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# One-Step Synthesis of a [20]Silafullerane with an Endohedral Chloride Ion**

*Jan Tillmann, Josef Heinrich Wender, Ute Bahr, Michael Bolte, Hans-Wolfram Lerner, Max C. Holthausen,* and Matthias Wagner**

*Dedicated to Professor Manfred Scheer on the occasion of his 60th birthday*

**Abstract:** *Silicon analogues of the most prominent carbon nanostructures, namely, hollow spheroidals such as $C_{60}$ and the fullerene family, have been unknown to date. Herein we show that discrete $Si_{20}$ dodecahedra, stabilized by an endohedral guest and valence saturation, are accessible in preparative yields through a chloride-induced disproportionation reaction of hexachlorodisilane in the presence of tri(n-butyl)amine. X-ray crystallography revealed that each silicon dodecahedron contains an endohedral chloride ion that imparts a net negative charge. Eight chloro substituents and twelve trichlorosilyl groups are attached to the surface of each cluster in a strictly regioregular arrangement, a thermodynamically preferred substitution pattern according to quantum-chemical assessment. Our results demonstrate that the wet-chemical self-assembly of a complex, monodisperse Si nanostructure is possible under mild conditions starting from simple $Si_2$ building blocks.*

Silicon is an essential material for the vast majority of electronic devices. Today's pervasive incorporation of digital technology into equipment of daily use and the increasing demand for lightweight, portable digital gadgets requires continuing miniaturization of all the components. As current silicon micropatterning methods, such as photolithography for the fabrication of integrated circuits, are approaching their natural limits, novel bottom-up strategies based on nanoscale silicon building blocks are required. In the case of the lower homologue carbon, the chemistry of 1D (e.g. *trans*-polyacetylene), 2D (e.g. graphene), and microtubular (e.g. buckytubes) nanomaterials is well established. By comparison, structurally defined linear polysilanes, silicon nanosheets, nanotubes, and clusters still mark new frontiers in an emerging field of research.[1] First and foremost, the discovery of $C_{60}$ and the fullerenes triggered the quest for their all-silicon analogues. However, despite the contiguity of carbon and silicon in the same group of the periodic table, their bonding behavior exhibits characteristic differences: While carbon atoms readily adjust their valence states to participate in single, double, and triple bonds, silicon atoms strongly prefer $sp^3$ hybridization and single bonds. Correspondingly, while the smallest possible fullerene molecule, the $C_{20}$ dodecahedron, does exist,[2] quantum-chemical predictions characterize the corresponding $Si_{20}$ fullerene as a highly unstable species.[3,4] A large body of theoretical work has convincingly shown that the architecture of thermodynamically stable silicon clusters is dominated by the compulsive tendency of silicon atoms to engage in fourfold binding interactions. For cluster sizes between 18 and 25 atoms, theory predicts low-energy prolate or oblate cluster shapes, both comprised of irregular, densely packed substructures containing a few highly coordinated atoms.[5,6]

While these results make the existence of stable all-silicon fullerenes unlikely, theory proposes two modes of stabilization of an $Si_{20}$ fullerene core: One concept rests upon the incorporation of a metal atom into the Si cage (e.g. $Th@Si_{20}$).[7–9] However, for most $M@Si_{20}$ fullerenes this strategy still falls short, as distorted or thermodynamically metastable structures are computed.[10–12] The second approach is based on the introduction of exohedral substituents to fully satisfy all four silicon valencies, and, indeed, an $I_h$-symmetric silafullerane cage has been identified as the $Si_{20}H_{20}$ global minimum.[13–15] A combination of both stabilizing factors should lead to particularly stable species, such as $E@Si_{20}H_{20}$, where $E = M$ or a halide ion.[16–18] Compared to the metal-encapsulated silicon cages $M@Si_{20}$, the host–guest interactions in the hydrogenated silicon fullerenes $M@Si_{20}H_{20}$ tend to be significantly weaker.[19]

In contrast to the plethora of theoretical studies on $Si_{20}H_{20}$, no experimental data are available for the parent compound or any of its derivatives, because $Si_{20}$ fulleroids

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[*] Dipl.-Chem. J. Tillmann, Dipl.-Chem. J. H. Wender, Dr. M. Bolte, Dr. H.-W. Lerner, Prof. Dr. M. C. Holthausen, Prof. Dr. M. Wagner
Institut für Anorganische Chemie, Goethe-Universität Frankfurt
Max-von-Laue-Strasse 7, 60438 Frankfurt (Main) (Germany)
E-mail: Max.Holthausen@chemie.uni-frankfurt.de
Matthias.Wagner@chemie.uni-frankfurt.de

Dr. U. Bahr
Institut für Pharmazeutische Chemie, Goethe-Universität Frankfurt
Max-von-Laue-Strasse 9, 60438 Frankfurt (Main) (Germany)

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have remained inaccessible to date. A glance at their carbon congener, dodecahedrane ($C_{20}H_{20}$), immediately reveals some of the challenges that would make the total synthesis of $Si_{20}$ fulleroids a formidable task: Paquette's milestone approach to dodecahedrane, at that time regarded as the "Mount Everest of alicyclic chemistry", requires 23 reaction steps and uses C=C unsaturated and carbanionic intermediates[20]—a comparably versatile synthetic set of intermediates is not available in silicon chemistry. On the other hand, the $Si_{20}$ dodecahedron occurs as a recurring structural motif within the expanded covalent frameworks of face-sharing polyhedra in the silicon clathrates $M_8Si_{46}$ and $M_xSi_{136}$ ($x \leq 24$; M = e.g. alkali metals).[21,22] Such alkali-metal-doped clathrates are accessible through thermal treatment of the corresponding Zintl phases, MSi, in an inert atmosphere.[23] We took this as an indication that a self-assembly strategy might be feasible to also prepare discrete, molecular silicon fulleroids. Along these lines, a further clue was provided by Pichierri et al., who explicitly predicted that halide ions, especially $Br^-$, are ideally suited to the anion-templated synthesis of $Si_{20}H_{20}$.[17]

Our research groups have already shown that the chloride-induced disproportionation reaction of hexachlorodisilane ($Si_2Cl_6$) furnishes perchlorinated cyclohexasilanes in preparatively useful yields.[24] We identified a dual role of $Cl^-$ ions in this self-assembly of higher oligosilanes: Apart from mediating the reaction, $Cl^-$ ions also play a structure-determining role, as they finally coordinate above and below the ring center, which provides the necessary thermodynamic thrust towards the formation of the cyclohexasilanes from a mixture of equilibrating oligosilanes. In this and related[25] cases, the underlying dynamic covalent chemistry strongly depends on the reaction temperature, the solvent, the stoichiometric reactant ratio, and the presence of additives such as tertiary amines. A systematic variation of these parameters ultimately allowed us to shift the course of the reaction from the mere production of six-membered ring structures to the generation of the first $Si_{20}$ dodecahedrane. In the optimized procedure, $Si_2Cl_6$ (20 equiv), $[nBu_4N]Cl$ (2 equiv), and $nBu_3N$ (1 equiv) react at room temperature in $CH_2Cl_2$ solution to furnish $[nBu_4N][Si_{32}Cl_{45}]$ in 27% yield (see the idealized balanced Equation (1) and the Supporting Information).

$$42\,Si_2Cl_6 + [R_4N]Cl \xrightarrow{\text{cat. } nBu_3N} [R_4N][Si_{32}Cl_{45}] + 52\,SiCl_4 \tag{1}$$

The literature-known cyclohexasilane chloride diadduct $[nBu_4N]_2[1,1\text{-}(SiCl_3)_2Si_6Cl_{10}\cdot 2\,Cl]$[24] forms as the major other product. Both compounds are separable by fractional crystallization. X-ray analysis firmly established the silafullerane cage as part of the $[nBu_4N][Si_{32}Cl_{45}]$ lattice. The use of the preparatively much less productive $[Et_4N]Cl$ as the chloride source avoided severe cation disorder in the solid state; we therefore discuss below structural parameters of $[Si_{32}Cl_{45}]^-$ from a high-quality $[Et_4N][Si_{32}Cl_{45}]\cdot 2\,SiCl_4$ crystal. Otherwise the choice of counterion has no noticeable structure-determining influence (see also the Supporting Information). For solubility reasons and because of the better availability of the compound, samples of $[nBu_4N][Si_{32}Cl_{45}]$ have been employed for all other investigations.

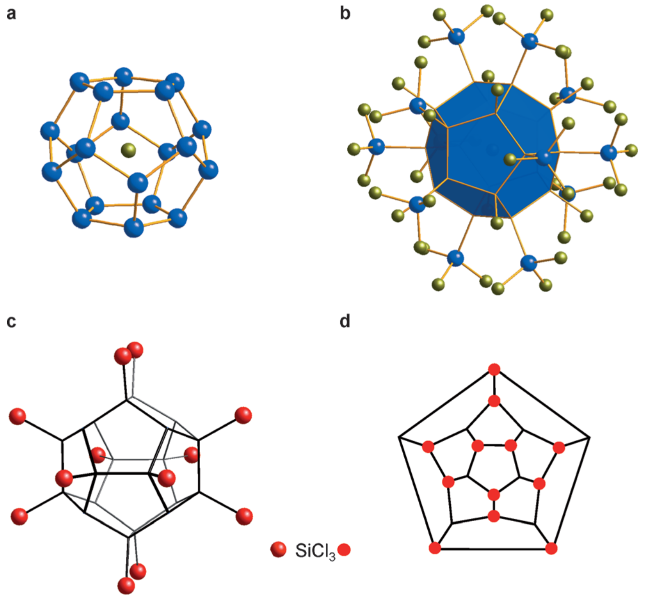
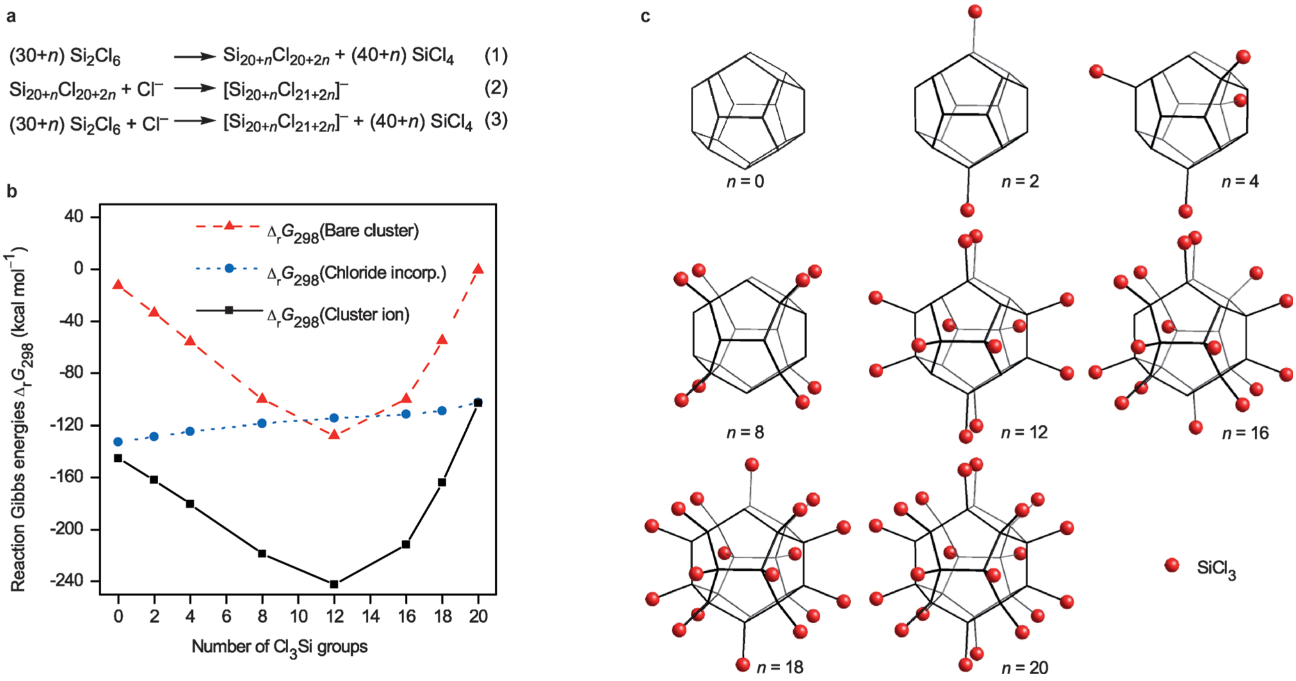


***Figure 1.*** Molecular structure of the silafullerane $[Si_{32}Cl_{45}]^-$.[27] a) Dodecahedral core with an endohedral $Cl^-$ ion. b) Full structure including substituents. c) Plot showing the pairwise octahedral arrangement of the twelve $Cl_3Si$ groups. d) Schlegel diagram illustrating the equivalence of all twelve five-membered rings (each of the red filled circles represents one $Cl_3Si$ substituent attached to an $Si^0$ cluster atom).

The $[Si_{32}Cl_{45}]^-$ cluster consists of a $Si_{20}$ dodecahedral core with an endohedral $Cl^-$ ion, from which the molecule acquires its net negative charge (Figure 1a). The largest nucleus-to-nucleus diameter spanning the silicon cage is 6.65 Å ($C_{60}$: 7.07 Å)[26] and the inner free volume amounts to 7.6 Å$^3$ (after removal of the endohedral $Cl^-$ ion and taking into consideration a van der Waals radius of 2.10 Å for the silicon atoms). The experimentally determined Si–Si bond lengths of the cage fall in the narrow range between 2.343(2) Å and 2.360(2) Å, and these metrics are in accord with those of the DFT-optimized structure ($Si^0$–$Si^0$: 2.360 Å, $Si^I$–$Si^0$: 2.371 Å). None of the endocyclic Si-Si-Si bond angles in either the X-ray or the DFT structure deviates by more than 3° from the ideal tetrahedral angle (109.5°), which illustrates why the dodecahedral framework is ideally suited to meet the geometric requirements of tetravalent Si atoms. The $Si_{20}$ core carries eight chloro and twelve trichlorosilyl substituents that saturate all four valencies of the silicon cluster atoms (Figure 1b). The perfection with which precisely twelve $Cl_3Si$ groups in $[Si_{32}Cl_{45}]^-$ are arranged pairwise towards the vertices of an octahedron (Figure 1c) is particularly remarkable and offers unique opportunities for the future fabrication of highly ordered silicon nano-networks. Finally, the Schlegel diagram (Figure 1d) illustrates the equivalence of all the five-membered rings constituting the substituted dodecahedron.

To understand the origin of the $T_h$-symmetric arrangement of $Cl_3Si$ substitutents, we studied the thermodynamic influence of different silyl substitution patterns and the endohedral $Cl^-$ ion on the silafullerane core by quantum-chemical means based on the set of idealized reactions shown



$$(30+n)\ Si_2Cl_6 \longrightarrow Si_{20+n}Cl_{20+2n} + (40+n)\ SiCl_4 \quad (1)$$

$$Si_{20+n}Cl_{20+2n} + Cl^- \longrightarrow [Si_{20+n}Cl_{21+2n}]^- \quad (2)$$

$$(30+n)\ Si_2Cl_6 + Cl^- \longrightarrow [Si_{20+n}Cl_{21+2n}]^- + (40+n)\ SiCl_4 \quad (3)$$

***Figure 2.*** Relative thermodynamic stabilities computed by employing double-hybrid DFT for [20]silafulleranes bearing different numbers (*n*) of exohedral trichlorosilyl substituents. a) Generalized (isodesmic) reaction equations depending on the number of $Cl_3Si$ substitutents for the formation of the empty silafullerane cages $Si_{20+n}Cl_{20+2n}$ from $Si_2Cl_6$ (1), the incorporation of the endohedral chloride ion (2), and the overall formation of silicon cluster ions $[Si_{20+n}Cl_{21+2n}]^-$ from $Si_2Cl_6$ and $Cl^-$ (3). b) Reaction Gibbs energies $\Delta_r G_{298}$ computed at the B2GP-PLYP-D/TZVPP level for reaction 1 (red graph), 2 (blue graph), and 3 (black graph). c) Plots illustrating the arrangements of $Cl_3Si$ groups on the cluster surface.

in Figure 2a. The replacement of up to twelve Cl substituents in $Si_{20}Cl_{20}$ by $Cl_3Si$ groups exerts an almost linear thermodynamic stabilization on the resulting clusters, with an increment of about $-11$ kcal mol$^{-1}$ per $Cl_3Si$ group (Figure 2b,c). Beyond this point, increased steric repulsion results in decreased cluster stabilities, which clearly documents the thermodynamic preference brought about by the experimentally observed substitution pattern. Encapsulation of a $Cl^-$ ion is strongly exergonic in all cases, but slightly less so as the degree of silyl substitution increases. In terms of the two fundamental concepts mentioned above for stabilization of the $Si_{20}$ cluster, we conclude that the effect of twelve exohedral $Cl_3Si$ groups is on a par with that of one endohedral $Cl^-$ ion and that their joint contributions render the experimentally observed structure particularly favorable.

A characteristic of the bulk material is that only three signals occur in the $^{29}Si$ NMR spectrum ($[D_8]$THF) of $[nBu_4N][Si_{32}Cl_{45}]$, in line with the proposed highly symmetric substituted silafullerane structure ($T_h$). The experimental (computed) chemical shift values of 31.1 (30.1), 10.3 (13.5), and $-60.3$ ($-63.3$) ppm correspond to the $Si^I$, $Si^{III}$, and $Si^0$ centers, respectively (Figure 3a).

A first hint at the reactivity of the $[Si_{32}Cl_{45}]^-$ cluster ions was obtained in a laser-desorption ionization (LDI) MS(−) experiment. Apart from the molecular ion signal at $m/z = 2492.8$ (correct isotope pattern; Figure 3b), a number of additional equidistant signals ($\Delta(m/z) = 99.0$) originate from a major fragmentation cascade resulting from multiple extrusions of $\{SiCl_2\}$ (see the Supporting Information); in this way, $Cl_3Si$ groups are successively transformed into Cl substituents. Tandem mass-spectrometry on mass-selected $[Si_{32}Cl_{45}]^-$ ions reveals a dominant signal for the $[Si_{31}Cl_{43}]^-$ ion after collision with He gas. Consequently, $\{SiCl_2\}$ extrusion from the molecular ion represents a viable dissociation path under gas-phase conditions, for example, inside the laser plume of the spectrometer source.

To demonstrate the fundamental ability of the [20]silafullerane to form derivatives, we carried out exhaustive Si−Cl/Si−H exchange. Upon reaction of $[nBu_4N][Si_{32}Cl_{45}]$ with $Li[AlH_4]$, the three $^{29}Si$ NMR signals attributable to the starting material vanished and three new resonances appeared at $-10.8$ (dm; SiH), $-58.9$ (s; Si), and $-93.5$ ppm (q; $SiH_3$). LDIMS(−) analysis of the evaporated reaction mixture revealed signals at $m/z = 168.9$ ($[AlCl_4]^-$) and $m/z = 977.5$ ($[Si_{32}H_{44}Cl]^-$). In conclusion: 1) an Al−H/Al−Cl exchange has taken place, 2) the Si−Cl/Si−H exchange is not restricted to the twelve $Cl_3Si$ groups but also involves the eight Si−Cl cluster vertices, and 3) the cage remained intact, because the endohedral $Cl^-$ ion was still present.

The one-step synthesis of the first [20]silafullerane paves the way to develop the chemistry of monodisperse nanoscale oligosilanes. Envisioning the most obvious next steps, we anticipate that the well-oriented $Cl_3Si$ substituents can be used as anchor groups for the targeted bottom-up fabrication of nanostructured 3D networks. Connectivity patterns and dimensionality may be tailored through a posteriori $\{SiCl_2\}$ extrusion from the parent $[Si_{32}Cl_{45}]^-$ ion. Also, variation of the endohedral guest could give access to [20]silafulleranes with

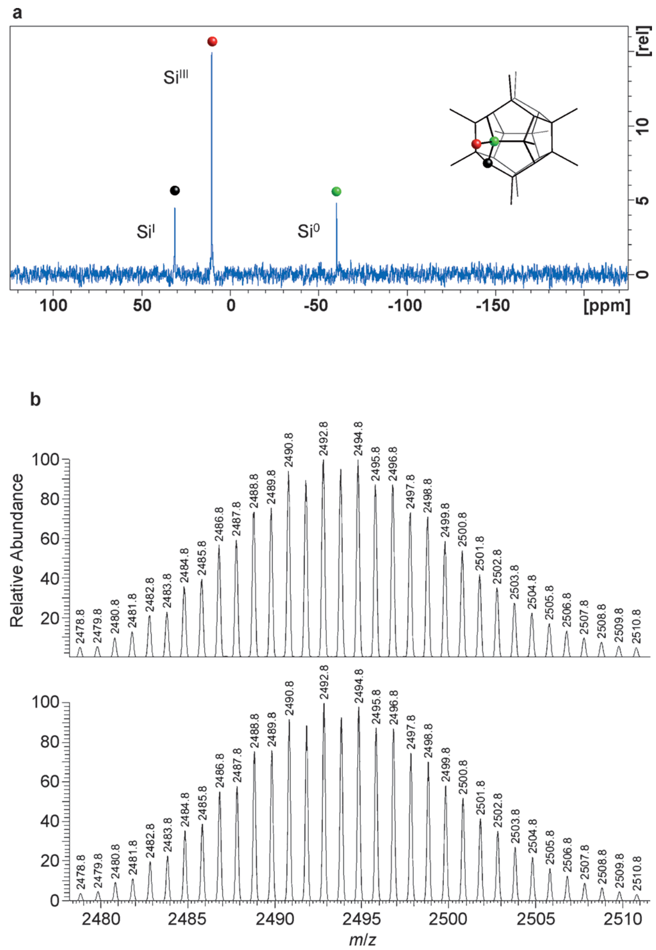


***Figure 3.*** NMR and mass spectra. a) $^{29}$Si NMR spectrum (99.4 MHz, [D$_8$]THF) of [$n$Bu$_4$N][Si$_{32}$Cl$_{45}$]. b) Isotopic pattern of the molecular ion signal of the silafullerane [Si$_{32}$Cl$_{45}$]$^-$ (top: LDI(−) mass spectrum; bottom: simulated signal pattern).

adjustable spin and charge properties. The novel [20]silafullerane thus provides a long-awaited molecular basis to study the fundamental characteristics of cage-shaped silicon nanoparticles, such as the influence of the strictly confined three-dimensional space on their electronic structure.

## *Experimental Section*

All reactions were carried out under dry argon or nitrogen using standard Schlenk or glove box techniques. CH$_2$Cl$_2$ was dried over CaH$_2$ and freshly distilled prior to use; [D$_8$]THF was dried over molecular sieves (4 Å). Si$_2$Cl$_6$, $n$Bu$_3$N, [Et$_4$N]Cl, [$n$Bu$_4$N]Cl, and [Ph$_4$P]Cl were purchased from commercial sources; the salts were dried in a dynamic vacuum at room temperature for 2 days. In rare cases, in which a batch of chloride salt was found to contain significant amounts of water, we prepared a calibrated solution in CH$_2$Cl$_2$ and stored it over molecular sieves (3 Å). Commercially obtained batches of [$n$Bu$_4$N]Cl were usually contaminated with trace amounts of KCl. [$n$Bu$_4$N]Cl was, therefore, routinely dissolved in CH$_2$Cl$_2$ and the insoluble KCl was removed by filtration. Elemental analyses were performed at the microanalytical laboratory Pascher, Remagen, Germany.

Synthesis of [$n$Bu$_4$N][Si$_{32}$Cl$_{45}$]: In a representative experiment, a screw-capped Schott vial was charged in an argon-filled glove box with [$n$Bu$_4$N]Cl (1.0 g, 3.6 mmol), Bu$_3$N (0.36 g, 1.9 mmol), and CH$_2$Cl$_2$ (9 mL). Neat Si$_2$Cl$_6$ (6.4 mL, 10 g, 37 mmol) was added by syringe in one portion with stirring at room temperature. The initially colorless solution immediately turned yellow. Stirring was continued for 2 days, whereupon the color of the solution intensified to orange-brown and a colorless precipitate formed. The precipitate was removed by filtration and found to consist mainly of the known cyclohexasilane chloride adduct [$n$Bu$_4$N]$_2$[1,1-(SiCl$_3$)$_2$Si$_6$Cl$_{10}$·2 Cl][24] ($^{29}$Si NMR spectroscopic control, X-ray diffraction). The slightly turbid filtrate was diluted with CH$_2$Cl$_2$ (10 mL) and the resulting clear solution was stored in a screw-capped Schott vial. After approximately one week, colorless single crystals had grown (columnar habitus with a hexagonal base). The brown mother liquor was decanted and the crystal crop was washed with CH$_2$Cl$_2$ (4×5 mL). Yield of [$n$Bu$_4$N][Si$_{32}$Cl$_{45}$]·2 CH$_2$Cl$_2$: 0.70 g (0.24 mmol; 27 %). $^{29}$Si NMR (99.4 MHz, [D$_8$]THF, see Figure 3 a): $\delta = 31.1$ (Si$^{\mathrm{I}}$), 10.3 (Si$^{\mathrm{III}}$), −60.3 ppm (Si$^0$); $^{13}$C{$^1$H} NMR (125.8 MHz, [D$_8$]THF): $\delta =$ 59.1 (N-CH$_2$) 24.3 (N-CH$_2$-*C*H$_2$), 20.4 (*C*H$_2$-CH$_3$), 13.8 ppm (CH$_2$-*C*H$_3$); $^1$H NMR (500.2 MHz, [D$_8$]THF): $\delta = 3.25$ (m, 8 H), 1.69 (m, 8 H), 1.42 (m, 8 H), 1.02 ppm (t, $J = 7.3$ Hz, 12 H); LDIMS(−): $m/z =$ 2492.8 [Si$_{32}$Cl$_{45}$]$^-$; LDIMS(+): $m/z = 242.3$ [$n$Bu$_4$N]$^+$. Elemental analysis calcd (%) for [$n$Bu$_4$N][Si$_{32}$Cl$_{45}$] [2736.58]·2 CH$_2$Cl$_2$ [84.93]: C 7.44, H 1.39, Cl 53.7 (hydrolyzable Cl), N 0.48, Si 31.0; found: C 7.46, H 1.53, Cl 54.2, N 0.42, Si 30.5. The presence of cocrystallized CH$_2$Cl$_2$ solvent molecules was proven by NMR spectroscopy. For a powder X-ray diffractogram see the Supporting Information.

**Keywords:** density functional calculations · nanostructures · self-assembly · silafulleranes · silanes

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[27] CCDC 1033606 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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