due to allyl η^3 to η^1 isomerization.

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Supplementary Material Available: Tables of thermal parameters and hydrogen atom coordinates (Tables III and IV) (2 pages); listings of observed and calculated structure factors (Tables V and VI) (11 pages). Ordering information is given on any current masthead page.

Catalytic Dehydrogenative Coupling of Secondary Silanes with Cp_2MCl_2/nBuLi

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The catalytic dehydrogenative coupling of secondary silanes has been achieved with the combination of Cp_2ZrCl_2 and 2 equiv of nBuLi in toluene at 90 °C. The products produced from $PhMeSiH_2$ contain disilane through pentasilanes after 2 days, and longer time periods produce oligomeric mixtures up to the octamer. Disilane through tetrasilane have been isolated as distillable, air-stable liquids and are produced as mixtures of stereoisomers. The distribution of oligomers has been determined under various conditions of temperature, time, solvent, and Si/Zr and Zr/Li ratios as well as with a combination of Cp_2ZrCl_2 with Grignard reagents. Disilane is formed from Ph_2SiH_2 even at 110 °C, although silafluorene condenses rapidly even at room temperature to a mixture of oligomers. The combination of Cp_2TiCl_2/nBuLi with $PhMeSiH_2$ provides oligomers from disilane through hexasilane, whereas Cp_2HfCl_2 produces disilane and trisilane. A possible mechanism for the coupling reaction is presented.

Introduction

The chemistry of short silicon chains is an undeveloped area in group XIV chemistry. The general method utilized to form silicon–silicon bonds is a Wurtz-type coupling reaction of halosilanes (usually chlorosilanes).[1] The products from this reaction are cyclopolysilanes or linear polysilanes depending on the reaction conditions employed. Although halogen-terminated oligomers are probable intermediates in the condensation reaction, these are rarely reported.[2] Thus, oligomers are usually prepared either by multistep routes that require the formation of a cyclopolysilane followed by ring opening or by some variant of a Wurtz-type coupling reaction of a dihalosilane in the presence of a monohalosilane as a chain terminator.[1c]

Harrod and co-workers have shown that it is possible to generate silicon oligomers from primary silanes in the presence of metallocene complexes. The best catalysts for the dehydrogenative coupling are those derived from Cp_2MR_2 (M = Ti, Zr; R = Me).[4] The condensation of $PhSiH_3$ produced the linear oligomers $H(PhSiH)_xH$ with an average degree of polymerization of 10 from Cp_2TiMe_2[5] and 20 from Cp_2ZrMe_2.[6] However, $BuSiH_3$ is converted to both linear and cyclic products with Dp values ranging between 2 and 8 with Cp_2ZrMe_2.[7]

Table I. Diastereomers of $H(PhMeSi)_xH$

	no. of stereoisomers		no. of Me resonances		no. of resonances
x	meso forms	d,l pairs	^1H	^{13}C[a]	^{29}Si[b]
2	1	1	4[c]	2	2
3	2	1	11[d]	7	7
4	2	4	24[e]	16	16

[a] Decoupled. [b] If observable. [c] Two doublets. [d] Four doublets and three singlets. A statistical mixture would contain 10 resonances of intensity 1 and the remaining resonance of intensity 2. [e] Eight doublets (four of intensity 1 and four of intensity 2) and eight singlets (four of intensity 1 and four of intensity 2).

The conversion of secondary silanes to oligomers has been much less successful. Dimerization of $PhMeSiH_2$ occurs with catalytic quantities of Cp_2ZrMe_2[8] and Cp_2TiMe_2[9] but only in the presence of an olefin in the latter case. Under rigorous conditions (110 °C) Cp_2TiPh_2 converts $PhMeSiH_2$ to disilanes and trisilanes and addition of an olefin improves conversion of the starting material and favors the trisilane product.[10]

There are disadvantages in the use of Cp_2MR_2 catalysts, which include the required synthesis from a metallocene dichloride and the fact that Cp_2ZrMe_2 undergos slow decomposition at room temperature. A more direct approach to catalysis by the metallocene complexes of the titanium triad would be generation in situ of an active species directly from the metallocene dichloride. Described in this report is the combination of commercially available Cp_2MCl_2 and nBuLi, which produces a catalyst capable of generating oligomers with more than three silicon atoms from secondary silanes, in contrast to the results reported for Cp_2MR_2.

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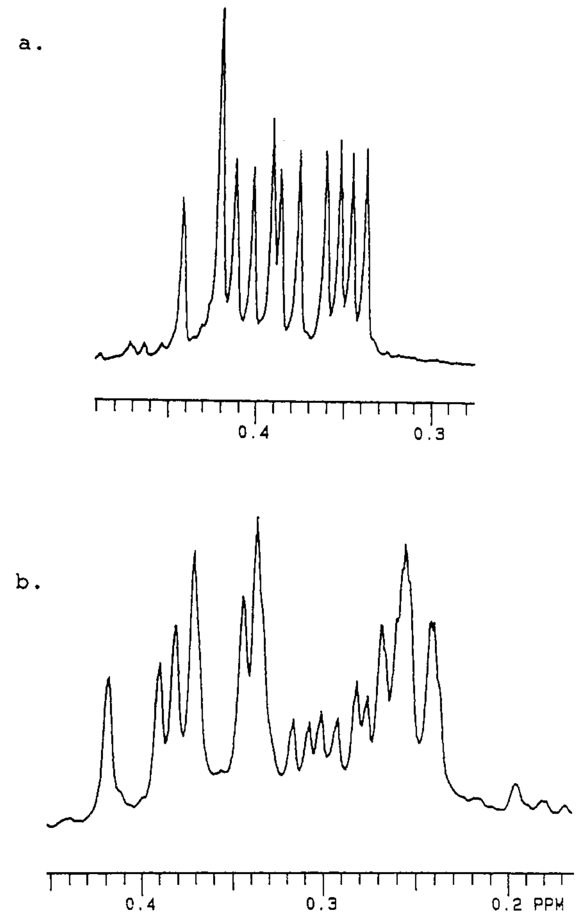
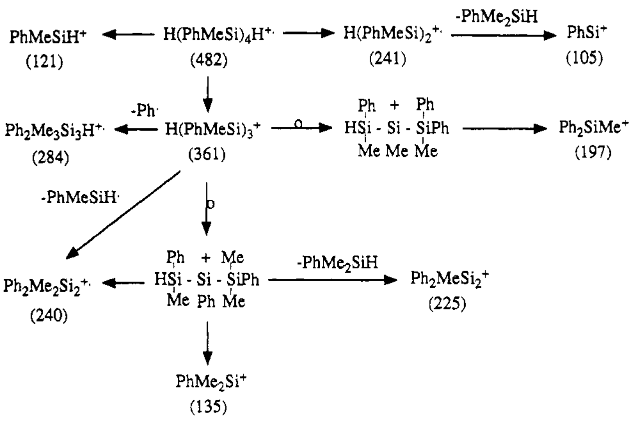


Figure 1. ^1H NMR spectra of the SiMe region collected on a Varian XL-300 spectrometer in $CDCl_3$, with internal TMS as standard: (a) $H(PhMeSi)_3H$; (b) $H(PhMeSi)_4H$.

Results

Characterization of Oligomers from $PhMeSiH_2$. To establish the conditions and the factors that influence the reaction of secondary silanes, $PhMeSiH_2$ was selected as a test system. In previous studies of the condensation of $PhMeSiH_2$[10,11] the disilane and trisilane formed were identified only by gas chromatography. The disilane $H(PhMeSi)_2H$ has been prepared by Mg coupling of PhMeHSiCl, but spectroscopic data were not provided.[12] Reactions of $H(PhMeSi)_3H$ have been described, but not the origin of the trisilane.[13] Formation of $H(PhMeSi)_4H$ as a 3% byproduct has been reported in the condensation of $PhMeSiCl_2$ with lithium. It was speculated that the linear tetrasilane was formed from ring opening of the cyclotetrasilane.[14]

Scheme I. **Fragmentation Scheme of $H(PhMeSi)_4H^{•+}$**



The ^1H NMR spectra for the SiMe region of the trisilane and the tetrasilane produced from $PhMeSiH_2$ are shown in Figure 1, and additional spectroscopic data are provided in the Experimental Section. The complex spectra arise from the fact that the silicon centers are chirotopic.[15] The ^1H and ^{13}C NMR spectral data for the trisilane are consistent with the formation of a statistical mixture of stereoisomers, as summarized in Table I. The eight resonances between 0.337 and 0.402 ppm consist of four pairs of doublets (J = 4.65 Hz). The three resonances corresponding to the internal SiMe's are furthest downfield (0.412–0.442 ppm). The trisilane generated from (m-$CH_3C_6H_4$)$MeSiH_2$ also exhibits the same pattern for the SiMe region. The tetrasilane spectrum is more complicated, with methyl resonances ranging from 0.241 to 0.417 ppm, and does not appear to correspond to a statistical mixture of stereoisomers. In addition, only half of the predicted ^{13}C resonances for the methyl groups in the tetrasilane were observed. It is possible that some stereospecificity occurs in the production of this chain length.[17] The ^{29}Si spectra show two regions separated by about 10–12 ppm. The region furthest upfield is assigned to the internal silicon centers by analogy to other polysilanes.[18]

The ^1H NMR spectrum of the previously described $H(PhMeSi)_4H$ exhibited only one singlet for the internal Me groups and one doublet for the terminal Me groups.[14] Clearly, only one of the stereoisomers was isolated in that case. The tetrasilane was also converted quantitatively to $H(PhMeSiO)_3(PhMeSi)H$ when exposed to air.[14] The tetrasilanes produced from dehydrogenative coupling are stable under normal laboratory conditions and produce only small quantities of $H(PhMeSiO)(PhMeSi)_3H$ (or its isomer) after 8 months under normal laboratory conditions.

Mass spectral data (70 eV) for selected isomers of the cyclic oligomers $(PhMeSi)_6$ and $(PhMeSi)_5$ have been published.[19] The cyclic compounds exhibit intense parent ions with major fragment ions of the type $Ph_xMe_{3-x}Si^+$ (x = 1, 2), which result from rearrangements of the P^+ ion. Fragments between P^+ and $Ph_xMe_{3-x}Si^+$ are weak (<10%). In contrast, the linear oligomers of $H(PhMeSi)_xH$ are characterized by weak molecular ions and intense ions of intermediate m/e values in addition to those of $Ph_xMe_{3-x}Si^+$. Silicon–silicon scission of the $H(PhMeSi)_xH^{•+}$ (P^+) ion produces cations with charge retention on either fragment. Rearrangement and subsequent silicon–silicon scission accounts for the intense fragments of intermediate mass. Scheme I illustrates a plausible pathway for the tetrasilane. The intensity of the parent ion, $H(PhMeSi)_xH^{•+}$ decreases with increasing chain length

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Table II. Product Distribution from Condensation of $PhMeSiH_2$

run no.	Si/Zr/Li[a]	temp, °C	solvent[b]	% condensn	% distribn[c] SiBu[d]	Si_2	Si_3	Si_4
1	30/1/2	20	Tol	14	3	9	0.3	
2		50	Tol	24	3	18	1.2	
3		70	Tol	43	8	22	11	0.4
4		90	Tol	45	6	20	16	1.8
5		110	Xyl	59	10	22	19	4[e]
6	30/1/1	90	Tol	28	1.4	23	2.2	
7	30/1/3	90	Tol	48	6	21	18	2.1
8	30/1/2	50	THF	23	3.2	18	0.8	
9	15/1/2	90	Tol	52	15	18	14	1.5
10	60/1/2	90	Tol	45	3.6	21	17	1.9
11	30/1/2[f]	90	Tol	38	5	18	12	1.1
12	30/1/2[g]	90	Tol	0				

[a] Initial molar ratios of $PhMeSiH_2/Cp_2ZrCl_2$/nBuLi except for run 12; 2 mL of solvent/1.0 g of silane. [b] Solvent key: Tol, toluene; Xyl, *m*-xylene; THF, tetrahydrofuran. [c] Products are given as area percentages determined by gas chromatography (see Experimental Section). [d] SiBu represents PhMeBuSiH (Bu = *n*-C_4H_9). [e] In addition Si_5 (0.4%). [f] 4 mL of solvent/1.0 of g silane. [g] $PhMeSiH_2/Cp^*{}_2ZrCl_2$/nBuLi; Cp* = C_5Me_5.

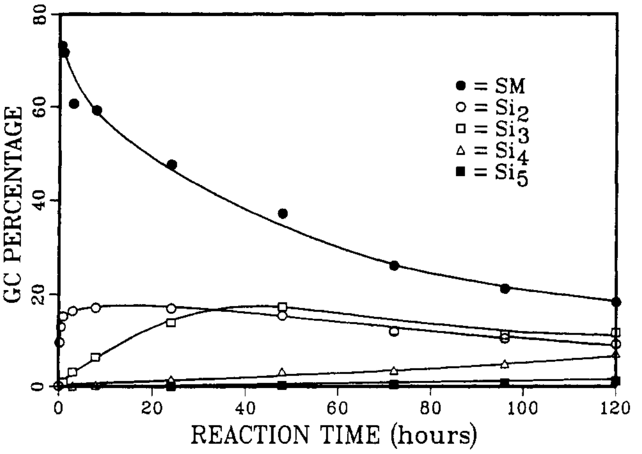

Figure 2. Relative percentages of $PhMeSiH_2$ and oligomers determined by gas chromatography as a function of reaction time. Conditions: 90 °C, Si/Zr = 30, Zr/Li = 0.5, 1.0 g of $PhMeSiH_2$, 2 mL of toluene.

and is not observed for oligomers with $x > 5$. The absence of intense ions in higher mass ranges for longer oligomers supports the absence of cyclic Si_5 and Si_6 species. All of the linear oligomers exhibit an intense SiH absorption in the infrared region near 2100 cm^{-1}.

Product Distribution. Several reaction variables were altered to determine the factors that influence not only the extent of conversion of the silane starting material but also the distribution of silicon in the product oligomers. Figure 2 shows the growth of oligomers formed from $PhMeSiH_2$ at 90 °C as determined by gas chromatography. The plot demonstrates the rapid growth of disilane, which maximizes at about 3 h. The conversion of disilane to trisilane (and higher oligomers) results in the decrease in concentration of the disilane. The higher oligomers are formed more slowly, and the trisilane maximizes after 36 h. These results are similar to those reported for the step-growth reaction of $PhSiH_3$.[20] The distribution of oligomers as a function of reaction temperature, solvent, and Si/Zr and Zr/Bu ratios have been determined, and typical results for a 24-h run are shown in Table II. Increasing the temperature increases the percent conversion and promotes the formation of higher oligomers (runs 1–5). At the same temperature the reaction results in THF and toluene (runs 4 and 8) are similar.

Table III. Organometallic Additives in the Cp_2ZrCl_2/RM Coupling of $PhMeSiH_2$

RM[a]	% conversn	% distribn PhMeRSiH[b]	x in H(PhMeSi)$_x$H 2	3	4
BuLi	50	3.2	23	18	3
iPrMgCl	52	8.0	21	19	1.7
EtMgBr	43	3.4	23	12.3	1.2
BuMgCl	34	5.3	22	6	0.3

[a] Ratio of Si/Zr/RM = 30/1/2. Reactions run in toluene at 90 °C for 24 h. [b] R derived from the given organometallic reagent.

Two molar equivalents of nBuLi is required per Cp_2ZrCl_2. Increasing the ratio of BuLi/Cp_2ZrCl_2 has little effect on the percent conversion of $PhMeSiH_2$, but decreasing the ratio to 1/1 reduces the conversion of starting material to a little more than half that observed for the stoichiometric ratio (runs 4, 6, and 7). Changing the ratio of Si/Zr (runs 4, 9, and 10) has a marginal effect on the production of oligomers, since the sum of unreacted starting material and PhMeBuSiH changes only by +2% in runs 9 and 10 relative to run 4. Decreasing the concentration of reactants slows the reaction (runs 4 and 11). The combination $Cp^*{}_2ZrCl_2$/nBuLi does not promote the condensation of hydrosilanes (run 12). Other organometallic reagents may be used with Cp_2ZrCl_2 for the condensation of $PhMeSiH_2$, and results are summarized in Table III.

Discussion

In contrast to Cp_2ZrMe_2, the combination of Cp_2ZrCl_2/nBuLi is an effective catalyst for the formation of short-chain oligomers from secondary silanes. The condensation of $PhMeSiH_2$ requires higher temperatures since disilane and only traces of trisilane are observed when reactions are performed at room temperature. After 48 h at room temperature the percent of disilane in product mixtures remains constant (about 11–12%) and slow formation of the disiloxane HPhMeSiOSiMePhH is observed. The formation of disiloxane may result from reaction with water, since samples of $PhMeSiH_2$ that have not been dried over molecular sieves rapidly produce HPhMeSiOSiPhMeH.[21] To produce reasonable quantities of oligomers with chain lengths of four silicon units or higher requires temperatures of about 90 °C for a period longer

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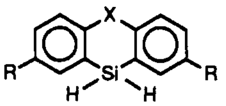
Table IV. Condensation of Secondary Silanes

silane	amt, g	conditions,[a] *b*/temp, °C/time, h	recovered products, g (%)[c]	% distribn Si	Si$_2$	Si$_3$	Si$_4$	Si$_{>4}$	method[d]
PhMeSiH$_2$	1.15	30/52/48	0.57 (49)	6[e]	54	19[f,g]			A
	2.26	32/90/48	1.68 (74)	3[e]	24	42	17	14	A
	2.33	30/90/96	1.81 (78)	14		39	23[f]	24	A
ArMeSiH$_2$[h]	1.10	29/88/48	0.91 (83)	4	12	48	37[f]		A
Ph$_2$SiH$_2$	0.81	22/90/72	0.74 (91)	18[i]	82	0			B
Ia[j]	0.35	15/23/2	0.36 (103)[k]	8[l]	71[m]	11			C
Ib	0.40	15/90/47	0.40 (100)	0[n]	62	28			C
Ic	0.51	15/90/47	0.51 (100)	100					C

[a] Reactions conducted in toluene (2 mL). [b] Silicon/zirconium ratio. [c] Weight percent based on weight of starting silane. [d] Key for method of determination (unless specified otherwise, data given are weight percent): A, separation by distillation; B, combination of separation of disilane and integration of SiH region in ^{1}H NMR spectrum of residue; C, integration of SiH region in ^{1}H NMR spectrum.[11] [e] PhMeBuSiH. [f] Contains detectable amounts of next highest oligomer (^{1}H NMR). [g] Remainder not identified. [h] Ar = m-$CH_3C_6H_5$–. [i] Starting material plus Ph$_2$BuSiH. [j] Silafluorene with tBu substituents in 3,7-positions. [k] Contains a small quantity of catalyst residue (^{1}H NMR). [l] Combination of starting material and nBu-substituted silafluorene. [m] Tentative assignment; mole percent based on integration of tBu resonances. [n] Unidentified product present, <20 mg.

than 3 days, as illustrated in Table IV.

The condensation reaction of secondary silanes beyond the disilane stage with Cp$_2$ZrCl$_2$/nBuLi is sensitive to the steric bulk of the substituents, as can be seen from the results for Ph$_2$SiH$_2$ as compared to those for PhMeSiH$_2$ (Table IV). Disilane and only traces of trisilane are produced from Ph$_2$SiH$_2$ even at temperatures up to 110 °C. The steric bulk of diarylsilanes can be reduced by tying the two phenyl groups in the position ortho to the silicon center to form the tricyclic series I. Since unsubstituted silafluorenes produce highly insoluble oligomer products,[22] the condensation of 3,7-di-*tert*-butylsilafluorene Ia was investigated.



Ia, X = –, R = *tert*-butyl
b, X = CH$_2$, R = H
c, X = CH$_2$CH$_2$, R = H

Silafluorenes react rapidly in the presence of Cp$_2$ZrCl$_2$/nBuLi even at room temperature. After 2 h, more than 90% conversion of Ia occurred and the major species in the product mixture was assigned to the disilane. However, additional oligomers with similar solubility properties are also present and the disilane could not be cleanly separated from the byproducts. The condensation of silaanthracene Ib occurs more slowly with the in situ catalyst than with Cp$_2$ZrMe$_2$. After 10 h at 90 °C the ratio of trisilane to disilane is >7 (99% conversion) with Cp$_2$ZrMe$_2$ whereas this ratio is 0.45 after 47 h with Cp$_2$ZrCl$_2$/nBuLi, at which point there is no detectable starting material. The silepin Ic does not react with either zirconium catalyst system at 90 °C.

Although more rigorous conditions are required for the condensation of secondary silanes, production of chains longer than three units can be produced from a zirconocene-based catalyst. It is also clear that an effective catalyst can be formed by addition of an active organometallic reagent to commercially available zirconocene dichloride. Since secondary silanes are not condensed in the presence of Cp$_2$TiMe$_2$ in the absence of olefin,[9] the approach of a combined catalyst system was extended to Cp$_2$TiCl$_2$/BuLi as well as to Cp$_2$HfCl$_2$/BuLi. The results are summarized in Table V. In contrast to the reactions that have been described for Cp$_2$TiMe$_2$, there is no induction period in the formation of oligomers from the Cp$_2$TiCl$_2$/nBuLi combined catalyst. Although the zirconium system seems to be more effective for chain extension than the titanocene system, chain growth does occur slowly and after 4 days oligomers up to the hexamer are observed in the presence of Cp$_2$TiCl$_2$/BuLi. After longer time periods disilane is still the major product with Cp$_2$HfCl$_2$/BuLi, and this particular system may be useful when disilane is the desired product.

Table V. Comparison of Cp$_2$MCl$_2$/BuLi (M = Ti, Zr, Hf) in the Condensation of PhMeSiH$_2$[a]

M	% conversn	% product distribn Si(Bu)	Si$_2$	Si$_3$	Si$_4$
Ti	39	0.2	23	10	1
Zr	50	3	23	18	3
Hf	44	2.3	34	6	

[a] Conditions: Si/M = 30; M/Bu = 1/2; 2 mL of toluene/g of silane; 90 °C; 24 h.

Mechanism. Three major questions must be addressed in the effort to develop a mechanism for the oligomerization of hydrosilanes: (1) the nature of the catalytic species generated from Cp$_2$ZrCl$_2$/nBuLi, (2) the intermediate leading to the coupling reaction, and (3) whether the Cp$_2$ZrCl$_2$/nBuLi system and Cp$_2$ZrMe$_2$ produce the same catalytic species.

The nature of the species formed from Cp$_2$ZrBu$_2$ at room temperature is not entirely clear, although the reactivity appears to suggest that it is a source of "zirconocene".[23] Buchwald and co-workers have shown that when solutions of Cp$_2$ZrBu$_2$ are warmed to room temperature in the presence of phosphine, the complex Cp$_2$Zr(butene)L (L = PMe$_3$) is formed in high yield.[24] This observation suggests the formation of Cp$_2$Zr(butene) from Cp$_2$ZrBu$_2$ and is the starting point for a possible catalytic cycle as outlined in Scheme II. The formation of PhMeBuSiH occurs rapidly even at 0 °C, and this product could be explained through the equivalent of hydrosilation of the coordinated butene leading to a species that reacts similarly to zirconocene. If "zirconocene" 3 is formed, it may mimic a carbene with insertion into an Si–H bond to provide the hydridosilylzirconium(IV) species 4. Isolation of PMe$_3$ adducts of hydrido silyl complexes was recently reported.[25] A σ-bond metathesis reaction through the intermediate 5, similar to

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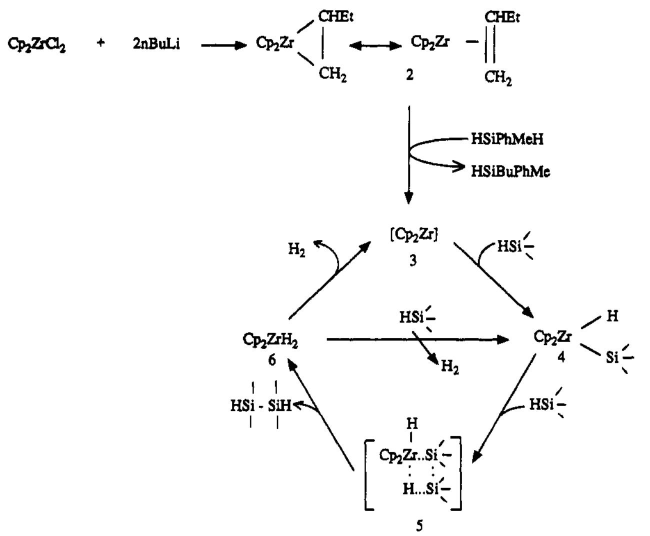
Scheme II. Proposed Mechanism for Dehydrogenative Coupling of Secondary Silanes



that proposed by Tilley,[20] followed by elimination of the silicon oligomer would then produce the hydride 6. Reductive elimination of H_2 or a second σ-bond metathesis reaction to return to 4 could then occur. Since tertiary silanes do not condense with catalytic quantities of Cp_2ZrCl_2/nBuLi, it is probable that the monosilane reacts preferentially with 3 and thus the growth of the chain occurs stepwise as suggested by the data summarized in Table II. Formation of disilane involves reaction of a monosilane with 4. Chain growth involves reaction of a disilane (or other oligomer) with 4. This latter process appears to be where steric problems may occur in the condensation of secondary silanes, as indicated in the chain lengths produced in the reaction of Ph_2SiH_2 as compared to that of $PhMeSiH_2$.

Although phosphine adducts of zirconocene have been reported,[26] free zirconocene would be expected to be highly reactive. In an earlier study of the reaction of Cp_2ZrBu_2 a two-step decomposition was proposed, with the first step involving elimination of butene to form $Cp_2ZrBu(H)$ (7).[23a] A σ-bond metathesis reaction of 7 with $PhMeSiH_2$ would also provide PhMeBuSiH as well as 6, which would enter into the cycle outlined in Scheme II.

Dimers related to 4 have been reported in the condensation of $PhSiH_3$ with Cp_2ZrMe_2,[8] but a species similar to 4 has been proposed by Harrod in the condensation of primary silanes.[4,27] An α-elimination of dihydrogen to a silylene complex of zirconocene, which then adds H_3SiR to the multiple bond, is the process favored for oligomer formation. Since such a sequence cannot occur beyond the disilane stage for a secondary silane, some other mechanism such as the one proposed in Scheme II must occur. The differences in rate and product distribution from Ib with Cp_2ZrMe_2 compared to that with Cp_2ZrCl_2/nBuLi suggest that different species or intermediates are present in the two catalyst systems. Additional studies on the condensation of primary silanes with the combined catalyst system are in progress in an attempt to address this issue.

The focus of the discussion has been on catalysis by the zirconium system. There is no requirement that the same mechanism occurs in the reactions of secondary silanes with Cp_2TiCl_2/nBuLi. Indeed, almost no Bu group transfer to $PhMeSiH_2$ occurs (Table V). Since Cp_2TiMe_2 is reported to couple secondary silanes to the disilane only in the presence of olefins, it is unlikely that the same catalytic species is responsible for both the preformed catalyst and that generated from Cp_2TiCl_2/nBuLi. Although Cp_2HfMe_2 does not promote the condensation of primary silanes even at 90 °C,[4] the combination of Cp_2HfCl_2/nBuLi may react in a sequence similar to the depicted in Scheme II.

Summary. The combination of Cp_2MCl_2/RM' (M = Ti, Zr, Hf; M' = Li, Mg) has been shown to be an effective catalyst for the condensation of secondary silanes. Chains three silicon atoms and longer as mixtures of diastereomers are produced from the zirconium and titanium systems, but not with hafnium. The condensation requires temperatures higher than those reported for reaction of primary silanes, and this observation is most likely related to the process involved in chain growth. A likely intermediate for the transfer of a silicon unit and subsequent chain growth is $Cp_2Zr(H)(SiHRR')$, produced from zirconocene dichloride with the organometallic additive possibly through "zirconocene".

Experimental Section

General Data. All reactions unless otherwise noted were carried out under an atmosphere of dry nitrogen or argon by using a combination of standard Schlenk techniques and a Vacuum Atmospheres HE-43 drybox. Solvents were dried by using standard techniques, and all glassware was dried in an oven at 110–120 °C prior to use. Commercial compounds Cp_2TiCl_2, Cp_2ZrCl, Cp_2HfCl_2, nBuLi, EtMgBr, BuMgBr, and iPrMgCl were used as supplied, and the following compounds were prepared by literature methods: $PhMeSiH_2$, m-$CH_3C_6H_4CH_3SiH_2$,[28] Ia,[22] Ib,[29] and Ic.[22]

^1H, ^{13}C, and ^{29}Si NMR spectra were recorded on a Varian XL-300 multinuclear spectrophotometer. Unless specified otherwise, data were collected in $CDCl_3$ with TMS as an internal standard. Mass spectral data were collected 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-m (HP-1) capillary column. Data for the nondistilled residues were obtained through the direct-insertion probe. Chromatographic separations were obtained on a 15 m × 0.32 mm i.d. 1.0-μm film DB-5 column (J&W Scientific) with a flow rate of 6 mL/min (helium) and a temperature program from 50 to 320 °C at 20 °C/min and recorded on a HP3394A integrator. The injection temperature was 200 °C, and that of the detector was 320 °C. Liquid chromatography was performed on a Perkin-Elmer Series 4 liquid chromatograph equipped with a C-18 reverse-phase analytical column and a Perkin-Elmer LC-95 UV/visible spectrophotometric detector set at a wavelength of 270 nm. Analyses were recorded on a Perkin-Elmer LCI-100 laboratory computing integrator. Infrared spectra were determined on a Perkin-Elmer Model 1600 FT-IR spectrophotometer as thin films.

Condensation of $PhMeSiH_2$ with Catalytic Cp_2ZrCl_2/nBuLi. In a typical reaction, a slurry of Cp_2ZrCl_2 (184 mg, 0.630 mmol) in dry toluene (2.0 mL) that had been cooled in an ice bath was degassed for 10 min before addition of nBuLi (0.80 mL, 1.6 M). When the Cp_2ZrCl_2 dissolved and a reddish yellow solution had formed, $PhMeSiH_2$ (2.33 g, 19.1 mmol) was injected and the reaction flask placed in a 90 °C oil bath. A dark red-brown color developed. After 96 h, hexane was added, resulting in discharge of the brown color and formation of a bright yellow solid, which was removed by filtration through Celite. Removal of the volatiles from the filtrate provided a pale yellow, viscous oil. Kugelrohr distillation provided a fraction boiling below 125 °C (0.1 mmHg) (174 mg), which contained disilane (>80%) and PhMeBuSiH. The oil that distilled from 140 to 240 °C (0.08 mmHg) (1.49 g) was

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redistilled to give disilane (105 mg), trisilane (761 mg, >90%), and tetrasilane contaminated with pentasilane (458 mg).

PhMeBuSiH. Mass spectrum (*m*/*e* (relative intensities)): 178 (P, 4.6), 121 (PhMeSiH, 100), 107 ($PhSiH_2$, 18), 105 (PhSi, 14), 100 (BuMeSi, 34). ^{1}H NMR (δ (J, Hz); $CDCl_3$ as a mixture with $Ph_2Me_2Si_2H_2$): 0.32 (d, SiMe, $^3J_{CHSiH} = 3.7$), 0.8–0.9 (br m, $SiCH_2$ + CH_3), 1.3–1.4 (br m, CH_2), 4.35 (m, SiH, $^2J_{CHSiH} = 3.7$), 7.2–7.6 (m, arom). ^{13}C NMR (δ; $CDCl_3$): −5.64 (SiMe), 13.11, 13.76, 26.18, 26.56 ($SiCH_2CH_2CH_2CH_3$), 127.82, 129.13, 143.29, 134.68 (arom).

H(PhMeSi)$_2$H. Bp: 100–115 °C (0.08 mmHg) (lit.[12] bp 105 °C (0.6 mmHg)). IR: ν_{SiH} 2108 cm^{-1}. Mass spectrum (*m*/*e* (relative intensities)): 242 (P, 6), 197 (Ph_2MeSi, 100), 121 (PhMeSiH, 52), 105 (PhSi, 41). ^{1}H NMR (δ (J, Hz); $CDCl_3$): 0.43 (2 d, SiMe, $^3J_{CHSiH} = 4.68$), 4.41 (2 overlapping q, SiH), 7.2–7.6 (m, arom). ^{13}C NMR (δ; $CDCl_3$): −7.65, −7.44 (SiMe), 127.94, 128.98, 134.73, 134.85 (arom). ^{29}Si NMR (δ; $CDCl_3$) −36.80, −36.37.

H(PhMeSi)$_3$H. Bp: 140–160 °C (0.08 mmHg). IR: ν_{SiH} 2104 cm^{-1}. Mass spectrum (*m*/*e* (relative intensities)): 362 (P, 6.5), 241 ($Ph_2Me_2Si_2H$, 88), 240 ($Ph_2Me_2Si_2$, 78), 225 (Ph_2MeSi_2, 38), 197 (90, Ph_2MeSi), 164 ($PhMe_2Si_2H$, 100), 163 ($PhMe_2Si_2$, 163), 135 ($PhMe_2Si$, 55), 121 (PhMeSiH, 31), 105 (PhSi, 105). ^{1}H NMR (δ (J, Hz); $CDCl_3$): 0.34–0.44 (4 d + 3 s, SiMe, $^3J_{CHSiH} = 4.65$ (av); see Figure 1a), 4.37–4.47 (m, SiH, 1.9), 7.2–7.4 (m, arom, 16.7). ^{13}C NMR (δ; $CDCl_3$): −7.95, −7.85, −7.72, −7.44, −7.28, −7.25, −7.17 (SiMe), 127.84, 128.40, 128.87, 128.98, 134.81, 134.87, 134.90, 135.09, 135.53 (arom). ^{29}Si NMR (δ; $CDCl_3$): −46.19, −46.00, −45.84, −34.29, −34.15 (Me).

H(PhMeSi)$_4$H. Bp: 200–230 °C (0.08 mmHg). IR: ν_{SiH} 2099 cm^{-1}. Mass spectrum (*m*/*e* (relative intensities)): 482 (P, 5), 361 ($Ph_3Me_3Si_3H$, 37), 284 ($Ph_2Me_3Si_3H$, 80), 283 ($Ph_2Me_3Si_3$, 24), 281 ($Ph_2Me_3Si_3 - 2H$), 241 ($Ph_2Me_2Si_2H$, 51), 240 ($Ph_2Me_2Si_2$, 66), 239 ($Ph_2Me_2Si_2 - H$, 56), 238 ($Ph_2Me_2Si_2 - 2H$, 24), 225 (Ph_2MeSi_2, 66), 224 ($Ph_2MeSi_2 - H$, 36), 206 ($PhMe_3Si_3$, 26), 197 (Ph_2MeSi, 79), 135 ($PhMe_2Si$, 87), 121 (PhMeSiH, 47), 105 (PhSi, 100). ^{1}H NMR (δ (J, Hz); $CDCl_3$): 0.24–0.42 (overlapping d + s (see Figure 1b), SiMe, 9.5), 4.38–4.43 (q, SiH, 1.7, $^3J_{CHSiH} = 4.54$), 7.1–7.3 (m, arom, 22.7). ^{13}C NMR (δ; $CDCl_3$): −7.45, −7.39, −7.36, −7.23, −7.21, −7.11, −6.99, −6.93 (Me), 127.69, 127.40, 127.77, 127.81, 128.14, 128.28, 128.63, 128.68, 128.73, 128.77, 134.80, 134.87, 134.98, 135.02, 135.82 (arom). ^{29}Si NMR (δ; $CDCl_3$ + $Cr(acac)_3$): −43.54, −43.30, −34.00, −33.85.

Attempts to isolate the pentasilane by distillation were not successful. However, the mass spectrum of the reaction residue (direct inlet) demonstrated the presence of both pentasilane and hexasilane. Mass spectrum for H(PhMeSi)$_5$H (*m*/*e* (relative intensities)): 602 (P, 1.4), 481 (9), 361 (18), 281 (12), 241 (11), 240 (12), 239 (13), 225 (18), 197 (49), 195 (22), 135 (48), 105 (51), 78 (100). Mass spectrum for H(PhMeSi)$_6$H (*m*/*e* (relative intensities)): 722 (P, <1%).

An HPLC trace of the combined, nondistilled portion (481 mg) was consistent with the presence of tetrasilane through octasilane. Retention times relative to that of disilane at a flow rate of 2 mL/min of acetonitrile (oligomer (time, min)): trisilane (0.40), tetrasilane (1.0), pentasilane (2.03), hexasilane (3.65), heptasilane (6.23), octasilane (10.64).

The isolated samples were used to verify the conditions for H(PhMeSi)$_x$H (x = 1–5) separation relative to the starting silane on a 15 m × 0.32 mm i.d. 1.0-μm film DB-5 column with a flow rate of 6 mL/min (helium), a temperature program from 50 to 320 °C at 20 °C/min (injection temperature was set at 200 °C and detector at 320 °C): PhMeSi(Bu)H (3.1 min), [$C_{16}H_{34}$, 5.4], disilane (5.7 min), trisilane (9.0 min), tetrasilane (11.3 min), pentasilane (13.3 min). Reaction conditions were varied by changing solvents, temperature, reactant/catalyst ratios and concentration, and organometallic additive. Aliquots were removed periodically, filtered through a small plug of Celite, and analyzed by gas chromatography. The results after 24 h are reported as integrated raw areas of peaks in Tables II, III, and V and Figure 2.

A GC analysis of samples of isolated disilane through tetrasilane that had been stored 8 months under ambient conditions showed the formation of small amounts of siloxanes H(PhMeSiO)(PhMeSi)$_x$H. The percentage of siloxanes produced from the original oligomer was x = 1 (4%), x = 2 (2.6%), and x = 3 (1.8%).

Condensation of $PhMeSiH_2$ with Cp_2TiCl_2/nBuLi. A slurry of Cp_2TiCl_2 (56 mg, 0.22 mmol) in dry toluene (2.0 mL) was reacted with nBuLi (0.36 mL, 1.25 M in hexane) at 0 °C before addition of $PhMeSiH_2$ (0.97 g, 8.0 mmol) to give a yellow-brown solution. After the mixture was heated to 90 °C, the solution turned blue-green. An aliquot removed after 24 h was analyzed, and the results are summarized in Table V. After 96 h hexane was added and the slurry filtered through Celite. Removal of the volatiles provided a viscous oil (0.70 g), which contained disilane through hexasilane as determined by a combination of GC and HPLC.

Condensation of $PhMeSiH_2$ with Catalytic Cp_2HfCl_2/nBuLi. In a similar fashion Cp_2HfCl_2 (90 mg, 0.24 mmol), nBuLi (0.38 mL, 1.25 M in hexane), and $PhMeSiH_2$ (0.95 g, 7.8 mmol) were reacted at 90 °C. Analysis of an aliquot removed after 24 h is summarized in Table V. Workup after 96 h provided a viscous oil (0.69 g) that contained disilane (68%), trisilane (25%), and tetrasilane (1.4%) by GC.

Oligomers from (m-$CH_3C_6H_4$)$MeSiH_2$. In a similar fashion (m-tolyl)$MeSiH_2$ (1.096 g, 8.06 mmol) was reacted with Cp_2ZrCl_2 (81 mg, 0.28 mmol) and nBuLi (0.35 mL, 1.6 M) for 46 h at 88 °C. After addition of hexane and removal of insoluble material the volatiles were removed and the residue was distilled to give a viscous oil. Kugelrohr distillation provided a fraction boiling below 120 °C (0.11 mmHg) (144 mg), which contained disilane and ArMeBuSiH. The oil that distilled from 130 to 200 °C (0.1 mmHg) (435 mg) contained primarily trisilane. ^{1}H NMR (δ (J, Hz); $CDCl_3$): 0.31–0.42 (4 d + 3 s, SiMe, 7, $^3J_{CHSiH} = 4.8$ Hz), 2.2–2.3 (4 s, CMe, 9), 4.37–4.53 (2 overlapping q, SiH, 2), 7.05–7.25 (m, arom, 12). ^{13}C NMR (δ; $CDCl_3$, in part): −7.89, −7.77, −7.64, −7.40, −7.25, −7.19, −7.0 (SiMe), 21.40 (arom Me). The residue was a thick yellow-brown residue (336 mg).

Reaction of Ia in the Presence of Cp_2ZrCl_2/nBuLi. The reaction of Ia (348 mg, 1.18 mmol) in the presence of Cp_2ZrCl_2 (23 mg, 0.78 mmol) and nBuLi (0.10 mL, 1.6 M in hexane) was conducted at room temperature in toluene (2 mL). After 2 h the solvent was removed, the residue dissolved in warm hexane/toluene, and this solution filtered through Celite. The ^{1}H NMR spectrum showed the presence of traces of Ia and one major and one minor product. ^{1}H NMR (δ; major product; in part): 1.082, 1.067 (2 s, tBu), 5.430 (s, SiH). ^{1}H NMR (δ; minor product): 1.031, 1.011 (2 s, tBu), 1.142, 1.128 (2 s, tBu), 5.029 (s, SiH). The ratio between the two sets of tBu singlets in the minor product remained constant at 2:1 in seven independent runs. The major product was tentatively assigned to disilane and the minor product to the trisilane. Integration of the tBu resonances showed a ratio of disilane to trisilane of 4.8. In a second run conducted under similar conditions but for 17 h, the ratio between disilane and trisilane was 1.5 and additional resonances appeared in the tBu region of the ^{1}H NMR spectrum. When reactions were conducted at higher temperatures or for longer periods of time, the tBu region became too complex to analyze.

Separation of oligomers from starting material and impurities, decomposition products, and catalyst residues was readily achieved by radial chromatography with 1% EtOAc in hexane, but no conditions were found that would separate disilane from trisilane. Attempts to recrystallize the oligomers that had been separated by chromatography were not successful from hydrocarbon solvents, and decomposition occurred in protic solvents. The oligomers were unstable under gas chromatographic conditions, and only odd mass fragment ions were observed at the highest mass regions in mass spectra obtained at 70 and 20 eV or under CI conditions.

Reaction of Ib in the Presence of Cp_2ZrCl_2/nBuLi. The reaction of Ib (401 mg, 2.0 mmol) with Cp_2ZrCl_2 (40 mg, 0.14 mmol) and nBuLi (0.17 mL, 1.6 M in hexane) was conducted in the same manner as that for $PhMeSiH_2$ at 90 °C, except that Ib was dissolved in degassed toluene (1 mL) prior to addition to the catalyst slurry in toluene (1 mL). After 47 h the solvent was removed, the resultant solid dissolved in hexane/toluene (1:1), and this solution filtered through a short silica gel column (100 mesh) to remove the catalyst. The disilane and trisilane in the product mixture were determined by ^{1}H NMR spectroscopy, as previously described.[21] An additional component (<20 mg) characterized by a singlet in the ^{1}H NMR spectrum at 4.63 ppm was formed, which was separated from the disilane and trisilane by radial chromatography. The component contained neither SiH nor SiO as determined by infrared spectroscopy and was not identified.

Reaction of Ic in the Presence of Cp$_2$ZrCl$_2$/nBuLi. The reaction of Ic (511 mg, 2.4 mmol) with Cp$_2$ZrCl$_2$ (47 mg, 0.16 mmol) and nBuLi (0.20 mL, 1.6 M in hexane) at 90 °C for 47 h was conducted as described for Ib. A ^{1}H NMR spectrum of the reaction residue after workup showed only the presence of Ic.

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Intramolecular Penta- and Hexacoordinate Tetraorganotin Compounds Containing the 8-(Dimethylamino)-1-naphthyl Ligand

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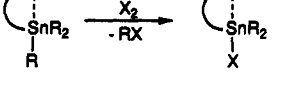
A series of novel tetraorganotin compounds, Sn[(8-Me$_2$N)C$_{10}$H$_6$-1]RR′R″, containing the 8-(dimethylamino)-1-naphthyl group, has been synthesized and characterized. For one of these compounds (R = R′ = R″ = Ph) the molecular structure in the solid state has been determined by X-ray diffraction methods: C$_{30}$H$_{27}$NSn, monoclinic, space group $P2_1/a$, and a = 24.8365 (7) Å, b = 12.3785 (4) Å, c = 17.1997 (6) Å, β = 109.102 (3)°, and Z = 8; final R = 0.031 for 7920 observed reflections. The tin center has a distorted trigonal-bipyramidal coordination geometry with the nitrogen atom (Sn–N = 2.884 (3) Å) and one of the phenyl groups at approximately axial positions. The structure of this tetraorganotin compound was compared with that of [8-(dimethylamino)-1-naphthyl]methylphenyltin bromide, for which the structure in the solid state has been determined by X-ray diffraction methods: C$_{19}$H$_{20}$BrNSn, monoclinic, space group $P2_1/a$, with a = 16.356 (3) Å, b = 13.922 (4) Å, c = 8.082 (2) Å, β = 102.91 (2); and Z = 4; final R = 0.042 for 2804 observed reflections. The tin center has a trigonal-bipyramidal coordination geometry in which the organic ligands occupy the equatorial sites, while the more electronegative Br and N ligands are in the axial positions. ^{1}H, ^{13}C, and ^{119}Sn NMR spectra of the tetraorganotin compounds show that, most likely as a result of the fixed orientation of the nitrogen atom with respect to the tin atom, also in solution these species are pentacoordinate. This may be concluded from the observations that (i) the ^{1}H and ^{13}C NMR spectra of chiral [8-(dimethylamino)-1-naphthyl]methylphenylneopentyltin show two resonances for the diastereotopic NMe$_2$ group, indicating that pyramidal inversion of the nitrogen atom is blocked, and (ii) the increase of the $^1J(^{119}\mathrm{Sn}-^{13}\mathrm{C}(1)_{\mathrm{naphthyl}})$ values compared to those of unsubstituted naphthyltin compounds points to a coordination number larger than 4. Moreover, the tetraorganotin compounds show an enhanced reactivity in redistribution reactions, which may be the result of the labilization of the Sn–C bond in a trans position with respect to the coordinating nitrogen atom.

Introduction

Although tetraorganotin compounds were previously regarded as being unable to extend their coordination number because of the poor acceptor properties of the tin center,[1] recently a few examples of tetraorganotin compounds have been reported in which the tin center may be regarded as penta-[2-4] or even hexacoordinate[5] as a result of intramolecular Sn–N coordination. Such coordination has been proposed to be responsible for the changes in the reactivity sequence observed in halodemetalation reactions of mixed tetraorganotin compounds, in which potentially coordinating groups (Y) are present in the γ-position with respect to the tin. It is thought that intramolecular assistance by those groups facilitates the cleavage of tin–carbon bonds trans to them (eq 1).[6-8]



(1)

The presence of pentacoordinate tin in such tetraorganotin compounds was confirmed by the X-ray crystal structure determination of (2-carbomethoxy-1,4-cyclohexadien-1-yl)trimethyltin.[9]

Previously we have reported on the synthesis and characterization of pentacoordinate triorganotin halides containing the bidentate 8-(dimethylamino)-1-naphthyl group, and it was shown that these contain a configurationally stable tin center.[10] Moreover, it appeared that

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