Improved Synthesis of $[Si_6Cl_{14}]^{2-}$ Salts as Precursors for Si_6H_{12} and other Novel Silanes

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BACKGROUND

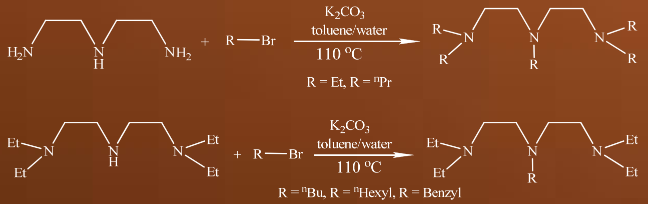
While studying the reaction of N,N,N',N',N"-pentaethyldiethylenetriamine (PEDETA) with $HSiCl_3$, an unexpected ionic compound containing a tetradecachlorocyclohexasilane dianion $[Si_6Cl_{14}]^{2-}$ was formed in high purity and low yield after refluxing for two days in CH_2Cl_2.[1] While there is precedent that amines may promote the formation of higher-order silanes (e.g., $N(CH_3)_3 + Si_2Cl_6 \rightarrow$-$(SiCl_2)_n$-oligomers)[2, 3] this triamine template reaction[1] was the first report where a cyclic product was formed from simple chlorosilanes. The novel synthesis of the $[Si_6Cl_{14}]^{2-}$ dianion from select triamines and trichlorosilane has led to a feasible feed stock of the cyclic Si_6H_{12} liquid silane. This precursor has enabled NDSU to examine the utility of liquid silanes as precursors for electronic materials via the following: electrospinning Si NWs for lithium-ion battery anodes; low-temperature PECVD growth of a-Si:H and SiN for solar cells; and printed transistors for solid-state lighting where 10 µm wide lines of a-Si:H have already been demonstrated using NDSU's Collimated Aerosol Beam Direct Write (CAB-DW)™. Given the strategic importance of these energy-relevant applications and our anticipated demand for developmental-scale quantities of Si_6H_{12}, the synthetic route to its precursor $[Si_6Cl_{14}]^{2-}$ is under active investigation. To this end, a series of alkyl triamines have been studied to better understand the underling chemistry of the complex triamine/chlorosilane interactions. These alkyl triamines have shown a similar reactivity with trichlorosilane producing complex salts of cationic hexacoordinate silane and the tetradecachlorocyclohexasilane dianion. The novel nature of these salts have also led to the discovery of new types of lewis acid-base adducts of cyclic Si_6X_{12}.

PURPOSE

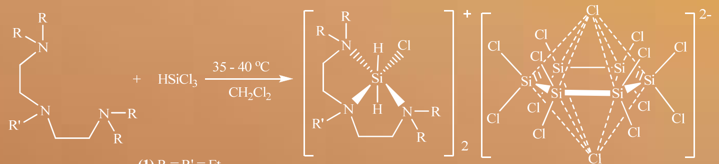
- Determine the reactivity of various peralkylated triamines on the dismutation and complexation of trichlorosilane.
- Explore the role of free tertiary amines in the reaction rate and yield the $[Si_6Cl_{14}]^{2-}$ synthesis.
- Understand the mechanism for chlorosilane condensation in the formation of $[Si_6Cl_{14}]^{2-}$.
- Utilize the various triamines with trichlorosilane in the synthesis of Si_6H_{12} for use in printed electronics.
- Further develop the synthesis of $[Si_6Cl_{14}]^{2-}$ as a precursor to Si_6Cl_{12} and its $L_2Si_6Cl_{12}$, $LSi_6Cl_{12}X^-$ and $Si_6Cl_{12}X_2^{2-}$ adducts.

REACTIONS

Synthesis of Peralkylated Triamines

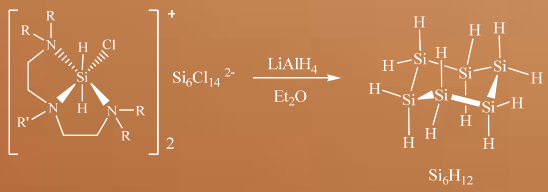


Synthesis of $[Si_6Cl_{14}]^{2-}$ Salts

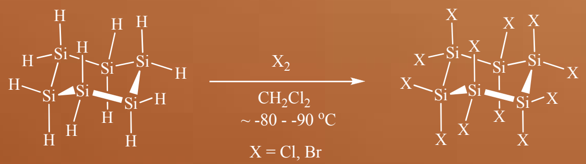


(1) R = R' = Et
(2) R = R' = ^{n}Pr
(3) R = Et, R' = ^{n}Bu
(4) R = Et, R' = ^{n}Hexyl
(5) R = Et, R' = Bz

Reduction of $[Si_6Cl_{14}]^{2-}$ Salt to Produce Cyclohexasilane



Synthesis of Perhalogenated Cyclohexasilane



RESULTS

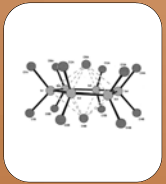
The reaction of excess $HSiCl_3$ with the aforementioned triamines led to the formation of $[Si_6Cl_{14}]^{2-}$ containing salts in all instances. The isolated complex salts were characterized using FT-IR and elemental analysis. IR spectra of these compounds showed characteristic Si-H stretching modes around 2100cm^{-1} due to the hexacoordinate silane cation and Si-Cl active modes near 528cm^{-1} as a result of the cyclic dianion. Reaction yields and elemental analysis (CHN) of the salts are summarized in the table below.

Compound	Percent Yield	Elemental Analysis (Theoretical)	Elemental Analysis (Experimental)
(1) $C_{28}H_{70}Cl_{16}N_6Si_8$	13.0%	C, 26.22; H, 5.50; N, 6.55	C, 26.37; H, 5.69; N, 6.49
(2) $C_{38}H_{90}Cl_{16}N_6Si_8$	10.4%	C, 32.07; H, 6.37; N, 5.91	C, 32.00; H, 6.20; N, 5.81
(3) $C_{32}H_{78}Cl_{16}N_6Si_8$	16.6%	C, 28.71; H, 5.87; N, 6.28	C, 28.96; H, 5.94; N, 6.34
(4) $C_{36}H_{86}Cl_{16}N_6Si_8$	17.6%	C, 30.99; H, 6.21; N, 6.02	C, 31.57; H, 6.46; N, 6.05
(5) $C_{38}H_{74}Cl_{16}N_6Si_8$	23.0%	C, 32.44; H, 5.30; N, 5.97	C, 31.77; H, 5.08; N, 5.66

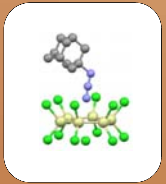
Reduction of salts **1-5** with $LiAlH_4$ led to the exclusive formation of cyclic Si_6H_{12} with yields >90%. This valued compound was further halogenated at low temperatures using Cl_2 or Br_2 to obtain dodecahalocyclohexasilanes. The reactivity of Si_6X_{12} was probed with a series of compounds to better understand the bonding between the silicon ring and axial moieties. Organic salts of form $^nBu_4NX$ (X = Cl, Br, I) were added to solutions of Si_6X_{12} in polar solvents to obtain crystals for X-Ray and ^{29}Si NMR analysis of these compounds.

^{29}Si NMR Data of Salts Compared to Free Si_6X_{12} in CD_2Cl_2				
	$^nBu_4NCl$	$^nBu_4NBr$	$^nBu_4NI$	Free
Si_6Cl_{12}	- 21.52	- 22.23	- 21.88	- 0.54
Si_6Br_{12}	- 37.44	- 37.40	- 37.92	- 25.92

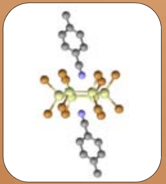
Recent studies on Si_6X_{12} interactions with isocyanides, azides, and other lewis bases has led to the discovery and isolation of a new class of neutral and ionic adducts of cyclic silanes. Further work in this field will likely uncover a broad range of donor molecules.



$Si_6Cl_{12}X_2^{2-}$
2000



$LSi_6Cl_{12}X^-$
2009



$L_2Si_6Cl_{12}$
2009

CONCLUSIONS

The reaction of peralkylated triamines with $HSiCl_3$ in dry CH_2Cl_2 gives ionic compounds based upon the tetradecachlorocyclohexasilane dianion. Several substituted triamines ($R_2NC_2H_4NR'C_2H_4NR_2$ where R = R'= Et, ^{n}Pr; R = Et, R'= ^{n}Bu, ^{n}Hexyl, Benzyl) were examined for this reaction and N,N,N',N'-tetraethyl-N"-benzyl-diethylenetriamine produced the best yields of $[Si_6Cl_{14}]^{2-}$ salt at 23% based on the amine reagent. This improvement in yield could be attributed to the decreased nucleophilicity of the central amine through increased steric hindrance of the alkyl substituents. The overall consequence of this substituent variation study has revealed new reagents for the synthesis of $[Si_6Cl_{14}]^{2-}$ salts and further demonstrated the ability of triamines to efficiently dismutate, complex, and condense chlorosilanes. The increased production of these salts has also opened a route for the study of Si_6X_{12} and its Lewis acid/base adducts.

ACKNOWLEDGEMENTS

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