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C4-Ferrocenylsilyl-bridged and -substituted N-heterocyclic carbenes: complexation of germanium chloride†

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While the 1 : 1 reaction of C4-trichlorosilyl-functionalized N-heterocyclic carbene (NHC) (2) with $[(\eta^5\text{-}C_5H_4Li)_2Fe]_3[TMEDA]_2$ (3) gives C4-sila[1]ferrocenophane-substituted NHC (4), C4-ferrocenylsilyl-bridged bis-NHC (6) is synthesized by combining 3 with C4-chlorodimethylsilyl-functionalized NHC (5) in a 1 : 2 ratio, (compound 5 is prepared by reaction of the anionic N-heterocyclic dicarbene (NHDC) $[:C\{[N(2,6\text{-}Pr^i{}_2C_6H_3)]_2CHCLi\}]_n$ (1) with Me_2SiCl_2). In addition, ligand 4- and 6-based $GeCl_2$ complexes (7 and 8) are also synthesized. Compounds 4–8 have been characterized by ^1H, ^{13}C, and ^{29}Si NMR spectroscopy and single crystal X-ray diffraction.

Although N-heterocyclic carbenes (NHCs) have been extensively utilized in organic and transition-metal catalysis,[1] the main group chemistry of these versatile ligands has also experienced enormous growth over the past two decades. In particular, a variety of unusual low-oxidation state main group species has been prepared *via* carbene stabilization.[2–16] The extensive utility of N-heterocyclic carbenes may be largely attributed to their strong σ-donating capabilities. Judicious chemical modification of the substituents on either the nitrogen atoms or the backbone of the imidazole ring may allow fine-tuning of the electronic and steric properties of N-heterocyclic carbenes.[17]

Ferrocene, a redox-active ligand, has been broadly employed as a building block in the synthesis of organometallic polymers.[18] The chemistry of *N*-ferrocenyl-substituted N-heterocyclic carbenes, such as (**I**) and (**II**) (Fig. 1) has attracted increased attention since these ligands have the potential to enhance the catalytic activity of the resulting catalyst.[17,19–22] Recently, N-heterocyclic carbenes containing 1,1′-disubstituted ferrocene have also been reported.[23,24] Notably, functionalization of the C4 position of N-heterocyclic carbenes is important as this may allow effective tuning of the electronic and steric properties of the C2 carbene centres.[25–28] However, the literature does not reveal any reports of C4-ferrocenyl-substituted NHCs or bis-NHCs. As an extension of our recent syntheses of a series of NHC-stabilized highly reactive main-group species[14,16] such as H–B═B–H,[29,30] E_2 (E = Si, P, As),[31–33] Si_2O_n (*n* = 3, 4),[34] and $(SiO_2)_2CO_2$,[35] we are interested in studying the following two aspects: (1) the effect of C4-ferrocenylsilyl functionalization of NHC on the stabilization of low-oxidation-state main group species; and (2) the utilization of C4-ferrocenylsilyl-bridged bis-NHCs in building polymers containing main group diatomic molecules [*i.e.*, E(0)$_2$, E = main group elements]. Herein, we report the syntheses[36] and molecular structures[36] of a C4-sila[1]ferrocenophane-substituted N-heterocyclic carbene (**4**), a C4-ferrocenylsilyl-bridged bis-N-heterocyclic carbene (**6**), and their germanium chloride derivatives (**7**) and (**8**).

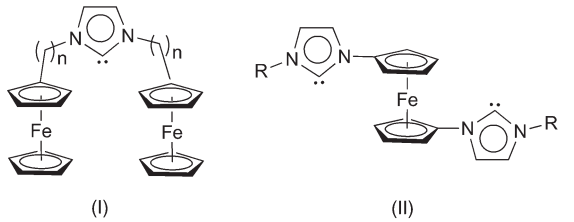

Fig. 1 Examples of ferrocene-*N*-functionalized N-heterocyclic carbenes.

This laboratory synthesized the first anionic N-heterocyclic dicarbene (NHDC, **1**)[37] *via* C4-lithiation of a NHC ligand $[:C\{N(2,6\text{-}Pr^i{}_2C_6H_3)CH\}_2]$. This has proven to be an effective platform to access various NHDC-based binuclear complexes, abnormal carbene-based complexes, poly-NHCs, and C4-functionalized N-heterocyclic carbenes.[38–40] For example, C4-trichlorosilyl-functionalized N-heterocyclic carbene (**2** in Scheme 1; R = 2,6-diisopropylphenyl) was facilely synthesized *via* reaction of **1** with $SiCl_4$.[41] Herein, we now report that the parallel reaction of **1** with Me_2SiCl_2 gives colourless

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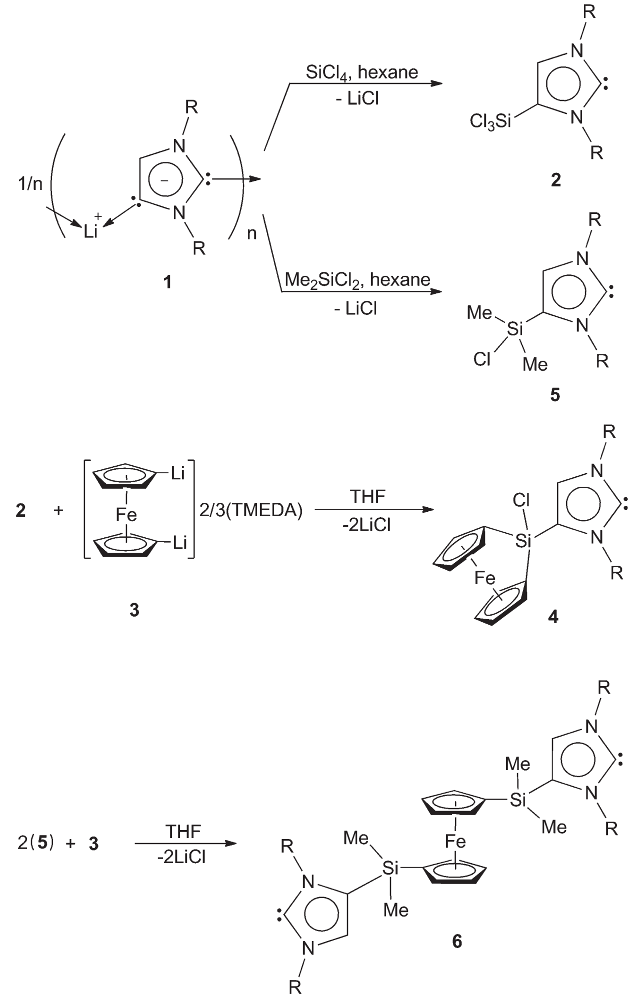
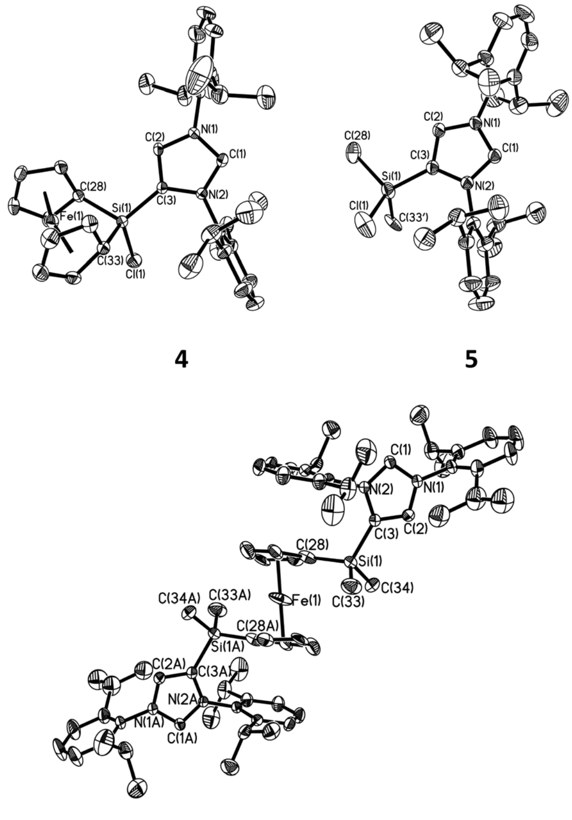


Scheme 1 Syntheses of compounds **2**, **4**, **5**, and **6**.

C4-chlorodimethylsilyl-functionalized NHC (**5**) (in 91.9% yield).[36] Further reaction of **2** with $[(\eta^5\text{-}C_5H_4Li)_2Fe]_3[TMEDA]_2$ (**3**)[42] in THF (in a 1 : 1 ratio) gives **4** as an orange powder (75.9% yield). The 2 : 1 combination of **2** with **3**, however, gives a mixture of **4** with unreacted **2**, but not the expected ferrocenyl-silyl-bridged bis-NHC ligand. Importantly, yellow bis-NHC ligand (**6**) can be synthesized (in 70.0% yield) by combining **5** with **3** (in a 2 : 1 ratio) in THF (Scheme 1). The reported poly-NHCs, including bis-NHCs, usually involve linkages of multiple NHC moieties *via* their nitrogen atoms.[43] Synthesis of **6** suggests that a variety of bis-NHC ligands may be readily accessed *via* C4-functionalization of NHDC (**1**). Indeed, **1** has been utilized in synthesizing C4-silyl-bridged bis-NHCs.[28] The ^{29}Si NMR chemical shift (in THF-d_8) of **5** (9.9 ppm) shifts downfield with compared to that (−13.5 ppm) for **2**.[41] In addition, the ^{29}Si NMR chemical shift (in C_6D_6) of **4** (−15.5 ppm) compares well to that (−15.4 ppm) for chlorosila[1]ferrocenophane $(\eta^5\text{-}C_5H_4)_2FeSi(H)Cl$ (**9**)[44] and that (−15.7 ppm) for **6**. The ^{1}H NMR imidazole resonances (in C_6D_6) of **4** (7.55 ppm), **5** (7.11 ppm), and **6** (6.91 ppm) are notable as they are indicative of the effective electronic effect of the corresponding C4-functionalization on the imidazole ring.

Single crystal X-ray structural analysis[36] shows that the asymmetric unit of the crystal of **6** contains half one molecule of **6** with the iron atom residing on an inversion centre, whereas the asymmetric unit of the crystal of **4** contains two independent molecules, which have very similar structural parameters (Fig. 2; for clarity, only one molecule of **4** is shown). Both the Me_2SiCl moiety in **5** and the $Fe\{\eta^5\text{-}C_5H_4(SiMe_2)\}_2$ unit in **6** involve crystallographic disorder. For clarity, only one data set is shown in the caption of Fig. 2. In **4** and **5**, chlorosila[1]ferrocenophane and Me_2SiCl moieties, respectively, bonds to the C4 carbon of the N-heterocyclic carbene. In contrast, for **6**, a $Fe\{\eta^5\text{-}C_5H_4(SiMe_2)\}_2$ fragment bridges two N-heterocyclic carbenes through silicon–carbon



4 **5**

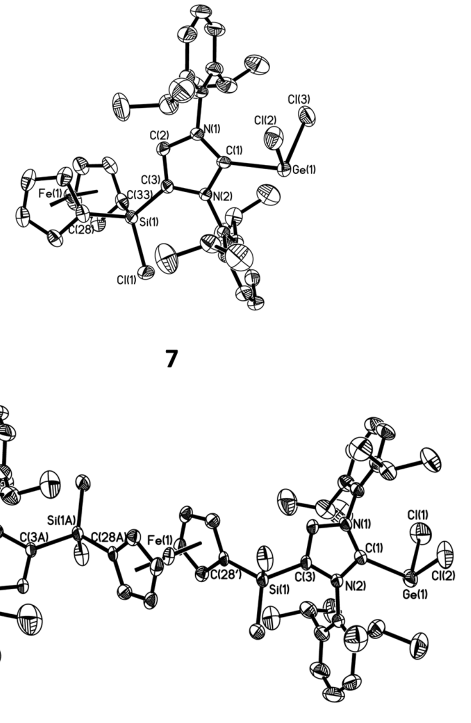
6

Fig. 2 Molecular structures of compounds **4**, **5**, and **6**. Thermal ellipsoids represent 30% probability: hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°) are as follows. For **4**, Si(1)–C(3) 1.842(4), Si(1)–C(28) 1.862(4), Si(1)–C(33) 1.866(4), Si(1)–Cl(1) 2.0524(16); C(3)–Si(1)–Cl(1) 111.21(13), C(3)–Si(1)–C(28) 110.79(18), C(3)–Si(1)–C(33) 117.06(19), C(28)–Si(1)–C(33) 99.22(18). For **5**, Si(1)–C(3) 1.859(2), Si(1)–C(28) 1.877(3), Si(1)–Cl(1) 2.046(4), Si(1)–C(33) 1.891(8); C(3)–Si(1)–Cl(1) 109.19(11), C(3)–Si(1)–C(28) 106.94(12), C(3)–Si(1)–C(33) 114.3(3). For **6**, Si(1)–C(3) 1.879(3), Si(1)–C(28) 1.869(10), Si(1)–C(33) 1.916(7), Si(1)–C(34) 1.866(6); C(3)–Si(1)–C(28) 111.9(5), C(3)–Si(1)–C(33) 107.9(3), C(3)–Si(1)–C(34) 105.9(3), C(33)–Si(1)–C(34) 106.0(5).

(*i.e.*, C4) bonds. All the silicon atoms in **4**–**6** are four-coordinate and adopt a distorted tetrahedral geometry. The Si–C$_{\mathrm{NHC}}$ bond distances in **4**–**6** [1.842(4)–1.879(3) Å] are marginally longer than that [1.819(3) Å] for **2**.[41] The Si–Cl bond distances (*ca.* 2.05 Å) of both **4** and **5** are also slightly longer than that (2.01 Å, av.) for **2**. The bonding character of the sila[1]ferrocenophane unit in **4** is very similar to that of **9**.[44]

Reactions of **4** and **6** with GeCl$_2$·dioxane afford the corresponding N-heterocyclic carbene–germanium chloride adducts **7** and **8**, respectively, in a quantitative yield (Scheme 2).[36] The ^{29}Si NMR chemical shift of **7** (−15.1 ppm in THF-d$_8$) is almost the same as that (−15.5 ppm in C$_6$D$_6$) for **4**, whereas the ^{29}Si NMR chemical shift (in THF-d$_8$) of **8** (−11.9 ppm) shifts downfield compared to that (−15.7 ppm) for **6**. The ^{1}H NMR imidazole resonances (in THF-d$_8$) of **7** and **8** are 8.40 and 7.42 ppm, respectively. The ^{13}C NMR resonance patterns of the substituted Cp rings in both **4** and **7** are consistent with those for **9**.[44] In addition, the ferrocenyl ^{13}C NMR resonance patterns of both **6** and **8** are similar to that for Fe{η^5-C$_5$H$_4$(SiMe$_2$OBpin)}$_2$.[45]

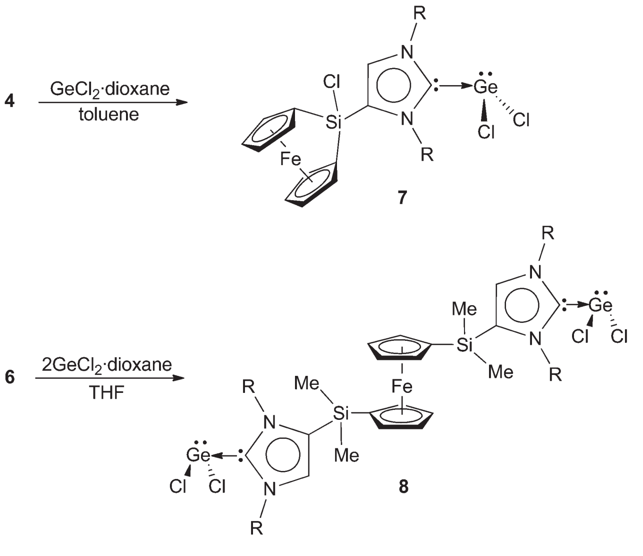
The existence of three-metal centres (one iron atom in the ferrocenylsilyl backbone between two NHC ligands and two germanium atoms attached to the C2 carbene centres, respectively) is the most intriguing structural feature of **8** (Fig. 3). Similar to **6**, compound **8** has an inversion centre at the iron atom. The substituted Cp rings in **8** are also disordered (only one data set is listed in the caption of Fig. 3). The C–Ge and Ge–Cl bond distances in both **7** and **8** [$d_{\mathrm{C-Ge}}$ = 2.132(5) Å, $d_{\mathrm{Ge-Cl}}$ = 2.264 Å (av.) for **7**; $d_{\mathrm{C-Ge}}$ = 2.107(4) Å, $d_{\mathrm{Ge-Cl}}$ = 2.264 Å (av.) for **8**] are comparable to those [$d_{\mathrm{C-Ge}}$ = 2.110(4) Å, $d_{\mathrm{Ge-Cl}}$ = 2.275 Å (av.)] for NHC-complexed GeCl$_2$ [NHC = :C{N(2,6-Pr$^i{}_2$C$_6$H$_3$)CH}$_2$].[46] The coordination about the germanium atoms in **7** and **8** may be described as trigonal pyramidal. Meanwhile, the Si–C$_{\mathrm{NHC}}$ bond distances of **7** [1.867(4) Å] and **8** [1.895(4) Å] are marginally longer than those in their ligand precursors **4** [1.842(4) Å] and **6** [1.879(3) Å], respectively. In both **7** and **8**, notably, the C–Ge bond tilts obviously to the flanking phenyl substituent, which is adjacent to the functionalized C4 carbon of the imidazole ring [Ge(1)–C(1)–N(1) angle = 138.0(3)°, Ge(1)–C(1)–N(2) angle = 117.1(3)° for **7**; Ge(1)–C(1)–N(1) angle = 136.8(3)°, Ge(1)–C(1)–N(2) angle = 118.1(3)° for **8**]. This structural feature may be due to Menshutkin interaction[47] between the germanium atom and the phenyl ring next to the substituted C4 carbon, which has also been observed in *m*-terphenyl-based heavier group 14 and 15 halides.[48,49]



7

8

Fig. 3 Molecular structures of compounds **7** and **8**. Thermal ellipsoids represent 30% probability: hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°) are as follows. For **7**, Si(1)–C(3) 1.867(4), Si(1)–Cl(1) 2.039(2) Si(1)–C(28) 1.858(6), Si(1)–C(33) 1.854(6), C(1)–Ge(1) 2.132(5), Ge(1)–Cl(2) 2.2618(19), Ge(1)–Cl(3) 2.267(2); C(3)–Si(1)–Cl(1) 113.12(17), C(3)–Si(1)–C(28) 113.3(2), C(3)–Si(1)–C(33) 111.6(3), C(28)–Si(1)–C(33) 100.0(2), C(1)–Ge(1)–Cl(2) 92.88(14), C(1)–Ge(1)–Cl(3) 96.49(15), Cl(2)–Ge(1)–Cl(3) 97.85(8). For **8**, Si(1)–C(3) 1.895(4), Si(1)–C(28′) 1.855(12), C(1)–Ge(1) 2.107(4), Ge(1)–Cl(1) 2.242(2), Ge(1)–Cl(2) 2.2861(16); C(3)–Si(1)–C(28′) 104.5(11), C(1)–Ge(1)–Cl(1) 96.86(12), C(1)–Ge(1)–Cl(2) 91.34(11), Cl(1)–Ge(1)–Cl(2) 96.08(8).



Scheme 2 Syntheses of compounds **7** and **8**.

Conclusions

Based on the anionic NHDC ligand (**1**), C4-silyl-functionalized NHCs (**2** and **5**) have been achieved. Further reactions of **2** and **5** with [(η^5-C$_5$H$_4$Li)$_2$Fe]$_3$[TMEDA]$_2$ give C4-sila[1]ferrocenophane-substituted NHC ligand (**4**) and C4-ferrocenylsilyl-bridged bis-NHC ligand (**6**), respectively. We also investigated the reactivity of **4** and **6** toward $GeCl_2$·dioxane, which afforded the corresponding carbene–germanium chloride adducts **7** and **8**, respectively. The reduction of both **7** and **8** is being studied in this laboratory.

Acknowledgements

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