Organometallics **1989,** *8,* 487–491

Table IV. Effect of Halide Substitution on $\Delta\delta$ (^{1}H NMR) of Neopentyl-, Ethyl-, and [(Trimethylsilyl)methyl]arsenic Compounds

R, X, n	$\Delta\delta$	
	AsR_nX_{3-n}	AsR_nX_{5-n}
Np,[a] Br, 1	2.08	
2	1.23	2.96
3	0.42	2.68
Et,[b] Cl, 1	0.85[c]	
2	0.45[c]	
3	0.00[c]	2.50[d]
Me_3SiCH_2,[a,e] Cl, 1	1.57	
2	1.16	
3	0.59	2.46

[a] Benzene solution. [b] References 28 and 30. [c] CH_2Cl_2 solution. [d] Neat, TMS reference. [e] Reference 29.

sistently downfield that of the methyl resonances for all the neopentyl arsenic compounds. The change in chemical shift, $\Delta\delta$ (^{1}H NMR), was defined as $\delta(CH_2) - \delta(CH_3)$ and was used to describe the environment about the arsenic center. The change in chemical shift between methyl and methylene protons has been used to approximate the environment about arsenic[28] compounds incorporating the ethyl group. Thus, the $\Delta\delta$ for the neopentylarsenic(III) compounds was shown to increase with halide substitution at the arsenic center as expected for the addition of electronegative substituents (Table IV). For comparison, the series AsR_nCl_{3-n} (R = Et, CH_iSiMe_3; n = 1–3)[28,29] exhibit similar increases in $\Delta\delta$ upon halide substitution. The $\Delta\delta$'s for the neopentylarsenic(V) derivatives were greater than those observed for the neopentylarsenic(III) compounds, consistent with the lowering of electron density at the arsenic center. Similarly, increased halide substitution at the As(V) center resulted in the expected increase in $\Delta\delta$. The ^{13}C NMR spectra exhibit similar trends for the secondary carbons, while the quaternary and primary carbons exhibit little change in chemical shift with halide substitution or change in oxidation state.

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Registry No. $AsNp_3$, 99715-59-0; $AsNP_3Br_2$, 118299-85-7; $AsNp_2Br$, 118299-86-8; $AsNpBr_2$, 118299-87-9; $AsNp_2Br_3$, 118299-88-0; NpMgCl, 13132-23-5; $AsCl_3$, 7784-34-1; neopentyl chloride, 753-89-9.

Supplementary Material Available: Tables of anisotropic displacement parameters and hydrogen atom coordinates (5 pages); a listing of observed and calculated structure amplitudes (10 pages). Ordering information is given on any current masthead page.

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Lewis Base Adducts to Diorganosilylenes

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Silylenes **2a–d** were generated photolytically at 77 K in 3-MP matrices doped with ethers, amines, sulfides, phosphines, and alcohols. The initially formed free silylenes react upon annealing of the matrix to give acid–base complexes observed by electronic spectroscopy. For R_2O, R_3N, and R_2S further warming of the matrix leads to the disilenes **3a–d**. Use of *i*-PrOH or *sec*-BuOH as bases led to silylene–alcohol complexes which ultimately yielded products of silylene insertion into the O–H bond.

Introduction

In the rapidly advancing field of silylene chemistry,[1,2] a topic of current interest is the formation of silaylides from the reaction of silylenes with Lewis bases. Acid–base complexes of silylenes were first proposed as intermediates by Seyferth et al. in 1978.[3] Beginning in 1980, Weber published a series of papers presenting evidence for the formation of silylene–donor adducts with a number of oxygen- and sulfur-substituted compounds.[4] The first spectroscopic evidence for complex formation came from an infrared spectroscopic study of the reaction of Si atoms with H_2O in Ar matrices in which a complex of hydroxysilylene (H–Si–OH) and H_2O was observed.[5] In the last

Table I. Absorption Maxima for Ether, Amine, and Sulfide Complexes (λ_{max} (nm))

base	substituents on silicon			
	Mes, Mes	Mes, *t*-Bu	Mes, OAr	Me, Me
3-MP	580	505	395	450
Et_2O	320	348	332	299
THF	328	350	330	280
2-MeTHF	326	350	330	294
2,5-MeTHF	327	350	322	290
Et_3N	350	345	348	287
n-Bu_3N	325	345	346	287
i-Pr_2NEt	329	339	328	288
t-Bu_2S	316	368	350	322
$\overline{\Delta\lambda}(R_2O)$	256	155	65	160
$\overline{\Delta\lambda}(R_3N)$	225	162	55	162

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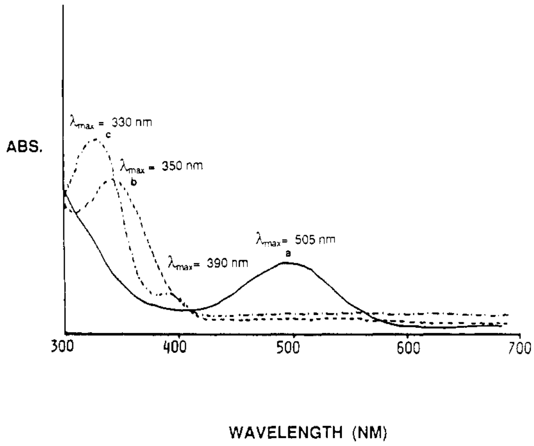
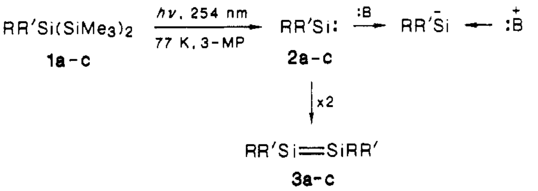


Figure 1. UV spectra of **1b** in 95:5 3-MP/2-MeTHF: a (—), after 15-min irradiation at 77 K; b (- - -), after annealing of the matrix; c (-··-), after further warming of the matrix.

year there have been reports on the possible intermediacy of Si–P ylides in the reaction of hexamethylsilirane with tantalum hydrides[6] and on the spectroscopic observation of silylene–donor complexes with ethers,[7] ketones, thioketones,[8] phosphines, and sulfur and nitrogen heterocycles.[9] Here we report our studies of silylene reactivity with Lewis bases in 3-methylpentane (3-MP) matrices including the first spectroscopic observation of a silylene–alcohol complex.

Results and Discussion

Generation of R_2Si: in 3-MP Matrices. The sterically hindered silylenes investigated in this study, **2a–c**, were generated by UV photolysis at 254 nm of the linear trisilanes $RR'Si(SiMe_3)_2$ (**1a–c**).[2] Dimethylsilylene (**2d**) was generated by similar irradiation of $(Me_2Si)_6$.[10] The silylenes were detected by their characteristic UV absorption bands for the n → p transition,[2] given in Table I.



(1)

a, R = R' = mesityl; b, R = mesityl, R' = t-Bu; c, R = mesityl, R' = 2,6-diisopropylphenoxy

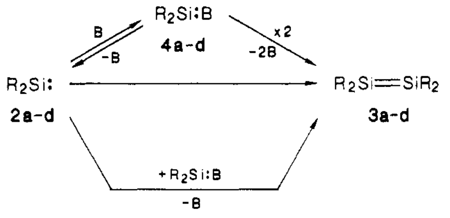
Reaction of R_2Si: with R_2O, R_2S, or R_3N in 3-MP. Silylene precursors **1a–d** were dissolved in a mixture of 95:5 3-MP/B: (B = R_2O, R_2S, R_3N), degassed, and frozen at 77 K. Irradiation of the resulting glass with 254-nm light produced a colored matrix, the electronic spectrum of which corresponded to that of free silylene (**2a–d**). As the matrix was warmed, the band for **2a–d** diminished and a new band grew in at shorter wavelength, which we assign to the silylene–base complex. Upon further warming the new band disappeared and was replaced by bands due to the disilene (**3a–d**).[11] The UV spectra for the reaction of **1b** with 2-MeTHF are shown in Figure 1.

Table II. Percent Yields of Trapping Reactions with EtOH[a]

R, R'	THF	Et_2O	2-MeTHF	Et_3N
Mes, Mes	69	100	77	100
Mes, t-Bu	89	90	74	82

[a] Yields determined by capillary GC.

Scheme I



In order to trap the silylene complex the same reactions were carried out in the presence of a 20-fold molar excess of ethanol. In these cases the free silylene bands were observed which upon warming gave way to the bands assigned to the silylene–base complexes. Upon further warming the bands of the complexes decayed and no new bands were observed. Analysis of the photolysates by GC–MS showed that only one new compound was formed, corresponding to the product of silylene insertion into the OH bond of ethanol. Results of some representative reactions are shown in Table II.[12]

Our results indicate that ethers, amines, and sulfides all behave similarly with silylenes. In every case, in the absence of trapping reagent formation of a silylene–base adduct was observed, followed by dimerization to yield the disilene. Three possible pathways to disilene formation are shown in Scheme I. One possibility is that the complexed silylene is in equilibrium with free silylene, this equilibrium being shifted toward the complex by the huge excess of donor molecules in the matrix. As the matrix warms, any free silylene formed would react with another free silylene to form disilene. The second pathway would involve attack of the electrophilic-free silylene by the silaylide to yield disilene and a free donor molecule. Thirdly, two molecules of the complex could react to yield disilene with loss of two molecules of base. The results of our experiments do not allow us to choose between these three mechanisms although the dimerization of two free silylene molecules seems most unlikely under the conditions employed.

The positions of the absorption maxima (λ_{max}) of these complexes provide an indication of the strength of the acid–base interaction between the silylene and the donor molecule. For each silylene, the position of the absorption maximum of the complex varies little over the series of ethers employed. This trend is also observed for the amines studied. The nature of the acid–base interaction for a series of similar donor substrates appears to be relatively insensitive to the steric and electronic properties of the base.

The electronic environment of the silylene does, however, appear to affect the nature of its interaction with the donor molecule. This is best seen through a comparison of $\overline{\Delta\lambda}(R_2O)$ and $\overline{\Delta\lambda}(R_3N)$, the average change in the ab-

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(11) In each case the disilene absorptions were observed to have the same λ_{max} as those found in pure 3-MP matrices; no evidence of disilene–base adducts was obtained.

(12) Slightly lower yields of trapped product were obtained in reactions with cyclic ethers present because of competing formation of C–O insertion compounds as reported in ref 7.

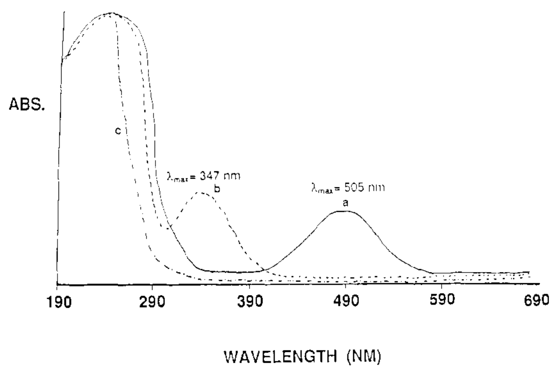


Figure 2. UV spectra of **1b** in 95:5 3-MP/*i*-PrOH: a (—), after 15-min irradiation at 77 K; b (- - -), after annealing of the matrix; c (- · · -), after further warming of the matrix.

Table III. Absorption Maxima for Silylene-Alcohol Complexes

R, R′	3-MP	EtOH	*i*-PrOH	*sec*-BuOH	*t*-BuOH[a]
Mes, Mes	580		322	325	(420)
Mes, *t*-Bu	505		328	333	(330, 309)
Mes, OAr	395		321	320	(390, 480)

[a] Bands due to disilene formation.

sorption maxima upon complexation with ethers and amines, respectively, from that in the free silylene (Table I). The blue shift observed upon complexation is the smallest for **2c**. This is consistent with intramolecular stabilization of **2c** by the lone-pair electrons of the oxy substituent,[13] reducing the electrophilicty of the silylene and weakening the silylene-donor interaction. The $\overline{\Delta\lambda}$ values for **2b** and **2d** are remarkably similar and are smaller than for **2a**. A possible explanation for these results is that conjugation between the silicon p orbital and the mesityl substituent takes place in **2a**, stabilizing the silaylide, leading to a larger blue shift in the observed absorption maximum. Such conjugation in the complex of **2b** may be precluded because of an unfavorable steric interaction between the ortho methyl groups of the mesityl substituent and the *tert*-butyl group.[14]

Reaction of R_2Si: with ROH. Trisilanes **1a–c** were dissolved in a mixture of 95:5 3-MP/ROH, degassed and frozen at 77 K. Irradiation of the matrix at 254 nm yielded free silylene as characterized by the usual UV absorption. The observed changes in the UV spectrum upon annealing of the matrix were dependent upon the steric bulk of the alcohol used. For ROH = ethanol (EtOH), as the matrix was warmed, the silylene band diminished and no new bands were observed. Analysis of the photolysate showed that a quantitative yield of the expected insertion product **4a–c** was obtained. For ROH = 2-propanol (*i*-PrOH) a new band was observed to grow in as the silylene band decreased, as shown in Figure 2 for **1b**. Upon further warming the new band decayed and no new bands were observed. Analysis of the resulting solution revealed a quantitative conversion to the expected insertion product RR′SiH(O-*i*-Pr) (**5a–c**). Similar results were obtained by using 2-butanol (*sec*-BuOH) with the final products being RR′SiH(O-*sec*-Bu) (**6a–c**). In the case of 2-methyl-2-propanol (*t*-BuOH), upon annealing of the matrix the silylene was observed to dimerize to disilene; no complex formation or trapped product was observed. Attempts to observe alcohol complexes using Me_2Si: resulted only in the formation of the expected trapping products.

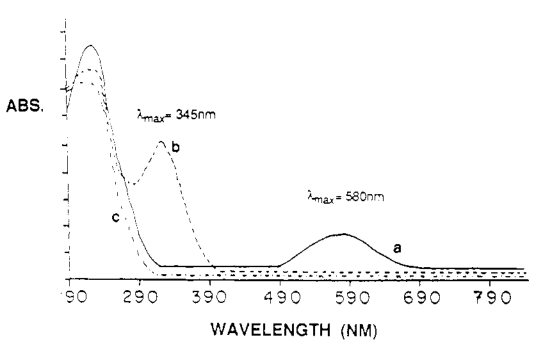
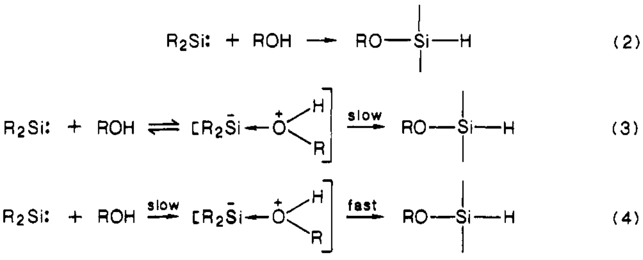


Figure 3. UV spectra of **1a** in 95:5 3-MP/*n*-Bu_3P: a (—), after 15-min irradiation at 254 nm at 77 K; b (- - -), after annealing of the matrix; c (- · · -), after complete melting of the matrix.

Table IV. Absorption Maxima for Silylene-Phosphine Complexes (λ_{max} (nm))

R, R′	3-MP	*n*-Bu_3P	Et_3P	Cy_3P
Mes, Mes	580	345	336	345
Mes, *t*-Bu	505	350	369	385
Mes, OAr	395	358	349	328, 375
Me, Me	450	390		306

Three principal mechanisms for silylene reaction with alcohols have been discussed previously (eq 2–4).[15] Steele



$$R_2Si: + ROH \longrightarrow RO-\overset{|}{\underset{|}{Si}}-H \qquad (2)$$

$$R_2Si: + ROH \rightleftharpoons \left[R_2\overset{-}{Si}\leftarrow\overset{+}{O}\begin{smallmatrix}H\\R\end{smallmatrix}\right] \xrightarrow{slow} RO-\overset{|}{\underset{|}{Si}}-H \qquad (3)$$

$$R_2Si: + ROH \xrightarrow{slow} \left[R_2\overset{-}{Si}\leftarrow\overset{+}{O}\begin{smallmatrix}H\\R\end{smallmatrix}\right] \xrightarrow{fast} RO-\overset{|}{\underset{|}{Si}}-H \qquad (4)$$

and Weber, based upon the results of deuterium isotope effect studies, were able to eliminate eq 4 as a possible mechanism; however the results did not afford a clear choice between eq 2 and 3. Although theoretical calculations have predicted the intermediate ylide to have a significant lifetime,[16] no direct observation of this intermediate has been previously reported. Our results lend strong support to the proposal of eq 3 as the mechanism of the O–H insertion reaction for the silylenes studied.

Reaction of R_2Si: with R_3P. Anaerobic stock solutions of silylene precursors **1a–d** in 3-MP were prepared. These solutions were added to a cuvette via syringe, and 5% (vol) of R_3P was added via syringe for R = Et or *n*-Bu. For R = cyclohexyl the phosphine was added in a dry box previous to the addition of the stock solution. The samples were then degassed and frozen at 77 K. After irradiation of the resulting glasses at 254 nm only the band for free silylenes was present, as shown in Figure 3 for **1a**. Warming of the glass resulted in the decay of the silylene band with concomitant growth of a new band, assigned to the silaylide, at shorter wavelength. The positions of the absorption maxima of a number of silylene–phosphine complexes are given in Table IV. Upon further warming the band assigned to the complex disappeared and no new bands were seen. This differs from the other nonhydroxylic bases used, which gave disilene as the final

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(13) Calculations on substituted silylenes by Apeloig et al. predict a blue shift of the n → p transition of silylenes by π-donor substituents. Apeloig, Y.; Karni, M. *J. Chem. Soc., Chem. Commun.* **1985**, *1048*.

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product upon warming. For phosphines only new, uncharacterized products are obtained. Attempts to determine the structure of these new compounds are in progress.

Experimental Section

General Procedures. All manipulations were carried out under dry nitrogen. The 3-methylpentane (Aldrich) used for matrix studies was deolefinated,[17] dried over $MgSO_4$, and distilled from $LiAlH_4$ prior to use. Toluene (NaK), hexane (Na/benzophenone), and THF (Na/benzophenone) used in syntheses were all distilled prior to use. All ethers, alcohols, and amines were distilled under nitrogen before use; ethers were distilled from Na/K alloy, alcohols from the corresponding Na alkoxide, and amines from CaH_2. Di-*tert*-butyl sulfide, triethylphosphine, tri-*n*-butylphosphine (Aldrich), and tricyclohexylphosphine (Alfa) were used without further purification. The trisilanes were prepared by literature methods[11] as was dodecamethylcyclohexasilane.[18] All ^{1}H NMR spectra were recorded on a Bruker WP-270 NMR spectrometer. ^{1}H chemical shifts were referenced to the resiudal protons of C_6D_6. Silicon-29 and ^{13}C NMR spectra were obtained on a Bruker AM-360 spectrometer. Silicon-29 chemical shifts were referenced to external tetramethylsilane. ^{13}C shifts were referenced to the C_6D_6 peaks. GC analysis was carried out on a Hewlett-Packard 5890A instrument equipped with a 0.53 mm × 15 m open tubular column coated with 5% phenylmethylsilicone and a 3390A integrating chart recorder. Preparative GC was done on a GOW-MAC Model 550P instrument equipped with a $^1/_4$ in. × 6 ft column packed with 10% SE-30 on Chromosorb W/AW/DMCS. High-resolution mass spectra were recorded on a Kratos MS-80 instrument. IR spectra were taken on a Mattson Instrument Polaris FT-IR. Values are reported in cm^{-1} referenced to polystyrene. UV spectra were recorded on a Perkin-Elmer Lambda Array Model 3840 spectrophotometer interfaced with a Motorola series 7000 computer. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Photolysis at Liquid-Nitrogen Temperature in 3-MP. In a typical experiment 1 mg of the silylene precursor was added to an oven-dried 1 mm × 10 mm Suprasil cuvette. Next, 0.95 mL of 3-MP and 0.05 mL of the appropriate dopant was added via syringe. After the sample was degassed by three freeze-pump-thaw cycles, the cuvette was placed into a quartz windowed Dewar filled with liquid nitrogen. The glass formed was then irradiated for 15–30 min in a Rayonet RPR-208 photoreactor equipped with low-pressure mercury lamps. After the UV spectrum of the matrix was taken, the liquid nitrogen was removed and the UV spectrum was monitored as the glass softened.

Analytical Scale Trapping Experiments. For yield determinations the average response factors relative to $C_{16}H_{34}$ for ethoxysilanes **4a**,**b** and trisilanes **1a**,**b** were determined from ten determinations. In a typical experiment 1 mL of a standard solution of trisilane and $C_{16}H_{34}$ in 3-MP was placed in a Suprasil cuvette. To this were added 50 μL of the Lewis base and a 20-fold molar excess (vs trisilane) of EtOH. The sample was then degassed by three freeze-pump-thaw cycles and irradiated for 15 min at 254 nm. After the initial photolysis the UV spectrum of the sample was recorded. In each case the UV spectrum was identical with that obtained in the absence of EtOH. Following 7–10 freeze-irradiate-thaw cycles (F-I-T), the yield of insertion product was then determined by GC analysis of the photolysate. GC-MS analysis was also conducted to insure that the product obtained was identical with the authentic insertion product.

Preparative Scale Trapping Experiments. In order to more fully characterize the trapping products, large-scale matrix experiments were conducted for each silylene-Lewis base couple studied. In a typical experiment 100 mg of **1a**,**b** was added to a quartz tube and dissolved in 5 mL of 3-MP. Next, 250 μL of the donor substrate and a 20-fold molar excess of EtOH was added. The sample was degassed and irradiated for 15–30 min. Analysis of the glasses by UV spectroscopy showed that they were identical with those obtained in the absence of alcohol. The sample was taken through 10–15 F-I-T cycles after which the products were isolated by preparative GC. All trapping products were characterized by comparison of their GC retention times, GC-MS, and ^{1}H NMR to those of authentic samples.

Synthesis of $Mes_2Si(OEt)H$ (4a). $Mes_2SiH(Cl)$ was synthesized by the method of Weidenbruch.[19] To a solution of 1.85 g (6.1 mmol) of $Mes_2SiH(Cl)$ and 50 mL of hexane was added 0.85 mL of Et_3N (4 equiv). Next, 0.33 mL of EtOH (1 equiv) was added via syringe. The reaction mixture was stirred at room temperature for 12 h after which the white amine hydrochloride salts were filtered off and washed with 4 × 100 mL portions of hexane. The solvent was removed at reduced pressure, and the resulting colorless oil was distilled to yield $Mes_2SiH(OEt)$ (70–75 °C at 0.1 Torr): ^{1}H NMR ($CDCl_3$) δ 6.79 (s, 4 H), 5.81 (s, 1 H), 3.76 (q, 2 H), 2.37 (s, 12 H), 2.25 (s, 6 H), 1.23 (t, 3 H); MS, calcd 312.1904, found 312.1900 for M$^+$; IR (neat) ν_{Si-H} 2150 cm^{-1}.

Synthesis of Mes(*t*-Bu)SiH(Cl). $Mes(H)SiCl_2$ was synthesized by the method of Weidenbruch.[19] A solution of 9.0 g of $Mes(H)SiCl_2$ (0.04 mol) in 100 mL of hexane was cooled to 0 °C. To this was slowly added 24.1 mL of 1.7 M *t*-BuLi (Aldrich) via syringe. After addition was complete, the solution was allowed to warm to room temperature and was stirred for 5 h. The reaction mixture was filtered, the solvent was removed in vacuo, and the product was isolated by Kugelrohr distillation (70 °C at 0.1 Torr) to yield 7.0 g (71%) of a colorless oil: ^{1}H NMR (C_6D_6) δ 6.66 (s, 2 H), 5.49 (s, 1 H); 2.42 (s, 6 H), 2.03 (s, 3 H), 1.03 (s, 9 H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 145.0, 140.5, 129.3, 125.2, 26.8, 24.5, 21.2, 21.1; ^{29}Si NMR ($CDCl_3$) δ 5.85 ($^1J_{Si-H}$ = 222.4 Hz, $^3J_{Si-H}$ = 7.4 Hz); IR (neat) ν_{Si-H} 2090 cm^{-1}; MS, M$^+$ (^{35}Cl) calcd 240.1096, found 240.1100, M$^+$ (^{37}Cl) calcd 242.1066, found 242.1063.

Synthesis of Mes(OAr)SiH(Cl). The lithium salt of 2,6-diisopropylphenol was prepared by the method of Schrock,[20] using 4.1 mL of the phenol (Aldrich). The salt was filtered, washed with hexane, and redissolved in dry THF. This solution was transferred via cannula to an addition funnel which was attached to a flask containing a solution of 5.0 g of $Mes(H)SiCl_2$ (23 mmol) and 15 mL of hexane. The hexane solution was cooled to 0 °C and the phenoxide was added dropwise over a 1-h period. The reaction mixture was then allowed to warm to room temperature and was stirred for 10 h. Following filtration and concentration in vacuo the product was isolated by Kugelrohr distillation (100 °C at 0.02 Torr) as a waxy, white solid (mp 62–66 °C): isolated yield 43%; ^{1}H NMR (C_6D_6) δ 7.15 (m, 3 H), 6.62 (s, 2 H), 6.09 (s, 1 H), 3.52 (sep, 2 H), 2.53 (s, 6 H), 1.99 (s, 3 H), 1.19, 1.17, 1.15, 1.13 (dd, 12 H); ^{13}C NMR (C_6D_6) δ 149.4, 144.4, 141.7, 139.3, 129.5, 124.3, 124.1, 27.8, 23.8, 22.7, 21.1; ^{29}Si NMR (C_6D_6) δ −17.8, ($^1J_{Si-H}$ = 267.6 Hz). MS, M$^+$ (^{35}Cl) calcd 360.1669, found, 360.1663, M$^+$ (^{37}Cl) calcd 362.1639, found 362.1607.

Synthesis of $Mes_2SiH(O$-*i*-Pr), Mes(*t*-Bu)SiH(O-*i*-Pr), and Mes(OAr)SiH(O-*i*-Pr). All of these compounds were made in a similar manner. In a typical experiment 3.0 g of the chlorosilane was dissolved in 50 mL of dry hexane. To this solution was added first 4 equiv of Et_3N and then 1 equiv of 2-propanol. After 12 h at hexane reflux the reaction was cooled, filtered, and concentrated in vacuo. Reactions gave quantitative yields by GC. The residue was distilled under reduced pressure to yield pure alkoxysilanes.

Mes(OAr)SiH(O-*i*-Pr) (5c): ^{1}H NMR (C_6D_6) δ 7.08–6.97 (m, 3 H), 6.83 (s, 2 H), 5.43 (s, 1 H), 4.15 (sep, 1 H, N J = 5.93 Hz), 3.35 (sep, 2 H, J = 6.81 Hz), 2.54 (s, 6 H), 2.28 (s, 3 H), 1.20, 1.17 (d, 6 H), J = 5.93 Hz), 1.14, 1.11 (d, 12 H, J = 6.82 Hz); ^{13}C{^{1}H} NMR (C_6D_6) δ 149.7, 144.6, 140.5, 139.4, 129.2, 124.0, 123.3, 67.2, 27.4, 25.5, 25.4, 23.8, 23.6, 23.0, 21.1; ^{29}Si NMR (C_6D_6) δ −32.9 ($^1J_{Si-H}$ = 238.9 Hz); IR (neat) ν_{Si-H} 2180 cm^{-1}. Anal. Calcd for $C_{24}H_{35}SiO_2$: C, 74.94; H, 9.44. Found: C, 74.74; H, 9.21.

$Mes_2SiH(O$-*i*-Pr) (5a): ^{1}H NMR (C_6D_6) δ 6.71 (s, 4 H), 6.16 (s, 1 H), 3.99 (sep, 1 H, J = 6.03 Hz), 2.51 (s, 12 H), 2.10 (s, 6 H), 1.12 (d, 6 H, J = 6.03 Hz); ^{13}C NMR (C_6D_6) δ 144.68, 139.51, 130.33, 129.43, 67.68, 25.24, 22.98, 21.14; ^{29}Si NMR (c_6D_6) δ −22.27, −25.17 ($^1J_{Si-H}$ = 206.5 Hz); IR (neat) ν_{Si-H} 2140 cm^{-1}; MS, M$^+$ calcd

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326.2058, found 326.2066. Anal. Calcd for $C_{21}H_{30}SiO$: C, 77.25; H, 9.27. Found: C, 76.89; H, 9.28.

Data for Mes(*t*-Bu)SiH(O-*i*-Pr) (**5b**) have been reported elsewhere.[7]

Mes(*t*-Bu)SiH(O-*sec*-Bu), Mes(OAr)SiH(O-*sec*-Bu), and Mes$_2$SiH(O-*sec*-Bu). All of these compounds were made by a similar method. In a typical experiment 3.0 g of the chlorosilane was dissolved in 50 mL of dry hexane. To this was added first 4 equiv of Et_3N and then 1 equiv of *sec*-BuOH (Aldrich). The reaction was heated at hexane reflux for 17 h after which the reaction mixture was cooled, filtered, and concentrated in vacuo. Analysis of the residue by GC showed that quantitative conversion to the alkoxysilane had occurred. The products were then purified by distillation under reduced pressure.

Mes(*t*-Bu)SiH(O-*sec*-Bu) (6b). An inseparable mixture of two diastereomers was obtained (1:1 by ^{1}H NMR): δ (C_6D_6) 6.75 (s, 4 H), 5.29 (s, 1 H), 5.27 (s, 1 H), 3.76 (m, 2 H), 2.54 (br s, 12 H), 2.11 (s, 6 H), 1.63–1.32 (m, 4 H), 1.15 (d, 3 H), 1.10 (s, 9 H), 1.09 (s, 9 H), 1.03 (d, 3 H); 0.90 (t, 3 H), 0.77 (t, 3 H); ^{29}Si NMR (C_6D_6) δ −1.17, −3.21 ($^1J_{\text{Si-H}}$ = 202.7 Hz), −1.78, −3.72 ($^1J_{\text{Si-H}}$ = 192.76 Hz); IR (neat) $\nu_{\text{Si-H}}$ 2130 cm^{-1}; MS, M$^+$ calcd 278.2058, found 278.2070 (1.55%), M$^+$ − 57 calcd 221.1356, found 221.1359 (74.3%). Anal. Calcd for $C_{17}H_{30}SiO$: C, 73.38; H, 10.79. Found: C, 73.07; H, 10.82.

Mes$_2$SiH(O-*sec*-Bu) (6a): ^{1}H NMR (C_6D_6) δ 6.72 (s, 4 H), 6.18 (s, 1 H), 3.81 (sextet, 1 H), 2.53 (s, 12 H), 2.09 (s, 6 H), 1.64–1.29 (m, 2 H), 1.10 (d, 3 H), 0.83 (5, 3 H); ^{13}C NMR (C_6D_6) δ 144.62, 139.40, 130.44, 128.16, 77.78, 32.23, 23.07, 22.33, 21.19, 9.96; ^{29}Si NMR (C_6D_6) δ −22.16, −24.27 ($^1J_{\text{Si-H}}$ = 207.52 Hz); IR (neat) $\nu_{\text{Si-H}}$ 2140 cm^{-1}; MS, M$^+$ calcd 340.2214, found 340.2219 (7.9%). Anal. Calcd for $C_{22}H_{32}SiO$: C, 77.59; H, 9.47. Found: C, 77.30; H, 9.12.

Mes(OAr)SiH(O-*sec*-Bu) (6c): ^{1}H NMR (C_6D_6) δ 7.11 (m, 3 H), 6.72 (s, 2 H), 5.71 (s, 1 H), 3.89 (sep, 2 H), 3.66 (m, 1 H), 2.65 (s, 3 H), 2.64 (s, 3 H), 2.06 (s, 3 H), 1.48 (m, 1 H), 1.35 (m, 1 H), 1.24, 1.23 (d, 6 H), 1.22, 1.21 (d, 6 H), 1.14 (d, 3 H), 0.80 (t, 3 H); ^{29}Si NMR (C_6D_6) δ −31.05, −33.50 ($^1J_{\text{Si-H}}$ = 243.4 Hz), −31.79, −34.24 ($^1J_{\text{Si-H}}$ = 243.4 Hz); IR (neat) $\nu_{\text{Si-H}}$ 2160 cm^{-1}; MS, M$^+$ − H calcd 397.2553, found 397.2578, M$^+$ − 120 calcd 278.1695, found 278.1710. Anal. Calcd for $C_{25}H_{38}SiO_2$: C, 75.33; H, 9.61. Found: C, 74.86; H, 9.63.

Registry No. **1a**, 79184-72-8; **1b**, 88526-27-6; **1c**, 111060-23-2; **2a**, 79184-71-7; **2b**, 89486-28-2; **2c**, 111060-25-4; **2d**, 6376-86-9; **3a**, 80785-72-4; **3b**, 116971-70-1; **3c**, 116971-69-8; **4a**, 51525-38-3; **4b**, 111060-31-2; **4c**, 111060-32-3; **5a**, 51525-40-7; **5b**, 117560-02-8; **5c**, 117581-34-7; **6a**, 51525-43-0; **6b** (diastereomer 1), 117560-03-9; **6b** (diastereomer 2), 117581-35-8; **6c**, 117560-04-0; THF, 109-99-9; 2-MeTHF, 96-47-9; 2,5-Me$_2$THF, 1003-38-9; *t*-Bu$_2$S, 107-47-1; Et_3P, 554-70-1; *n*-Bu$_3$P, 998-40-3; Cy$_3$P, 2622-14-2; (Me$_2$Si)$_6$, 4098-30-0; Mes$_2$SiH(Cl), 50490-74-9; Mes(*t*-Bu)SiH(Cl), 111060-34-5; Mes(H)SiCl$_2$, 117560-00-6; Mes(OAr)SiH(Cl), 117560-01-7; EtOH, 64-17-5; *i*-PrOH, 67-63-0; *sec*-BuOH, 78-92-2; *t*-BuOH, 75-65-0; Et_2O, 60-29-7; Et_3N, 121-44-8; *n*-Bu$_3$N, 102-82-9; *i*-Pr$_2$NEt, 7087-68-5; Mes$_2$Si(Et$_2$O), 117581-36-9; Mes$_2$Si(THF), 112400-75-6; Mes$_2$Si(2-MeTHF), 111060-30-1; Mes$_2$Si(2,5-Me$_2$THF), 117581-37-0; Mes$_2$Si(Et$_3$N), 117581-38-1; Mes$_2$Si(*n*-Bu$_3$N), 117605-83-1; Mes$_2$Si(*i*-Pr$_2$NEt), 117624-51-8; Mes$_2$Si(*t*-Bu$_2$S), 117605-84-2; Mes(*t*-Bu)Si(Et$_2$O), 117581-39-2; Mes(*t*-Bu)Si(THF), 117581-40-5; Mes(*t*-Bu)Si(2-MeTHF), 111060-27-6; Mes(*t*-Bu)Si(2,5-Me$_2$THF), 117605-78-4; Mes(*t*-Bu)Si(Et$_3$N), 117581-41-6; Mes(*t*-Bu)Si(*n*-Bu$_3$N), 117581-42-7; Mes(*t*-Bu)Si(*i*-Pr$_2$NEt), 117605-85-3; Mes(*t*-Bu)Si(*t*-Bu$_2$S), 117581-43-8; Mes(OAr)Si(Et$_2$O), 117605-86-4; Mes(OAr)Si(THF), 117581-44-9; Mes(OAr)Si(2-MeTHF), 111060-28-7; Mes(OAr)Si(2,5-Me$_2$THF), 117581-45-0; Mes(OAr)Si(Et$_3$N), 117581-46-1; Mes(OAr)Si(*n*-Bu$_3$N), 117581-47-2; Mes(OAr)Si(*i*-Pr$_2$NEt), 117605-87-5; Mes(OAr)Si(*t*-Bu$_2$S), 117581-48-3; Me$_2$Si(Et$_2$O), 113686-62-7; Me$_2$Si(THF), 113686-61-6; Me$_2$Si(2-MeTHF), 117605-88-6; Me$_2$Si(2,5-Me$_2$THF), 117581-49-4; Me$_2$Si(Et$_3$N), 113686-63-8; Me$_2$Si(*n*-Bu$_3$N), 117581-50-7; Me$_2$Si(*i*-Pr$_2$NEt), 117605-89-7; Me$_2$Si(*t*-Bu$_2$S), 117581-51-8; Mes$_2$Si(*n*-Bu$_3$P), 112400-74-5; Mes(*t*-Bu)Si(*n*-Bu$_3$P), 117581-52-9; Mes(OAr)Si(*n*-Bu$_3$P), 117581-53-0; Me$_2$Si(*n*-Bu$_3$P), 117581-54-1; Mes$_2$Si(Et$_3$P), 117581-55-2; Mes(*t*-Bu)Si(Et$_3$P), 117581-56-3; Mes(OAr)Si(Et$_3$P), 117581-57-4; Mes$_2$Si(Cy$_3$P), 117581-58-5; Mes(*t*-Bu)Si(Cy$_3$P), 117581-59-6; Mes(OAr)Si(Cy$_3$P), 117581-60-9; Me$_2$Si(Cy$_3$P), 117581-61-0; 2,6-diisopropylphenol, lithium salt, 72727-49-2.