Dalton Transactions

PAPER

View Article Online
View Journal | View Issue

Open Access Article. Published on 15 January 2014. Downloaded on 3/16/2026 2:08:51 PM.
This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.

Cite this: *Dalton Trans.*, 2014, **43**, 5175

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

Anukul Jana, Moumita Majumdar, Volker Huch, Michael Zimmer and David Scheschkewitz*

Received 10th January 2014,
Accepted 14th January 2014

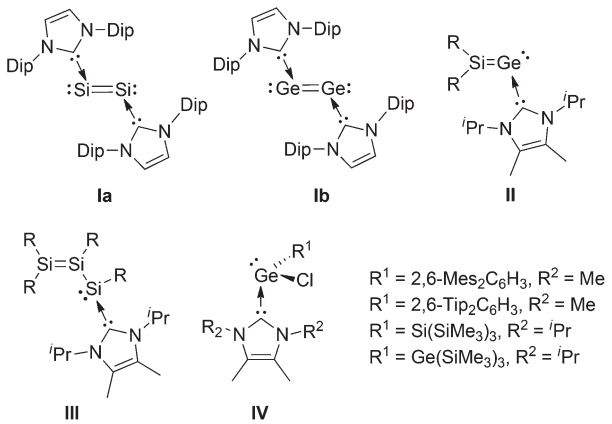
DOI: 10.1039/c4dt00094c

www.rsc.org/dalton

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 (Tip_2Cl)Si-(Tip)Si═Ge·NHC^{iPr_2Me_2} (**4**-*E*/*Z*; Tip = 2,4,6-$^iPr_3C_6H_2$; NHC^{iPr_2Me_2} = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene) is available as an *E*/*Z*-equilibrium mixture from Tip_2Si═Si(Tip)Li and NHC^{iPr_2Me_2}·$GeCl_2$. 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.

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, Tip_2Si═Ge·NHC^{iPr_2Me_2} **II** (NHC^{iPr_2Me_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 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]



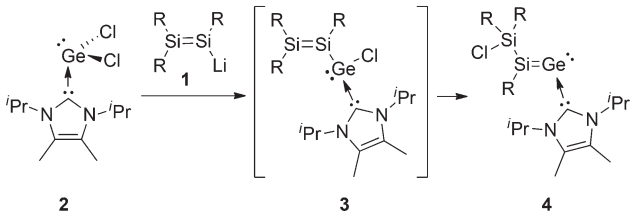
Scheme 1 Chemical structures of **Ia**, **Ib**, **II**, **III**, and **IV** (Dip = 2,6-$^iPr_2C_6H_3$, R = Tip = 2,4,6-$^iPr_3C_6H_2$, Mes = 2,4,6-$Me_3C_6H_2$).

Our recent isolation of a stable NHC^{iPr_2Me_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, NHC^{iPr_2Me_2}·$GeCl_2$ **2**[9c] (Scheme 2). Monosubstituted NHC-coordinated chlorogermylenes **IV** (Scheme 1) have been prepared *via* similar approaches.[19]

Krupp-Chair of General and Inorganic Chemistry, Saarland University, 66125 Saarbrücken, Germany. E-mail: scheschkewitz@mx.uni-saarland.de

† 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

Open Access Article. Published on 15 January 2014. Downloaded on 3/16/2026 2:08:51 PM.
This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.



Scheme 2 Synthesis of 4 (R = Tip = 2,4,6-$^{i}Pr_3C_6H_2$).

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. 126–128 °C) (Scheme 2) with an additional peripheral Si–Cl functionality (see the Experimental section). The reaction plausibly proceeds through the NHC-stabilized chloro(disilenyl)germylene **3** as a transient followed by 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 the 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 L mol^{-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 the Tomasi's polarized continuum model (PCM) at the B3LYP/6-31G(d,p) level of theory.† The calculated lowest-energy excitation of **II** at 439 nm is predominantly associated with 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]

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),[13] whereas

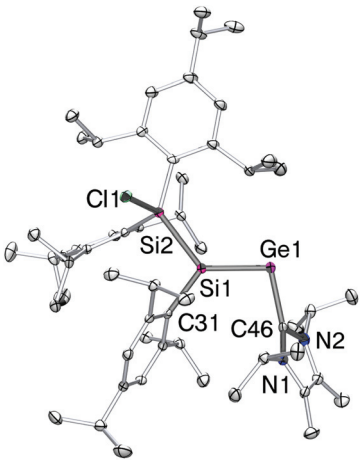


Fig. 1 Structure of **4**-*E* in the solid state (thermal ellipsoids at 30%). Hydrogen atoms are omitted. Selected bond lengths [Å]: Si1–Ge1 = 2.2757(10), Ge1–C46 = 2.061(4), Si1–Si2 = 2.3776(13), Si2–Cl1 = 2.1179(13).

it is almost identical with that of the bulkily substituted silagermene ($^{t}Bu_3Si)_2Si{=}GeMes_2$ (2.2769(8) Å; Mes = 2,4,6-$Me_3C_6H_2$).[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]

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 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 $NHC^{iPr_2Me_2}$.[20]

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-$^{i}Pr_2C_6H_3$ 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 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*.[17]

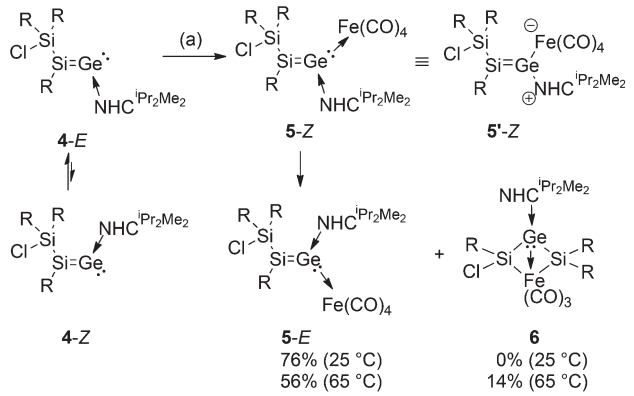
Mills *et al.* had obtained the first structurally characterized transition metal complexes of diphenylvinylidene from diphenylketene and $Fe(CO)_5$.[21] The reaction of **4**-*E*/*Z* with $Fe_2(CO)_9$ in

Table 1 $^{29}Si\{^1H\}$[a], $^{13}C\{^1H\}$ 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 (N*C*N)	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.

Open Access Article. Published on 15 January 2014. Downloaded on 3/16/2026 2:08:51 PM.
This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.



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-$^iPr_3C_6H_2$; $NHC^{iPr_2Me_2}$ = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene).

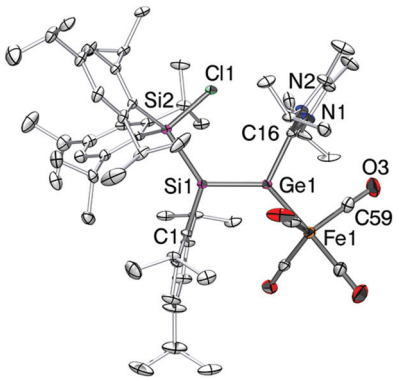


Fig. 2 Structure of **5**-*E* in the solid state (thermal ellipsoids at 30%). Hydrogen atoms are omitted. Selected bond lengths [Å]: Si1–Ge1 = 2.2480(10), Ge1–C16 = 2.020(3), Ge1–Fe1 = 2.3780(6), Fe1–C59 = 1.772(4), C59–O3 = 1.162(5), Si1–Si2 = 2.3767(12), Si2–Cl1 = 2.1118(11).

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 $NHC^{iPr_2Me_2}$ ligand in **4**-*E* (Scheme 3) (see the Experimental section). The iron germenylidene complex **5**-*Z* was isolated as a red-brown solid (mp. 140–142 °C) in 63% yield. In the 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 $NHC^{iPr_2Me_2}$, 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 $NHC^{iPr_2Me_2}$ ligand in **4**-*E*/*Z*, which, however, can readily be explained by the comparatively larger $Fe(CO)_4$ moiety (Scheme 3) (see the Experimental section). 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 stronger σ-donors compared to, for instance, the N-heterocyclic carbene, NHC^{Dip} ($NHC^{Dip}Fe(CO)_4$:[23a] ν = 2035, 1947, 1928, 1919 cm^{-1}) (NHC^{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-$^iPr_2C_6H_3N)_2$}). 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]

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 (∑ 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 planes of C1–Si–Si2 and Fe1–Ge1–C16. The bond length of Ge1–C16 is by 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-$^iPr_2C_6H_3N)_2$}). The C16–Ge1–Si1 bond angle is by 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_2Si═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 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** is 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 $SiTip_2Cl$ 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 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 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 $NHC^{iPr_2Me_2}$-stabilized germylene moiety so that an analogous electronic description (**6**′, Scheme 4) probably contributes less than a zwitterionic resonance form of allylic type (**6**″).

Open Access Article. Published on 15 January 2014. Downloaded on 3/16/2026 2:08:51 PM.
This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.

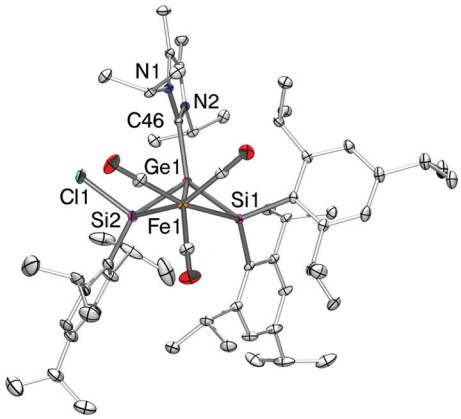
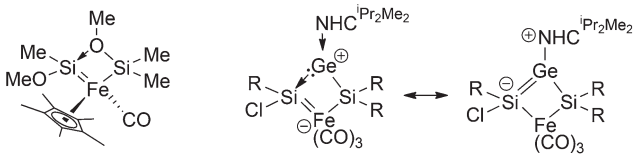


Fig. 3 Structure of 6 in the solid state (thermal ellipsoids at 30%). Hydrogen atoms are omitted. Selected bond lengths [Å]: Ge1–C46 = 2.053(2), Ge1–Si1 = 2.3870(7), Ge1–Si2 = 2.3249(7), Fe1–Si1 = 2.3520(7), Fe1–Si2 = 2.3166(8), Ge1–Fe1 = 2.6875(4).



Scheme 4 Chemical structures of **7** and canonical forms of **6** (R = Tip = 2,4,6-$^{i}Pr_3C_6H_2$).

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 that in the tetracarbonyl iron 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 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]

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-d_6, toluene-d_8, and THF-d_8 were dried and distilled over potassium under argon. ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced to the peaks of residual protons of the deuterated solvent (^1H) or the deuterated solvent itself (^{13}C). $^{29}Si\{^1H\}$ 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 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-d_6, TMS): δ 7.08 (s, 4H, Tip*H*), 7.03 (s, 2H, Tip*H*), 5.38 (2H, sept, N^iPr–C*H*), 4.47–3.96 (m and br, altogether 6H, *o*-^iPr–C*H*), 2.83–2.65 (m, 3H, *p*-^iPr–C*H*), 1.52 (s, 6H, $CH_3C{=}C$), 1.33–1.11 (br and m, altogether 48H, ^iPr–CH_3), 1.01 (d, 6H, ^iPr–CH_3), 0.85 (d, 12 H, N^iPr–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^iPr–*C*H), 35.74, 34.79, 34.53, 34.42 (^iPr–*C*H), 25.64, 25.25, 24.95, 24.29, 24.09, 24.05 (^iPr–CH_3), 20.69 (N ^iPr–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 L mol^{-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 $P2(1)/c$, 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, 48 361 reflections, 14 017 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 h. The ratio of the two isomers was approximately 0.84 : 0.16 (**4**-*E*/**4**-*Z*). **4**-*Z*: ^1H 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^iPr–C*H*), 4.75–4.54 (m and br, altogether 2H, *o*-^iPr–C*H*), 3.76–3.64 (m, 2H, *o*-^iPr–C*H*), 1.80 (d, 3H, ^iPr–CH_3), 1.76–1.69 (m, 6H, ^iPr–CH_3), 1.61 (s, 6H, $CH_3C{=}C$), 0.61 (d, 3H, ^iPr–CH_3), 0.47 (d, 3H, ^iPr–CH_3), 0.40 (d, 3H, ^iPr–CH_3), 0.30 (d, 3H, ^iPr–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).

 This journal is © The Royal Society of Chemistry 2014

Open Access Article. Published on 15 January 2014. Downloaded on 3/16/2026 2:08:51 PM.
This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.

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 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. ^{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–C*H*$_3$), 1.67–1.51 (s and m, altogether 15H, ^{i}Pr–C*H*$_3$ and C*H*$_3$C=C), 1.45–1.39 (s and m, altogether 6H, ^{i}Pr–C*H*$_3$ and C*H*$_3$C=C), 1.34–1.25 (m, 9H, ^{i}Pr–C*H*$_3$), 1.22 (d, 6H, ^{i}Pr–C*H*$_3$), 1.17–1.16 (m, 9H, ^{i}Pr–C*H*$_3$), 1.09–1.03 (m, 6H, ^{i}Pr–C*H*$_3$), 0.48 (d, 3H, ^{i}Pr–C*H*$_3$), 0.43 (d, 3H, ^{i}Pr–C*H*$_3$), 0.37 (d, 3H, ^{i}Pr–C*H*$_3$), 0.20–0.11 (m, 9H, ^{i}Pr–C*H*$_3$) ppm. ^{13}C NMR (75.4 MHz, toluene-d$_8$, TMS): δ 217.56 (*C*O), 165.81 (N*C*N) ppm. (We were unable to assign other signals correctly, because they 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 under 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–C*H*$_3$), 1.79 (d, 3H, ^{i}Pr–C*H*$_3$), 1.68–1.46 (s and m, altogether 30H, ^{i}Pr–C*H*$_3$ and C*H*$_3$C=C), 1.27–1.21 (m, 12H, ^{i}Pr–C*H*$_3$), 1.19–1.15 (m, 12H, ^{i}Pr–C*H*$_3$), 0.56 (d, 3H, ^{i}Pr–C*H*$_3$), 0.43 (d, 3H, ^{i}Pr–C*H*$_3$), 0.34 (d, 3H, ^{i}Pr–C*H*$_3$), 0.24 (d, 3H, ^{i}Pr–C*H*$_3$) 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 (Tip*C*$_{quart}$ 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–*C*H$_3$) 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 (L mol^{-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 $P\bar{1}$, 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, 105 034 reflections, 28 114 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 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%). **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–C*H*$_3$), 1.68 (s, 3H, C*H*$_3$C=C), 1.66 (s, 3H, C*H*$_3$C=C), 1.56–1.37 (m, altogether 18H, ^{i}Pr–C*H*$_3$), 1.31–1.04 (m, altogether 30H, ^{i}Pr–C*H*$_3$), 0.72 (d, 3H, ^{i}Pr–C*H*$_3$), 0.48 (d, 3H, ^{i}Pr–C*H*$_3$), 0.45 (d, 3H, ^{i}Pr–C*H*$_3$), 0.19 (d, 3H, ^{i}Pr–C*H*$_3$) 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, C*H*$_3$C=C), 2.35 (s, 3H, C*H*$_3$C=C), 1.85 (d, 3H, ^{i}Pr–C*H*$_3$), 1.62 (d, 3H, ^{i}Pr–C*H*$_3$), 1.58–1.49 (m, altogether 9H, ^{i}Pr–C*H*$_3$), 1.44 (d, 3H, ^{i}Pr–C*H*$_3$), 1.24 (d, 3H, ^{i}Pr–C*H*$_3$), 1.20–1.11 (m, altogether 21H, ^{i}Pr–C*H*$_3$), 1.08–1.03 (m, altogether 9H, ^{i}Pr–C*H*$_3$), 0.88 (d, 3H, ^{i}Pr–C*H*$_3$), 0.45 (d, 3H, ^{i}Pr–C*H*$_3$), 0.18–0.14 (m, altogether 6H, ^{i}Pr–C*H*$_3$), −0.20 (d, 3H, ^{i}Pr–C*H*$_3$) 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 ((Tip*C*$_{quart}$), 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

Open Access Article. Published on 15 January 2014. Downloaded on 3/16/2026 2:08:51 PM.
This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.

(SiTip$_2$) 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 = 11 955.0(6) Å^3; Z = 8, ρ_c = 1.216 g cm^{-3}, T = 132(2) K, λ = 0.71073 Å, 104 743 reflections, 14 312 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}.

Conclusions

We have shown an 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 ease of migration of the residual chlorine functionality.

Acknowledgements

Support for this study was provided by the EPSRC (EP/H048804/1), the Alfried Krupp von Bohlen und Halbach Foundation. We thank Dr Carsten Präsang for assistance with the IR measurement.

Notes and references

1 (*a*) J. Barrau, J. Escudié and J. Satgé, *Chem. Rev.*, 1990, **90**, 283–319; (*b*) J. Barrau and G. Rima, *Coord. Chem. Rev.*, 1998, **178–180**, 593–622; (*c*) V. Y. Lee and A. Sekiguchi, *Organometallic Compounds of Low-Coordinate Si, Ge, Sn, Pb: From Phantom Species to Stable Compounds*, Wiley, Chichester, U.K., 2010; (*d*) M. Asay, C. Jones and M. Driess, *Chem. Rev.*, 2011, **111**, 354–396; (*e*) Y. Mizuhata, T. Sasamori and N. Tokitoh, *Chem. Rev.*, 2009, **109**, 3479–3511.

2 (*a*) D. H. Harris and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 1974, 895–896; (*b*) P. B. Hitchcock, M. F. Lappert, B. J. Samways and E. L. Weinberg, *J. Chem. Soc., Chem. Commun.*, 1983, 1492–1494; (*c*) A. Meller and C. P. Gribe, *Chem. Ber.*, 1985, **118**, 2020–2029; (*d*) T. Fjeldberg, P. B. Hitchcock, M. F. Lappert, S. J. Smith and A. J. Thorne, *J. Chem. Soc., Chem. Commun.*, 1986, 939–941; (*e*) P. Jutzi, A. Becker, H. G. Stammler and B. Neumann, *Organometallics*, 1991, **10**, 1647–1648; (*f*) W. A. Herrmann, M. Denk, J. Behm, W. Scherer, F.-R. Klingan, H. Bock, B. Solouki and M. Wagner, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1485–1488.

3 (*a*) M. Stender, A. D. Phillips, R. J. Wright and P. P. Power, *Angew. Chem., Int. Ed.*, 2002, **41**, 1785–1787; (*b*) Y. Sugiyama, T. Sasamori, Y. Hosoi, Y. Furukawa, N. Takagi, S. Nagase and N. Tokitoh, *J. Am. Chem. Soc.*, 2006, **128**, 1023–1031; (*c*) R. C. Fischer and P. P. Power, *Chem. Rev.*, 2010, **110**, 3877–3923; (*d*) J. Li, C. Schenk, C. Goedecke, G. Frenking and C. Jones, *J. Am. Chem. Soc.*, 2011, **133**, 18622–18625.

4 (*a*) P. B. Hitchcock, M. F. Lappert, S. J. Miles and A. J. Thorne, *J. Chem. Soc., Chem. Commun.*, 1984, 480–482; (*b*) D. E. Goldberg, P. B. Hitchcock, M. F. Lappert, K. M. Thomas, A. J. Thorne, T. Fjeldberg, A. Haaland and B. E. R. Schilling, *J. Chem. Soc., Dalton Trans.*, 1986, 2387–2394; (*c*) V. Y. Lee, K. McNeice, Y. Ito and A. Sekiguchi, *Chem. Commun.*, 2011, **47**, 3272–3274.

5 (*a*) K. M. Baines and J. A. Cooke, *Organometallics*, 1992, **11**, 3487–3488; (*b*) M. Ichinohe, Y. Arai and A. Sekiguchi, *Organometallics*, 2001, **20**, 4141–4143; (*c*) M. Igarashi, M. lchinohe and A. Sekiguchi, *Heteroat. Chem.*, 2008, **19**, 649–653.

6 (*a*) M. C. Kuchta and G. Parkin, *J. Chem. Soc., Chem. Commun.*, 1994, 1351–1352; (*b*) R. Okazaki and N. Tokitoh, *Acc. Chem. Res.*, 2000, **33**, 625–630; (*c*) L. Li, T. Fukawa, T. Matsuo, D. Hashizume, H. Fueno, K. Ta-naka and K. Tamao, *Nat. Chem.*, 2012, **4**, 361–365.

7 Y. Wang, Y. Xie, P. Wei, R. B. King, H. F. Schaefer III, P. von R. Schleyer and G. H. Robinson, *Science*, 2008, **321**, 1069–1071.

8 (*a*) D. Martin, M. Soleilhavoup and G. Bertrand, *Chem. Sci.*, 2011, **2**, 389–399; (*b*) Y. Wang and G. H. Robinson, *Inorg. Chem.*, 2011, **50**, 12326–12337; (*c*) Y. Xiong, S. Yao and M. Driess, *Angew. Chem., Int. Ed.*, 2013, **52**, 4302–4311; (*d*) R. S. Ghadwal, R. Azhakar and H. W. Roesky, *Acc. Chem. Res.*, 2013, **46**, 444–456.

9 (*a*) P. Jutzi, H. J. Hoffmann, D. J. Brauer and C. Krüger, *Angew. Chem., Int. Ed. Engl.*, 1973, **12**, 1002–1003; (*b*) T. Fjeldberg, A. Haaland, B. E. R. Schilling, M. F. Lappert and A. J. Thorne, *J. Chem. Soc., Dalton Trans.*, 1986, 1551–1556; (*c*) P. A. Rupar, V. N. Staroverov, P. J. Ragogna and K. M. Baines, *J. Am. Chem. Soc.*, 2007, **129**, 15138–15139.

10 A. Sidiropoulos, C. Jones, A. Stasch, S. Klein and G. Frenking, *Angew. Chem., Int. Ed.*, 2009, **48**, 9701–9704.

11 (*a*) M. Veith, S. Becker and V. Huch, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1237–1238; (*b*) Y. Ding, Q. Ma, I. Usón, H. W. Roesky, M. Noltemeyer and H.-G. Schmidt, *J. Am. Chem. Soc.*, 2002, **124**, 8542–8543; (*c*) S. Yao, Y. Xiong and M. Driess, *Chem. Commun.*, 2009, 6466–6468; (*d*) A. Jana, D. Ghoshal, H. W. Roesky, I. Objartel, G. Schwab and D. Stalke, *J. Am. Chem. Soc.*, 2009, **131**, 1288–1293.

12 (*a*) S. P. Green, C. Jones, P. C. Junk, K.-A. Lippert and A. Stasch, *Chem. Commun.*, 2006, 3978–3980; (*b*) S. Nagendran, S. S. Sen, H. W. Roesky, D. Koley, H. Grubmüller, A. Pal and R. Herbst-Irmer, *Organometallics*, 2008, **27**, 5459–5463; (*c*) C. Jones, S. J. Bonyhady, N. Holzmann, G. Frenking and A. Stasch, *Inorg. Chem.*, 2011, **50**, 12315–12325.

13 A. Jana, V. Huch and D. Scheschkewitz, *Angew. Chem., Int. Ed.*, 2013, **52**, 12179–12182.

14 (*a*) M. I. Bruce, *Chem. Rev.*, 1991, **91**, 197–257; (*b*) M. I. Bruce, *Chem. Rev.*, 1998, **98**, 2797–2858; (*c*) A. M. Lozano-Vila,

 This journal is © The Royal Society of Chemistry 2014

Open Access Article. Published on 15 January 2014. Downloaded on 3/16/2026 2:08:51 PM.
This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.

S. Monsaert, A. Bajek and F. Verpoort, *Chem. Rev.*, 2010, **110**, 4865–4909.

15 For a report on the trapping of a base-stabilized stannavinylidene in an iron complex, see: W.-P. Leung, W.-K. Chiu and T. C. W. Mak, *Inorg. Chem.*, 2013, **52**, 9479–9486.

16 (*a*) R. Waterman, P. G. Hayes and T. D. Tilley, *Acc. Chem. Res.*, 2007, **40**, 712–719; (*b*) K. E. Litz, J. E. Bender IV, J. W. Kampf and M. M. B. Holl, *Angew. Chem., Int. Ed.*, 1997, **36**, 496–498; (*c*) P. G. Hayes, C. W. Gribble, R. Waterman and T. D. Tilley, *J. Am. Chem. Soc.*, 2009, **131**, 4606–4607; (*d*) M. E. Fasulo and T. D. Tilley, *Chem. Commun.*, 2012, **48**, 7690–7692; (*e*) D. Gallego, A. Brück, E. Irran, F. Meier, M. Kaupp, M. Driess and J. F. Hartwig, *J. Am. Chem. Soc.*, 2013, **135**, 15617–15626.

17 M. J. Cowley, V. Huch, H. S. Rzepa and D. Scheschkewitz, *Nat. Chem.*, 2013, **5**, 876–879.

18 D. Scheschkewitz, *Angew. Chem., Int. Ed.*, 2004, **43**, 2965–2967.

19 (*a*) A. C. Filippou, O. Chernov, B. Blom, K. W. Stumpf and G. Schnakenburg, *Chem.–Eur. J.*, 2010, **16**, 2866–2872; (*b*) N. Katir, D. Matioszek, S. Ladeira, J. Escudié and A. Castel, *Angew. Chem., Int. Ed.*, 2011, **50**, 5352–5355.

20 N. Kuhn and T. Kratz, *Synthesis*, 1993, 561–562.

21 O. S. Mills and A. D. Redhouse, *Chem. Commun.*, 1966, 444–445.

22 In ^{13}C NMR, the carbenic carbon of $NHC^{iPr_2Me_2}\cdot GeCl_2$ **2** appears at δ = 169.11 ppm in [d_6]-benzene, see Fig. S5 in the ESI.†

23 (*a*) S. Warratz, L. Postigo and B. Royo, *Organometallics*, 2013, **32**, 893–897; (*b*) L. W. Pineda, V. Jancik, J. F. Colunga-Valladares, H. W. Roesky, A. Hofmeister and J. Magull, *Organometallics*, 2006, **25**, 2381–2383; (*c*) C. Löwe, H.-U. Hund and H. Berke, *J. Organomet. Chem.*, 1989, **372**, 295–309; (*d*) A. Jana, P. P. Samuel, H. W. Roesky and C. Schulzke, *J. Fluorine Chem.*, 2010, **131**, 1096–1099.

24 T.-l. Nguyen and D. Scheschkewitz, *J. Am. Chem. Soc.*, 2005, **127**, 10174–10175.

25 D. Himmel, I. Krossing and A. Schnepf, *Angew. Chem., Int. Ed.*, 2014, **53**, 370–374.

26 (*a*) K. Ueno, H. Tobita, M. Shimoi and H. Ogino, *J. Am. Chem. Soc.*, 1988, **110**, 4092–4093; (*b*) H. Tobita, K. Ueno, M. Shimoi and H. Ogino, *J. Am. Chem. Soc.*, 1990, **112**, 3415–3420; (*c*) K. Ueno, S. Ito, K. Endo, H. Tobita, S. Inomata and H. Ogino, *Organometallics*, 1994, **13**, 3309–3314.

27 H. Hashimoto, K. Suzuki, W. Setaka, C. Kabuto and M. Kira, *J. Am. Chem. Soc.*, 2004, **126**, 13628–13629.

28 (*a*) C. Leis, D. L. Wilkinson, H. Handwerker and C. Zybill, *Organometallics*, 1992, **11**, 514–529; (*b*) L. Christian and C. Zybill, *Polyhedron*, 1991, **10**, 1163–1171.

29 T. Iwamoto, H. Masuda, C. Kabuto and M. Kira, *Organometallics*, 2005, **24**, 197–199.

30 H. K. Sharma and K. H. Pannell, *Chem. Rev.*, 1995, **95**, 1351–1374.

31 H. Wagner, J. Baumgartner, T. Müller and C. Marschner, *J. Am. Chem. Soc.*, 2009, **131**, 5022–5023.