr₂C₆H₃, Mes = 2,4,6-Me₃C₆H₂).

^aKrupp-Chair for General and Inorganic Chemistry, Saarland University, 66123 Saarbrücken, Germany. E-mail: scheschkewitz@mx.uni-saarland.de

^bInorganic Solid-State Chemistry, Saarland University, 66123 Saarbrücken, Germany

^cCoordination Chemistry, Saarland University, 66123 Saarbrücken, Germany

^dPhysical Chemistry and Chemistry Education, Saarland University, 66123 Saarbrücken, Germany

^eLondon Centre for Nanotechnology, University College London, London WC1H 0AH, UK

† Electronic supplementary information (ESI) available: Details on the synthetic procedures and analyses, SC-XRD, NMR and IR spectroscopic data and DFT calculations. CCDC 2427550 (**2b**) and 2427551 (**3**). For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d5qi00678c>



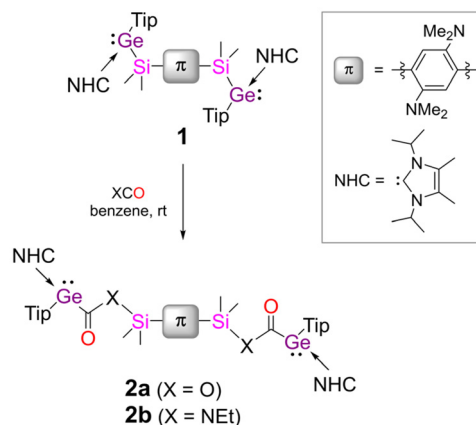
II.^{5b} In contrast, in the reaction of an N-heterocyclic imino (NHI) di-substituted germylene, the carbonyl group adds in a [2 + 2]-cycloaddition across the Ge–N bonds to provide four-coordinate germylene **III**.^{5c} The only known examples for reactions of the germanium center at the CO₂ carbon atom are hydrogermylenation reactions with heteroleptic hydrido germynes, in which carboxy germynes with Ge–C bonds, such as **IV**, are obtained instead.^{5d,e} Such germynes 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 CO₂ derivatization by main-group systems.^{5g} Certain digermynes undergo related insertion reactions of the C=O bond, forming germynyl 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 CO₂ 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 CO₂ 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 CS₂ 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 ¹³C{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 germynes **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 CO₂ and ethyl isocyanate, respectively, to carboxy- and amide-functionalized NHC-bis(germylene)s **2a,b** (Tip = 2,4,6-trisopropylphenyl).

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 ²⁹Si{¹H} NMR peaks at 2.09 and 2.05 ppm are considerably downfield shifted compared to the germynyl substituted silicon atoms of the starting material **1** (–11.07, –11.19 ppm).¹⁰ Such low-field shifts are indeed characteristic for silanols, 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 ²⁹Si{¹H} NMR peaks with equal intensities in addition to two sets of signals for the phenylene, the NMe₂ and SiMe₂ groups in the ¹³C{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 germynyl 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 germynyl 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 $\Delta G = 11.4$ 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-



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 $^{13}\text{C}\{^1\text{H}\}$ 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 $^{29}\text{Si}\{^1\text{H}\}$ 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 ($\text{PhMe}_2\text{SiNR}_2$: -5 to -1 ppm)^{17e} in comparison to the corresponding silanole (PhMe_2SiOH : 7 ppm), for instance.^{17d}

The appearance of two $^{13}\text{C}\{^1\text{H}\}$ carbonyl carbon resonances for **2b** in addition to the somewhat larger separation of the two $^{29}\text{Si}\{^1\text{H}\}$ 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 $^{29}\text{Si}\{^1\text{H}\}$ 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 $\Delta G^\ddagger \sim 60 \text{ kJ mol}^{-1}$ (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; $\Sigma_{\text{Ge}}^\circ = 308.4^\circ$ to 317.7°),^{10,12} the pyramidalization in **2b** ($\Sigma_{\text{Ge1}}^\circ = 296.0(2)^\circ$) 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 ($\Sigma_{\text{Ge1}}^\circ = 253.4^\circ$ 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

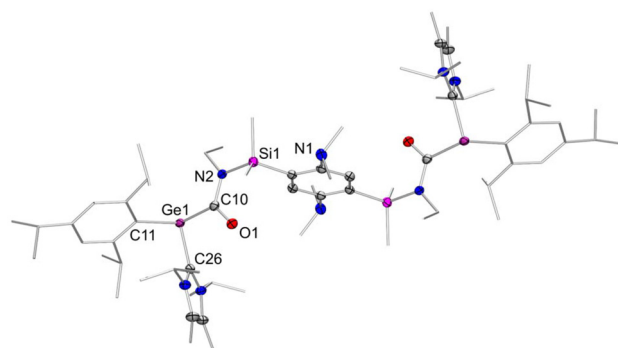
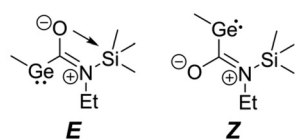


Fig. 1 Molecular structure of amide-functionalized NHC-bis(germylene) **2b** in the solid state (co-crystallized solvent molecules and hydrogen atoms omitted for clarity, thermal ellipsoids at 50%). Selected bond lengths [Å] and angles [°]: Ge1-C26 2.078(2), Ge1-C10 2.066(2), N2-C10 1.382(3), C10-O1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



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

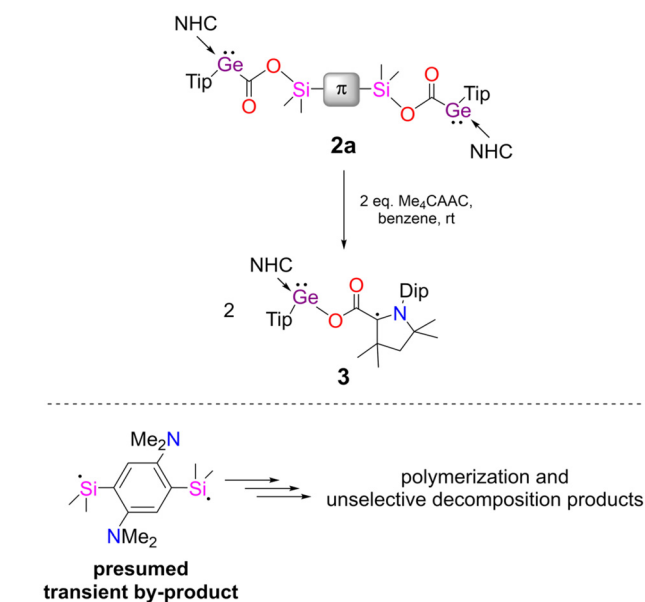


environment of the nitrogen centers are perfectly planar ($\angle_{\text{N}_2} = 360.0(5)^\circ$) and the carbonyl group only slightly deviates ($\text{Si1-N2-C10-O1 } 9.1(2)^\circ$) from the presumably favored *E*-conformation (*vide supra*).

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 $\text{C}=\text{X}$ ($\text{X} = \text{N}, \text{O}$) 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 $\text{Si}-\text{X}$ 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 $\text{Ge}=\text{C}$ bonds¹⁰ nor the corresponding bis(digermene) with $\text{Ge}=\text{Ge}$ 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 $\text{Ge}=\text{C}$ 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



Scheme 4 Synthesis of paramagnetic NHC-germylene **3** (NHC = 1,3-diisopropylimidazol-4,5-dimethyl-2-ylidene, $\text{CAAC}^{\text{Me}} = 1$ -(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

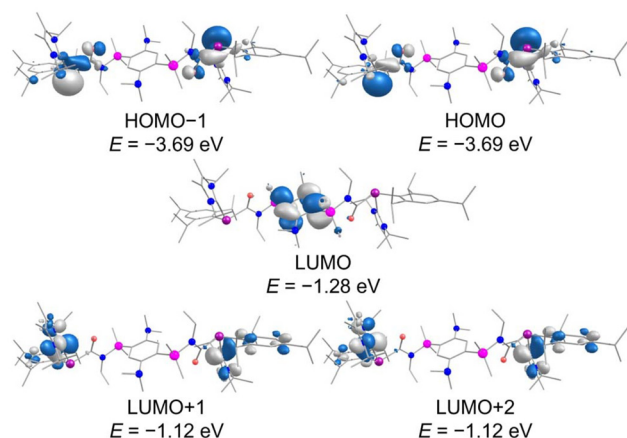


Fig. 2 Selected frontier orbitals of amide-functionalized NHC-bis(germylene) **2b** (contour value 0.036). Hydrogen atoms omitted for clarity.

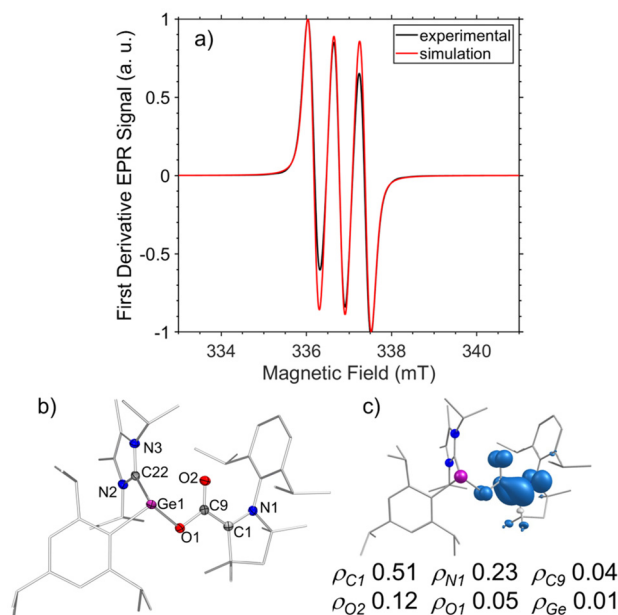


Fig. 3 (a) Experimental and simulated continuous-wave EPR spectra of a C_6D_6 solution of **3** (simulation parameters: $g = 2.0035$, $A(^{14}\text{N}) = 6.0$ G). (b) Molecular structure of NHC-germylene radical **3** in the solid state (co-crystallized solvent molecules and hydrogen atoms omitted for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



smaller than in germylenyl substituted CAAC-radicals (2.0070, 2.0075; $A(^{14}\text{N}) = 5.0, 5.3 \text{ G}$),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 ($A(^{14}\text{N}) = 6.0 \text{ G}$), 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}–CO₂ (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 ($\Sigma_{\text{Ge}^{\circ}} = 288.2(1)^{\circ}$), comparable to a reported siloxy aryl NHC-germylene ($\epsilon_{\text{Ge}^{\circ}} = 283.7^{\circ}$),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 $A(^{14}\text{N}) = 4.2 \text{ G}$ 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 CO₂ and EtNCO with a *para*-silylenephénylene-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.

Acknowledgements

We thank the Fonds der Chemischen Industrie for a Kekulé fellowship for A.-L. T. and the German Research Foundation for funding ("Solar-Driven Chemistry: Light-Induced Small Molecule Fixation by Diradicals"; DFG SCHE 906/9-1). We acknowledge the instrumentation facilities provided by the service center for X-ray analysis established with the financial support from Saarland University and the German Research Foundation (INST 256/506-1 and INST 256/582-1). We thank Prof. Stella Stopkowicz for access to the computational cluster.

References

- Reviews: (a) R. Akhtar, K. Gaurav and S. Khan, Applications of low-valent compounds with heavy group-14 elements, *Chem. Soc. Rev.*, 2024, **53**, 6150–6243; (b) S. Sinha and J. Jiang, Main group elements in electrochemical hydrogen evolution and carbon dioxide reduction, *Chem. Commun.*, 2023, **59**, 11767–11779; (c) M. Pérez-Jiménez, H. Corona,



- F. de la Cruz-Martínez and J. Campos, Donor-Acceptor Activation of Carbon Dioxide, *Chem. – Eur. J.*, 2023, **29**, e202301428; (d) A. Saddington, S. Yao and M. Driess, Recent advances in low-valent silicon chemistry, in *Advances in Inorganic Chemistry*, ed. K. Meyer and R. van Eldik, Academic Press, 2023, vol. 82, pp. 119–156; (e) F. Dankert and C. Hering-Junghans, Heavier group 13/15 multiple bond systems: synthesis, structure and chemical bond activation, *Chem. Commun.*, 2022, **58**, 1242–1262; (f) S. Fujimori and S. Inoue, Small Molecule Activation by Two-Coordinate Acyclic Silylenes, *Eur. J. Inorg. Chem.*, 2020, 3131–3142; (g) C. Shan, S. Yao and M. Driess, Where silylene–silicon centres matter in the activation of small molecules, *Chem. Soc. Rev.*, 2020, **49**, 6733–6754; (h) Y. Su and R. Kinjo, Small molecule activation by boron-containing Heterocycles, *Chem. Soc. Rev.*, 2019, **48**, 3613–3659; (i) R. L. Melen, Frontiers in molecular p-block chemistry: From structure to reactivity, *Science*, 2019, **363**, 479–484; (j) T. J. Hadlington, M. Driess and C. Jones, Low-valent group 14 element hydride chemistry: towards catalysis, *Chem. Soc. Rev.*, 2018, **47**, 4176–4197; (k) C. Weetman and S. Inoue, The Road Travelled: After Main-Group Elements as Transition Metals, *ChemCatChem*, 2018, **10**, 4213–4228; (l) T. Chu and G. I. Nikonov, Oxidative Addition and Reductive Elimination at Main-Group Element Centers, *Chem. Rev.*, 2018, **118**, 3608–3680; (m) X. Wang, C. Xia and L. Wu, Homogeneous carbon dioxide reduction with p-block element-containing reductants, *Green Chem.*, 2018, **20**, 5415–5426; (n) S. Yadav, S. Saha and S. S. Sen, Compounds with Low-Valent p-Block Elements for Small Molecule Activation and Catalysis, *ChemCatChem*, 2016, **8**, 486–501; (o) B. Blom and M. Driess, Recent Advances in Silylene Chemistry: Small Molecule Activation En-Route Towards Metal-Free Catalysis, in *Functional Molecular Silicon Compounds II. Structure and Bonding*, ed. D. Scheschkewitz, Springer International Publishing, 2014, vol. 156, pp. 85–123.
- 2 (a) N. Wiberg, W. Niedermayer, K. Polborn and P. Mayer, Reactivity of the Isolable Disilene $R^*PhSi=SiPhR^*$ ($R^*=Si$, Bu_3), *Chem. – Eur. J.*, 2002, **8**, 2730–2739; (b) D. Gau, R. Rodriguez, T. Kato, N. Saffon-Merceron, A. de Cózar, F. P. Cossío and A. Baceiredo, Synthesis of a Stable Disilyne Bisphosphine Adduct and Its Non-Metal-Mediated CO_2 Reduction to CO, *Angew. Chem., Int. Ed.*, 2011, **50**, 1092–1096, (*Angew. Chem.*, 2011, **123**, 1124–1128); (c) J. Li, M. Hermann, G. Frenking and C. Jones, The Facile Reduction of Carbon Dioxide to Carbon Monoxide with an Amido-Digermine, *Angew. Chem., Int. Ed.*, 2012, **51**, 8611–8614, (*Angew. Chem.*, 2012, **124**, 8739–8742); (d) D. Wendel, T. Szilvási, D. Henschel, P. J. Altmann, C. Jandl, S. Inoue and B. Rieger, Precise Activation of Ammonia and Carbon Dioxide by an Iminodisilene, *Angew. Chem., Int. Ed.*, 2018, **57**, 14575–14579, (*Angew. Chem.*, 2018, **130**, 14783–14787); (e) A. Kostenko and M. Driess, Geometrically Compelled Disilene with λ^4 -Coordinate SiIII Atoms, *J. Am. Chem. Soc.*, 2018, **140**, 16962–16966.
- 3 (a) A. Caise, L. P. Griffin, C. McManus, A. Heilmann and S. Aldridge, Reversible Uptake of CO_2 by Pincer Ligand Supported Dimetallynes, *Angew. Chem., Int. Ed.*, 2022, **61**, e202117496, (*Angew. Chem.*, 2022, **134**, e202117496); (b) J. Fan, S. Quek, M.-C. Yang, Z.-F. Zhang, M.-D. Su and C.-W. So, Reversible CO_2 activation by a N-phosphinoamidinato digermine, *Chem. Commun.*, 2022, **58**, 1033–1036.
- 4 (a) P. Jutzi, D. Eikenberg, A. Möhrke, B. Neumann and H.-G. Stammer, Decamethylsilicocene Chemistry: Unprecedented Multistep Reactions of a Silicon(II) Compound with the Heterocumulenes CO_2 , COS, CS_2 , and RNCS (R = Methyl, Phenyl), *Organometallics*, 1996, **15**, 753–759; (b) S. Yao, Y. Xiong, M. Brym and M. Driess, An Isolable Silanoic Ester by Oxygenation of a Stable Silylene, *J. Am. Chem. Soc.*, 2007, **129**, 7268–7269; (c) X. Liu, X.-Q. Xiao, Z. Xu, X. Yang, Z. Li, Z. Dong, C. Yan, G. Lai and M. Kira, Reactions of an Isolable Dialkylsilylene with Carbon Dioxide and Related Heterocumulenes, *Organometallics*, 2014, **33**, 5434–5439; (d) K. Junold, M. Nutz, J. A. Baus, C. Burschka, C. Fonseca Guerra, F. M. Bickelhaupt and R. Tacke, The Donor-Stabilized Silylene Bis[N,N' -diisopropylbenzamidinato(–)]silicon(II): Synthesis, Electronic Structure, and Reactivity, *Chem. – Eur. J.*, 2014, **20**, 9319–9329; (e) F. M. Mick, J. A. Baus, M. Nutz, C. Burschka, J. Poater, F. M. Bickelhaupt and R. Tacke, Reactivity of the Donor-Stabilized Silylenes [$iPrNC(Ph)NiPr$] $_2Si$ and [$iPrNC(Ni,Pr_2)NiPr$] $_2Si$: Activation of CO_2 and CS_2 , *Chem. – Eur. J.*, 2015, **21**, 16665–16672; (f) D. Wendel, A. Porzelt, F. A. D. Herz, D. Sarkar, C. Jandl, S. Inoue and B. Rieger, From Si(II) to Si(IV) and Back: Reversible Intramolecular Carbon–Carbon Bond Activation by an Acyclic Iminosilylene, *J. Am. Chem. Soc.*, 2017, **139**, 8134–8137; (g) A. V. Protchenko, P. Vasko, D. C. Huan Do, J. Hicks, M. Á. Fuentes, C. Jones and S. Aldridge, Reduction of Carbon Oxides by an Acyclic Silylene: Reductive Coupling of CO, *Angew. Chem., Int. Ed.*, 2019, **58**, 1808–1812, (*Angew. Chem.*, 2019, **131**, 1822–1826); (h) M.-P. Luecke, E. Pens, S. Yao and M. Driess, An Isolable Bis(Silano-Borane) Adduct, *Chem. – Eur. J.*, 2020, **26**, 4500–4504; (i) Y. Xiong, S. Yao, A. Ruzicka and M. Driess, Distinctly different reactivity of bis(silylenyl)- versus phosphanyl-silylenyl-substituted o-dicarborene towards O_2 , N_2O and CO_2 , *Chem. Commun.*, 2021, **57**, 5965–5968.
- 5 (a) L. R. Sita, J. R. Babcock and R. Xi, Facile Metathetical Exchange between Carbon Dioxide and the Divalent Group 14 Bisamides $M[N(SiMe_3)_2]_2$ (M = Ge and Sn), *J. Am. Chem. Soc.*, 1996, **118**, 10912–10913; (b) A. Bückner, C. Wölper and S. Schulz, Activation of heteroallenes by metal-substituted electron-rich tetrylenes, *Polyhedron*, 2024, **247**, 116702; (c) L. Groll, J. A. Kelly and S. Inoue, Reactivity of NHI-Stabilized Heavier Tetrylenes towards CO_2 and N_2O , *Chem. – Asian J.*, 2024, **19**, e202300941; (d) A. Jana, D. Ghoshal, H. W. Roesky, I. Objartel, G. Schwab and D. A. Stalke, A Germanium(II) Hydride as an Effective Reagent for Hydrogermylation Reactions, *J. Am. Chem. Soc.*,



- 2009, **131**, 1288–1293; (e) G. Tan, W. Wang, B. Bloma and M. Driess, Mechanistic studies of CO₂ reduction to methanol mediated by an N-heterocyclic germylene hydride, *Dalton Trans.*, 2014, **43**, 6006–6011; (f) A. Jana, G. Tavčar, H. W. Roesky and M. John, Germanium(II) hydride mediated reduction of carbon dioxide to formic acid and methanol with ammonia borane as the hydrogen source, *Dalton Trans.*, 2010, **39**, 9487–9489; (g) T. J. Hadlington, C. E. Kefalidis, L. Maron and C. Jones, Efficient Reduction of Carbon Dioxide to Methanol Equivalents Catalyzed by Two-Coordinate Amido-Germanium(II) and -Tin(II) Hydride Complexes, *ACS Catal.*, 2017, **7**, 1853–1859.
- 6 (a) J. R. Babcock, L. Liable-Sands, A. L. Rheingold and L. R. Sita, Syntheses, Structural Characterizations, and Heterocumulene Metathesis Studies of New Monomeric Bis(triorganosilylamido)tin(II) Derivatives, *Organometallics*, 1999, **18**, 4437–4441; (b) A. Jana, H. W. Roesky, C. Schulzke and A. Döring, Reactions of Tin(II) Hydride Species with Unsaturated Molecules, *Angew. Chem., Int. Ed.*, 2009, **48**, 1106–1109, (*Angew. Chem.*, 2009, **121**, 1126–1129); (c) D. A. Dickie, E. N. Coker and R. A. Kemp, Formation of a Reversible, Intramolecular Main-Group Metal–CO₂ Adduct, *Inorg. Chem.*, 2011, **50**, 11288–11290; (d) S. Weiß, M. Widemann, K. Eichele, H. Schubert and L. Wesemann, Low valent lead and tin hydrides in reactions with heteroallenes, *Dalton Trans.*, 2021, **50**, 4952–4958; (e) A. V. Protchenko, M. Á. Fuentes, J. Hicks, C. McManus, R. Tirfoin and S. Aldridge, Reactions of a diborylstannylene with CO₂ and N₂O: diboration of carbon dioxide by a main group bis(boryl) complex, *Dalton Trans.*, 2021, **50**, 9059–9067; (f) D. Sarkar, L. Groll, D. Munz, F. Hanusch and S. Inoue, Ligand Assisted CO₂ Activation and Catalytic Valorization by an NHI-Stabilized Stannylene, *ChemCatChem*, 2022, **14**, e202201048.
- 7 Reviews: (a) W. P. Neumann, Germylenes and Stannylenes, *Chem. Rev.*, 1991, **91**, 311–334; (b) N. N. Zemlyanskii, I. V. Borisova, M. S. Nechaev, V. N. Khrustalev, V. V. Lunin, M. Y. Antipin and Y. A. Ustynyuk, Divalent silicon, germanium, and tin compounds with element-heteroatom bonds, *Russ. Chem. Bull. Int. Ed.*, 2004, **53**, 980–1006; (c) Y. Mizuhata, T. Sasamori and N. Tokitoh, Stable Heavier Carbene Analogues, *Chem. Rev.*, 2009, **109**, 3479–3511; (d) M. Asay, C. Jones and M. Driess, N-Heterocyclic Carbene Analogues with Low-Valent Group 13 and Group 14 Elements: Syntheses, Structures, and Reactivities of a New Generation of Multitalented Ligands, *Chem. Rev.*, 2011, **111**, 354–396; (e) J. A. Cabeza and P. García-Álvarez, Polydentate Amidinato-Silylenes, -Germylenes and -Stannylenes, *Chem. – Eur. J.*, 2024, **30**, e202400786.
- 8 Reviews: (a) N. Mukherjee and M. Majumdar, Diverse Functionality of Molecular Germanium: Emerging Opportunities as Catalysts, *J. Am. Chem. Soc.*, 2024, **146**, 24209–24232; (b) X. Gao, Y. He and J. Cui, Charting the frontiers of Bis-germylene chemistry, *J. Organomet. Chem.*, 2024, **1012**, 123146; (c) S. Yao, A. Saddington, Y. Xiong and M. Driess, Chelating Bis-silylenes As Powerful Ligands To Enable Unusual Low-Valent Main-Group Element Functions, *Acc. Chem. Res.*, 2023, **56**, 475–488.
- 9 (a) L. Klemmer, A.-L. Thömmes, M. Zimmer, V. Huch, B. Morgenstern and D. Scheschkewitz, Metathesis of Ge=Ge double bonds, *Nat. Chem.*, 2020, **13**, 373–377; (b) A.-L. Thömmes, T. Büttner, B. Morgenstern, O. Janka, G. Kickelbick, B.-J. Niebuur, T. Kraus, M. Gallei and D. Scheschkewitz, Near-Infinite-Chain Polymers with Ge=Ge Double Bonds, *Angew. Chem., Int. Ed.*, 2024, **63**, e202415103, (Nahezu unendlich lange Polymere mit Ge=Ge-Doppelbindungen, *Angew. Chem.*, 2024, **136**, e202415103).
- 10 A.-L. Thömmes, B. Morgenstern, M. Zimmer, D. M. Andrada and D. Scheschkewitz, σ,π -Conjugated Bis(germylene) Adducts with NHC and CAACs, *Chem. – Eur. J.*, 2023, **29**, e202301273.
- 11 V. S. Ajithkumar, N. Khilari, P. B. Ghanwat, G. Venugopal, D. Koley and S. S. Sen, Activation of carbon disulfide by a hypersilyl germylene, *Dalton Trans.*, 2024, **53**, 10814–10818.
- 12 (a) K. L. Hurni, P. A. Rugar, N. C. Payne and K. M. Baines, Stabilization of a Transient Diorganogermylene by an N-Heterocyclic Carbene, *Organometallics*, 2007, **26**, 4109–4111; (b) A. J. Ruddy, P. A. Rugar, K. J. Bladec, C. J. Allan, J. C. Avery and K. M. Baines, On the Bonding in N-Heterocyclic Carbene Complexes of Germanium(II), *Organometallics*, 2010, **29**, 1362–1367.
- 13 (a) A. Jana, V. Huch and D. Scheschkewitz, NHC-Stabilized Silagermynylidene: A Heavier Analogue of Vinylidene, *Angew. Chem., Int. Ed.*, 2013, **52**, 12179–12182, (NHC-Stabilisiertes Silagermynylid: ein schweres Analogon von Vinyliden, *Angew. Chem.*, 2013, **125**, 12401–12404); (b) A. Jana, V. Huch, H. S. Rzepa and D. Scheschkewitz, A Multiply Functionalized Base-Coordinated GeII Compound and Its Reversible Dimerization to the Digermene, *Angew. Chem., Int. Ed.*, 2015, **54**, 289–292, (Eine mehrfach funktionalisierte Basenkoordinierte GeII-Verbindung und ihre reversible Dimerisierung zum Digermen, *Angew. Chem.*, 2015, **127**, 291–295); (c) D. Nieder, C. B. Yildiz, A. Jana, M. Zimmer, V. Huch and D. Scheschkewitz, Dimerization of a marginally stable disilyl germylene to tricyclic systems: evidence for reversible NHC-coordination, *Chem. Commun.*, 2016, **52**, 2799–2802; (d) D. Nieder, V. Huch, C. B. Yildiz and D. Scheschkewitz, Regiodiscriminating Reactivity of Isolable NHC-Coordinated Disilyl Germylene and Its Cyclic Isomer, *J. Am. Chem. Soc.*, 2016, **138**, 13996–14005.
- 14 (a) A. B. Terent'ev, V. I. Dostovalova and R. K. Freidlina, Carbon-13 N.m.r. Spectra of Branched Carboxylic Acids and their Derivatives, *Org. Magn. Reson.*, 1977, **9**, 301–307; (b) K. L. Williamson, M. U. Hasan and D. R. Clutter, Conformational Analysis by NMR. ¹³C Nuclear Magnetic Resonance Spectra of Saturated and Unsaturated Carboxylic Acids and Their Corresponding Esters and Anhydrides, *J. Magn. Reson.*, 1978, **30**, 367–383.
- 15 N. N. Zemlyansky, I. V. Borisova, V. N. Khrustalev, M. Y. Antipin, Y. A. Ustynyuk, M. S. Nechaev and



- V. V. Lunin, New Stable Gemylenes, Stannylenes, and Related Compounds. 3. Stable Monomers $XGeOCH_2CH_2NMe_2$ ($X = Cl, OCOME$) with Only One Intramolecular Coordination Metal–Nitrogen Bond: Synthesis and Structure, *Organometallics*, 2003, **22**, 5441–5446.
- 16 (a) K. Igawa, N. Kokan and K. Tomooka, Asymmetric Synthesis of Chiral Silacarboxylic Acids and Their Ester Derivatives, *Angew. Chem., Int. Ed.*, 2010, **49**, 728–731; (b) K. Igawa, Y. Kawasaki, S. Nozaki, N. Kokan and K. Tomooka, Ozone Oxidation of Silylalkene: Mechanistic Study and Application for the Synthesis of Silacarboxylic Acid Derivatives, *J. Org. Chem.*, 2020, **85**, 4165–4171.
 - 17 Ph_3SiOH (-13 ppm)^{17d} constitutes an exception to the general trend and was omitted from the discussion for clarity; (a) J. Schraml, V. Chvalovský, M. Mägi and E. Lippmaa, The role of electronic and steric effects in ²⁹Si-NMR spectra of compounds with Si–O–C group, *Collect. Czech. Chem. Commun.*, 1981, **46**, 377–390; (b) I. Zicmane, E. Liepins, L. M. Ignatovich and E. Lukevics, A ¹³C, ¹⁷O, ¹⁹Si NMR study of some silicon, germanium and tin acylox- yderivatives, *J. Organomet. Chem.*, 1991, **417**, 355–362; (c) P. Lassacher, A. G. Brook and A. J. Lough, Reactions of Silenes: A New Silene to Silene Thermal Rearrangement, *Organometallics*, 1995, **14**, 4359–4365; (d) Y. Okada, M. Oba, A. Arai, K. Tanaka, K. Nishiyama and W. Ando, Diorganotelluride-Catalyzed Oxidation of Silanes to Silanols under Atmospheric Oxygen, *Inorg. Chem.*, 2010, **49**, 383–385; (e) A. I. Ojeda-Amador, J. Munarriz, P. Alamán-Valtierra, V. Polo, R. Puerta-Oteo, M. V. Jiménez, F. J. Fernández-Alvarez and J. J. Pérez-Torrente, Mechanistic Insights on the Functionalization of CO₂ with Amines and Hydrosilanes Catalyzed by a Zwitterionic Iridium Carboxylate-Functionalized Bis-NHC Catalyst, *ChemCatChem*, 2019, **11**, 5524–5535.
 - 18 S. Fortier, Y. Zhang, H. K. Sharma and K. H. Pannell, Formation of Silicon–Carbon Bonds by Photochemical Irradiation of $(\eta^5-C_5H_5)Fe(CO)_2SiR_3$ and $(\eta^5-C_5H_5)Fe(CO)_2Me$ to Obtain R_3SiMe , *Organometallics*, 2010, **29**, 1041–1044.
 - 19 P. C. Bulman Page, S. S. Klair and S. Rosenthal, Synthesis and Chemistry of Acyl Silanes, *Chem. Soc. Rev.*, 1990, **19**, 147–195.
 - 20 L. Klemmer, Y. Kaiser, V. Huch, M. Zimmer and D. Scheschke, Persistent Digermenes with Acyl and α -Chlorosilyl Functionalities, *Chem. – Eur. J.*, 2019, **25**, 12187–12195.
 - 21 Y.-R. Luo, *Comprehensive Handbook of Chemical Bond Energies*, Taylor & Francis, Boca Raton, 2007, vol. 1, pp. 455–480.
 - 22 X. Wang, J. Zhang, L. Wang and L. Deng, High-Spin Iron(II) Alkynyl Complexes with N-Heterocyclic Carbene Ligation: Synthesis, Characterization, and Reactivity Study, *Organometallics*, 2015, **34**, 2775–2782.
 - 23 M. U. Hasan, ¹³C NMR Spectra of some Amides and Imides. Effect of Inductive and Mesomeric Interactions, Cyclization and Hydrogen Bonding on ¹³C NMR Chemical Shifts, *Org. Magn. Reson.*, 1980, **14**, 447–450.
 - 24 (a) L. W. Reeves, R. C. Shaddick and K. N. Shaw, Nuclear Magnetic Resonance Studies of Multi-site Chemical Exchange. III. Hindered Rotation in Dimethylacetamide, Dimethyl Trifluoroacetamide, and Dimethyl Benzamide, *Can. J. Chem.*, 1971, **49**, 3683–3691; (b) M. Feigel, Rotation Barriers of Amides in the Gas Phase, *J. Phys. Chem.*, 1983, **87**, 3054–3058; (c) V. S. Dimitrov and J. A. Ladd, Dynamic NMR: comparison of the experimental barriers to internal rotation in *N,N*-dimethylformamide with those calculated by the ab initio SCF MO method, *J. Mol. Struct.*, 1987, **159**, 107–112.
 - 25 (a) T. Threlfall, The infrared spectra of amides. Part 1. The stretching vibrations of primary carboxamides, *Vib. Spectrosc.*, 2022, **121**, 103386; (b) H. F. Shurvell, Spectra-Structure Correlations in the Mid- and Far-infrared, in *Handbook of Vibrational Spectroscopy*, ed. P. Griffiths and J. M. Chalmers, John Wiley & Sons, Chichester, 2006, vol. 1, pp. 1783–1816.
 - 26 (a) M. Chen, B. Lei, X. Wang, H. Rong, H. Song and Z. Mo, A Silylene-Stabilized Germanium Analogue of Alkynylaluminum, *Angew. Chem., Int. Ed.*, 2022, **61**, e202204495, (*Angew. Chem.*, 2022, **134**, e202204495); (b) R. S. C. Charman, N. J. Evans, L. E. English, S. E. Neale, P. Vasko, M. F. Mahon and D. J. Liptrot, The structures and reactivity of NHC-supported copper(I) triphenylgermyls, *Chem. Sci.*, 2024, **15**, 584–593; (c) L. K. Saunders, H. Nowell, L. E. Hatcher, H. J. Shepherd, S. J. Teat, D. R. Allan, P. R. Raithby and C. C. Wilson, Exploring short strong hydrogen bonds engineered in organic acid molecular crystals for temperature dependent proton migration behaviour using single crystal synchrotron X-ray diffraction (SCSXR), *CrystEngComm*, 2019, **21**, 5249–5260; (d) J. R. Holden, C. Dickinson and C. M. Bock, The Crystal Structure of 2,4,6-Trinitroaniline, *J. Phys. Chem.*, 1972, **76**, 3597–3602.
 - 27 A. Pratap Singh, P. P. Samuel, H. W. Roesky, M. C. Schwarzer, G. Frenking, N. S. Sidhu and B. A. Dittrich, A Singlet Biradicaloid Zinc Compound and Its Nonradical Counterpart, *J. Am. Chem. Soc.*, 2013, **135**, 7324–7329.
 - 28 M. M. Siddiqui, S. K. Sarkar, S. Sinhababu, P. N. Ruth, R. Herbst-Irmer, D. Stalke, M. Ghosh, M. Fu, L. Zhao, D. Casanova, G. Frenking, B. Schwederski, W. Kaim and H. W. Roesky, Isolation of Transient Acyclic Germanium(I) Radicals Stabilized by Cyclic Alkyl(amino) Carbenes, *J. Am. Chem. Soc.*, 2019, **141**, 1908–1912.
 - 29 D. Sarkar, C. Weetman, S. Dutta, E. Schubert, C. Jandl, D. Koley and S. Inoue, N-Heterocyclic Carbene-Stabilized Germa-acylium Ion: Reactivity and Utility in Catalytic CO₂ Functionalizations, *J. Am. Chem. Soc.*, 2020, **142**, 15403–15411.
 - 30 (a) C. D. Martin, M. Soleilhavoup and G. Bertrand, Carbene-stabilized main group radicals and radical ions, *Chem. Sci.*, 2013, **4**, 3020–3030; (b) S. Kundu, S. Sinhababu, V. Chandrasekhar and H. W. Roesky, Stable cyclic (alkyl) (amino)carbene (cAAC) radicals with main group substituents, *Chem. Sci.*, 2019, **10**, 4727–4741; (c) K. Breitwieser, H. Bahmann, R. Weiss and D. Munz, Gauging Radical



- Stabilization with Carbenes, *Angew. Chem., Int. Ed.*, 2022, **61**, e202206390, (*Angew. Chem.*, 2022, **134**, e202206390).
- 31 (a) K. C. Mondal, H. W. Roesky, M. C. Schwarzer, G. Frenking, I. Tkach, H. Wolf, D. Kratzert, R. Herbst-Irmer, B. Niepötter and D. Stalke, Conversion of a Singlet Silylene to a stable Biradical, *Angew. Chem., Int. Ed.*, 2013, **52**, 1801–1805, (Umwandlung eines Singulett-Silylens in

ein stabiles Biradikal, *Angew. Chem.*, 2013, **125**, 1845–1850); (b) J. Böhnke, T. Dellermann, M. A. Celik, I. Krummenacher, R. D. Dewhurst, S. Demeshko, W. C. Ewing, K. Hammond, M. Heß, E. Bill, E. Welz, M. I. S. Röhr, R. Mitrić, B. Engels, F. Meyer and H. Braunschweig, Isolation of diborenes and their 90°-twisted diradical congeners, *Nat. Commun.*, 2018, **9**, 1197.

