Indirect and Direct Grafting of Transition Metals to Siliconoids

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Dedicated to Professor Reinhold Tacke on the occasion of his 70th birthday

Abstract: Unsatrated charge-neutral silicon clusters (siliconoids) are important as gas-phase intermediates between molecules and the elemental bulk. With stable zirconocene- and hafnocene-substituted derivatives, we here report the first examples containing directly bonded transition-metal fragments that are readily accessible from the ligato-lithiated Si₆ siliconoid (1Li) and Cp₂MCl₂ (M = Zr, Hf). Charge-neutral siliconoid ligands with pending tetrylene functionality were prepared by the reaction of amidinato chloro tetrylenes [PhC(NtBu)₂]ECl (E = Si, Ge, Sn) with 1Li, thus confirming the principal compatibility of such low-valent functionalities with the unsaturated Si₆ cluster scaffold. The pronounced donor properties of the tetrylene/siliconoid hybrids allow for their coordination to the Fe(CO)₄ fragment.

The synthesis of stable unsaturated silicon clusters (siliconoids)[1] has attracted considerable interest because of the presumed intermediacy of the parent species in gas-phase deposition processes[2] as well as the fact that the unsubstituted vertices are reminiscent of the free valencies of bulk and nano silicon surfaces.[3] Since the report of the first stable siliconoid,[4] a variety of further examples have been prepared by the groups of Wiberg,[5] Kyushin,[6] Iwamoto[7] Brecher,[8] Fässler,[9] Lips[10] and our group.[11] The two recent syntheses of regioisomeric lithiated Si₆ siliconoids (benzpolarenes)[12] and their facile functionalization with suitable electrophiles considerably enlarged the scope of this emerging field towards the related Zintl anions (polyanionic, deltahedral clusters without any substituents). The presence of organic substituents in siliconoids confers higher solubility, while the electronic properties are retained as manifest in the wide dispersion of ²⁹Si NMR shifts.[4,6,8,11,12] While Zintl anions of Group 14 elements heavier than silicon have been frequently applied in the synthesis of partially substituted metalloid clusters,[13] the grafting of substituents to silicon-based Zintl anions has only been achieved very recently by the groups of Korber[14] and Fässler,[15] who independently reported the protonation of silicon Zintl anions to the partially H-substituted anionic clusters [HSi₉]⁻, [H₂Si₉]⁻, and [HSi₄]⁻.[16] In addition, the Fässler group successfully transferred silyl substituents to Si₄⁻.[9]

Zintl silicid anions have been employed as extraordinarily electron-rich ligands towards transition-metal centers.[17] Conversely, the coordination of neutral siliconoids to metals has thus far remained elusive. Here, with zirconocene and hafnocene derivatives, we report the first examples of siliconoids bearing covalently attached transition-metal functionalities. As attempts to coordinate charge-neutral siliconoids to transition-metal fragments in a dative manner remained inconclusive, we resorted to the grafting of amidinato tetrylene residues PhC(NBu)₂ECl (E = Si, Ge, Sn) to the Si₆ scaffold. Given that tetrle(II) species are well established as ligands in catalysis,[21] it was conceivable that tetrylene functionalization would facilitate the coordination of electron-rich siliconoid moieties to transition-metal centers. As will be elaborated further on, the targeted tetrylene-siliconoid hybrids are stable and indeed readily transformed into the corresponding Fe(CO)₄ complexes.

Treatment of Cp₂MCl₂ (M = Zr, Hf) with the ligato-lithiated siliconoid 1Li results in rapid and uniform conversion into the corresponding Group 4 metalated siliconoids 2a and 2b (Scheme 1). In contrast, reaction with one equivalent of titanocene dichloride led to a complicated mixture of products, presumably because of competing redox reactions. The diagnostically wide dispersion of ²⁹Si signals confirmed the presence of uncompromised benzopolarene scaffolds.[11d,e] The signals of the provo-silicon atoms appear at the usual low field at 162.6 (2a) and 162.8 ppm (2b), while the two unsubstituted nudo-vertices give rise to two individual signals.

1Li + Cp₂MCl₂ (M = Zr, Hf) → 2a, 2b

Scheme 1. Synthesis of ligato-metalloocene-substituted Si₆ siliconoids 2a and 2b. 2a: M = Zr; 2b: M = Hf. Tip = triisopropylphenyl. The “naked” positions 1 and 3 are referred to as nudo, the NMR-desheilded position 2 as provo, the mono-substituted positions 4 and 6 as ligato, and the remote position 5 as remote.[11]
Table 1: Selected analytical data of metallocene-substituted siliconoids 2a and 2b.

|            | δ(29Si)2 | δ(29Si1/3) | Si1–Si3 | Si4–M | Si4–M | \(\delta_{\text{exp}}\) | \(\delta_{\text{calc}}\) |
|------------|----------|------------|---------|--------|--------|----------------|----------------|
| 2a (M = Zr)| 162.6    | −233.5     | 2.588(2)| 2.782(1)| 2.741 | 521            |                 |
| 2b (M = Hf)| 162.8    | −232.1     | 2.588(1)| 2.770(1)| 2.738 | 497            |                 |

at characteristically high field at −233.5 and −240.6 ppm for 2a and −232.1 and −240.3 ppm for 2b (Table 1). The apparent symmetry reduction is typical for ligato-substituted benzpolarenes and has been attributed to hindered rotation of the pending functionality. The other 29Si NMR chemical shifts are located within the usual range for saturated silicon atoms and vary only slightly with the introduced ligand (see the Supporting Information).

The longest-wavelength absorptions in the UV/Vis spectra are at \(\lambda_{\text{exp}} = 521\) nm (2a) and 497 nm (2b), and therefore slightly red-shifted in comparison with previously reported ligato-substituted siliconoids (\(\lambda_{\text{max}} = 364–477\) nm). Single crystals were obtained by crystallization from hexane/toluene in 53% (2a) and 66% (2b) yield, and their structures were confirmed by X-ray diffraction in the solid state (Figure 1).

Figure 1: Representative molecular structure of siliconoid 2b in the solid state. Hydrogen atoms omitted for clarity. Thermal ellipsoids set at 50% probability. For the structure of 2a, see the Supporting Information.

The distances between the unsubstituted bridgehead silicon atoms Si1 and Si3 (2a: 2.588(2) Å; 2b: 2.588(1) Å) are significantly shorter than those of the peraryl-substituted global-minimum isomer and in line with previously reported persilabenzpolarenes with electropositive groups in the ligato-position. The electronic nature of the substituent apparently affects the electron density available for cluster bonding.

The Zr–Si bond length of 2.782(1) Å in 2a is in between that reported for a disilanyl-substituted zirconocene chloride on the one hand (2.7611 Å) and silyl-substituted zirconocene complexes on the other hand (2.813–2.8214 Å). Similarly, the Hf–Si bond of 2.770(2) Å in 2b is shorter than those reported for tetracoordinated hafnium compounds (2.835–2.888 Å). The experimental bond lengths were satisfactorily reproduced by DFT calculations for 2a and 2b at the BP86 + D3(BJ)/def2-SVP level of theory (Table 1).

In solution, even smallest traces of water lead to the progressive hydrolysis of ligato-zirconocene-functionalized siliconoid 2a as indicated by the gradual appearance of a second set of signals, including a characteristic Si–H resonance at 4.103 ppm, in the 1H NMR spectrum. The Si–H bond of ligato-hafnocene-functionalized siliconoid 2b exhibits a considerably higher stability towards hydrolysis (see the Supporting Information for details). In view of the instability of the covalent silicon–metal bond in 2a and 2b, it is unsurprising that attempts to directly graft later transition metals to siliconoids have failed thus far. In the same vein, the dative coordination of charge-neutral siliconoids to transition metals is also unknown. We therefore considered the functionalization of the Si4 scaffold with an auxiliary tetrylene ligand in order to facilitate coordination.

Tetrylenes are known for their excellent o-donating properties. As the reaction of ligato-lithiated benzpolarene 11Li with Jutzi’s silicocene affords the cluster-expanded Si7 siliconoid instead of the simple substitution product, we chose the N-heterocyclic chloro tetrylenes of the Roesky type for the isolation of a silylene-functionalized Si6 siliconoid. In fact, the tetrylenes [PhC(NBu)2]ECl are known to readily undergo nucleophilic substitution of the chlorine substituent. Treatment of the ligato-lithiated benzpolarene 11Li with 1.1 equivalents of [PhC(NBu)2]ECl indeed leads to rapid conversion into uniform products (E = Si, Ge, Sn; Scheme 2).

Scheme 2. Synthesis of the tetrylene-functionalized Si4 siliconoids 3a–c. 3a: E = Si; 3b: E = Ge; 3c: E = Sn.

The occurrence of two sets of signals each in the 29Si and 119Sn NMR spectra of 3b and 3c suggested the presence of rotational isomers in solution. Indeed, 29Si and 119Sn solid-state NMR spectra of 3a–c show just a single set of signals (Table 2 and the Supporting Information). A VT-NMR study accompanied by precipitation of LiCl. 29Si NMR analysis showed the diagnostic wide dispersion of chemical shifts (as discussed above for 2a and 2b), and thus confirmed the anticipated integrity of the benzpolarene scaffolds suggesting the formation of siliconoids 3a–c. An additional signal in the 29Si NMR spectrum of 3a was assigned to the pending silylene center.
in toluene solution revealed the onset of coalescence at 343 K for germylene-substituted 3b although the barrier proved to be too high to allow for accurate determination of the coalescence temperature (> 70°C). The $^{29}$Si and $^1$H NMR spectra of stannylene-substituted 3c show broad signals with poor signal-to-noise ratios at room temperature, suggesting that the coalescence temperature may be within reach. Accordingly, VT-NMR analysis of 3c at low temperature (226 K) revealed sharpened signals in the $^1$H NMR spectrum as well as a second set of less intense signals in the $^{29}$Si NMR spectrum (Table 2).

The longest-wavelength absorption bands in the UV/Vis spectra are at $\lambda_{\text{max}}$ = 472 nm (3a), 436 nm (3b), and 436 nm (3c). Single crystals were obtained in 72% (3a), 78% (3b), and 74% (3c) yield, and the structures were confirmed by X-ray diffraction studies (Figure 2). The structure of the Si6 cluster core is hardly influenced by the nature of the tetrylene ligand. The distances between the unsubstituted bridgehead silicon atoms Si1 and Si3 (3a: 2.6039(9) Å; 3b: 2.612(2) Å; 3c: 2.6149(8) Å) are slightly shorter than in the global-minimum isomer Si6Tip$_2$[13g] and in line with previously reported ligato-functionalized siliconoids with electropositive groups.[11b,14] The bonds between Si4 and the pending tetrylene (3a: 2.4294(9) Å; 3b: 2.493(2) Å; 3c: 2.6753(6) Å) are longer than typical single bonds.[24−27]

In order to probe the suitability of 3a−c as neutral ligands towards transition metals, we attempted the coordination to Fe(CO)$_4$ in a proof-of-principle study (Scheme 3). Complexes 4a−c are obtained in a straightforward manner by stirring a benzene solution of 3a−c with 4 (4a), 5 (4b), or 1.5 (4c) equivalents of Fe(CO)$_4$[18,19a,28] at room temperature. Complexes 4a−c were fully characterized by X-ray diffraction on single crystals, elemental analysis, as well as multinuclear NMR, UV/Vis, and IR spectroscopy.

| Table 2: Selected NMR shifts of the tetrylene-functionalized siliconoids 3a−c. |
|-----------------|---------------|---------------|---------------|---------------|---------------|
|                  | $\delta(\text{Si2})$ | $\delta(\text{Si1/3})$ | $\delta(\text{Si2})$ | $\delta(\text{Si1/3})$ | $\delta(\text{l}^{119}\text{Sn})$ |
|                  | [ppm]         | [ppm]         | solid          | [ppm]         | solid          | [ppm]         |
| 3a               | 166.7         | −244.6        | 160.0          | −250.5        | −260.7         |
|                  |               |               | 160.0          | −250.5        | −260.7         |
| 3b               | 167.3         | −245.4        | 163.4          | −248.9        | −261.2         |
| major            |               |               | 163.4          | −248.9        | −261.2         |
| 3b               | 165.6         | −233.9        | −238.1         | −236.9        | −267.8         |
| minor            |               |               | −238.1         | −236.9        | −267.8         |
| 3c               | 162.3         | −232.6        | −236.9         | −269.3        | 336.5          |
| major            |               |               | −236.9         | −269.3        | 336.5          |
| 3c               | 168.8         | −242.3        | 162.9          | −244.3        | 336.5          |
| minor            |               |               | 162.9          | −244.3        | 336.5          |

![Figure 2. Representative molecular structure of silylene-functionalized siliconoid 3a in the solid state.[13] Hydrogen atoms omitted for clarity. Thermal ellipsoids set at 50% probability. For the structures of 3b and 3c, see the Supporting Information.](image)

![Scheme 3. Reaction of the tetrylene-functionalized Si6 siliconoids 3a−c with Fe(CO)$_4$ to afford the corresponding Fe(CO)$_4$ complexes 4a−c.](image)

Table 3: Selected NMR shifts of Fe(CO)$_4$ complexes of tetrylene-substituted siliconoids 4a−c.

|                  | $\delta(\text{Si2})$ | $\delta(\text{Si1/3})$ | $\delta(\text{Si2})$ | $\delta(\text{Si1/3})$ | $\delta(\text{l}^{119}\text{Sn})$ |
|-----------------|---------------|---------------|---------------|---------------|---------------|
|                  | [ppm]         | [ppm]         | solid          | [ppm]         | solid          | [ppm]         |
| 4a              | 165.1         | −198.2        | 158.2          | −195.9        | −231.2         |
| 4b              | 163.7         | −203.0        | 156.7          | −202.2        | −233.4         |
| 4c              | 160.2         | −201.7        | 154.1          | −200.3        | 456.3          | 469.2         |
ex.\[26a,28a\] with CO stretching modes at $\nu = 1899, 1913, 1948, 2022 \text{ cm}^{-1}$ (4a), 1908, 1918, 1949, 2025 cm$^{-1}$ (3b), and 1902, 1914, 1942, 2015 cm$^{-1}$ (4c). The donor strength of 4a-c can be classified by the asymmetric carbonyl absorptions at $\nu = 2022 \text{ cm}^{-1}$ (4a), 2025 cm$^{-1}$ (4b), and 2015 cm$^{-1}$ (4c), which indicate a slightly lower ligand-to-metal $\sigma$-donation compared to other tetrylene Fe(CO)$_4$ complexes such as $[\text{PhC(NR}_3\text{Bu)}_2\text{SiO]}\text{Fe(CO)}_4$ ($\nu = 2026 \text{ cm}^{-1}$)\[28a\] and $[\text{PhC(NR}_3\text{Bu)}_2\text{GeC]}\text{Fe(CO)}_4$ ($\nu = 2042 \text{ cm}^{-1}$)\[28b\]. Single crystals of 4a-c were obtained in 75% (4a), 60% (4b), and 70% (4c) yield, and the structures were confirmed to be isosteric by X-ray diffraction studies (Figure 3). The distances between the bridgehead silicon atoms Si1–Si3 (4a: 2.566(1) Å; 4b: 2.566(1) Å; 4c: 2.5756(7) Å) are slightly shorter than in 3a-c. This is indicative of increased electron density within the cluster scaffold upon formation of the transition-metal complex. The bonds Si–E in 4a-c (4a: 2.384(1) Å; 4b: 2.4422(8) Å; 4c: 2.5896(5) Å) are equally shortened compared to 3a-c and now in the typical range of Si–E single bonds (E = Si, Ge, Sn).\[24–27\] The Fe(CO)$_4$ complexes 4a-c exhibit typical Fe–E distances (4a: 2.279(1) Å; 4b: 2.3496(5) Å; 4c: 2.4957(3) Å).\[18,19a,28a–c\]

**Figure 3.** Representative molecular structure of the Fe(CO)$_4$ complex of 4a in the solid state.\[29\] Hydrogen atoms omitted for clarity. Thermal ellipsoids set at 50% probability. For the structures of 4b and 4c, see the Supporting Information.

In conclusion, with 2a and 2b, we have reported the first transition-metal-substituted neutral siliconoids. The reaction of an anionic Si, siliconoid with PhC(NR$_3$Bu)$_2$ECl (E = Si, Ge, Sn) gave rise to siliconoids with pending Roesky-type silylene, germylene, and stannylene moieties, an unprecedented feature in silicon cluster chemistry. Unlike in the case of the previously attempted grafting of a Cp*-substituted silylene fragment,\[114\] the electrophilicity of the tetrylenes of the Roesky type is sufficiently low, thereby avoiding the otherwise observed expansion of the cluster core. As proof of concept for the suitability of these novel ligands in the coordination to transition metals, we synthesized and characterized the corresponding Fe(CO)$_4$ complexes 4a-c.

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**Conflict of interest**

The authors declare no conflict of interest.

**Keywords:** clusters · ligands · low-valent species · silicon · siliconoids

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