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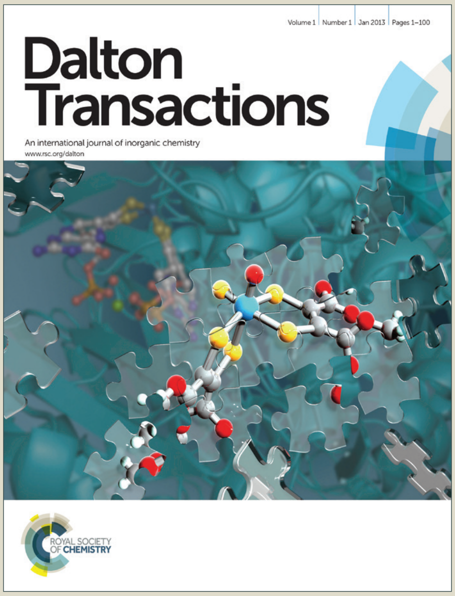

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PAPER

A stable NHC-Coordinated Silagermenylidene Functionalized in Allylic Position and its Behaviour as a Ligand†

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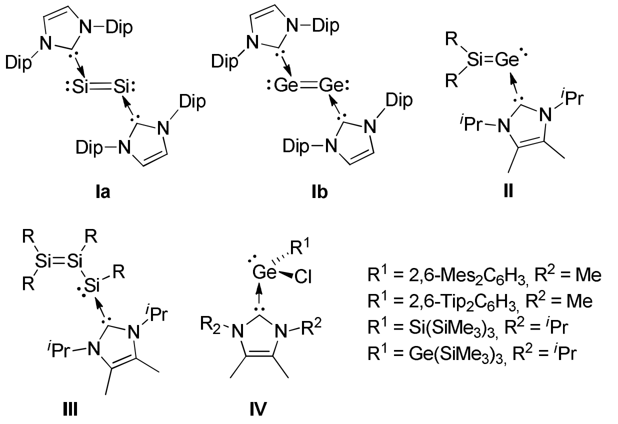
Vinylidenes are common in transition metal chemistry with catalytic applications in alkene and alkyne metathesis. We here report the isolation of a heavier analogue of vinylidene, an α-chlorosilyl functionalized silagermenylidene stabilized by an *N*-heterocyclic carbene (NHC). Silagermenylidene $(\text{Tip}_2\text{Cl})\text{Si-(Tip)Si=Ge}\cdot\text{NHC}^{i\text{Pr}_2\text{Me}_2}$ (**4**-*E/Z*; Tip = $2,4,6\text{-}^i\text{Pr}_3\text{C}_6\text{H}_2$; $\text{NHC}^{i\text{Pr}_2\text{Me}_2}$ = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene) is available as an *E*/*Z*-equilibrium mixture from $\text{Tip}_2\text{Si=Si(Tip)Li}$ and $\text{NHC}^{i\text{Pr}_2\text{Me}_2}\cdot\text{GeCl}_2$. Reaction of **4**-*E/Z* with $\text{Fe}_2(\text{CO})_9$ 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 germylenes[2] and digermynes,[3] as well as three-coordinate digermenes,[4] silagermenes,[5] and germachalcogenones[6] 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.* dihalogermylenes,[9] digermanium(0) **Ib**[10]), and inherently polar/ polarizable multiple bonds (*e.g.* germachalcogenones,[11] digermynes[12]) 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, $\text{Tip}_2\text{Si=Ge}\cdot\text{NHC}^{i\text{Pr}_2\text{Me}_2}$ **II** ($\text{NHC}^{i\text{Pr}_2\text{Me}_2}$ = 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 vinylidene complexes in catalysis,[14] an open question remained 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]



Scheme 1 Chemical structures of **Ia**, **Ib**, **II**, **III**, and **IV** (Dip = $2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3$, R = Tip = $2,4,6\text{-}^i\text{Pr}_3\text{C}_6\text{H}_2$, Mes = $2,4,6\text{-Me}_3\text{C}_6\text{H}_2$).

Our recent isolation of a stable $\text{NHC}^{i\text{Pr}_2\text{Me}_2}$-stabilized aryl(disilenyl)silylene **III**[17] encouraged us to target the corresponding disilenyl-substituted chlorogermylene **3**. We thus reacted disilenide **1**[18] and NHC-coordinated germanium(II)chloride, $\text{NHC}^{i\text{Pr}_2\text{Me}_2}\cdot\text{GeCl}_2$ **2**[9c] (Scheme 2). Monosubstituted NHC-coordinated chlorogermylenes **IV** (Scheme 1) had been prepared via similar approaches.[19]

Results and discussion

Surprisingly, instead of the targeted **3** the 1:1 reaction of **1**[18] and **2**[9c] in toluene at −78 °C affords the NHC-coordinated silagermenylidene **4** in 62% yield (mp. 126-8 °C) (Scheme 2) with an additional peripheral Si-Cl functionality.‡ The reaction plausibly proceeds through the NHC-stabilized chloro(disilenyl)germylene **3** as a transient followed by

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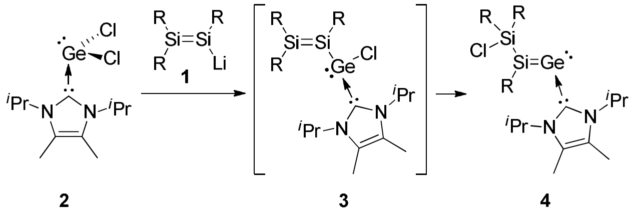
† Electronic Supplementary Information (ESI) available: NMR and UV/vis spectra of all new compounds, X-ray crystallographic data (CIF) for **4**-*E*, **5**-*E*, and **6**, and computational details. Crystallographic data have also been deposited with the Cambridge Structural Database: CCDC-953520 (**4**-*E*), -953522 (**5**-*E*), and -953521 (**6**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/

subsequent 1,3-migration of chlorine from germanium to the *β*-silicon. In solution, the ^{29}Si resonances of **4** at 162.5 and 7.3 ppm served as first indication of the formation of a silagermenylidene due to the close similarity to the low-field resonance of **II** (158.9 ppm).[13] The red color of **4** is due to the longest wavelength absorption in the UV/vis spectrum at λ_{max} = 451 nm (Table 1, ε = 9220 Lmol^{-1}cm^{-1}), which almost matches with that of compound **II** (λ_{max} = 455 nm). In contrast to **II**, however, the second absorption of **4** appears as a shoulder (**4**: λ_{max} = 389 nm, **II**: λ_{max} = 365 nm). To gain more information about the origins of the UV/vis absorptions, we performed TD-DFT calculations of the silagermenylidene **II** on the basis of the experimentally determined molecular structure in the solid state. Solvent effects were approximated using Tomasi's Polarized Continuum Model (PCM) at the at the B3LYP/6-31G(d,p) level of theory.[†] The calculated lowest-energy excitation of **II** at 439 nm is predominantly associated to the π-π* transition (HOMO→LUMO), in very good agreement with the experimental value of 455 nm. The second experimental absorption band at λ_{max} = 365 nm is due to various excitations, but does contain a significant component originating from the n-π* transition (HOMO−1→LUMO) as suspected in our previous communication.[13]



Scheme 2 Synthesis of **4** (R = Tip = 2,4,6-^{i}Pr$_3$C$_6$H$_2$).

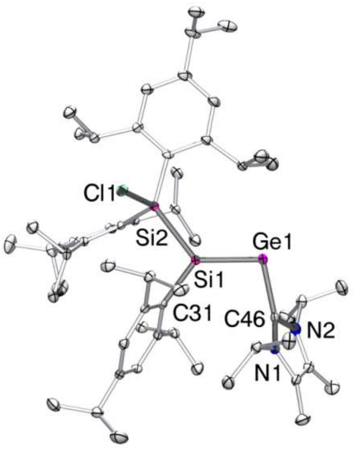


Fig. 1 Structure of **4**-*E* in the solid state (thermal ellipsoids at 30%). Hydrogen atoms omitted. Selected bond lengths [Å]: Si1-Ge1 = 2.2757(10), Ge1-C46 = 2.061(4), Si1-Si2 = 2.3776(13), Si2-Cl1 = 2.1179(13).

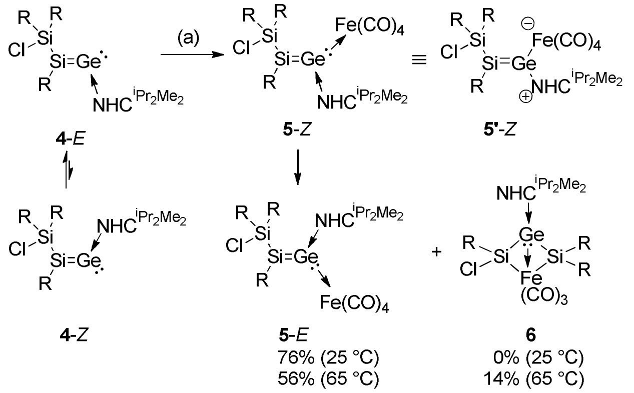
Crystals of **4** suitable for X-ray diffraction analysis were obtained from pentane at 25 °C. The structure in the solid state (Figure 1) confirmed the constitution of **4** as the sterically most favorable *E*-stereoisomer. The Ge1-Si1 bond length is with 2.2757(10) Å slightly longer than in **II** (2.2521(5) Å),[13] whereas it is almost identical with that of the bulkily substituted silagermene (^{t}Bu$_3$Si)$_2$Si=GeMes$_2$ (2.2769(8) Å; Mes = 2,4,6-Me$_3$C$_6$H$_2$).[5c] 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 silagermenylidene **II** (2.0474(18) Å) and the GeCl$_2$ precursor **2** (2.106(3) Å).[9c]

Table 1 ^{29}Si{^{1}H}^{a}, ^{13}C{^{1}H} NMR, UV/vis data of **4-*E***, **4-*Z***, **5-*Z***, **5-*E***, and **6**

	4-E^b	4-Z^b	5-Z^c	5-E^c	6^c
δ^{29}Si (SiTip)	162.5 (159.5)	134.0 (90.4)	100.7	98.1	113.7 (138.3)
δ^{29}Si (SiTip$_2$)	7.3 (1.7)	−0.2 (−9.8)	3.0	−3.9	91.5 (110.7)
δ^{13}C (NCN)	178.4 (168.4)	178.3(165.1)	165.8	167.0	-
δ^{13}C Fe(CO)$_4$	-		217.6	216.8	219.0, 216.0
λ_{max} [nm]	451, 389		503	512; 427	368^d

^{a} Calculated values in parentheses. ^{b}In d_6-benzene. ^{c}In d_8-toluene. ^{d}In THF.

Interestingly, in solution **4**-*E* slowly converts to a new compound with ^{29}Si NMR resonances at 134.0 and −0.2 ppm, which we assign to stereoisomer **4**-*Z* (Scheme 3). Equilibrium is reached after approximately 4h 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$^{iPr2\,Me2}$.[20]



Scheme 3 Equilibrium of **4**-*E* to **4**-*Z* and Synthesis of Transition Metal Complexes **5**-*Z*, **5**-*E* and **6** (a: THF, Fe$_2$(CO)$_9$; R = Tip = 2,4,6-^{i}Pr$_3$C$_6$H$_2$; NHC^{iPr2Me2} = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene).

The calculated ^{29}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 **4Dip**-*E* and **4Dip**-*Z* (R = Dip = 2,6-^{i}Pr$_2$C$_6$H$_3$ instead of Tip) are 159.5, 1.7 and 90.4, −9.8 ppm, respectively.[†] Although the experimental trend is reproduced, the absolute agreement of calculated and 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*.[17]

Mills et al. had obtained the first structurally characterized transition metal complexes of diphenylvinylidene from diphenylketene and Fe(CO)$_5$.[21] The reaction of **4**-*E*/*Z* with Fe$_2$(CO)$_9$ in THF at room temperature initially affords only the *Z*-stereoisomer of the silagermenylidene complex **5,** which corresponds to the relative orientation of the chlorosilyl group and the NHC$^{i\mathrm{Pr2Me2}}$ ligand in **4**-*E* (Scheme 3).‡ The iron germenylidene complex **5**-*Z* was isolated as red-brown solid (mp. 140-142 °C) in 63 % yield. In case of germylenes, similar complexes have been reported.[16b] In the ^{13}C NMR of **5**-*Z*, the two downfield resonances at 216.8 and 167.0 ppm were assigned to the carbonyl ligands at the Fe-center and coordinated NHC$^{i\mathrm{Pr2Me2}}$, respectively.[22] The ^{29}Si NMR exhibits signals at 100.7 and 3.0 ppm; the formal *sp*^{2}-Si is substantially upfield shifted compared to that of the free ligand **4**-*E* (Table 1). As shown by the new ^{29}Si signals at 98.1 and −3.9 ppm in a 1:1 ratio, **5**-*Z* slowly – but in this case irreversibly – rearranges to the stereoisomer, **5**-*E* (mp. 158-160 °C) in solution. This is in contrast to the steric preferences of the NHC$^{i\mathrm{Pr2\,Me2}}$ ligand in **4**-*E*/*Z*, which, however, can readily be explained by the comparatively larger Fe(CO)$_4$ moiety (Scheme 3).‡ In the IR, the most intense carbonyl stretching bands of **5**-*Z* and **5**-*E* are observed at 2018, 2010, 1923, 1899 cm^{-1} and 2011, 2008, 1917, 1897 cm^{-1}, respectively. Apparently, silagermenylidenes **4**-*E*/*Z* are somewhat weaker σ-donors compared to, for instance, the *N*-heterocyclic carbene, NHC$^{\mathrm{Dip}}$ (NHC$^{\mathrm{Dip}}$Fe(CO)$_4$):[23a] ν = 2035, 1947, 1928, 1919 cm^{-1}) (NHC$^{\mathrm{Dip}}$ = C{N(Ar)CH}$_2$, Ar = 2,6-diisopropylphenyl) and intramolecularly base-coordinated germylene LGeOH[23b] (CO stretching frequencies of LGe(OH)Fe(CO)$_4$: ν = 2039, 1956, 1942 cm^{-1}) (L = CH{(CMe)$_2$(2,6-^{i}Pr$_2$C$_6$H$_3$N)$_2$}). Incidentally, the carbonyl stretching frequencies of **5**-*Z* and **5**-*E* are very similar to those of the carbon-based vinylidene complex H(CHO)C=C=Fe(CO)$_2$(P(OMe)$_3$)$_2$ (ν = 2015, 2007 cm^{-1}).[23c]

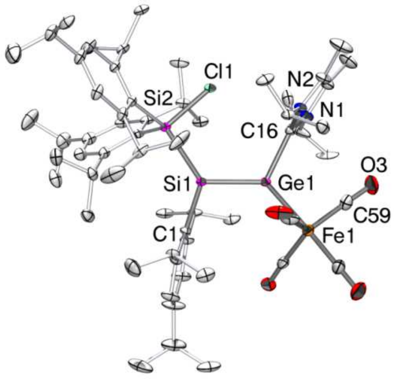


Fig. 2 Structure of **5**-*E* in the solid state (thermal ellipsoids at 30%). Hydrogen atoms omitted. Selected bond lengths [Å] Si1-Ge1 = 2.2480(10), Ge1-C16 = 2.020(3), Ge1-Fe1 = 2.3780(6), Fe1-C59 = 1.772(4), C59-O3 = 1.162(5), Si1-Si2 = 2.3767(12), Si2-Cl1 = 2.1118(11).

The iron complex **5**-*E* crystallizes from concentrated pentane solution (Fig. 2). The structural model confirmed that the Si=Ge bond is retained upon coordination (Ge1-Si1 2.2480(10) Å). Both formally *sp*^{2}-hybridized heavier atoms, Si and Ge, are pyramidalized (Σ of angles: Ge1 354.74°; Si1 351.25°). The Si=Ge bond adopts a strongly *trans*-bent geometry (Si1: 30.27 (1)°, Ge1: 21.07 (8)°). Another noteworthy feature of **5**-*E* is the twisting angle of 17.09(1)° between the plane of C1-Si-Si2 and Fe1-Ge1-C16. The bond length of Ge1-C16 is with 2.020(3) Å significantly shorter than in the free ligand (**4**-*E*: 2.061(4) Å). The Ge1-Fe1 bond length (2.3780(6) Å) is slightly longer than in germylene-coordinated iron(0)tetracarbonyl complexes, (LGeOH Å 2.330(1) Å,[23b] LGeF 2.3262(7) Å,[23d] L = CH{(CMe)$_2$(2,6-^{i}Pr$_2$C$_6$H$_3$N)$_2$}). The C16-Ge1-Si1 bond angle is with 115.59(10)° much wider than that in silagermenylidenes (**II**,[13] C31-Ge-Si 98.90(5)° and **4**-*E*, C(46)-Ge(1)-Si(1) 101.90(10)°). These structural parameters are reminiscent of the η^1-vinyl coordination mode in Tip$_2$Si=SiTip-(Cl)ZrCp$_2$.[24] In the light of the current discussion on the use of arrows in the context of donor acceptor interactions[25] it should be noted that obviously a 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** is formed in 14% yield (Scheme 3) along with the major product **5**-*E* (56%).‡ Notably, **6** cannot be obtained by heating an isolated sample of **5**-*E*. Spatial proximity between the Fe(CO)$_4$ and SiTip$_2$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 ^{29}Si NMR, both resonances of silicon appear at 113.7 (SiTip) and 91.5 (SiTip$_2$) ppm, which hints at the absence of saturated silicon atoms, such as in the chlorosilyl side chain in of **5**-*Z*/*E*.

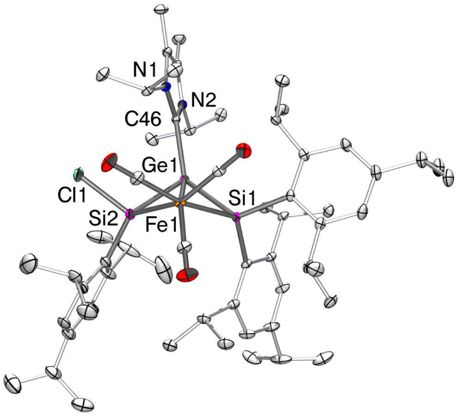
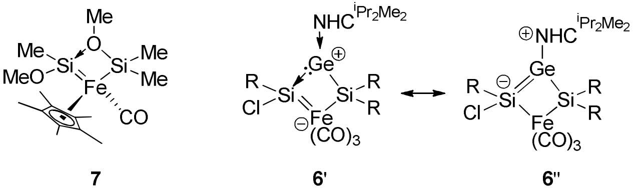


Fig. 3 Structure of **6** in the solid state (thermal ellipsoids at 30%). Hydrogen atoms omitted. Selected bond lengths [Å]: Ge1-C46 = 2.053(2), Ge1-Si1 = 2.3870(7), Ge1-Si2 = 2.3249(7), Fe1-Si1 = 2.3520(7), Fe1-Si2 = 2.3166(8), Ge1-Fe1 = 2.6875(4).

An X-ray diffraction study on single crystals of **6** revealed a bicyclo[1.1.0]butane-like butterfly structure with the Fe1 and Ge1 in the bridgehead positions (Fig. 3). Apparently, a chlorine migration from the SiTip$_2$ moiety to the SiTip moiety took place during conversion from **5**-*Z* to **6**. The ^{29}Si NMR shifts of **6** are close to those of Ogino's alkoxy- and amido-bridged bis(silylene)iron complexes **7** (Scheme 4).[26] In the present case, however, the bridging unit is the NHC$^{i\mathrm{Pr2\,Me2}}$-stabilized germylene moiety so that an analogous electronic description (**6**', Scheme 4) probably contributes less than a zwitterionic resonance form of allylic type (**6**'').



Scheme 4 Chemical Structures of **7** and Canonical Forms of **6** (R = Tip = 2,4,6-^{i}Pr$_3$C$_6$H$_2$).

This assertion 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 in the tetracarbonyliron complexes of a *Z*-1,2-dichlorodisilene (2.4358(6) Å, average distance),[27] but longer than the Si-Fe distances in silylene-iron complexes $((CO)_4Fe{=}Si(Me)_2\cdot HMPA$,[28a] 2.280(1) and 2.294(1) Å for two crystallographic independent molecules; $(CO)_4Fe{=}Si(S^tBu)_2\cdot HMPA$[28b] (2.278(1) Å) (HMPA = $(NMe_2)_3PO$/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, average distance).[29] The mechanism for the formation of **6** remains obscure. However, the intramolecular activation of a silicon-silicon bond in oligosilyl iron complexes has been reported[30] and recently Marschner et al. demonstrated the Lewis acids catalyzed shuttling of germanium atoms into branched polysilanes.[31]

Conclusions

In conclusion, we have shown the efficient method for the synthesis of side chain-functionalized silagermenylidene stabilized by coordination of an *N*-heterocyclic carbene. Its suitability as a ligand for transition metal complexes was demonstrated by coordination to the $Fe(CO)_4$ fragment. Moreover, the resulting silagermenylidene iron complex thermally rearranges to an apparently more stable complex of unprecedented allylic structure, which is undoubtedly a consequence of the readily migrating residual chlorine functionality.

ACKNOWLEDGMENT

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Notes and references

‡ **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-d_6, Toluene-d_8, and THF-d_8 were dried and distilled over potassium under argon. ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced to the peaks of residual protons of the deuterated solvent (^{1}H) or the deuterated solvent itself (^{13}C). ^{29}Si{^{1}H} NMR spectra were referenced to external $SiMe_4$. 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 Varian 2000 FT-IR FTS 2000 spectrometer. Melting points were determined under argon in closed NMR tubes and are uncorrected. Elemental analyses were performed on Leco CHN-900 analyzer.

Synthesis of **4**-*E***:** A precooled (–78 ºC) 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 up slowly to room temperature and stirred for 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 in vacuum to yield 1.90 g (62 %) of **4**-*E*. Single crystals suitable for X-ray diffraction were obtained from saturated pentane solution after keeping 2 days at room temperature. Mp: 126-128 °C. ^{1}H NMR (300 MHz, benzene-d_6, TMS): δ 7.08 (s, 4H, Tip*H*), 7.03 (s, 2H, Tip*H*), 5.38 (2H, sept, N^{i}Pr-C*H*), 4.47-3.96 (m and br, altogether 6H, *o*-^{i}Pr-C*H*), 2.83-2.65 (m, 3H, *p*-^{i}Pr-C*H*), 1.52 (s, 6H, CH_3C=C), 1.33-1.11 (br and m, altogether 48H, ^{i}Pr-CH_3), 1.01 (d, 6H, ^{i}Pr-CH_3), 0.85 (d, 12 H, N^{i}Pr-CH_3) ppm. ^{13}C NMR (75.4 MHz, benzene-d_6, TMS): δ 178.45 (N*C*N), 154.41, 153.96, 149.51, 149.17, 142.48, 138.44 (TipC_{quart}), 126.43 (N*CC*N), 122.51, 121.64 (Tip*C*H), 53.92 (N^{i}Pr-*C*H), 35.74, 34.79, 34.53, 34.42 (^{i}Pr-*C*H), 25.64, 25.25, 24.95, 24.29, 24.09, 24.05 (^{i}Pr-CH_3), 20.69 (N ^{i}Pr-CH_3), 10.05 (CH_3C=C) ppm. ^{29}Si NMR (59.5 MHz, benzene-d_6, TMS): δ 162.50 (*Si*Tip), 7.3 (*Si*Tip$_2$) ppm. UV/vis (hexane): $\lambda_{max}(\varepsilon)$ = 451 nm (9220 Lmol^{-1}cm^{-1}), 389 nm (sh). Anal. Calcd. for $C_{56}H_{89}ClGeN_2Si_2$ (954.58): C, 70.46; H, 9.40; N, 2.93. Found: C, 70.47; H, 9.47; N, 2.93. Crystallographic data: $C_{56}H_{89}ClGeN_2Si_2$, M_r = 954.51, monoclinic, space group *P*2(1)/c, a = 20.3816(11), b = 10.9027(6), c = 25.5288(13) Å, β = 90.840(3) °, V = 5672.3(5) Å^3; Z = 4, ρ_c =1.118 g cm^{-3}, T = 133(2) K, λ = 0.71073 Å, 48361 reflections, 14017 independent (R_{int} = 0.1264), R_1 = 0.0619 ($I > 2\,\sigma(I)$) and wR_2(all data) = 0.1332, *GooF* = 0.970, max/min residual electron density: 0.827/−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 hrs. The ratio of the two isomers was approximately 0.84:0.16 (**4**-*E*/**4**-*Z*). **4**-*Z*: ^{1}H NMR (300 MHz, benzene-d_6, TMS): δ 7.24 (br, 2H, Tip*H*), 7.21 (br, 1H, Tip*H*), 6.97 (br, 1H, Tip*H*), 6.77 (br, 1H, Tip*H*), 5.67 (2H, sept, N^{i}Pr-C*H*), 4.75-4.54 (m and br, altogether 2H, *o*-^{i}Pr-C*H*), 3.76-3.64 (m, 2H, *o*-^{i}Pr-C*H*), 1.80 (d, 3H, ^{i}Pr-CH_3), 1.76-1.69 (m, 6H, ^{i}Pr-CH_3),1.61 (s, 6H, CH_3C=C), 0.61 (d, 3H, ^{i}Pr-CH_3), 0.47 (d, 3H, ^{i}Pr-CH_3), 0.40 (d, 3H, ^{i}Pr-CH_3), 0.30 (d, 3H, ^{i}Pr-CH_3) ppm. ^{13}C NMR (75.4 MHz, [D$_6$]benzene, TMS): δ 178.33 (N*C*N) ppm. ^{29}Si NMR (59.5 MHz, [D$_6$]benzene, TMS): δ 134.02 (*Si*Tip), −0.20 (*Si*Tip$_2$) 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 $Fe_2(CO)_9$ (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 filtered to remove insoluble impurities. The hexane is 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. ^{1}H NMR (300 MHz, toluene-d_8, TMS): δ 7.26, 7.18, 6.86, 6.81, 6.65 (d, each having 1H, Tip*H*), another Tip-H signal is masked by residual proton signals of toluene-d_8, 5.83 (sept, 1H, ^{i}Pr-C*H*), 5.09 (sept, 1H, ^{i}Pr-C*H*), 5.00 (sept., 1H, ^{i}Pr-C*H*), 4.55 (sept, 1H, ^{i}Pr-C*H*), 4.07 (sept, 1H, ^{i}Pr-C*H*), 3.80-3.62 (m, 2H, ^{i}Pr-C*H*), 2.78 (sept, 1H, ^{i}Pr-C*H*), 2.70-2.53 (m, 2H, ^{i}Pr-C*H*), 2.48 (sept, 1H, ^{i}Pr-C*H*), 1.73 (d, 3H, ^{i}Pr-CH_3), 1.67-1.51 (s and m, altogether 15H, ^{i}Pr-CH_3 and CH_3C=C), 1.45-1.39 (s and m, altogether 6H, ^{i}Pr-CH_3 and CH_3C=C), 1.34-1.25 (m, 9H, ^{i}Pr-CH_3), 1.22 (d, 6H, ^{i}Pr-CH_3), 1.17-1.16 (m, 9H, ^{i}Pr-CH_3), 1.09-1.03 (m, 6H, ^{i}Pr-CH_3), 0.48 (d, 3H, ^{i}Pr-CH_3), 0.43 (d, 3H, ^{i}Pr-CH_3), 0.37 (d, 3H, ^{i}Pr-CH_3), 0.20-0.11 (m, 9H, ^{i}Pr-CH_3) ppm. ^{13}C NMR (75.4 MHz, toluene-d_8, TMS): δ 217.56 (*C*O), 165.81 (N*C*N) ppm. (Other signals we were unable to assign correctly, because it overlap with its isomer **5**-*E*). ^{29}Si NMR (59.5 MHz, toluene-d_8, TMS): δ 100.67 (*Si*Tip), 2.98 (*Si*Tip$_2$) ppm. Mp.: 140-142 °C. UV/vis (hexane): $\lambda_{max}(\varepsilon)$ = 503 nm (8260 Lmol^{-1}cm^{-1}). IR (KBr, cm^{-1}): ν = 2018 (s), 2010 (s), 1923 (s), 1899 (s). Anal. Calcd. for $C_{60}H_{89}ClFeGeN_2O_4Si_2$ (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 in vacuum and the solid residue extracted with 70 mL of hexane. The solution was concentrated to about 20 mL and after keeping at −20 °C for a week afforded brown-red crystals of **5**-*E* (0.77 g, 76%). Mp: 158-160 °C. ^{1}H NMR (300 MHz, toluene-d_8, TMS): δ 7.27-7.23 (m, 2H, Tip*H*), 7.21 (d, 1H, Tip*H*), 7.05 (1H, Tip*H*, masked by toluene-d_8), 6.96 (d, 1H, Tip*H*), 6.73 (d, 1H, Tip*H*), 5.72 (sept, 1H, N^{i}Pr-C*H*), 5.51 (sept, 1H, N^{i}Pr-C*H*), 4.62 (sept, 1H, ^{i}Pr-C*H*), 4.54 (sept, 1H, ^{i}Pr-C*H*),4.30 (sept, 1H, ^{i}Pr-C*H*), 3.67 (sept, 1H, ^{i}Pr-C*H*), 3.57 (sept, 1H, ^{i}Pr-C*H*), 2.88-2.62 (m, 4H, ^{i}Pr-C*H*), 2.00 (d, 3H, ^{i}Pr-CH_3), 1.79 (d, 3H, ^{i}Pr-CH_3), 1.68-1.46 (s and m, altogether 30H, ^{i}Pr-CH_3 and CH_3C=C), 1.27-1.21 (m, 12H, ^{i}Pr-CH_3), 1.19-1.15 (m, 12H, ^{i}Pr-CH_3), 0.56 (d, 3H, ^{i}Pr-CH_3), 0.43 (d, 3H, ^{i}Pr-CH_3), 0.34 (d, 3H, ^{i}Pr-CH_3), 0.24 (d, 3H, ^{i}Pr-CH_3) ppm. ^{13}C NMR (75.4 MHz, toluene-d_8, TMS): δ 216.85 (*C*O), 166.99 (N*C*N), 156.72, 155.76, 155.69, 154.05, 153.23, 152.37, 151.32, 150.41, 137.67, 133.07, 130.55, 127.35, 127.00 (TipC_{quart} and N*CC*N), 124.07, 123.37, 122.53, 122.40, 122.12, 120.96 (Tip*C*H), 55.53, 54.84 (N^{i}Pr-*C*H), 38.48, 38.11, 37.20, 35.24, 34.81, 34.62, 34.47, 33.97, 31.04 (^{i}Pr-*C*H), 32.00, 30.66, 27.80, 27.30, 26.00, 25.36, 25.16, 24.83, 24.30, 24.16, 24.02, 23.97, 23.92, 23.87, 23.05, 22.50, 22.43, 22.40, 21.87, 20.83, 14.29 (^{i}Pr-CH_3)

10.17, 9.92 (*C*H$_3$C=C) ppm. ^{29}Si NMR (59.5 MHz, toluene-d$_8$, TMS): δ 98.14 (*Si*Tip), −3.89 (*Si*Tip$_2$) ppm. UV/vis (hexane): $\lambda_{max}(\varepsilon)$ = 512 nm (7050 Lmol^{-1}cm^{-1}), 427 nm (6670) nm (Lmol^{-1}cm^{-1}). IR (KBr, cm^{-1}): ν = 2011 (s), 2008 (s), 1917 (s) 1897 (s). Anal. Calcd. for $C_{60}H_{89}ClFeGeN_2O_4Si_2$ (1122.47): C, 64.20; H, 7.99; N, 2.50. Found: C, 64.15; H, 7.90; N, 2.26. Crystallographic data: $C_{60}H_{89}ClFeGeN_2O_4Si_2\cdot 0.25C_5H_{12}$, M_r = 1140.44, triclinic, space group *P*-1, a = 13.2910(4), b = 19.9842(5), c = 24.8636(7) Å, α = 89.1430(10), β = 95.311(2), γ = 76.122(2) °, V = 6407.6(3) Å^3; Z = 4, ρ_c =1.182 g cm^{-3}, T = 123(2) K, λ = 0.71073 Å, 105034 reflections, 28114 independent (R_{int} = 0.0436), R_1 = 0.0619 ($I > 2\,\sigma(I)$) and wR_2(all data) = 0.1744, *GooF* = 1.427, max/min residual electron density: 2.142/−0.789 e Å^{-3}.

Synthesis of **6:** A solution of **5**-*Z* (0.50 g, 0.44 mmol) in toluene (30 mL) was stirred in a sealed Schlenk flask overnight at 65 °C. All the volatiles were removed in 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%). **6**: Mp: 197-199 °C. ^{1}H NMR (300 MHz, toluene-d$_8$, TMS): δ 7.23 (d, 1H, Tip*H*), 7.13 (1H, Tip*H*, masked by toluene-d8), 7.02 (sept, 1H, N^{i}Pr-C*H*), 7.01 (1H, Tip*H*, masked by toluene-d$_8$), 6.98-6.95 (m, 2H, Tip*H*), 6.87 (d, 1H, Tip*H*), 6.41 (sept, 1H, N^{i}Pr-C*H*), 5.25 (sept, 1H, ^{i}Pr-C*H*), 4.86 (sept, 1H, ^{i}Pr-C*H*), 4.35 (sept, 1H, ^{i}Pr-C*H*), 4.22 (sept, 1H, ^{i}Pr-C*H*), 3.61 (sept, 1H, ^{i}Pr-C*H*), 3.44 (sept, 1H, ^{i}Pr-C*H*), 2.79 (sept, 1H, ^{i}Pr-C*H*), 2.77 (sept, 1H, ^{i}Pr-C*H*), 2.65 (sept, 1H, ^{i}Pr-C*H*), 1.87-1.78 (m, 6H, ^{i}Pr-CH_3), 1.68 (s, 3H, CH_3C=C), 1.66 (s, 3H, CH_3C=C), 1.56-1.37 (m, altogether 18H, ^{i}Pr-CH_3), 1.31-1.04 (m, altogether 30H, ^{i}Pr-CH_3), 0.72 (d, 3H, ^{i}Pr-CH_3), 0.48 (d, 3H, ^{i}Pr-CH_3), 0.45 (d, 3H, ^{i}Pr-CH_3), 0.19 (d, 3H, ^{i}Pr-CH_3) ppm. ^{1}H NMR (300 MHz, thf-d$_8$, TMS): δ 7.03 (d, 1H, Tip*H*), 6.96 (d, 1H, Tip*H*), 6.95 (sept, 1H, N^{i}Pr-C*H*), 6.80 (d, 1H, Tip*H*), 6.76 (d, 1H, Tip*H*), 6.71 (d, 1H, Tip*H*), 6.67 (d, 1H, Tip*H*), 6.19 (sept, 1H, N^{i}Pr-C*H*), 4.82 (sept, 1H, ^{i}Pr-C*H*), 4.61 (sept, 1H, ^{i}Pr-C*H*), 4.15 (sept, 1H, ^{i}Pr-C*H*), 3.82 (sept, 1H, ^{i}Pr-C*H*), 3.34-3.18 (m, 2H, ^{i}Pr-C*H*), 2.87-2.68 (m, 2H, ^{i}Pr-C*H*), 2.63 (sept, 1H, ^{i}Pr-C*H*), 2.41 (s, 3H, CH_3C=C), 2.35 (s, 3H, CH_3C=C), 1.85 (d, 3H, ^{i}Pr-CH_3), 1.62 (d, 3H, ^{i}Pr-CH_3), 1.58-1.49 (m, altogether 9H, ^{i}Pr-CH_3), 1.44 (d, 3H, ^{i}Pr-CH_3), 1.24 (d, 3H, ^{i}Pr-CH_3), 1.20-1.11 (m, altogether 21H, ^{i}Pr-CH_3), 1.08-1.03 (m, altogether 9H, ^{i}Pr-CH_3), 0.88 (d, 3H, ^{i}Pr-CH_3), 0.45 (d, 3H, ^{i}Pr-CH_3), 0.18-0.14 (m, altogether 6H, ^{i}Pr-CH_3), −0.20 (d, 3H, ^{i}Pr-CH_3) ppm. ^{13}C NMR (75.4 MHz, thf-d$_8$, TMS): δ 218.99, 215.98 (*C*O), 157.19, 156.89, 155.09, 154.75, 154.08, 152.28, 150.90, 150.71, 149.48, 143.26, 142.18, 136.52 ((TipC_{quart}), 129.52, 129.26 (N*CC*N), 123.68, 122.72, 122.66, 122.06, 121.88, 121.43 (Tip*C*H), 56.24, 54.08 (N^{i}Pr-*C*H), 38.20, 36.65, 36.46, 35.29, 35.39, 34.98, 34.83, 34.16, 30.24 (^{i}Pr-*C*H), 28.21, 26.76, 26.28, 25.97, 25.65, 25.48, 24.91, 24.38, 24.36, 24.28, 24.18, 23.99, 23.90, 23.84, 23.40, 22.88, 22.23, 21.98 (^{i}Pr-*C*H$_3$), 11.21, 10.73 (*C*H$_3$C=C) ppm (we did not observe the carbenic carbon resonance). ^{29}Si NMR (59.5 MHz, toluene-d$_8$, TMS): δ 113.66 (*Si*Tip), 91.46 (*Si*Tip$_2$) ppm. ^{29}Si NMR (59.5 MHz, [D$_8$]THF, TMS): δ 111.36 (*Si*Tip), 88.27 (*Si*Tip$_2$) ppm. UV/vis (THF): $\lambda_{max}(\varepsilon)$ = 368 nm (6820 Lmol^{-1}cm^{-1}). IR (KBr, cm^{-1}): ν = 1982 (s), 1920 (s), 1916 (s). Anal. Calcd. for $C_{59}H_{89}ClFeGeN_2O_3Si_2$ (1094.46): C, 64.75; H, 8.20; N, 2.56. Found: C, 65.35; H, 8.08; N, 2.38. Crystallographic data: $C_{59}H_{89}ClFeGeN_2O_3Si_2$, M_r = 1094.39, orthorhombic, space group P_{bca}, a = 19.6288(5), b = 24.6607(7), c = 24.6974(7) Å, V = 11955.0(6) Å^3; Z = 8, ρ_c =1.216 g cm^{-3}, T = 132(2) K, λ = 0.71073 Å, 104743 reflections, 14312 independent (R_{int} = 0.0577), R_1 = 0.0442 ($I > 2\,\sigma(I)$) and wR_2(all data) = 0.1131, *GooF* = 1.022, max/min residual electron density: 1.184/−0.536 e Å^{-3}.

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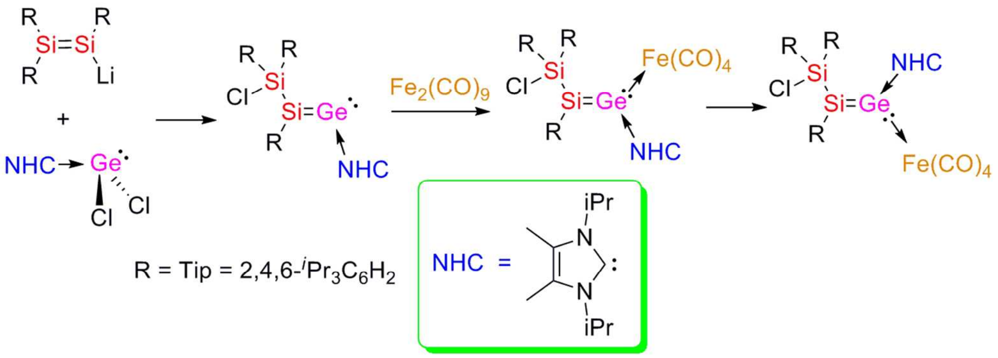

Vinylidenes are common in transition metal chemistry with catalytic applications in alkene and alkyne metathesis. We here report the isolation of a heavier analogue of vinylidene, an α-chlorosilyl functionalized silagermenylidene stabilized by an N-heterocyclic carbene (NHC). Silagermenylidene $(Tip_2Cl)Si$-$(Tip)Si=Ge•NHC^{iPr2Me2}$ (**4**-*E*/*Z*; Tip = 2,4,6-$iPr_3C_6H_2$; $NHC^{iPr2Me2}$ = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene) is available as an *E*/*Z*-equilibrium mixture from $Tip_2Si=Si(Tip)Li$ and $NHC^{iPr2Me2}•GeCl_2$. Reaction of **4**-*E*/*Z* with $Fe_2(CO)_9$ 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.
118x42mm (300 x 300 DPI)