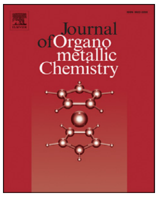
Journal of Organometallic Chemistry 768 (2014) 140–144

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem



N-Methylaniline-induced Si—Si bond cleavages of perchlorooligosilanes

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ARTICLE INFO

Article history:
Received 2 April 2014
Received in revised form
26 June 2014
Accepted 30 June 2014
Available online 8 July 2014

Keywords:
Si—Si bond cleavage
Disproportionation
Heterolytic cleavage
Aminochlorosilane

ABSTRACT

This study describes Si—Si bond cleavage of perchlorooligosilane using an amine. *N*-Methylaniline-induced Si—Si bond cleavage reactions of cyclic perchlorosilanes Si_5Cl_{10} (**1**) and Si_4Cl_8 (**2**), and acyclic perchlorosilanes Si_5Cl_{12} (**3**) and Si_2Cl_6 (**4**) yielded the *N*,*N*-methylphenylamino-substituted monosilanes, $(NMePh)_{3-n}SiHCl_n$ (**5**; $n = 2$, **6**; $n = 1$, **7**; $n = 0$) and $(NMePh)_{4-n}SiCl_n$ (**8**; $n = 2$, **9**; $n = 3$). Products and yields depended on the perchlorooligosilanes used. In addition, disproportionation between Si—N and Si—Cl bonds was observed in reactions of compounds **5** and **9**.

Introduction

Amine-induced disproportionation reactions of halogenated monosilanes and disilanes have been widely investigated [1]. In particular, the redistribution reaction of Si_2Cl_6 induced by Et_3N to yield dodecachloroneopentasilane [2] (Si_5Cl_{12}) and the reaction of $HSiCl_3$ with pentaethyldiethylenetriamine (PEDETA) to yield tetradecachlorocyclohexasilane dianion [3] $[(Si_6Cl_{14})^{2-}]$ are highly applicable synthetic methods. The reaction of $HSiCl_3$ with substituted pyridines forms stable solid adducts of $HSiCl_3\cdot(Rpy)_2$ as octahedral complexes. Disproportionation reactions of $HSiCl_3\cdot(Rpy)_2$ complexes in polar solvents at elevated temperature yield mixtures of $HSiCl_3\cdot(Rpy)_2$, $H_2SiCl_2\cdot(Rpy)_2$ and $SiCl_4\cdot(Rpy)_2$ [4]. Aminolysis reaction of $SiCl_4$ with various amines and disproportionation reactions of $SiCl_{4-n}(NR_2)_n$ ($n = 1, 2, 3, 4$) show exchanges between Si—N and Si—Cl bonds in aminochloromonosilanes. [5]

Wilkins reported that Si—Si bonds of Si_2Cl_6 are cleaved in the presence of excess NMe_3 [6], leading to many studies on this reaction along with plausible mechanisms. Recently, low-temperature two-dimensional HETCOR NMR and computational studies confirmed silylene-base adducts ($SiCl_2\cdot NR_3$) as key intermediates (Scheme 1 with NR_3 as base), defining the principle of the base-induced disproportionation of perchlorinated silanes [7]. With pyridine as a base, positively and negatively charged intermediates ($py\cdot Cl_3Si^{+}\cdots{}^{-}SiCl_3$) are generated through polarization of the Si—Si bond of Si_2Cl_6 by coordination with pyridine in a 1:1 M ratio. A subsequent addition reaction to the pyridine ring yields the 1,4-dihydro-1,4-bis(trichlorosilyl)pyridine. [8] The heterolytic cleavage mechanism was also demonstrated in the reaction of Si_2Cl_6 with tetramethylethylenediamine (TMEDA), suggested by the trapping reactions of $Si_2Cl_6\cdot TMEDA$ with MeX (X = Cl, I) and Me_3SiN_3 [9].

No reports have investigated Si—Si bond cleavage of cyclic silanes using amines. Thus, we studied the reactivity of decachlorocyclopentasilane in the presence of excess Et_3N and observed no change. However, we found that the secondary amine *N*-methylaniline reacted with decachlorocyclopentasilane. We report *N*-methylaniline-mediated Si—Si bond cleavage reactions of the cyclic perchlorosilanes Si_5Cl_{10} (**1**) and Si_4Cl_8 (**2**), and the acyclic perchlorosilanes Si_5Cl_{12} (**3**) and Si_2Cl_6 (**4**). In addition, we describe a plausible cleavage mechanism and demonstrate disproportionation of aminochlorosilanes.

Results and discussion

Decachlorocyclopentasilane [10] (**1**) and octachlorocyclotetrasilane [11] (**2**) were prepared using known

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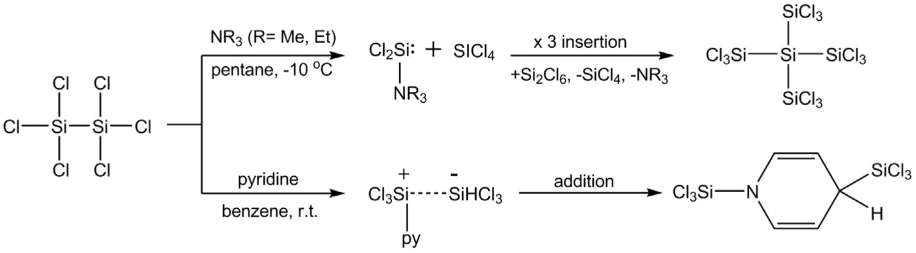
http://dx.doi.org/10.1016/j.jorganchem.2014.06.030



Scheme 1. Reactivity of $Cl_3SiSiCl_3$ to NR_3 (R = Me, Et) and pyridine.

procedures. Reactions of *N*-methylaniline with perchlorocyclosilanes (**1** and **2**) were carried out in benzene at room temperature.

All Si—Si bond cleavages of Si_5Cl_{10} (**1**) produced *N*,*N*-methylphenylamino-substituted chlorosilanes (**5**, **6**, and **7**) in quantitative yields (^{1}H NMR yield) (Scheme 2). Si—N bonds and Si—H bonds were formed in the products and all Si—Si bonds of **1** were cleaved.

The reaction of Si_4Cl_8 (**2**) with *N*-methylaniline yielded cleaved products (Scheme 3). Interestingly, not only nonprotonated **8** was obtained as a major product but also yields of **6** and **7** were different from those in Scheme 2; **6** was major product in the reaction of **1** while it was minor in the reaction of **2**. Different ring strains of the cyclosilanes likely affected the results, since compound **2** has larger ring strain than **1**. Accordingly, **2** was easily decomposed by UV-light to give perchloropolysilanes ($-(SiCl_2)_n-$) [12], while **1** was not. In comparison, compounds **1** and **2** did not react with Et_3N and reaction of **1** and **2** with dialkylamines (Et_2NH, $^iPr_2NH$) gave numerous mixtures respectively. It is noteworthy that compounds **1** and **2** were indifferent towards Et_3N as a tertiary amine, which was implying that secondary amines were important for the cleavage of Si—Si bonds.

A single crystal of compound **7** suitable for X-ray analysis was obtained by recrystallization from benzene. The structure of **7** has C_3 symmetry and the Si atom has a tetrahedral structure (Fig. 1). The Si—N bond length of 1.723(2) Å was similar to the bond length in arylaminosilanes [13] (av. 1.723(8) Å), and slightly longer than the length in alkylaminosilanes [14] (av. 1.709(8) Å). The bond angles around nitrogen atom ($\Sigma N = 359.9°$) showed planar geometry.

In the process of product-isolation, unfortunately, we were not able to isolate them except for compound **7**. This was because of the thermal disproportionation reaction of monosilanes containing Si—N and Si—Cl bonds during distillations at reduced pressure and separation using prep. GC. Therefore, we synthesized authentic compounds of products **5**, **6**, **8**, and **9** using aminolysis reactions of $SiCl_4$ or $HSiCl_3$ with *N*-methylaniline respectively (Scheme 4)

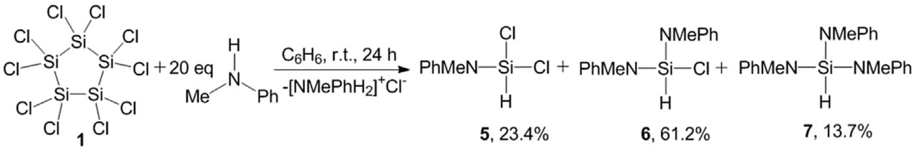
The novel all cleavage of Si—Si bonds of compounds **1** and **2** by a secondary amine prompted us to extend our study the corresponding reactivity of acyclic perchlorosilanes. The reactions of dodecachloroneopentasilane (**3**) and hexachlorodisilane (**4**) with *N*-methylaniline gave products, **8**, **9** (Scheme 5) and **6**, **7**, **8** and **9** (Scheme 6), respectively. All Si—Si bond cleavages of acyclic compounds were similar to cleavages of cyclic perchlorosilanes. Interestingly, the reaction of **3** yielded only nonprotonated species **8** and **9**, which were obtained at almost 79% yield (^{1}H NMR yield).

To investigate the possible mechanism that yielded the products of the reaction of perchlorosilanes with *N*-methylaniline, we carried out reactions in condition of different amounts of *N*-methylaniline. In conditions (a), 3 h reaction of 4 equivalents of *N*-methylaniline with **4** at room temperature gave $HSiCl_3$ (33.4%), **5** (17.5%), **8** (20.6%) and **9** (28.1%, ^{1}H NMR yield) and then (b), adding excess *N*-methylaniline into the reaction mixtures to give **6**, **7**, **8**, and **9** (Scheme 7). These final products were the same as the products from the reaction of **4** with 12 equivalents of *N*-methylaniline shown in Schemes 6 and 7. Protonated species ($HSiCl_3$ and **5**) were 50.9% of the yield and nonprotonated species (**8** and **9**) were 48.7% with a ratio of protonated to nonprotonated of nearly 1:1 under experimental condition (a). The formation of $HSiCl_3$ and a 1:1 ratio of protonated to nonprotonated products indicated that Si—Si bonds might be cleaved through positively- and negatively-charged intermediate. The product $HSiCl_3$ was formed from H abstraction by a negatively-charged Si atom and the counterpart aminosilane **9** was formed by bond formation between an N atom and a positively charged Si atom. The final compounds **6**, **7** and **8** could be formed by aminolyses of $HSiCl_3$, **5** and **9**, respectively.

We also studied ligand exchanges between Si—N and Si—Cl bonds in compounds **5** and **9** (Scheme 8). A major product was **6** in reaction (a) and **8** in reaction (b), which were monitored by ^{1}H NMR and GC/MS in 70.3% and 71.8%, respectively.

Conclusion

Reaction of *N*-methylaniline with the cyclic perchlorosilanes (**1** and **2**) and the acyclic perchlorosilanes (**3** and **4**) yielded the Si—Si bond-cleaved aminated products, $(NMePh)_{3-n}SiHCl_n$, ($n = 0–2$) and $(NMePh)_{4-n}SiCl_n$, ($n = 2–3$). We propose a plausible mechanism of an aminolysis reaction followed by the formation of positively- and negatively-charged intermediates through the coordination of *N*-methylaniline with silicon atoms. The negatively charged silicon atom acquires the proton on the nitrogen atom of the coordinated *N*-methylaniline to form a Si—H bond and simultaneously the positively-charged silicon atom forms a Si—N bond. In addition, disproportionation reactions of compounds **5** and **9** were observed at elevated temperatures.



Scheme 2. Reaction of Si_5Cl_{10} (**1**) with *N*-methylaniline.