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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 nebulas mixing with each other. In front, two metals complexes with different structural motifs are depicted.

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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 (Cp⁴) substituted four-membered N-heterocyclic silylene [{PhC(NtBu)₂Si(C₅Me₄H)}] is reported first. Then, selected reactions with transition metal and a calcium precursor are shown. The proton of the Cp⁴-unit is labile. This results in two different reaction pathways: (1) deprotonation and (2) rearrangement reactions. Deprotonation was achieved by the reaction of [{PhC(NtBu)₂Si(C₅Me₄H)}] with suitable zinc precursors. Rearrangement to [{PhC(NtBu)₂(C₅Me₄SiH)}, featuring a formally tetravalent silicon R₂C=Si(R')–H unit, was observed when the proton of the Cp⁴ ring was shifted from the Cp⁴-ring to the silylene in the presence of a Lewis acid. This allows for the coordination of the Cp⁴-ring to a calcium compound. Furthermore, upon reaction with transition metal dimers [MCl(cod)]₂ (M = Rh, Ir; cod = 1,5-cyclooctadiene) the proton stays at the Cp⁴-ring and the silylene reacts as a sigma donor, which breaks the dimeric structure of the precursors.

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 [{PhC(NtBu)₂SiCl}] emerged as one of the most valuable silylene reagents reported to date.^{6,8–19} [{PhC(NtBu)₂SiCl}] 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 [{PhC(NtBu)₂Si(C₅Me₅)}] (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.

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 (Cp⁴) 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} [{PhC(NtBu)₂Si(C₅Me₄H)}] (**1**) was synthesized in a rational approach from [{PhC(NtBu)₂SiCl}] and KCp⁴ 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 *P*2₁/*c* with one molecule in the asymmetric unit (Fig. 1). As predicted, the silylene binds to the Cp⁴-ring at the position of the C1 carbon and bears a proton and no methyl group. The Si–

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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 $P2_1/c$ 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).



of **2** shows the Si–H valence stretching mode at 2204 cm^{-1} , which is absent in the spectrum of **1**.

Interestingly this rearrangement of compound **1** to **2** does not occur in the presence of an excess amount of KCp^4 , as adding two equivalents of KCp^4 to one equivalent of SiCl did not yield compound **2**. Furthermore, NMR studies showed that the slow rearrangement of **1** to **2** described before is not accelerated in the presence of excess KCp^4 . Another interesting point is that while we observed rearrangement from compound **1** to **2** we did not observe the back reaction from **2** to **1**. A flame sealed NMR sample of freshly dissolved crystals of compound **2** did not show any traces of compound **1** even after several weeks of continuous heating.

Both **1** and **2** have different possibilities for coordination to metal atoms. Compound **1** is a silylene and thus should coordinate as a soft Lewis-base *via* the Si atom to metal atoms, while for **2**, which formally is a Si(IV) species, a coordination *via* the Cp⁴-ring is expected. By deprotonation of either **1** or **2** an anion is formed, which may either act like a substituted cyclopentadienyl ligand or a silyl anion. All these different coordination modes were realized and are now described in the following sections.

Deprotonation

After studying the rearrangement process, we investigated the deprotonation of **1** in the next reaction. After several failed attempts, we finally found $[\text{ZnCp}_2^*]$ to be a suitable deprotonating agent. Thus, $[\text{ZnCp}_2^*]$ was treated in a straightforward reaction with compound **1** in toluene (Scheme 4), which led to the formation of $\{[\text{PhC}(\text{NtBu})_2](\text{C}_5\text{Me}_4)\text{Si}\{\text{Zn}(\text{C}_5\text{Me}_5)\}\}$ (**3**) as an orange precipitate (starting from compound **2** yields the same result). Upon recrystallization from the hot mother liquor, crystals suitable for X-ray diffraction studies were formed. During the course of the reaction one Cp^{*} ligand was protonated and cleaved off.³⁷ The remaining $[\text{ZnCp}^*]^+$ fragment was bulky enough to provide steric shielding of the Zn atom.^{38–40}

Compound **3** crystallizes in the monoclinic space group $P2_1/n$ with one molecule in the asymmetric unit (Fig. 3). The solid-state structure of compound **3** also shows that the Cp⁴-ring is arranged as in compound **2** as sila-fulvene but the proton is completely removed from the ligand. The resulting silyl anion is bound to the $[\text{ZnCp}^*]$ fragment, with a short Zn–Si bond distance of $2.3105(11)\text{ \AA}$.^{26,27,41} Additionally this is one of very few examples of a $[\text{ZnR}]^+$ -fragment bound directly to a silicon atom.^{42,43} Due to the rearrangement and deprotonation the



Scheme 4 Synthesis of $\{[\text{PhC}(\text{NtBu})_2](\text{C}_5\text{Me}_4)\text{Si}\{\text{Zn}(\text{C}_5\text{Me}_5)\}\}$ (**3**) and $\{[\text{PhC}(\text{NtBu})_2](\text{C}_5\text{Me}_4)\text{Si}\{\text{Zn}(\text{C}_5\text{Me}_4\text{iPr})\}\}$ (**4**).



Fig. 3 Solid state structure of compound **4**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Zn–Si 2.3056(9); Zn–Cp_{centr.} 1.885(2); Si–N1 1.839(3); Si–N2 1.844(3); Si–C1 1.777(3); N1–C22 1.332(4); N2–C22 1.325(4); C1–C2 1.438(4); C1–C5 1.435(4); C2–C3 1.384(4); C3–C4 1.429(5); C4–C5 1.374(4); N1–C22–N2 106.3(3); N1–Si–Zn 109.99(8); N2–Si–Zn 106.14(9); C1–Si–Zn 122.55(10); N1–Si–C1 117.20(13); N2–Si–C1 118.84(13); Si–C1–C2 125.5(2); Si–C1–C5 128.0(2); C2–C1–C5 106.4(3).

coordination of the silyl anion is different from that of typical silylene zinc species, which feature a dative bond between zinc complexes ZnR_2 and silylene. The difference in coordination can be attributed to the Cp⁴-ring, which due to its labile proton acts as non-innocent substituent on the silylene. Since the sila fulvene unit is similar to compound **2**, the bond distances and angles are almost equal. The Si–C1 distance is again in the range of the literature known Si–C double bonds.^{31–33} The $[\text{ZnCp}^*]$ fragment shows a short distance between Zn and the Cp^{*} centroid of $1.9118(5)\text{ \AA}$. In the ²⁹Si NMR spectrum of compound **3**, a peak at 6.0 ppm is detected. Compared to that for compound **1** (39.7 ppm) this signal is significantly high field shifted, whereas compared to that for the more similar compound **2** (–18.6 ppm) a downfield shifted is seen.

Since the bulky substituents on zinc in $[\text{ZnCp}_2^*]$ were the key for successful coordination of the silylene, we next used the even more bulky zirconocene $[\text{Zn}(\text{Cp}^{\text{iPr}4})_2]$ (Cp^{iPr4} = 1-iso-propyl-2,3,4,5-methylcyclopentadienyl) as the precursor (Scheme 4). The reaction of $[\text{Zn}(\text{Cp}^{\text{iPr}4})_2]$ with **1** resulted in the product $\{[\text{PhC}(\text{NtBu})_2](\text{C}_5\text{Me}_4)\text{Si}\{\text{Zn}(\text{C}_5\text{Me}_4\text{iPr})\}\}$ (**4**), which was isolated as orange crystals. The product crystallizes in the chiral, monoclinic space group *Pc* with one molecule in the asymmetric unit (Fig. 4). The chirality is caused by the iso-propyl group on the Cp^{4iPr}-ring, which cannot freely rotate and forms a kind of paddle-wheel geometry. The structure is similar to compound **3** except for the slightly disordered iso-propyl group on the Cp^{4iPr}-ring bound to the zinc atom. The bond length and angles correspond well with those of compound **3** and the NMR spectra show only the additional peaks corresponding to the iso-propyl group.

Carbon coordination

A coordination of compound **2** *via* the carbon atoms of the Cp⁴-ring was realized in $\{[\text{PhC}(\text{NtBu})_2]\text{SiH}(\text{C}_5\text{Me}_4)\{\text{Ca}(\text{C}_5\text{Me}_5)\text{I}\}\}$ (**5**)





Fig. 4 Solid state structure of compound **3**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Zn–Si 2.3105(11); Zn–Cp_{centr.} 1.9118(5); Si–N1 1.835(3); Si–N2 1.843(3); Si–C1 1.779(3); N1–C20 1.346(4); N2–C20 1.329(4); C1–C2 1.447(5); C1–C5 1.442(5); C2–C3 1.389(5); C3–C4 1.421(6); C4–C5 1.387(5); N1–C10–N2 105.8(3); N1–Si–Zn 109.00(10); N2–Si–Zn 107.67(10); C1–Si–Zn 120.62(12); N1–Si–C1 118.1(2); N2–Si–C1 120.17(14); Si–C1–C2 124.6(3); Si–C1–C5 128.6(3); C2–C1–C5 106.7(3).



Scheme 5 Synthesis of $\{[\text{PhC}(\text{NtBu})_2\text{SiH}(\text{C}_5\text{Me}_4)]\{\text{Ca}(\text{C}_5\text{Me}_5\text{I})\}$ (**5**).

(Scheme 5). When $[\text{Ca}(\text{C}_5\text{Me}_5)\text{I}]$ was stirred together with **1** in toluene overnight a rearrangement of **1** to **2** takes place first, followed by coordination of **2** to the Ca atom (starting from compound **2** yields the same result). As a result, compound **5**



Fig. 5 Solid state structure of compound **5**. Hydrogen atoms are omitted for clarity (except H1). Selected bond lengths [Å] and angles [°]: Ca–I 3.0851(6); Ca–Cp_{centr.} 2.368(2); Ca–C1 2.637(3); Ca–C2 2.681(3); Ca–C3 2.780(3); Ca–C4 2.825(3); Ca–C5 2.744(3); Si–N1 1.798(2); Si–N2 1.812(2); Si–C1 1.795(2); Si–H1 1.35(3); N1–C20 1.329(3); N2–C20 1.346(3); C1–C2 1.432(3); C1–C5 1.437(3); C2–C3 1.388(4); C3–C4 1.426(4); C4–C5 1.390(3); Cp*–Ca–Cp*⁴ 143.51(13); N2–C20–N1 106.1(2); C1–Si–H1 119.5(12); C1–Si–N1 116.75(11); C1–Si–N2 121.33(10); N1–Si–H1 106.9(13); N2–Si–H1 110.0(12); Si–C1–C2 128.5(2); Si–C1–C5 123.1(2); C2–C1–C5 106.9(2).

was formed as an orange residue, which could be recrystallized from the hot mother liquor to obtain crystals suitable for X-ray diffraction studies.

Compound **5** crystallizes in the triclinic space-group $P\bar{1}$ with one molecule in the asymmetric unit (Fig. 5). The $\{[\text{PhC}(\text{NtBu})_2\text{SiH}(\text{C}_5\text{Me}_4)]\}$ moiety of the structure has nearly the same structural parameters (bonds and angles) as described before in structure **2**, **3** and **4**. In contrast to the zinc compounds described above, no deprotonation took place during the course of the reaction and the sila fulvene structure of **2** is preserved upon coordination featuring long (C1–C2 1.432(3), C1–C5 1.437(3), and C3–C4 1.426(4) Å) and short (C2–C3 1.388(4) and C4–C5 1.390(3) Å) C–C bonds. Consequently, the calcium atom cannot bind to the silicon atom and a coordination of the Cp⁴-ring of the sila fulvene is thus observed. Since bond lengths of the C–C double bonds are not influenced upon coordination and the Ca–C1 bond (2.637(3) Å) is the shortest of all Ca–C bonds, we anticipate an electrostatic interaction between the partially negatively charged carbon atom C1 and the calcium atom. π -Coordination of the alkene functions does not seem to play an important role. The calcium atom is coordinated to η^5 -Cp* and the Cp⁴-ring as well as to the iodide. Cp* and the Cp⁴-ring are bent out of plane, enclosing a 143.51(13)° angle. In contrast to many similar structural motifs known in the literature, compound **5** does not dimerize *via* an iodine bridge.^{44–48}

The proton on the silicon atom was detected by NMR and IR spectroscopy. In the ¹H NMR spectrum of compound **5**, the corresponding signal is seen at 3.27 ppm, which is in contrast to the data of compound **2**. In the ²⁹Si NMR spectrum no resonance was observed. The IR spectrum shows the Si–H valence stretching mode at 2205 cm^{−1}.⁴⁹

Silylene coordination

Besides carbon coordination, we were also interested in binding compound **1** *via* the Si atom to transition metals to fully explore the coordination potential of this ligand. Silylenes are known for their ability to bind to, among others, low-valent transition metal complexes.^{6,20,28,41,50–56} For this purpose, compound **1** was treated with group 9 dimers $[\text{RhCl}(\text{cod})]_2$ and $[\text{IrCl}(\text{cod})]_2$ (cod = 1,5-cyclooctadiene) to give $\{[\text{PhC}(\text{NtBu})_2(\text{C}_5\text{Me}_4\text{H})\text{Si}\{\text{RhCl}(\text{cod})\}]\}$ (**6**) and $\{[\text{PhC}(\text{NtBu})_2(\text{C}_5\text{Me}_4\text{H})\text{Si}\{\text{IrCl}(\text{cod})\}]\}$ (**7**) (Scheme 6). Starting from compound **2** gave the same result.



Scheme 6 Synthesis of $\{[\text{PhC}(\text{NtBu})_2(\text{C}_5\text{Me}_4\text{H})\text{Si}\{\text{RhCl}(\text{cod})\}]\}$ (**6**) and $\{[\text{PhC}(\text{NtBu})_2(\text{C}_5\text{Me}_4\text{H})\text{Si}\{\text{IrCl}(\text{cod})\}]\}$ (**7**).



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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