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A cyclopentadienyl functionalized silylene – a flexible ligand for Si- and C-coordination

We report on a cyclopentadienyl functionalized silylene, which can bind to various metals in different coordination modes. The picture shows two of these coordination modes in the form of spheres, which attract each other. As described in our contribution the silylene (yellow sphere) coordinates to zinc (greyish sphere) and the Cp ring (shown as the five smaller black spheres) coordinates to calcium (purple sphere). The attraction between these spheres is showcased as a nebula mixing with each other. In front, two metals complexes with different structural motifs are depicted.

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Introduction

The earliest report of a stable silicon(II) compound (decamethylsilocene) in 1986 was a landmark achievement in low-valent silicon(II) chemistry, which was only known by matrix-isolations before.^{1–3} The next significant step towards stable and reactive low-valent main group compounds was achieved in 1991 with the synthesis of N-heterocyclic carbenes.⁴ This concept was successfully migrated to silicon(II) chemistry with the synthesis of the stable N-heterocyclic silylene (NHSi) in 1994.⁵ Following this initial milestone, several other NHSi compounds were synthesized and characterized.^{6,7} Among others, the four-membered NHSi $[\{\text{PhC}(\text{NtBu})_2\}\text{SiCl}]$ emerged as one of the most valuable silylene reagents reported to date.^{6,8–19} $[\{\text{PhC}(\text{NtBu})_2\}\text{SiCl}]$ can easily be derivatized by substitution of the chlorine atom. A wide variety of substituents was applied over the last decade.^{6,20–25} We recently presented a pentamethylcyclopentadienyl (Cp^*) substituted version $[\{\text{PhC}(\text{NtBu})_2\}\text{Si}(\text{C}_5\text{Me}_5)]$ (Scheme 1) and explored its coordination behavior towards transition metals and its reactivity with chalcogens.^{26–28} In these complexes, we always observed a 1,2-silicon shift of the silylene on the Cp^* -ring.

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A cyclopentadienyl functionalized silylene – a flexible ligand for Si- and C-coordination†

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The synthesis of a 1,2,3,4-tetramethylcyclopentadienyl (Cp^4) substituted four-membered N-heterocyclic silylene $[\{\text{PhC}(\text{NtBu})_2\}\text{Si}(\text{C}_5\text{Me}_4\text{H})]$ is reported first. Then, selected reactions with transition metal and a calcium precursor are shown. The proton of the Cp^4 -unit is labile. This results in two different reaction pathways: (1) deprotonation and (2) rearrangement reactions. Deprotonation was achieved by the reaction of $[\{\text{PhC}(\text{NtBu})_2\}\text{Si}(\text{C}_5\text{Me}_4\text{H})]$ with suitable zinc precursors. Rearrangement to $[\{\text{PhC}(\text{NtBu})_2\}(\text{C}_5\text{Me}_4)\text{SiH}]$, featuring a formally tetravalent silicon $\text{R}_2\text{C}=\text{Si}(\text{R}')\text{H}$ unit, was observed when the proton of the Cp^4 ring was shifted from the Cp^4 -ring to the silylene in the presence of a Lewis acid. This allows for the coordination of the Cp^4 -ring to a calcium compound. Furthermore, upon reaction with transition metal dimers $[\text{MCl}(\text{cod})_2]$ ($\text{M} = \text{Rh}, \text{Ir}$; $\text{cod} = 1,5$ -cyclooctadiene) the proton stays at the Cp^4 -ring and the silylene reacts as a sigma donor, which breaks the dimeric structure of the precursors.

Results and discussion

Synthesis

Following our previous results, we were interested in the reaction behaviour of a NHSi with a cyclopentadienyl substituent, which has at least one hydrogen atom at the five membered ring to enable a subsequent deprotonation. 1,2,3,4-Tetramethylcyclopentadienyl (Cp^4) emerged as a feasible substituent having one acidic proton at the central ring. Furthermore, due to its relatively high steric demand, the 1,2-silicon shift should be suppressed.^{26–29} $[\{\text{PhC}(\text{NtBu})_2\}\text{Si}(\text{C}_5\text{Me}_4\text{H})]$ (**1**) was synthesized in a rational approach from $[\{\text{PhC}(\text{NtBu})_2\}\text{SiCl}]$ and KCp^4 in good yields (89%, Scheme 2). In contrast to its analogue, Cp^* substituted compound **1** is soluble in all common but halogen-free solvents. In contrast, halogen-containing solvents cause degradation of the silylene. Compound **1**, which was recrystallized from hot *n*-heptane, crystallizes in the monomeric space group $P2_1/c$ with one molecule in the asymmetric unit (Fig. 1). As predicted, the silylene binds to the Cp^4 -ring at the position of the C1 carbon and bears a proton and no methyl group. The Si-



Scheme 1 Comparison of the previous and herein published silylene.



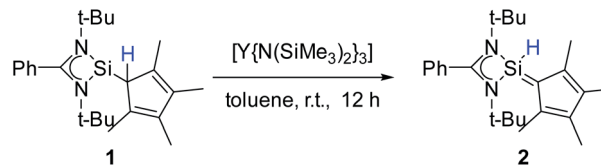
Scheme 2 Synthesis of $[\{\text{PhC}(\text{NtBu})_2\}\text{Si}(\text{C}_5\text{Me}_4\text{H})]$ (**1**).Scheme 3 Synthesis of $[\{\text{PhC}(\text{NtBu})_2\}(\text{C}_5\text{Me}_4)\text{SiH}]$ (**2**).

Fig. 1 Solid state structure of compound **1**. Hydrogen atoms are omitted for clarity (except H1). Selected bond lengths [Å] and angles [°]: Si–N1 1.8731(13); Si–N2 1.8732(12); N1–C10 1.342(2); N2–C10 1.339(2); Si–C1 1.972(2); C1–C2 1.492(2); C1–C5 1.499(2); C2–C3 1.352(2); C3–C4 1.462(2); C4–C5 1.353(2); N1–C10–N2 105.50(12); N1–Si–C1 102.71(6); N2–Si–C1 105.45(6); Si–C1–H1 100.3(9); Si–C1–C2 116.86(10); C2–C1–C5 104.07(12); C2–C1–H1 114.4(10); Si–C1–C5 107.29(10); C5–C1–H1 114.2(10).

C1 bond length (1.972(2) Å) is in the range of literature known carbon–silicon single bonds (1.88–1.98 Å).^{26,30} The ¹H NMR spectrum of **1** shows the expected signals for the $[\text{PhC}(\text{NtBu})_2]$ amidinate ligand as well as a set of three signals, which correspond to the methyl groups and the proton of the Cp⁴-ring. The ²⁹Si NMR spectrum shows a strong doublet at 38.0 ppm (²J_{Si,H} = 4.0 Hz) as well as a small doublet at –18.6 (¹J_{Si,H} = 234 Hz). The second signal, which we first deemed to be an impurity, was detected in all samples and proved to be an indicator for another silylene species, which was formed during the prolonged ²⁹Si NMR measurements due to a rearrangement reaction. This formation is rather slow at room temperature and can be accelerated at higher temperatures, which could be proven by heating an NMR sample for several days at 80 °C and measuring after different times.

Rearrangement

To enforce this rearrangement reaction, compound **1** was treated with $[\text{Y}\{\text{N}(\text{SiMe}_3)_2\}_3]$ as a weak and well soluble Lewis acid at room temperature to give the isomer $[\{\text{PhC}(\text{NtBu})_2\}(\text{C}_5\text{Me}_4)\text{SiH}]$ (**2**) (Scheme 3). Compound **2** crystallizes in the monomeric space group *P*2₁/*c* with one molecule in the

asymmetric unit (Fig. 2). Upon rearrangement from **1** to **2** a 1,2-H-shift from the Cp⁴-carbon ring atom to the silicon atom took place. As a consequence, structural changes in the Cp⁴-Si bond occur, e.g., the Si–C1 bond is much shorter than that in **1**. The observed bond length (1.761(2) Å) is in the range of literature known Si=C double bonds and is, apart from NHC–Si (NHC = N-heterocyclic carbene) interactions, one of only a few known examples of a Si=C double bond in which a NHSi is involved.^{5,11,31–35} Furthermore, the Si–C1 bond is now in-plane with the C–Me bonds of the Cp⁴-ring and the average C–C bond length within the Cp⁴-ring is shorter than that in **1**. This leads us to the conclusion that Cp⁴ and the silylene atom form a conjugated system similar to fulvene. The proton H1 of the silicon atom was located and freely refined in the difference Fourier map. The Si–H bond length (1.35(2) Å) is in agreement with those in the literature.^{24,36} Compared to **1**, only minor structural changes are seen in the amidinate backbone of the silylene. In the ¹H NMR spectrum of compound **2**, the resonance for the proton coordinated to silylene is detected at 5.92 ppm. This is a low field shift of around 3.6 ppm, compared to that in **1**. Concomitantly, the resonance for the silylene in the ²⁹Si NMR spectrum is shifted to a higher field (–18.6 ppm) and is observed as a doublet due to ¹J_{Si,H} coupling (234 Hz) with the proton. This resonance is in the exact same position as that for the impurity in the NMR spectra for compound **1**, leading us to the conclusion that the “impurity” in **1** is in fact compound **2**, which formed over a prolonged period of time. The IR spectrum



Fig. 2 Solid state structure of compound **2**. Hydrogen atoms are omitted for clarity (except H1). Selected bond lengths [Å] and angles [°]: Si–H1 1.35(2); Si–N1 1.8219(13); Si–N2 1.8149(13); Si–C1 1.761(2); N1–C10 1.333(2); N2–C10 1.345(2); C1–C2 1.448(2); C1–C5 1.440(2); C2–C3 1.382(2); C3–C4 1.427(2); C4–C5 1.381(2); N1–C10–N2 105.72(12); N1–Si–C1 122.30(6); N2–Si–C1 122.15(6); N1–Si–H1 103.8(7); N2–Si–H1 107.4(7); C1–Si–H1 119.4(7); Si–C1–C2 125.59(11); Si–C1–C5 127.53(11); C2–C1–C5 106.88(12).



interaction is found (for details see the ESI†). In both cases examined, the strength of the SiC bonds changes only insignificantly compared to the situation in the respective uncoordinated ligands.

Conclusions

In summary, we have synthesized the newly functionalized four-membered silylene (NHSi) [$\{\text{PhC}(\text{NtBu})_2\}\text{Si}(\text{C}_5\text{Me}_4\text{H})$] with a Cp⁴-unit attached to the silylene unit. Due to the labile proton at the Cp⁴-unit the ligand can be either deprotonated or rearranged to a sila fulvene structure. Both forms were isolated. Depending on the reaction conditions and the metal precursor, the ligand or its derivatives can be coordinated in all three forms: silylene (A), anion (B), and sila fulvene (C) (Scheme 7). This flexibility, which is to the best of our knowledge unique, makes [$\{\text{PhC}(\text{NtBu})_2\}\text{Si}(\text{C}_5\text{Me}_4\text{H})$] a versatile and flexible (pro) ligand for a wide range of metal complexes.

Conflicts of interest

There are no conflicts to declare.

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