# Chemical Science

## EDGE ARTICLE

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Cite this: Chem. Sci., 2019, 10, 4523

All publication charges for this article have been paid for by the Royal Society of Chemistry

Received 14th December 2018 Accepted 7th March 2019

DOI: 10.1039/c8sc05591b

rsc.li/chemical-science

### Introduction

Partially substituted neutral silicon clusters (siliconoids)1-4 are fleeting intermediates during the production of silicon from molecular precursors and can typically only be detected in the gas phase.<sup>5-9</sup> The synthesis of stable derivatives has attracted considerable interest as the unsubstituted vertices of siliconoids are reminiscent of the free valences at bulk and nano surfaces of silicon, the so-called "dangling bonds".<sup>10-13</sup> Since the report on the first stable siliconoid Si<sub>5</sub>R<sub>6</sub> with one "naked" vertex in a hemispheroidal coordination environment by one of us,14 numerous examples have been prepared by the groups of Wiberg,15 Breher,16 Kyushin,17,18 Iwamoto,19 Fässler20 and ourselves.<sup>14,21–23</sup> The  $Si_6R_6$  isomers 1 (ref. 22) and 2 (ref. 23) are lower energy isomers of the hypothetical hexasilabenzene and as such prime examples of the often drastic differences between carbon and silicon (Scheme 1). While of the known C<sub>6</sub>H<sub>6</sub> isomers, benzene is by far the lowest in energy, the tricyclic 2 corresponds to the global minimum isomer of Si<sub>6</sub>H<sub>6</sub> and can therefore be considered as the silicon analogue of benzene on grounds of thermodynamic stability.23,24

The functionalization of such clusters is a prerequisite for the further development of their chemistry and ultimately the



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The recent progress in the synthesis of partially substituted neutral silicon clusters (siliconoids) revealed unique structures and electronic anisotropies that are reminiscent of bulk and nano surfaces of silicon. Here, we report the selective 2-lithiation of the global minimum  $Si_6R_6$  siliconoid at a different vertex than in the previously reported isomeric 4-lithiated derivative ( $R = 2,4,6^{-i}Pr_3C_6H_2$ ). In order to enable an intuitive distinction of the vertices of the global minimum  $Si_6R_6$  scaffold (which can be considered the silicon analogue of benzene in terms of thermodynamic stability), we introduce a novel nomenclature in analogy to the *ortho-meta-para* nomenclature of disubstituted benzenes. By treatment of the 2lithiated  $Si_6$  cluster with Me<sub>3</sub>SiCl, SiCl<sub>4</sub> H<sub>3</sub>B·SMe<sub>2</sub>, (Me<sub>2</sub>N)<sub>2</sub>PCl as well as with carboxylic acid chlorides RCOCl ( $R = {}^{t}Bu$ , Ph) various 2-functionalized  $Si_6$  clusters were obtained and characterized in solution and – in most cases – the solid state. The structural and spectroscopic effect of the position of the newly introduced functional group is discussed by comparison to the corresponding 4-functionalized derivatives.

application of their fascinating electronic properties in extended materials. Compared to the related Zintl anions of the heavier group 14 elements,<sup>25–31</sup> which are (poly)anionic, completely unsubstituted deltahedral clusters, siliconoids are partially substituted yet exhibit a similarly wide dispersion of <sup>29</sup>Si NMR shifts.<sup>14,16–18,22,24</sup> Very recently, the protonation of silicon Zintl anions to partially H-substituted anionic siliconoids was reported independently by the groups of Fässler and Gschwind/Korber.<sup>30,31</sup> We had previously described the reductive functionalization of the dismutational Si<sub>6</sub>R<sub>6</sub> isomer **1** to the



Scheme 1 Synthesis of 3Li (ref. 32) and 4Li (this work) from dismutational hexasilabenzene isomer 1 and from the global minimum isomer 2 (Tip = 2,4,6-triisopropylphenyl).

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<sup>†</sup> Electronic supplementary information (ESI) available: CCDC 1877380 (5a), 1877381 (5b), 1877378 (4Li), 1877379 (6a), 1877382 (6c), 1877383 (6f). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8sc05591b

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anionic siliconoid **3Li** as well as its reactivity with several representative electrophiles of groups 13 to 15.<sup>32,33</sup>

Herein, we show that reduction of the global minimum isomer 2 under similar conditions selectively affords the regiomeric anionic Si<sub>6</sub> siliconoid **4Li** instead of **3Li** by cleavage of an aryl substituent in the 2-position of the bridged propellane scaffold (Scheme 1). In order to account for the rapidly increasing number of species with the thermodynamically favored bridged-propellane scaffold and unequivocally distinguish between the different vertices, we propose a novel terminology for this structural motif, inspired by the wellestablished *ortho-meta-para* nomenclature for disubstituted benzenes.<sup>34-37</sup> The functionalization of **3Li** and **4Li** with selected electrophiles is shown to result in several sets of regiomeric derivatives allowing for the systematic comparison of the structural and spectroscopic consequences of the functional group's position.

### Results and discussion

#### Nomenclature of Si<sub>6</sub> siliconoids

Structures with [1.1.1.]propellane motif have intrigued experimentalists and theorists alike ever since the early 1970s,38,39 because of their non-classical structure containing bridgehead atoms in an umbrella-type hemispheroidal coordination environment. The bonding situation between the bridgehead atoms of [1.1.1]propellanes can be described by biradical or ionic contributions to the electronic ground state<sup>40-43</sup> and was discussed by Shaik et al. as a "charge-shift-bond".44,45 The Si<sub>6</sub> siliconoids 2 and 3Li show a closely related structure having two propeller blades bridged by one SiTip<sub>2</sub> moiety. Strongly deshielded <sup>29</sup>Si NMR signals had been explained by a clusterlike delocalization of the two electrons in question.<sup>23</sup> Electron density determinations of the Si<sub>6</sub> siliconoid 2 confirmed the absence of direct bonding between the bridgehead silicon vertices.46 For nomenclature purposes,47,48 the Si<sub>6</sub> scaffold is nonetheless formally considered as tetracyclic system with a direct connection between the hemispheroidally coordinated vertices that are depicted in the schemes as a dashed line.

The high thermodynamic stability of Si<sub>6</sub> siliconoid 2 as the alleged global minimum of the Si<sub>6</sub>H<sub>6</sub> potential energy surface<sup>23,24</sup> suggests a considerable prevalence of this structural motif. This received first corroboration by the successful synthesis of mixed group 14 systems49 and a Sn<sub>6</sub> derivative recently.50 Saturated variations of the six-atom scaffold occur in numerous other species throughout main group chemistry.51-54 In the past, the tetracyclic core structure has been variously referred to as "edge-capped trigonal bipyramid"55 "doubly edgebridged tetrahedron"56 or "bridged propellane".23 As these terminologies do not seem to do justice to the ubiquity of the structural motif, we propose a novel term that echoes the relationship to the iconic benzene molecule and - at the same time - takes into account the extraordinary polarization of 2 and related species.39,57-64 We thus suggest the term "benzpolarene"in analogy to benzvalene - for the tetracyclic arrangement of vertices in the cluster core of 2 and 3Li. In addition, we feel that the availability of the first Si<sub>6</sub> siliconoid regiomers described

herein requires a descriptive nomenclature not unlike the wellestablished *ortho*, *meta* and *para* prefixes used for disubstituted benzenes. The prefixes thus proposed in the following reflect the characteristic bonding situation of each vertex (Chart 1).

The latin words for "naked" (lat. nudus), "bonded" (lat. ligatus), "remote" (lat. remotus) and "deprived" (lat. privus) served as inspirations. The *nudo* prefix is assigned to the unsubstituted ("naked") bridgehead silicon atoms in 1,3-position, the *ligato* prefix to the mono-substituted vertices (4,6-position) bonded to one substituent each, the *remoto* prefix to the remote bridge in 5-position and the *privo* prefix to the characteristically deshielded ("deprived" of electrons) atom in 2-position.

#### Functionalization in ligato position

In addition to the previously reported persilabenzpolarenes,<sup>32,33</sup> we investigated two further reactions of siliconoid **3Li** with electrophiles. The novel *ligato* functionalized siliconoids **5a,b** were thus obtained by treatment of **3Li** in benzene at room temperature with Me<sub>3</sub>SiCl and benzoyl chloride, respectively (Scheme 2). The reactions proceed quantitatively according to <sup>29</sup>Si NMR spectroscopy. The siliconoids **5a,b** were isolated as single crystals and fully characterized by X-ray analysis, NMR spectroscopy, UV/Vis (Table 1) and by IR spectroscopy in case of the CO containing species.

The <sup>29</sup>Si NMR spectra of **5a,b** show the typical distribution of chemical shifts for ligato functionalized persilabenzpolarenes as recently reported by our group for 5c-f:<sup>32,33</sup> the two unsubstituted bridgehead silicon atoms give rise to two <sup>29</sup>Si signals in a range of -257 to -280 ppm (Table 1). The  $C_{2v}$  symmetry of the benzpolarene scaffold of 2 is lowered to  $C_s$  in the substituted cases. As we had shown by VT NMR studies for some of the ligato-functionalized species,32 hindered rotation further reduces the symmetry so that the two seemingly identical nudo atoms become diastereotopic. The resonances of the SiTip<sub>2</sub> groups in privo position are strongly deshielded with signals at 169.9 (5a) and 174.7 ppm (5b). The surprisingly downfield shifted signals (for tetracoordinate silicon atoms) had been rationalized by invoking magnetically induced cluster currents or - in a complementary manner - by the strong LUMO contribution at this atom.<sup>49,65,66</sup> The <sup>29</sup>Si NMR chemical shifts of the remaining cluster vertices are located in the typical range for saturated silicon atoms and vary only slightly with the introduced functionality. The longest wavelength absorption bands in the UV/Vis are observed at  $\lambda_{max} = 459$  nm (5a) and 477 nm (5b). The characteristic CO stretching mode in the IR of 5b at v= 1605  $\text{cm}^{-1}$  compares well with that of 5c.<sup>32,33</sup> Single crystals



**Chart 1** Proposed prefixes for unique assignment of vertices in bridged propellane-type ("benzpolarene") siliconoids.

Scheme 2 Synthesis of ligato-functionalized siliconoids 5a-f. Reagents: (a) Me<sub>3</sub>SiCl, (b) PhCOCl, (c) <sup>t</sup>BuCOCl, (d) ClP(NMe<sub>2</sub>)<sub>2</sub>, (e) SiCl<sub>4</sub>, (f) BH<sub>3</sub>·SMe<sub>2</sub>. **5a**:  $E = Me_3Si$ , **5b**: E = COPh and the previously reported<sup>32</sup> **5c**:  $E = CO^{t}Bu$ , **5d**:  $E = P(NMe_{2})_{2}$ , **5e**:  $E = SiCl_{3}$ , **5f**:  $E = BH_{3}^{-1}$ 

were obtained in 45% (5a) and 66% (5b) yield and the structures confirmed by X-ray diffraction studies (Fig. 1).<sup>67</sup> The distances between the unsubstituted bridgehead silicon atoms Si1 and Si3 are slightly shorter than in the global minimum isomer,<sup>23</sup> in line with the observations for the previously reported ligato functionalized persilabenzpolarenes 3Li and 5c-f.32,33 The distance between the ligato positions Si4 and Si6 of 5a-f increases with decreasing distance between the nudo positions Si1 and Si3, presumably in order to minimize strain (Table 1). Apparently, the variation of the *ligato* functionality of the benzpolarene structures 5a-f directly influences the bonding between the unsubstituted silicon atoms Si1 and Si3.

#### Synthesis of privo lithiated siliconoid 4Li

The reduction of the dismutational isomer of hexasilabenzene 1 had yielded the lithiated siliconoid with a benzpolarene scaffold 3Li and thus a functionalized derivative of the Si<sub>6</sub>H<sub>6</sub> global minimum isomer 2.32,33 In order to probe the possible intermediacy of 2, its reduction with lithium/naphthalene was investigated (Scheme 3).

Treatment of 2 with 2.2 equivalents of Li/C<sub>10</sub>H<sub>8</sub> in Et<sub>2</sub>O and thf indeed results in the complete and uniform conversion into a novel anionic Si<sub>6</sub> species as confirmed by <sup>29</sup>Si NMR spectroscopy. The six resonances show a similar chemical shift distribution as in 3Li, but with distinctly different values suggesting the functionalization had taken place in another position of the benzpolarene scaffold (Table 1). The reduction product 4Li was fully characterized by X-ray diffraction on single crystals, NMR spectroscopy and UV/Vis spectroscopy.

A strongly deshielded <sup>29</sup>Si NMR signal at 267.9 ppm is significantly broadened (presumably due to coupling to the quadrupolar <sup>7</sup>Li-nucleus) and only shows a cross-peak to the aromatic H atoms of a single Tip ligand in the 2D  $^{1}$ H/ $^{29}$ Si correlation spectrum. These observations led us to conclude that the anionic functionality of 4Li is located at the tetracoordinate silicon atom in the privo position Si2. The <sup>29</sup>Si chemical shift of 267.9 ppm is particularly remarkable as saturated silyl anions typically show resonances at much higher field often deep in the negative ppm region.<sup>69</sup> According to our previous calculations,66 the magnetically induced cluster currents circumvent the privo position and thus cause its pronounced deshielding even in case of the peraryl-substituted benzpolarene 2. On the basis of a complementary explanation referring to the topology of the LUMO,49 this phenomenon is probably due to the pronounced silylene character of the privo atom. The presence of a directly attached electron-releasing substituent could lead to an increased localization of the vacant p orbital in the privo position and thus to the observed even more pronounced deshielding. The signals for the remoto SiTip<sub>2</sub> and the two *ligato* SiTip units appear at  $\delta = 15.3$  and 100.2/-43.8 ppm, respectively. The reason for the large difference between the chemical shifts is unclear although the electronic environments of the *ligato* atoms are certainly dominated by their relative position to the anionic functionality and the lithium counter cation in privo position. The unsubstituted bridgehead silicon atoms in the nudo positions are apparently

Table 1 Comparison of NMR spectroscopic and structure data of ligato functionalized siliconoids 5a-f and privo functionalized siliconoids 6a-f

Position						$\lambda_{max}$	_	_		
of E	Comp.	Functional group (E)	Si1, Si3 [ppm]	Si2 [ppm]	Si4 [ppm]	[nm]	ΔSi1–Si3 [Å]	ΔSi4–Si6 [Å]	$\sigma_{ m m}{}^{a,67}$	Hemispheroidality <sup>b</sup> $\phi$ [Å]
_	2	Tip <sup>23</sup>	-274.2	174.6	-7.5	473	2.7076(8)	2.9037	0.08	1.3535
ligato	3Li	Li <sup>32</sup>	-230.9, -232.6	152.2	-66.8	364	2.5506(9)	3.2243		1.2805
privo	4Li	Li	-222.2, -231.4	267.9	-43.8	468	2.5562(10)	2.9171(11)	_	1.3078
ligato	5a	TMS	-257.8, -266.6	169.9	-3.7	459	2.6176(5)	2.9643(8)	-0.04	1.3283
ligato	5b	COPh	-263.0, -279.0	174.7	-26.5	477	2.6598(9)	2.8854(8)	0.34	1.3333
ligato	5 <b>c</b>	CO <sup>t</sup> Bu <sup>32</sup>	-264.7, -271.1	171.8	-27.4	475	2.6430(6)	2.9095	0.27	1.3458
ligato	5d	$P(NMe_2)_2$ (ref. 32)	-256.0, -261.4	168.7	-33.8	475	2.6231(5)	2.9508	0.18	1.3498
ligato	5e	SiCl <sub>3</sub> (ref. 32)	-252.3, -264.2	175.4	12.9	460	2.635(1)	2.8920	0.48	1.3409
ligato	5f	BH <sub>3</sub> (ref. 32)	-257.3, -265.0	161.2	-4.8	475	2.620(1)	2.9988	-0.48	1.3153
privo	6a	TMS	-242.0, -253.3	193.6	-15.9	469	2.6118(6)	2.9482(6)	-0.04	1.3308
privo	6b	COPh	-268.5, -271.1	166.2	-16.2	_	_	_	0.34	_
privo	6c	CO <sup>t</sup> Bu	-263.1, -265.8	173.1	-14.5	473	2.6350(5)	2.9641(7)	0.27	1.3439
privo	6d	$P(NMe_2)_2$	-246.0, -256.1	186.5	-16.9	_	_	_ ``	0.18	_
privo	6e	SiCl <sub>3</sub>	-251.6, -258.9	161.7	-6.4	_	_	_	0.48	_
privo	6f	$BH_3^-$	-243.3, -255.6	237.3	-28.8	454	2.6024(8)	2.9431(7)	-0.48	1.3155

<sup>a</sup> For substituents BH<sub>3</sub><sup>-</sup> and Tip no Hammett parameters are available. The Hammett parameters of similar compounds were used for the correlation plots in Fig. 4:  $B(OH)_3^-$  for  $BH_3^-$  and  $(C_6H_5^-4-CHMe_2)$  for the Tip substituent (see ref. 68). <sup>b</sup> The hemispheroidality  $\phi$  is the distance of a naked cluster vertex from the plane spanned by its three substituents. Its value is taken as a measure for the degree of hemispheroidality of the vertex. For a detailed explanation see ref. 4.



Fig. 1 Structures of 5a,b in the solid state (thermal ellipsoids at 50% probability). Hydrogen atoms and co-crystallized pentane omitted. a:  $E = SiMe_3$ , b: E = COPh.



Scheme 3 Synthesis of privo-lithiohexasilabenzpolarene 4Li by reduction with 2 equivalents of  $Li/C_{10}H_8$ .

not compromised by the reduction and give rise to two signals at the usual high field at  $\delta = -222.2$  and -231.4 ppm, comparable to the corresponding signals of the *ligato* lithiated **3Li**. The constitution of the reduction product of benzpolarene **2** was finally proven as the *privo* functionalized **4Li** by X-ray diffraction on single crystals (Fig. 2).<sup>67</sup>

The distance between the bridgehead silicon atoms (Si1–Si3 2.5562(10) Å) is similar to that in **3Li**, but shorter than in the fully Tip-substituted siliconoid 2 and the *ligato* functionalized siliconoids **5a–b**. This shortening is tentatively attributed to delocalization of the lone-pair of the anionic silicon vertex into cluster bonding orbitals. The formation of the two regioisomeric derivatives is predominantly a consequence of the



Fig. 2 Structure of 4Li in the solid state (thermal ellipsoids at 50% probability). Hydrogen atoms and co-crystallized solvent molecules omitted.

different topologies of the LUMOs of both the dismutational  $Si_6R_6$  isomer 1 and the benzpolarene isomer 2. The initial reduction plausibly occurs at the unsubstituted vertices of the starting materials (A, D), which provide dominant contributions to the respective LUMOs.<sup>22,23</sup> Other important LUMO contributions are located precisely at the silicon vertices to which the preferentially eliminated aryl groups are bonded. The subsequent isomerizations are likely driven by the very low energy of the benzpolarene scaffold (Scheme 4). The lithiated regioisomer **3Li** is formed due to a *syn* TipLi elimination (B) followed by a cyclobutene–bicyclobutane rearrangement (C). In case of the reduction of the benzpolarene isomer **2**, we suggest an orbital-and strain-controlled TipLi elimination followed by a 1,2-migration of the lithium counteraction (F) to yield **4Li**.

#### Functionalization in privo position

In order to evaluate the suitability of *privo* lithiated siliconoid **4Li** as nucleophilic transfer reagent for the intact unsaturated Si<sub>6</sub> scaffold, we treated it with several electrophiles (Me<sub>3</sub>SiCl, PhCOCl, <sup>t</sup>BuCOCl, ClP(NMe<sub>2</sub>)<sub>2</sub>, SiCl<sub>4</sub>, BH<sub>3</sub>·SMe<sub>2</sub>). Indeed, the corresponding *privo* substituted siliconoids **6a–f** are obtained by straightforward combination of the reagents in toluene at room temperature (Scheme 5).

According to <sup>29</sup>Si NMR spectra, the reactions lead to full conversion of **4Li** to the *privo* functionalized siliconoids **6a-f**. Crystallization of **6a,c,f** from concentrated hexane solutions affords single crystals in moderate to good yields (**6a**: 66%; **6c**: 27%; **6f**: 78%), which were fully characterized by multinuclear NMR spectroscopy, UV/Vis spectroscopy and X-ray diffraction (Fig. 3).<sup>67</sup> In case of **6b,d,e**, the reactions were only performed on the NMR scale and characterized by multinuclear NMR spectroscopy. The <sup>29</sup>Si NMR data of the *privo* substituted species display a similarly wide dispersion in chemical shifts as the corresponding *ligato* isomers. The <sup>29</sup>Si NMR spectra of **6a-f** thus show two signals in the high-field region for the *nudo* positions and a strongly deshielded signal for the *privo* silicon atom, which carries one Tip substituent and the functional group E in this case.

The UV/Vis spectra of the isolated products **6a,c,f** and **4Li** show the position of the longest wavelength absorption



Scheme 4 Mechanistic explanation of the regioselective formation of 3Li and 4Li.



Scheme 5 Synthesis of *privo*-functionalized siliconoids **6a–d**. Reagents: (a) Me<sub>3</sub>SiCl, (b) PhCOCl, (c) <sup>t</sup>BuCOCl, (d) ClP(NMe<sub>2</sub>)<sub>2</sub>, (e) SiCl<sub>4</sub>, (f) BH<sub>3</sub>·SMe<sub>2</sub>. **6a**:  $E = Me_3Si$ , **6b**: E = COPh, **6c**: E = CO<sup>t</sup>Bu, **6d**:  $E = P(NMe_2)_2$ , **6e**:  $E = SiCl_3$ , **6f**:  $E = BH_3^-$ .

maximum to strongly depend on the substituents of the Si<sub>6</sub> scaffold ( $\lambda_{max}$ ; **6a** 469 nm; **6c** 473 nm; **6f** 454 nm; **4Li** 468 nm). As in case of the *ligato* functionalized species, it can presumably be assigned to the vertical HOMO–LUMO singlet excitation.

The distances between the bridgehead silicon atoms Si1–Si3 in the crystal structure of **6a,c,f** (**6a** 2.6118(6), **6c** 2.6350(5), **6f** 2.6024(6) Å) are longer than in the *ligato* lithiated siliconoid **3Li**<sup>32,33</sup> and *privo* lithiated siliconoid **4Li**, but slightly shorter than

in the *ligato* functionalized siliconoids **5a,c,f**. This is in line with a more effective  $\sigma$  donation in the *privo* position. While for siliconoids **5a–f**, a reciprocal interdependency between the distances of Si1–Si3 and Si4–Si6 is observed, no such relationship is present in case of the *privo* functionalized siliconoids **6a–f**.

The <sup>29</sup>Si NMR resonances of the *privo* silicon atom are strongly influenced by the nature of the pending functionality. The signal is shifted to higher field with increasing electron-withdrawing power of the substituent: Li > BH<sub>3</sub> > TMS > P(NMe<sub>2</sub>)<sub>2</sub> > Tip > CO<sup>t</sup>Bu > COPh > SiCl<sub>3</sub>. This sequence correlates nicely with the Hammett parameter  $\sigma_{\rm m}$ ,<sup>70-73</sup> which is based on the relative reaction kinetics of a second substitution in the *meta* position of benzene relative to the functionality in question.

#### Correlation with Hammett parameters $\sigma$

Fig. 4 shows the two correlations between the <sup>29</sup>Si NMR chemical shift at the *privo* position of compounds **2**, **5a–f** and **6a–f** and the Hammett parameter  $\sigma_m$  drawn separately for the two synthetically accessible positions of the functional group. The correlations with the  $\sigma_p$  Hammett parameter are similar, but slightly less satisfactory (see ESI†).

The plot for the *ligato* functionalized compounds **5a–f** (Fig. 3, top) shows a linear relationship ( $R^2 = 0.912$ ). The response of the <sup>29</sup>Si chemical shift, however, is moderate as indicated in its range (160 to 180 ppm) and the resulting slope (m = 14.346 ppm). Electron-withdrawing substituents in *ligato* position result in a stronger deshielding of the *privo* atom in the <sup>29</sup>Si NMR (**5b,c,d,e**) while electron-donating groups exert the opposite effect (**5a,f**). The  $\sigma_m$  value for the Tip substituent (red triangle in Fig. 4) had to be approximated by that of C<sub>6</sub>H<sub>5</sub>-4-CHMe<sub>2</sub> (ref. 68) and was therefore disregarded for the linear fit. Surprisingly, there is no apparent correlation of the *nudo* silicon atoms Si1 and Si3 (Table 1).

In case of the privo functionalized benzpolarenes (6a-f), the correlation of the Hammett parameters  $\sigma_m$  is even better with a very good linear dependency ( $R^2 = 0.978$ ). This is due to a markedly stronger response than in case of ligato functionalization with a slope of m = -79.76 ppm and a consequently larger chemical shift range (160 to 240 ppm). The stronger influence of the functional group is readily explained by its direct attachment to the silicon atom in question (Si2) vs. an additional distance of two Si-Si bonds in case of ligato functionalization. Remarkably, the slope of the linear fit is negative proving a reciprocal relationship between the electron-withdrawing strength of the substituent and its deshielding effect in the privo position. We had shown previously that the formal substitution of the nudo silicon atoms by germanium or tin results in a pronounced deshielding of the privo positions as well, which we tentatively rationalized by the strong influence of the LUMO shape on the paramagnetic contribution to the chemical shift.49

In contrast to our findings, in the case of mono-substituted carbon-based benzenes, the correlation of the Hammett parameter  $\sigma_p$  with the chemical shift of the *para*-carbon atom is known,<sup>74</sup> *i.e.* the ring atom opposite to the one carrying the functional group.



Fig. 3 Structures of 6a, 6c and 6f in the solid state (thermal ellipsoids at 50% probability). Hydrogen atoms and co-crystallized solvent molecules omitted. a: E = TMS, c:  $E = CO^{t}Bu$ , f:  $E = BH_{3}^{-}$ .



Fig. 4 Plots of the Hammett parameters  $\sigma_m$  vs. <sup>29</sup>Si chemical shifts of the *privo* silicon vertices of *ligato* (5a–f; top) and *privo* functionalized hexasilabenzpolarenes (6a–f; bottom). The data pair marked with red triangles corresponds to the unfunctionalized hexaaryl derivative 2.

### Conclusion

 $Si_6$  siliconoids 1 and 2 can be selectively reduced to yield derivatives of the global minimum isomer of the  $Si_6H_6$  potential energy surface with an anionic functionality at distinct vertices. In order to distinguish between the different positions of the

tricyclic Si<sub>6</sub> scaffold, we propose a nomenclature that refers to the characteristic environment of the four conceivable symmetry-independent positions: nudo, privo, ligato and remoto. The anisotropic electronic structure of the global minimum Si<sub>6</sub>H<sub>6</sub> scaffold is accounted for by the introduction of "benzpolarene" as unique name for this ever more frequently occurring structural motif. The privo lithiated hexasilabenzpolarene is accessible by reductive cleavage of one of the Tip groups of the perarylated derivative, while the ligato lithiated isomer had been obtained from the dismutational isomer previously. The privo derivative is shown to be an equally suitable nucleophilic reagent for the transfer of the uncompromised benzpolarene framework. The electronic influence of the functional groups in two distinct positions is rationalized on the basis of linear correlations with the Hammett parameter  $\sigma_{\rm m}$ . With the possibility of functionalization in different positions of the Si<sub>6</sub> scaffold the construction of larger systems comprising Si6 siliconoid motifs has become a viable option, which is currently being investigated in our laboratory.

### Conflicts of interest

There are no conflicts to declare.

### Acknowledgements

Funding by the Deutsche Forschungsgemeinschaft (DFG SCHE906/4-1 and 4-2) and COST Action CM1302 (Smart Inorganic Polymers) is gratefully acknowledged.

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