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ARTICLE

Halide-Ion Diadducts of Perhalogenated Cyclopenta- and Cyclohexasilanes

Julian Teichmann,[a] Benedikt Köstler,[a] Jan Tillmann,[a] Maximilian Moxter,[a] Robin Kupec,[a] Michael Bolte,[a] Hans-Wolfram Lerner,*[a] and Matthias Wagner*[a]

Dedicated to Prof. Alexander C. Filippou on the Occasion of his 60th Birthday

Abstract. The halosilicates(II) $[n\mathrm{Bu_4N}]_2[\mathrm{Si_6Br_{12}{\cdot}2Br}]$ and $[n\mathrm{Bu_4P}]_2[\mathrm{Si_6I_{12}{\cdot}2I}]$ were prepared by mere addition of the appropriate halide salt to the corresponding disilane $\mathrm{Si_2}X_6$ (X = Br, I). In the first case, the $\mathrm{Br_3Si}$-substituted derivative $[n\mathrm{Bu_4N}]_2[\mathrm{Si_7Br_{14}{\cdot}2Br}]$ formed as a second product. We have been able to obtain single crystals of $[\mathrm{Ph_4P}]_2[\mathrm{Si_7Br_{14}{\cdot}2Br}]$ by switching the $\mathrm{Br^-}$ salt from $[n\mathrm{Bu_4N}]\mathrm{Br}$ to $[\mathrm{Ph_4P}]\mathrm{Br}$. All three compounds, $[n\mathrm{Bu_4N}]_2[\mathrm{Si_6Br_{12}{\cdot}2Br}]$ (monoclinic, $P2_1/c$), $[n\mathrm{Bu_4P}]_2[\mathrm{Si_6I_{12}{\cdot}2I}]$ (triclinic, $P\bar{1}$), and $[\mathrm{Ph_4P}]_2[\mathrm{Si_7Br_{14}{\cdot}2Br}]$ (triclinic, $P\bar{1}$) were structurally characterized by X-ray crystallography and found to form "inverse sandwich complexes", in which two X^- ions are located above and below a planarized $\mathrm{Si_6}$ ring. The free periodated cyclohexasilane $\mathrm{Si_6I_{12}}$ is accessible from $[n\mathrm{Bu_4N}]_2[\mathrm{Si_6Cl_{12}{\cdot}2Cl}]$ and $\mathrm{BI_3}$ (1:5 molar ratio; $\mathrm{CH_2Cl_2}$) via a decomplexation/halide-exchange cascade. $\mathrm{Si_6I_{12}}$ (monoclinic, $C2/c$) adopts a puckered chair conformation in the solid state. The cyclopentasilane diadduct $[n\mathrm{Bu_4P}]_2[\mathrm{Si_5Cl_{10}{\cdot}2Cl}]$ forms at –78 °C from $\mathrm{Si_5Cl_{10}}$ and 2 equiv. of $[n\mathrm{Bu_4P}]\mathrm{Cl}$ in $\mathrm{CH_2Cl_2}$. An X-ray analysis of $[n\mathrm{Bu_4P}]_2[\mathrm{Si_5Cl_{10}{\cdot}2Cl}]{\cdot}2\mathrm{CH_2Cl_2}$ (monoclinic, $C2/c$) again revealed the structure of an "inverse sandwich complex". Crystalline $[n\mathrm{Bu_4P}]_2[\mathrm{Si_5Cl_{10}{\cdot}2Cl}]{\cdot}2\mathrm{CH_2Cl_2}$ is stable at room temperature. However, in $\mathrm{CH_2Cl_2}$ solution the compound quantitatively undergoes ring-expansion reactions to furnish cyclohexasilane derivatives. This behavior is in striking contrast to that of $[n\mathrm{Bu_4N}]_2[\mathrm{Si_6Cl_{12}{\cdot}2Cl}]$, which persists at room temperature both in solution and the solid state. Competition experiments revealed free $\mathrm{Si_5Cl_{10}}$ and $\mathrm{Si_6Cl_{12}}$ to have comparable $\mathrm{Cl^-}$ affinities, even though the distance between the two apical $\mathrm{Cl^-}$ ions in $[\mathrm{Si_5Cl_{10}{\cdot}2Cl}]^{2-}$ (4.292 Å) is larger by 0.456 Å than that in $[\mathrm{Si_6Cl_{12}{\cdot}2Cl}]^{2-}$ (3.836 Å).

Introduction

Perhalogenated oligosilanes are of great technological importance, because they find use in the synthesis of silicon-containing polymers and also as precursor molecules for the deposition of amorphous or crystalline silicon.[1] A deeper understanding of the intrinsic properties of perhalogenated oligosilanes can best be gained by investigating samples of monodisperse, cyclic species to avoid spurious chain-length and end-group effects. The classical route to cyclic oligosilanes Si_nX_{2n} (n = 4, 5, 6; X = Cl, Br, I) proceeds via phenyl/halogen exchange on $\mathrm{Si}_n\mathrm{Ph}_{2n}$ using HX in the presence of $\mathrm{Al}X_3$.[2–5] The required perphenylated cyclosilanes are typically prepared through Wurtz-type coupling of $\mathrm{Ph_2SiCl_2}$ with alkali metals.[6,7] However, the coupling reaction is not size-selective and mixtures of $\mathrm{Si_4Ph_8}$, $\mathrm{Si_5Ph_{10}}$ (main product), and $\mathrm{Si_6Ph_{12}}$ are usually obtained, which poses problems with regard to product separation and reduces the product yields.[6–8]

In 2001, *Boudjouk* et al. reported an alternative synthesis of $\mathrm{Si_6Cl_{12}}$, starting from $\mathrm{HSiCl_3}$ and pedeta in $\mathrm{CH_2Cl_2}$ (40 °C, 48 h; pedeta = 1,1,4,7,7-pentaethyldiethylenetriamine).[9] The compound was isolated in the form of the chlorosilicate(II) "inverse sandwich complex" $[(\mathrm{pedeta})\mathrm{H_2SiCl}]_2[\mathrm{Si_6Cl_{12}{\cdot}2Cl}]$, in which two additional $\mathrm{Cl^-}$ ions are coordinated in μ^6 modes above and below the planarized $\mathrm{Si_6}$ ring. The chloride diadduct can be converted to parent cyclohexasilane, $\mathrm{Si_6H_{12}}$, by employing $\mathrm{LiAlH_4}$ as the hydride source.[9,10] Subsequent treatment of $\mathrm{Si_6H_{12}}$ with elemental $\mathrm{Cl_2}$ or $\mathrm{Br_2}$ at low temperatures results in exhaustive H/X exchange to afford $\mathrm{Si_6Cl_{12}}$ or $\mathrm{Si_6Br_{12}}$, respectively.[2,5,10,11]

Recently, our group has established convenient access to $[\mathrm{Si_6Cl_{12}{\cdot}2Cl}]^{2-}$ and to its $\mathrm{Cl_3Si}$-substituted congeners $[\mathrm{Si_7Cl_{14}{\cdot}2Cl}]^{2-}$ and $[\mathrm{Si_8Cl_{16}{\cdot}2Cl}]^{2-}$ via the chloride-induced disproportionation of $\mathrm{Si_2Cl_6}$ (Scheme 1).[12–14] We also found ways to liberate the free cyclohexasilane $\mathrm{Si_6Cl_{12}}$ from $[\mathrm{Si_6Cl_{12}{\cdot}2Cl}]^{2-}$ by means of $\mathrm{AlCl_3}$.[15] It turned out that the Lewis acidity of $\mathrm{Si_6Cl_{12}}$ is comparable to that of $\mathrm{BCl_3}$,[15] and a number of stable diadducts with Lewis bases (L) other than the $\mathrm{Cl^-}$ ion have been reported.[10,11]

The information gathered so far on Si_nX_{2n} immediately raises the following questions, which are answered in this paper:

(1) Is it possible to prepare also the bromo- and iodosilicates(II) $[\mathrm{Si_6}X_{12}{\cdot}2X]^{2-}$ (X = Br, I) in ways similar to the synthesis of $[\mathrm{Si_6Cl_{12}{\cdot}2Cl}]^{2-}$ from $\mathrm{Si_2Cl_6/Cl^-}$?

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* Dr. H.-W. Lerner
Fax: +49 69 79829260
E-Mail: lerner@chemie.uni-frankfurt.de
* Prof. Dr. M. Wagner
E-Mail: matthias.wagner@chemie.uni-frankfurt.de
[a] Institut für Anorganische Chemie
Goethe-Universität Frankfurt
Max-von-Laue-Str. 7
60438 Frankfurt, Germany

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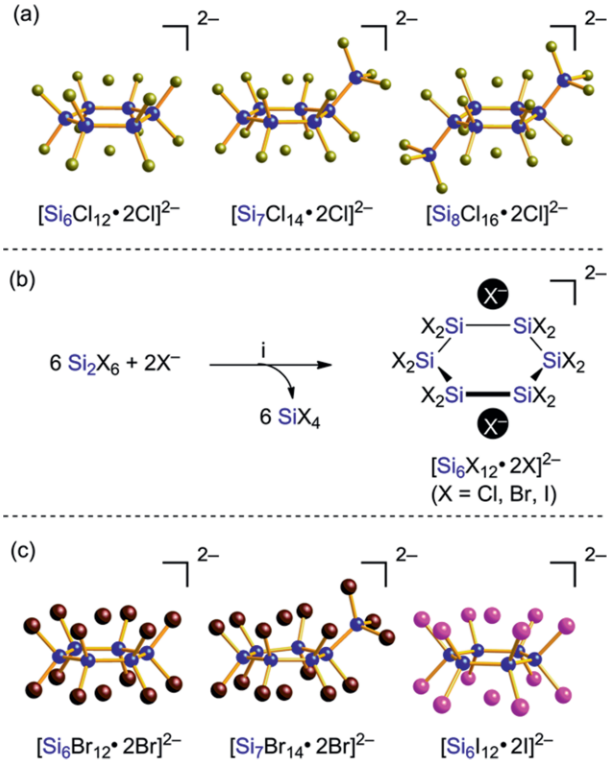


Scheme 1. (a) Solid-state structures of $[n\mathrm{Bu_4N}]_2[\mathrm{Si_6Cl_{12}{\cdot}2Cl}]$ and its $\mathrm{Cl_3Si}$-substituted congeners $[\mathrm{Ph_4P}]_2[\mathrm{Si_7Cl_{14}{\cdot}2Cl}]$ and $[\mathrm{Ph_4P}]_2[\mathrm{Si_8Cl_{16}{\cdot}2Cl}]$ (cations omitted for clarity).[13] (b) Synthesis of $[\mathrm{Si_6}X_{12}{\cdot}2X]^{2-}$ through disproportionation of $\mathrm{Si_2}X_6$ (X = Cl, Br, I) with the corresponding X^- ions; in the cases of X = Cl, Br, several $X_3\mathrm{Si}$-substituted derivatives are formed in addition to the perhalogenated cyclohexasilanes (i: $\mathrm{CH_2Cl_2}$, room temperature or 80 °C). (c) Solid-state structures of $[n\mathrm{Bu_4N}]_2[\mathrm{Si_6Br_{12}{\cdot}2Br}]$, $[\mathrm{Ph_4P}]_2[\mathrm{Si_7Br_{14}{\cdot}2Br}]$, and $[n\mathrm{Bu_4P}]_2[\mathrm{Si_6I_{12}{\cdot}2I}]$ (cations omitted for clarity).

(2) Is the stability of chlorosilicates(II) ring-size dependend and can, apart from $[\mathrm{Si_6Cl_{12}{\cdot}2Cl}]^{2-}$, also the cyclopentasilane diadduct $[\mathrm{Si_5Cl_{10}{\cdot}2Cl}]^{2-}$ be isolated and fully characterized?

Results and Discussion

Synthesis and Characterization of $[\mathrm{Si_6}X_{12}{\cdot}2X]^{2-}$, Starting from $\mathrm{Si_2}X_6/X^-$ (X = Br, I)

The precursor compounds $\mathrm{Si_2Br_6}$[16] and $\mathrm{Si_2I_6}$,[17] were prepared according to literature procedures. From a broad variety of available soluble halide salts, $[n\mathrm{Bu_4N}]\mathrm{Br}$, $[\mathrm{Ph_4P}]\mathrm{Br}$, or $[n\mathrm{Bu_4P}]\mathrm{I}$ were chosen such as to generate the reaction product with the highest degree of crystallinity.

First, we investigated the reactions of $\mathrm{Si_2Br_6}$ with $[n\mathrm{Bu_4N}]\mathrm{Br}$ and $[\mathrm{Ph_4P}]\mathrm{Br}$, respectively. Treatment of $\mathrm{Si_2Br_6}$ with $[n\mathrm{Bu_4N}]\mathrm{Br}$ (8:3 molar ratio; $\mathrm{CH_2Cl_2}$) resulted in an immediate reaction, whereupon the mixture quickly became heterogeneous. A $^{29}\mathrm{Si}$ NMR spectrum showed that the resonance of $\mathrm{Si_2Br_6}$ [$\delta(^{29}\mathrm{Si}) = -35.9$ ppm][16] had completely vanished. Newly developed signals were assignable to $\mathrm{SiBr_4}$ [$\delta(^{29}\mathrm{Si}) = -90.2$; lit: –92.7 ppm[18]] and the bromosilicates(II) $[\mathrm{Si_6Br_{12}{\cdot}2Br}]^{2-}$ [$\delta(^{29}\mathrm{Si}) = -38.1$; lit: –37.4 ppm[11,19]] and $[\mathrm{Si_7Br_{14}{\cdot}2Br}]^{2-}$ (Scheme 1). $[n\mathrm{Bu_4N}]_2[\mathrm{Si_6Br_{12}{\cdot}2Br}]$ could be separated from $[n\mathrm{Bu_4N}]_2[\mathrm{Si_7Br_{14}{\cdot}2Br}]$ and $\mathrm{SiBr_4}$ by crystallization. $[n\mathrm{Bu_4N}]_2[\mathrm{Si_6Br_{12}{\cdot}2Br}]$ crystallizes in the monoclinic space group $P2_1/c$ and represents a polymorph of a published structure (the latter sample had been prepared through the addition of $[n\mathrm{Bu_4N}]\mathrm{Br}$ to free $\mathrm{Si_6Br_{12}}$).[11] In the solid state, $[n\mathrm{Bu_4N}]_2[\mathrm{Si_6Br_{12}{\cdot}2Br}]$ reveals an essentially planar $\mathrm{Si_6}$ ring (rms deviation: 0.026 Å; average Si–Si bond length = 2.342 Å). Two $\mathrm{Br^-}$ anions are located above and below the ring centroid (COG) with distances of 2.061 Å and 2.059 Å for COG···Br(1) and COG···Br(2), respectively (Scheme 1; selected bond lengths and angles are listed in the caption of Figure 1S, Supporting Information). The distances of the apical Br(1) and Br(2) ions to the Si atoms within the six-membered ring (average value: 3.12 Å) are shorter than the sum of the van der Waals radii [r_{vdw}(SiBr): 3.95 Å],[20] but longer than the sum of the covalent radii [r_{cov}(SiBr): 2.31 Å].[21]

Overall, the structural parameters of our $[\mathrm{Si_6Br_{12}{\cdot}2Br}]^{2-}$ dianion are close to those found in the polymorphic structure (triclinic, $P\bar{1}$).[11] The main difference between the two polymorphs is that the triclinic structure has just half a $\mathrm{Si_6Br_{12}}$ molecule, one $\mathrm{Br^-}$ anion and one $[n\mathrm{Bu_4N}]^+$ cation in the asymmetric unit, whereas the asymmetric unit of the monoclinic polymorph contains one complete $\mathrm{Si_6Br_{12}}$ molecule, two $\mathrm{Br^-}$ anions and two $[n\mathrm{Bu_4N}]^+$ cations. In the triclinic polymorph, the planes of all $\mathrm{Si_6}$ rings are exactly coplanar; in the monoclinic structure, half of the ring planes are tilted by 43.9° with respect to the other half. The distance between the $\mathrm{Br^-}$ anion and the N atom of the $[n\mathrm{Bu_4N}]^+$ cation is shorter in the triclinic (4.71 Å) than in the monoclinic form (average value: 5.05 Å). In the triclinic form, all four N–C–C–C torsion angles adopt a *trans* conformation, whereas in the monoclinic form, one of the eight N–C–C–C torsion angles adopts a gauche conformation.

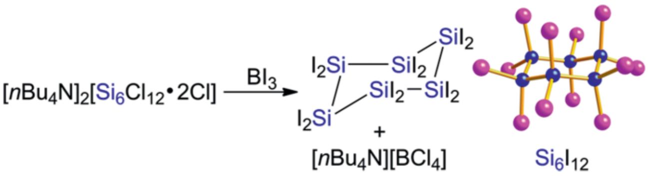
The reaction of $\mathrm{Si_2Br_6}$ with a solution of $[\mathrm{Ph_4P}]\mathrm{Br}$ in $\mathrm{CD_2Cl_2}$ again led to the bromosilicate(II) anions $[\mathrm{Si_6Br_{12}{\cdot}2Br}]^{2-}$ and $[\mathrm{Si_7Br_{14}{\cdot}2Br}]^{2-}$ and to $\mathrm{SiBr_4}$ as necessary byproduct (Scheme 1). The disilane was quantitatively consumed after 1 h at room temperature ($^{29}\mathrm{Si}$-NMR spectroscopic control). Single crystals of $[\mathrm{Ph_4P}]_2[\mathrm{Si_7Br_{14}{\cdot}2Br}]$ (triclinic, $P\bar{1}$, $Z = 2$), grew at room temperature in the NMR tube directly from the reaction solution. The structure of the dianionic moiety $[\mathrm{Si_7Br_{14}{\cdot}2Br}]^{2-}$ is shown in Scheme 1 (selected bond lengths and angles are listed in the caption of Figure 2S, Supporting Information). As was the case for $[n\mathrm{Bu_4N}]_2[\mathrm{Si_6Br_{12}{\cdot}2Br}]$, the six-membered ring of $[\mathrm{Ph_4P}]_2[\mathrm{Si_7Br_{14}{\cdot}2Br}]$ is by and large planar (rms deviation 0.054 Å). The distances between the two coordinated bromide anions and the ring centroid amount to COG···Br(1) = 2.071 Å and COG···Br(2) = 2.078 Å, which is slightly longer than in the case of $[n\mathrm{Bu_4N}]_2[\mathrm{Si_6Br_{12}{\cdot}2Br}]$ and likely attributable to the steric demand of the $\mathrm{Br_3Si}$ substituent.

Next, we prepared the iodosilicate(II) $[n\mathrm{Bu_4P}]_2[\mathrm{Si_6I_{12}{\cdot}2I}]$ by heating an equimolar mixture of $\mathrm{Si_2I_6}$ and $[n\mathrm{Bu_4P}]\mathrm{I}$ in $\mathrm{CD_2Cl_2}$ for 20 h to 80 °C (flame-sealed NMR tube; Scheme 1). We applied the elevated temperatures and used the significantly overstoichiometric amount of $[n\mathrm{Bu_4P}]\mathrm{I}$ (cf. Scheme 1) with the aim to promote a reaction of the poorly soluble Si_2I_6. After cooling to room temperature, colorless single crystals of $[nBu_4P]_2[Si_6I_{12}{\cdot}2I]$ formed (90 % yield). In the crystal lattice (triclinic, $P\bar{1}$), $[Si_6I_{12}{\cdot}2I]^{2-}$ shows a planar six-membered ring (rms deviation 0.021 Å), located on a crystallographic center of inversion, with an average Si–Si bond length of 2.382 Å. Two I^- anions are coordinated to establish an "inverse sandwich complex" with a COG···I distance of 2.285 Å (Scheme 1; selected bond lengths and angles are listed in the caption of Figure 3S, Supporting Information). Similar to the case of $[nBu_4N]_2[Si_6Br_{12}{\cdot}2Br]$, the average distance between the Si atoms and the apical halide ions of $[nBu_4P]_2[Si_6I_{12}{\cdot}2I]$ (3.30 Å) is smaller than the sum of the van der Waals radii [r_{vdw}(SiI): 4.08 Å],[20] but larger than the sum of the covalent radii [r_{cov}(SiI): 2.50 Å] of Si and I.[21]

A ^{29}Si NMR spectroscopic investigation of the mother liquor revealed the presence of chlorinated side products, such as $SiCl_4$, which likely originate from I/Cl-exchange reactions between the iodosilanes and the solvent CD_2Cl_2[22] (see Figure 7S, Supporting Information, for a $^{13}C\{^1H\}$ NMR spectrum of the reaction solution showing the resonance of CD_2ICl). This observation is a caveat concerning a possible chloride contamination of $[nBu_4P]_2[Si_6I_{12}{\cdot}2I]$. Unfortunately, the poor solubility of $[nBu_4P]_2[Si_6I_{12}{\cdot}2I]$ in all common inert solvents precluded its characterization by solution-state NMR spectroscopy, which would otherwise have been a powerful diagnostic tool to distinguish between SiI_2 and $SiICl/SiCl_2$ fragments within the sample. The key quality criteria of the X-ray crystal-structure analysis of $[nBu_4P]_2[Si_6I_{12}{\cdot}2I]$ (i.e., Si–I bond lengths, shapes and sizes of the thermal ellipsoids, residual electron density) gave no indication for significant chloride contamination. To finally resolve the issue, we repeated the synthesis of $[nBu_4P]_2[Si_6I_{12}{\cdot}2I]$ in 1,2-dichlorobenzene. This time, an NMR spectroscopic investigation of the reaction mixture did not reveal any halide-exchange reaction with the solvent. Again, we obtained single crystals of $[nBu_4P]_2[Si_6I_{12}{\cdot}2I]$. X-ray diffraction gave precisely the same results as before.

We emphasize at this point that the addition of $[nBu_4N]I$ to Si_6Cl_{12} in CH_2Cl_2 cleanly affords the I^- diadduct $[nBu_4N]_2[Si_6Cl_{12}{\cdot}2I]$ with no indication of Cl/I scrambling at the silicon atoms.[11] It is thus barely surprising that also in the case of the synthesis of $[nBu_4P]_2[Si_6I_{12}{\cdot}2I]$ in CD_2Cl_2 the chlorosilane side products are not converted back to corresponding iodosilanes by the excess amount of $[nBu_4P]I$. On the other hand, when we generated $[SiCl_3]^-$ from the $Si_2Cl_6/[R_4N]Cl$ system[12,13,15,25] and attempted to trap the anion in situ with BI_3, we did not detect any $[Et_4N][I_3B–SiCl_3]$, but rather isolated the $[SiI_3]^-$ adduct $[Et_4N][I_3B–SiI_3]$.[22] According to quantum-chemical calculations, the quantitative Cl/I exchange between $[SiCl_3]^-$ and BI_3 is overall strongly exergonic and therefore provides a thermodynamic thrust toward $[I_3B–SiI_3]^-$ formation.[22]

Given this background, we decided to examine the reaction between $[nBu_4N]_2[Si_6Cl_{12}{\cdot}2Cl]$ and 5 equiv. of BI_3 with the aim to obtain free Si_6I_{12} in a combined decomplexation/halide-exchange process (Scheme 2). In CH_2Cl_2 solution, an immediate reaction occurred between both starting materials already at ambient temperature and the colorless periodated cyclohexasilane (Si_6I_{12}) precipitated from the mixture. The precipitate was allowed to age for 6 d to grow single crystals suitable for X-ray crystallography.



Scheme 2. Synthesis and solid-state structure of the periodated cyclohexasilane Si_6I_{12}.

Not only the I^- diadduct $[nBu_4P]_2[Si_6I_{12}{\cdot}2I]$, but also the free cyclohexasilane Si_6I_{12} is not sufficiently soluble to record ^{29}Si NMR spectra. An IR spectrum of Si_6I_{12} revealed two characteristic bands at 405 cm^{-1} (s) and 468 cm^{-1} (w).[5] Nevertheless, the above-mentioned caveat regarding the possibility of minor Cl contamination of the iodosilicate(II) also applies to Si_6I_{12}.

The cyclohexasilane Si_6I_{12} crystallizes in the monoclinic space group $C2/c$ (Scheme 2; selected bond lengths and angles are listed in the caption of Figure 4S, Supporting Information). The molecule is located on a crystallographic center of inversion. The Si_6 ring adopts a regular chair conformation with approximate D_{3d} symmetry. The average dihedral angle between the best planes through four central Si_6-ring atoms and the corresponding flap planes can be taken as a measure of the ring puckering. In the solid-state structure of centrosymmetric Si_6I_{12}, there are three such dihedral angles: Si(2)Si(3)Si(2A)Si(3A)//Si(2)Si(1)Si(3A) = 42.9°, Si(1)Si(2)Si(1A)Si(2A)//Si(2)Si(3)Si(1A) = 43.2°, and Si(1)Si(3A)Si(1A)Si(3)//Si(1)Si(2)Si(3) = 44.3°. Their average value amounts to 43.5° (cf. Scheme 2 and Figure 4S, Supporting Information). A chair conformation is the intuitive minimum for cyclohexane analogues such as Si_6X_{12}, because it helps to avoid angular strain.

In a series of thorough theoretical studies, a *pseudo*-Jahn-Teller (PJT) effect has been identified as an important factor inducing ring puckering.[11,23,24] An interaction of the unoccupied MOs of Si_6X_{12}, which are basically composed of $\sigma^*(Si–X)$ orbitals, with electron lone pairs of apically coordinated X^- ions suppresses the PJT distortion, induces a planarization of the Si_6 ring and leads to a stabilizing effect in the "inverse sandwich complexes" $[Si_6X_{12}{\cdot}2X]^{2-}$.[11,23,24] The bonding of X^- ions to the six-membered ring in $[Si_6X_{12}{\cdot}2X]^{2-}$ is not entirely covalent in nature, but also benefits from Coulomb attraction between the positively polarized Si ring atoms and the anionic guests.[23] It has been computed that, irrespective of the halogen pattern, the degree of covalency in complexes $[Si_6X_{12}{\cdot}2X]^{2-}$ is approximately 45 %.[23]

With the molecular structures of $[nBu_4P]_2[Si_6I_{12}{\cdot}2I]$ and Si_6I_{12} at hand, we are now in a position to compare the key structural parameters of the entire series of compounds $[Si_6X_{12}{\cdot}2X]^{2-}$ and Si_6X_{12} (X = Cl, Br, I; Table 1 and Table 2). For the diadducts $[Si_6X_{12}{\cdot}2X]^{2-}$, computed bond lengths [B3LYP/6-311++g(d,p)][23] are available in addition to the X-ray crystallographically determined ones. As a general trend,

Table 1. Comparison of computed and experimentally determined structural parameters of $[Si_6X_{12}{\cdot}2X]^{2-}$ (X = Cl, Br, I). To ensure maximum comparability we only included examples with $[nBu_4N]^+$ or $[nBu_4P]^+$ counterions. Note: In this table, X' denotes an apical X^- ion.

	Si–Si (avg) /Å	Si–X (avg) /Å	Si···X' (avg) /Å	X···X' (avg) /Å	X'···X' /Å
$[Si_6Cl_{12}{\cdot}2Cl]^{2-}$ calcd. a)	2.372	2.123	3.085	3.729	
$[Si_6Cl_{12}{\cdot}2Cl]^{2-}$ exp. b)	2.322	2.078	3.010	3.635	3.836
$[Si_6Br_{12}{\cdot}2Br]^{2-}$ calcd. a)	2.368	2.290	3.090	3.805	
$[Si_6Br_{12}{\cdot}2Br]^{2-}$ exp.	2.342 b)	2.251 b)	3.118 b)	3.786 b)	4.119 b)
	2.343 c)	2.247 c)	3.125 c)	3.789 c)	4.136 c)
$[Si_6I_{12}{\cdot}2I]^{2-}$ calcd. a)	2.447	2.571	3.429	4.147	
$[Si_6I_{12}{\cdot}2I]^{2-}$ exp. b)	2.382	2.496	3.300	4.018	4.570

a) *Vedha* et al.[23] b) Prepared through the halogen-induced disproportionation of Si_2X_6 (this work and reference[13]). c) Prepared by *Boudjouk* et al. through the addition of 2 equiv. of $[nBu_4N]Br$ to Si_6Br_{12}[11,24].

the calculated Si–Si and Si–X bond lengths are slightly too long (≤ 0.065 Å for Si–Si; 0.045 Å for Si–Cl, ≤ 0.043 Å for Si–Br, 0.075 Å for Si–I), but still agree well with the averaged experimentally determined parameters. Along both series $[Si_6X_{12}{\cdot}2X]^{2-}$ and Si_6X_{12}, the nature of the halogen atom has a surprisingly small influence on the Si–Si bond lengths. The coordination of X^- ions to Si_6X_{12} leads to a slight contraction of the Si–Si bonds in the case of $X^- = Cl^-$ and to an elongation in the case of $X^- = I^-$; Si_6Br_{12} and $[Si_6Br_{12}{\cdot}2Br]^{2-}$ possess the same average Si–Si bond length. We hypothesize that these structural changes are necessary to maintain an optimal interaction of the respective Si_6 ring with the small Cl^- the medium-sized Br^-, and the large I^- ion. An expansion is evident for the Si–X bonds of the diadducts, likely due to electron donation from the apical X^- ions into antibonding σ*(Si–X) orbitals.

Table 2. Comparison of structural parameters of Si_6X_{12} (X = Cl, Br, I).

	Si–Si (avg) /Å	Si–X (avg) /Å	Si–Si–Si (avg) /°	Flap angle (avg) /°
Si_6Cl_{12} a)	2.342	2.029	112.9	45.4
Si_6Br_{12} a)	2.341	2.196	113.2	44.2
Si_6I_{12} b)	2.355	2.435	113.5	43.5

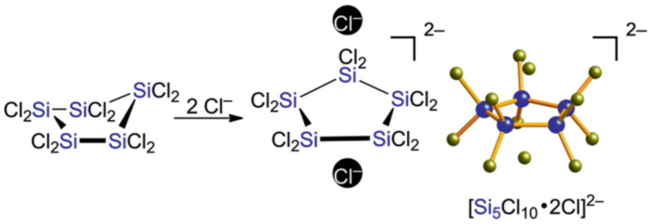
a) Prepared through exhaustive H/X exchange on Si_6H_{12} using X_2[10]. b) Prepared through decomplexation and exhaustive Cl/I exchange on $[Si_6Cl_{12}{\cdot}2Cl]^{2-}$ using BI_3.

We finally note that also the Si–Si–Si bond angles and the flap angles of Si_6X_{12} are independent from X, thereby pointing toward a similar degree of PJT distortion in all three cyclohexasilanes.

Synthesis and Structural Characterization of $[nBu_4P]_2[Si_5Cl_{10}{\cdot}2Cl]$

The Cl^--induced disproportionation of Si_2Cl_6, followed by decomplexation of the primary product $[Si_6Cl_{12}{\cdot}2Cl]^{2-}$ with $AlCl_3$, arguably provides the most time- and cost-efficient route for the synthesis of Si_6Cl_{12}.[15] Unfortunately, until todate this protocol is restricted to the preparation of cyclohexasilanes; compounds of other ring sizes have never been isolated from the product mixtures. For our investigations of the Cl^- diadduct $[Si_5Cl_{10}{\cdot}2Cl]^{2-}$, we thus had to rely on Hengge's classical synthesis of Si_5Cl_{10}.[3]

A solution of the perhalogenated cyclopentasilane in CH_2Cl_2 was added at –78 °C to a solution of $[nBu_4P]Cl$ in the same solvent. The mixture was stored at –72 °C for 7 d to grow colorless single crystals of $[nBu_4P]_2[Si_5Cl_{10}{\cdot}2Cl]{\cdot}2CH_2Cl_2$ in a yield of 76 % (monoclinic, $C2/c$). Similar to $[Si_6Cl_{12}{\cdot}2Cl]^{2-}$, the dianion $[Si_5Cl_{10}{\cdot}2Cl]^{2-}$ forms an "inverse sandwich complex" with a planar Si_5 ring (rms deviation: 0.011 Å) located on a twofold rotation axis (Scheme 3; selected bond lengths and angles are listed in the caption of Figure 5S, Supporting Information). All Si–Si bond lengths fall in the narrow range between 2.340(1) Å and 2.346(1) Å. The average value of 2.344 Å is close to the average Si–Si bond length of the cyclohexasilane diadduct $[nBu_4N]_2[Si_6Cl_{12}{\cdot}2Cl]$ (2.322 Å). The same is true for the average Si–Cl bond lengths in the Si_5 diadduct (2.094 Å) compared to the Si_6 diadduct (2.078 Å). The distance between the two apical Cl^- ions, however, is larger by as much as 0.456 Å in $[Si_5Cl_{10}{\cdot}2Cl]^{2-}$ (4.292 Å) than in the Si_6 analog (3.836 Å). These decisive structural differences likely result from the fact that the void spaces above and below the ring planes are more limited in the case of the five-membered ring species.



Scheme 3. Synthesis of $[nBu_4P]_2[Si_5Cl_{10}{\cdot}2Cl]$ and solid-state structure of the dianion $[Si_5Cl_{10}{\cdot}2Cl]^{2-}$. $[nBu_4P]Cl$ was used as Cl^- source.

Most key structural parameters of $[Si_5Cl_{10}{\cdot}2Cl]^{2-}$ have been correctly predicted by a recent DFT study.[26] The most significant deviation between the computed and experimentally determined values is evident for the Cl^-···Cl^- distance (calcd: 4.215 Å vs. exp: 4.292 Å). Nevertheless, also the DFT calculations unequivocally confirm much farther separated Cl^- ions in the Si_5 compared to the Si_6 diadduct. To rationalize the planar conformation of the Si_5 ring in $[Si_5Cl_{10}{\cdot}2Cl]^{2-}$, the authors offer a similar explanation as previously discussed for the $[Si_6X_{12}{\cdot}2X]^{2-}$ diadducts.[26]

Yet, contrary to the theoretical prediction of "substantial Si_5Cl_{10} ring stabilization due to the exocyclic chlorine", our experiments suggest a *destabilizing* effect of Cl^- coordination on the Si_5Cl_{10} scaffold:

Even though crystalline $[nBu_4P]_2[Si_5Cl_{10}{\cdot}2Cl]{\cdot}2CH_2Cl_2$ remains unchanged at room temperature, its CH_2Cl_2 solutions persist only at low temperatures. Upon warming to ambient temperature, the complex undergoes rearrangement reactions to afford cyclohexasilane diadducts such as $[Si_6Cl_{12}{\cdot}2Cl]^{2-}$ and $[Si_7Cl_{14}{\cdot}2Cl]^{2-}$. In stark contrast, free Si_5Cl_{10}/Si_6Cl_{12} as well as the complexed cyclohexasilane $[nBu_4N]_2[Si_6Cl_{12}{\cdot}2Cl]$ are stable at room temperature under inert conditions. It is also worth mentioning that room temperature-stable diadducts $[Si_5Cl_{10}{\cdot}2NCR]$ of Si_5Cl_{10} with nitrile ligands have been reported (*R* = *p*-tolyl, 1-adamantyl).[27] To assess the affinity of Si_5Cl_{10} toward Cl^- ions, we performed a number of competition experiments at room temperature on an NMR scale (CD_2Cl_2). While the cyclopentasilane behaves inert to $[nBu_4N][AlCl_4]$, it quantitatively decomposes to numerous unidentified products upon addition of 2 equiv. of $[nBu_4N][BCl_4]$.

In agreement with this observation, we succeeded in the clean liberation of Si_5Cl_{10} by adding crystals of $[nBu_4N]_2[Si_5Cl_{10}{\cdot}2Cl]{\cdot}2CH_2Cl_2$ to a suspension of 2.5 equiv. of $AlCl_3$ in CH_2Cl_2 (see also reference[15] in this context). Attempts to reproduce this reaction using BCl_3 as the Lewis acid failed and furnished complex product mixtures. We therefore conclude that the Cl^- affinity of Si_5Cl_{10} roughly matches that of BCl_3 but is too low to outcompete $AlCl_3$. It should be noted that Si_5Cl_{10}, like Si_6Cl_{12},[15] is a donor-free storage form of dichlorosilylene $SiCl_2$. Treatment of Si_5Cl_{10} with strong ligands, such as NMe_2Et or 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene, in C_6H_6 results in the quantitative formation of the corresponding dichlorosilylene adducts (NMR spectroscopic control). These adducts have already been described in the literature.[28,29]

We finally prepared a 1:1 mixture of Si_5Cl_{10} and $[nBu_4N]_2[Si_6Cl_{12}{\cdot}2Cl]$ in CD_2Cl_2 and recorded ^{29}Si NMR spectra of the sample at room temperature. The signal of Si_5Cl_{10} [$\delta(^{29}Si) = -2.17$; lit.: –1.70 ppm[27]] had completely vanished. Instead, we observed resonances assignable to $SiCl_4$, $[Si_6Cl_{12}{\cdot}2Cl]^{2-}$, $[Si_7Cl_{14}{\cdot}2Cl]^{2-}$,[13] and 1,1-$[Si_8Cl_{16}{\cdot}2Cl]^{2-}$,[13] together with signals of yet unidentified products. We therefore conclude that Si_5Cl_{10} rivals Si_6Cl_{12} in terms of Cl^- affinity, because it is apparently capable of abstracting Cl^- ions from $[Si_6Cl_{12}{\cdot}2Cl]^{2-}$ and subsequently undergoes the skeletal rearrangement mentioned above.

Summary and Conclusions

The X^- induced disproportionation of Si_2X_6 (*X* = Cl, Br, I) provides convenient access not only to the "inverse sandwich complex" $[nBu_4N]_2[Si_6Cl_{12}{\cdot}2Cl]$, but also to its heavier congeners $[nBu_4N]_2[Si_6Br_{12}{\cdot}2Br]$ and $[nBu_4P]_2[Si_6I_{12}{\cdot}2I]$. In all cases, these halosilicates(II) are colorless, crystalline solids. $[nBu_4N]_2[Si_6Cl_{12}{\cdot}2Cl]$ and $[nBu_4N]_2[Si_6Br_{12}{\cdot}2Br]$ persist at room temperature in CH_2Cl_2 solution; $[nBu_4P]_2[Si_6I_{12}{\cdot}2I]$ is virtually insoluble in all common inert solvents. Irrespective of the nature of *X*, we found no indication for a destabilizing effect of coordinated X^- ions on the Si_6X_{12} ring.

The opposite is true for the perchlorinated cyclopentasilane Si_5Cl_{10}: Even though a corresponding Cl^- diadduct $[nBu_4P]_2[Si_5Cl_{10}{\cdot}2Cl]{\cdot}2CH_2Cl_2$ can be prepared and isolated in excellent yields at low temperatures of –78 °C, the compound readily undergoes a ring-expansion reaction to form $[nBu_4P]_2[Si_6Cl_{12}{\cdot}2Cl]$ and Cl_3Si-substituted derivatives thereof in CH_2Cl_2 solutions at ambient temperature.

This observation is of immediate relevance for an understanding of the reaction mechanism underlying the synthesis of perchlorinated cyclohexasilanes via the Cl^--induced heterolysis of Si_2Cl_6: The exclusive formation of Si_6 rings does not necessarily imply a size selectivity of the actual ring-closure process. It is well conceivable that, besides Si_6 rings, also cyclic Si_5 intermediates are formed, which subsequently undergo a Cl^--mediated rearrangement to furnish cyclohexasilane products.

Moreover, we found similar Cl^- affinities for Si_5Cl_{10} and Si_6Cl_{12}. The significantly longer distances between the apical Cl^- ions and the ring planes in $[Si_5Cl_{10}{\cdot}2Cl]^{2-}$ compared to $[Si_6Cl_{12}{\cdot}2Cl]^{2-}$ are therefore not indicative of pronounced differences in the interaction between the individual components of the two "inverse sandwich complexes".

Moreover, we developed an efficient decomplexation/halogen-exchange protocol, which starts from $[nBu_4N]_2[Si_6Cl_{12}{\cdot}2Cl]$ and BI_3 (5 equiv.) and provides free Si_6I_{12} in excellent yields. This convenient reaction is remarkable, because treatment of $[nBu_4N]_2[Si_6Cl_{12}{\cdot}2Cl]$ with BCl_3 fails to provide free Si_6Cl_{12}.[15]

In summary, we have expanded the scope of the X^--induced disproportionation reaction of Si_2X_6 beyond the scope of chlorosilanes and demonstrated its versatility for generating various useful silicon species.

Experimental Section

General Considerations: All reactions and manipulations were carried out in dry, oxygen-free nitrogen or argon by using standard Schlenk ware or an argon-filled M. Braun glovebox. CH_2Cl_2 and CD_2Cl_2 were dried with CaH_2 and freshly distilled prior to use. C_6H_6 and C_6D_6 were dried with sodium/benzophenone and freshly distilled prior to use. Si_2Br_6,[16] Si_2I_6,[17] and Si_5Cl_{10}[3] were prepared according to published procedures. The commercially available ammonium and phosphonium halides, $[nBu_4P]Cl$ (*Sigma Aldrich*), $[nBu_4N]Br$ (*Sigma Aldrich*), $[Ph_4P]Br$ (*Sigma Aldrich*), and $[nBu_4P]I$ (*Sigma Aldrich*) were used as received. $AlCl_3$ was freshly prepared from aluminum metal and dry HCl gas. The NMR spectra were recorded with Bruker Avance 300 and Avance 500 spectrometers.

Synthesis of $[nBu_4N]_2[Si_6Br_{12}{\cdot}2Br]$ and $[nBu_4N]_2[Si_7Br_{14}{\cdot}2Br]$: An NMR tube was charged with neat solid Si_2Br_6 (0.43 g, 0.80 mmol). A solution of $[nBu_4N]Br$ (0.11 g, 0.34 mmol) in CD_2Cl_2 (0.8 mL) was added at room temperature. After few minutes, the reaction mixture turned brownish and a colorless precipitate formed. The NMR tube was flame-sealed. The ^{29}Si NMR spectrum of the reaction solution revealed resonances assignable to $SiBr_4$ (–90.2 ppm),[18] $[Si_6Br_{12}{\cdot}2Br]^{2-}$ (see below),[11] and $[Si_7Br_{14}{\cdot}2Br]^{2-}$ (see below). Single crystals of $[nBu_4N]_2[Si_6Br_{12}{\cdot}2Br]$ suitable for X-ray crystallography were harvested after storing the reaction solution for 3 d at room temperature.

[*n*Bu$_4$N]$_2$[Si$_6$Br$_{12}$·2Br]: ^{29}Si NMR (CD$_2$Cl$_2$, 59.6 MHz, 298 K): δ = –38.1 ppm (cf. reference[11,19]).

[*n*Bu$_4$N]$_2$[Si$_7$Br$_{14}$·2Br]: ^{29}Si NMR (CD$_2$Cl$_2$, 59.6 MHz, 298 K): δ = –57.2 (1 Si, SiBr), –41.7 (2 Si, SiBr$_2$), –37.6 (1 Si, SiBr$_2$), –37.4 (2 Si, SiBr$_2$), –18.1 ppm (1Si, SiBr$_3$).

Crystallization of [Ph$_4$P]$_2$[Si$_7$Br$_{14}$·2Br]: An NMR tube was charged with neat Si$_2$Br$_6$ (0.51 g, 0.95 mmol). A solution of [Ph$_4$P]Br (0.11 g, 0.26 mmol) in CD$_2$Cl$_2$ (0.8 mL) was added at room temperature. After few minutes, the reaction mixture turned brownish and a colorless precipitate formed. Single crystals of [Ph$_4$P]$_2$[Si$_7$Br$_{14}$·2Br] suitable for X-ray crystallography were harvested after storing the reaction solution for 3 d at room temperature.

Synthesis of [*n*Bu$_4$P]$_2$[Si$_6$I$_{12}$·2I]: Neat solid Si$_2$I$_6$ (0.100 g, 0.122 mmol) was added to a CD$_2$Cl$_2$ solution (0.5 mL) of [*n*Bu$_4$P]I (0.047 g, 0.122 mmol) in an NMR tube at room temperature. Even though most of the Si$_2$I$_6$ remained undissolved, the color of the mixture turned yellow. The NMR tube was flame-sealed and heated in a sand bath to 80 °C for 20 h. After cooling to room temperature, colorless crystals of [*n*Bu$_4$P]$_2$[Si$_6$I$_{12}$·2I] had formed. Yield: 0.045 g, 0.018 mmol (90 %).

The reaction solution was investigated by ^{13}C{^{1}H} and ^{29}Si NMR spectroscopy. The ^{13}C{^{1}H} NMR spectrum contained signals of [*n*Bu$_4$P]$^+$ and CD$_2$ICl.[30,31] CD$_2$ICl likely originates from a Cl/I exchange reaction between CD$_2$Cl$_2$ and iodosilanes (cf. reference[22]). Correspondingly, the ^{29}Si NMR spectrum showed a resonance assignable to SiCl$_4$ (–18.9 ppm)[13] and two more signals at –20.8 ppm and –21.9 ppm. For comparison, we note that the chemical shift values of [Si$_6$Cl$_{12}$·2Cl]$^{2-}$ and [Si$_6$Cl$_{12}$·2I]$^{2-}$ are –21.7 ppm[13] and –21.9 ppm,[11,32] respectively.

NMR spectra of [*n*Bu$_4$P]$_2$[Si$_6$I$_{12}$·2I] could not be recorded due to the poor solubility of this compound in all common inert solvents. We therefore picked four different crystals of the product and identified all of them as [*n*Bu$_4$P]$_2$[Si$_6$I$_{12}$·2I] by X-ray diffraction.

Synthesis of Si$_6$I$_{12}$: A brown glass flask was charged with a solution of [*n*Bu$_4$N]$_2$[Si$_6$Cl$_{12}$·2Cl] (0.100 g, 0.087 mmol) in CH$_2$Cl$_2$ (10 mL). A solution of BI$_3$ (0.167 g, 0.426 mmol) in CH$_2$Cl$_2$ (10 mL) was added dropwise at room temperature. Upon mixing, the solution turned yellow and very small crystals precipitated. After storing the reaction solution for 6 d at room temperature, the crystals had grown to a size suitable for X-ray crystallography. The crystals were isolated by filtration and rinsed with CH$_2$Cl$_2$ (4 mL). Yield: 0.107 g, 0.063 mmol (73 %). NMR spectra of Si$_6$I$_{12}$ could not be recorded due to its poor solubility in all common inert solvents. Instead, four different crystals were picked and each of them identified as Si$_6$I$_{12}$ by X-ray diffraction.

Synthesis of [*n*Bu$_4$P]$_2$[Si$_5$Cl$_{10}$·2Cl]: A solution of Si$_5$Cl$_{10}$ (0.500 g, 1.01 mmol) in CH$_2$Cl$_2$ (3 mL) was added dropwise at –78 °C to a solution of [*n*Bu$_4$P]Cl (0.596 g, 2.02 mmol) in CH$_2$Cl$_2$ (3 mL). Crystals of [*n*Bu$_4$P]$_2$[Si$_5$Cl$_{10}$·2Cl]·2CH$_2$Cl$_2$ suitable for X-ray analysis were harvested after the reaction solution had been stored at –72 °C for 7 d. Yield: 0.958 g, 0.764 mmol (76 %).

[*n*Bu$_4$P]$_2$[Si$_5$Cl$_{10}$·2Cl]: ^{29}Si NMR (CD$_2$Cl$_2$, 99.4 MHz, 298 K): δ = –36.6 ppm. *Note*: Due to the instability of the compound at room temperature in solution, the sample must be measured immediately after preparation.

Crystal Structure Determinations of [*n*Bu$_4$N]$_2$[Si$_6$Br$_{12}$·2Br], [Ph$_4$P]$_2$[Si$_7$Br$_{14}$·2Br], [*n*Bu$_4$P]$_2$[Si$_6$I$_{12}$·2I], Si$_6$I$_{12}$, and [*n*Bu$_4$P]$_2$[Si$_5$Cl$_{10}$·2Cl]·2CH$_2$Cl$_2$: Data collections were performed with a STOE IPDS II two-circle diffractometer with a Genix Microfocus tube with mirror optics using Mo-K_α radiation (λ = 0.71073 Å) and data were scaled using the frame-scaling procedure in the X-AREA program system.[33] The structures were solved by direct methods using the program SHELXS and refined against F^2 with full-matrix least-squares techniques using the program SHELXL.[34] All non-hydrogen atoms were refined anisotropically, whereas the hydrogen atoms were treated with a riding model.

Crystallographic data for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1824864 ([*n*Bu$_4$N]$_2$[Si$_6$Br$_{12}$·2Br]), CCDC-1824862 ([*n*Bu$_4$P]$_2$[Si$_6$I$_{12}$·2I]), CCDC-1824865 ([Ph$_4$P]$_2$[Si$_7$Br$_{14}$·2Br]), CCDC-1824863 (Si$_6$I$_{12}$), and CCDC-1835244 ([*n*Bu$_4$P]$_2$[Si$_5$Cl$_{10}$·2Cl]·2CH$_2$Cl$_2$) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Supporting Information (see footnote on the first page of this article): ORTEP and crystallographic data of [*n*Bu$_4$N]$_2$[Si$_6$Br$_{12}$·2Br], [Ph$_4$P]$_2$[Si$_7$Br$_{14}$·2Br], [*n*Bu$_4$P]$_2$[Si$_6$I$_{12}$·2I], Si$_6$I$_{12}$, and [*n*Bu$_4$P]$_2$[Si$_5$Cl$_{10}$·2Cl]·2CH$_2$Cl$_2$. ^{29}Si NMR spectrum of the reaction solution of the mixture of Si$_2$Br$_6$/[*n*Bu$_4$N]Br in CD$_2$Cl$_2$. ^{13}C{^{1}H} and ^{29}Si NMR spectra of the solution phase of the reaction mixture Si$_2$I$_6$/[*n*Bu$_4$P]I in CD$_2$Cl$_2$.

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Keywords: Bromine; Iodine; Silicon, Cyclopentasilane; Cyclohexasilane

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J. Teichmann, B. Köstler, J. Tillmann, M. Moxter, R. Kupec, M. Bolte, H.-W. Lerner, M. Wagner** **1–8**

Halide-Ion Diadducts of Perhalogenated Cyclopenta- and Cyclohexasilanes