Synthesis of (Chloromethyl)silanes by the Low-Temperature Reaction of Chlorosilanes and in Situ Generated (Chloromethyl)lithium in Tetrahydrofuran

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Received December 10, 1990

The reaction between chlorosilanes and (chloromethyl)lithium, generated in situ from bromochloromethane and *n*-butyllithium, was used to synthesize (chloromethyl)silanes. The method is applicable to a wide variety of chlorosilanes and is particularly useful for silanes that contain such reactive bonds as Si–Si, Si–H, Si–vinyl, and Si–allyl. The corresponding (chloromethyl)silanes are generally prepared in high yield. The method may be extended successfully to bromomethylation and iodomethylation of chlorosilanes, and also to the chloromethylation of the other group 14 element (Ge, Sn, and Pb) halides.

Introduction

α-(Halomethyl)silanes are versatile starting materials for the synthesis of organosilicon compounds.[1] They are particularly useful in the synthesis of transition-metal derivatives, $L_nMCH_2SiR_3$,[2] formation of silylmethyl Grignard, lithium, and main-group derivatives,[1b] and formation of the α-carbanion $LiCHClSiR_3$ by metalation of α-hydrogen.[3] These reagents are widely applied to organic syntheses as a synthon of the C_1 unit.[4] (Halomethyl)silanes also are useful for functionalizing siloxanes and their related polymers.[5]

Despite the widespread application of these compounds, there are only a few standard methods for their synthesis, usually, but not only, involving some form of direct halogenation.[6,7] These methods are not applicable to the formation of (halomethyl)silanes that contain other functionalities such as Si–H, Si–Si, Si–vinyl, or Si–allyl bonds. Given the recent surge in interest in the chemistry of oligo- and polysilanes, the synthesis of α-functional silanes containing Si–Si bonds was of interest. We wish to report on the scope of a new route for the formation of α-(chloromethyl)silanes containing the Si–Si, Si–H, Si–Cl, Si–vinyl, and Si–allyl functionalities. A preliminary account of this work has appeared.[8]

The synthetic procedure involves the alkylation of chlorosilanes by in situ generated (chloromethyl)lithium (Scheme I) and is a modification of a procedure used by Kauffmann for the formation of Ph_3ECH_2I, E = Si, Ge, Pb.[9a] It is also related to a recently published procedure in which Me_3SiCl and $PhCH_2Cl$ were added at −100 °C to a solution of LDA to form $Me_3SiCHClPh$[9b] and the insertion of halocarbenoids into the Si–C bond of 1-silacyclobutane.[9d]

Scheme I

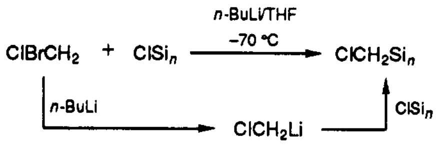

Table I. Possible Synthetic Methods

substrate	reagent(s)	comments[a]	ref
CH_3–Si	$Cl_2/h\nu$	A, B	6
CH_3–Si	Cl_2SO_2/BPO	A, B	7
H–Si	PhHgCHBrCl	C, D, F	10
H–Si	$PhHgCX_2Cl/Bu_3SnH$	C, E	11
H–Si	ClC(R)	G	9d
Li–Si	CH_2Cl_2	D, F	12
Cl–Si	CH_2N_2	C, D	13
Cl–Si	$ClBrCH_2$/Li	A, D	14
Cl–Si	I_2CH_2/PhLi	G	9a
Cl–Si	I_2CH_2/Zn	H	15
$ClCH_2SiMe_2Cl$	R_3SiLi	A	16
$ClCH_2SiMe_2Cl$	RLi	F	17
MeO–$CH_2SiMe_2SiMe_3$	BCl_3	I	18

[a] A = Poor selectivity, multiple products. B = Cleavage of Si–Si, Si–H bonds. C = Disposal and use of hazardous reagents. D = Poor yields. E = Multiple steps. F = Not widely applicable. G = Potentially useful. H = Inappropriate for silicon compounds. I = No target compounds produced.

Results and Discussion

The methods currently known for the formation of α-(halomethyl)silanes are listed in Table I. However, there is a need for a more general procedure since the methods listed in Table I suffer from numerous practical problems including low selectivity, low yield, lack of functional group tolerance, use of hazardous reagents, and lack of general applicability. In general the direct chlorination of CH_3–Si groups is used most frequently. This is, in part, because no reasonable alternative synthetic procedures are avail-

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able. Direct chlorination is essentially inapplicable if the methylsilanes contain Si–H or Si–Si bonds since the halogen will also rupture such linkages. Also, the presence of unsaturated substituents, e.g., vinyl, allyl, etc., precludes the effective use of direct halogenation.

A most attractive route for producing substituted silanes is the direct displacement of chloride from chlorosilanes. This is generally the preferred route for the formation of many alkyl-, aryl-, and transition-metal-substituted silanes and has been exhaustively studied both kinetically and stereochemically. The direct replacement of $[Cl]^-$ by $[CH_2Cl]^-$ thus seems appropriate, especially since chlorosilanes are available with a wide range of other functional groups bound to silicon.

Kumada and co-workers briefly noted the use of the reagent $ClBrCH_2/Li$ as a route to form (1-chloromethyl)heptamethyltrisilane from (1-chloro)heptamethyltrisilane.[14] We reinvestigated this procedure and found it a poor route to the desired compounds, probably due to the inability to control, let alone prevent, side reactions. In this regard, Augê recently reported that the same type of reagent, i.e. CH_2X_2/Li, X = Cl, Br, upon reaction with Me_3SiCl led to very high yields of the disubstituted product, i.e. $(Me_3Si)_2CH_2$.[19] It seems that the metallic Li will further react with the initially formed $ClCH_2Si$ group.

We chose to use the reagent $ClCH_2Li$ as a suitable vehicle for introduction of the CH_2Cl functionality onto silicon. This reagent is known to be very unstable even at low temperature but has been generated and used successfully in situ.[20] It may be generated by one of two methods: (A) from $ClXCH_2$ (X = Br, I) and lithium metal; (B) from $ClXCH_2$ (X = Br, I) and RLi (R = *n*-Bu, *s*-Bu, Me, Ph). The latter route is more frequently used, and the in situ generation and use has been applied successfully to methylenation and chloromethylation of organic carbonyl and organic boron compounds.[20,21] In both cases the reaction procedure is essentially the same: to a cooled THF solution of substrate and $ClXCH_2$ is added RLi dropwise at low temperature. The organolithium reagent first reacts with $ClXCH_2$ to give $ClCH_2Li$, which then reacts with the substrate.

We therefore expected a similar behavior in the three-component system RLi, $BrClCH_2$, and R_3SiCl, especially since there are several reports that RLi does not always react with chlorosilanes in the presence of other more reactive reagents. The syntheses of arylsilanes, eq 1, acylsilanes, eq 2, and fluoroallylsilanes, eq 3, represent good examples of such behavior.[22,23,41]

$$Me_3SiCl + PhBr \xrightarrow{n\text{-BuLi}} Me_3SiPh \qquad (1)$$

$$Me_3SiCl + CO \xrightarrow{RLi} Me_3SiCOR \qquad (2)$$

$$R = n\text{-Bu},\ i\text{-Bu},\ t\text{-Bu, etc.}$$

$$Me_3SiCl + CF_2{=}CHCH_2Br \xrightarrow{n\text{-BuLi}} Me_3SiCF_2CH{=}CH_2 \qquad (3)$$

Table II. Investigation of Reaction Conditions

$ClSiMe_2SiMe_3 \rightarrow XCH(R)SiMe_2SiMe_3$

dihaloalkane	alkyllithium	solvent	temp, °C	yield
$ClBrCH_2$	*n*-BuLi	THF	−60 to −70	80
$ClBrCH_2$	*s*-BuLi	THF	−60 to −70	76
$ClBrCH_2$	*n*-BuLi	Et_2O	−60 to −70	trace
$ClBrCH_2$	*n*-BuLi	THF	−5 to −10	trace
Br_2CH_2	*n*-BuLi	THF	−60 to −70	63
Br_2CHMe	*n*-BuLi	THF	−60 to −70	64
I_2CH_2	*n*-BuLi	THF	−60 to −70	32

Table III. Synthesis of (Chloromethyl)oligosilanes

$$ClSi_n \xrightarrow[-70\ °C]{n\text{-BuLi}/ClBrCH_2} ClCH_2Si_n$$

substrate	product	yield
$ClSiMe_2SiMe_2SiMe_3$	$ClCH_2SiMe_2SiMe_2SiMe_3$	77
$ClSiMe(SiMe_3)_2$	$ClCH_2SiMe(SiMe_3)_2$	84
$ClSiMe_2SiMe_2SiMe_2SiMe_3$	$ClCH_2SiMe_2SiMe_2SiMe_2SiMe_3$	88
$ClSiMe_2SiMe_2Ph$	$ClCH_2SiMe_2SiMe_2Ph$	63
$ClSiPhMeSiMe_3$	$ClCH_2SiPhMeSiMe_3$	79
$ClSiPhMeSiMePh_2$	$ClCH_2SiPhMeSiMePh_2$	68
$ClSiPhMeSiMe_2SiMe_3$	$ClCH_2SiPhMeSiMe_2SiMe_3$	69

For our initial study we chose to investigate the use of the in situ process with 1-chloropentamethyldisilane to optimize conditions. A summary of these results is presented in Table II. Isolated yields after distillation are reported. We did not examine the use of $IClCH_2$ as a precursor for $ClCH_2Li$ due to the success obtained by using the less expensive $BrClCH_2$. Similarly, since *n*-BuLi in hexane and *s*-BuLi in cyclohexane are readily available commercially and were effective for our purpose, no other organolithium reagents were investigated. THF is critical as the solvent since diethyl ether did not promote the reaction. The reaction temperature also is a key factor; reaction at 5–10 °C did not produce significant amounts of the desired product. Finally, although Villieras et al. have reported on the efficacy of added LiBr in stabilizing $ClCH_2Li$,[24] in our hands such addition did not improve the reaction yields. The standard conditions we used, as described in the Experimental Section, involved a temperature between −60 and −70 °C, use of *n*-BuLi, and the substrate in THF.

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Table IV. Syntheses of (Chloromethyl)cyclooligosilanes

$$\mathrm{Cl(Me)Si(SiMe_2)}_n \xrightarrow[-70\ ^\circ\mathrm{C}]{n\text{-BuLi/BrClCH}_2} \mathrm{ClCH_2(Me)Si(SiMe_2)}_n$$

substrate	product	yield
Cl(Me)Si(SiMe$_2$)$_4$	ClCH$_2$(Me)Si(SiMe$_2$)$_4$	81
Cl(Me)Si(SiMe$_2$)$_5$	ClCH$_2$(Me)Si(SiMe$_2$)$_5$	84

Table V. Syntheses of Functionalized (Chloromethyl)silanes

substrate	ratio of ClCH$_2$Li/ substrate	product	yield
Cl$_2$SiMe$_2$	2	(ClCH$_2$)$_2$SiMe$_2$	75
ClSiMe$_2$SiMe$_2$Cl	2	ClCH$_2$SiMe$_2$SiMe$_2$CH$_2$Cl	76
ClSiMe$_2$SiMe$_2$Cl	1	ClCH$_2$SiMe$_2$SiMe$_2$Cl	35
ClSiMe$_2$SiMe$_2$SiMe$_2$Cl	2	ClCH$_2$SiMe$_2$SiMe$_2$SiMe$_2$CH$_2$Cl	87
Cl$_2$SiMePh	1	ClCH$_2$ClSiMePh	39
ClSiMePhH	1	ClCH$_2$SiMePhH	61
ClSiMe$_2$CH$_2$CH=CH$_2$	1	ClCH$_2$SiMe$_2$CH$_2$CH=CH$_2$	71
ClSiMe$_2$CH=CH$_2$	1	ClCH$_2$SiMe$_2$CH=CH$_2$	71

Table VI. Chloromethylation of Ph$_3$EX (E = Si, Ge, Sn, and Pb; X = Cl, Br)

$$\mathrm{XEPh_3} \xrightarrow[-70\ ^\circ\mathrm{C}]{n\text{-BuLi/ClBrCH}_2} \mathrm{ClCH_2EPh_3}$$

substrate	product	yield
ClSiPh$_3$	ClCH$_2$SiPh$_3$	79
BrGePh$_3$	ClCH$_2$GePh$_3$	76
ClSnPh$_3$	ClCH$_2$SnPh$_3$	65
ClPbPh$_3$	ClCH$_2$PbPh$_3$	68

As noted from Table II, we also used Br$_2$CH$_2$, Br$_2$CHMe, and I$_2$CH$_2$ as sources of (halomethyl)lithium reagents. α-Methyl substitution on the dihalocarbon did not inhibit the coupling reaction. However, in the case of I$_2$CH$_2$, (iodomethyl)pentamethyldisilane was obtained in rather low yield.

The data in Table II convinced us that the use of in situ generated (halomethyl)lithium was an excellent new route to functional (halomethyl)silanes. The yields of ClCH(R)SiMe$_2$SiMe$_3$ were not only superior to those obtained by the "traditional" route, Me$_3$SiSiMe$_3$ + SO$_2$Cl$_2$, but the procedure also represented a potentially general synthesis. The application of the reaction to other organosilicon substrates is outlined below.

Syntheses of (Chloromethyl)oligosilanes. The applicability of this new method for the syntheses of (chloromethyl)oligosilanes from the corresponding chlorooligosilanes is outlined in Table III. Primary and secondary chlorosilanes are excellent substrates. However, we have been unable to successfully use tertiary chlorosilanes, e.g. (Me$_3$Si)$_3$SiCl. Both α-phenyl- and β-phenyl-substituted chlorooligosilanes are suitable substrates. Of the compounds in Table III, only ClCH$_2$(SiMe$_2$)$_2$SiMe$_3$[14] and ClCH$_2$SiMe$_2$SiMe$_2$Ph[17] have been reported, illustrating the potential of the technique.

Synthesis of (Chloromethyl)cyclooligosilanes. There are no examples in the literature of (chloromethyl)cyclooligosilanes. The new technique was used with Cl(Me)Si(SiMe$_2$)$_4$ and Cl(Me)Si(SiMe$_2$)$_5$ as substrates, i.e. the five- and six-membered silicon rings. In both cases good yields of the new chloromethyl derivatives were obtained (Table IV). The success of these reactions opens up an opportunity to study α-functional cyclooligosilanes for the first time.

Syntheses of Functionalized (Chloromethyl)silanes. Various functionally substituted (chloromethyl)silanes synthesized by the new procedure are listed in Table V. From this method, dichlorosilanes were converted to bis(chloromethyl)silanes in high yield. In contrast, conventional direct chlorination of (CH$_3$)$_2$SiCl$_2$ gives complex reaction mixtures, which include (chloromethyl)chlorosilanes, bis(chloromethyl)silanes, (dichloromethyl)silanes, and polychlorinated higher boiling residues.[6] Our attempts to partially chloromethylate dichlorosilanes gave nearly statistical mixtures of dichlorosilane, chloro(chloromethyl)silane, and bis(chloromethyl)silane (1:2:1 determined by GLC peak area ratio), eq 4.

$$\mathrm{Cl_2SiMePh} \xrightarrow{n\text{-BuLi/BrClCH}_2\text{/THF}} \mathrm{Cl_2SiMePh} + \mathrm{ClCH_2(Cl)SiMePh} + \mathrm{(ClCH_2)_2SiMePh} \quad (4)$$

α,ω-Dichlorooligosilanes are also readily converted to their corresponding α,ω-bis(chloromethyl) analogues. Alternative routes produce the desired compounds in very low yield or result in a complex mixture of isomeric materials.[18,25]

The new reaction is tolerant toward the H–Si bond, another distinct advantage compared with direct radical chlorination of CH$_3$–Si groups, and also may be used with advantage to chloromethylate chlorosilanes with vinyl and allyl groups. These examples demonstrate the great versatility of the new synthetic procedure.

Chloromethylation of Group 14 Element Halides. The general procedure described above also can be applied to the synthesis of chloromethyl derivatives of the Ph$_3$E system, E = Si, Ge, Sn, Pb (Table VI). High yields again typify the reaction. Given the total inapplicability of radical chlorination for Sn and Pb compounds, the in situ use of ClCH$_2^-$Li$^+$ will be the method of choice for such transformations. It is such a system that Kauffmann et al. have previously published, i.e. formation of iodomethyl derivatives.[9]

Conclusion

The coupling reaction between (chloromethyl)lithium, generated in situ, and chlorosilanes, is an excellent preparative method for (chloromethyl)silanes. Using this method, we have been able to synthesize not only the regular (chloromethyl)(methyl)(phenyl)silanes, but also silanes with reactive functionalities such as Si–Si, Si–H, Si–vinyl, and Si–allyl bonds. The reaction also may be used with effect to produce known bis(chloromethyl)silanes efficiently without the side products associated with other published procedures. The (chloromethyl)oligosilanes, both linear and cyclic, are a new class of α-functional compounds.

Experimental Section

NMR spectra were recorded on a Bruker NMR 200-MHz spectrometer in CDCl$_3$ solvent unless stated otherwise, and IR spectra were recorded on a Perkin-Elmer 580B spectrometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. All reactions were performed in a dry N$_2$ or argon atmosphere with dry, oxygen-free solvents.

Starting silicon compounds, Me$_3$SiSiMe$_3$, Cl$_2$SiMe$_2$, Cl$_2$SiMePh, ClSiMe$_2$Ph, ClSiMePh$_2$, ClSiPh$_3$, ClSiMePhH, ClSiMe$_2$CH$_2$CH=CH$_2$, and ClSiMe$_2$CH=CH$_2$ were purchased from Hüls America (Petrarch), Bristol, PA, GePh$_4$, ClSnPh$_3$, and ClPbPh$_3$ were purchased from Alfa Products, Ward Hill, MA, Br$_2$CHMe was obtained from Pfaltz & Bauer, Inc., Waterbury, CT, and ClBrCH$_2$, Br$_2$CH$_2$, n-BuLi, and s-BuLi were obtained

Table VII. Spectroscopic and Analytical Data for XCH_2(silanes) Synthesized

$BrCH_2SiMe_2SiMe_3$
bp: 84–85 °C/29 mmHg (lit.[18] 57 °C/9 mmHg)
^1H: 0.06 ($SiMe_3$), 0.10 ($SiMe_2$), 2.50 ppm (CH_2)
^{13}C: −3.90 ($SiMe_2$), −1.52 ($SiMe_3$), 18.15 ppm (CH_2)
^{29}Si: −19.35 ($SiMe_3$), −14.58 ppm ($SiMe_2$)

$BrCHMeSiMe_2SiMe_3$
bp: 88–90 °C/32 mmHg
anal. Calcd: C, 35.13; H, 8.00. Found: C, 35.54; H, 7.80
^1H: 0.08 (Me_3, Me), 0.10 (Me), 1.66 (d, J = 7.7 Hz, CH_3–CHBr), 3.43 ppm (q, J = 7.7 Hz, CH_3–*CH*Br)
^{13}C: −4.85 (SiMe), −4.52 (SiMe), −1.22 ($SiMe_3$), 21.93 (q, J_{CH} = 42.5 Hz, CH_3–CHBr), 37.69 ppm (d, J_{CH} = 27.4 Hz, CHBr)
^{29}Si: −19.21 ($SiMe_3$), −9.75 ppm ($SiMe_2$)

$ICH_2SiMe_2SiMe_3$
bp: 90–92 °C/22 mmHg (lit.[26] 96–97 °C/23 mmHg)
^1H: 0.09 (Me), 2.06 ppm (CH_2)
^{13}C: −11.93 (CH_2I), −2.27 ($SiMe_2$), −1.52 ppm ($SiMe_3$)
^{29}Si: −19.70 ($SiMe_3$), −13.08 ppm ($SiMe_2$)

$ClCH_2SiMe_2SiMe_2SiMe_2CH_2Cl$
bp: 94 °C/0.07 mmHg
Anal. Calcd: C, 35.14; H, 8.11. Found: C, 35.50; H, 8.16
^1H: 0.15 (Si–$SiMe_2$–Si), 0.16 ($SiMe_2$–Si–$SiMe_2$), 2.85 ppm (CH_2)
^{13}C: −6.07 (Si–$SiMe_2$–Si), −4.01 ($SiMe_2$–Si–$SiMe_2$), 31.56 ppm (CH_2)
^{29}Si: −48.84 (Si*Si*Si), −11.12 ppm (*Si*Si*Si*)

$ClCH_2SiMe_2SiMe_2Ph$
bp: 150–158 °C/33 mmHg (lit.[16] 130 °C/27 mmHg)
^1H: 0.29 ($SiMe_2$), 0.54 ($SiMe_2$), 2.95 (CH_2), 7.3–7.7 ppm (Ph)
^{13}C: −4.57 (Si*Me*$_2$$CH_2Cl$), −3.11 ($SiMe_2Ph$), 31.41 ($CH_2$), 128.5, 129.2, 134.3, 138.8 ppm (Ph)
^{29}Si: −21.68 (SiPh), −14.79 ppm ($SiCH_2Cl$)

$ClCH_2SiPhMeSiMe_3$
bp: 88–90 °C/32 mmHg
Anal. Calcd: C, 54.39; H, 7.88. Found: C, 53.69; H, 7.98
^1H: 0.37 ($SiMe_3$), 0.67 (Me), 3.28, 3.30 (AB d, J = 13.4 Hz, CH_AH_BCl), 7.4–7.8 ppm (Ph)
^{13}C: −6.25 (Si*Me*CH_2Cl), −1.03 ($SiMe_3$), 30.31 (CH_2), 128.6, 129.8, 134.69, 136.39 ppm (Ph)
^{29}Si: −18.05, −18.59 ppm

$ClCH_2SiPhMeSiMePh_2$
bp: 184–194 °C/0.35 mmHg
Anal. Calcd: C, 68.72; H, 6.32. Found: C, 68.16; H, 6.24
^1H: 0.79 (Me), 0.95 (Me), 3.35 (CH_2), 7.3–8.0 ppm (Ph)
^{13}C: −5.63 ($SiMePh_2$), −3.31 (Si*Me*CH_2Cl), 30.13 (CH_2), 128.6, 129.8, 129.9, 135.0, 135.4, 135.6, 135.8 ppm (Ph)
^{29}Si: −22.68, −18.94 ppm

$ClCH_2SiPhMeSiMe_2SiMe_3$
bp: 112 °C/0.30 mmHg
Anal. Calcd: C, 51.87; H, 8.37. Found: C, 51.38; H, 8.52
^1H: 0.15 ($SiMe_3$), 0.31 ($SiMe_2$), 0.63 (Me), 3.25 (CH_2), 7.3–7.7 ppm (Ph)
^{13}C: −5.74 (Me_2,Me) −1.13 ($SiMe_3$), 30.57 (CH_2), 128.4, 129.6, 134.5, 136.6 ppm (Ph)
^{29}Si: −47.93, −15.59, −14.80 ppm

$ClCH_2SiMe_2SiMe_2Cl$
bp: 89–90 °C/35 mmHg (lit.[7a] 79.5 °C/17 mmHg)
^1H: 0.21 ($ClCH_2Si$*Me*$_2$), 0.48 ($SiMe_2Cl$), 2.88 ppm (CH_2)
^{13}C: −5.37 ($ClCH_2Si$*Me*$_2$), 2.95 ($SiMe_2Cl$), 29.9 ppm (CH_2)
^{29}Si: −14.19 ($SiCH_2Cl$), 22.00 ppm (SiCl)

$ClCH_2SiMePhCl$
bp: 129 °C/33 mmHg (lit.[27] 130 °C/32 mmHg)
^1H: 0.87 (Me), 3.17 (CH_2Cl), 7.3–7.8 ppm (Ph)
^{13}C: −1.11 (Me), 30.31 (CH_2Cl), 128.8, 131.7, 132.7, 134.3 ppm (Ph)
^{29}Si: 12.35 ppm

$ClCH_2SiMePhH$
bp: 112 °C/36 mmHg (lit.[27] 110 °C/30 mmHg)
IR (neat): 2141.9 cm^{-1} (Si–H)
^1H: 0.61 (d, J = 3.7 Hz, Me), 3.11 (d, J = 3.3 Hz, CH_2), 4.68 (m, SiH), 7.4–7.8 ppm (m, Ph)
^{13}C: −6.63 (Me), 28.54 (CH_2), 128.5, 130.7, 135.1 ppm (Ph)
^{29}Si: −14.76 ppm

$ClCH_2SiMe_2CH_2CH{=}CH_2$
bp: 77 °C/80 mmHg (lit.[28] 80 °C/83 mmHg)
^1H: 0.13 ($SiMe_2$), 1.5–1.75 (–CH_2–), 2.77 (CH_2Cl), 4.7–5.1 ($CH_2{=}$), 5.5–6.2 ppm (–CH=)

$ClCH_2SiMe_2CH{=}CH_2$
bp: 114–115 °C (lit.[29] 119–120 °C)
^1H: 0.21 (Me_2), 2.82 (CH_2), 5.5–6.3 ppm ($CH{=}CH_2$)

$ClCH_2SiPh_3$
mp: 118.4–119.8 °C (lit.[11] 114–116 °C)
^1H: 3.57 (CH_2Cl), 7.3–7.7 ppm (Ph)
^{29}Si: −14.55 ppm

$ClCH_2GePh_3$
mp: 115.5–116.0 °C (lit.[11] 118–120.5 °C)
^1H (C_6D_6): 3.36 (CH_2Cl), 7.2–7.6 ppm (Ph)

$ClCH_2SnPh_3$
mp: 90.3–92.0 °C
Anal. Calcd: C, 57.13; H, 4.29. Found: C, 57.21; H, 4.32
^1H: 3.63 (CH_2Cl), 7.3–7.8 ppm (Ph)

$ClCH_2PbPh_3$
mp: 81.0–82.0 °C
Anal. Calcd: c, 46.77; H, 3.51. Found: C, 46.91; H, 3.53
^1H: 4.08 (CH_2Cl), 7.3–7.9 ppm (Ph)

$Ph_2SiMeSiMe_2SiMe_3$
bp: 144–148 °C/0.3 mmHg
Anal. Calcd: C, 65.78; H, 8.59. Found: C, 64.98; H, 8.51
^1H: 0.19 ($SiMe_3$), 0.41 ($SiMe_2$), 0.85 (SiMe), 7.4–7.8 ppm (Ph)
^{13}C: −5.34 (Me_2), −3.24 (Me), −0.85 (Me_3), 128.4, 129.4, 135.5, 138.4 ppm (Ph)
^{29}Si: −47.79 ($SiMe_2$), −18.78 (SiMe), −15.47 ($SiMe_3$)

$ClCH_2SiMe(SiMe_2)_4$ (Waxy Solid)
bp: 120–140 °C/0.9 mmHg
^1H: 0.13, 0.18, 0.24 (SiMe), 3.04 ppm (CH_2)
^{13}C: −7.45 (Si*Me*CH_2Cl), −6.30, −6.10 ($SiMe_2$), 30.25 ppm (CH_2Cl)
^{29}Si: −42.15 (4Si), −32.17 ppm ($SiCH_2Cl$)

$ClCH_2SiMe(SiMe_2)_5$ (Waxy Solid)
bp: 175–185 °C/0.2 mmHg
^1H: 0.10 (4 Me), 0.12 (2 Me), 0.17 (4 Me), 0.24 (Me), 3.06 ppm (CH_2)
^{13}C: −8.01 (Si*Me*CH_2Cl), −6.22, −6.05, −5.44, −4.95 (SiMe), 31.11 ppm (CH_2Cl)
^{29}Si: −42.37 (1 Si), −42.16 (2 Si), −41.94 (2 Si), −33.91 ppm ($SiCH_2Cl$)

from Aldrich Chemical Co., Milwaukee, WI. Other starting materials were prepared by published procedures: $ClSiMe_2SiMe_3$,[30] $ClSiMe_2SiMe_2Cl$,[30] $ClSiMe_2SiMe_2SiMe_3$,[31] $ClSiMe(SiMe_3)_2$,[32] $ClSiMe_2SiMe_2SiMe_2SiMe_3$,[33] $ClSiMe_2SiMe_2Ph$,[34] $ClSiPhMeSiMe_3$,[35] $BrGePh_3$.[36] Other starting organosilicon compounds were synthesized by modifications of published procedures: $ClSiMe_2SiMe_2SiMe_2Cl$ (bp 112 °C/40 mmHg (lit.[37] 89–92 °C/15 mmHg) was prepared in 93% yield by $AlCl_3$-catalyzed chlorodephenylation with HCl of $PhSiMe_2SiMe_2SiMe_2Ph$[38] in essentially the same manner published for the preparation of Cl-$SiMe_2SiMe_2SiMe_2SiMe_2Cl$[34] from $PhSiMe_2SiMe_2SiMe_2SiMe_2Ph$. $ClSiPhMeSiMePh_2$ (bp 186 °C/0.40 mmHg, 43% yield from $Ph_2SiMeSiMePh_2$[39]) and $ClSiPhMeSiMe_2SiMe_3$ (bp 104–108 °C/0.35 mmHg, 70% yield from $Ph_2SiMeSiMe_2SiMe_3$) were prepared by using the same technique as published for $ClSiPhMeSiMe_3$.[35] These two compounds are previously unreported; however, we used them directly for transformation to their chloromethyl derivatives, which were completely characterized (Table VII). $Ph_2SiMeSiMe_2SiMe_3$ was prepared by the reaction between $Ph_2MeSiLi$ and $ClSiMe_2SiMe_3$ in 80% yield. This is also unreported, and full characterization is provided in Table VII. Syntheses of $ClMeSi(SiMe_2)_4$ and $ClMeSi(SiMe_2)_5$ were performed with published procedures.[40]

The typical experimental procedures for the synthesis of the chloromethyl compounds outlined below are representative of the technique. Yields reported in the tables are of isolated, purified materials. A (chloromethyl)oligosilane synthesis appears in the preliminary communication of this study.[8]

Synthesis of $ClCH_2(Me)Si(SiMe_2)_4$. Into a 500-mL three-necked flask equipped with a magnetic stirring bar, rubber septum, nitrogen inlet tube, and low-temperature thermometer were placed 16.0 g (0.05 mol) of $ClSiMe(SiMe_2)_4$ and $BrCH_2Cl$, 6.6 g (0.05 mol) in 150 mL of dry THF. To this mixture, maintained between −70 and −60 °C, was added on the cold wall of the flask, via syringe over 50 min, 32 mL (0.05 mol) of a 1.6 M solution of *n*-butyllithium in hexane. The solution was warmed to room temperature during 1 h and then hydrolyzed and extracted with hexane. The extract was washed with water and dried over $CaCl_2$. The solvent was removed, and the residue was distilled, by using a 20-cm Vigreux column, at 120–140 °C/0.9 mmHg to give 13.5 g (0.04 mol, 81%) of $ClCH_2(Me)Si(SiMe_2)_4$ as a waxy solid. We have been unable to obtain elemental analytical data within 1% of the calculated values. The relatively high boiling point and waxy nature of the compound and the (chloromethyl)cyclohexasilane may be responsible for this lack of success. We have used both chloromethyl derivatives to synthesize transition-metal complexes of the type L_nMCH_2–cyclosilane, which have been completely characterized, including single-crystal structures, and these data will be part of a forthcoming publication.

Synthesis of $ClCH_2(Cl)SiMePh$. Into a 500-mL three-necked flask equipped with a magnetic stirring bar, rubber septum, nitrogen inlet tube, and low-temperature thermometer were placed 11.9 g (0.06 mol) of $Cl_2SiMePh$ and $BrCH_2Cl$, 8.0 g (0.06 mol) in 75 mL of dry THF. To this mixture, maintained between −70 and −60 °C, was added on the cold wall of the flask, via syringe over 1 h, 38.8 mL (0.06 mol) of a 1.6 M solution of *n*-butyllithium in hexane. The solution was warmed to room temperature during 70 min, and the solvent was evaporated in vacuo. The residue was extracted into dry hexane (50 mL), and the resulting solution was filtered. The residue was washed with hexane (25 mL × 2), and all filtrates were combined. Subsequent to removal of the solvent in vacuo, distillation on a 20-cm Vigreux column at 129 °C/33 mmHg yielded 5.0 g (0.02 mol, 39%) of $ClCH_2(Cl)SiMePh$.

Synthesis of $ClCH_2SiMePhH$. Into a 500-mL three-necked flask equipped with a magnetic stirring bar, rubber septum, nitrogen inlet tube, and low-temperature thermometer were added 8.0 g (0.05 mol) of $ClSiMePhH$ and $BrCH_2Cl$, 6.6 g (0.05 mol) in 150 mL of dry THF. To this mixture, maintained between −70 and −60 °C, was added on the cold wall of the flask, via syringe over 30 min, 31.9 mL (0.05 mol) of a 1.6 M solution of *n*-butyllithium in hexane. The solution was warmed to room temperature during 50 min. The mixture was hydrolyzed and extracted with hexane and the extract washed with water and dried over $CaCl_2$. The solvent was removed, and the residue was distilled on a 20-cm Vigreux column at 112 °C/36 mmHg to give 5.3 g (0.03 mol, 61%) of $ClCH_2SiMePhH$.

Synthesis of $ClCH_2SiMe_2CH_2CH{=}CH_2$. Into a 500-mL three-necked flask equipped with a magnetic stirring bar, rubber septum, nitrogen inlet tube, and low-temperature thermometer were added 9.7 g (0.07 mol) of $ClSiMe_2CH_2CH{=}CH_2$ and $BrCH_2Cl$, 9.3 g (0.07 mol) in 150 mL of dry THF. To this mixture, maintained between −70 and −60 °C, was added on the cold wall of the flask, via syringe over 40 min, 45 mL (0.07 mol) of a 1.6 M solution of *n*-butyllithium in hexane. The solution was permitted to warm to room temperature, and the mixture was then hydrolyzed and extracted with hexane. The extract was washed with water and dried over $CaCl_2$. The solvent was removed, and the residue was distilled on a 20-cm column packed with raschig rings at 77 °C/80 mmHg to give 7.6 g (0.05 mol, 71%) of $ClCH_2SiMe_2CH_2CH{=}CH_2$.

Synthesis of $ClCH_2PbPh_3$. Into a 500-mL three-necked flask equipped with a magnetic stirring bar, rubber septum, nitrogen inlet tube, and low-temperature thermometer were added 3.0 g (0.006 mol) of $ClPbPh_3$ and $BrCH_2Cl$, 0.8 g (0.006 mol) in 50 mL of dry THF. To this mixture, maintained between −70 and −60 °C, was added on the cold wall of the flask, via syringe over 45 min, 4.0 mL (0.006 mol) of a 1.6 M solution of *n*-butyllithium in hexane. The solution was permitted to warm to room temperature over 45 min, and the mixture was hydrolyzed and extracted with CH_2Cl_2. The extract was washed with water and dried over $CaCl_2$. The solvent was removed in vacuo to give a white solid (3.0 g), which was recrystallized from hot hexane (10 mL) to give $ClCH_2PbPh_3$, 1.58 g (0.003 mol, 52%, mp 79.0–80.5 °C). The mother liquid was evaporated in vacuo, and the residue was recrystallized from hot hexane (5 mL) to give the second crop, 0.50 g (0.001 mol, 16%). An analytical sample was obtained by further recrystallization from hexane (mp 81.0–82.0 °C).

Acknowledgment. This research was supported by the DOD, Defense Logistics Agency, Directorate of Stockpile Management, Grant DN-009, administered by the University of Texas at El Paso Institute of Manufacturing and Materials Management.