NHC-coordinated silagermenylidene functionalized in allylic position and its behaviour as a ligand†

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Vinylidenes are common in transition metal chemistry with catalytic applications in alkene and alkyne metathesis. We report here the isolation of a heavier analogue of vinylidene, an α-chlorosilyl functionalized silagermenylidene stabilized by an N-heterocyclic carbene (NHC). Silagermenylidene (Tip2Cl)Si·(Tip)Si–Ge·NHCiPr2Me2 (4-E/Z; Tip = 2,4,6-iPr3C6H2; NHCiPr2Me2 = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene) is available as an E/Z-equilibrium mixture from Tip2Si–Si(Tip)Li and NHCiPr2Me2·GeCl2. Reaction of 4-E/Z with Fe2(CO)9 affords a silagermenylidene Fe(CO)4 complex, which slowly isomerizes to its E-isomer at 25 °C. A rearranged Fe(CO)3 complex with an allylic SiGeSi ligand is obtained as a side product at 65 °C.

Introduction

The chemistry of low-coordinate germanium has received considerable attention in recent years.1 Important bonding motifs experimentally realized include two-coordinate germynes,2 and digermynes,3 as well as three-coordinate digermerenes,4 silagermenes,5 and germachalcogenones6 on the other hand. Since Robinson et al. reported the NHC-stabilized disilicon(0) species Ia,7 the use of strong donors for the isolation of highly reactive low-valent species by raising the coordination number has drastically increased.8 In germanium chemistry, germylene-type compounds (e.g. dihalogermynes,9 digermanium(0) Ib10), and inherently polar/polarizable multiple bonds (e.g. germachalcogenones,11 digermynes12) are prominent examples that are stabilized by base-coordination under retention of remarkable reactivity. Very recently, we reported on a N-heterocyclic carbene stabilized silagermenylidene, Tip2Si–Ge–NHCiPr2Me2 II (NHCiPr2Me2 = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene, Scheme 1).13 With the Si–Ge bond, the lone pair of electrons and the coordination site of the NHC, compound II offers various potential sites for further manipulation. Initially, we demonstrated the clean [2 + 2] cycloaddition of an alkyne to the Si–Ge bond.13 In view of the prominent role of carbon-based vinylidenes in catalysis,14 an open question remains the coordination behavior of isolable heavier vinylidenes towards transition metals.15 In the case of heavier analogues of carbenes, transition metal coordination compounds are known.16

Our recent isolation of a stable NHCiPr2Me2-stabilized aryl (disilanyl)silylene III17 encouraged us to target the corresponding disilanyl-substituted chlorogermylene 3. We thus reacted disilene 118 and NHC-coordinated germanium(iv) chloride, NHCiPr2Me2·GeCl2 29 (Scheme 2). Monosubstituted NHC-coordinated chlorogermylenes IV (Scheme 1) have been prepared via similar approaches.19

†Electronic supplementary information (ESI) available: NMR and UV/vis spectra of all new compounds, X-ray crystallographic data (CIF) for 4-E, 5-E, and 6, and computational details, CCDC 953520–953522. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4dt00094c

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Results and discussion

Surprisingly, instead of the targeted 3 the 1:1 reaction of 1\textsuperscript{18} and 2\textsuperscript{9c} in toluene at −78 °C affords the NHC-coordinated silagermenyldene 4 in 62% yield (mp. 126–128 °C) (Scheme 2) with an additional peripheral Si-Cl functionality (see the Experimental section). The reaction plausibly proceeds through the NHC-stabilized chlorodisilenylgermylene 3 as a transient followed by subsequent 1,3-migration of chlorine from germanium to the β-silicon. In solution, the \(^{29}\text{Si}\) resonances of 4 at 162.5 and 7.3 ppm served as the first indication of the formation of a silagermenyldene due to the close similarity to the low-field resonance of II (158.9 ppm).\textsuperscript{13} The red color of 4 is due to the longest wavelength absorption in the UV/vis spectrum at \(\lambda_{\text{max}} = 451\) nm (Table 1, \(\varepsilon = 9220\) L mol\(^{-1}\) cm\(^{-1}\)), which almost matches with that of compound II (\(\lambda_{\text{max}} = 455\) nm). In contrast to II, however, the second absorption of 4 appears as a shoulder (4: \(\lambda_{\text{max}} = 389\) nm, II: \(\lambda_{\text{max}} = 365\) nm). To gain more information about the origins of the UV/vis absorptions, we performed TD-DFT calculations of the silagermenyldene II on the basis of the experimentally determined molecular structure in the solid state. Solvent effects were approximated using the Tomasi’s polarized continuum model (PCM) at the B3LYP/6-31G(d,p) level of theory.\textsuperscript{†} The calculated lowest-energy excitation of 4 at 439 nm is predominantly associated with the \(\pi-\pi^*\) transition (HOMO → LUMO), in very good agreement with the experimental value of 455 nm. The second experimental absorption band at \(\lambda_{\text{max}} = 365\) nm is due to various excitations, but does contain a significant component originating from the \(n-\pi^*\) transition (HOMO−1 → LUMO) as suspected in our previous communication.\textsuperscript{13}

Crystals of 4 suitable for X-ray diffraction analysis were obtained from pentane at 25 °C. The structure in the solid state (Fig. 1) confirmed the constitution of 4 as the sterically most favorable E-stereoisomer. The Ge1–Si1 bond length is by 2.2757(10) Å slightly longer than in II (2.2521(5) Å),\textsuperscript{11} whereas it is almost identical with that of the bulkily substituted silagermene (\(\text{Bu}_3\text{Si})_2\text{Si} = \text{GeMes}_2\) (2.2769(8) Å; Mes = 2,4,6-Me\(_3\)C\(_6\)H\(_3\)).\textsuperscript{9c} As in II, the NHC coordinates to germanium in a near-orthogonal manner with respect to the Si1–Ge1 bond vector (C46–Ge1–Si1 101.90(10)°). The Ge1–C46 distance in 4-E (2.061(4) Å) is between that of the simple silagermenyldene II (2.0474(18) Å) and the GeCl\(_2\) precursor 2 (2.106(3) Å).\textsuperscript{9c}

Interestingly, in solution, 4-E slowly converts to a new compound with \(^{29}\text{Si}\) NMR resonances at 134.0 and −0.2 ppm, which we assign to stereoisomer 4-Z (Scheme 3). Equilibrium is reached after approximately 4 h in benzene-\(d_6\) at an \(E/Z\) ratio of 0.85 : 0.15, essentially unaffected by temperature (+70 to −60 °C) or the presence of excess NHC\textsubscript{2Pr}(Me\(_2\)).\textsuperscript{20}

The calculated \(^{29}\text{Si}\) shifts [GIAO/B3LYP/6-31G(d,p) for H, C, N, 6-311+G(2d,p) for Si, Ge, Cl] of the truncated model systems for both isomers 4-Dip-E and 4-Dip-Z (R = Dip = 2,6-iPr\(_2\)C\(_6\)H\(_3\) instead of Tip) are 159.5, 1.7 and 90.4, −9.8 ppm, respectively.\textsuperscript{†} Although the experimental trend is reproduced, the absolute agreement of the calculated and the experimental values is better for the major isomer 4-E. The deviations presumably arise from the neglect of dispersive forces that should affect the sterically unfavorable isomer 4-Z considerably more than 4-E.\textsuperscript{17}

Mills et al. had obtained the first structurally characterized transition metal complexes of diphenylvinylidene from diphenylketene and Fe(CO)\(_5\).\textsuperscript{21} The reaction of 4-E/Z with Fe\(_2\)(CO)\(_9\) in

![Diagram](image-url)
THF at room temperature initially affords only the Z-stereoisomer of the silagermenyldene complex 5, which corresponds to the relative orientation of the chlorosilyl group and the NHCPr2Me2 ligand in 4-E (Scheme 3) (see the Experimental section). The iron germylenyldene complex 5-Z was isolated as a red-brown solid (mp. 140°C) in 63% yield. In the case of germylenes, similar complexes have been reported. In the 13C NMR of 5-Z, the two downfield resonances at 216.8 and 167.0 ppm were assigned to the carbonyl ligands at the Fe- and center and coordinated NHC iPr2Me2, respectively. The 29Si NMR exhibits signals at 100.7 and 3.0 ppm; the formal sp2-Si center and coordinated NHC iPr2Me2, respectively. The α-carbon signals at 2015, 2010, 1923, 1899 cm−1 of 5-E: 2.061(4) Å). The Ge1–Fe1 bond length (2.3780(6) Å) is slightly longer than in germyle-coordinated iron(tetra-carbonyl complexes (LGeOH Å 2.330(1) Å, LGeF Å 2.326(7) Å). In the light of the current discussion on the use of arrows in the context of donor–acceptor interactions it should be noted that obviously the formulation of 5-Z as zwitterionic complex 5′-Z is equally valid.

When the isomerization process of 5-Z was carried out at 65 °C, an additional product 6 was formed in 14% yield (Scheme 3) along with the major product 5-E (56%) (see the Experimental section). Notably, 6 cannot be obtained by heating an isolated sample of 5-E. Spatial proximity between the Fe(CO)4 and Si(Tip2)Cl moieties seems to be required for the isomerization under loss of one CO ligand. By fractional crystallization, we isolated 6 as yellow blocks (mp. 197–199 °C). In 29Si NMR, both resonances of silicon appear at 113.7 (SiTip2) and 91.5 (Si(Tip2)) ppm, which hints at the absence of saturated silicon atoms, such as in the chlorosilyl side chain of 5-Z/E.

An X-ray diffraction study on single crystals of 6 revealed a bicyclo[1.1.0]butane-like butterfly structure with the Fe and Ge in the bridgehead positions (Fig. 3). Apparently, a chlorine migration from the Si(Tip2) moiety to the Si(Tip2) moiety took place during conversion from 5-Z to 6. The 29Si NMR shifts of 6 are close to those of Ogino’s alkox- and amido-bridged bis(silylene)iron complexes 7 (Scheme 4). In the present case, however, the bridging unit is the NHCPr2Me2-stabilized germyle moiety so that an analogous electronic description (6', Scheme 4) probably contributes less than a zwitterionic resonance form of allylic type (6′).
This averaged finds support in the pertinent structural features of 6. The averaged distance between Fe1 and Si1/Si2 in 6 is 2.3343(7) Å, shorter than that in the tetracarbonyl iron complexes of a Z-1,2-dichlorodisilene (2.4358(6) Å, average distance), but longer than the Si–Fe distances in silylene–iron complexes ([Co]Fe=Si(Me)2·HMPA, 2.280(1) Å and 2.294(1) Å for two crystallographic independent molecules; [Co]Fe=Si(SiMe2)2·HMPA, 2.278(1) Å) (HMPA = (NMe2)3PO/hexamethylphosphoric triamide). The average distance between silicon and germanium in 6 is 2.3560(7) Å, considerably longer than that of the reported 2-germadisilaallene (2.2370(7) Å) (HMPA = (NMe2)3PO/hexamethylphosphoric triamide). The mechanism for formation of 6 remains obscure. However, the intramolecular activation of a silicon–sulfur bond in oligosilyl iron complexes has been reported and recently Marschner et al. demonstrated the Lewis acids catalyzed shuttling of germanium atoms into branched polysilanes.

Experimental section

General remarks

All experiments were carried out under a protective atmosphere of argon applying standard Schlenk techniques or in a glove box. All the solvents were refluxed over sodium/benzophenone, distilled and stored under argon. Benzene-d8, toluene-d8, and THF-d8 were dried and distilled over potassium under argon. 1H and 13C[1H] NMR spectra were referenced to the peaks of residual protons of the deuterated solvent (1H) or the deuterated solvent itself (13C). 29Si[1H] NMR spectra were referenced to external SiMe4. UV/vis spectra were acquired using a Perkin-Elmer Lambda 35 spectrometer using quartz cells with a path length of 0.1 cm. IR spectra were recorded using a Varian 2000 FT-IR FTS 2000 spectrometer. Melting points were determined under argon in closed NMR tubes and are uncorrected. Elemental analyses were performed using a Leco CHN-900 analyzer.

Synthesis of 4-E: A precooled (−78 °C) solution of 1 (2.70 g, 3.17 mmol, in 30 mL of toluene) was transferred by cannula to a suspension of 2 (1.02 g, 3.17 mmol, in 15 mL of toluene) at −78 °C. The reaction mixture was allowed to warm slowly to room temperature and stirred overnight. All the volatiles were removed under vacuum and the solid residue dissolved in 30 mL of hexane. After filtration, the solution was concentrated to about 10 mL and kept overnight at room temperature. The red precipitate was separated from the supernatant solution, washed with 5 mL of pentane and dried under vacuum to yield 1.90 g (62%) of 4-E. Single crystals suitable for X-ray diffraction were obtained from a saturated pentane solution after keeping for 2 days at room temperature. Mp: 126–128 °C.

1H NMR (300 MHz, benzene-d6, TMS): δ 7.08 (s, 4H, TipH), 7.03 (s, 2H, TipH), 5.38 (2H, sept, NPr–CH2), 4.47–3.96 (m and br, altogether 6H, oPr–CH2), 2.83–2.65 (m, 3H, pPr–CH2), 1.52 (s, 6H, CH3–C=C–C), 1.33–1.11 (br and m, altogether 48H, 1Pr–CH2), 0.85 (d, 12 H, NPr–CH3) ppm.

13C NMR (75.4 MHz, benzene-d6, TMS): δ 162.50 (StTip), 7.3 (StTip) ppm. UV/vis (hexane): λmax(em) = 451 nm (9220 L mol–1 cm–1), 389 nm (sh). Anal. Calcd for C56H89ClGeN2Si2: C, 70.46; H, 9.40; N, 2.93. Found: C, 70.47; H, 9.47; N, 2.93. Crystallographic data: C56H89ClGeN2Si2, M = 954.51, monoclinic, space group P2(1)/c, a = 20.8316(11), b = 10.99027(6), c = 25.5288(13) Å, β = 90.840(3)°, V = 5672.3(5) Å3; Z = 4, μ = 1.118 g cm–3, T = 133(2) K, λ = 0.71073 Å, 48.361 reflections, 14 017 independent (Rint = 0.1264), R1 = 0.0619 (I > 2σ(I)) and wR2(all data) = 0.1332, Goof = 0.970, max/min residual electron density: 0.8272/–0.923 e Å–3.

Equilibrium between 4-E and 4-Z and NMR data of 4-Z: In solution 4-E isomerizes to 4-Z reaching equilibrium after about 4 h. The ratio of the two isomers was approximately 0.84:0.16 (4-E:4-Z). 4-E: 1H NMR (300 MHz, benzene-d8, TMS): δ 7.24 (br, 2H, TipH), 7.21 (br, 1H, TipH), 6.97 (br, 1H, TipH), 6.77 (br, 1H, TipH), 5.67 (2H, sept, NPr–CH2), 4.75–4.54 (m and br, altogether 2H, oPr–CH2), 3.76–3.64 (m, 2H, oPr–CH2), 1.80 (d, 3H, pPr–CH3), 1.76–1.69 (m, 6H, pPr–CH3), 1.61 (s, 6H, CH3–C=C–C), 0.61 (d, 3H, pPr–CH3), 0.47 (d, 3H, pPr–CH3), 0.40 (d, 3H, pPr–CH3), 0.30 (d, 3H, pPr–CH3) ppm.

13C NMR (75.4 MHz, benzene-d8, TMS): δ 178.33 (NCN) ppm. 29Si NMR (59.5 MHz, benzene-d8, TMS): δ 138.02 (StTip), −0.20 (StTip) ppm (minor isomer).
Synthesis of 5-Z: Dry and degassed THF (30 mL) was added to a Schlenk flask containing compound 4-E (1.90 g, 1.99 mmol) and Fe₂(CO)₉ (0.80 g, 2.19 mmol) at room temperature. The color of the reaction mixture changed immediately to deep red. The reaction mixture was stirred for another 4 h and all the volatiles were removed under vacuum. The solid residue was extracted with 80 mL of hexane and the resulting solution was filtered to remove insoluble impurities. The hexane was distilled off under vacuum. After addition of 20 mL of pentane, 1.40 g (63%) of 5-Z were isolated as a dark-red solid. Mp: 140–142 °C. ¹H NMR (300 MHz, toluene-d₈, TMS): δ 7.26, 7.18, 6.86, 6.81, 6.65 (d, each having 1H, Tipf), another Tip-H signal is marked by residual proton signals of toluene-d₈, 5.83 (sept, 1H, Tip-Ch), 5.09 (sept, 1H, Tip-Ch), 5.00 (sept., 1H, Tip-Ch), 4.55 (sept, 1H, Tip-Ch), 4.07 (sept, 1H, Tip-Ch), 3.80–3.62 (m, 2H, Tip-Ch), 2.78 (sept, 1H, Tip-Ch), 2.70–2.53 (m, 2H, Tip-Ch), 2.48 (sept, 1H, Tip-Ch), 1.73 (d, 3H, CH₃-C), 1.67–1.51 (s and m, altogether 15H, Tip-Ch₂ and CH₃-C=C), 1.45–1.39 (s and m, altogether 6H, Tip-Ch and CH₃-C=C), 1.34–1.25 (m, 9H, Tip-Ch₃), 1.22 (d, 6H, Tip-Ch₃), 1.17–1.16 (m, 9H, Tip-Ch₃), 1.09–1.03 (m, 6H, Tip-Ch₃), 0.48 (d, 3H, Tip-Ch₂), 0.43 (d, 3H, Tip-Ch₂), 0.37 (d, 3H, Tip-Ch₂), 0.20–0.11 (m, 9H, Tip-Ch₂) ppm. ²⁹Si NMR (75.4 MHz, toluene-d₈, TMS): δ 217.56 (CO), 165.81 (NCN) ppm. (We were unable to assign other signals correctly, because they overlap with its isomer 5-E). ²⁹Si NMR (59.5 MHz, toluene-d₈, TMS): δ 100.67 (SiTip), 2.98 (SiTip₂) ppm. Mp.: 140–142 °C. UV/vis (hexane): λmax (d) = 503 nm (8260 Lmol⁻¹cm⁻¹). IR (KBr, cm⁻¹): ν = 2018 (s), 1923 (s), 1899 (s). Anal. Calcd for Ca₉H₉₅ClFeGe₅N₂O₄Si₂ (1122.47): C, 64.20; H, 7.99; N, 2.50. Found: C, 64.10; H, 7.74; N, 2.63.

Synthesis of 5-E: A solution of 5-Z (1.00 g, 0.89 mmol) in toluene (60 mL) was stirred for five days at room temperature. All volatiles were removed under vacuum and the solid residue extracted with 70 mL of hexane. The solution was concentrated to about 20 mL and after keeping at 65 °C. All the volatiles were removed under vacuum and the solid residue extracted with 40 mL of hexane. The solution was concentrated to about 20 mL and after keeping at room temperature for two days afforded yellow blocks of 6 (0.075 g, 14%). Keeping the mother liquor at −20 °C for a week afforded brown-red crystals of 5-E (0.28 g, 56%). Mp: 197–199 °C. ¹H NMR (300 MHz, toluene-d₈, TMS): δ 7.23 (1H, Tipf), 7.13 (1H, Tipf, masked by toluene-d₈), 7.02 (sept, 1H, N'Pr-Ch), 7.01 (1H, Tipf, masked by toluene-d₈), 6.98–6.95 (m, 2H, Tipf), 6.87 (d, 1H, Tipf), 6.41 (sept, 1H, N'Pr-Ch), 5.25 (sept, 1H, Tip-Ch), 4.86 (sept, 1H, Tip-Ch), 4.35 (sept, 1H, Tip-Ch), 4.22 (sept, 1H, Tip-Ch), 3.61 (sept, 1H, Tip-Ch), 2.47 (sept, 1H, Tip-Ch), 2.77 (sept, 1H, Tip-Ch), 2.65 (sept, 1H, Tip-Ch), 1.67–1.78 (m, 6H, Tip-Ch), 1.68 (s, 3H, CH₃-C=C), 1.66 (s, 3H, CH₃-C=C), 1.56–1.57 (m, altogether 18H, Tip-Ch), 1.31–1.04 (m, altogether 30H, Tip-Ch), 0.72 (d, 3H, Tip-Ch₂), 0.48 (d, 3H, Tip-Ch₂), 0.45 (d, 3H, Tip-Ch₂), 0.19 (d, 3H, Tip-Ch₂) ppm. ²⁹Si NMR (300 MHz, thf-d₈, TMS): δ 7.03 (1H, Tipf), 6.96 (d, 1H, Tipf), 6.95 (sept, 1H, N'Pr-Ch), 6.80 (d, 1H, Tipf), 6.76 (d, 1H, Tipf), 6.71 (d, 1H, Tipf), 6.67 (1H, Tipf), 6.19 (sept, 1H, N'Pr-Ch), 4.82 (sept, 1H, Tip-Ch), 4.61 (sept, 1H, Tip-Ch), 4.15 (sept, 1H, Tip-Ch), 3.82 (sept, 1H, Tip-Ch), 3.34–3.18 (m, 2H, Tip-Ch), 2.87–2.68 (m, 1H, Tip-Ch), 2.63 (sept, 1H, Tip-Ch), 2.41 (s, 3H, CH₃-C=C), 2.35 (s, 3H, CH₃-C=C), 1.85 (s, 3H, Tip-Ch), 1.62 (d, 3H, Tip-Ch), 1.58–1.49 (m, altogether 9H, Tip-Ch), 1.44 (d, 3H, Tip-Ch), 1.24 (d, 3H, Tip-Ch), 1.20–1.11 (m, altogether 21H, Tip-Ch), 1.08–1.03 (m, altogether 9H, Tip-Ch), 0.88 (d, 3H, Tip-Ch), 0.45 (d, 3H, Tip-Ch), 0.18–0.14 (m, altogether 6H, Tip-Ch), 0.20 (d, 3H, Tip-Ch) ppm. ¹³C NMR (75.4 MHz, thf-d₈, TMS): δ 218.99, 215.98 (CO), 157.19, 156.89, 155.09, 154.75, 154.08, 152.28, 150.90, 150.71, 149.48, 143.26, 142.18, 136.52 (Tip-Ch₂), 129.52, 129.26 (NCN), 123.68, 122.72, 122.66, 122.06, 121.88, 121.43 (Tip-Ch), 56.24, 54.08 (N'Pr-Ch), 38.20, 36.65, 36.46, 35.29, 35.39, 34.98, 34.83, 34.16, 30.24 (Tip-Ch), 28.21, 26.76, 26.28, 25.97, 25.65, 24.58, 24.91, 24.38, 24.36, 24.28, 24.18, 23.99, 23.90, 23.84, 23.40, 22.88, 22.23, 21.98 (Tip-Ch), 11.21, 10.73 (CH₃-C=C) ppm (we did not observe the carbonic carbon resonance). ²⁹Si NMR (59.5 MHz, toluene-d₈, TMS): δ 113.66 (SiTip), 91.46 (SiTip₂) ppm. ²⁹Si NMR (59.5 MHz, D₂O,THF, TMS): δ 111.36 (SiTip), 88.27
Conclusions

We have shown an efficient method for the synthesis of side chain-functionalized silagermylidene stabilized by coordination of an N-heterocyclic carbene. Its suitability as a ligand for transition metal complexes was demonstrated by coordination to the Fe(αCO₃) fragment. Moreover, the resulting silagermylidene iron complex thermally rearranges to an apparently more stable complex of unprecedented allylic structure, which is undoubtedly a consequence of the ease of migration of the residual chlorine functionality.

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Notes and references


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22 In $^{13}$C NMR, the carbenic carbon of NHC$_{iPr^2Me^2}$–GeCl$_2$ appears at $\delta = 169.11$ ppm in [d$_6$]-benzene, see Fig. S5 in the ESI.$^\dagger$


