Preparation of Chlorosilyl Enolates†

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A variety of chlorosilyl enolates has been prepared starting from esters, thiol esters, acylsilanes, and ketones. Two general methods are involved, direct enolsilylation with trichlorosilyl triflate and diisopropylethylamine, and a number of methods based on electrophilic substitution of either *C*- or *O*-silyl or stannyl carbonyl compounds. The most useful method is a $Hg(OAc)_2$-catalyzed transsilylation from trimethylsilyl to trichlorosilyl enol ethers, providing a wide range of ketone enolates in good to high yield.

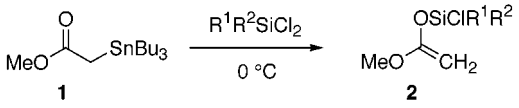
Introduction

Recent reports from these laboratories have described the chemistry of a new class of aldolization reagents based on electron-deficient silyl enolates.[1] These species exhibit remarkable reactivity patterns, spontaneously reacting with aldehydes at or below ambient temperature. More importantly, these reactions are accelerated by the addition of catalytic quantities of Lewis bases (chiral phosphoramides). When cyclic enolates are used, aldol adducts are formed with high syn-diastereoselectivity in the uncatalyzed reactions, suggestive of a closed, boatlike transition structure.[1b,e] In contrast, reactions catalyzed by chiral phosphoramides typically provide products resulting from closed, chairlike transition structures, often with good to excellent enantioselectivity.[1b,e] Although several chlorosilyl enolates were known[2,3] when our work commenced, new, more efficient methods of synthesis were needed to provide access to certain classes of enolates and to enhance the general utility of this aldol reaction. We describe herein general methods for the synthesis of these unique and useful reagents.

Results

Enolates Derived from Esters and Ester-Surrogates. The first chlorosilyl enolates reported in the literature were those derived from methyl acetate, prepared by the metathesis of alkyl (trialkyl)stannyl acetates with chlorosilanes.[2] We have also found this to be the most general procedure for the generation of such acetate-derived chlorosilyl enolates. Treatment of methyl (tributylstannyl)acetate (**1**)[4] with an excess of the appropriate chlorosilane at 0−25 °C led to the formation of the chlorosilyl enolates **2**, Table 1. Excess chlorosilane was typically used to control the quantity of bis(enoxy)chlorosilane byproducts formed by reaction of the primary chlorosilyl enolate with starting stannyl acetate. When the reaction was complete, excess chlorosilane was removed and the products were distilled at 0−25 °C under reduced pressure. These manipulations must be carried out at the lowest possible temperature, as the chlorosilyl enolates **2** are unstable with respect to their *C*-silyl isomers and isomerization occurs rapidly at 70−90 °C.[2d] These *C*-(chlorosilyl) esters are inert in the subsequent aldol reactions and do not revert back to the O-bound trichlorosilyl enolates under common reaction conditions.

Table 1. Synthesis of Acetate Chlorosilyl Enolates by the Stannane Method



1 **2**

entry	silane	R^1	R^2	product	yield,[a] %
1	$HSiCl_3$	H	Cl	**2a**	48
2	$SiCl_4$	Cl	Cl	**2b**	65
3	$MeSiCl_3$	Me	Cl	**2c**	57
4	$PhSiCl_3$	Ph	Cl	**2d**	23
5	Me_2SiCl_2	Me	Me	**2e**	18
6	$(CH_2)_3SiCl_2$	$-(CH_2)_3-$		**2f**	19

[a] Yield of distilled product.

Although the reaction proved to be general for the synthesis of various chlorosilyl enolates[1c] the yields of the process were moderate at best. The lower yields of enolates in entries 4−6 (Table 1) reflect the lower volatility of these enolates and the greater difficulty in separating them from Bu_3SnCl and from the *C*-(chlorosilyl) isomers. That these substances are O-bound silyl enolates (enoxychlorosilanes) was readily confirmed by examination of the ^1H NMR spectrum of trichlorosilyl

† The Chemistry of Chlorosilyl Enolates. 9.

(1) (a) Denmark, S. E.; Winter, S. B. D.; Su, X.; Wong, K.-T. *J. Am. Chem. Soc.* **1996**, *118*, 7404. (b) Denmark, S. E.; Wong, K.-T.; Stavenger, R. A. *J. Am. Chem. Soc.* **1997**, *119*, 2333. (c) Denmark, S. E.; Winter, S. B. D *Synlett* **1997**, 1087. (d) Denmark, S. E.; Stavenger, R. A.; Wong, K. T. *J. Org. Chem.* **1998**, *63*, 918. (e) Denmark, S. E.; Stavenger, R. A.; Wong, K.-T. *Tetrahedron* **1998**, *54*, 10389. (f) Denmark, S. E.; Stavenger, R. A. *J. Org. Chem.* **1998**, *63*, 9524.

(2) (a) Burlachenko, G. S.; Khasapov, B. N.; Petrovskaya, L. I.; Baukov, Yu. I.; Lutsenko, I. F. *J. Gen. Chem. USSR (Engl. Transl.)* **1966**, *36*, 532. (b) Lutsenko, I. F.; Baukov, Yu. I.; Burlachenko, G. S.; Khasapov, B. N. *J. Organomet. Chem.* **1966**, *5*, 20. (c) Burlachenko, G. S.; Baukov, Yu. I.; Dzherayan, T. G.; Lutsenko, I. F. *J. Gen. Chem. USSR (Engl. Transl.)* **1975**, *45*, 73. (d) Buakov, Yu. I.; Lutsenko, I. F.; *Moscow University Chem. Bull. (Engl. Transl.)* **1970**, *25*, 72. (e) Ponomarev, S. V.; Baukov, Yu. I.; Dudukina, O. V.; Petrosyan, I. V.; Petrovskaya, L. I. *J. Gen. Chem. USSR (Engl. Transl.)* **1967**, *37*, 2092. (f) Burlachenko, G. S.; Baukov, Yu. I.; Lutsenko, I. F. *J. Gen. Chem. USSR (Engl. Transl.)* **1970**, *40*, 88.

(3) (a) Benkeser, R. A.; Smith, W. E. *J. Am. Chem. Soc.* **1968**, *90*, 5307. (b) Walkup, R. D. *Tetrahedron Lett.* **1987**, *28*, 511. (c) Walkup, R. D.; Obeyesekere, N. U. *J. Org. Chem.* **1988**, *53*, 920. (d) Walkup, R. D.; Obeyesekere, N. U.; Kane, R. R. *Chem. Lett.* **1990**, 1055. (e) Kaye, P. T.; Learmonth, R. A.; Ravindran, S. S. *Synth. Commun.* **1993**, *23*, 437. (f) Shea, K. J.; Zandi, K. S.; Staab, A. J.; Carr, R. *Tetrahedron Lett.* **1990**, *31*, 5885. (g) Gillard, J. W.; Fortin, R.; Grimm, E. L.; Maillard, M.; Tjepkema, M.; Bernstein, M. A.; Glaser, R. *Tetrahedron Lett.* **1991**, *32*, 1145.

(4) Zapata, A.; Acuña, A. C. *Synth. Commun.* **1984**, *14*, 27.

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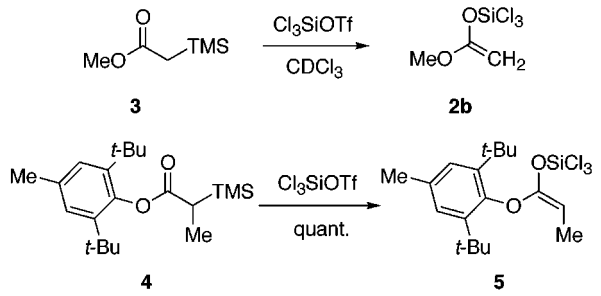
Scheme 1

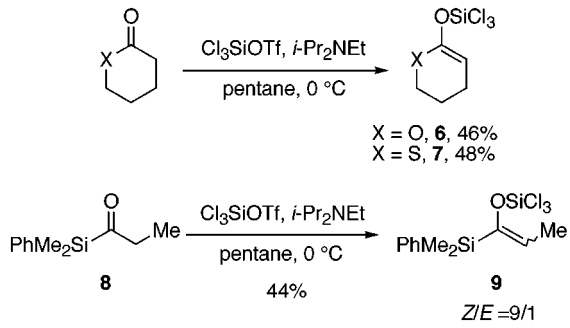


enolate **2b**, which was contaminated with a small amount of the *C*-silyl isomer.[5] The spectrum of the enolate (*O*-silyl) displayed two doublets at δ 3.41 and δ 3.65 ppm (1 H each) and a singlet at δ 3.65 ppm (3 H), whereas the *C*-(trichlorosilyl)acetate displayed two singlets at δ 3.75 ppm (3 H) and δ 2.78 ppm (2 H). Similar procedures using various alkyl (tributylstannyl)propanoates and $SiCl_4$ led to complex mixtures, with the dominant products being the *C*-(trichlorosilyl)propanoate derivatives.

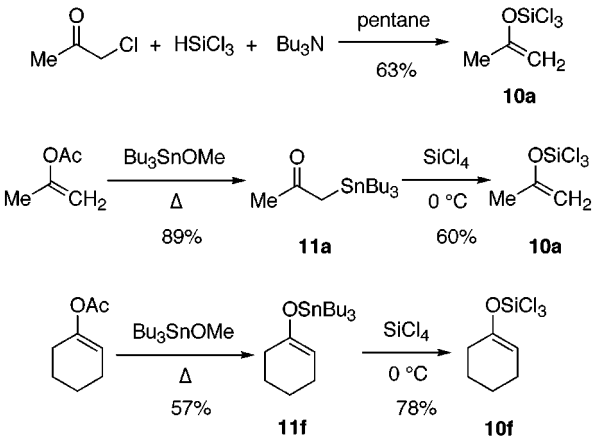
To avoid the use of tin compounds in stoichiometric amounts, other routes to chlorosilyl enolates were investigated. A conceptually similar process can be envisioned that employs an alkylsilane as the electrofugal group. Unfortunately, combination of $SiCl_4$ with various alkyl *C*-(trimethylsilyl) esters led to no reaction. However, when trichlorosilyl triflate[6] was used as the trichlorosilylating reagent, relatively clean conversion to the trichlorosilyl enolate was observed, Scheme 1. Treatment of methyl *C*-(trimethylsilyl)acetate (**3**) with trichlorosilyl triflate in $CDCl_3$ at room temperature led to fast (<10 min) conversion to the *O*-(trichlorosilyl) enolate **2b**. The bulky ester enolate **5**[7] was synthesized by treatment of the silane **4** with trichlorosilyl triflate at room temperature though here conversion was slow, requiring over 30 h for completion. The enolate **5** (assumed to be of *E* configuration[7]) could be obtained in reasonably pure form (^1H and ^{19}F NMR analysis) in essentially quantitative yield by simple treatment of **4** with trichlorosilyl triflate followed by removal of the byproduct TMSOTf under reduced pressure.

The extreme reactivity of trichlorosilyl triflate also proved useful in the direct enolsilylation of carbonyl compounds. Initial experiments revealed that esters and ketones were inert to the action of $SiCl_4$ and a variety of amine bases. Furthermore, reaction of chlorosilanes with alkali metal enolates proved ineffective. However, when trichlorosilyl triflate was used in conjunction with *i*-Pr_2NEt, rapid conversion to the trichlorosilyl enolates was accomplished for ketones, cyclic esters, and thiol esters. Acyclic esters reacted very slowly under these conditions and led only to poor conversion to the *C*-(trichlorosilyl) esters. Amides were inert, and acyl oxazolidinones provided complex mixtures of products.

Scheme 2



Scheme 3



Other tertiary amine bases (Proton Sponge, pentamethylpiperidine, Et_3N, Me_2NEt) seemed to offer no advantage, and pyridine and its derivatives were wholly ineffective in this transformation. Although the reaction proceeded well in chlorinated solvents, difficulties involved in the isolation of the chlorosilyl enolates led to the use of pentane as solvent, so that the majority of the amine salts could be removed by Schlenk filtration. Thus, trichlorosilyl enolates **6** and **7** were obtained after distillation in modest yield directly from the corresponding carbonyl compounds. This method was also found to be effective for acylsilanes, Scheme 2. Treatment of **8**[8] under the standard conditions led to the formation of the enolate **9** as a 9/1 mixture of *Z*/*E* isomers (assignment of configuration tentative) in 44% yield.

Enolates Derived from Ketones. Ketone-derived chlorosilyl enolates have also been prepared previously. For example, the acetone enolate **10a** was generated by a reductive chlorosilylation reaction reported by Benkeser,[3] Scheme 3. We were able to reproduce the Benkeser procedure, i.e., treatment of chloroacetone with trichlorosilane and Bu_3N to prepare the trichlorosilyl enolate **10a**. Curiously, Et_3N and *i*-Pr_2NEt seemed unable to effect this transformation. In addition, in our hands the use of pentane was found to be superior to THF (the solvent used in the Benkeser report), providing cleaner reaction and allowing easier separation of the solvent from the volatile chlorosilyl enolate. The enolate **10a** could be purified reproducibly by vacuum-transfer of the reaction mixture away from the ammonium salts, concentration of the crude distillate, and redistillation of the residue. However, due to the necessity of this vacuum-transfer step, only relatively volatile enolates are

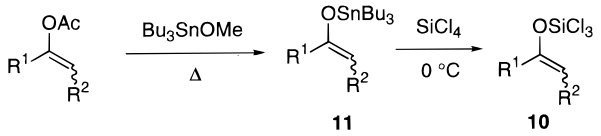
(5) All acetate enolates in this study were contaminated with small quantities of the corresponding *C*-silyl isomer. Complete removal is neither necessary, nor practical, as the *O*-silyl enolate does isomerize slowly, even when stored at −20 °C.

(6) (a) Bassindale, A. R.; Stout, T. *J. Organomet. Chem.* **1984**, *271*, C1. (b) Rüdinger, C.; Beruda, H.; Schmidbaur, H. *Z. Naturforsch. B* **1994**, *49b*, 1348.

(7) The corresponding lithium enolate has been used in aldol reactions by Heathcock, see: (a) Heathcock, C. H.; Young, S. D.; Hagen, J. P.; Pirrung, M. C.; White, C. T.; VanDerveer, D. *J. Org. Chem.* **1980**, *45*, 3846. (b) Heathcock, C. H.; Pirrung, M. C.; Montgomery, S. H, Lampe, J. *Tetrahedron* **1981**, *37*, 4087.

(8) Fujiwara, T.; Sawabe, K.; Takeda, T. *Tetrahedron* **1997**, *53*, 8349.

Table 2. Synthesis of Ketone Trichlorosilyl Enolates by the Stannane Method



entry	stannane	R^1	R^2	enolate	yield,[a] %
1	**11b**	*t*-Bu	H	**10b**	54
2	**11c**	Ph	H	**10c**	67
3	**11d**	Ph	Me	**10d**[b]	83
4	**11e**	$-(CH_2)_3-$		**10e**	27
5	**11f**	$-(CH_2)_4-$		**10f**	78
6	**11g**	$-(CH_2)_5-$		**10g**	63

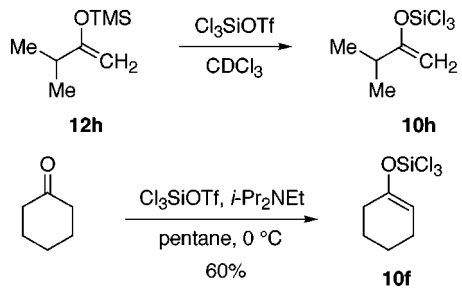
[a] Yield of distilled product. [b] *Z*/*E* > 50/1.

amenable to this procedure, and it remains our method of choice for the preparation of **10a**.

As noted above, the stannane route is also quite useful for the preparation of certain ketone-derived chlorosilyl enolates, though the method is limited by the availability of regiochemically pure stannyl ketone derivatives **11**,[9] often from the corresponding enol acetates, Scheme 3. Both the trichlorosilyl enolates derived from acetone and cyclohexanone[2e] can be prepared by this three-step procedure in moderate yield from the starting ketone. In most cases, purification of the stannyl ketone is not required, thus simplifying the overall process. Treatment of the enol acetate with Bu_3SnOMe at roughly 100 °C,[10] followed by removal of the methyl acetate and direct treatment of the crude stannyl ketones with excess $SiCl_4$ (again to preclude formation of poly(enoxy)silanes), led to the pure trichlorosilyl enolates **10b**−**g** in moderate to good yield after distillation, Table 2. In the case of propiophenone, excellent *Z* selectivity (>50/1) was observed in the formation of the trichlorosilyl enolate. Unlike their ester counterparts, these enolates are thermally stable and can be distilled at temperatures up to 140 °C under reduced pressure without complication. In fact, we have yet to observe a *C*-(trichlorosilyl) ketone in the course of these studies, and it is likely that the *O*-silyl isomers are significantly more thermodynamically stable.

The use of trichlorosilyl triflate in the synthesis of ketone enolates has also been investigated, both in trans-silylation reactions and direct enolsilylation. Though *C*-(trialkylsilyl) ketones have not been utilized, when the TMS enol ether **12h** was treated with trichlorosilyl triflate in $CDCl_3$, rapid trans-silylation to form the chlorosilyl enolate **10h** occurred, Scheme 4. Unfortunately, on a preparative scale, pure samples of the enolate could not be obtained. Direct enolsilylation of cyclohexanone proceeded as above with *i*-Pr_2NEt and trichlorosilyl triflate, and though good yields could sometimes be obtained, the reaction as currently developed is too capricious for general preparative purposes. Attempts at direct enolsilylation of methyl isobutyl ketone with trichlorosilyl triflate and various amine bases led only to complex mixtures.

Scheme 4



The most general method yet discovered for the synthesis of chlorosilyl enolates of ketones is an interesting trans-silylation catalyzed by soft, electrophilic metal salts, especially $Hg(OAc)_2$. It was known that treatment of *C*-mercurioesters[2b] or stannylated esters[2a] with halosilanes provided mixtures of the *C*-silylesters and *O*-silyl esters. In addition, *C*-mercurioketones[11] and *C*-(trichlorostannyl)ketones[12] were known to be formed cleanly from TMS enol ethers and the corresponding metal salts. We therefore reasoned that a Lewis acidic species could function as a catalyst for the trans-silylation from alkylsilyl to chlorosilyl enol ethers. Initial studies using 1 equiv of $SiCl_4$ and 10 mol % of $TiCl_4$, $BF_3{\cdot}OEt_2$, or $SnCl_4$ were not encouraging; only $SnCl_4$ seemed to promote reaction with the TMS enol ether of pinacolone (**12b**), and this proved to be neither general nor amenable to large-scale reactions. However, when softer Lewis acids such as $Hg(OAc)_2$, $Hg(OTFA)_2$, $Tl(OTFA)_3$, and $Pd(OAc)_2$ were used at 5 mol % loading, clean conversion to the trichlorosilyl enolate was observed.

The TMS enol ether derived from methyl isopropyl ketone (**12h**) was used as a test substrate to examine several reaction parameters. Curiously, although a slight excess (2−3 equiv) of $SiCl_4$ did help reduce the amount of bis(enoxy)dichlorosilane formed, larger excesses (5 equiv) slowed the reaction dramatically. In addition, conducting the reaction at concentrations higher than 1 M led to significant reduction in overall rate. In general, all of the salts behaved similarly, though $Tl(OTFA)_3$ was slower than the others, and when $Pd(OAc)_2$ was used with cyclic ketone substrates, poor conversion was noted, along with formation of a palladium mirror on the reaction vessel. From these studies it was determined that 5 mol % loading of $Hg(OAc)_2$ and 2 equiv of $SiCl_4$ afforded the best combination of rate and monoenoxysilane selectivity; the corresponding trichlorosilyl enolates could be isolated in reproducibly good yield, Table 3. It was also demonstrated that other chlorosilane derivatives participated in this reaction, with the hydridodichlorosilyl enolate **13** being formed in moderate yield using 4 mol % $Hg(OAc)_2$, Table 3, entry 3.

This procedure has been used to create an extensive collection of methyl ketone-derived enolates now using only 1 mol % $Hg(OAc)_2$, Table 4. Common protecting groups (Table 4, entries 5 and 8−10) and other acid

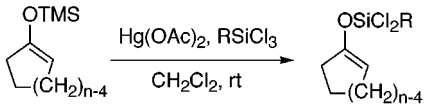
(9) For leading references on alkyltin enolates see: (a) Yasuda, M.; Katoh, Y.; Shibata, I.; Baba, A.; Matsuda, H.; Sonoda, N. *J. Org. Chem.* **1994**, *59*, 4386. (b) Shibata, I.; Baba, A. *Org. Prep. Proced. Int.* **1994**, *26*, 85. Recently, an interesting asymmetric aldol addition utlizing such stannanes directly has appeared appeared; see: (c) Yanagisawa, A.; Matsumoto, Y.; Nakashima, H.; Asakawa, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1997**, *119*, 9319.

(10) Pereyre, M.; Bellegarde, B.; Mendelsohn, J.; Valade, J. *J. Organomet. Chem.* **1968**, *11*, 97.

(11) (a) House, H. O.; Auerbach, R. A.; Gall, M.; Peet, N. P. *J. Org. Chem.* **1973**, *38*, 514. (b) Yamamoto, Y.; Maruyama, K. *J. Am. Chem. Soc.* **1982**, *104*, 2323. (c) Bluthe, N.; Malacria, M.; Gore, J. *Tetrahedron* **1984**, *40*, 3277. (d) Drouin, J.; Boaventura, M.-A.; Conia, J.-M. *J. Am. Chem. Soc.* **1985**, *107*, 1726.

(12) (a) Nakamura, E.; Kuwajima, I. *Chem. Lett.* **1983**, 59. (b) Nakamura, E.; Kuwajima, I. *Tetrahedron Lett.* **1983**, *24*, 3347. (c) Annunziata, R.; Benaglia, M.; Cinquini, M.; Cozzi, F.; Raimondi, L. *Tetrahedron* **1994**, *50*, 5821. (d) Kuwajima, I.; Nakamura, E. *Acc. Chem. Res.* **1985**, *18*, 181.

Table 3. Synthesis of Cyclic Ketone Chlorosilyl Enolates by Trans-Silylation

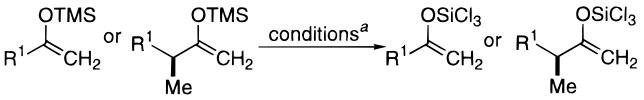


12

entry	*n*	enol ether	$Hg(OAc)_2$, mol %	R	enolate	yield,[a] %
1	5	**12e**	5	Cl	**10e**	73
2	6	**12f**	5	Cl	**10f**	68
3	6	**12f**	4	H	**13**	59
4	7	**12g**	5	Cl	**10g**	78

[a] Yield of distilled product.

Table 4. Synthesis of Methyl Ketone Trichlorosilyl Enolates by Trans-Silylation

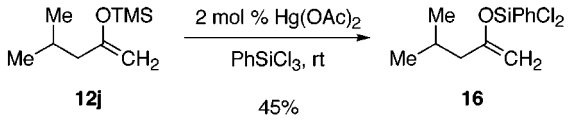


12 **14** **10** **15**

entry	enol ether	R^1	enolate	yield,[b] %
1	**12h**	*i*-Pr	**10h**	83
2	**12i**	*n*-Bu	**10i**	83
3	**12j**	*i*-Bu	**10j**	74
4	**12b**	*t*-Bu	**10b**	81
5	**12k**	$TBSOCH_2$	**10k**	65
6	**12l**	$CH_2{\equiv}CH$	**10l**	61
7	**12c**	Ph	**10c**	69
8	**14a**	OTBS	**15a**	71
9	**14b**	OPiv	**15b**	78
10	**14c**	OBn	**15c**	60

[a] 1 mol % $Hg(OAc)_2/SiCl_4/CH_2Cl_2$/rt. [b] Yield of distilled product.

Scheme 5



12j 45% **16**

sensitive substrates (Table 4, entry 6) are compatible with this reagent combination so long as care is taken to perform the reaction under anhydrous conditions. In addition, unsymmetrical methyl ketone enolates are now easily available from the TMS enol ethers, whereas with the tin-based method such substrates would be difficult to obtain in regiochemically pure form. In further studies with TMS enol ether **14a** it was found that as little as 0.25 mol % $Hg(OAc)_2$ could be used effectively in the transformation with only slight reduction in rate (roughly 30−60 min reaction time at room temperature). The phenyldichlorosilyl enolate **16** was also available in modest yield via the mercury-catalyzed trans-silylation reaction, Scheme 5. The efficacy of this catalytic trans-silylation has allowed the use of trichlorosilyl enolates as aldolization reagents without the need for purification. Thus, treatment of TMS enol ethers with $SiCl_4$ and catalytic $Hg(OAc)_2$ followed by concentration provides crude trichlorosilyl enolate of sufficient purity to be used in subsequent asymmetric aldol additions without significantly changed yield or selectivity.[1d,1f]

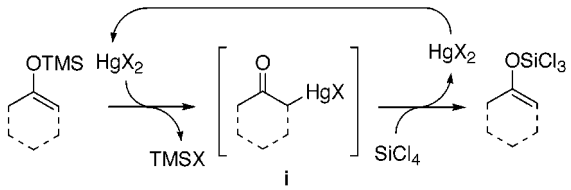
Discussion

The synthesis of chlorosilyl enolates of both esters and ketones by the silicon−tin metathesis reaction is certainly general, though purification of the products is both necessary and tedious due the presence of Bu_3SnCl and, in some instances, excess chlorosilane. Although the preparation of ketone enolates by this method is general and reasonably efficient when the desired enol acetate is conveniently prepared, the limited availability of regiochemically pure enol acetates does present a barrier to the general utility of this method.

The use of trichlorosilyl triflate as a trichlorosilylating reagent allows for the use of metathetical reactions using substrates with weaker electrofuges, i.e., alkylsilanes. These reactions seem to be fairly general over a range of ester and ketone substrates, though the preparative utility is low due to the complicated mixtures often observed and the ready decomposition of the product in the reaction mixture (even in cases where the isolated trichlorosilyl enolates are known to be stable). These problems may stem from undetected impurities in trichlorosilyl triflate or be due to impurities formed during the course of the reactions. The use of trichlorosilyl triflate (or perhaps related reagents) in direct enolsilylation is potentially the most convenient and powerful method for the synthesis of trichlorosilyl enolates, though it is currently hampered by limited substrate generality and the capricious nature of the reaction even with substrates amenable to the process.

The trans-silylation reaction from TMS enol ethers catalyzed by $Hg(OAc)_2$ is currently the most general and efficient method for the preparation of chlorosilyl enolates of ketones. Indeed, for methyl ketones the process is extremely facile, with good results being obtained even at 400/1 substrate/catalyst ratio. Cyclic ketones are much less reactive in this process (presumably due to steric hindrance of one or both of the steps in the process), and hence, more catalyst (4−5 mol %) is required, in addition to longer reaction times (18−24 h versus 1−2 h for methyl ketones). The largest problem in the reaction is the formation of 10−15% of the bis(enoxy)dichlorosilane, lowering the overall yield of the process, though the crude reaction mixture seems to contain only mono- and bis-(enoxy) species and TMSCl. A cursory investigation of other metal salts demonstrated that, of those surveyed, $Hg(OAc)_2$ was the most selective for the mono(enoxy) species. The dramatic drop in rate when either overall concentration of the reaction or a large (3−5 equivalents) excess of $SiCl_4$ is used is intriguing. Presumably, this is due to a catalyst deactivation pathway, though the process involved is not clear at the present time. We feel that, from the precedent of both House[11] and Baukov,[2] the mercury salt electrophilically adds to the starting enol ether, forming a transient α-mercurio ketone, with loss of the trimethylsilyl group, Scheme 6. Coordination of $SiCl_4$ to the carbonyl and assisted loss of the mercury electrofuge would then form the trichlorosilyl enolate and reform an active mercury salt for the next catalytic cycle.

Scheme 6



i

We recognize that this is a primitive mechanistic picture as we are not certain of the exact nature of the

chlorosilylating species nor of the nucleophile that assists the loss of the mercury electrofuge. A detailed mechanistic study is in progress.

In conclusion, we have accomplished the syntheses of 26 chlorosilyl enolates (most of which have been applied to aldol addition reactions) by a number of independent methods. Although capricious, trans-silylation and direct enolsilylation with trichlorosilyl triflate are both promising processes for the general preparation of chlorosilyl enolates, while the mercury-catalyzed trans-silylation seems to be a much preferred method over the traditional stannane−silicon metathesis route. Efforts toward the selective synthesis of both *E*- and *Z*-configured enolates of simple ethyl ketones and more direct methods for the synthesis of chlorosilyl enolates continue.

Experimental Section

General Methods. See the Supporting Information.

Trichloro[(1-methoxyethenyl)oxy]silane (2b). Methyl (tributylstannyl)acetate (**1**)[4] (18.46 g, 50.8 mmol) was added to $SiCl_4$ (35 mL, 306 mmol, 6 equiv) at room temperature under argon with vigorous stirring. The mixture was maintained at room temperature until ^{1}H NMR spectra of aliquots indicated that the stannyl ester had been consumed (typically 6−24 h). The excess $SiCl_4$ was removed under reduced pressure, and the residue was distilled at reduced pressure (two to three distillations were usually required) to give 6.82 g (65%) of the silyl ketene acetal **2b**[2a] as a clear, colorless liquid: bp 25 °C (5 mmHg); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.65 (d, J = 4.0, 1 H), 3.64 (s, 3 H), 3.41 (d, J = 3.9, 1 H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 158.33, 64.70, 56.13; IR (neat) 1672 (s) cm^{-1}; MS (CI) *m*/*z* 209 (9), 207 (8), 75 (100); HRMS calcd for $C_3H_6{}^{35}Cl^{37}Cl_2O_2Si$ 210.9144, found 210.9145. Anal. Calcd for $C_3H_5Cl_3O_2Si$ (207.52): C, 17.36; H, 2.43; Cl, 51.25. Found: C, 17.53; H, 2.53; Cl, 51.08.

Data for dichloro[(1-methoxyethenyl)oxy]silane (2a): bp 0 °C (5 mmHg); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.73 (s, 1 H), 3.63 (s, 3 H), 3.58 (d, J = 3.7, 1 H), 3.34 (d, J = 3.9, 1 H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 158.88, 63.55, 55.99; IR (neat) 1677 (s) cm^{-1}; MS (CI) *m*/*z* 177 (12), 175 (52), 173 (75), 171 (15), 75 (100); HRMS calcd for $C_3H_5{}^{35}Cl_2O_2Si$ 170.9436, found 170.9429. Anal. Calcd for $C_3H_6Cl_2O_2Si$ (173.07): Cl, 40.97. Found: Cl, 41.18.

Data for dichloro[(1-methoxyethenyl)oxy]methylsilane (2c): bp 25 °C (0.5 mmHg); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.61 (s, 3 H), 3.57 (d, J = 3.6, 1 H), 3.34 (d, J = 3.6, 1 H), 0.89 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 159.02, 63.64, 55.79, 4.95; IR (neat) 1764 (s), 1747 (s) cm^{-1}; MS (CI) *m*/*z* 187 (M + 1, 27) 186 (11), 151 (100); HRMS calcd for $C_4H_9{}^{35}Cl_2O_2Si$ 186.9749, found 186.9747.

Data for dichloro[(1-methoxyethenyl)oxy]phenylsilane (2d): bp 65 °C (0.02 mmHg); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.79 (br d, J = 7.2, 2 H), 7.55 (br t, J = 7.5, 1 H), 7.47 (t, J = 7.4, 2 H), 3.64 (d, J = 3.6, 1 H), 3.60 (s, 3 H), 3.37 (d, J = 3.6, 1 H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 159.05, 133.65, 132.67, 130.18, 128.30, 64.05, 55.81; IR (neat) 1733 (m), 1666 (s) cm^{-1}; MS (FI) *m*/*z* 252 (18), 248 (100).

Data for chloro[(1-methoxyvinyl)oxy]dimethylsilane (2e): bp 25 °C (0.5 mmHg); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.58 (s, 3 H), 3.45 (d, J = 3.2, 1 H), 3.24 (d, J = 3.2, 1 H), 0.58 (s, 6 H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 160.32, 62.09, 55.44, 2.43, 2.40.

Data for chloro[(1-methoxyethenyl)oxy]silacyclobutane (2f): bp 25 °C (0.02 mmHg); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.46 (d, J = 3.4, 1 H), 3.60 (s, 3 H), 3.27 (d, J = 3.4, 1 H), 2.01−1.79 (m, 4 H), 1.78−1.68 (m, 2 H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 159.74, 62.08, 55.67, 25.03, 12.55; IR (neat) 1728 (s), 1666 (s) cm^{-1}; MS (CI) *m*/*z* 179 (M + 1, 6), 75 (100); HRMS calcd for $C_6H_{12}{}^{35}ClO_2Si$ 179.0295, found 179.0296.

Trichloro[(1-cyclohexenyl)oxy]silane (10f). Tributyl[(1-cyclohexenyl)oxy]stannane[9c] (52.0 g, 134 mmol) was added via an addition funnel to cold (0 °C) $SiCl_4$ (46.0 mL, 403 mmol, 3.0 equiv) over 3 h with vigorous stirring. After complete addition, the mixture was warmed to room temperature and stirred for an additional 3 h. Excess $SiCl_4$ was removed by simple distillation, and the residue was fractionated twice through a 5-cm Vigreux column under reduced pressure to afford 24.2 g (78%) of the trichlorosilyl enolate **10f** as a colorless liquid: bp 76−78 °C (11 mmHg); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.31−5.28 (m, 1 H), 2.17−2.13 (m, 2 H), 2.09−2.04 (m, 2 H), 1.74−1.68 (m, 2 H), 1.58−1.52 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 148.07, 109.13, 28.54, 23.56, 22.74, 21.65; IR ($CHCl_3$) 1459 (m) cm^{-1}; MS (EI) *m*/*z* 234 (28), 233 (26), 232 (73), 231 (56), 230 (73), 229 (47), 202 (100). Anal. Calcd for $C_6H_9Cl_3OSi$ (231.58): C, 31.12; H, 3.92; Cl, 45.93. Found: C, 31.49; H, 4.08; Cl, 45.54.

Trichloro[1-phenyl-[(1-propenyl)oxy]silane (10d). 1-Phenyl-[(1-propenyl)oxy]acetate[13] (18.95 g, 107.5 mmol) and tributyltin methoxide (31.0 mL, 107.5 mmol, 1.0 equiv) were heated to 100 °C (bath temperature) for 4 h. The methyl acetate formed was continuously removed via a 10-cm Vigreux column. The mixture was cooled to room temperature, and the flask was carefully evacuated to 0.05 mmHg and heated to 100 °C (bath temperature) for 30 min to provide tributyl[(1-phenyl-1-propenenyl)oxy]stannane, which was used without further purification. The tributylstannyl compound was then added to cold (0 °C) $SiCl_4$ (37.0 mL, 323 mmol, 3.0 equiv) through an addition funnel over 2.5 h. The mixture was warmed to room temperature and stirred for an additional 3 h. Excess $SiCl_4$ was removed by distillation, and the residue was fractionated twice through a 5-cm Vigreux column to give 23.8 g (83%) of the trichlorosilyl enolate **10d** as a pale yellow liquid: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.53−7.51 (m, 2 H), 7.40−7.31 (m, 3 H), 5.63 (q, J = 7.1, 1 H), 1.88 (d, J = 7.1, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 147.66, 135.72, 128.38, 128.25, 125.03, 108.82, 11.94; IR (neat) 1496 (m) cm^{-1}; MS (EI) *m*/*z* 270 (6), 269 (11), 268 (17), 267 (25), 266 (18), 265 (24). Anal. Calcd for $C_9H_9Cl_3OSi$ (267.62): C, 40.39; H, 3.39; Cl, 39.74. Found: C, 40.19; H, 3.38; Cl, 39.65.

4-Methyl-2,6-bis(1,1-dimethylethyl)phenyl 2-(Trimethylsilyl)propanoate (4). *n*-Butyllithium (6.2 mL of a 1.72 M solution in hexanes, 10.7 mmol, 1.01 equiv) was added quickly to a cold (0 °C) solution of *i*-Pr_2NH (1.50 mL, 10.7 mmol, 1.2 equiv) in THF (40 mL). The resulting solution was stirred at 0 °C for 10 min and then cooled to −75 °C (internal). A solution of ester[7] (2.8 mL, 10.5 mmol) in THF (10 mL) was then added dropwise over 30 min. After the final addition, the reaction mixture was stirred at −75 to −77 °C for 30 min, and then TMSCl (1.90 mL, 15.0 mmol, 1.5 equiv) was added quickly, during which time the temperature rose to −71 °C. The mixture was allowed to warm to room temperature slowly and stirred for 12 h. Volatile components were removed under reduced pressure (0.3 mmHg), pentane (30 mL) was added, and the resulting slurry was Schlenk filtered. The filtrate was concentrated under reduced pressure (0.3 mmHg) to give a residue that was crystallized from hexane to provide 2.45 g (67%) of the *C*-TMS compound **4** as white crystals: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.11 (s, 1 H), 7.11 (s, 1 H), 2.30 (s, 3 H), 2.26 (q, J = 7.3, 1 H), 1.45 (d, J = 7.3, 3 H), 1.34 (s, 9 H), 1.33 (s, 9 H), 0.19 (s, 9 H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 175.47, 146.64, 142.14, 141.83, 134.10, 127.07, 126.78, 35.33, 35.21, 31.66, 31.49, 31.27, 21.44, 11.34, −1.68.

Trichloro[[[4-methyl-2,6-bis(1,1-dimethylethyl)phenoxy]propenyl]oxy]silane (5). Trichlorosilyl triflate[6] (95 μL, 0.55 mmol, 1.2 equiv) was added quickly to a cold (0 °C) solution of ester **4** in $CDCl_3$ (0.5 mL). The reaction mixture was allowed to stand at room temperature for 30 h, at which time no starting silane was observed in the ^{1}H NMR spectrum. Removal of the volatile components under reduced pressure (0.1 mmHg) provided the trichlorosilyl enolate **5** in essentially quantitative yield: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.10 (s, 2 H), 4.07 (q, J = 6.8, 1 H), 2.36 (s, 3 H), 1.46 (s, 18 H), 1.1 (d, J = 6.8, 3 H).

(13) Foss, V. L.; Sorokin, N. M.; Avrutov, I. M.; Lutsenko, I. F. *J. Organomet. Chem.* **1974**, *78*, 115.

Trichloro[(3,4-dihydro-2*H*-pyran-6-yl)oxy]silane (6). Trichlorosilyl triflate (1.0 mL, 5.76 mmol, 1.3 equiv) was added dropwise to δ-valerolactone (0.4 mL, 4.3 mmol) in dry pentane (50 mL) at 0 °C. After 10 min at this temperature, *i*-Pr_2NEt (0.8 mL, 5.76 mmol, 1.3 equiv) was added dropwise over 30 min. A white precipitate formed during the addition. The mixture was stirred at 0 °C for 45 min and then was warmed to room temperature, Schlenk filtered under argon, and concentrated under reduced pressure (~40 mmHg). The residue was purified by distillation (bulb-to-bulb) to give 0.506 g (48%) the silyl ketene acetal **6** as a colorless liquid: bp 25 °C ABT (0.02 mmHg); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.21 (t, J = 3.7, 1 H), 4.14 (br t, J = 5.1), 2.09 (td, J = 6.4, 3.7, 2 H), 1.84−1.79 (m, 2 H).

Data for trichloro[(3,4-dihydro-2*H*-thiapyran-6-yl)oxy]silane (7): bp 80 °C ABT (0.3 mmHg); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.41 (t, J = 3.9, 1 H), 2.99−2.96 (m, 2 H), 2.28−2.21 (m, 2 H), 1.98−1.90 (m, 2 H).

Data for trichloro[[(1-(dimethylphenylsilyl)propenyl]oxy]silane (9): bp 120 °C ABT (0.03 mmHg); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.57−7.54 (m, 2 H), 7.40−7.35 (m, 3 H), 6.07 (q, J = 7.4, *E*), 4.37 (q, J = 6.8, *Z*), 1.69 (d, J = 6.9, *Z*), 1.50 (d, J = 7.3, *E*), 0.48 (s, *E*) 0.45 (s, *Z*).

Trichloro[(1-methylethenyl)oxy]silane (10a). Chloroacetone (6.37 mL, 80.0 mmol) was added dropwise over 15 min to a 0 °C solution of *n*-Bu_3N (19.06 mL, 80.0 mmol, 1.0 equiv) and trichlorosilane (8.07 mL, 80.0 mmol, 1.0 equiv) in pentane (40 mL). During the addition, an oily phase appeared that eventually solidified. After the addition, the heterogeneous mixture was warmed to room temperature and stirred for 18 h. The volatile materials were then vacuum transferred at 0.2 mmHg to a new flask. The pentane was removed at reduced pressure (200 mmHg), and the resulting oil was distilled twice through a 7.5 cm Vigreux column to give 9.65 g (63%) of the trichlorosilyl enolate **10a** as a clear, colorless liquid: bp 63−64 °C (110 mmHg); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.55 (br d, J = 1.1, 1 H), 4.42 (br s, 1 H), 1.92 (s, 3 H); ^{13}C NMR ($CDCl_3$, 126 MHz) 152.62, 96.94, 21.44; IR (neat) 1659 (s) cm^{-1}; MS (CI) *m*/*z* 197 (15), 195 (14), 193 (6), 191 (2), 59 (100); HRMS calcd for $C_3H_6Cl_3OSi$ 190.9254, found 190.9250.

Trichloro[(1-butylethenyl)oxy]silane (10i). Silicon tetrachloride (9.18 mL, 80.0 mmol, 2.0 equiv) was added quickly to a suspension of $Hg(OAc)_2$ (127.0 mg, 0.40 mmol, 0.01 equiv) in CH_2Cl_2 (40 mL). During the addition, the mercury salt dissolved. Silyl enol ether **12i**[14] (6.89 g, 40.0 mmol) was then added to the solution dropwise over 10 min, and the solution was stirred at room temperature for an additional 50 min. During this time, the reaction mixture became somewhat cloudy once again. Removal of an aliquot and ^{1}H NMR analysis indicated that the reaction was complete. The mixture was concentrated at reduced pressure (100 mmHg), and the resulting oil was distilled twice through a 7.5 cm Vigreux column to give 7.76 g (83%) of the trichlorosilyl enolate **10i** as a clear, colorless oil: bp 68−70 °C (15 mmHg); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.56 (br d, J = 1.9, 1 H), 4.41 (br s, 1 H), 2.16 (t, J = 7.1, 2 H), 1.49 (m, 2 H), 1.35 (sext, J = 7.5, 2 H), 0.92 (t, J = 7.3, 3 H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 156.43, 95.62, 34.77, 28.41, 21.94, 13.78; IR (neat) 1655 (s) cm^{-1}; MS (CI) *m*/*z* 239 (4), 237 (4), 235 (10), 233 (11), 180 (100). Anal. Calcd for $C_6H_{11}Cl_3OSi$ (233.60): C, 30.85; H, 4.75; Cl, 45.53. Found: C, 30.93; H, 5.04; Cl, 45.54.

Data for trichloro[[1-(2-methylpropyl)ethenyl]oxy]silane (10j): bp 98−99 °C (90 mmHg); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.58 (br d, J = 2.1, 1 H), 4.39 (br d, J = 1.1, 1 H), 2.01 (d, J = 7.1, 2 H), 1.88 (sept, J = 6.8, 1 H), 0.93 (d, J = 6.6, 6 H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 155.36, 96.77, 44.49, 25.34, 22.09; IR (neat) 1655 (s) cm^{-1}; MS (CI) *m*/*z* 239 (2), 237 (3), 235 (6), 233 (12), 83 (100). Anal. Calcd for $C_6H_{11}Cl_3OSi$ (233.60): C, 30.85; H, 4.75; Cl, 45.53. Found: C, 30.80; H, 5.00; Cl, 45.27.

(14) (a) Haslouin, J.; Rouessac, F. *Bull. Chem. Soc. Fr.* **1976**, 1122. (b) Camici, L.; Dembech, P.; Ricci, A.; Seconi, G.; Taddei, M. *Tetrahedron* **1988**, *44*, 4197.

Data for dichloro[[1-(2-methylpropyl)ethenyl]oxy]-phenylsilane (16): bp 77 °C (0.15 mmHg); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.78 (dd, J = 8.1, 1.3, 2 H), 7.56 (tt, J = 7.5, 2.0, 1 H), 7.48 (t, J = 7.5, 2 H), 4.57 (d, J = 1.6, 1 H), 4.33 (d, J = 1.6, 1 H), 2.04 (d, J = 7.1, 2 H), 1.91 (nonet, J = 7.3, 1 H), 0.93 (d, J = 6.6, 6 H).

Data for trichloro[[1-(methylethyl)ethenyl]oxy]silane (10h): bp 78−80 °C (75 mmHg); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.51 (d, J = 2.4, 1 H), 4.15 (dd, J = 2.4, 0.8, 1 H), 2.36 (sept d, J_{sept} = 6.8, J_d = 0.2, 1 H), 1.09 (d, J = 6.8, 6 H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 161.63, 93.18, 33.60, 20.03; IR (neat) 1647 (m) cm^{-1}; MS (CI) *m*/*z* 221 (1), 219 (1), 60 (100). Anal. Calcd for $C_5H_9Cl_3OSi$ (219.57): C, 27.35; H, 4.13; Cl, 48.44. Found: C, 27.15; H, 4.41; Cl, 48.50.

Data for trichloro[[1-(1,1-dimethylethyl)ethenyl]oxy]-silane (10b): bp 90−91 °C (80 mmHg); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.47 (d, J = 2.8, 1 H), 4.46 (d, J = 2.7, 1 H), 1.11 (s, 9 H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 164.23, 92.06, 36.23, 27.66; IR (neat) 1643 (s) cm^{-1}; MS (CI) *m*/*z* 237 (1), 235 (2), 233 (2), 101 (100). Anal. Calcd for $C_6H_{11}Cl_3OSi$ (233.60): C, 30.85; H, 4.75; Cl, 45.53. Found: C, 30.69; H, 4.76; Cl, 45.61.

Data for trichloro[(1-phenylethenyl)oxy]silane (10c): bp 85−87 °C (3 mmHg); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.59−7.56 (m, 2 H), 7.40−7.35 (m, 3 H), 5.23 (d, J = 2.9, 1 H), 4.92 (d, J = 2.9, 1 H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 152.94, 134.31, 129.24, 128.46, 125.16, 95.93; IR (neat) 1631 (s) cm^{-1}; MS (CI) *m*/*z* 255 (1), 253 (2), 105 (100). Anal. Calcd for $C_8H_7Cl_3OSi$ (253.59): C, 37.89; H, 2.78; Cl, 41.94. Found: C, 37.96; H, 2.96; Cl, 41.91.

Data for trichloro[[1-[[[dimethyl(1,1-dimethylethyl)-silyl]oxy]methyl]ethenyl]oxy]silane (10k): bp 74−75 °C (3 mmHg); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.76 (br s, 1 H), 4.71 (br s, 1 H), 4.06 (br t, J = 1.1, 2 H), 0.92 (s, 9 H), 0.09 (s, 6 H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 154.54, 95.29, 62.82, 25.81, 18.33, −5.46; IR (neat) 1663 (s) cm^{-1}; MS (CI) *m*/*z* 327 (4), 325 (12), 323 (23), 321 (18). Anal. Calcd for $C_9H_{19}Cl_3O_2Si_2$ (321.78): C, 33.59; H, 5.95; Cl, 33.05. Found: C, 33.89; H, 6.27; Cl, 33.16.

Data for trichloro[(1-butadienyl)oxy]silane (10*l*): bp 63−64 °C (65 mmHg); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.19 (dd, J = 17.0, 6.2, 1 H), 5.53 (d, J = 17.0, 1 H), 5.24 (d, J = 6.4, 1 H), 4.82 (m, 1 H), 4.68 (d, J = 2.2, 1 H).

Data for (*S*)-trichloro[[1-[[[dimethyl(1,1-dimethylethyl)silyl]oxy]ethyl]ethenyl]oxy]silane (15a): bp 140 °C (ABT, 12 mmHg); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.75 (dd, J = 2.2, 0.9, 1 H), 4.62 (d, J = 2.2, 1 H), 4.16 (q, J = 6.4, 1 H), 1.29 (d, J = 6.2, 3 H), 0.91 (s, 9 H), 0.08 (s, 3 H), 0.08 (s, 3 H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 158.58, 94.05, 68.54, 25.76, 22.04, 18.17, −4.94, −5.10; MS (CI) *m*/*z* 337 (15), 335 (16); HRMS calcd for $C_{10}H_{22}Cl_3O_2Si_2$ 335.0224, found 335.0225.

Data for (*S*)-[1-methyl-2-[(trichlorosilyl)oxy]-2-propenyl]-2,2-dimethylpropanoate (15b): bp 140 °C (ABT, 8 mmHg); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.28 (q, J = 6.6, 1 H), 4.72 (app q, J = 2.8, 2 H), 1.37 (d, J = 6.6, 3 H), 1.21 (s, 9 H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 177.36, 154.03, 96.76, 69.31, 38.71, 27.04, 17.63.

Data for (*S*)-trichloro[(1-(phenylmethoxy)ethenyl)-oxy]silane (15c): bp 130 °C (ABT, 0.3 mmHg); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.37−7.29 (m, 5 H), 4.79 (dd, J = 2.4, 0.7, 1 H), 4.74 (d, J = 2.4, 1 H), 4.66 (d, J = 11.9, 1 H), 4.42 (d, J = 12.0, 1 H), 3.88 (q, J = 6.4, 1 H), 1.37 (d, J = 6.4, 3 H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 155.18, 138.07, 128.42, 127.70, 127.67, 96.80, 74.92, 70.58, 19.13.

Data for trichloro[(cyclopentenyl)oxy]silane (10e): bp 45−46 °C (7 mmHg); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.10 (pent, J = 2.0, 1 H), 2.44−2.40 (m, 2 H), 2.36−2.31 (m, 2 H), 1.98−1.90 (m, 2 H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 150.75, 108.38, 32.14, 28.30, 20.99; IR (neat) 1657 (s) cm^{-1}; MS (EI) *m*/*z* 222 (3), 220 (5), 218 (11), 216 (18), 55 (100). Anal. Calcd for $C_5H_7Cl_3OSi$ (217.55): C, 27.60; H, 3.24; Cl, 48.89. Found: C, 27.61; H, 3.35; Cl, 48.60.

Data for dichloro[(cyclohexenyl)oxy]silane (13): bp 84−85 °C (30 mmHg); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.66 (s, 1 H), 5.22−2.19 (m, 1 H), 2.14−2.08 (m, 2 H), 2.07−2.02 (m, 2 H), 1.74−1.66 (m, 2 H), 1.57−1.50 (m, 2 H).

Data for trichloro[(cycloheptenyl)oxy]silane (10g): bp 84−85 °C (10 mmHg); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.44 (t, J = 6.5, 1 H), 2.38−2.35 (m, 2 H), 2.05 (br q, J = 4.9, 2 H), 1.73−1.50 (m, 6 H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 152.80, 113.78, 34.16, 30.68, 27.06, 24.93, 24.00; IR (neat) 1673 (s) cm^{-1}; MS (EI) m/z 247 (2), 245 (2), 55 (100). Anal. Calcd for $C_7H_{11}Cl_3OSi$ (245.61): C, 34.23; H, 4.51; Cl, 43.30. Found: C, 34.05; H, 4.67; Cl, 43.48.

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Supporting Information Available: Full experimental procedures and characterization data for all compounds described (35 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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