Direct Reaction of Silicon with α−ω Dichloroalkanes: Direct Formation of Dichlorosilacyclopentane

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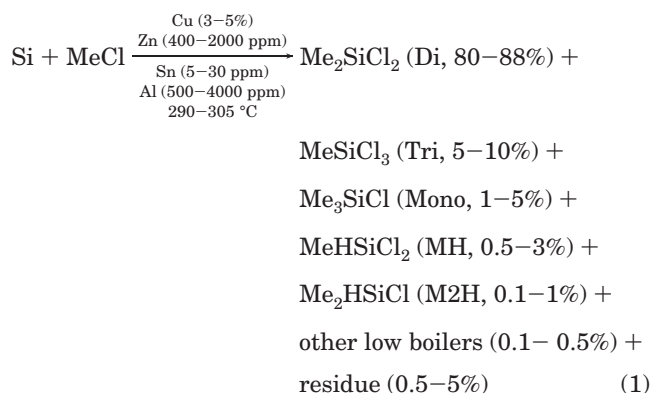*GE Global Research Center, 1 Research Circle, Niskayuna, New York 12309*

The direct reaction of silicon with 1,4-dichlorobutane in the presence of a CuCl catalyst gives high selectivity for dichlorosilacyclopentane under some conditions. The effects of residence time, temperature, and promoters are explored, and the highest selectivity occurs at short residence time and in the presence of a Cd promoter. The reaction of silicon with methyl chloride is discussed as well. The methyl chloride reaction is usually promoted by Zn and not by Cd. The reaction of silicon with 1,3-dichloropropane and with 1,5-dichloropentane was also explored; however poor selectivity to any product occurred with these other dichloroalkanes. The origin of the selectivity for the silacyclopentane is discussed in terms of low activation energy for ring closure in the five-membered ring case. Other low activation options such as reaction of silylene intermediate with C−H vs C−Cl prevent good selectivity in the dichloropropane and dichloropentane reactions.

Introduction

The direct reaction of silicon and methyl chloride, also known as the Rochow process, is the industrial process for production of methylchlorosilanes, eq 1.[1]

$$\text{Si} + \text{MeCl} \xrightarrow[\substack{\text{Sn (5−30 ppm)} \\ \text{Al (500−4000 ppm)} \\ \text{290−305 °C}}]{\substack{\text{Cu (3−5\%)} \\ \text{Zn (400−2000 ppm)}}} \text{Me}_2\text{SiCl}_2 \text{ (Di, 80−88\%) +}$$

$$\text{MeSiCl}_3 \text{ (Tri, 5−10\%) +}$$

$$\text{Me}_3\text{SiCl (Mono, 1−5\%) +}$$

$$\text{MeHSiCl}_2 \text{ (MH, 0.5−3\%) +}$$

$$\text{Me}_2\text{HSiCl (M2H, 0.1−1\%) +}$$

$$\text{other low boilers (0.1− 0.5\%) +}$$

$$\text{residue (0.5−5\%)} \qquad (1)$$

Processes for direct formation of chlorosilanes with groups other than methyl have been less well developed.[2] The ethylchlorosilane[3,4] process was fairly well worked out in the Soviet chemical industry, and other alkylchlorsilane[5,6] direct reactions were also reported. Phenylchlorosilanes were first prepared shortly after the discovery of the methyl process.[7] Concerns about poly-chlorinated biphenyl formation have limited the direct reaction of phenyl chloride with silicon. Reactions of silicon with vinyl halides have also been reported.[8]

Perhaps the most extensive research on direct silicon reactions with RCl (R ≠ Me) have been performed by the Jung group in Korea. Jung has reported reactions of silicon with methylene chloride,[9] chloromethylsilanes,[10] and allyl chloride.[11] An interesting direct reaction of silicon with 1,2-bis(chloromethyl) benzene has been shown to give the silacycle shown in eq 2.[12]
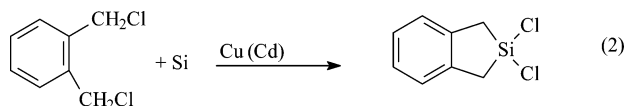
Dichlorosilacyclopentane, **1**, was prepared in the 1950s by Grignard[13] and by alkyllithium[14] reactions of silicon tetrachloride with 1,4-dichlorobutane. Compound **1** was also prepared in about 30% yield from the direct reaction of 1,4-dichlorobutane with silicon in a tube reactor.[15] Copolymers obtained by hydrolysis of Me$_2$SiCl$_2$ and **1** indicated higher thermal stability than

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(1) Lewis, L. N. Recent Advances in the Direct Process. In *The Chemistry of Organosilicon Compoinds*; Rappoport, Z., Apeloig, Y., Eds.; John Wiley & Sons: 1998; Vol. 2, Chapter 26, p 1581.

(2) Kanner, B.; Lewis, K. M. Commercial Production of Silanes by the Direct Synthesis. In *Catalyzed Direct Reactions of Silicon*; Lewis, K. M., Rethwisch, D. G., Eds.; Elsevier: New York, 1993; p 1.

(3) Trishkin, V. Ya.; Koval'chuk, D. S.; Paravoi, E. I.; Kocherga, V. D.; Golubtsov, S. A.; Mangalin, E. G. Selection of an optimality criterion for the synthesis of organosilicon monomers. *Vopr. Khim. Khimicheskoi Tekhnol.* **1973**, *No. 28*, 52−6. CAN 80:27734.

(4) Moskovtsev, V. V.; Golubtsov, S. A.; Andrianov, K. A.; Lobusevich, N. P. Directed synthesis of ethyldichloro and diethyldichlorosilanes. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1970**, 1079−82, CAN 73:66660.

(5) Topchiev, A. V.; Nametkin, N. S. Direct synthesis of alkyl and *arylhalosilanes*. *J. Gen. Chem. U.S.S.R.* **1953**, *23*, 73−8.

(6) Sadykh-Zade, S. I.; Petrov, A. D. Direct synthesis of chloro (3-chloro-2-butenyl)silanes. *Dokl. Akad. Nauk S.S.S.R.* **1954**, *96*, 765−8; CAN 49:45931.

(7) Rochow, E. G.; Gilliam, W. F. *J. Am. Chem. Soc.* **1945**, *67*, 1772.

(8) Hurd, D. T. *J. Am. Chem. Soc.* **1945**, *67*, 1813.

(9) Jung, Il. N.; Yeon, S. H.; Lee, B. W. Preparation of polychlorobis-(silyl)alkanes. U.S. Patent 5,235,083, 1993.

(10) Jung, Il. N.; Lee, G. H.; Yeon, S. H.; Suk, M. Y. Direct synthesis of trisilaalkanes. *Bull. Korean Chem. Soc.* **1991**, *12*, 445−9.

(11) Yeon, S. H.; Lee, B. W.; Kim, S. Il.; Jung, Il. N. Problems and solutions involved in direct synthesis of allylchlorosilanes. *Organometallics* **1993**, *12*, 4887−91.

(12) Jung, Il. N.; Yeon, S. H.; Han, J. S. Direct synthesis of 2,2-dichloro-2-silaindan. *Bull. Korean Chem. Soc.* **1993**, *14*, 315−16.

(13) Kumada, M. Synthesis of some organosilicon compounds by the Grignard method. *J. Inst. Polytech. Osaka City Univ.* **1951**, *Ser. C, 2*, 11−8.

(14) West, R.; Rochow, E. G. Alkyldilithium compounds and organosilicon spiranes. *Naturwissenschaften* **1953**, *40*, 142.
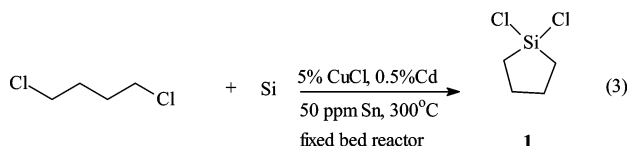
those polymers obtained without **1** (polydimethysiloxanes).[16] In addition Cella reported that dimethoxysilacyclopentane (prepared from methanol and **1**) imparted improved cure performance when combined with standard components of a room-temperature vulcanizable siloxane.[17]

1
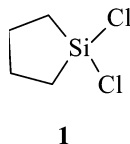
This report describes our efforts to better understand the direct formation of **1** and briefly explore the reactions of silicon with other dichloroalkanes.

Results and Discussion

Selectivity and Yield of Dichlorosilacyclopentane, 1. Our fixed bed reactor has been described previously, and it enables us to react solid mixtures of silicon and metal catalysts with gaseous reagents such as methyl chloride.[18] By use of a syringe pump and a carrier flow gas we can also use the fixed bed reactor to react silicon and reagents that are liquid at ambient temperature in place of gases.[19] In a typical methylchlorosilane direct reaction, eq 1, powdered silicon, 5% of a CuCl catalyst, 0.5% Zn, and 50 ppm tin were reacted with methyl chloride gas at 300 °C. When 1,4-dichlorobutane was used in place of methyl chloride, the recovered condensable materials were composed of many compounds and no single product was made in more than a few percent. Jung employs Cd and not zinc in all of his reports.[9−12] No mention of promoters was made in the 1950s work.[15] The reaction between silicon and 1,4-dichlorobutane was repeated, but cadmium was used in place of zinc as a promoter and high selectivity for **1** occurred, eq 3.

$$Cl\diagdown\diagup\diagdown Cl \ + \ Si \xrightarrow[\substack{50\ ppm\ Sn,\ 300^{\circ}C \\ fixed\ bed\ reactor}]{5\%\ CuCl,\ 0.5\%Cd} \ \ \mathbf{1} \tag{3}$$

The yield and selectivity for **1** were determined as follows. The silicon utilization was determined by mass balance before and after reaction. Formation of **1** was confirmed by comparison of ^{1}H NMR and gas chromatography (GC) to pure standards. Finally conversion of 1,4-dichlorobutane (DCB) to products and specifically

(15) Petrov, A. D.; Smetankina, N. P.; Nikishin, G. I. Direct synthesis of 1,1-dichloro-1-silacyclopentane. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1958**, 1468−71; CAN 53:45158.

(16) Sobolevskii, M. V.; Nazarova, D. V.; Lotarev, M. B. Polyorganosiloxanes based on 1,1-dichloro-1-silacyclopentane. *Plasticheskie Massy* **1968**, 30−2; CAN 70:5834.

(17) Cella, J. A.; Burnell, T. B. Room-temperature-vulcanizable silicones comprising difunctional organosilicon compounds U.S. Patent 5,610,259, 1997.

(18) Lewis, L. N.; Ward, W. J. Use of a Fixed Bed Reactor to Evaluate the Interactions of Catalysts and Promoters in the Methyl Chlorosilane Reaction and to Determine the Effect of Cu in the Form of Eta Phase on Theis Reaction. *Ind. Eng. Chem. Res.* **2002**, *41*, 397−402.

(19) Lewis, L. N.; Schattenmann, F. J.; Jordan, T. M.; Carnahan, J. C.; Flanagan, W. P.; Wroczynski, R. J.; Lemmon, J. P. Reaction of Silicate Minerals to Form Tetramethylsilane. *Inorg. Chem.* **2002**, *41*, 2608.
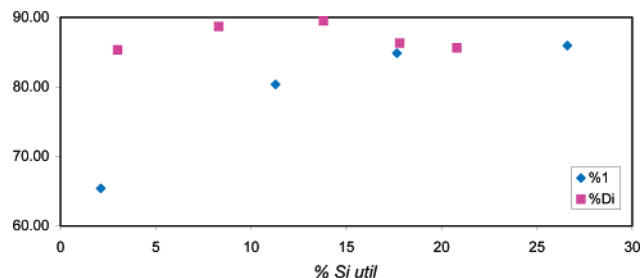

Figure 1. Typical plot of % Di (dimethyldichlorosilane) in product mixture from reaction of silicon with methyl chloride and % formation of **1** from the reaction of silicon and 1,4-dichlorobutane.
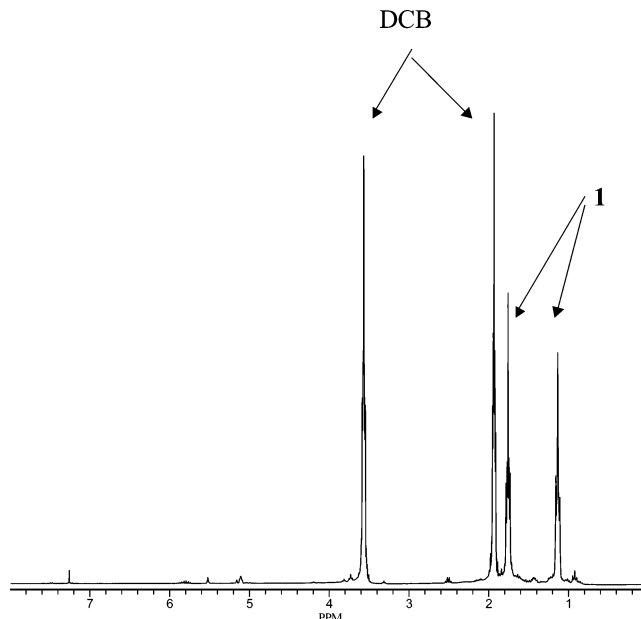
Figure 2. ^{1}H NMR spectrum of "crude" product mixture from reaction of 1,4-dichlorobutane (DCB) with Si to form dichlorosilacyclopentane (**1**) in a fixed bed reactor.

to **1** was determined. In a typical methyl chloride reaction with silicon, the formation of dimethyldichlorosilane (Di) vs silicon utilization is plotted in order to determine the quality of the product mixture obtained, as shown in Figure 1.

In a like manner, formation of **1**, from eq 3, as a percent of the total of all products vs silicon utilization was plotted and is also shown in Figure 1; these data were obtained from GC analysis. In the fixed bed experiment, samples of condensed liquid are collected periodically and then analyzed. The error on percent selectivity is about 2%. The first sample from the reaction in eq 3 was analyzed by GC and ^{1}H NMR, Figure 2. Both analyses showed that the mixture was about 70% unreacted DCB and 30% **1**. GC-MS analysis showed that other trace products included unsaturated species such as

$$Cl_3Si\diagdown\diagup\diagdown\diagup$$
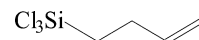
The NMR in Figure 2 shows the trace peaks due to unsaturated products between 5 and 6 ppm and small peaks due to saturated resonances.

We explored the effect of residence time of the feed reactant, DCB, on conversion and selectivity. There were two ways to control the residence time of DCB over
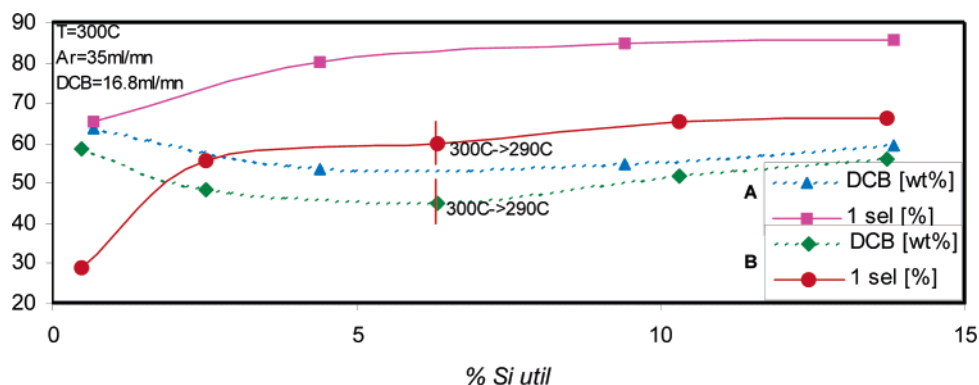
Figure 3. (A) Reaction of Si with 1,3-dichloropropane. (B) Reaction of Si with 1,3-dichloropropane, 300 °C vs 290 °C.
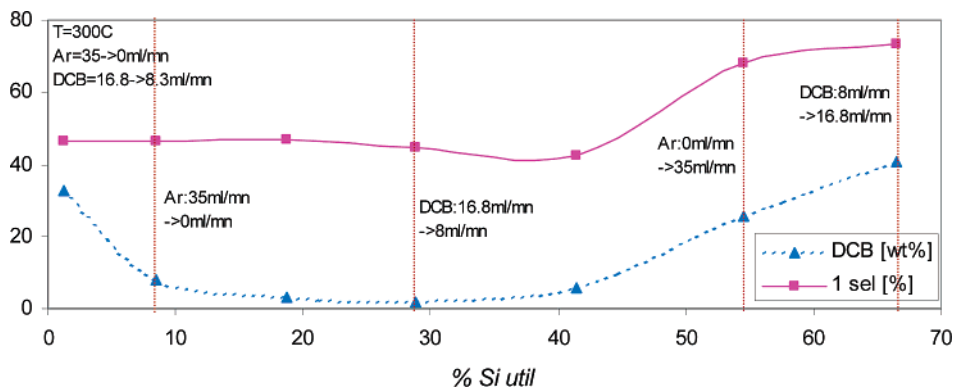
Figure 4. Reaction of Si with 1,4-dichlorobutane, effect of residence time and partial pressure.

the silicon-catalyst bed: syringe pump feed rate and carrier gas flow. Initial conditions employed a flow rate of DCB of 16.8 mL/min using an Ar carrier gas flow rate of 35 mL/min and a temperature of 300 °C. Figure 3A shows the course of the reaction with consumption of DCB and formation of **1**.

The reaction in eq 3 was repeated except that in the course of the reaction the temperature was lowered from 300 °C to 290 °C with only a small decrease in yield and small change in formation of **1**, Figure 3B. Note that the methylchlorosilane reaction will run very poorly at 290 °C.[20]

The reaction of eq 3 was repeated a third time by making changes in residence time. Residence time and partial pressure of DCB were varied first by shutting off the carrier gas flow, and then the syringe pump feed rate was shortened. In both cases significant changes in the DCB conversion and product selectivity occurred. When the carrier gas was turned off, nearly complete conversion of DCB occurred (vs only about 50% conversion). However selectivity for **1** was extremely poor. At this point, lowering the feed rate had no substantial effect on yield or selectivity. When the carrier gas flow was re-established (still lower syringe pump feed rate), the yield decreased and the selectivity for formation of **1** increased.

Thus with a short residence time, 50% conversion and ca. 85% selectivity to **1** occurred, but when the residence time was long, nearly quantitative conversion of DCB to products occurred but with only about 50% selectivity for **1**, Figure 4. The effects observed were due to simultaneous change in residence time and partial

pressure, but no experiments were performed that could distinguish the effect of partial pressure and residence time.

Another factor promoting formation of **1** was the choice of Cd vs Zn as a promoter. ^{1}H NMR and GC analysis of the collected condensables from the reaction in eq 3 but using Zn in place of Cd showed a multitude of peaks. The origin of the difference between Cd and Zn is not known. However, one attempt was made to improve the reaction of eq 3 with Zn as the promoter. We and others reported that improved selectivity in the methylchlorosilane reaction occurred when low levels of zinc were used and about 500 ppm of phosphorus was added to the silicon−catalyst mixture.[21] For example, in eq 1, the selectivity for Me_2SiCl_2 improved from about 85% to over 90%. The reaction of eq 3 was repeated using Zn at 700 ppm instead of 1800 ppm and with 580 ppm of phosphorus in the form of Cu_3P, and conversion of DCB to products was about 40% and selectivity for **1** improved to about 60%. The use of phosphorus improved the selectivity for **1** when Zn was the promoter, but Cd alone was a superior promoter for selectively forming **1**. The use of Cd as a promoter for the methyl chlorosilane direct reaction will be the subject of a future publication.

Reactions of Silicon with Other α,ω-Dichloroalkanes. Attempts were made to prepare the four- and six-membered silacycles from 1,3-dichloropropane (DCP) and 1,5-dichloropentane (DCPent) respectively, eqs 4 and 5.

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(20) Voorhoeve, R. J. H. *Organohalosilanes*; Elsevier: New York, 1967; pp 139−45.

(21) Ward, W. J.; Lewis, L. N.; Bablin, J. M. Exploring the Effects of Phosphorus in the Direct Process with a Fixed Bed Reactor. Oye, H. A., Rong, H. M., Nygaard, L., Schussler, G., Tuset, J. Kr., Eds. In *Silicon for the Chemical Industry V*; Trondheim: Norway, 2000; p 309.

(4)

(5)

Scheme 1
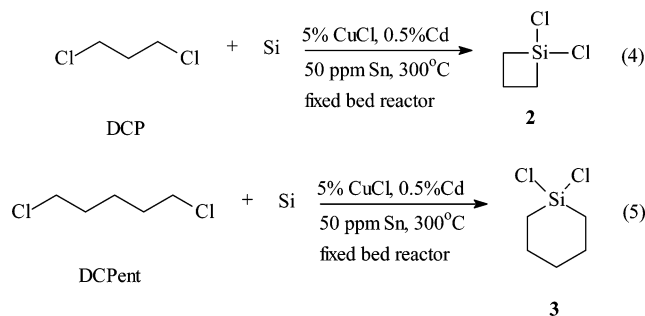
The reaction of DCP was investigated under a variety of carrier gas flow rates and DCP injection rates. The "optimal" Cu/Cd/Sn conditions from eq 3 were employed in all cases. While DCP conversion greater than 50% could be achieved, selectivity for **2** was never higher than about 15%. ^{1}H NMR and GC analyses of the collected condensed products from eq 4 showed a multitude of products. The condensed materials from eq 4 included saturated and unsaturated groups. GC-MS analysis indicated that most of the products were not the cyclic species desired. The GC-MS analysis did confirm the presence of **2**, a species with 174 amu mass, consistent with $Cl_3SiC_3H_5$ (allyl), and the biggest peak in the spectrum had a mass of 308 amu, consistent with $Cl_3SiCH_2CH_2CH_2SiCl_3$. The corresponding compound, $Cl_3Si(CH_2)_4SiCl_3$, was NOT found in GC-MS analysis of the condensables from the reaction of eq 3. Even less selective was the reaction of eq 5. In the reaction of 1,5-dichloropentane with Si, only a trace of product **3** was observed by GC-MS analysis.

Clearly, only the formation of the five-membered ring, **1**, proceeded with any reasonable selectivity. The thermodynamic stability and/or formation of the three silacycles, **1**, **2**, and **3**, were investigated.

Scheme 1 is a proposal that supports the observed formation of **1** under some conditions. Formation of a silylene intermediate in methyl chloride direct reaction from reaction of MeCl and a copper−silicon alloy like Cu_3Si η-phase has been well established.[22] Silylene **4** is the likely silylene from reaction of 1,4-dichlorobutane with copper silicon alloy. Formation of Si−H-, Si−Si-, and Si−C-containing products can be explained by silylene reaction with C−H (or HCl), SiCl, or C−Cl, respectively. There is a high probability for reaction of C−H with the silylene intermediate to give undesirable products. However, reaction of dichlorobutane is special because of the close proximity of the second C−Cl bond to the silylene. Thus silylene reaction with the 4-C−Cl position to permit ring closure and formation of **1** is competitive with reaction with C−H and intermolecular C−Cl. In the reactions of silylene, in eqs 4 and 5, the second intramolecular C−Cl is not positioned to make silylene reaction with it favorable.

Computational Details

To address the observation that the five-membered silacycle is preferred over the four- and six-memberd silacycles, we sought to model the transition state intermediates for the reaction and compare computed
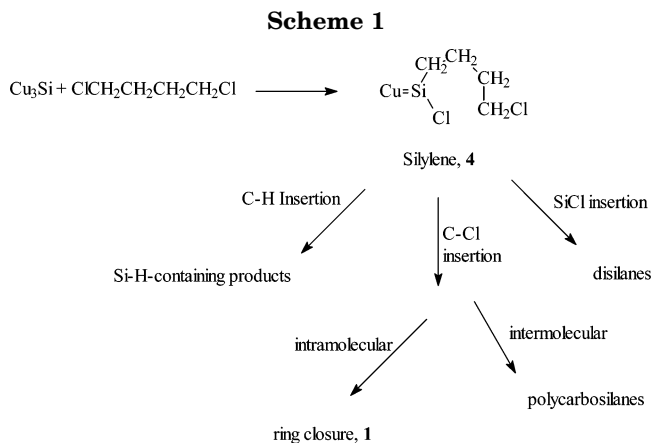
steric, electronic, and thermodynamic properties. In setting up such a comparison, a number of approximations are required. The reactions were modelled in the gas phase and removed from a continuous silicon surface. There is good reason to believe the initial reaction between the chloroalkane and η-phase silicon does not depend on the length of the alkane moiety. Rather, the reactions depart at the point where a copper-bound silicon atom engages in insertion and other side reactions. Initially we explored copper-stabilized silylenes, but these had convergence issues. Therefore, we modelled the simplest case, namely, naked silylenes for the three cases under investigation (Table 1). Models were computed using Wavefunction's Spartan 2004[23] on a Pentium 4 computer. Energy is reported as the *total* energy,[24] not the classical heat of formation from the elements typically available using semiempirical models.

The silylenes in Table 1 were subjected to a global conformation search at the PM3 level with the lowest energy conformers geometry-optimized at the HF/6-31G* level. Conformers that showed an apparent intramolecular interaction between the silylene and a neighboring atom were selected for additional geometry optimization at the B3LYP/6-31G* level. These results are listed in Table 2. Linear silylenes **5a** and **6a** demonstrate only one acceptable cyclic intermediate, **5b** and **6b**, respectively, while **7a** shows two acceptable cyclic intermediates, **7b** and **7c**. These conformers all show an intramolecular interaction between the silylene and hydrogen or chlorine atoms five or six atoms away at an average of 2.789 Å. The silylene−H or silylene−Cl interaction is probably the initial geometric arrangement required for a silylene insertion process into the heteroatom−carbon bond. Further evidence for the silylene insertion process is seen by computing and visualizing the HOMO. The molecular orbital extends from the silylene across space to the "bonded" heteroatom. The carbon atom bond distances are considerably further away for these pre-transition state intermediates, with an average of 3.615 Å. In general, these conformers are less stable and suffer a smaller entropic penalty than their linear isomers.

To address the question of experimental product silacycle preference, the cyclic intermediates in Table

(22) Okamoto, M.; Onodera, S.; Okano, T.; Susuki, E.; Ono, Y. Intermediacy of Surface Silylene in the Direct Synthesis of Methylchlorosilanes. *J. Organomet. Chem.* **1997**, *531*, 67.

(23) *Spartan 2004*; Wavefunction, Inc.: Irvine, CA 92612.
(24) The ab initio calculation methods provide energy for the process of separating the molecule into bare nuclei and electrons.

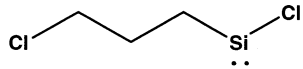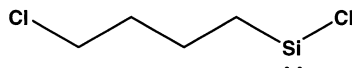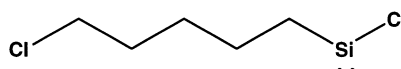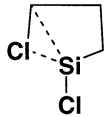**Table 1. Model Structure for Computation Study (B3LYP/6-31G*)**
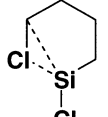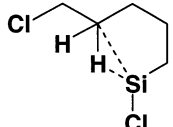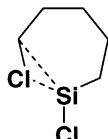
	Chain-elongated Silylene Structures	E (kcal/mol)	G° (kcal/mol)	S° (kcal/mol°C)	H° (kcal/mol)
5a		-833227.886	-833196.058	9.456E-02	-833167.865
6a		-857897.482	-857849.103	1.023E-01	-857818.610
7a		-882567.442	-882501.607	1.045E-01	-882470.464

Table 2. Pre-silacycle Conformers (B3LYP/6-31G*)

	Pre-silacycle Structure	G° (kcal/mol)	Energy Difference [a] (kcal/mol)	Entropy Difference [b] (kcal/mol°C)	Silicon to carbon distance (A)	Silicon to heteroatom distance (A)
5b		-833198.038	-1.98	-6.540E-03	3.426	2.759
6b		-857848.351	0.752	-9.228E-03	3.570	2.743
7b		-882500.086	1.521	2.577E-03	3.437	2.778
7c		-882497.046	4.561	-2.064E-01	4.028	2.874

[a] Gibbs free energy difference between cyclic and liner isomers (negative = favored). [b] Entropy difference between cyclic and linear isomers (positive = favored).

2 were subjected to transition state optimization at the B3LYP/6-31G* level. Convergence difficulty was encountered with most of the cyclic intermediates in that one single large amplitude imaginary frequency was not observed. The exception was with **6b**, where a good transition state was identified with a single imagery vibration frequency of i328.56 cm^{-1}. Animation of the vibration shows an insertion process. The bonding distances in the transition state **6c** are as follows: Si−C = 2.846 Å, Si−Cl = 2.324 Å, and C−Cl = 2.473 Å.

Due to the difficulty in obtaining transition state geometries for the cyclic intermediates, we constrained the bond distances for **5c** and **7d** to match those listed above for **6c**. The analogous operation with **7c** was not preformed due to the lack of a transition state distance for the Si−H bond. The constrained structures were then subjected to optimization at the B3LYP/6-31G* level. These results are listed in Table 3.

Using this technique, we obtained single imagery frequencies for **5c** = i307.05 cm^{-1} and **7d** = 489.69 cm^{-1}.

Table 3. Transitions State Results (B3LYP/6-31G*)

	Transition State	Gº (kcal/mol)	Energy Difference [a] (kcal/mol)	Entropy Difference [b] (kcal/mol°C)
5c		-833166.996	31.042	-4.876E-04
6c		-857820.388	27.963	-1.831E-03
7d		-882466.131	30.915	-4.961E-03

[a] Gibbs free energy difference between cyclic and liner isomers (negative = favored). [b] Entropy difference between cyclic and linear isomers (positive = favored).

The energy barrier for the formation of the silacyclopentane is 3 kcal/mol less than the others. This is significant enough to anticipate an order of magnitude preference for the formation of the silacyclopentane over the other ring-forming reactions. The entropic differences also illustrate a degree of preference. Note that **5c** pays a smaller entropy penalty for ring formation than either **6c** or **7d**. This may help explain the experimental observation for the formation of a small quantity of silacyclobutane. In the case of silacyclohexane, not only does it have the largest entropy penalty, but inspection of the transition state structure shows the methylene hydrogen in the ring to be 2.871 Å away from the chlorine atom involved in the insertion reaction. This is a disfavored steric situation and adds to the observation that formation of the silacyclohexane is inhibited. The analogous interaction for **5c** measures 2.976 Å, and **6c** measures 2.944 Å.

Experimental Section

Measurements. GC measurements were made using a Hewlett-Packard model 6890 instrument with a thermal conductivity detector and a 30 m HP 1 column (0.32 mm i.d. and 0.25 μM film thickness). GC-MS data were recorded using a JEOL SX 102 high-resolution, double-focusing magnetic sector instrument with a 30 m DB 5 capillary column. NMR spectra were recorded in $CDCl_3$ with TMS as an internal standard on a GE QE-300 instrument, ^{1}H and ^{13}C NMR at 300.15 and 75.48 MHz, respectively. Pulverized silicon was used in the reactions. The silicon was produced by Elkem Chemicals and was taken from a standard lot made for plant feed. A large quantity of this silicon was ground, and the resulting ground powder was used as feed to the lab reactors. The surface area was 0.38 m^2/g. The silicon had a particle size of 50 μm. The elemental composition of the silicon was the same as previously reported.[18]

Procedures. Reactions were performed in a fixed bed reactor as described previously.[18,19,21] The reactor was a glass tube (20 cm long; 1 cm inner diameter) with a porous glass grid to hold the silicon/catalyst/promoter sample. The reactor was centered vertically in a Nichrome ribbon wound glass tube (5 cm outer diameter). Two pairs of electrodes were fitted to the Nichrome to create two heated zones. The top-heating zone was used to preheat the dichloroalkane/carrier gas mixture, and the bottom section was for the reactor itself. The Nichrome wound tube was centered in a quartz glass tube (6.4 cm outer diameter) for insulation and safety purposes. The carrier gas stream was regulated using a mass flow controller (MKS Instruments type 1179A) connected to a four-channel readout device (MKS Instruments type 247D). The dichloroalkane was added into the carrier gas stream (typically argon) above the upper heating zone through a septum via motor driven syringe. The reactor downstream was collected using a water-chilled condenser.

Prior to using cuprous chloride (copper(I) chloride Alpha Aesar 99.999% metals basis), the CuCl was ground to a particle size of 2–5 μm by first preparing a mixture of 3:1 hexane/CuCl in a plastic jar containing 1 cm porcelain balls. Because the amount of tin is so low, for convenience and accuracy tin powder (Aldrich 325 mesh, 99.8%) was added to the CuCl slurry prior to grinding to obtain a final tin concentration in the contact mass of 50 ppm. The jar was sealed with Teflon tape and placed on a roller mill for 12–16 h. A finely dispersed CuCl/Sn suspension resulted and was transferred to a glass 150 mL bottle with a clean stir bar.

A contact mass was prepared by blending lab grind silicon powder, the CuCl/Sn suspension, and additional hexane in order to make the resultant slurry homogeneous. A known amount of the silicon powder was placed in a clean, dry 150 mL quartz reaction thimble. While the CuCl/Sn suspension(s) was stirred by magnetic stir bar, amounts were removed via Pasteur pipet and placed into the silicon until the desired mass was obtained. Finally an amount of hexane (Merck GC/LC solvent grade) was added in order to thoroughly disperse the CuCl. The slurry was then mixed for ~5 min. This homogenized slurry was then dried free of hexane by sweeping nitrogen over the top of it in a fume hood for at least 2 h. Completing the removal of all the hexane solvent, the semi-dried silicon and CuCl cake was vacuum-dried for at least 0.5 h. The thimble containing the dried mixture was placed in a furnace, set at 320 °C, through which argon (g) flowed at ~200 sccm. Within 0.5 h after applying heat the reduction of CuCl to Cu began, indicated by the presence of $SiCl_4$ (Q) in the exit gas stream. The exit gas was easily monitored for Q by passing the vent tube through and/or over ammonium hydroxide solution (Baker reagent grade). At the peak of the Q reaction, the exit gas from the furnace became a dense fog. When the fog was no longer visible (after ~2 h), the Q reaction was determined to be complete, the furnace was shut off, opened, and cooled, and the reaction thimble was then removed. The resulting contact mass was weighed, sealed, and then stored in a dry glovebox until further use.

Typical Procedure. The contact mass (typically 6 g) was combined with the promoter (either Zn or Cd powder) and then charged to the reactor and heated to the desired temperature with dichloroalkane injection and the Ar carrier gas. The condensable products were collected and weighed and then analyzed by GC, GC-MS, and ^{1}H and ^{13}C NMR analysis.