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Halide Coordination of Perhalocyclohexasilane Si_6X_{12} (X = Cl or Br)

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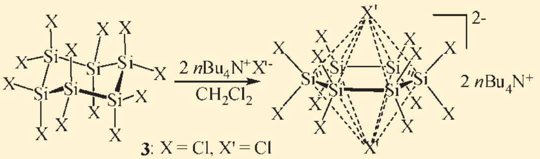
Supporting Information

ABSTRACT: The addition of halide anions (X′ = Cl^-, Br^-, or I^-) to perhalocyclohexasilane Si_6X_{12} (X = Cl or Br) led to the formation of complexes comprising $[Si_6X_{12}X'_2]^{2-}$ dianions. An upfield shift in the ^{29}Si NMR spectra was noted upon coordination, and structural determination by X-ray crystallography showed that the dianions adopt an "inverse sandwich" structure where the six cyclic silicon atoms form a planar hexagon with the two halide anions X′ located on the 6-fold axis equally disposed above and below the plane of the Si_6 ring. Additionally, these apical X′ atoms are within the van der Waals bonding distance to the silicon ring atoms, indicating a strong interaction between X′ and silicon atoms. These results detail crystallographic variations within the halogen series providing further insight into the nature of the Lewis acid sites above and below the Si_6X_{12} ring, where interactions with hard Lewis bases such as halide anions are observed. Interestingly, the stereochemistry of the silicon atoms in $[Si_6X_{12}X'_2]^{2-}$ is not affected much by the size or electronegativity of the halogen atoms.



3: X = Cl, X′ = Cl
4: X = Cl, X′ = Br
5: X = Cl, X′ = I
6: X = Br, X′ = Cl
7: X = Br, X′ = Br
8: X = Br, X′ = I

INTRODUCTION

During the study of the reactivity between triamine and chlorosilane, we recently found a straightforward preparation of Si_6H_{12}.[1] A key intermediate in the preparation of Si_6H_{12} is a salt comprising a tetradecachlorocyclohexasilane dianion $[Si_6Cl_{14}]^{2-}$ that forms during disproportionation and redistribution of trichlorosilane with an amine-promoting reagent, pentaethyldiethylenetriamine (PEDETA).[1] The dianion exhibits an interesting "inverse sandwich" structure in the solid state where the six silicon atoms form a planar hexagon with the two apical chlorides located on the 6-fold axis equally disposed above and below the plane of the Si_6 ring, and each chloride equally coordinated to six silicon atoms. The density functional theory (DFT) simulation has demonstrated that Si_6Cl_{12} coodination with chloride anions leads to occupation of the orbitals responsible for a Jahn−Teller effect, and the stabilization of such orbitals leads to suppression of the Jahn−Teller effect, which may explain why the planar configuration of $[Si_6Cl_{14}]^{2-}$ is more stable.[2]

Compared to carbon, silicon offers a wider variety of coordination schemes and hypercoordinate silicon chemistry is well established.[3] A small number of hypercoordinate silicon complexes that feature two or more neutral silicon atoms anchored by another donor ligand feature unusual structures and stereodynamic behavior. Tamao et al. reported a pentacoordinate anionic silicate $[o\text{-}C_6H_4(SiPhF_2)_2F]^-$ that contains a bent fluoride bridge between two silicon atoms (Scheme 1A).[4] Similar μ^2 bridging has been reported for other atoms such as the oxygen atom of carbonyl (Scheme 1B)[5] and chloride (Scheme 1C).[6] Jung and Xia reported that three silicon atoms in 12-silacrown-3 could complex with either one chloride or one bromide anion (Scheme 1D),[7] and Brondani et al. found that a fluoride anion quickly exchanges between three silicon atoms in trisilacyclohexane (Scheme 1E).[7] In all examples, none of the donors was shared by more than three silicon atoms of the host molecule.

The $[Si_6Cl_{14}]^{2-}$ dianion exhibits novel μ^6 coordination of the X′ atoms where each of the apical chloride bridges all six silicon atoms of the ring. Even though the formation of the $[(PEDETA)(H_2SiCl)]_2[Si_6Cl_{14}]$ salt is not yet fully understood, the unique structure of the dianion represents an interesting area of hypercoordinate silicon chemistry. Given recent synthetic advances,[8] we are now able to prepare gram quantities of Si_6X_{12} (X = Cl or Br) by molecular halogenation of Si_6H_{12} and use these perhalocyclosilanes to further investigate the coordination chemistry. We recently determined that organic donor organocyanides coordinate to the Si_6X_{12} or Si_5Cl_{10} ring to give adducts (Scheme 1F,G).[8] Herein we report additional details on the synthesis, structure, and reactivity of Si_6X_{12} and $[Si_6X_{12}X'_2]^{2-}$ adducts (X = Cl or Br; X′ = Cl^-, Br^-, or I^-).

EXPERIMENTAL SECTION

General Considerations. All experiments were carried out in a dry nitrogen atmosphere using a glovebox and standard Schlenk-line

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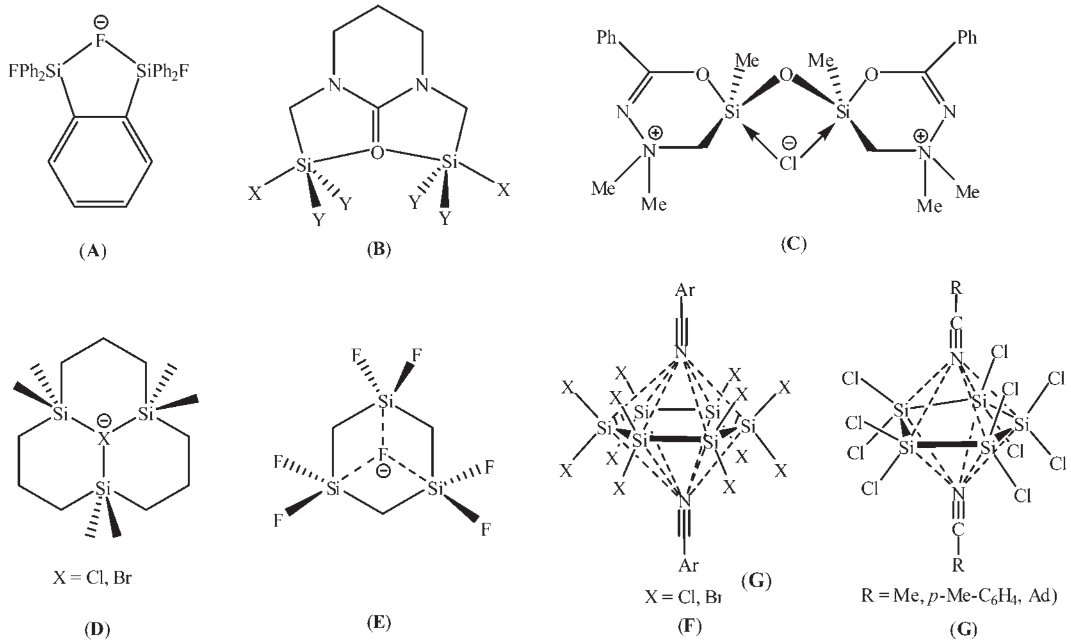
Scheme 1. Examples of Hypercoordinated Silicon Complexes



techniques as necessary. Methylene chloride and hexane were passed through solvent purification columns and then dried over activated 4 Å molecular sieves (240 °C/8 h dynamic vacuum). All deuterated solvents were sparged with nitrogen, dried over 4 Å molecular sieves, and stored under nitrogen. ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded on a JEOL ECA 400 MHz NMR spectrometer at 400 and 100.5 MHz, respectively, and at 25 °C unless otherwise noted. The spectra were indirectly referenced to tetramethylsilane using residual solvent signals as internal standards. UV–vis spectra were collected using a Cary 5000 UV–vis–near-IR spectrophotometer. Elemental analyses were performed on a LECO CHNs-932 elemental combustion analyzer and a VTF-900 oxygen analyzer. Si_6Cl_{12} and Si_6Br_{12} were synthesized according to the literature[8a] with tetrabutylammonium chloride, tetrabutylammonium bromide, and tetrabutylammonium iodide purchased from Sigma-Aldrich and used as received.

Synthesis of $[n\text{-}Bu_4N]_2[Si_6Cl_{14}]$ (**3**). A solution of Si_6Cl_{12} (300 mg, 0.500 mmol) in 3.0 mL of CH_2Cl_2 was treated with *n*-Bu_4NCl (278 mg, 1.00 mmol), and the resulting mixture was stirred for 2 h to give a cloudy mixture. Hexane (0.5 mL) was added to the reaction mixture and stirred for 2 min. A colorless solid was formed and collected by filtration to give 357 mg of a crude product (yield 61.8%). The isolated solid was recrystallized from CH_2Cl_2 at −30 °C to give analytically pure **3**. ^{1}H NMR (CD_2Cl_2): δ 3.12 (t, 2H, $NCH_2CH_2CH_2CH_3$), 1.58 (m, 2H, $NCH_2CH_2CH_2CH_3$), 1.44 (m, 2H, $NCH_2CH_2CH_2CH_3$), 0.98 (t, 3H, $NCH_2CH_2CH_2CH_3$). ^{13}C NMR (CD_2Cl_2): δ 59.20, 24.22, 19.87, 13.59. ^{29}Si NMR (CD_2Cl_2): δ 21.52. Elem anal. Calcd for $C_{32}H_{72}Cl_{14}N_2Si_6$: C, 33.43; H, 6.31; N, 2.44. Found: C, 33.16; H, 6.37; N, 2.47.

Synthesis of $[n\text{-}Bu_4N]_2[Si_6Cl_{12}Br_2]$ (**4**). This synthesis followed the same procedure as that described for **3** by using Si_6Cl_{12} (300 mg, 0.500 mmol) and *n*-Bu_4NBr (322 mg, 1.00 mmol). The colorless crude product (410 mg; yield 65.9%) was recrystallized from CH_2Cl_2 at −30 °C to give analytically pure **4**. ^{1}H NMR (CD_2Cl_2): δ 3.11 (t, 2H, $NCH_2CH_2CH_2CH_3$), 1.58 (m, 2H, $NCH_2CH_2CH_2CH_3$), 1.43 (m, 2H, $NCH_2CH_2CH_2CH_3$), 0.99 (t, 3H, $NCH_2CH_2CH_2CH_3$). ^{13}C NMR (CD_2Cl_2): δ 59.00, 24.10, 19.77, 13.55. ^{29}Si NMR (CD_2Cl_2): δ 22.23. Elem anal. Calcd for $C_{32}H_{72}Br_2Cl_{12}N_2Si_6$: C, 31.03; H, 5.86; N, 2.26. Found: C, 31.03; H, 5.80; N, 2.33.

Synthesis of $[n\text{-}Bu_4N]_2[Si_6Cl_{12}I_2]$ (**5**). This synthesis followed the same procedure as that described for **3** using Si_6Cl_{12} (300 mg, 0.500 mmol) and *n*-Bu_4NI (370 mg, 1.00 mmol). Colorless crystals precipitated without the addition of hexane, giving 340 mg (yield 50.7%) of analytically pure **5**. Single crystals for X-ray diffraction were obtained by recrystallization from CH_2Cl_2 at 0 °C. ^{1}H NMR (CD_2Cl_2): δ 3.11 (t, 2H, $NCH_2CH_2CH_2CH_3$), 1.59 (m, 2H, $NCH_2CH_2CH_2CH_3$), 1.43 (m, 2H, $NCH_2CH_2CH_2CH_3$), 0.99 (t, 3H, $NCH_2CH_2CH_2CH_3$). ^{13}C NMR (CD_2Cl_2): δ 59.04, 24.10, 19.78, 13.54. ^{29}Si NMR (CD_2Cl_2): δ 21.88. Elem anal. Calcd for $C_{32}H_{72}Cl_{12}I_2N_2Si_6$: C, 28.84; H, 5.45; N, 2.10. Found: C, 28.57; H, 5.26; N, 2.19.

Synthesis of $[n\text{-}Bu_4N]_2[Si_6Br_{12}Cl_2]$ (**6**). A solution of Si_6Br_{12} (285 mg, 0.250 mmol) in 3.0 mL of CH_2Cl_2 was treated with *n*-Bu_4NCl (140 mg, 0.500 mmol), giving a cloudy solution immediately. After stirring for 1 h, the colorless solid was collected by filtration to give 245 mg (yield 57.6%) of product. ^{1}H NMR (CD_2Cl_2): δ 3.12 (t, 2H, $NCH_2CH_2CH_2CH_3$), 1.58 (m, 2H, $NCH_2CH_2CH_2CH_3$), 1.45 (m, 2H, $NCH_2CH_2CH_2CH_3$), 0.99 (t, 3H, $NCH_2CH_2CH_2CH_3$). ^{13}C NMR (CD_2Cl_2): δ 59.07, 24.16, 19.86, 13.60. ^{29}Si NMR (CD_2Cl_2): δ 37.44. Elem anal. Calcd for $C_{32}H_{72}Br_{12}Cl_2N_2Si_6$: C, 22.83; H, 4.31; N, 1.66. Found: C, 21.90; H, 4.16; N, 1.60.

Synthesis of $[n\text{-}Bu_4N]_2[Si_6Br_{14}]$ (**7**). This synthesis followed the same procedure as that described for **6** using Si_6Br_{12} (290 mg, 0.260 mmol) and *n*-Bu_4NBr (163 mg, 0.510 mmol). The colorless solid was collected by filtration to give 350 mg (yield 77.3%) of analytically pure **7**. Single crystals suitable for structural determination by X-ray analysis were obtained by recrystallization from CH_2Cl_2 at 0 °C. ^{1}H NMR (CD_2Cl_2): δ 3.13 (t, 2H, $NCH_2CH_2CH_2CH_3$), 1.60 (m, 2H, $NCH_2CH_2CH_2CH_3$), 1.46 (m, 2H, $NCH_2CH_2CH_2CH_3$), 1.00 (t, 3H, $NCH_2CH_2CH_2CH_3$). ^{13}C NMR (CD_2Cl_2): δ 59.01, 24.18, 19.89, 13.62. ^{29}Si NMR (CD_2Cl_2): δ 37.40. Elem anal. Calcd for $C_{32}H_{72}Br_{14}N_2Si_6$: C, 21.69; H, 4.10; N, 1.58. Found: C, 21.53; H, 4.09; N, 1.63.

Synthesis of $[n\text{-}Bu_4N]_2[Si_6Br_{12}I_2]$ (**8**). This synthesis followed the same procedure as that described for **6** using Si_6Br_{12} (280 mg, 0.250 mmol) and *n*-Bu_4NI (185 mg, 0.500 mmol). The colorless solid was collected by filtration to give 340 mg (yield 73.1%) of analytically pure **8**. Single crystals suitable for structural determination by X-ray analysis

Table 1. Crystallographic Data for Compounds **1**, **5**, **7**, and **8**

	1	**5**	**7**	**8**
formula	$Cl_{12}Si_6$	$C_{33}H_{74}Cl_{14}I_2N_2Si_6$	$C_{32}H_{72}Br_{14}N_2Si_6$	$C_{32}H_{72}Br_{12}I_2N_2Si_6$
fw	593.95	1417.58	1448.95	1866.18
cryst syst	monoclinic	monoclinic	triclinic	triclinic
space group	$C2/c$	$P2(1)/n$	$P\bar{1}$	$P\bar{1}$
a, Å	17.624(12)	18.115(7)	11.106(4)	11.083(3)
b, Å	9.765(7)	19.081(7)	12.084(4)	12.203(4)
c, Å	13.506(9)	18.331(7)	12.741(4)	12.885(4)
α, deg	90.00	90.00	107.503(6)	107.899(5)
β, deg	109.914(9)	97.360(8)	91.912(6)	91.885(5)
γ, deg	90.00	90.00	115.239(6)	115.169(5)
V, Å^3	2185.38	6284(4)	1449.0(9)	1473.5(8)
Z	4	4	1	1
D_{calcd}, g/mL	1.805	1.498	2.031	2.103
cryst size, mm^3	0.60 × 0.55 × 0.22	0.60 × 0.42 × 0.30	0.34 × 0.32 × 0.06	0.74 × 0.40 × 0.24
μ, cm^{-1}	1.83	1.736	9.821	9.350
F(000)	1152	2856	852	888
reflns collected	8800	51 767	13 955	14 088
unique reflns	2145	12 371	6882	7000
reflns obsd	1878	6595	4381	5750
R indices $[I > 2\sigma(I)]^*$	R1 = 0.032, wR2 = 0.0801	R1 = 0.0759, wR2 = 0.2380	R1 = 0.0509, wR2 = 0.1371	R1 = 0.0547, wR2 = 0.1788
R indices (all data)	R1 = 0.0371, wR2 = 0.0835	R1 = 0.1376, wR2 = 0.2947	R1 = 0.0972, wR2 = 0.1710	R1 = 0.0671, wR2 = 0.1922

[*] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = \{[\Sigma[(F_o)^2 - (F_c)^2]^2]/[\Sigma w(F_o{}^2)^2]\}^{1/2}$ for $F_o{}^2 > 2\sigma(F_o{}^2)$, $w = [\sigma^2(F_o)^2 + (AP)^2 + BP]^{-1}$, where $P = [(F_o)^2 + 2(F_c)^2]/3$; A (B) = 0.0359 (3.1345) for **1**, A (B) = 0.1736 (2.0412) for **5**, A (B) = 0.1027 (0.0000) for **7**, and A (B) = 0.0967 (14.1034) for **8**.

were obtained by recrystallization from CH_2Cl_2 at 0 °C. ^1H NMR (CD_2Cl_2): δ 3.13 (t, 2H, $NCH_2CH_2CH_2CH_3$), 1.60 (m, 2H, $NCH_2CH_2CH_2CH_3$), 1.45 (m, 2H, $NCH_2CH_2CH_2CH_3$), 1.00 (t, 3H, $NCH_2CH_2CH_2CH_3$). ^{13}C NMR (CD_2Cl_2): δ 59.11, 24.17, 19.88, 13.60. ^{29}Si NMR (CD_2Cl_2): δ 37.92. Elem anal. Calcd for $C_{32}H_{72}Br_{12}I_2N_2Si_6$: C, 20.60; H, 3.89; N, 1.50. Found: C, 20.61; H, 3.85; N, 1.59.

X-ray Structural Determination. Single crystals of **1**, **5**, **7**, and **8** were mounted under mineral oil on glass fibers and immediately placed in a cold nitrogen stream ($T < -15$ °C) on a Siemens diffractometer with a 1K CCD area detector [graphite-monochromated Mo Kα radiation (crystals protected with Paratone N)]. The structures were solved by direct methods and refined on F^2 using the *SHELXTL* V6.14 package (after absorption corrections with *SADABS*). Non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were included in idealized positions. Crystallographic data for **1**, **5**, **7**, and **8** are given in Table 1.

■ RESULTS AND DISCUSSION

Synthesis and Characterization of Si_6X_{12} (X = Cl or Br). We recently reported the synthesis of perhalogenated cyclohexasilanes Si_6X_{12} [X = Cl (**1**) or Br (**2**)] via molecular halogenation of Si_6H_{12} with Cl_2 and Br_2, respectively.[8a] The reactions proceed rapidly in high yield (>85%), and the ^{29}Si NMR spectra of the products are consistent with a previous report.[9] Crystals of Si_6Cl_{12} suitable for structural determination by X-ray analysis were prepared by recrystallization from CH_2Cl_2 at −30 °C. Similar to the solid-state structure of Si_6Br_{12},[8a] Si_6Cl_{12} adopts a chair conformation with an inversion center in the middle of the Si_6 ring. The Si−Si bond distances are ~2.34 Å, the Si−Cl bond distances are ~2.03 Å, and the Si−Si−Si angles vary from 112 to 114° (Figure 1). It is worthwhile mentioning that no intermolecular halide−halide interaction is observed for Si_6Cl_{12} in the solid state, which stands in contrast to Si_6Br_{12}.[8a]

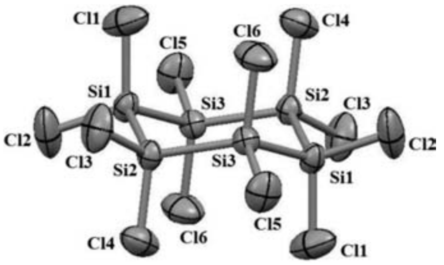
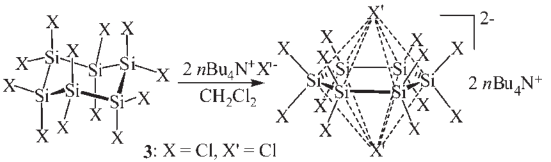


Figure 1. Molecular structure of **1**. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (deg): Si1−Si2 2.346(2), Si2−Si3 2.337(2), Si3−Si1 2.344(2), Si1−Cl1 2.030(2), Si1−Cl2 2.022(1), Si2−Cl3 2.029(2), Si2−Cl4 2.033(2), Si3−Cl5 2.029(2), Si3−Cl6 2.031(1); Si1−Si2−Si2 111.85(4), Si2−Si3−Si1 114.34(4), Si3−Si1−Si2 112.36(4).

Reaction of Si_6X_{12} (X = Cl or Br) with n-Bu_4NX' (X′ = Cl^-, Br^-, or I^-) and Adduct Characterization. The addition of n-Bu_4NX' (X′ = Cl^-, Br^-, or I^-) to a stirred solution of Si_6Br_{12} in CH_2Cl_2 led to the immediate formation of colorless precipitates. By way of comparison, the reaction of n-Bu_4NX' with Si_6Cl_{12} was not immediate but colorless crystal precipitation was noted for n-$Bu_4N^+I^-$ and n-$Bu_4N^+Br^-$ after stirring for 15 and 20 min, respectively. No precipitate was observed in the reaction of n-$Bu_4N^+Cl^-$ with Si_6Cl_{12}, with the mixture becoming turbid after stirring (1 h), with the colorless powder isolated after the addition of hexane. In all cases, products are colorless solids that form in good yield (55−78%). Elemental analysis indicates that all of these complexes consist of one Si_6X_{12} (X = Cl or Br) and

Scheme 2. Reaction of Si_6X_{12} (X = Cl or Br) with Halides



3: X = Cl, X′ = Cl
4: X = Cl, X′ = Br
5: X = Cl, X′ = I
6: X = Br, X′ = Cl
7: X = Br, X′ = Br
8: X = Br, X′ = I

Table 2. ^{29}Si NMR Chemical Shifts for **3**−**8** and Si_6X_{12} (X = Cl or Br)

	n-Bu_4NCl	n-Bu_4NBr	n-Bu_4NI	uncoordinated
Si_6Cl_{12}	−21.52 (**3**)	−22.23 (**4**)	−21.88 (**5**)	−0.54 (**1**)
Si_6Br_{12}	−37.44 (**6**)	−37.40 (**7**)	−37.92 (**8**)	−25.92 (**2**)

two n-Bu_4NX' (X′ = Cl^-, Br^-, or I^-) molecules, suggestive of the "inverse sandwich" geometry (Scheme 2).

All products have very low solubility in common organic solvents with NMR spectra collected in CD_2Cl_2 requiring long scanning times. ^{1}H and ^{13}C NMR spectra exhibit the anticipated resonances for tetra-n-butylammonium group with little variance in the chemical shifts among the different compounds. All ^{29}Si NMR spectra show a single sharp singlet that is shifted upfield compared to the uncoordinated perhalocyclohexasilanes **1** and **2** (Table 2). For Si_6Cl_{12} adducts (**3**−**5**), the ^{29}Si NMR signals shift from −0.54 to about −22.0 ppm, while for Si_6Br_{12} adducts (**6**−**8**), they are less shifted, from −25.92 to about −37.0 ppm. The silicon shifts for complexes **3**−**8** are comparable to that observed for the trisilacyclohexane complex (Scheme 1E), where the silicon ring atoms shift from −2.38 to −25.56 ppm when coordinated by fluoride, F^-.[10] It is also of note that almost no chemical shift was observed for the silicon ring atoms when Si_6Br_{12} was μ^6-coordinated by the nitrogen atom of p-tolunitrile (i.e., ^{29}Si = −25.77 ppm),[8a] which indicates the extent of the electrostatic interactions (Scheme 1F). It is interesting to note, in spite of the marked variance in the size and polarizability of the halogen atoms, that there is very little difference in the chemical shift of the silicon atoms that comprise the Si_6 ring. One might speculate that it is the geometry change of the Si_6 ring upon coordination [i.e., chair (D_{3d}) to planar (D_{6h})] that leads to this observation. To further probe the nature of this adduct chemistry, preliminary DFT calculations were performed for chair (D_{3d}) and planar (D_{6h}) isomers of Si_6X_{12} (X = Cl or Br) as well as the Cl^--, Br^--, and I^--coordinated $Si_6X_{12}X'_2{}^{2-}$ species (D_{6h}). The following trend is well-illustrated in the chemical shift calculations (see the Supporting Information): δ Si_6X_{12} (planar) > Si_6X_{12} (chair) > $Si_6X_{12}X'_2{}^{2-}$. These theoretical data support the notion that halide coordination is the most important factor contributing to the upfield changes noted in Table 2.

Complexes **3**−**8** were characterized by UV−vis spectroscopy and compared to the parent perhalogenated cyclohexasilanes (Figure 2). For free Si_6Cl_{12}, three absorbances were observed [λ_{max} = 241 nm (ε = 5500), 285 nm (ε = 900), and 325 nm (ε = 300)], in agreement with Hengge's results for a cyclohexane solution.[11] Interestingly, all three of these Si_6Cl_{12} peaks disappear in compounds **3**−**5**. A similar relationship was observed for compounds **6**−**8**, with the absorbance of Si_6Br_{12} [λ_{max} = 255 nm (ε = 5800), 282 nm (ε = 1200), 315 nm (ε = 700), and 345 nm (ε = 300)] disappearing upon halide coordination. Hengge pointed out that these weak absorptions are at low energy and are possibly due to intramolecular charge transfer. Our results suggested that such intramolecular interactions are minimized for cyclohexasilane complexes that maintain a planar Si_6 ring.

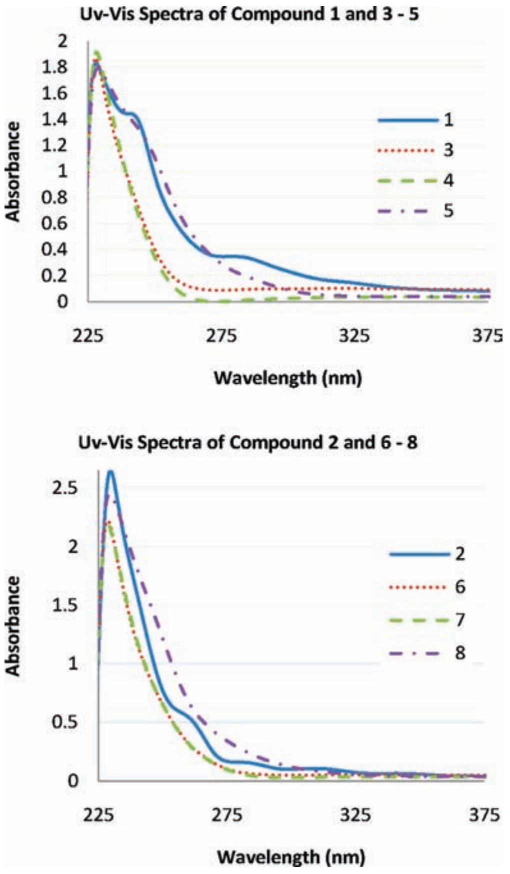


Figure 2. UV−vis spectra of **1** and **3**−**5** (above) and **2** and **6**−**8** (below) in CH_2Cl_2.

X-ray Structures of 5, 7, and8. Crystals of **5**, **7**, and **8** were grown from methylene chloride at 0 °C, and single-crystal X-ray diffraction analysis indicates that all contain a $[Si_6X_{12}X'_2]^{2-}$ dianion adopting the "inverse sandwich" structure and two tetra-n-butylammonium groups as the countercations (Figures 3−5). The "inverse sandwich" complexes in this work contain planar Lewis acids coordinated by Lewis bases. By way of comparison, most literature reports for "inverse sandwich" complexes have planar Lewis base rings (e.g., benzene, cyclopentadienyl, etc.) coordinated by Lewis acids both above and below the ring.[12]

Both complexes **7** and **8** have an inversion center in the middle of the Si_6 ring. For **5**, **7**, and **8**, the Si−Si distances in the Si_6 ring were 2.33−2.36 Å with very small deviations in the locations of the various halides for either equatorial or apical positions. The Si−Si−Si angles for **5**, **7**, and **8** are nearly 120°, giving a Si_6 planar hexagonal ring. These Si−Si distances are similar to those of a number of compounds: Si_6Br_{12} (2.34 Å),[8] $[PEDETA(SiH_2Cl)]_2[Si_6Cl_{14}]$ (2.32 Å),[1] neutral permethylated cyclohexasilane $[SiMe_2]_6$ (2.34 Å),[13] $[Si(Me)Ph]_6$ (2.35−2.36 Å),[14] and $[Si(H)CH_2Ph]_6$ (2.33 Å).[15] The Si−Br(equatorial) distances in **7**

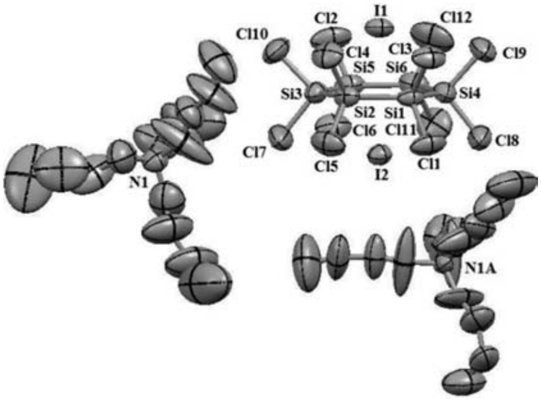


Figure 3. Molecular structure of **5**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms and a solvent molecule CH_2Cl_2 are omitted for clarity. Selected bond lengths (Å) and angles (deg): Si1–Si2 2.322(4), Si1–Si4 2.338(4), Si2–Si3 2.351(4), Si3–Si5 2.338(5), Si4–Si6 2.337(5), Si5–Si6 2.334(5), Si1–Cl1 2.079(4), Si1–Cl3 2.079(4), Si2–Cl5 2.078(4), Si2–Cl4 2.090(4), Si3–Cl7 2.084(4), Si3–Cl10 2.095(4), Si4–Cl8 2.078(4), Si4–Cl9 2.087(4), Si5–Cl2 2.087(4), Si5–Cl6 2.089(4), Si6–Cl12 2.066(5), Si6–Cl11 2.089(5); Si1–Si2–Si3 119.9(2), Si1–Si4–Si6 119.9(2), Si2–Si3–Si5 120.3(2), Si2–Si1–Si4 120.6(2), Si3–Si5–Si6 119.9(2), Si4–Si6–Si5 119.9(2). Contacts for Si–I1 (Å): 3.297, 3.268, 3.301, 3.334, 3.296, 3.291. Contacts for Si–I2 (Å): 3.286, 3.302, 3.229, 3.280, 3.272, 3.318.

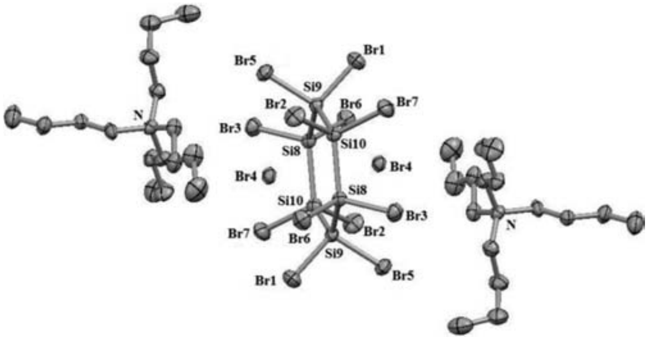


Figure 4. Molecular structure of **7**. Thermal ellipsoids are shown at the 50% probability level with hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): Si8–Si10 2.339(3), Si8–Si9 2.350(3), Si9–Si10 2.341(2), Si9–Br1 2.2433(19), Si10–Br2 2.2487(19), Si8–Br3 2.253(2), Si9–Br5 2.256(2), Si8–Br6 2.2535(19), Si10–Br7 2.229(2); Si8–Si9–Si10 119.7(1), Si9–Si8–Si10 121.7(1), Si8–Si10–Si9 118.3(1). Contacts for Si–Br4 (Å): 3.061, 3.115, 3.153, 3.140, 3.139, 3.141.

(2.23–2.26 Å) and **8** (2.27–2.28 Å) are slightly longer than that in free Si_6Br_{12} (2.20 Å),[8] indicating a possible weakening of the Si–Br bonds when the chair conformation of the cyclosilane Si_6Br_{12} is forced into planarity.

One of the most interesting features of these dianions is the strong interaction between silicon and apical halides. The contacts between the silicon and apical iodine atoms in both **5** ($[Si_6Cl_{12}I_2]^{2-}$) and **8** ($[Si_6Br_{12}I_2]^{2-}$) are very similar (~3.2–3.3 Å). These distances are significantly shorter than a typical Si–I van der Waals bond [r_{vdw}(Si–I) = 4.08 Å][16] but longer than the sum of the covalent radii [r_{cov}(Si–I) = 2.50 Å].[17] For **7** ($[Si_6Br_{14}]^{2-}$), the contacts between the silicon and apical bromine atoms (~3.1–3.2 Å) are significantly shorter than a typical Si–Br van der Waals bond [r_{vdw}(Si–Br) = 3.95 Å][16] but longer than the sum of the covalent radii [r_{cov}(Si–Br) = 2.31 Å].[17] The Si–X′(apical) interactions could be even more significant if the ionic radii were considered (i.e., Cl^-, Br^-, and I^- = 1.81, 1.96, and 2.20 Å, respectively).[18]

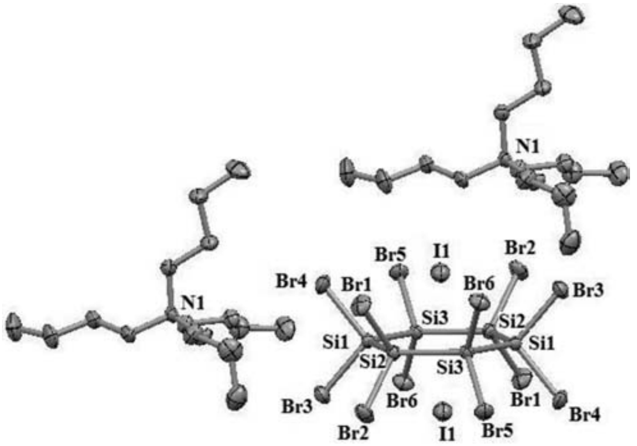
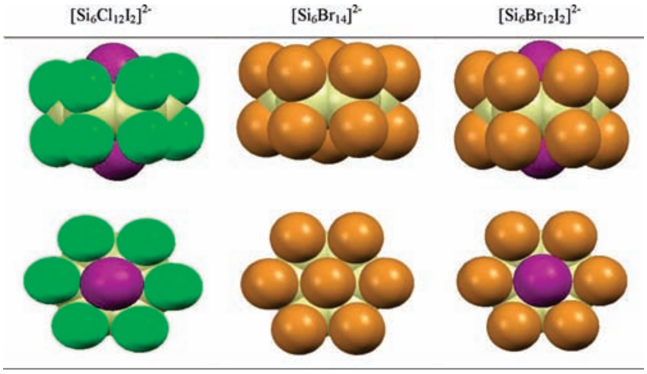


Figure 5. Molecular structure of **8**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Si1–Si2 2.356(3), Si1–Si3 2.352(2), Si2–Si3 2.360(4), Si3–Br6 2.276(2), Si3–Br5 2.245(2), Si1–Br4 2.273(2), Si1–Br3 2.293(2), Si2–Br2 2.269(2), Si2–Br1 2.272(2); Si1–Si2–Si3 121.5(1), Si1–Si3–Si2 118.5(1), Si2–Si1–Si3 119.9(1). Contacts for Si–I1 (Å): 3.254, 3.251, 3.239, 3.238, 3.159, 3.219.

Table 3. Spacefill Model of the Dianions in X-ray Structures[a]



[a] Atom color legend: chlorine, green; bromine, brown; iodine, purple; silicon, gray.

While the Si–X′(apical) interactions are important in the formation of these complexes, the equatorial halides must also play a key role in the adduct formation as Si_6Me_{12} does react with *n*-Bu_4NX' halides. The average X(equatorial)–X′(apical) distances in $[Si_6Cl_{12}I_2]^{2-}$, $[Si_6Br_{14}]^{2-}$, and $[Si_6Br_{12}I_2]^{2-}$ are 3.752, 3.787, and 3.837 Å, respectively. These distances are all very close to the sum of the van der Waals radii of two halogen atoms [r_{vdw}(Cl) = 1.75 Å, r_{vdw}(Br) = 1.85 Å, and r_{vdw}(I) = 1.98 Å][16] and slightly shorter than the sum of the van der Waals radius and ionic halide radius of halide. These results suggest that intramolecular halogen–halogen interactions are minimal. However, the electron-withdrawing nature of the 12 halogen atoms around the Si_6 ring likely leads to strong Lewis acid sites above and below the hexagonal ring. Spacefill models of the anions (Table 3) show

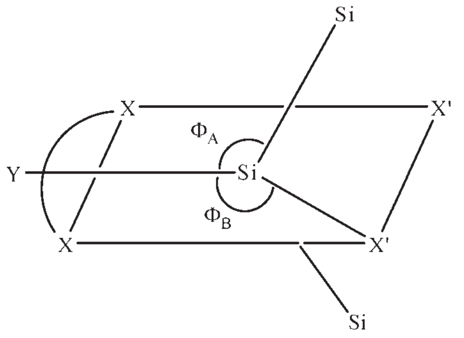


Figure 6. General stereochemistry for the silicon atoms in dianions.

Table 4. Stereochemical Parameters for Silicon Atoms of Dianions

	b^a	Φ_A	Φ_B	Si−Si/Si−X′
$[Si_6Cl_{14}]^{2-}$	1.535	120.04	140.60	0.774
$[Si_6Cl_{12}I_2]^{2-}$	1.566	120.01	135.24	0.710
$[Si_6Br_{14}]^{2-}$	1.546	120.03	138.56	0.750
$[Si_6Br_{12}I_2]^{2-}$	1.556	120.02	136.89	0.731

[a] $b = 2 \sin(\alpha/2)$, where $\alpha = (XSiX + X'SiX' + SiSiSi)/3$.

that the apical halides sit just above and below the Si_6 rings and are nearly contained inside the pocket formed by the Si_6X_{12} rings without noticeable X(equatorial)−X′(apical) interactions.

Weak hydrogen-bonding interactions between alkyl hydrogen atoms and halides (C−H···X) were observed, with **5** exhibiting two types of C−H···X contacts as follows: one interaction with a solvent molecule $C(CH_2Cl_2)$−H···Cl(equatorial) and one interaction with an ammonium alkyl group C−H···I(apical), with H···Cl and H···I distances of 2.790 and 3.173 Å, respectively. Compound **7** exhibits more complicated interactions between ammonium alkyl groups and the halides because each $[Si_6Br_{14}]^{2-}$ anion symmetrically bonds to six adjacent tetra-*n*-butylammonium groups through C−H···Br(equatorial) interactions (H···Br distances = 2.984, 3.014, and 3.035 Å). Compound **8** stands in contrast with only two symmetric C−H···Br(equatorial) interactions (H···Br distance = 3.031 Å). All of these H···X distances are slightly shorter than the corresponding sum of the van der Waals radii [$r_{vdw}(H) = 1.20$ Å, $r_{vdw}(Cl) = 1.75$ Å, $r_{vdw}(Cl) = 1.85$ Å, and $r_{vdw}(I) = 1.98$ Å].[16]

Stereochemistry of the Six-Coordinated Silicon Atoms. Each silicon atom in **3**−**8** adopts a distorted octahedral geometry. The stereochemistry for each silicon atom was approximated using the $[M(\text{bidentate})(\text{unidentate})_4]^{X\pm}$ system because all complexes contain two mirror planes (XXX′X′ and SiSiSi in X where equatorial halide and X′ apical halide; see Figure 6).[19] Therefore, the stereochemistry was defined by normalized bite *b* [$b = 2 \sin(\alpha/2)$, where $\alpha = (XSiX + X'SiX' + SiSiSi)/3$] and the angular parameters Φ_A and Φ_B, where the coordinate Φ is defined as the angle between the silicon−halide (or silicon−silicon) bond and the axis (Si−Y) passing through the silicon atom and bisecting the X−X edge. Because of the symmetry of the dianion structure, the SiSiSi plane is perpendicular to the XXX′X′ plane and the Si−Y axis represents the line that intersects these two planes.

The stereochemical parameters of the dianion silicon atoms for **5**, **7**, and **8** and $[PEDETA(SiH_2Cl)]_2[Si_6Cl_{14}]$[1] are shown in Table 4, with each reported value representing the average of the six silicon atoms. The normalized bite *b* for all four complexes is around 1.54−1.56, which is increased from the regular octahedral value (i.e., $2^{1/2} = 1.414$). The *b* value is larger than those of most of the six-coordinated metal complexes because Si−X′ is not a typical covalent bond, with longer Si−X′ distances giving larger *b* values. Φ_A is about 120° instead of the 90° observed for regular octahedral geometry, with Φ_B increased only slightly from 135°. In general, the stereochemistries of the silicon atoms in each dianion are very similar irrespective of the size or electronegativity of the halides, either at equatorial or apical positions.

CONCLUSION

"Inverse sandwich" complexes were prepared by the coordination of halide X′ (Cl^-, Br^-, or I^-) to perhalocyclohexasilanes Si_6X_{12} (X = Cl or Br). X-ray structures show that these halides coordinate to silicon atoms above and below the Si_6 ring. Both ^{29}Si NMR shift and X-ray structure data indicate strong interactions between coordinated halides and silicon atoms.

ASSOCIATED CONTENT

Supporting Information. Details for DFT calculations and crystallographic information files. This material is available free of charge via the Internet at http://pubs.acs.org.

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REFERENCES

(1) (a) Boudjouk, P. R.; Kim, B.-K.; Remington, M. P.; Chauhan, B. U.S. Patent 5,942,637, 1999. (b) Choi, S.-B.; Kim, B.-K.; Boudjouk, P.; Grier, D. G. *J. Am. Chem. Soc.* **2001**, *123*, 8117–8118.

(2) Pokhodnya, K.; Olson, C.; Dai, X.; Schulz, D. L.; Boudjouk, P.; Sergeeva, A. P.; Boldyrev, A. I. *J. Chem. Phys.* **2011**, *134*, 041405.

(3) (a) Chuit, C.; Corriu, R. P.; Reye, C.; Young, J. C. *Chem. Rev.* **1993**, *93*, 1371–1448. (b) Holmes, R. R. *Chem. Rev.* **1990**, *90*, 17. (c) Kost, D.; Kalikhman, I. *Acc. Chem. Res.* **2009**, *42*, 303. (d) Voronkov, M. G.; Trofimova, O. M.; Bolgova, Y. I.; Chernov, N. F. *Russ. Chem. Rev.* **2007**, *76*, 825.

(4) (a) Tamao, K.; Hayashi, T.; Ito, Y. *J. Organomet. Chem.* **1996**, *506*, 85. (b) Tamao, K.; Hayashi, T.; Ito, Y.; Shiro, M. *J. Am. Chem. Soc.* **1990**, *112*, 2422. (c) Tamao, K.; Hayashi, T.; Ito, Y.; Shiro, M. *Organometallics* **1992**, *11*, 2099.

(5) Sidorkin, V. F.; Belogolova, E. F.; Pestunovich, V. A. *Chem.—Eur. J.* **2006**, *12*, 2021.

(6) Kalikhman, I.; Girshberg, O.; Lameyer, L.; Stalke, D.; Kost, D. *J. Am. Chem. Soc.* **2001**, *123*, 4709.

(7) Jung, M. E.; Xia, H. *Tetrahedron Lett.* **1988**, *29*, 297.

(8) (a) Dai, X.; Schulz, D. L.; Braun, C.; Ugrinov, A.; Boudjouk, P. *Organometallics* **2010**, *29*, 2203. (b) Dai, X.; Anderson, K.; Schulz, D. L.; Boudjouk, P. *Dalton Trans.* **2010**, *39*, 11188.

(9) Kovar, D.; Utvary, K.; Hengge, E. *Monatsh. Chem.* **1979**, *110*, 1295.

(10) Brondani, D.; Carre, F. H.; Corriu, R. J. P.; Moreau, J. J. E.; Man, M. W. C. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 324.

(11) Stuger, H.; Hengge, E. *Monatsh. Chem.* **1988**, *119*, 873.

(12) (a) Bernard, M.; Rohmer, M.-M.; Lopez, X.; Theopold, K. H. *Angew. Chem., Int. Ed.* **2008**, *47*, 5597. (b) Buchin, B.; Gemel, C.; Cadenbach, T.; Schmid, R.; Fischer, R. A. *Angew. Chem., Int. Ed.* **2006**, *45*, 1074. (c) Freeman, W. P.; Don Tilley, T.; Liable-Sands, L. M.; Rheingold, A. L. *J. Am. Chem. Soc.* **1996**, *118*, 10457. (d) Jones, J. N.; Macdonald, C. L. B.; Gorden, J. D.; Cowley, A. H. *J. Organomet. Chem.* **2003**, *666*, 3. (e) Krieck, S.; Gorls, H.; Yu, L.; Reiher, M.; Westerhausen, M. *J. Am. Chem. Soc.* **2009**, *131*, 2977. (f) Nikiforov, G. B.; Crewdson, P.; Gambarotta, S.; Korobkov, I.; Budzelaar, P. H. M. *Organometallics* **2007**, *26*, 48. (g) Schier, A.; Wallis, J. M.; Mueller, G.; Schmidbaur, H. *Angew. Chem.* **1986**, *98*, 742. (h) Schmidbaur, H.; Nowak, R.; Schier, A.; Wallis, J. M.; Huber, B.; Mueller, G. *Chem. Ber.* **1987**, *120*, 1829. (i) Schmidbaur, H.; Nowak, R.; Steigelmann, O.; Mueller, G. *Chem. Ber.* **1990**, *123*, 1221. (j) Schumann, H.; Winterfeld, J.; Esser, L.; Kociok-Koehn, G. *Angew. Chem., Int. Ed. Engl.* **1993**, *105*, 1212. (k) Tsai, Y.-C.; Wang, P.-Y.; Chen, S.-A.; Chen, J.-M. *J. Am. Chem. Soc.* **2007**, *129*, 8066. (l) Wessel, J.; Behrens, U.; Lork, E.; Mews, R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 443.

(13) Carrell, H. L.; Donohue, J. *Acta Crystallogr., Sect. B* **1972**, *28*, 1566.

(14) Chen, S. M.; David, L. D.; Haller, K. J.; Wadsworth, C. L.; West, R. *Organometallics* **1983**, *2*, 409.

(15) Li, H.; Butler, I. S.; Harrod, J. F. *Organometallics* **1993**, *12*, 4553.

(16) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(17) Cordero, B.; Gomez, V.; Platero-Prats, A. E.; Reves, M.; Echeverria, J.; Cremades, E.; Barragan, F.; Alvarez, S. *Dalton Trans.* **2008**, 2832.

(18) (a) Pauling, L. *The Nature of Chemical Bond*, 2nd ed.; Cornell University Press: Ithaca, NY, 1948; pp 187−193. (b) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

(19) Kepert, D. L. In *Progress in Inorganic Chemistry*; Lippard, S. J., Ed.; John Wiley & Sons, Inc.: New York, 1977; Vol. 23, p 1.