Synthesis and structural investigation of R₂Si (R = Me, Ph) bridged di-N-heterocyclic carbenes

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Functionalization of the C4 carbon of an imidazol-derived N-heterocyclic carbene (NHC) may allow fine-tuning of the electronic and steric properties of the C2 carbene center. A facile route to silyl-functionalyzed di-N-heterocyclic carbenes (Di-NHCS) is described. Treatment of the polymeric lithiated NHC, Li[(IPrH)]₄ (1) [(IPrH) = \{N-2,6-iPr₂C₆H₃\}], with a dichlorosilane affords monomeric silyl-functionalized Di-NHCS, Ph₂Si[(IPrH)]₂ (R = Ph, Me, 3). Interestingly, silyl-functionalized mono-NHC, Ph₂Si[(IPrH)] (4) with a pendant chloro-substituent can also be exclusively isolated maintaining the reactants 1 and Ph₂SiCl₂ ratio. NHCs 2 and 4 readily form copper complexes, Ph₂Si[(IPrH)CuCl] (5) and Ph₂Si[(IPrH)CuCl] (6), on reaction with CuCl. Straightforward conversion of an NHC to a Di-NHC (2 or 3) via C4 functionalization is reported for the first time. Molecular structures of 2, 4, 5 and 6 have been established by single crystal X-ray diffraction studies.

Introduction

N-heterocyclic carbenes (NHCs), which were originally considered as simple phosphine mimics, have established exceptional applications beyond ligands in organometallic and transition metal catalysis.1–5 The utility of NHCs has expanded from the stabilization of elusive compounds with a low-valent main group element6 or complexes with a metal in the high-oxidation state2 to the pharmaceuticals4 and materials science.5 The success of NHCs as ligands in catalysis is largely attributed to their strong σ-donor properties and relatively high covalent contribution to the metal–C(carbene) bond.6 A very small modification in the structure may have a significant impact on the properties of an NHC and hence derived metal complexes as well as related species.7 A unique structural feature allows fine-tuning of NHCs in more ways, therefore a variety of NHCs with variable structural and electronic properties has been prepared.8 Interesting poly-NHCs featuring two or more carbene functionalities have been reported; however, a majority of them is linked via the nitrogen atom of the imidazol ring.9–14 In addition to their applications as ligands in catalysis,9 such poly-NHCs have shown their potential as building-blocks to design a new class of structurally dynamic materials.14

Among available methods of fine-tuning, functionalization of NHCs impacts the properties as well as allows access to a new class of NHCs.15–22 The prospect of direct access to functionalized NHCs from an NHC, with p-block moieties in particular, is enormous as it enables the synthesis of new ligands. Functionalization of an imidazol-2-ylidene with a phosphalkene was first observed by Gates et al. to yield a 4-phosphino-substituted NHC (Scheme 1, I).16 Bertrand et al. developed a method for the preparation of 4-substituted imidazol-2-ylidenes (Scheme 1, II) by deprotonation of a C2-substituted imidazolium salt.17 Formation of II presumably occurs via 1,3 rearrangement of an imidazol-4-ylidene (mesoionic carbene) intermediate. Nevertheless, stable metal-free imidazol-4-ylidenes have also been reported by the same group.23 Functionalization of an NHC has also been achieved with a silylene (IPr)SiCl₂, when treated with adamantyl azide (Scheme 1, III).18 Robinson et al. revealed a facile route to a lithiated NHC, Li[(IPr₃) (I) Li[(IPr₃) = \{(N-2,6-iPr₂C₆H₃)₂CHClI\}]C₆H₅] (1).19 which has

Scheme 1  C4 functionalized mono-NHCS.
facilitated the access to new molecular scaffolds with interesting properties and applications.\(^{20}\)

Treatment of an NHC-precursor, 1-methyl-3-\textit{t}ert-butyl-imidazol-2-thione (Scheme 2, IV), with \textit{n}BuLi in the presence of a phosphine affords phosphino-bridged di-thiones (\textbf{V}).\(^{22}\) Interestingly, in contrast to the established protocol to NHCs,\(^{24}\) reaction of (\textbf{V}) with potassium metal does not yield the expected phosphino-bridged Di-NHC (\textbf{VI}) but an imidazolium phosphonide zwitterion (\textbf{VII}).\(^{22}\) Silyl-functionalized mono-NHCs (Scheme 1, II and III) can be prepared starting from an NHC (Scheme 1);\(^{17-19}\) however, to the best of our knowledge no Di-NHC has been synthesized so far. Therefore, we became interested in developing a protocol for synthesis of Di-NHCs via direct C4-functionalization of an NHC.

Herein, we report a straightforward route to C4-bridged Di-NHCs, R\(_2\)Si(\textit{IPr})\(_2\) (R = Ph, 2; Me, 3) and a copper complex Ph\(_3\)Si[(\textit{IPr})\(_3\)]CuCl\(_2\) (5) (Schemes 3 and 4). A similar protocol also allows access to silyl-functionalized mono-NHC, Ph\(_3\)ClSi(\textit{IPr}) (4) with a pendant chloro-substituent.

**Results and discussion**

Di-NHCs 2 and 3 have been prepared (Scheme 3) in almost quantitative yield on treatment of \((\textit{Li}(\textit{IPr})\(_3\))_n\) (1) with an appropriate dihalosilane. Silyl-functionalized mono-NHC, Ph\(_3\)ClSi(\textit{IPr}) (4) is also accessible on treatment of 1 with one equiv. of Ph\(_2\)SiCl\(_2\) (Scheme 3) in 82% yield. Compounds 2–4 are colorless crystalline solids, which are soluble in common organic solvents (benzene, toluene, and THF). They are stable under an inert atmosphere of nitrogen or argon gas. The El-mass spectrum of 2 exhibits the molecular ion peak at 956.6 amu. A comparison of the NMR spectral data of 2–4 with those of the unfunctionalized NHC, IPr (IPr = \{N-2,6-\textit{i}Pr\(_2\)C\(_6\)H\(_3\)CH\(_2\)\(_2\):C\}) exhibits significant differences. For instance, imidazol backbone protons (NCH) of 2 appear as a singlet at \(\delta\) 7.65 ppm (in C\(_6\)D\(_6\)), which are shifted by \(\delta\) 1.03 ppm down field when compared with IPr (\(\delta\) 6.62 ppm in C\(_6\)D\(_6\)).\(^{25}\) This significant chemical shift may be attributed due to the presence of electron withdrawing phenyl groups on the silicon atom. As expected, NCH protons of 3 exhibit a singlet at \(\delta\) 7.16 ppm (in THF-d\(_8\)), which are shifted slightly up field than those of IPr (\(\delta\) 7.18 ppm, in THF-d\(_8\)), the \(\text{\textit{H}}\) NMR spectrum of 2 shows a remarkably high field signal for two isopropyl groups (NCH) of 2, which are shifted by \(\delta\) 0.65 ppm, 12H, HCMes), which may be inferred as the shielding contributions from the \(\pi\)-current density of adjacent phenyl substituents of the SiPh\(_2\) moiety. This is consistent with the solid state structure of 2 and thus the structure is maintained in the solution state. This feature is not available in 3, therefore HCMes protons appear in the expected region. The \(\text{\textit{C}}\) NMR spectrum of 2 and 3 each exhibits resonances consistent with their \(\text{\textit{H}}\) NMR spectral data. Each of the NHCs 2 and 3 shows a signal at \(\delta\) 225.19 and 225.12 ppm for the carbene carbon atom. Each of the compounds 2 (\(\delta\) –31.17) and 3 (\(\delta\) –22.14 ppm) exhibits a signal in the \(\text{\textit{C}}\) NMR spectrum, which is consistent with those observed for four-coordinate organosilicon compounds.\(^{17-19,26}\) The \(\text{\textit{H}}\) and \(\text{\textit{C}}\) NMR signals of 4 are fully in agreement with its solid state structure. Compound 4 exhibits a signal at \(\delta\) –9.19 ppm in the \(\text{\textit{C}}\) NMR spectrum.\(^{26a}\)

The molecular structure of 2 was established by a single crystal X-ray diffraction study, which clearly reveals the formation of a Di-NHC (Fig. 1). Compound 2 crystallizes in the monoclinic space group \(\text{P2}_1/\text{c}\). The silicon atom in 2 is fourfold coordinated and bridges two flanking NHC moieties. Each of the imidazol-rings features a delocalized \(\pi\)-electron system with short single and long double bonds. The N1–C2–N3 bond

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**Scheme 2** Reaction of di-thione (\textbf{V}) with potassium metal.

**Scheme 3** Reaction synthesis of NHCs 2 and 3 and mono-NHC 4.

**Scheme 4** Synthesis of NHC copper complexes (5) and (6).
The four-fold coordinated silicon atom adopts a distorted tetrahedral geometry.

NHCs 2 and 4 each reacts with CuCl and affords complexes Ph₅Si(((IPr)CuCl)₂ (5) and Ph₂(Cl)Si(((IPr)CuCl) (6), respectively (Scheme 4). Complexes 5 and 6 are colorless crystalline solids, soluble in THF and CH₂Cl₂, and stable under an inert gas atmosphere. Formation of 5 and 6 is supported by the appearance of the corresponding molecular ion peak in the EI-mass spectrum. The ¹H NMR spectrum of each of compounds 5 and 6 shows signals for NHC moieties. Appearance of a new signal in the ¹³C NMR spectrum of 5 at δ 186.3 ppm is assigned for the carbene carbon atom (C–Cu). Complexes 5 and 6 show a ²⁹Si[¹H] NMR resonance at δ −30.10 and −10.95 ppm.¹⁷⁻¹⁹,²⁶

Complex 5 crystallizes in the orthorhombic space group Pna₂₁.²⁵ The molecular structure of 5 reveals that each of the carbene centers coordinates to a CuCl moiety (Fig. 3). The Cu–C(carbene) bond length of 1.886 Å (av.) and slightly distorted linear geometry with C–Cu–Cl angles of 174.14° (av.) are consistent with those of reported NHC-copper complexes.¹⁷,²⁸ The Cu–Cl bond length of 2.11 Å (av.) may be assigned for the terminal CuCl.¹⁷,²⁸ The four-fold coordinated silicon atom adopts distorted tetrahedral geometry with a significant decrease in the C₄–Si–C₉ bond angle of 98.63°(14). The molecular structure of 6 is shown in Fig. 4. Complex 6 crystallizes in the monoclinic space group P2₁/c. The copper atom in 6 features a distorted linear geometry with C₂–Cu₁–C₁₁ bond angle of 174.02(5)°. As expected for both complexes 5 and 6, the N–C–N bond angle increases by 2.9° (av.) on coordination of the carbene carbon to CuCl.

**Fig. 1** Molecular structure of Di-NHC 2. Isopropyl groups and hydrogen atoms have been omitted for clarity; anisotropic displacement parameters are depicted at the 50% probability level. Selected bond lengths [Å] and angles [°]: N1–C2 1.367(2), N1–C5 1.385(2), N3–C2 1.3669(19), C4–C5 1.358(2), Si1–C4 1.8791(16), Si1–C5 1.8760(17); N1–C2–N3 101.65(13), N3–C4–C5 103.50(13), C4–Si1–C5 107.08(7), C4–Si1–C9 104.24(7).

angle of 101.65(13) further supports the carbene character of the C₂ carbon.⁸ The Si₁–C₄ (imidazol) and Si₁–C₅₉ (Ph) (av. 1.87 Å) bond lengths are equal to the sum of the covalent radii of Si and C.²⁷

Compound 4 crystallizes in the triclinic space group P1. The molecular structure of 4 shows functionalization of the C₄ carbon atom with Si(Cl)H₂ (Fig. 2). The Si₁–C₁₁ bond length of 2.0701(8) Å is consistent with those measured for the compounds with four coordinate silicon atoms.²⁶,²⁷ The four-fold coordinated silicon atom adopts a distorted tetrahedral geometry.

NHCs 2 and 4 each reacts with CuCl and affords complexes Ph₅Si(((IPr)CuCl)₂ (5) and Ph₂(Cl)Si(((IPr)CuCl) (6), respectively (Scheme 4). Complexes 5 and 6 are colorless crystalline solids, soluble in THF and CH₂Cl₂, and stable under an inert gas atmosphere. Formation of 5 and 6 is supported by the appearance of the corresponding molecular ion peak in the EI-mass spectrum. The ¹H NMR spectrum of each of compounds 5 and 6 shows signals for NHC moieties. Appearance of a new signal in the ¹³C NMR spectrum of 5 at δ 186.3 ppm is assigned for the carbene carbon atom (C–Cu). Complexes 5 and 6 show a ²⁹Si[¹H] NMR resonance at δ −30.10 and −10.95 ppm.¹⁷⁻¹⁹,²⁶

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**Fig. 2** Molecular structure of mono-NHC 4. Hydrogen atoms have been omitted for clarity; anisotropic displacement parameters are depicted at the 50% probability level. Selected bond lengths [Å] and angles [°]: N1–C2 1.3732(19), N1–C5 1.3799(19), N3–C2 1.3678(19), C4–C5 1.355(2), Si1–C4 1.8791(16), Si1–C5 1.8760(17); N1–C2–N3 101.65(13), N3–C4–C5 103.50(13), C4–Si1–C5 107.08(7), C4–Si1–C9 104.24(7).

Ph₅Si(((IPr)CuCl)₂ (5) and Ph₂(Cl)Si(((IPr)CuCl) (6), respectively (Scheme 4). Complexes 5 and 6 are colorless crystalline solids, soluble in THF and CH₂Cl₂, and stable under an inert gas atmosphere. Formation of 5 and 6 is supported by the appearance of the corresponding molecular ion peak in the EI-mass spectrum. The ¹H NMR spectrum of each of compounds 5 and 6 shows signals for NHC moieties. Appearance of a new signal in the ¹³C NMR spectrum of 5 at δ 186.3 ppm is assigned for the carbene carbon atom (C–Cu). Complexes 5 and 6 show a ²⁹Si[¹H] NMR resonance at δ −30.10 and −10.95 ppm.¹⁷⁻¹⁹,²⁶

Complex 5 crystallizes in the orthorhombic space group Pna₂₁.²⁵ The molecular structure of 5 reveals that each of the carbene centers coordinates to a CuCl moiety (Fig. 3). The Cu–C(carbene) bond length of 1.886 Å (av.) and slightly distorted linear geometry with C–Cu–Cl angles of 174.14° (av.) are consistent with those of reported NHC-copper complexes.¹⁷,²⁸ The Cu–Cl bond length of 2.11 Å (av.) may be assigned for the terminal CuCl.¹⁷,²⁸ The four-fold coordinated silicon atom adopts distorted tetrahedral geometry with a significant decrease in the C₄–Si–C₉ bond angle of 98.63°(14). The molecular structure of 6 is shown in Fig. 4. Complex 6 crystallizes in the monoclinic space group P2₁/c. The copper atom in 6 features a distorted linear geometry with C₂–Cu₁–C₁₁ bond angle of 174.02(5)°. As expected for both complexes 5 and 6, the N–C–N bond angle increases by 2.9° (av.) on coordination of the carbene carbon to CuCl.

**Fig. 3** Molecular structure of dicopper complex 5. Isopropyl groups and hydrogen atoms have been omitted for clarity; anisotropic displacement parameters are depicted at the 50% probability level. Selected bond lengths [Å] and angles [°]: C₁–C₂ 1.898(5), C₁–C₁₁ 2.1116(15), C₂–C₇ 1.875(5), C₂–C₁₂ 2.1152(14), N₁–C₁₂ 1.362(6), N₁–C₅ 1.367(7), N₃–C₂ 1.350(6), C₄–C₅ 1.350(7), Si₁–C₄ 1.855(8), Si₁–C₉ 1.858(5); C₂–Cu₁–C₁₁ 174.84(15), N₁–C₂–N₃ 104.5(4), N₃–C₄–C₅ 104.6(4), C₄–Si₁–C₅₉ 108.9(2), C₄–Si₁–C₉ 98.63(14).
Experimental

General

All synthesis and manipulations were carried out under an inert atmosphere of dry argon gas using Schlenk line techniques or glove-box. C$_6$D$_6$ and THF-d$_8$ were dried over K-benzophenone ketyl and distilled under dry argon atmosphere prior to use. CD$_2$Cl$_2$ was dried over CaH$_2$ and distilled under dry argon prior to use. All other solvents were dried and purified by a MBRAUN solvent purification system (MB SPS 800).

$^1$H, $^{13}$C, and $^{29}$Si NMR spectra were recorded using a Bruker Avance III 300 spectrometer. EI-mass spectra were recorded with MAT 95 (70 eV). Elemental analyses were performed at the Institute for Inorganic Chemistry, Universität Göttingen.

Synthesis of Ph$_2$Si(IPrH)$_2$ (2). To a 100 mL toluene suspension of Li(IPrH)$_2$ (1) (6.38 g, 16.17 mmol) was added a 40 mL toluene solution of Ph$_2$SiCl$_2$ (2.04 g, 8.08 mmol) at 78 °C with constant stirring. The resulting reaction mixture was brought to room temperature and stirred overnight. During this time the yellowish reaction mixture turned to brown suspension. The reaction mixture was further stirred at 90 °C for 4 h. Filtration through Celite afforded a wine red solution. Removal of the volatiles under vacuum gave a brown solid. The resulting solid was re-dissolved in a 30 mL n-hexane-toluene (2:1) mixture and stored at 4 °C for two days to yield colorless crystals of Ph$_2$Si(IPrH)$_2$. Yield: 6.48 g, 84%. Anal calcld for C$_{16}$H$_{30}$N$_2$Si (957): C 82.79, H 8.42, N 5.85; found C 82.72, H 8.44, N 5.66. $^1$H NMR (300 MHz, C$_6$D$_6$, 25 °C): $\delta$ 0.65 (d, 12H, $J = 6.82$ Hz, HCMc$_2$); 1.19 (d, 12H, $J = 6.97$ Hz, HCMc$_2$); 1.22, 125 (dd, 24H, $J = 6.74$ Hz, 6.79 Hz, HCMc$_2$); 2.64 (sept, 4H, $J = 6.79$ Hz, HCMc$_2$); 3.14 (sept, 4H, $J = 6.90$ Hz, HCMc$_2$); 6.76 (d, 4H, $J = 7.76$ Hz, m-C$_6$H$_{3}$); 6.91 (d, $J = 7.45$ Hz, m-C$_6$H$_{3}$); 7.00 (m, 6H, o-C$_6$H$_{3}$); 7.10–7.19 (m, 4H, m-C$_6$H$_{3}$); 7.29 (t, 4H, p-C$_6$H$_{3}$); 7.65 (s, 2H, NCH) ppm. $^{13}$C$_1$[H] NMR (75 MHz, C$_6$D$_6$, 25 °C): $\delta$ 21.02, 24.10, 24.23, 26.18 (HCMc$_2$); 28.62, 29.01 (HCMc$_2$); 122.84, 123.70, 130.10, 134.54, 136.54, 138.19, 139.12 (CHCH$_2$, C$_6$H$_{3}$, C$_6$H$_{3}$), 146.02 (ipso-C$_6$H$_{3}$), 225.19 (NCN) ppm. $^{29}$Si$_1$[H] NMR (59 MHz, C$_6$D$_6$, 25 °C): $\delta$ –31.17 ppm. El-MS: m/z (%): 956.6 (85) [M$^+$], 387.4 (100) [IPrH$^+$].

Synthesis of Me$_3$Si(IPrH)$_2$ (3). Compound 3 was prepared in 79% yield adopting a similar method as described for the compound 2, using (1) (2.23 g, 5.65 mmol) and Me$_3$SiCl (0.35 mL, 2.90 mmol). Anal calcld for C$_{66}$H$_{80}$N$_4$Si (957): C 82.79, H 8.42, N 5.85; found C 82.72, H 8.44, N 5.66. $^1$H NMR (300 MHz, THF-d$_8$, 25 °C): $\delta$ -0.30 (s, 6H, SiMe$_2$), 1.04 (d, 12H, $J = 6.94$ Hz, HCMc$_2$); 1.11 (d, 12H, $J = 6.67$ Hz, HCMc$_2$); 1.16, 1.18 (dd, 24H, HCMc$_2$); 2.62 (sept, 4H, $J = 6.83$ Hz, HCMc$_2$); 2.82 (sept, 4H, $J = 6.91$ Hz, HCMc$_2$); 7.16 (s, 2H, NCH), 7.22 (m, 8H, m-C$_6$H$_3$); 7.35 (m, 4H, p-C$_6$H$_3$) ppm. $^{13}$C$_1$[H] NMR (75 MHz, THF-d$_8$, 25 °C): $\delta$ 0.49 (SiMe$_2$), 22.76, 24.37, 24.66, 25.49 (HCMc$_2$); 29.65, 29.82, 30.10 (HCMc$_2$); 123.08, 124.33, 124.49, 124.63, 124.79, 129.94, 130.20, 131.71, 134.06, 139.58, 140.23, 140.88 (C$_6$H$_3$), 147.05, 147.32, 147.62 (ipso-C$_6$H$_3$), 225.12 (NCN) ppm. $^{29}$Si$_1$[H] NMR (59 MHz, THF-d$_8$, 25 °C): $\delta$ –22.14 ppm.

Synthesis of Ph$_2$(Cl)Si(IPrH) (4). To a toluene suspension of (1) (1.87 g, 4.74 mmol) was added a 50 mL toluene solution of Ph$_2$SiCl$_2$ (1 mL, 4.74 mmol) at –78 °C. The reaction mixture was brought to room-temperature and stirred overnight. Filtration through Celite afforded yellowish solution. Removal of all the volatiles under vacuum yielded a yellow solid. Colorless crystals of 4 (2.36 g, 82%) were recovered after one week on storage of a saturated toluene solution at –25 °C. $^1$H NMR (300 MHz, THF-d$_8$, 25 °C): $\delta$ 0.74 (d, 6H, $J = 6.86$ Hz, HCMc$_2$); 1.06 (d, 6H, $J = 6.79$ Hz, HCMc$_2$); 1.18 (d, 6H, $J = 6.85$ Hz, HCMc$_2$); 1.22 (d, 6H, $J = 6.94$ Hz, HCMc$_2$); 2.52 (sept, 2H, $J = 6.85$ Hz, HCMc$_2$); 2.87 (sept, 2H, $J = 6.92$ Hz, HCMc$_2$); 7.06 (d, 2H, $J = 7.80$ Hz, m-C$_6$H$_3$); 7.25–7.44 (m, 15H, C$_6$H$_{3}$, C$_6$H$_{3}$, NCH) ppm. $^{13}$C$_1$[H] NMR (75 MHz, THF-d$_8$, 25 °C): $\delta$ 21.25, 24.02, 24.28, 26.05 (HCMc$_2$), 28.99, 29.52 (HCMc$_2$), 123.51, 123.89, 125.83, 126.58, 126.88, 129.23, 129.35, 129.46, 131.43, 132.63, 135.57, 136.34, 138.57, 139.51 (C$_{6}$H$_{3}$, C$_{6}$H$_{3}$), 146.35, 146.83 (ipso-C$_6$H$_3$), 225.88 (NCN) ppm. $^{29}$Si$_1$[H] NMR (59 MHz, THF-d$_8$, 25 °C): $\delta$ –9.19 ppm.
Synthesis of Ph₃Si([IPrH])CuCl₂ (5). To a Schlenk flask containing 2 (0.52 g, 0.54 mmol) and anhydrous CuCl (0.11 g, 1.11 mmol) was added 20 mL of THF. Resulting suspension was stirred overnight at room temperature. The solution was filtered under vacuum through a glass filter, and the filtrate was concentrated to 5 mL of CH₂Cl₂ and combined with 10 mL of n-hexane. The solution was stored at −35 °C to obtain colorless crystals of 5 in 81% (0.51 g) yield. Anal. calc. for C₆₈H₇₃Cl₂CuS₄I₂: C 68.61, H 6.98, N 4.85; found C 67.55, H 6.85, N 4.91.

1H NMR (300 MHz, CDCl₃, 25 °C): δ 0.50 (d, 12H, J = 6.63 Hz, HCMc2); 1.14 (d, 12H, J = 6.79 Hz, HCMc2); 1.31 (m, 24H, HCMc2); 2.18 (sept, 4H, J = 6.77 Hz, HCMc2); 2.64 (sept, 4H, J = 6.88 Hz, HCMc2); 6.85 (m, 8H, m-C₆H₃); 7.08 (t, 4H, J = 7.70 Hz, p-C₆H₃); 7.19 (t, 2H, J = 7.79 Hz, p-C₆H₃); 7.31 (t, 2H, J = 6.99 Hz, m-C₆H₃); 7.41 (d, 4H, J = 7.76 Hz, o-C₆H₃); 7.50 (s, 2H, NCF2); 7.61 (t, 2H, J = 7.77 Hz, m-C₆H₃) ppm. 13C{1H} NMR (75 MHz, CDCl₃, 25 °C): δ 21.42, 24.44, 29.40, 27.21 (CH₂); 29.18, 29.39 (HCMe₂); 124.27, 124.90, 126.49, 129.58, 131.17, 131.26, 131.33, 134.27, 134.48, 138.85, 136.48, 145.69, 146.02 (C₆H₅, C₆H₃), 186.27 (NCN) ppm. 29Si{1H} NMR (59 MHz, CDCl₃, 25 °C): δ −30.10 ppm. EI-MS: m/z: 1154.3 (M⁺), 1054.5 (M⁻ − CuCl₂), 956.6 (M⁻ − 2CuCl₂).

Synthesis of Ph₃Si([IPrH])CuCl₂ (6). To a 100 mL Schlenk flask containing 4 (360 mg, 0.66 mmol) and anhydrous CuCl (60 mg, 0.66 mmol) was added 50 mL toluene and stirred overnight. Filtration through Celite afforded yellowish solution, which was concentrated (20 mL) under vacuum and stored at 0 °C to yield colorless crystals of 7 (335 mg, 80%). Anal. calc. for C₆₇H₆₇Cl₂Cu₂N₂SiCl₂: C 72.44, H 8.76, N 4.47; found C 72.34, H 8.76, N 4.43.

1H NMR (300 MHz, THF-d₈, 25 °C): δ 0.75 (d, 6H, J = 6.81 Hz, HCMc₂), 1.26 (d, 6H, J = 3.99 Hz, HCMc₂), 1.28 (d, 6H, J = 4.07 Hz, HCMc₂), 1.32 (d, 6H, J = 6.88 Hz, HCMc₂), 2.41 (sept, 2H, J = 6.81 Hz, HCMc₂), 2.69 (sept, 2H, J = 6.90 Hz, HCMc₂), 7.19 (d, 2H, J = 7.83 Hz, m-C₆H₃), 7.35-7.52 (m, 15H, C₆H₅, C₆H₃), 7.89 (s, 1H, NCH) ppm. 13C{1H} NMR (75 MHz, THF-d₈, 25 °C): δ 22.20, 24.13, 24.34, 24.91 (HCMe₂), 25.10, 27.07, 29.92, 30.14 (HCMe₂), 125.05, 125.08, 125.79, 129.35, 129.45, 131.41, 131.56, 131.70, 135.96, 137.38 (C₆H₅, C₆H₃), 146.64, 147.02 (ipso-C₆H₃), 186.82 (NCN) ppm. 29Si{1H} NMR (59 MHz, THF-d₈, 25 °C): δ −10.95 ppm. MS (EI): m/z: 703.9 (M), 603.1 (M − CuCl₂), 387.28 (IPr).
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Notes and references


22. See ESI† for details.


