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Conversion of hydrosilanes to alkoxysilanes catalyzed by $Cp_2TiCl_2/^nBuLi$

Thomas C. Bedard and Joyce Y. Corey
Department of Chemistry, University of Missouri—St. Louis, St. Louis, MO 63121 (USA)

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Abstract

The combination of Cp_2TiCl_2 and ^nBuLi provides an effective catalyst for alcoholysis of the model silanes n-$HexSiH_3$, $PhMeSiH_2$, Ph_2SiH_2 and $PhMe_2SiH$ by ethanol, isopropanol, t-butyl alcohol and phenol. Increasing the steric bulk of the substituents on either the alcohol or the silane generally requires longer reaction periods and/or increasing temperature. All SiH bonds are converted to SiOEt groups by ethanol and a single SiH bond in secondary silanes and two SiH bonds in tertiary silanes are replaced by t-butyl alcohol. Diols including pinacol, 2,4-pentanediol and 2,5-hexanediol react with $PhRSiH_2$ (R = Me, Ph) to give 1,3-dioxa-2-silacyclopentanes, -hexanes and -heptanes, respectively. Attempts to form caged structures by condensation of primary silanes and triols was unsuccessful. Hydrolysis of $PhRSiH_2$ is promoted by $Cp_2TiCl_2/^nBuLi$ and the siloxane is produced in quantitative yield when R = Ph and a mixture of linear disiloxanes and trisiloxanes in addition to cyclopolysilanes are produced when R = Me. Other protic reagents including acids, mercaptans, amines and enolizable ketones did not react. The effects of reaction parameters such as temperature, silane to catalyst ratio, solvent, transition metal and replacements for ^nBuLi were also determined.

Introduction

The silicon–oxygen linkage associated with silyl ethers has been employed by both organic and inorganic chemists in a variety of applications from protective groups in organic synthesis to sol-gel preparations. The most common methods for formation of silyl ethers are the reaction of chlorosilanes either with an alcohol in the presence of an HCl acceptor or with an alkoxide [1].

Hydrosilanes may also be converted to alkoxysilanes but catalysis is usually required. Several electron rich complexes including $Co_2(CO)_8$, $RhCl(PPh_3)_3$, $RuCl_2(PPh_3)_3$, $ClRu(CO)_2(PMe_3)_2$, $ClIr(CO)(PMePh_2)_2$ and $Rh_2(pfb)_4$ (pfb = perfluorobutyrate) have been found effective for this process [1–3]. In addition, only two electron poor complexes, Cp_2TiPh_2 and $ArCr(CO)_2(\eta^2\text{-}HSiHPh_2)$, have been reported to promote alcoholysis of monosilanes [4,5]. Many of these com-

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Correspondence to: Dr. J.Y. Corey, Department of Chemistry, University of Missouri—St. Louis, St. Louis, MO 63121, USA.

Table 1

Alcoholysis of hydrosilanes promoted by $Cp_2TiCl_2/^nBuLi$

Alcohol	Silane	Conditions [a]		Yield [b]	Product (%)
		h	Temperature		
EtOH	n-$HexSiH_3$	1	A	89	n-$HexSi(OEt)_3$
	$MePhSiH_2$	0.17	A	95(88)	$MePhSi(OEt)_3$
	Ph_2SiH_2	0.67	A	95	$Ph_2Si(OEt)_3$
	$(^nPr)_2SiH_2$	1	A	–(68)	$(^nPr)_2Si(OEt)_2$
	Me_2PhSiH	24	A	85	$Me_2PhSi(OEt)$
^iPrOH	n-$HexSiH_3$	1	A	86(75)	n-$HexSi(O^iPr)_3$
	$MePhSiH_2$	1	A	90	$MePhSi(O^iPr)_2$
	Ph_2SiH_2	8	B	93	$Ph_2Si(O^iPr)_2$
	$(^nPr)_2SiH_2$	24	B	48	$(^nPr)_2SiH(O^iPr)$
				41	$(^nPr)_2Si(O^iPr)_2$
	Me_2PhSiH	48	B	N.R.	–
^tBuOH	n-$HexSiH_3$	2	B	76(78)	n-$HexSiH(O^tBu)_2$
	$MePhSiH_2$	0.17	A	94	$MePhSiH(O^tBu)$
	Ph_2SiH_2	1	B	66	$Ph_2SiH(O^tBu)$
	$(^nPr)_2SiH_2$	48	B	N.R	–
	Me_2PhSiH	48	B	N.R.	–
Phenol	n-$HexSiH_3$	20	B	84(80)	n-$HexSi(OPh)_3$
	$MePhSiH_2$	18	B	77	$MePhSi(OPh)_2$
	Ph_2SiH_2	20	B	52	$Ph_2Si(OPh)_2$
	Me_2PhSiH	18	B	11	$Me_2PhSi(OPh)$

[a] Reactions carried out in THF solvent. A = room temperature; B = reflux. [b] GC yields (±5%); isolated yield in parentheses.

plexes require rigorous conditions and/or provide moderate to low yields and few are effective with tertiary silanes at room temperature. For most transition metal catalyzed alcoholyses hydrosilylation of the multiple bonds of olefins and carbonyls is a competing process.

The dehydrocondensation of an HSi bond with HEl (El = C, Si, N, O, etc.) could be an effective alternative to processes that involve chlorosilanes and El^- anions if the appropriate catalyst can be developed. We have reported that the combination $Cp_2MCl_2/^nBuLi$ is an effective catalyst for the dehydrocoupling of primary and secondary silanes to silicon oligomers [6]. In the course of these investigations, it was discovered that the combination of $Cp_2TiCl_2/^nBuLi$ is also effective for promotion of alcoholysis of hydrosilanes under mild to moderate reaction conditions and provides silyl ethers in generally high yields.

Results

Hydrosilanes and ROH

Reactions between selected primary, secondary and tertiary silanes and representative monofunctional alcohols including ethanol, isopropanol, tert-butanol and phenol in the presence of $Cp_2TiCl_2/^nBuLi$ are summarized in Table 1.

Primary silanes and secondary silanes containing at least one phenyl substituent react with ethanol in less than 1 h at room temperature to convert all available

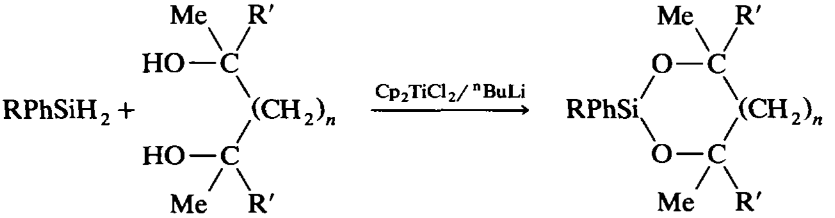
Si–H bonds to alkoxy substituents in 89% or greater yields. Reaction with isopropanol also provides good conversion of starting silanes but requires longer time periods and/or heating. The tertiary silane Me_2PhSiH forms the ethoxysilane in 24 h at room temperature but provides no reaction with isopropanol even after 48 h at reflux. Tertiary-butyl alcohol replaces only one hydrogen in secondary silanes $RPhSiH_2$ (R = Me, Ph) and replaces two hydrogens in the primary silane, but provides no reaction with $(n\text{-}Pr)_2SiH_2$ or Me_2PhSiH after 48 h at reflux. In contrast to several electron rich catalysts [2], $Cp_2TiCl_2/^nBuLi$ successfully promotes the reaction of hydrosilanes with phenol in 18–20 h at reflux to replace all reactive hydrogens in the cases studied.

The alcoholysis reaction appears to occur stepwise when there is more than one replaceable hydrogen per silicon since partially substituted alkoxy silanes RR'SiH(OR) and $RSiH_2(OR)$ or $RSiH(OR)_2$ were observed from secondary and primary silanes, respectively, at earlier stages of the reaction. Attempts to control hydrogen substitution at the mono addition stage by reducing the quantity of alcohol were unsuccessful. When reactions of $RPhSiH_2$ were conducted with a single equivalent of alcohol, a mixture of silane, mono-, and disubstituted alkoxysilanes were obtained even at −78°C. The failure to observe partial subsititution may be due to rapid redistribution of RR'SiH(OR) or $RSiH_2(OR)$.

Reaction conditions generally become more rigorous as the degree of substitution on the reacting alcohol increases from primary through tertiary. In the case of tert-butyl alcohol, a decreased degree of substitution of all silanes is observed. Reaction conditions must also be more rigorous as the degree of substitution increases on silicon as shown through comparison of data for $RPhSiH_2$ (R = Me, Ph) and Me_2PhSiH. Di-n-propylsilane is found to be generally less reactive than either diphenyl or methylphenylsilanes and the alkyl silane does not react with tert-butyl alcohol.

Hydrosilanes and polyfunctional alcohols

The reaction of secondary silanes with diols to produce 1,3-dioxa-2-silacycloalkanes was successfully accomplished in the presence of $Cp_2TiCl_2/^nBuLi$ as shown in eq. 1.

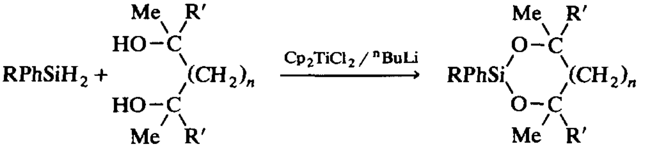


(1)

These reactions generally require refluxing conditions for 40 min to 48 h and produce isomeric mixtures in the cases where structural or stereo isomers are possible. The results are summarized in Table 2. Similar 1,3-dioxa-2-silacycles have been reported by Cragg and Lane from the reaction of dichlorosilanes with diols in yields that fall between 20 and 50% [7]. Dimers of 1,3-dioxa-2-silacycles are sometimes observed during the synthesis from silicon halides [7a]. In the current study no evidence for dimers was obtained under the GC conditions employed

Table 2

Reaction of secondary silanes with diols promoted by Cp_2TiCl_2 / ^nBuLi



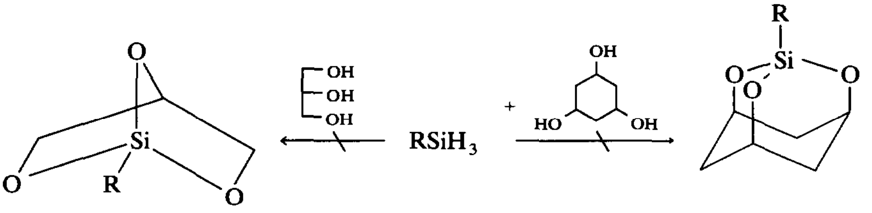
Diol	R	Product		Conditions [a] (h)	Yield [b]
		n	R′		
Pinacol	Me	0	Me	24	92(75) [c]
	Ph			48	85(66)
2,4-Pentanediol	Me	1	H	0.67	90(80)
	Ph			24	65
2,5-Hexanediol	Me	2	H	1	82
	Ph			24	89(84)

[a] Refluxing THF for the specified number of hours. [b] GC yield; isolated yield in parentheses. [c] Yield corrected for aliquots removed.

although decomposition of such species on the column cannot be precluded. However, when selected 1,3-dioxa-2-silacycles were isolated by distillation, the yields were comparable to the GC yields which suggests that dimers are probably not produced to a significant extent.

If the reaction of secondary silanes with diols occurs stepwise, a hydroalkoxysilane would form and cyclization would produce the 1,3-dioxa-2-silacycle. For the secondary silanes listed in Table 2, intramolecular cyclization occurs faster than intermolecular condensation to give oligomers (or polymers). However, when a primary silane was condensed with either pinacol or 2,4-pentanediol, insoluble solids or oils were obtained which contained weak residual SiH and OH stretches in the IR spectra. Therefore it was not possible to prepare silafunctional 1,3-dioxa-2-silacycles by the dehydrocoupling route although this has been successfully accomplished from $RSiCl_3$ by Cragg and Lane [7c].

Reaction of triols with primary silanes could lead to interesting caged structures as shown in eq. 2.



(2)

The reaction of either *cis,cis*-cyclohexanetriol or glycerol with both phenylsilane and hexylsilane at room temperature gave high melting solids with the former and insoluble oils with the latter. As in the case of reaction of primary silanes with diols, the isolated products exhibited residual SiH and OH stretches in the IR spectrum. In the course of the study with polyols the reaction of triethanolamine was also examined and in this case high yields of silatranes were realized.

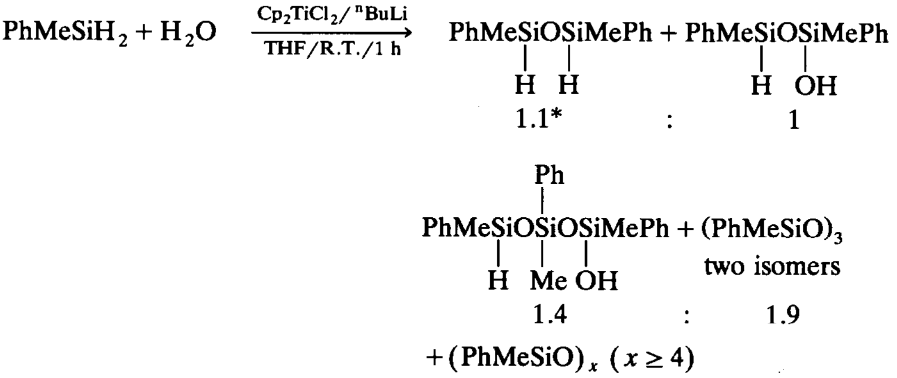
However, the reaction occurs to give the same products (and yields) in the absence of $Cp_2TiCl_2/{}^nBuLi$. The observation that the reaction of a hydrosilane with an amino alcohol is autocatalytic is not new [8] but does not appear to have been previously utilized in the synthesis of silatranes [9].

Hydrosilanes and other HEl reagents

When $RPhSiH_2$ (R = Me, Ph) is reacted with *N*-methylaniline or diethylamine no reaction occurs and only starting materials are recovered. However, if ethanol is added to the reaction mixture before workup, ethanolysis products are formed in high yield. Other HN-containing reagents such as diethylammonium hydrochloride and benzamide also do not react to give SiN coupling products although benzamide provides non-silicon containing products.

When acetic acid is added to $PhMeSiH_2/Cp_2TiCl_2/{}^nBuLi$ the solution turns bright green but no reaction of the silane occurs. The addition of thiophenol to silane-catalyst mixtures produced a purple color. No reaction of the silane occurs, however, PhSSPh is formed but does not exceed 20% (GC).

An interesting extension to the reactions of alcohols with hydrosilanes is the condensation that occurs in the presence of water. Reactions of both Ph_2SiH_2 and $PhMeSiH_2$ with water were monitored and products characterized by GCMS and ^1H NMR spectroscopy. The initial reaction of either secondary silane with water probably results in the formation of a silanol which can itself then react as an alcohol producing condensation products. The only product formed from Ph_2SiH_2 is the disiloxane, $Ph_2HSiOSiHPh_2$, in quantitative yield. However, condensation of $PhMeSiH_2$ is more complex and shows intermediate siloxanes and silanols as shown in eq. 3.



$$PhMeSiH_2 + H_2O \xrightarrow[\text{THF/R.T./1 h}]{Cp_2TiCl_2/{}^nBuLi} \underset{1.1^*}{\underset{H\quad H}{PhMeSiOSiMePh}} + \underset{1}{\underset{H\quad OH}{PhMeSiOSiMePh}} \qquad (3)$$

$$\underset{1.4}{\underset{H\quad Me\quad OH}{PhMeSiO\overset{Ph}{Si}OSiMePh}} + \underset{1.9}{\underset{\text{two isomers}}{(PhMeSiO)_3}}$$

$$+ (PhMeSiO)_x \ (x \geq 4)$$

* Weight ratio approximated from GC data.

In addition, there is a non-distilled portion which contains only aromatic and aliphatic methyl resonances indicative of higher order cyclopolysiloxanes.

Hydrosilanes and ketones

Substrates whose reactivity is of interest are enolizable ketones. In this case dehydrocoupling of the enol and a hydrosilane and/or reduction of the carbonyl is possible.

The reactions of ethylmethylketone, acetylacetonate and dimedone with n-$HexSiH_3$, $PhMeSiH_2$ and Me_2PhSiH failed to give products identifiable as either vinylsilyl ethers or as addition products of the hydrosilane to the carbonyl. However, several minor products (usually less than 15% of the reaction mixture) were observed from the ketone although these were not isolated. In order to determine whether the catalyst was still capable of effecting alcoholysis after addition of the ketone, ethanol was added. Only in the case of the reaction of Me_2PhSiH and EtCOMe was some formation of $Me_2PhSiOEt$ observed.

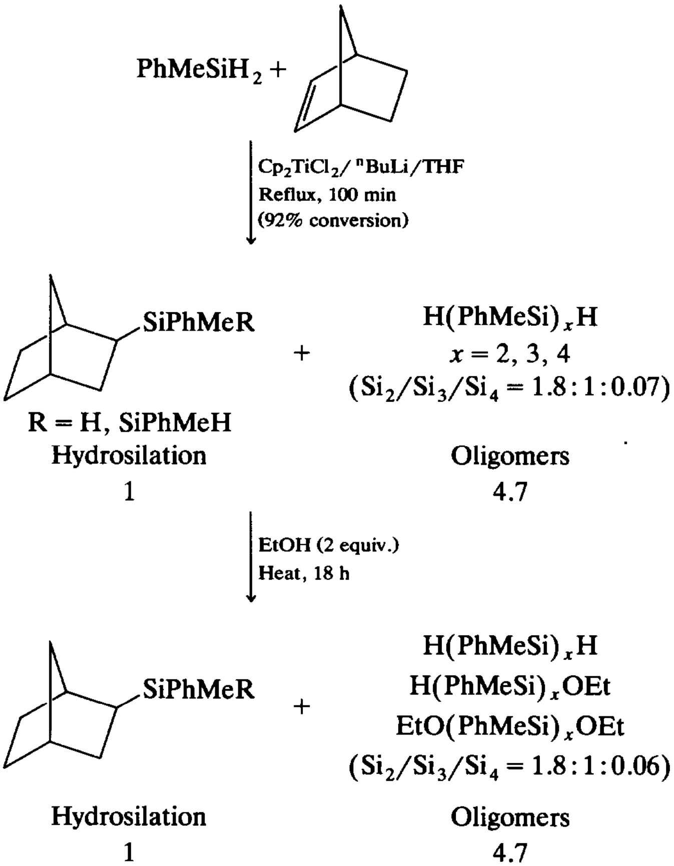
When benzophenone was added to Me_2PhSiH in the presence of the catalyst system, no reaction of the silane takes place but benzophenone is almost completely consumed. The addition of ethanol failed to convert the silane to $Me_2PhSiOEt$.

Discussion

The alcoholysis of hydrosilanes with the electron deficient catalyst Cp_2TiPh_2 has been reported [4]. The reactions were carried out in refluxing toluene with Ph_2SiH_2 and 2 equiv. of alcohol and product distributions determined by GC. With EtOH 100% of the silane was consumed and $Ph_2Si(OEt)_2$ (83%) and $Ph_2SiH(OEt)$ (9%) were produced. With ^iPrOH, 97% conversion of silane was observed after 12 h and the products formed were $Ph_2SiH(O^iPr)$ (88%) and $Ph_2SiH(O^iPr)$ (12%). The reaction of ^tBuOH was very slow with only 7% conversion after 86 h [$Ph_2SiH(O^tBu)$, 86%] [4]. Comparison of the results obtained using Cp_2TiPh_2 with those reported here shows that $Cp_2TiCl_2/^nBuLi$ effects alcoholysis of diphenylsilane in higher yields and under milder conditions. As an example, 97% conversion of Ph_2SiH_2 with ^iPrOH provided a mixture of mono and dialkoxy products in a 7 : 1 ratio after 12 h (refluxing toluene) with Cp_2TiPh_2 in comparison to 93% of the dialkoxy product in 8 h (refluxing THF) with $Cp_2TiCl_2/^nBuLi$. Since Cp_2TiPh_2 must be synthesized the catalyst system $Cp_2TiCl_2/^nBuLi$ has the advantage that the reagents in the combination are commercially available.

The reaction of secondary silanes with diols in the presence of $Cp_2TiCl_2/^nBuLi$ provides a good entry into five-, six- and seven-membered 1,3-dioxa-2-silacycles. The alcoholysis of Ph_2SiH_2 with 1,2-diols to give cyclic products in the presence of the electron rich transition metal catalyst $Rh_2(pfb)_4$ [3] was not successful but alcoholysis of Ph_2SiH_2 with 2,3-butanediol to the dioxasilacycle occurred in quantitative yield in the presence of Cp_2TiPh_2 [4]. The condensation of diols or triols with primary silanes in the presence of $Cp_2TiCl_2/^nBuLi$ did not provide monomer products but primary silanes are converted with *cis*-phloroglucitol to 2,4,10-trioxa-3-silaadamantanes with $ClRh(PPh_3)_3$ [9].

The elaboration of polysilane and polysiloxane oligomers in a directed fashion without disproportionation of the backbone is one of the goals in producing precursors to new materials. The development of a systematic approach to the synthesis of oligosiloxanes has been reported where one of the basic reactions is hydroxylation of $Me_3SiO(Me_2SiO)_nSiMe_2H$. This was successfully accomplished through the use of Pd/C as a catalyst [11]. The alcoholysis of $-[MeHSiO]_{0.3}$-$[MeSi(O)_{1.5}]_{0.7}-$ in the presence of Cp_2TiMe_2 at 20°C has provided $-[Me(RO)$-$SiO]_{0.3}[MeSi(O)_{1.5}]_{0.7}-$ [12]. Because of our interest in developing the chemistry of silicon oligomers the alcoholysis of $H(PhMeSi)_xH$ ($x = 2, 3$) was studied. The same



$H(PhMeSi)_2H/H(PhMeSi)_2OEt/EtO(PhMeSi)_2OEt = 12:12:1$
$H(PhMeSi)_3H/H(PhMeSi)_3OEt = 6.5:1$

Scheme 1. Oligomerization/Alcoholysis.

catalyst system has been found effective for both the condensation of hydrosilanes to oligomers as well as alcoholysis and it was possible to perform both processes without the isolation of the intermediate hydrosilane oligomers as shown in Scheme 1. The alcoholysis is quite slow since a tertiary silane is involved, but curiously the alcoholysis of the disilane occurs more readily than the trisilane. Both the condensation of $PhMeSiH_2$ to oligomers and the alcoholysis were monitored by gas chromatography and the products were verified by GCMS. The production and characterization of the oligomers has been previously described [6]. Although the alcoholysis may be too slow to be practical the reaction does occur without the disproportionation of the oligomers observed in the absence of ethanol [13].

In an attempt to gain some understanding of the factors which might influence the alcoholysis, several reaction parameters were varied including the transition metal, the ^{n}BuLi to Cp_2TiCl_2 ratio and alkoxide replacements for ^{n}BuLi. When either $MePhSiH_2$ or Ph_2SiH_2 were reacted with ethanol by the general alcoholysis procedure substituting zirconocene dichloride for titanocene dichloride, alcoholysis to both mono and diethoxysilanes occurred although in greatly reduced yields. After 1 h at room temperature the ratio of $PhRSiH_2$/PhRSiH(OEt)/$PhRSi(OEt)_2$ was 20:1.8:1 (R = Me) and 100:5:1 (R = Ph).

The ratio of $Cp_2TiCl_2/^nBuLi$ was varied from the 1:2 used for standard alcoholysis to 1:1 and 1:3, both of which produced variations that differed from the results obtained for the 1:2 ratio. With 2 equiv. of the lithium reagent, dark brown or brown-green mixtures are generated and complete alcoholysis occurs after 10 min at room temperature. With 1 equiv. of ^nBuLi, light green reaction mixtures were obtained. The ratio of $PhMeSi(OEt)_2/PhMeSiH_2$ changed from 5 after 1 h to 8.4 after 2 h and complete comsumption of starting silane was observed at 24 h. With 3 equiv. of ^nBuLi, dark reaction mixtures were produced and although $PhMeSiH_2$ is consumed within 1 h the products consist of $PhMeSi(OEt)_2$/[PhMeBuSiH + PhMeSiH(OEt)] in a 2:1 ratio. After 18 h this ratio is 14. These results indicate that the most efficient catalyst for conversion of both SiH bonds in the secondary silane occur when the ratio of Ti/Li is 2.

Alkoxide bases were briefly examined as replacements for ^nBuLi. When Cp_2TiCl_2 and 1 equiv. of LiOEt was used in the ethanolysis of $MePhSiH_2$, no reaction of the silane occurred after 48 h at room temperature. However, when 2 equiv. of LiOEt were used, vigorous reaction accompanied by gas evolution was observed and $PhMeSi(OEt)_2$ was produced. Similar results were obtained with 2 equiv. of NaOEt.

As previously indicated, Cp_2TiPh_2 has been successfully employed to promote the alcoholysis of Ph_2SiH_2 [4]. The redistribution of the hydrosilanes $(EtO)_2MeSiH$ and $-[MeHSiO]_x-$ to $2(EtO)_3MeSi$ and $-[MeHSiO]_{0.3}[MeSi(O)_{1.5}]_{0.7}-$ (and $MeSiH_3$) is promoted by Cp_2TiMe_2 and in the latter instance addition of MeOH results in conversion of the majority of the SiH groups in the polymer to SiOMe groups [12,14]. No mechanism for either alcoholysis reaction was proposed but a bimetallic Ti^{III} complex has been suggested for the redistribution of $(EtO)_2MeSiH$ [14].

The nature of the intermediate produced from the combination of $Cp_2TiCl_2/^nBuLi$ (or Cp_2TiCl_2/LiOEt) has not yet been determined. It is probable that a lower valent Ti species is present in these systems and the reaction chemistry in the presence of ketones and thiophenol lend some support for this speculation. In an earlier study of the related reaction of Cp_2TiCl_2 with ^iPrMgBr investigators proposed that Ti^{III} species are produced which varied as a function of the Ti/Mg ratio [15]. Cp_2TiBr, Cp_2TiR (R = C_3H_7 and/or H) and $Cp_2TiH_2^-$ were suggested for Ti/Mg ratios of 1:1 to 1:2 to 1:3, respectively. The formation and isolation of Cp_2TiBu_2 from Cp_2TiCl_2 and 2 equiv. of ^nBuLi at low temperatures is possible but the dialkyltitanocene decomposes on warming although the metal containing products were not identified [16]. The formation of Cp_2TiH from Cp_2TiCl_2 and ^nBuLi is suggested by the fact that addition to olefins occurs to give Cp_2TiR products [17]. The reaction of Cp_2TiCl_2 and BuLi in the presence of H_2 and Bu_3P led to the isolation of $Cp_2TiH(PBu_3)$ [18].

The results from the current study also indicate that different species may be present as a function of the $Cp_2TiCl_2/^nBuLi$ and Cp_2TiCl_2/LiOEt ratio. The 1:1 ratio does not produce a catalyst capable of promoting the alcoholysis reaction in the case of Cp_2TiCl_2 and LiOEt and the 1:1 and 1:3 $Cp_2TiCl_2/^nBuLi$ systems effect alcoholysis at a slower rate than the 1:2 ratio. It is probable that Cp_2TiH is formed when the ratio of Ti/Li exceeds 1. Addition of alcohol could convert Cp_2TiH to Cp_2TiOR. A subsequent metathesis reaction with the hydrosilane would transfer the alkoxy group to the silicon and regenerate Cp_2TiH. Transfer of an alkoxy group from Cp_2TiOR to Si has been suggested as part of the cycle for the Cp_2TiPh_2 promoted additions of hydrosilanes to carbonyl groups [19]. A similar sequence could also occur from $Cp_2TiH_2^-$ although the rates may not be the same. Alternative possibilities could include the formation of silyltitanium(III) species which are then solvolyzed by the added alcohol.

The combination of $Cp_2TiCl_2/^nBuLi$ serves as a readily prepared catalyst system which provides silyl ethers from hydrosilanes and alcohols in high yields under mild to moderate reaction conditions. The catalyst is effective for primary, secondary and tertiary hydrosilanes and alcohols and also for the formation of five-, six- and seven-membered ring 1,3-dioxa-2-silacycles from suitable diols. In addition, this catalyst combination promotes hydrolysis although the product distribution will be a function of the nature of the groups on silicon. The addition of carbonyl containing reagents appears to eliminate the species which promotes alcoholysis. The combination of $Cp_2TiCl_2/^nBuLi$ can also function as a hydrosilylation catalyst for acyclic olefins but not for cyclic olefins [13]. These latter two will limit the functional groups that can be present on the alcohol used to form the alkoxysilane.

Experimental

General

All reactions were carried out under an atmosphere of dry nitrogen through the use of standard Schlenk techniques in glassware which was dried in an oven at 110–120°C for 12 h prior to use. Tetrahydrofuran (THF) was freshly distilled from sodium/benzophenone under nitrogen. Commercial alcohols and diols not packaged under anhydrous conditions were dried by simple distillation from potassium carbonate, or magnesium powder in the case of ethanol. The commercial reagents Cp_2TiCl_2, ^nBuLi in hexanes, anhydrous ethyl ether and n-hexylsilane were used as supplied. The following compounds were prepared by standard procedures from chlorosilane and $LiAlH_4$: $PhMeSiH_2$ [20], Ph_2SiH_2 [20], $PhSiH_3$ [21], $(^nPr)_2SiH_2$ [22] and Me_2PhSiH [23].

^1H and ^{13}C spectra were recorded in $CDCl_3$ unless otherwise noted. Measurements were made on a Varian XL-300 spectrophotometer with the residual protons of the deuterated solvent used as the internal standard at 7.24 ppm or relative to TMS when specified. The characteristic solvent peaks centered at 77.0 ppm were used as an internal reference for ^{13}C spectra. Mass spectral data were obtained on a Hewlett-Packard 5988A GC/MS instrument equipped with an RTE-A data system, and gas chromatographic separations were performed in a split injection mode using a 12.5 μm (HP-1) capillary column. The GC data were collected on a Varian Aerograph Series 1400 Gas Chromatograph with a 15 m × 0.54 mm i.d., 1.5 m film DB-17 column (J & W Scientific) (Column A) at a flow rate of 6 mL/min helium, temperature programming 50–240°C (20°C/min) and recorded on an HP3394 A integrator. Alternatively data were collected on a Shimadzu GC-14A Gas Chromatograph with a 15 m × 0.54 mm i.d., 1.5 μm film DB-5 column (J & W Scientific) (Column B) with a flow rate of 6 mL/min helium and the same programming. The injection temperature was 240°C and the detector set at 260°C for Column A and 200°C and 320°C for Column B, respectively. Melting point determinations were obtained on a Hoover oil bath apparatus and are uncorrected.

Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

General procedure for the alcoholysis of hydrosilanes in the presence of Cp_2TiCl_2/ ^nBuLi

n-Butyllithium (2 equiv., 1.6 *M* in hexanes, 0.42 mL) was added to titanocene dichloride (0.0829 g, 0.33 mmol) in anhydrous THF (10 mL) at 0°C under nitrogen and stirred for 15 min. An immediate dark brown or black solution resulted. Hydrosilane (10 mmol) was added via syringe to the solution with stirring. Alcohol (11 mmol for tertiary silanes, 22 mmol for secondary silanes and 33 mmol for primary silanes) or polyol (11 mmol) was then added via syringe dropwise to the reaction mixture at a rate to keep gas evolution controlled. Upon completion of the addition, the mixture was allowed to warm to room temperature over 10 min and then stirred or heated to reflux as required. At various times, aliquots were removed via syringe, diluted with anhydrous ether and filtered through celite. GC analysis was used to estimate percent conversion of the starting hydrosilane and formation of products. Reactions were terminated by fitting the reaction vessel with a drying tube and exposing the mixture to air until a yellow colored solution resulted. Volatile materials were removed on a rotary evaporator.

Analysis of the reaction mixtures was performed by gas chromatography and percentages are uncorrected. Previously reported compounds were characterized by GCMS and isolated in some cases by vacuum distillation. Parent ions and peaks exhibiting relative intensities > 20% of the base peak with mass values over 100 amu in the GCMS analyses are recorded. Plausible assignments are supplied for the fragments. Previously reported alkoxysilanes are indicated with a reference and representative examples have been isolated and characterized in the present study. In most cases the only byproducts that arise are due to the presence of siloxanes caused by incomplete drying of the alcohols.

The results are grouped by alcohol and are on the scale described for the general alcoholysis procedure unless otherwise noted.

Reaction of ethanol

n-Hexylsilane. Reaction of $(n\text{-Hex})SiH_3$ and EtOH produced $(n\text{-Hex})SiH(OEt)_2$ within 10 min and $(n\text{-Hex})Si(OEt)_3$ [25] in 89% (GC) after 1 h. $C_{12}H_{28}SiO_2$ *m/e* 248 (M^+, 0.4%), 163 ($M^+ - C_6H_{13}$), 119 [$HSi(OEt)_2{}^+$].

Methylphenylsilane. Reaction of $MePhSiH_2$ (1.37 g, 11.0 mmol) and EtOH (1.4 mL, 1.10 g, 22.0 mmol) provided $MePhSi(OEt)_2$ in 95% (GC) after 10 min at room temperature. Kugelrohr distillation provided the ethoxysilane (2.08 g, 88%), b.p. 40–60°C/0.5 mm (lit. b.p. 75–78°C/4.0 mmHg) [26]. $C_{11}H_{18}SiO_2$ *m/e* 210 (M^+, 5.5%), 195 ($M^+ - CH_3$), 151 [$PhSi(H)OEt^+$].

In a separate experiment, $PhMeSiH_2$ and EtOH were reacted according to the general alcoholysis procedure with the omission of the catalyst. After 24 h at room temperature analysis (GC) showed only unreacted starting silane.

Diphenylsilane. Reaction of Ph_2SiH_2 and EtOH produced $Ph_2Si(OEt)_2$ [27] in 95% (GC) after 40 min. $C_{16}H_{20}SiO_2$ *m/e* 272 (M^+, 7%), 195 ($M^+ - C_6H_5$), 194 ($M^+ - C_6H_6$), 183 (Ph_2SiH^+), 151 [$PhSi(H)OEt^+$], 139 [$PhSi(OH)_2{}^+$], 123 [$PhSiH(OH)^+$], 104.

In a separate experiment the catalyst/silane mixture was cooled to −78°C prior to addition of ethanol. The mixture was stirred cold for 2 h before oxygen was introduced until the catalyst turned yellow. Analysis (GC) of the reaction mixture indicated a ratio of $PhMeSiH_2$/PhMeSiH(OEt)/$PhMeSi(OEt)_2$ of 15 : 5 : 1.

Di(n-propyl)silane. Reaction of $(^nPr)_2SiH_2$ and EtOH was terminated after 60 min at room temperature. Kugelrohr distillation provided $(^nPr)_2Si(OEt)_2$ (1.40, 68%), b.p. 70–80°C/7.5 mmHg (lit. b.p. 85°C/20.0 mmHg [28]). ^1H NMR: 3.65 (q, 4H), 1.32 (m, 4H), 1.10 (t, 6H), 0.87 (t, 6H), 0.52 (m, 4H) ppm. ^{13}C NMR: 58.20, 18.60, 18.23, 16.63, 15.42 ppm. $C_{10}H_{24}SiO_2$ *m/e* 204 (M^+).

When the reaction of $(^nPr)_2SiH_2$ and EtOH was conducted in the presence of cyclooctene (1.10 g, 10 mmol), complete consumption of the starting silane occurred within 20 min at room temperature. The only observed product was $(^nPr)_2Si(OEt)_2$.

Dimethylphenylsilane. Reaction of Me_2PhSiH and EtOH produced Me_2PhSi-OEt [29] in (85%, GC) and unreacted silane (11%, GC) after 24 h at room temperature. $C_{10}H_{16}SiO$ *m/e* 180 (M^+, 6%), 165 ($M^+ - CH_3$), 137 [PhMeSi-$(OH)^+$], 121 ($PhMeSiH^+$).

Reaction of isopropanol

n-Hexylsilane. Reaction of (n-Hex)SiH_3 and ^iPrOH was complete after 1 h at room temperature. After workup, Kugelrohr distillation provided (n-Hex)$Si(O^iPr)_3$ (2.10 g, 75%), b.p. 65–75°C/0.5 mmHg. ^1H NMR: 4.18 (sep, 3H), 1.2–1.4 (m, 8H), 1.16 (d, 18H), 0.8–0.9 (m, 2H), 0.5–0.6 (m, 3H) ppm. ^{13}C NMR: 64.95, 33.18, 31.71, 25.75, 23.14, 22.80, 14.32, 12.19 ppm. $C_{15}H_{34}SiO_3$ *m/e* 275 ($M^+ - CH_3$), 205 ($M^+ - C_6H_{13}$), 163, 121.

Methylphenylsilane. Reaction of $MePhSiH_2$ and ^iPrOH provided MePhSi-$(O^iPr)_2$ [30] in > 90% (GC) after 60 min at room temperature. $C_{13}H_{22}SiO_2$ *m/e* 238 (M^+, 1%), 223 ($M^+ - CH_3$), 160, 139 [$PhSi(OH)_2{}^+$].

Diphenylsilane. Reaction of Ph_2SiH_2 and ^iPrOH provided $Ph_2Si(O^iPr)_2$ [31] in 93% (GC) after 8 h at reflux. $C_{18}H_{24}SiO_2$ *m/e* 300 (M^+), 258 ($M^+ - CH_3$, 1.3%), 241 (Ph_2SiOPr^+), 222 ($M^+ - C_6H_6$), 199, 181 [$M^+ - (^iPrO + {}^iPrOH)$], 164,139 [$PhSi(OH)_2{}^+$].

Di-n-propylsilane. Reaction of $(^nPr)_2SiH_2$ and ^iPrOH was conducted at room temperature for 24 h after which $(^nPr)_2SiH(O^iPr)$ [32] and $(^nPr)_2Si(O^iPr)_2$ were formed in 48% and 41% yield, respectively. $C_{12}H_{28}SiO_2$ *m/e* 217 ($M^+ - CH_3$), 189 ($M^+ -$ Pr), 147 [$M^+ - (Pr + C_3H_6)$], 105 [$PrOSi(OH)H^+$]. $C_9H_{22}SiO$ *m/e* 174 (M^+, 2.1%), 159 ($M^+ - CH_3$), 131 ($M^+ - C_3H_7$), 117 [$M^+ - (CH_3 + C_3H_6)$].

Dimethylphenylsilane. No reaction of Me_2PhSiH and ^iPrOH occurred after 48 h at reflux.

Reaction of tert-butyl alcohol

n-Hexylsilane. Reaction of n-HexSiH_3 with ^tBuOH for 2 h at reflux gave n-HexSi(H)$(O^tBu)_2$ in 78% (GC). Kugelrohr distillation provided the product (2.06 g, 78%), b.p. 55–65°C/0.7 mmHg. ^1H NMR: 4.65–4.71 (m, 1H), 1.2–1.4 (m, 26H), 0.8–0.9 (m, 3H), 0.5–0.6 (m, 2H) ppm. ^{13}C NMR: 72.93, 32.82, 32.14, 31.89, 31.83, 22.81, 22.75, 17.41 ppm. $C_{14}H_{32}SiO_3$ m/e 260 (M^+, 0.8%), 245 ($M^+ - CH_3$), 189 [$MeSi(O^tBu)_2$], 175 [$HSi(O^tBu)_2^+$], 147, 131, 129, 119 [$^tBuOSi(OH)H^+$], 117, 113.

Methylphenylsilane. Reaction of $MePhSiH_2$ and ^tBuOH provided $MePhSiH(O^tBu)$ [33] in 95% (GC) after 10 min at room temperature. Attempts to incorporate further substitution at silicon by refluxing for 2 h were unsuccessful. $C_{11}H_{18}SiO$ m/e 194 (M^+).

The reaction of $MePhSiH_2$ was also conducted in toluene and after 10 min at room temperature quantitative conversion to $MePhSiH(O^tBu)$ occurred. Heating the mixture at reflux for 24 h failed to provide any evidence for the formation of $MePhSi(O^tBu)_2$.

Diphenylsilane. Reaction of Ph_2SiH_2 and ^tBuOH provided $Ph_2SiH(O^tBu)$ [34] in 66% after 1 h at reflux (unreacted silane, 29%). Attempts to incorporate a second alkoxy group through refluxing an additional 24 h were unsuccessful. $C_{16}H_{20}SiO$ m/e 256 (M^+, 1.7%), 241 ($M^+ - CH_3$), 199 ($M^+ - C_4H_9$), 181 [$M^+ - (OC_4H_9 + H_2)$], 178 [$PhSi(O^tBu)^+$], 123 [$PhSiH(OH)^+$], 122, 105 ($PhSi^+$).

Di-n-propylsilane. After 24 h at reflux no reaction of $(^nPr)_2SiH_2$ and ^tBuOH was observed.

Dimethylphenylsilane. After 48 h at reflux no reaction occurred between Me_2PhSiH and ^tBuOH.

Reaction of phenol

n-Hexylsilane. Reaction of n-$HexSiH_3$ and HOC_6H_5 provided n-$HexSi(OPh)_3$ in 84% after 20 h at reflux. Kugelrohr distillation provided the product (3.26 g, 80%), b.p. 165–175°C/0.7 mmHg. ^1H NMR: 7.0–7.4 (m, 15H), 1.5–1.6 (m, 2H), 1.2–1.4 (m, 6H), 1.0–1.1 (m, 2H), 0.8–1.0 (m, 3H) ppm. ^{13}C NMR: 153.14, 129.74, 122.42, 119.67, 32.33, 31.23, 22.41, 22.11, 14.02, 10.51 ppm. $C_{24}H_{28}SiO_3$ m/e 392 (M^+, 100%), 289, 215 [$HSi(OPh)_2)^+$], 213, 197, 121 ($SiOPh^+$).

Methylphenylsilane. Reaction of $MePhSiH_2$ and HOC_6H_5 provided $MePhSi(OPh)_2$ [35] in 77% (GC) after 18 h at reflux. $C_{19}H_{18}SiO_2$ m/e 306 (M^+, 100%), 291 ($M^+ - CH_3$), 273, 213 ($M^+ - OC_6H_5$), 197, 121 ($SiOPh^+$).

Diphenylsilane. Reaction of Ph_2SiH_2 and HOC_6H_5 provided $Ph_2Si(OPh)_2$ [36] in 52% (GC) after 20 h at reflux. $C_{24}H_{20}SiO_2$ m/e 368 (M^+, 65%), 275 ($M^+ - OC_6H_5$), 197 [$M^+ - (OC_6H_5 + C_6H_6)$].

Dimethylphenylsilane. Reaction of Me_2PhSiH and HOC_6H_5 provided $Me_2PhSi(OC_6H_5)$ [37] in 11% (GC) after 20 h at reflux. $C_{14}H_{16}SiO$ m/e 228 (M^+, 42%), 213 ($M^+ - CH_3$), 135 ($M^+ - OC_6H_5$).

Reaction of pinacol

Methylphenylsilane. Reaction of $MePhSiH_2$ (1.24 g, 10.0 mmol) and pinacol (1.41 g, 12.0 mmol) provided 2,4,4,5,5-pentamethyl-2-phenyl-1,3-dioxa-2-silacyclopentane in 92% (GC) after 24 h at reflux and no detectable dimer. Kugelrohr distillation provided the product as a clear liquid (1.61 g, 67%; 92% by GC), b.p. 55–80°C/0.4 mmHg (lit. b.p. 84°C/0.2 mmHg [7a,c]). ^1H NMR: 7.3–7.7 (m, arom, 5), 1.33 (s, CH_3, 6), 1.25 (s, CH_3, 6), 0.50 (s, $SiCH_3$, 3) ppm. ^{13}C NMR: 135.29, 133.42, 130.10, 127.71, 81.76, 25.76, −0.55 ppm. $C_{13}H_{20}SiO_2$ m/e 236 (M^+, 34%), 221 ($M^+ - CH_3$), 179, 178, 177, 163 [$M^+ - (CH_3 + OC(CH_3)_2$], 150, 139

[$PhSi(OH)_2^+$], 137 ($PhSiO_2^+$), 121, 120, 119, 118, 105 ($PhSi^+$). Samples stored for 9 months exhibited no change.

Diphenylsilane. Reaction of Ph_2SiH_2 and pinacol provided 4,4,5,5-tetramethyl-2,2-diphenyl-1,3-dioxa-2-silacyclopentane [7a,c] in 85% (GC) after 48 h at reflux and no detectable dimer. Kugelrohr distillation provided the product as a clear liquid (1.85 g, 66%), b.p. 120–135°C/1.0 mmHg (lit. b.p. 160/0.2 mmHg [7a]). ^1H NMR: 7.3–7.8 (m, 10H), 1.36 (s, 12H) ppm. ^{13}C NMR: 135.16, 133.58, 130.80, 128.00, 82.52, 26.19 ppm. $C_{18}H_{22}SiO_2$ m/e 298 (M^+, 21%), 283 ($M^+ - CH_3$), 199, 181 [$M^+ - HOC(CH_3)_2C(CH_3)_2O$], 139 [$PhSi(OH)_2^+$], 123 [$PhSiH(OH)^+$].

Phenylsilane. After 24 h at reflux reaction of $PhSiH_3$ (1.20 g, 11.0 mmol) and $HOC(CH_3)_2C(CH_3)_2OH$ (1.30 g, 11.0 mmol) resulted in the consumption of starting silane. Removal of the solvent provided a yellow solid, m.p. > 250°C which could not be redissolved. Weak residual SiH (2158 cm^{-1}) and OH (3452 cm^{-1}) stretches in the IR (KBr pellet) were observed.

Reaction of 2,4-pentanediol

Methylphenylsilane. Reaction of $MePhSiH_2$ (1.40 g, 11.0 mmol) and 2,4-pentanediol (1.32 g, 13.0 mmol) for 30 min at reflux provided 2,4,6-trimethyl-2-phenyl-1,3-dioxa-2-silacyclohexane as three diastereomers in a 1 : 1.1 : 1.4 ratio (90%), $PhMeSiH_2$ (3%), pentanediol (3.6%) and HPhMeSiOSiPhMeSiH (1.5%). Kugelrohr distillation provided the product as a clear liquid (2.04 g, 80%; 95% by GC), b.p. 75–80°C/1.0 mmHg [lit. b.p. 90°C/1.2 mmHg [7a,c]]. ^1H NMR: 7.3–7.7 (m, 5H), 4.0–4.6 (m, 2H), 1.5–1.9 (m, 2H), 1.1–1.4 (m, 6H), 0.4–0.6 (m, 3H) ppm. ^{13}C NMR: 137.32, 135.94, 135.72, 134.01, 133.87, 133.63, 130.45, 130.16, 130.12, 128.17, 128.00, 69.95, 69.61, 67.24, 66.68, 65.47, 46.00, 42.94, 24.77, 24.62, 24.46, 23.79, 23.68, 23.62, −0.36, −1.31, −3.39 ppm. $C_{12}H_{18}SiO_2$ m/e 222 (M^+, 5%), 207 ($M^+ - Me$), 163 ($M^+ - C_3H_6OH$), 144 ($M^+ - C_6H_6$), 137 ($PhSiO_2^+$), 129. After 9 months, the sample contained 77% of diastereomers of the 1,3-dioxa-2-silacyclohexane.

A mixture of $PhMeSiH_2$ and 2,4-pentanediol did not react after 3 h at reflux in the absence of the catalyst mixture.

Diphenylsilane. Reaction of Ph_2SiH_2 and 2,4-pentanediol provided 4,6-dimethyl-2,2-diphenyl-1,3-dioxa-2-silacyclohexane [7a,c] as a mixture of diastereomers in 65% (GC) after 24 h at reflux in addition to unreacted starting materials (34%) and siloxane (1%). $C_{17}H_{20}SiO_2$ m/e 284 (M^+, 13%), 269 ($M^+ - CH_3$), 225 ($M^+ - C_3H_7O$), 206 ($M^+ - C_6H_6$), 199, 197, 191 [$M^+ - (CH_3 + C_6H_6)$], 163, 154, 139 [$PhSi(OH)_2^+$], 123 [$Ph(H)SiOH^+$].

Phenylsilane. Reaction of $PhSiH_3$ (1.11 g, 10.0 mmol) and 2,4-pentanediol (1.13 mL, 1.07 g, 10.0 mmol) for 24 h at room temperature provided a slightly soluble oil which did not distill below 200°C/0.01 mmHg. The ^1H NMR spectrum of the oil exhibited the presence of OH resonances exchangeable with D_2O and residual SiH resonances.

Reaction of 2,5-hexanediol

Methylphenylsilane. Reaction of $MePhSiH_2$ and 2,5-hexanediol provided 2,4,7-trimethyl-2-phenyl-1,3-dioxa-2-silacycloheptane [7b] as three diastereomers (64%), siloxane (2%) and dimer (6%) (GC) after 1 h at reflux in addition to unreacted starting materials. Longer heating periods produced additional dimer.

$C_{13}H_{20}SiO_2$ *m/e* 236 (M^+, 0.8%), 221 ($M^+ - CH_3$), 177 ($M^+ - OC_3H_7$), 158 ($M^+ - C_6H_6$), 139 [$PhSi(OH)_2)^+$], 137, 123, 105 ($PhSi^+$).

Diphenylsilane. Reaction of Ph_2SiH_2 with 2,5-hexanediol provided 4,7-dimethyl-2,2-diphenyl-1,3-dioxa-2-silacycloheptane [7b] as a mixture of two diastereomers in 89% (GC) after 24 h at reflux in addition to unreacted starting materials. Kugelrohr distillation provided the product as a colorless solid (2.50 g, 84%), b.p. 105–120°C/0.7 mmHg, m.p. 66–75°C (lit. b.p. 130–140°C/0.1 mmHg, m.p. 55–75°C [7b]). ^1H NMR: 7.2–7.7 (m, 10H), 4.1–4.4 (m, 2H), 1.5–1.9 (m, 4H), 1.1–1.3 (m, 6H) ppm. ^{13}C NMR: 134.89, 134.81, 134.61, 134.17, 130.26, 130.12, 130.07, 128.02, 127.96, 127.83, 71.28, 71.19, 38.93, 35.14, 25.32, 23.74 ppm. $C_{18}H_{22}SiO_2$ *m/e* 298 (M^+, 3%), 220 ($M^+ - C_6H_6$), 199 (Ph_2SiOH^+), 181, 176 ($PhSiOC_4H_7{}^+$), 139 [$PhSi(OH)_2{}^+$].

Reaction of cis-*1,4-but-2-enediol*

Diphenylsilane. Reaction of diphenylsilane (1.79 g, 9.7 mmol) and *cis*-1,4-but-2-enediol (0.94 g, 10 mmol) provided 2,2-diphenyl-1,3-dioxa-2-silacyclohept-4-ene (90%), alcohol (5.5%) and an unidentified product (4.2%) after 3 h at room temperature. Kugelrohr distillation provided the product as a colorless liquid (1.98 g, 76%), b.p. 130–155°C/0.5 mmHg. ^1H NMR: 7.4–7.8 (m, 10H), 5.80 (s, 2H), 4.62 (d, 4H) ppm. ^{13}C NMR: 134.65, 131.69, 130.49, 129.66, 127.80, 62.09 ppm. $C_{16}H_{16}SiO_2$ *m/e* 268 (M^+, 23%), 190 ($M^+ - C_6H_6$), 161, 160.

Reaction of triethanolamine

Phenylsilane. Reaction of $PhSiH_3$ and $N(CH_2CH_2OH)_3$ was conducted for 60 min at reflux whereupon a solid was produced. Additional THF (15 mL) was added and the phenylsilatrane product was collected by vacuum filtration as a colorless solid (2.11 g, 89%), m.p. 203–205°C (lit. m.p. 208–209°C [38]). ^1H NMR: 7.2–7.8 (m, 5H), 3.88 (t, 6H), 2.86 (t, 6H) ppm. ^{13}C NMR: 142.34, 134.24, 127.74, 127.32, 57.84, 51.10 ppm.

When the reaction was carried out in the absence of $Cp_2TiCl_2/{}^nBuLi$, the same results were obtained.

n-Hexylsilane. Reaction of $n\text{-}HexSiH_3$ and $N(CH_2CH_2OH)_3$ was conducted for 24 h at room temperature. Filtration of the reaction mixture followed by removal of the solvent provided a colorless oil which solidified on standing. Recrystallization from ethanol provided product as a colorless solid (0.4 g), m.p. 72–75°C. Kugelrohr distillation of the mother liquor provided further product as a solid (1.45 g, 70% combined), b.p. 140–155°C/0.8 mmHg, m.p. 72–75°C. A sample was further purified for analysis by flash chromatography over silica gel in a 1:1 mixture of ethyl acetate and methylene chloride, m.p. 79–80°C. ^1H NMR: 3.73 (t, 6H), 2.76 (t, 6H), 1.1–1.4 (m, 6H), 0.8–0.9 (m, 4H), 0.3–0.4 (m, 3H) ppm. ^{13}C NMR: 57.96, 51.18, 33.69, 31.83, 25.05, 22.72, 16.46, 14.21 ppm. Anal. Found: C, 56.08; H, 9.32. $C_{12}H_{25}SiNO_3$ calc.: C, 55.56; H, 9.71%.

Reaction of cis,cis-*cyclohexanetriol*

n-Hexylsilane. Reaction of $n\text{-}HexSiH_3$ (0.67 g, 6.0 mmol) and *cis,cis*-cyclohexanetriol (0.78 g, 6.0 mmol) at room temperature for 90 min followed by heating at reflux for 24 h resulted in consumption of the starting silane. Removal of the solvent provided a thick yellow, semi-solid. Purification of the entire sample by flash chromatography over silica gel in methylene chloride provided a yellow solid (0.083 g, 6%) m.p. > 250°C. The IR spectrum showed weak, residual SiH (2160 cm^{-1} and OH (3452 cm^{-1}) stretches (KBr disk).

Phenylsilane. Reaction of $PhSiH_3$ (0.62 g, 6.0 mmol) and *cis,cis*-cyclohexanetriol (0.78 g, 6.0 mmol) was conducted in THF (35 mL) for 24 h at reflux. Removal of the solvent provided a colorless solid, m.p. > 240°C. The IR spectrum showed weak, residual SiH (2158 cm^{-1}) and OH (3452 cm^{-1}) stretches (KBr disk).

Reaction of glycerol

n-Hexylsilane. Reaction of n-$HexSiH_3$ and glycerol was conducted for 24 h at reflux. Analysis (GC) revealed no new peaks in addition to unreacted glycerol. Removal of the solvent provided an insoluble viscous oil. The IR spectrum exhibited weak, residual SiH (2158 cm^{-1}) and OH (3450 cm^{-1}) stretches (KBr disk).

Phenylsilane. Reaction of $PhSiH_3$ and glycerol was conducted for 24 h at reflux. Analysis (GC) revealed no new peaks in addition to unreacted glycerol and removal of the solvent provided an insoluble viscous oil. The IR spectrum exhibited weak, residual SiH (2160 cm^{-1}) and OH (3452 cm^{-1}) stretches (KBr disk).

Reaction of other protic reagents

All of the following reactions were conducted utilizing the general alcoholysis procedure.

N-*Methylaniline.* Reaction of $MePhSiH_2$ (1.13 g, 9.3 mmol) and PhNMeH (2.18 g, 0.020 mol) was conducted for 1 h at reflux. GCMS analysis indicated the presence of several new products (totalling < 10% by weight), none of which corresponded to species resulting from NH/HSi coupling or reduction of the carbonyl. Ethanol (2 mL) was added to the cooled reaction mixture and vigorous bubbling occurred. GCMS analysis showed complete consumption of the starting silane and formation of $PhMeSi(OEt)_2$.

The reaction of Ph_2SiH_2 (1.79 g, 10 mmol) and PhNMeH (2.3 g, 21 mmol) for 1 h gave similar results. Addition of ethanol resulted in complete consumption of Ph_2SiH_2 and formation of $Ph_2Si(OEt)_2$.

Diethylammonium hydrochloride. Reaction of $MePhSiH_2$ and $Et_2NH_2{}^+Cl^-$ was conducted for 24 h at reflux. Analysis (GC) showed that no reaction of the starting silane had occurred.

Benzamide. Addition of $PhCONH_2$ to $MePhSiH_2$ and the catalyst mixture resulted in the formation of a deep purple color. After 24 h at reflux GCMS analysis indicated formation of several new products none of which corresponded to species resulting from N–Si coupling or reduction of the carbonyl. Addition of alcohol resulted in no further reaction.

Thiophenol. Addition of PhSH to $MePhSiH_2$ and the catalyst mixture in toluene (10 mL) resulted in the formation of a deep purple color. After 48 h at reflux no conversion of the starting silane occurred but PhSSPh was formed (20% by GC).

Acetic acid. Addition of CH_3CO_2H to $MePhSiH_2$ and the catalyst mixture resulted in the formation of a bright green color. After 3 h at room temperature analysis showed that no reaction of the silane had taken place.

Reaction with water

Methylphenylsilane. Methylphenylsilane (1.30 g, 11 mmol) and water (0.21 g, 12 mmol) were reacted for 2 h at room temperature. Analysis (GC) showed the presence of the following components (assignments based on GCMS): $PhMeSiH_2$ (1.4%), PhMeSi(OH)H [39] (2.3%), HPhMeSiOSiPhMeH [40] (19%), HPhMeSiOSiPhMe(OH) (17%), HPhMeSiOSiPhMeOSiPhMe(OH) (23%). $(PhMeSiO)_3$ [41] (two isomers, 32%) and two components of longer retention time of 0.5% each. Kugelrohr distillation provided a fraction, b.p. 90–175°C which contained the disiloxanes and trisiloxanes (1.09 g, 73% of original mass). Both the ^1H and ^{13}C NMR spectra of the nondistilled residue (0.31 g, 21%) exhibited only aliphatic methyl and aromatic resonances indicative of higher cyclic siloxanes $(PhMeSiO)_x$ $(x > 3)$.

Reaction with ketones

Reactions were conducted according to the general procedure outlined for the alcoholysis.

Ethylmethylketone. After reaction of n-$HexSiH_3$ and MeCOEt at reflux for 150 min no detectable products were observed. After the reaction mixture had cooled to room temperature, ethanol was added and no evolution of gases occurred. After 24 h no alcoholysis of the $^nHexSiH_3$ was observed.

Similarly, $MePhSiH_2$ and MeCOEt were reacted for 150 min at reflux. Analysis showed the presence of starting silane and several minor products which totalled less that 15% (GC). None of the products corresponded to addition of SiH to the carbonyl group. After cooling to room temperature ethanol was added and after 24 h no further reaction occurred.

In a similar fashion Me_2PhSiH and MeCOEt were reacted and after 90 min at reflux starting silane and several minor products none of which were > 3% were observed. The reaction mixture was cooled to room temperature and EtOH (0.46 g, 1.1 equiv.) was added. GC analysis of the reaction mixture after an additional 24 h at room temperature showed the presence of starting silane (36%) and $Me_2PhSiOEt$ (56%). GCMS analysis of the minor products showed that none were consistent with addition of SiH across the carbonyl group.

Benzophenone. Analysis of the reaction mixture produced from Me_2PhSiH and PhCOPh after 90 min at reflux showed the starting silane and minor products none of which were > 3% by weight and complete consumption of benzophenone. The reaction mixture was cooled to room temperature and ethanol was added without any evolution of gases. After 24 h at room temperature starting silane was still present in addition to the minor components.

Acetylacetone. Analysis of the reaction mixture from $MePhSiH_2$ and $CH_3COCH_2COCH_3$ after 24 h at reflux showed only unreacted starting materials.

Dimedone. Addition of dimedone to $PhMeSiH_2$ in THF (15 mL) resulted in the formation of a purple color. Analysis of the reaction mixture after 3 h at room temperature showed the presence of only the starting materials.

Alcoholysis of $H(PhMeSi)_xH$

The catalyst system was prepared as described for the general alcoholysis and $PhMeSiH_2$ (1.25 g, 10.0 mmol) and norbornylene (0.95 g, 10 mmol) were added. The mixture was heated to reflux for 100 min after which time analysis (GC) showed the following composition: $MePhSiH_2$ (8%), $MePhHSiC_7H_{11}$ (5%), $H(PhMeSi)_2C_7H_{11}$ (8%), HPhMeSiOSiPhMeH (2.5%), $H(PhMeSi)_2H$ (38%), $H(PhMeSi)_3H$ (21%) and $H(PhMeSi)_4H$ (1.4%). The reaction mixture was cooled to room temperature and ethanol (1.01 g, 20.0 mmol) was added whereupon vigorous bubbling was observed. The mixture was heated at reflux for an additional 18 h when analysis (GC) showed the following composition: $PhMeSi(OEt)_2$ (12–13%), $MePhHSiC_7H_{11}$ (5%), $H(PhMeSi)_2C_7H_{11}$ (6.5%), EtOPhMeSiOSiMePh-OEt (2.8%), $H(PhMeSi)_2H$ (18.7%), EtOPhMeSiSiMePhH (19.1%), EtO $(PhMeSi)_2OEt$ (1.6%), $H(PhMeSi)_3H$ (19%), $EtO(PhMeSi)_3H$ (2.9%) and $H(PhMeSi)_4H$ (1.2%).

Variations of general alcoholysis conditions

$Cp_2ZrCl_2/{}^nBuLi$. The reaction of $MePhSiH_2$ (0.71 g, 5.8 mmol) and EtOH (0.59 g, 13 mmol) was conducted in the presence of Cp_2ZrCl_2 (57 mg, 0.20 mmol) and ^nBuLi (0.40 mmol). After 1 h at room temperature GC analysis showed the presence of $PhMeSiH_2$ (80%), PhMeSiH(OEt) (7%) and $PhMeSi(OEt)_2$ (4%).

Similarly, reaction of Ph_2SiH_2 (0.96 g, 5.2 mmol) and EtOH (0.53 g, 12 mmol) in the presence of Cp_2ZrCl_2 (51 mg, 0.17 mmol) and ^nBuLi (0.34 mmol) after 1 h at room temperature showed the presence of Ph_2SiH_2 (74%), $Ph_2SiH(OEt)$ (3.5%), $Ph_2Si(OEt)_2$ (0.7%) and $HPh_2SiOSiH_2H$ (6.8%).

$PhRSiH_2/Cp_2TiCl_2 = 60$. The reaction of $PhMeSiH_2$ and EtOH was conducted in the presence of Cp_2TiCl_2 (41 mg, 0.17 mmol) and ^nBuLi (0.33 mmol). In 10 min at room temperature conversion of silane to $PhMeSi(OEt)_2$ (95% by GC) had occurred.

The reaction of Ph_2SiH_2 and EtOH was similarly conducted. Analysis showed the following percentages of components at 10 min, 1 h and 24 h: Ph_2SiH_2 (25, 12, 2); $Ph_2SiH(OEt)$ (62, 46, 0) and $Ph_2Si(OEt)_2$ (13, 40, 95).

$Cp_2TiCl_2/{}^nBuLi = 1$. The reaction of $PhMeSiH_2$ and EtOH was conducted in the presence of Cp_2TiCl_2 (83 mg, 0.33 mmol) and ^nBuLi (0.33 mmol). A light green-colored solution was formed. Analysis showed the following percentages of components at 1 h, 2 h and 24 h: $PhMeSiH_2$ (13, 10, 0); $PhMeSi(OEt)_2$ (50, 84, 94); HPhMeSiOSiPhMeH (–, 0.8, 0.3); HPhMeSiOSiPhMe(OEt) (–, 1.0, 0.1); $[(EtO)PhMeSi]_2O$ (–, 1.8, 3.7).

$Cp_2TiCl_2/{}^nBuLi = 3$. The reaction of $PhMeSiH_2$ and EtOH was conducted in the presence of Cp_2TiCl_2 (83 mg, 0.33 mmol) and ^nBuLi (0.99 mmol). A dark green-black colored solution was formed. Analysis showed the following percentages of components at 1 h, 2 h and 18 h: PhMeBuSiH + PhMeSiH(OEt) (31, 22, 6.2); $PhMeSi(OEt)_2$ (61, 71, 87); HPhMeSiOSiPhMeH (1.8, 0.9, 0.2); HPhMe-SiOSiPhMe(OEt) (3.5, 2.4, 1.4); $[(EtO)PhMeSi]_2O$ (1.4, 2.2, 3.8).

$Cp_2TiCl_2/LiOEt = 1$. Lithium ethoxide, prepared from EtOH (0.36 mmol) and ^nBuLi (0.33 mmol) in THF (5 mL) was added to Cp_2TiCl_2 (83 mmol) in THF (5 mL) at 0°C whereupon an orange colored solution formed. The cold solution was stirred for 15 min prior to addition of $MePhSiH_2$ followed by EtOH. After 48 h at room temperature, no reaction of the starting silane had occurred.

$Cp_2TiCl_2/LiOEt = 2$. Lithium ethoxide prepared from EtOH (0.72 mmol) and ^nBuLi (0.66 mmol) in THF (5 mL) was added to Cp_2TiCl_2 (83 mg, 0.33 mmol) in THF (5 mL) at 0°C whereupon a bright yellow-colored solution formed. Addition of the $MePhSiH_2$ resulted in the formation of a dark green-colored solution.

Ethanol was then added with an immediate evolution of gas. After 1 h at room temperature, the reaction mixture contained $MePhSi(OEt)_2$ (95%) and HPhMeSiOSiPhMeH (5%).

$Cp_2TiCl_2/NaOEt = 2$. Sodium ethoxide, prepared by addition of sodium metal (33 mg, 1.40 mmol) to EtOH (1.47 mL, 25 mmol) was added to Cp_2TiCl_2 (0.178 g, 0.72 mmol) in THF (10 mL) at 0°C to give a bright yellow-colored solution which was stirred for 15 min. Upon addition of $PhMeSiH_2$ (10 mmol) a dark green-colored solution resulted and gas evolution occurred. After 1 h at room temperature, the reaction mixture contained $MePhSi(OEt)_2$ (98%) and HPhMeSiOSiPhMeH (2%).

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