Coupling of Deuteriosilanes in the Presence of Cp_2MCl_2/nBuLi

Joyce Y. Corey,* Jean L. Huhmann, and Xiao-Hong Zhu

Department of Chemistry, University of Missouri—St. Louis, St. Louis, Missouri 63121

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The condensation reactions of secondary deuteriosilanes to give oligomer products in the presence of the catalyst precursor Cp_2MCl_2/nBuLi have been investigated. The products from $PhMeSiD_2$ with M = Zr are not the expected deuterium-terminated chains $D(PhMeSi)_xD$ but a mixture of isotopomers with an average deuterium content near two per oligomer, as determined by mass spectroscopy and with deuterium located at silicon as well as the methyl groups, as shown by ^2H NMR of isolated oligomers. Deuterium scrambling in the oligomers was not observed in the condensation of $PhEtSiD_2$ with all three catalyst systems and only marginally in the products produced from the condensation of $PhCH_2(Me)SiD_2$ (M = Zr). The cocondensation of $PhMeSiD_2$ and $TolMeSiH_2$ provides a near-statistical distribution of combinations of disilanes through tetrasilanes with deuterium scattered almost equally within each combination including those that contain only TolMeSi units. The monosilane product PhMeBuSiD which is believed to form from hydrosilylation of coordinated butene in $[Cp_2Zr(butene)]$ contains from three to eight deuteriums with an average between four and five. Mechanisms for enhanced deuterium incorporation in PhMeBuSiD and deuterium scrambling in the oligomers produced from $PhMeSiD_2$ are proposed that have features in common.

Introduction

The condensation of primary and secondary hydrosilanes to give oligo- and polysilanes is promoted by a variety of transition metal derivatives.[1] The longest chain lengths are formed in the presence of metallocene complexes of the titanium triad and silicon–silicon bond formation in this case most likely occurs by a sequence of σ-bond metathesis steps.

We have developed the combination catalyst Cp_2MCl_2/nBuLi (M = Ti, Zr, Hf) for the condensation of both secondary and primary silanes.[2,3] The disilane, trisilane, and tetrasilane which are produced from the condensation of $PhMeSiH_2$ have been isolated and characterized. Although a statistical mixture of trisilanes is produced, the spectroscopic properties of the tetrasilane do not appear to be consistent with a statistical mixture of diastereomers.[2] In the condensation of $RSiH_3$ one of the diastereomers is produced preferentially under concentrated reaction conditions.[3] A related study has shown that the polyphenylsilane produced from $PhSiH_3$ exhibits a syndiotactic microstructure consistent with diastereomeric induction in the growth process.[4]

In an effort to obtain labeled oligomers (eq 1) and to further probe the mechanistic details of the condensation process, the reaction of secondary deuteriosilanes with Cp_2MCl_2/nBuLi (M = Ti, Zr, Hf) was studied. Although uniquely labeled oligomers were not obtained, a process

$$RR'SiD_2 \xrightarrow[\text{toluene}]{Cp_2MCl_2/nBuLi} D(RR'Si)_xD \qquad (1)$$

in addition to silicon–silicon bond formation was discovered that is unique to the zirconium catalyst system.

Experimental Section

General Considerations. All reactions unless otherwise noted were carried out under an atmosphere of dry nitrogen or argon with standard Schlenk techniques. Transfer of Cp_2ZrCl_2 was performed in a Vacuum Atmospheres HE-43 drybox. Solvents were dried using standard techniques, and all glassware was dried in an oven at 110–120 °C prior to use.

The commercial compounds, Cp_2MCl_2 (M = Ti, Zr, Hf), $LiAlD_4$, nBuLi in hexanes, CD_3MgI in THF (1 M), norbornylene, and chlorosilanes were used as supplied. The preparation of the $H(PhMeSi)_xH$ oligomers has been previously described[1] and $PhMeSiD_2$ was prepared according to the literature method.[5]

^1H NMR spectral data were recorded either on a 360 or an XL-300 spectrometer, ^2H and ^{13}C NMR spectral data were recorded on an XL-300 spectrometer equipped with a broadband tunable probe, and unless otherwise noted, all ^{13}C NMR and ^1H NMR data were collected in $CDCl_3$ with TMS as an internal standard and all ^2H NMR data were collected in $CHCl_3$ with $CDCl_3$ or acetone-d_6 as an internal standard. Mass spectral data were collected on a Hewlett Packard Model 5988A GC/MS instrument equipped with a RTE-A data system, and gas chromatographic separations were performed in a split injection mode using a 12.5-m (HP-1) capillary column. SIM data are normalized to the most intense peak in the cluster. Gas chromatographic separations were obtained on a Shimadzu GC-14A gas chromatograph, using a J&W Scientific 15-m × 0.53-mm-i.d., 1.5-μm film, DB-5 column with a flow rate of 6 mL/min (helium) and a temperature program from 60 to 320 °C, isothermic at 60 °C/2 min, then ramped at 20 °C/min with the injector temperature at 275 °C and the detector temperature at 350 °C. Integrations were recorded on a Shimadzu CR601 Chromatopac

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integrator and are uncorrected. Infrared spectra were obtained on a Perkin-Elmer Model 1600 FT-IR spectrophotometer as thin films.

$PhEtSiD_2$. A solution of $PhEtSiCl_2$ (36.6 g, 0.179 mol) in Et_2O was added dropwise to a slurry of $LiAlD_4$ (5.0 g, 0.12 mol) and the mixture allowed to stir at room temperature for 16 h. After hydrolysis with NH_4Cl (saturated, aqueous) the ether layer was separated and dried over anhydrous $MgSO_4$. After removal of the volatile material distillation provided $PhEtSiD_2$, bp 159–162 °C (11 g, 43%; 98% by GC) (lit.[6] bp 73–74 °C/30 mmHg). MS *m/e* (relative intensities) 139 (12.4), 138 (100), 137 (41.2), 136 (15), 135 (8.8); IR (thin film) 1544 (st, SiD), 1428 (wk, SiPh) cm^{-1}; ^1H NMR ($CDCl_3$, TMS) δ 0.8–1.2 (m, 5, CH_2CH_3), 7.2–7.7 (m, 5, arom).

$PhCH_2(Me)SiD_2$. The Grignard reagent prepared from $PhCH_2Cl$ (15.2 g, 0.120 mol) and Mg (2.9 g, 0.12 mol) was added to an ether solution of $MeSiCl_3$ (20 g, 0.13 mol) and the mixture stirred for 2 h prior to addition of $LiAlD_4$ (3.0 g, 0.071 mol). After workup, $PhCH_2(Me)SiD_2$, bp 158–160 °C (9.4 g, 58%; 100% by GC), was obtained. MS *m/e* (relative intensities) 140 (3.3), 139 (13), 138 (100), 137 (37), 136 (27), 135 (59), 134 (4.9); IR (thin film) 1560 (st, SiD) cm^{-1}; ^1H NMR ($CDCl_3$, TMS) δ 0.8 (s, 2.5, CH_3), 2.3 (s, 1.8 CH_2), 7.0–7.4 (5.8, m, arom).

$PhCD_3SiH_2$. A sample of $PhSiH_3$ (4.34 g, 40.0 mmol) was dissolved in hexanes (10 mL) and the solution cooled to −78 °C before reaction with $SnCl_4$ (11 g, 43 mmol). The reaction mixture was warmed slowly to −23 °C, then to 0 °C, and finally to room temperature and stirred for 1 h. Most of the reaction occurred at 0 °C. The slurry that formed was cannulated onto a glass frit and filtered to provide a hexane solution of $PhSiClH_2$ which was not isolated (hydrolysis of an aliquot shows the presence of $PhH_2SiOSiH_2Ph$, 90%, and $PhSiH_3$, 2%). To the hexane solution was added CD_3MgI (40 mL, 40 mmol) and the mixture stirred at room temperature for 2 h. After aqueous workup, $PhCD_3SiH_2$,[7] bp 120–140 °C (1.9 g, 38% overall yield), was obtained in 96% purity (GC analysis). MS *m/e* (relative intensities) 127 (3.2), 126 (13), 125 (79), 124 (100), 123 (38), 122 (2.4); IR (thin film) 2137 (st, SiH), 1428 (wk, SiPh) cm^{-1}; ^1H NMR ($CDCl_3$, TMS) δ 4.3 (1.9, s, SiH), 7.2–7.8 (5.1, m, arom).

General Conditions for the Condensation of $RR'SiD_2$ with Catalytic Cp_2MCl_2/nBuLi. A slurry of the metallocene dichloride in dry toluene was cooled in an ice bath and degassed for 10 min prior to the addition of 2 equiv of nBuLi. When the metal halide had dissolved, $RR'SiD_2$ was injected and the reaction flask placed in a 90 °C oil bath. On heating, the reaction mixture became dark colored within 30 min. Aliquots were removed at periodic intervals, added to hexanes, and filtered through Celite prior to analysis. The relative concentration of oligomers was determined by GC and the distribution of deuterium in the products was determined by GCMS including SIM analysis for weak molecular ions and in selected cases by ^2H NMR spectroscopy. Determination of the residual deuterium content of unreacted starting materials under the conditions employed (70 eV) is not possible since the $[P-1]^+$ and $[P-2]^+$ (proton and/or deuterium stripping) is so extensive (as an example, see Table I for a comparison of the parent clusters for $PhMeSiH_2$ and $PhMeSiD_2$). A similar problem is encountered for fragment ions which contain overlapping clusters which vary in hydrogen or deuterium content; thus analyses of products were carried out only on molecular ions. In the condensation of $PhMeSiH_2$ both the PhMeBuSiH and $H(PhMeSi)_2H$ products exhibit a minor $[P-1]^+$ ion. To simplify the calculations, the possible contribution of the $[P-1]^+$ in such cases was ignored and thus the deuterium content of these products is approximate.

Condensation of $PhMeSiD_2$ with Catalytic Cp_2ZrCl_2/nBuLi, Si/Zr = 35. To the catalyst prepared from Cp_2ZrCl_2 (0.335 g, 1.15 mmol) and nBuLi (1.8 mL, 1.3 M) in dry toluene (10 mL) was added $PhMeSiD_2$ (5.0 g, 41 mmol) and the reaction flask placed in a 90 °C oil bath. Aliquots were taken at 1, 5, 24 h and every 24 h subsequently. After 8 days, hexane was added, resulting in the discharge of color and formation of a yellow solid which was removed by filtration. Removal of the volatiles from the filtrate provided a viscous oil (3.5 g). Analysis by GC showed the following composition (%): PhMeBuSiH (9.4), disilane (34.4), trisilane (37.0), tetrasilane (11.4), plus five additional minor components ranging from 1.0 to 2.7%.

SIM (2 days): $SiC_7H_{10-x}D_x$, *m/e* 126 (5.5), 125 (21.4), 124 (68.7), 123 (94.2), 122 (100), 121 (49.7), 120 (16.9); $SiC_{11}H_{18-x}D_x$, *m/e* 187 (11.7), 186 (11.1), 185 (22.7), 184 (49.7), 183 (100), 182 (67.3), 181 (24.8); $Si_2C_{14}H_{18-x}D_x$, *m/e* 248 (2.7), 247 (8.4), 246 (24.6), 245 (59.4), 244 (100), 243 (70.5), 242 (27.7); $Si_3C_{21}H_{26-x}D_x$, *m/e* 368 (5.6), 367 (16.1), 366 (39.1), 365 (74.8), 364 (100), 363 (71.2), 362 (17.3); $Si_4C_{28}H_{34-x}D_x$, *m/e* 486 (48.4), 485 (82.7), 484 (100), 483 (58.4), 482 (13.7).

SIM (8 days): $SiC_7H_{10-x}D_x$, *m/e* 126 (8.1), 125 (26.9), 124 (63.6), 123 (100), 122 (99.6), 121 (58.8), 120 (19.0); $SiC_{11}H_{18-x}D_x$, *m/e* 186 (13.2), 185 (21.4), 184 (51.1), 183 (100), 182 (96.2), 181 (33.6), 180 (14.6); $Si_2C_{14}H_{18-x}D_x$, *m/e* 247 (20.3), 246 (46), 245 (79.2), 244 (100), 243 (79.6), 242 (32.5); $Si_3C_{21}H_{26-x}D_x$, *m/e* 368 (19.1), 367 (41.7), 366 (70.3), 365 (97.2), 364 (100), 363 (64.4), 362 (23.4); $Si_4C_{28}H_{34-x}D_x$, *m/e* 489 (8.1), 488 (19.2), 487 (47.2), 486 (66.7), 485 (100), 484 (90.6), 483 (58.4), 482 (20.1).

The residual oil was distilled and each fraction redistilled to obtain a center cut for each oligomer $D(PhMeSi)_xD$ with GC % >90%.

Disilane ($x = 2$): bp 95–105 °C/0.17 mmHg; ^1H NMR ($CDCl_3$, TMS) δ 0.42–0.45 (m, 6.5, $SiCH_{3-x}D_x$), 4.37–4.44 (m, 1.0, Si*H*); ^2H NMR ($CHCl_3$, acetone-d_6) δ 0.36 (br s, 2.0, $CD_{3-x}H_x$), 4.39 (br s, 1.0, Si*D*).

Trisilane ($x = 3$): bp 170–175 °C/0.03 mmHg; ^1H NMR ($CDCl_3$) δ 0.39–0.50 (m, 15, $CH_{3-x}D_x$), 4.46–4.54 (m, 1.0, Si*H*); ^2H NMR ($CDCl_3$, acetone-d_6) δ 0.32 (br s, 2.16, $CD_{3-x}H_x$), 4.39 (br s, 1.0, Si*D*).

Tetrasilane ($x = 4$): bp 185–190 °C/ 0.03 mmHg; ^1H ($CDCl_3$) δ 0.25–0.44 (m, 22, $CH_{3-x}D_x$), 4.38–4.44 (m, 1.0, Si*H*); ^2H NMR ($CDCl_3$, acetone-d_6) δ 0.24 (br s, 2.23, $CD_{3-x}H_x$), 4.35 (br s, 1.0, Si*D*).

Condensation of $PhMeSiD_2$ with Catalytic Cp_2ZrCl_2/nBuLi, Si/Zr = 60. The condensation of $PhMeSiD_2$ (3.8 g, 31 mmol) was conducted in the presence of Cp_2ZrCl_2 (0.15 g, 0.51 mmol) and nBuLi (0.80 mL, 1.3 M) for 6 days at 90 °C. After removal of the catalyst and volatile components a mixture of oligomers was obtained (2.2 g). GC analysis showed the following composition (%): disilane (19.1), trisilane (49.8), tetrasilane (26.8), pentasilane (4.3).

SIM (2 days): $SiC_7H_{10-x}D_x$, *m/e* 126 (4.0), 125 (16.6), 124 (100), 123 (94.6), 122 (94.5), 121 (32.3), 120 (12.4); $SiC_{11}H_{18-x}D_x$, *m/e* 186 (9.5), 185 (21.5), 184 (46.7), 183 (100), 182 (34.7), 181 (13.3); $Si_2C_{14}H_{18-x}D_x$, *m/e* 246 (9.1), 245 (27.1), 244 (100), 243 (26.2), 242 (5.5), 241 (1.1); $Si_3C_{21}H_{26-x}D_x$, *m/e* 366 (15.9), 365 (37.4), 364 (100), 363 (21.8), 362 (3.0); $Si_4C_{28}H_{34-x}D_x$, *m/e* 486 (30.6), 485 (59.3), 484 (100), 483 (21.9).

SIM (6 days): $SiC_7H_{10-x}D_x$, *m/e* 126 (3.2), 125 (19.8), 124 (71.7), 123 (96.5), 122 (100), 121 (45.1), 120 (15.7), 119 (4.5); $SiC_{11}H_{18-x}D_x$, *m/e* 186 (13.7), 185 (25.7), 184 (51.0), 183 (100), 182 (83.4), 181 (32.8); $Si_2C_{14}H_{18-x}D_x$, *m/e* 247 (7.6), 246 (21.5), 245 (53.4), 244 (100), 243 (64.8), 242 (17.0); $Si_3C_{21}H_{26-x}D_x$, *m/e* 368 (7.6), 367 (19.3), 366 (44.6), 365 (80.1), 364 (100), 363 (60.4), 362 (15.6); $Si_4C_{28}H_{34-x}D_x$, *m/e* 489 (4.8), 488 (12.7), 487 (30.6), 486 (59.5), 485 (93.2), 484 (100), 483 (55.8), 482 (12.5).

Reaction of $PhMeSiD_2$ with Cp_2ZrCl_2/nBuLi in C_7D_8, Si/Zr = 25. The condensation of $PhMeSiD_2$ (0.50 g, 0.40 mmol) was conducted in the presence of Cp_2ZrCl_2 (48 mg, 0.016 mmol) and nBuLi (0.25 mL, 1.3 M) for 2 days at 90 °C. After removal of the catalyst the mixture exhibited the following composition (GC, %): $PhMeSiD_2$ (33.1), PhMeBuSiD (3.4), disiloxane (5.5), disilane (25.0), trisilane (15.2), and tetrasilane (4.1). Removal of volatile components provided a mixture of oligomers (0.32 g).

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Table I. Condensation of $PhMeSiD_2$ in the Presence of Cp_2ZrCl_2/nBuLi: Deuterium Distribution in Products

	$PhMeSiH_2$ toluene Si/Zr = 30	$PhMeSiD_2$ toluene Si/Zr = 35		$PhMeSiD_2$ toluene Si/Zr = 60		$PhMeSiD_2$ toluene-d_8 Si/Zr = 32
		2 days	8 days	2 days	6 days	
$PhMeSiH_2$ or $SiC_7H_{10-x}D_x$[a]						
126			1.2			
125		3.6	5.3	3.9	3.0	
124	(35.8)[b]	17.7	15.1	27.2	18.9	24.2
123	(29.4)	26.0	26.6	26.0	27.4	30.2
122	32.9 (27.5)	30.3	28.4	28.6	31.2	29.4
121	45.6 (7.3)	15.4	17.5	9.8	14.3	11.6
120	18.7	5.4	5.9	3.9	5.2	4.6
119	2.9					
PhMeBuSiH or $SiC_{11}H_{18-x}D_x$[c]						
186 (D_8)		3.2	3.5	3.3	3.7	
185 (D_7)		5.8	4.3	6.4	6.3	5.8
184 (D_6)		13.7	11.9	15.4	12.8	11.2
183 (D_5)		38.7	30.4	50.4	33.5	26.8
182 (D_4)		27.7	33.1	17.4	30.7	27.8
181 (D_3)		10.9	11.4	7.1	13.0	18.8
180 (D_2)			5.4			9.4
179						
178	92.8					
177	7.2					
av no. of D[d]		4.9	4.6	5.1	3.9	4.3
$H(PhMeSi)_2H$ or $Si_2C_{14}H_{18-x}D_x$[c]						
247 (D_5)		1.0	2.9			
246 (D_4)		3.4	9.0		3.0	
245 (D_3)		14.6	19.4		13.4	4.3
244 (D_2)		37.3	29.6	75.0	43.1	60.1
243		29.2	26.9	19.9	31.6	26.1
242	87.8	12.1	12.3	4.2	8.9	6.9
241	12.2					
av no. of D[d]		1.69	1.95	1.70	1.70	1.62
$H(PhMeSi)_3H$ or $Si_3C_{21}H_{26-x}D_x$						
368 (D_6)			1.9			
367 (D_5)		1.5	6.0		1.9	
366 (D_4)		5.2	12.4		6.6	
365 (D_3)		17.3	21.8		19.8	3.9
364 (D_2)		35.6	28.2	79.4	37.3	63.9
363		31.9	20.9	17.9	26.7	27.1
362	100	8.6	8.9	2.6	7.6	4.6
av no. of D		1.83	2.33	1.77	1.97	1.67
$H(PhMeSi)_4H$ or $Si_4C_{28}H_{32-x}D_x$						
487 (D_5)			8.0		2.6	
486 (D_4)		5.1	8.3		7.7	
485 (D_3)		17.9	24.9	5.9	22.0	
484 (D_2)		40.0	27.7	75.6	38.0	78.4
483		29.2	22.0	18.5	29.7	16.1
482	100	7.8	9.1			5.4
av no. of D		1.83	2.31	1.87	2.06	1.73

[a] GCMS data with cluster sum set to 100. [b] $PhMeSiD_2$. [c] SIM data adjusted for isotopic distribution of carbon and silicon and cluster sum set to 100. [d] Numbers are not corrected for the presence of P – 1 contribution. [e] GCMS data.

SIM (1 day): $SiC_7H_{10-x}D_x$, *m/e* 126 (3.3), 125 (13.4), 124 (88.1), 123 (100), 122 (95.5), 121 (37.0), 120 (13.7), 119 (2.0); $SiC_{11}H_{18-x}D_x$, *m/e* 186 (20.0), 185 (34.3), 184 (68.6), 183 (100), 182 (53.5); $Si_2C_{14}H_{18-x}D_x$, *m/e* 246 (9.1), 245 (27.7), 244 (100), 243 (42.6), 242 (12.2); $Si_3C_{21}H_{26-x}D_x$, *m/e* 367 (3.7), 366 (16.3), 365 (40.5), 364 (100), 363 (38.9), 362 (6.2); $Si_4C_{28}H_{34-x}D_x$, *m/e* 486 (25.1), 485 (50.1), 484 (100), 483 (35.2), 482 (5.4).

SIM (2 days): $SiC_7H_{10-x}D_x$, *m/e* 126 (3.2), 125 (13.8), 124 (84.6), 123 (100), 122 (95.5), 121 (40.5), 120 (16.1), 119 (2.4); $SiC_{11}H_{18-x}D_x$, *m/e* 185 (29.7), 184 (61.5), 183 (100), 182 (56.2), 181 (18.8), 180 (4.3); $Si_2C_{14}H_{18-x}D_x$, *m/e* 247 (7.2), 246 (17.9), 245 (43.9), 244 (100), 243 (46.6), 242 (11.1); $Si_3C_{21}H_{26-x}D_x$, *m/e* 367 (4.1), 366 (16.3), 365 (40.8), 364 (100), 363 (44.4), 362 (6.8).

Reaction of $PhMeSiD_2$ and Cp_2TiCl_2/nBuLi. $PhMeSiD_2$ (1.0 g, 8.1 mmol) was added to the catalyst prepared from Cp_2TiCl_2 (64.2 mg, 0.258 mmol) and nBuLi (0.40 mL, 1.3 M) in dry toluene (2 mL), and the mixture was heated at 90 °C for 5 days. After removal of the catalyst the reaction mixture exhibited the following composition (GC, %): $PhMeSiD_2$ (37.3), disilane (20.7), trisilane (18.4), tetrasilane (6.1), siloxanes (10.9), and three additional unidentified components (4.7). The volatile material was removed under vacuum at room temperature to give an oil. ^2H NMR ($CHCl_3$, acetone-d_6) δ 0.3 (br s, 1.0, $CD_{3-x}H_x$), 4.32, 4.43 (br s, 12, Si*D*).

SIM (5 days): $SiC_7H_{10-x}D_x$, *m/e* 125 (10.1), 124 (57.5), 123 (96.0), 122 (100), 121 (42.3), 120 (18.5); $Si_2C_{14}H_{18-x}D_x$, *m/e* 245 (29.2), 244 (100), 243 (79.3), 242 (10.5); $Si_3C_{21}H_{26-x}D_x$, *m/e* 366 (17.2), 365 (42.9), 364 (100), 363 (71.5), 362 (17.6); $Si_4C_{28}H_{34-x}D_x$, *m/e* 486 (20.7), 485 (44.6), 484 (100), 483 (54.6), 482 (12.1).

Reaction of $PhMeSiD_2$/Norbornene and Cp_2TiCl_2/nBuLi. $PhMeSiD_2$ (1.0 g, 8.1 mmol) and then norbornene (0.76 g, 8.1 mmol) dissolved in dry toluene (2 drops) were added to the catalyst prepared from Cp_2TiCl_2 (67.4 mg, 0.271 mmol) and nBuLi (0.42 mL, 1.3 M) in dry toluene (2 mL), and the reaction mixture was placed in a 90 °C oil bath. Generally, all the starting material had reacted after several hours. The composition after 22 h (GC, %) was disilane (3.8), trisilane (34.8), tetrasilane (15.9), pentasilane (1.7), hydrosilylation products (32.4), and four unidentified components (11.5). After 1 or 2 days, hexanes were added, the slurry was filtered through Celite, and the volatiles were removed to give an orange viscous oil. ^{2}H NMR (CHCl$_3$, acetone-d_6) δ 4.48 (br s, Si*D*).

SIM (0.5 h): $Si_2C_{14}H_{18-x}D_x$, *m/e* 245 (28.3), 244 (90.5), 243 (100), 242 (32.6); $Si_3C_{21}H_{26-x}D_x$, *m/e* 366 (14.5), 365 (39.3), 364 (100), 363 (84.0), 362 (24.8), 361 (1.9); $Si_4C_{28}H_{34-x}D_x$, *m/e* 486 (21.2), 485 (49.9), 484 (100), 483 (59.0), 482 (15.6).

SIM (22 h): $Si_2C_{14}H_{18-x}D_x$, absent; $Si_3C_{21}H_{26-x}D_x$, *m/e* 366 (14.2), 365 (40.3), 364 (94.5), 363 (100), 362 (43.5), 361 (2.7); $Si_4C_{28}H_{34-x}D_x$, *m/e* 486 (19.5), 485 (49.1), 484 (100), 483 (74.1), 482 (34.4).

When reactions were run at room temperature in the presence of norbornylene or in C_7D_8 (room temperature in the presence of norbornene), the oligomers that were formed contained terminal SiH as determined by the ^{1}H NMR spectrum.

Reaction of $PhMeSiD_2$ and Cp_2HfCl_2/nBuLi. $PhMeSiD_2$ (1.0 g, 8.1 mmol) was added to the catalyst prepared from Cp_2HfCl_2 (104 mg, 0.274 mmol) and nBuLi (0.42 mL, 1.3 M) in dry toluene (2 mL), and the mixture was heated at 90 °C for 7 days when analysis of the mixture showed the following composition (GC, %): PhMeBuSiD (1.3), disilane (81.1), disiloxane (4.6), trisilane (9.0), and three unidentified components (4.0). After workup the ratio of disilane to trisilane was 9/1. ^{2}H NMR (CHCl$_3$, acetone-d_6) δ 4.40 (br s, Si*D*).

SIM (7 days): $Si_2C_{14}H_{18-x}D_x$, *m/e* 247 (1.5), 246 (9.0), 245 (26.2), 244 (100), 243 (35.7), 242 (9.4), 241 (1.9); $Si_3C_{21}H_{26-x}D_x$, *m/e* 367 (4.1), 366 (15.5), 365 (38.6), 364 (100), 363 (35.0), 362 (5.8); $Si_4C_{28}H_{34-x}D_x$, absent.

When the reaction was run in C_7D_8, the oligomers that formed contained terminal SiH, as determined by the ^{1}H NMR spectrum.

The reaction was run on the same scale in *m*-xylene at 125 °C for 3 days to give 0.18 g of oil after removal of the catalyst residues and volatile material. Composition of the oligomer mixture according to GC analysis (%): disilane (51.2), trisilane (26.8), siloxanes (6.4), and six additional components (10.9).

GCMS (2 days): $SiC_7H_{10-x}D_x$, *m/e* 126 (3.6), 125 (15.4), 124 (97), 123 (100), 122 (95.1), 121 (36.6), 120 (15.7), 119 (2.4).

SIM (3 days): $Si_2C_{14}H_{18-x}D_x$, *m/e* 247 (1.6), 246 (9.4), 245 (26.6), 244 (100), 243 (31.4), 242 (7.5), 241 (1.4); $Si_3C_{21}H_{26-x}D_x$, *m/e* 367 (4.1), 366 (16.1), 365 (38.5), 364 (100), 363 (29.4), 362 (5.2); $Si_4C_{28}H_{34-x}D_x$, absent.

Reaction of $PhEtSiD_2$ with Cp_2TiCl_2/nBuLi. $PhEtSiD_2$ (0.45 g, 3.3 mmol) was added to the catalyst prepared from Cp_2TiCl_2 (33 mg, 0.13 mmol) and nBuLi (0.18 mL, 1.45 M) in toluene (1 mL). After 3 days the GC analysis showed $PhEtSiD_2$ (20%), siloxane (6.6%), disilane (49.1%), trisilane (9.5%), and four unidentified components (7.7%). The ^{1}H NMR spectrum of the isolated oligomer mixture exhibited a ratio of SiEt to SiH of about 26.

GCMS (3 days): $SiC_8H_{10-x}D_x$, *m/e* 140 (4.1), 139 (14.5), 138 (100), 137 (71.2), 136 (27.6), 135 (13.1), 134 (9.9), 133 (6.4); $Si_2C_{16}H_{20-x}D_x$, *m/e* 275 (1.8), 274 (10.0), 273 (29.1), 272 (100), 271 (57.1), 270 (9.6); $Si_2C_{16}H_{20-x}D_x$, *m/e* 275 (1.7), 274 (8.1), 273 (28.0), 272 (100), 271 (56.0), 270 (9.6); $Si_3C_{24}H_{30-x}D_x$, not observed; $Si_3C_{22}H_{25-x}D_x$, *m/e* 379 (13), 378 (41.3), 377 (100), 376 (61.9).

$PhEtSiD_2$ (0.50 g, 3.6 mmol) and norbornene (0.34 g, 3.6 mmol) were added to the catalyst prepared from Cp_2TiCl_2 (30 mg, 0.12 mmol) and nBuLi (0.18 mL, 1.45 M) in toluene (1.0 mL). The mixture was heated in an oil bath at 90 °C for 4 days to give disilane (14%, GC), trisilane (75%, GC), and two unidentified components (11%).

SIM (4 days): $Si_2C_{16}H_{20-x}D_x$, *m/e* 274 (10.0), 273 (26.8), 272 (97.8), 271 (100), 270 (27.9); $Si_3C_{24}H_{30-x}D_x$, *m/e* 408 (10), 407 (45.5), 406 (100), 405 (99.1), 404 (33.4).

After the catalyst residue was separated, material boiling up to 150 °C/0.3 mmHg, was removed. The nondistilled material contained trisilane (85% by GC). ^{1}H NMR (CDCl$_3$, TMS) δ 0.7–1.0 (br s, 26, C*H*$_2$C*H*$_3$), 4.3–4.5 (m, 1.0, Si*H*); ^{2}H NMR (CHCl$_3$, acetone-d_6) δ 4.34 (br s, 4.34, Si*D*).

Reaction of $PhEtSiD_2$ with Cp_2ZrCl_2/nBuLi. $PhEtSiD_2$ (0.50 g, 3.62 mmol) was added to the catalyst prepared from Cp_2ZrCl_2 (34.3 mg, 0.121 mmol) and nBuLi (0.15 mL, 1.6 M) in dry toluene (1 mL), and the mixture was heated at 90 °C for 5 days when GC analysis showed the following composition (%): $PhEtSiH_{2-x}D_x$ (40.0), PhEtBuSiD(H) (4.9), disiloxane (1.5), disilane (47.5), trisilane (3.6), and one unidentified component (2.5). After removal of the catalyst residues and volatile material (bp up to 100 °C/0.1 mmHg) a pale yellow viscous oil with the following composition was obtained (GC, %): disilane (75), trisilane (14), siloxanes (8.0), and an unidentified component (2.0). ^{1}H NMR (CDCl$_3$, TMS) δ 4.4 (m, SiH); ^{2}H NMR (CHCl$_3$, acetone-d_6) δ 4.32 (br s, SiD).

GCMS (2 days): $SiC_{12}H_{20-x}$, *m/e* 198 (25.9), 197 (100), 196 (90.4), 195 (18.7).

SIM (2 days): $SiC_8H_{10-x}D_x$, *m/e* 140 (6.0), 139 (22.3), 138 (100), 137 (53.5), 136 (21.1), 135 (13.6), 134 (10.3), 133 (6.7); $Si_2C_{16}H_{20-x}D_x$, *m/e* 275 (1.4), 274 (12.2), 273 (23.1), 272 (100), 271 (41.7), 270 (5.6); $Si_3C_{24}H_{30-x}D_x$, *m/e* 409 (4.5), 408 (17.0), 407 (41.5), 406 (100), 405 (38.4), 404 (5.2).

Reaction of $PhEtSiD_2$ with Cp_2HfCl_2/nBuLi. In a similar fashion, $PhEtSiD_2$ (0.50 g, 3.62 mmol) was reacted with Cp_2HfCl_2 (45.9 mg, 0.121 mmol) and nBuLi (0.15 mL, 1.6 M) at 90 °C for 3 days when analysis showed the following composition (GC, %): $PhEtSiD_2$ (5.6), PhEtBuSiD (6.5), disilane (76.0), trisilane (2.1), and three unidentified components (9.8). After removal of the catalyst residues and volatile material a colorless oil was obtained. ^{1}H NMR (CDCl$_3$, TMS) δ 4.3 (br m, Si*H*); ^{2}H NMR (CHCl$_3$, acetone-d_6) δ 4.36, 4.28 (br s, Si*D*).

GCMS (3 days): $SiC_{12}H_{20-x}D_x$, *m/e* 197 (56.8), 196 (100), 195 (62.1). SIM (3 days): $SiC_8H_{10-x}D_x$, *m/e* 140 (3.8), 139 (12.7), 138 (100), 137 (50.5), 136 (20.1), 135 (9.1), 134 (7.1), 133 (4.9); $Si_2C_{16}H_{20-x}D_x$, *m/e* 275 (1.2), 274 (9.5), 273 (28.2), 272 (100), 271 (41.1), 270 (5.5).

Reaction of $PhCH_2(Me)SiD_2$ with Cp_2ZrCl_2/nBuLi. $PhCH_2(Me)SiD_2$ (0.56 g, 4.5 mmol) was reacted with the catalyst prepared from Cp_2ZrCl_2 (35 mg, 0.12 mmol) and nBuLi (0.15 mL, 1.6 M) in toluene (1 mL) at 90 °C for 3 days. Analysis of an aliquot after 2 days showed the following product mixture (GC, %): $PhCH_2(Me)SiH_2$ (35), $PhCH_2(Me)(Bu)SiD$ (1.9), disilane (27), trisilane (17), tetrasilane (1.7), and five unidentified components (9.0). Workup after 3 days provided 0.36 g of a viscous oil. Removal of the volatile material with bp 25–150 °C/0.3 mmHg provided a residue enriched in trisilane. ^{1}H NMR (CDCl$_3$) δ 0–0.2 (complex multiplet, 28, SiC*H*$_3$), 3.75–3.9 (m, 1, Si*H*). ^{2}H NMR (CHCl$_3$, CDCl$_3$) δ 0 (br s, 1.3, $CH_{3-x}D_x$), 2.1 (br s, 1.0, $CH_{2-x}D_x$Ph), 3.8 (br s, 20, Si*D*).

GCMS (2 days): $SiC_8H_{12-x}D_x$, *m/e* 140 (4.9), 139 (18.5), 138 (100), 137 (64.5), 136 (39.5), 135 (14), 134 (7.9), 133 (2.2); $Si_2C_{16}H_{22-x}D_x$, not observed; $Si_2C_9H_{15-x}D_x$, *m/e* 184 (1.45), 183 (8.90), 182 (26.4), 181 (100), 180 (38.3), 179 (25.7), 178 (28.8), 177 (5.6); $Si_3C_{24}H_{32-x}D_x$, not observed; $Si_3C_{17}H_{25-x}D_x$, *m/e* 318 (4.1), 317 (17.0), 316 (40.3), 315 (100), 314 (41.8), 313 (15.4), 312 (29.0), 311 (13.7), 310 (17.9), 309 (11.5), 308 (3.1), 307 (2.5).

Cocondensation of $PhMeSiD_2$ and (*p*-Tol)$MeSiH_2$ in the Presence of Cp_2ZrCl_2/nBuLi. To the catalyst system prepared from Cp_2ZrCl_2 (60 mg, 0.20 mmol) and nBuLi (0.26 mL, 1.6 M) in toluene (2 mL) was added $PhMeSiD_2$ (0.56 g, 4.5 mmol) and (*p*-Tol)$MeSiH_2$ (0.57 g, 4.2 mmol) and the mixture heated at 90 °C for 4 days. The composition after 4 days was determined by GC (A = PhMeSi; B = (*p*-Tol)MeSi) (%): AH_2 (13.4), BH_2 (14.0), ABuH (2.2), BBuH (2.6), HAAH (4.3), HABH (8.1), HBBH (3.8), HA_3H (5.6), HA_2BH (11.6), HAB_2H (9.1), HB_3H (2.7), HA_4H (1.6), HA_3B (4.6), HA_2B_2H (5.7), HAB_3H (3.2), HB_4H (0.9), and Si_5 components (unresolved, 4.8).

SIM (2 days): $SiC_7H_{10-x}D_x$, *m/e* 126 (1.2), 125 (6.2), 124 (33.1), 123 (75.2), 122 (100), 121 (72.0), 120 (26.4), 119 (4.4); $SiC_8H_{12-x}D_x$, *m/e* 139 (9.3), 138 (47.4), 137 (93.3), 136 (100), 135 (53.3), 134 (16.4), 133 (4.3); $Si_2C_{14}H_{18-x}D_x$, *m/e* 246 (6.0), 245 (21.7), 244 (65.2), 243 (100), 242 (60.4), 241 (10.3), 240 (2.6); $Si_2C_{15}H_{20-x}D_x$, *m/e* 261 (1.5), 260 (6.3), 259 (23.0), 258 (67.4), 257 (100), 256 (61.0), 255 (9.8). $Si_2C_{16}H_{22-x}D_x$, *m/e* 275 (1.3), 274 (5.9), 273 (22.0), 272 (65.7), 271 (100), 270 (58.1); $Si_3C_{21}H_{26-x}D_x$, *m/e* 367 (3.0), 366 (11.3), 265 (33.0), 364 (76.0), 363 (100), 362 (48.8), 361 (3.5); $Si_3C_{23}H_{30-x}D_x$, *m/e* 395 (3.3), 394 (12.4), 393 (33.9), 392 (75.1), 391 (100), 390

(51.2), 389 (3.1); $Si_3C_{24}H_{32-x}D_x$, *m/e* 409 (3.4), 408 (12.9), 407 (36.0), 406 (81.8), 405 (100), 404 (51.4), 403 (2.9); $Si_4C_{28}H_{30-x}D_x$, *m/e* 486 (17.0), 485 (43.9), 484 (84.8), 483 (100), 482 (47.8); $Si_4C_{29}H_{36-x}D_x$, *m/e* 500 (16.9), 499 (41.8), 498 (84.9), 497 (100), 496 (49.4).

Reaction of $PhCD_3SiH_2$ with Cp_2ZrCl_2/nBuLi. The catalyst mixture was prepared from Cp_2ZrCl_2 (40 mg, 0.14 mmol) in toluene (1.0 mL) and nBuLi (0.23 mL, 1.18 M). After injection of $PhMe_DSiH_2$ (0.31 g, 2.5 mmol) the tube was evacuated, sealed, and heated at 90 °C for 8 days. The catalyst and volatile material were removed to give an oil residue. ^2H NMR ($CHCl_3$, $CDCl_3$) δ 0.32, 0.22 (s, $SiCD_3$).

SIM: $SiC_{11}H_{18-x}D_x$, *m/e* 183 (5.3), 182 (19.0), 181 (100), 180 (9.8); $Si_2C_{14}H_{18-x}D_x$, *m/e* 251 (2.0), 250 (10.5), 249 (29.0), 248 (100), 247 (20.0), 246 (3.5); $Si_3C_{21}H_{26-x}D_x$, *m/e* 374 (4.5), 373 (17.6), 372 (40.8), 371 (100), 370 (12.0).

The reaction was repeated with $PhMe_DSiH_2$ (0.50 g, 4.9 mmol) and catalyst prepared from Cp_2ZrCl_2 (40 mg, 0.14 mmol) and nBuLi (0.25 mL, 1.18 M) for 30 days at 90 °C in toluene. GC analysis showed the following composition (%): $PhMe_DSiH_2$ (68), $PhMe_DBuSiH$ (3.9), disilane (12.9), trisilane (5.9), tetrasilane (1.7), and six additional minor components ranging from 0.5 to 1.2%. After removal of the catalyst and volatile material a pale yellow oil was obtained. ^2H NMR ($CHCl_3$) δ 0.2–0.8 (3 broad overlapping singlets, 14, $SiCD_{3-x}H_x$), 4.3–4.6 (2 overlapping singlets, 1.0, SiD).

SIM: $SiC_7H_{10-x}D_x$, *m/e* 127 (8.9), 126 (35.4), 125 (81.4), 124 (100), 123 (63.8), 122 (25.6); $SiC_{11}H_{18-x}D_x$, *m/e* 184 (1.7), 183 (9.2), 182 (43.6), 181 (100), 180 (16.7), 179 (1.3); $Si_2C_{14}H_{18-x}D_x$, *m/e* 251 (5.2), 250 (17.2), 249 (55.9), 248 (100), 247 (90.7), 246 (47.2), 245 (17.4), 244 (4.4); $Si_3C_{21}H_{26-x}D_x$, *m/e* 374 (10.1), 373 (30.6), 372 (69.4), 371 (100), 370 (79.9), 369 (45.4), 368 (21.4); $Si_4C_{28}H_{32-x}D_x$, *m/e* 497 (16.2), 496 (44.3), 495 (88.5), 494 (100), 493 (59.0), 492 (23.9).

Results

Starting Silanes. Reduction of dichlorosilanes with $LiAlD_4$ provides $RR'SiD_2$ and was employed for the production of $PhMeSiD_2$[5] and $PhEtSiD_2$ from commercially available starting materials. $PhEtSiD_2$ was previously prepared by the addition of EtMgBr to $PhSiD_2Br$.[6] Addition of $PhCH_2MgBr$ to $MeSiCl_3$ followed by reduction with $LiAlD_4$ provided the previously unreported $PhCH_2MeSiD_2$. The secondary deuteriosilanes exhibited no SiH band in the IR spectra or SiH resonance in the NMR spectra. The reaction of CD_3MgI with $PhSiCl_3$ followed by addition of $LiAlH_4$ provided a mixture of $PhSi(CD_3)_xH_{3-x}$ (x = 1–3) which could be used for condensation studies, but $PhCD_3SiH_2$[7a] could be obtained in >95% purity from monochlorination of $PhSiH_3$ with $SnCl_4$ followed by reaction with CD_3MgI. After our work was completed a similar preparation of $PhSiH_2SiCl$ was described[7b] and more recently the monochlorination of $PhSiH_3$ with $CuCl_2$/CuI has been reported.[7c]

$PhMeSiD_2$/Cp_2MCl_2/nBuLi. The ^1H NMR spectrum of the oligomer mixture produced from the condensation of $PhMeSiD_2$ with Cp_2ZrCl_2/nBuLi revealed the presence of SiH resonances, suggesting that the overall reaction outlined in eq 1 was not realized. The oligomerization reaction was run at two different Si/Zr ratios as well as in toluene-d_8. The GCMS and SIM analysis for reaction mixtures after 2 days as well as at the time of workup are provided in Table I with data for condensation of $PhMeSiH_2$ provided for comparison. The deuterium content for "unreacted" $PhMeSiD_2$ is consistently lower relative to starting $PhMeSiD_2$. The data in Table I show that the PhMeBuSiD which is produced from transfer of a Bu group from Zr to Si contains from 2 to 8 deuterium atoms with an average near 5. The deuterium content of the oligomers formed is initially less than 2 but with longer time periods rises to an average of 2 or more expected per oligomer. However, each oligomer is a mixture of isotopomers with a range of D_0 to D_5. When the reaction is run in toluene-d_8 the oligomers produced also contain terminal SiH and exhibit deuterium scrambling.

Table II. Condensation of $PhMeSiD_2$ in the Presence of Cp_2MCl_2/nBuLi (M = Ti, Hf): Distribution of Deuterium in Products

	$PhMeSiD_2$ toluene Cp_2TiCl_2 90 °C Si/Ti = 31 5 days	$PhMeSiD_2$ toluene Cp_2TiCl_2 + olefin Si/Ti = 30 0.5 h	 22 h	$PhMeSiD_2$ toluene Cp_2HfCl_2 90 °C Si/Hf = 30 7 days	$PhMeSiD_2$ xylene Cp_2HfCl_2 125 °C Si/Hf = 30 3 days
	$PhMeSiH_2$ or $SiC_7H_{10-x}D_x$[a]				
125	0.4	*b*		*b*	4.2[c]
124	15.4				26.7
123	29.5				27.5
122	33.8				26.2
121	14.3				10.1
120	6.7				4.3
	$H(PhMeSi)_2H$ or $Si_2C_{14}H_{18-x}D_x$[d]				
244 (D_2)	47.6	33.8		67.3	70.7
243	46.1	48.8		24.7	22.7
242	6.3	17.4		6.6	5.5
241				1.4	1.1
av no. of D[e]	1.41	1.16		1.59	1.64
	$H(PhMeSi)_3H$ or $Si_3C_{21}H_{26-x}D_x$[d]				
365 (D_3)	1.9		1.6		
364 (D_2)	45.7	40.4	29.7	69.1	73.0
363	41.2	45.0	45.1	26.2	22.7
362	11.2	14.6	23.6	4.7	4.3
av no. of D	1.41	1.26	1.09	1.64	1.69
	$H(PhMeSi)_4H$ or $Si_4C_{28}H_{32-x}D_x$[d]				
484 (D_2)	54.3	51.1	40.5	*f*	*f*
483	36.6	37.5	36.9		
482	9.1	11.5	22.6		
av no. of D	1.45	1.40	1.18		

[a] GCMS data with cluster sum set to 100. [b] Starting silane consumed. [c] GCMS data after 2 days. [d] SIM data adjusted for isotopic distribution of carbon and silicon and cluster sum set to 100. [e] Numbers are not corrected for the presence of P – 1 contribution. [f] Tetrasilane not observed.

The deuterium scrambling in the oligomers requires that deuterium be located in positions other than terminal silicon centers. Each of the oligomers was isolated in >90% purity, and the ^2H NMR spectra show that D is located at silicon and at the carbon of the methyl group and is absent from the phenyl groups. The ratio of deuterium at carbon to deuterium at silicon was found to be 1.97 in the disilane, 2.16 in the trisilane, and 2.23 in the tetrasilane.

The deuterium distribution in the oligomers produced with the titanium and hafnium catalysts are given in Table II. Deuterium is lost from unreacted starting material, as is observed with zirconium. However, the oligomers do not exhibit deuterium scrambling and the average number of deuteriums per oligomer is lower, around 1.4 from titanium and about 1.6 to 1.7 from hafnium. The ^2D NMR spectra show that deuterium is located on the terminal silicon with no evidence for the presence of deuterium at carbon.

The enhancement of the rate of silane condensation in the presence of olefins has been previously demonstrated.[2b] The reaction of $PhMeSiD_2$ and norbornene with Cp_2TiCl_2/nBuLi was studied and the results are also included in Table II. Disilane through tetrasilane are formed within 0.5 h (90 °C) with essentially complete consumption of starting silane, but the deuterium content of each oligomer is lower than that observed after 5 days in the absence of

Table III. Condensation of $PhEtSiD_2$ in the Presence of Cp_2MCl_2/nBuLi: Deuterium Distribution in Products

	$PhEtSiD_2$ toluene Cp_2TiCl_2 3 days Si/Ti = 25	$PhEtSiD_2$ toluene Cp_2TiCl_2 + olefin 4 days Si/Ti = 30	$PhEtSiD_2$ toluene Cp_2TiCl_2 4 days Si/Ti = 30	$PhEtSiD_2$ toluene Cp_2HfCl_2 3 days Si/Hf = 30
		$PhEtSiD_2$[a]		
138 (D_2)	42.8	*b*	51.0	52.0
137	32.1		27.1	26.7
136 (73.2)[c]	12.2		10.6	10.6
135 (13.1)	5.5		5.0	4.5
134 (8.0)	4.3		3.7	3.6
133 (4.6)	3.1		2.7	2.7
		$SiC_{12}H_{20-x}D_x$[d]		
198 (D_6)	*b*	*b*	3.1	
197 (D_5)			42.6	19.7
196 (D_4)			44.7	47.1
195 (D_3)			9.6	33.1
av no. of D			4.39	3.86
		$Si_2C_{16}H_{22-x}D_x$		
272 (D_2)	56.6[d]	36.5[d]	63.4[d]	66.3[e]
271	36.9	48.7	32.1	29.6
270 (97.6)[d,f]	6.5	14.8	4.3	4.1
269 (2.4)				
av no. of D[g]	1.50	1.22	1.60	1.62
		$Si_3C_{24}H_{32-x}D_x$		
406 (D_2)	[54.8][d,h]	32.7	66.9	*b*
405	[45.2]	48.3	28.9	
404 (100)[d,i]		19.0	4.2	
av no. of D		1.14	1.63	

[a] GCMS data with cluster sum set to 100. [b] Not observed. [c] Data for $PhCD_3SiH_2$ (unreacted). [d] GCMS data adjusted for isotopic distribution of carbon and silicon and cluster sum set to 100. [e] SIM data adjusted for isotopic distribution of carbon and silicon and cluster sum set to 100. [f] $H(PhEtSi)_2H$. [g] Numbers are not corrected for the presence of P − 1 contribution. [h] Parent not observed. Data given are for $[P - Et]^+$ (*m/e* 377 and 376). [i] $H(PhEtSi)_3H$.

norbornene. With time the oligomers redistribute and continue to lose deuterium.

$PhEtSiD_2/Cp_2MCl_2$/nBuLi. The distribution of deuterium in the oligomers produced from the condensation of $PhEtSiD_2$ is given in Table III. With all three metals the highest oligomer observed is the trisilane. The data for unreacted starting material are consistent with some deuterium stripping, as is observed in the condensation of $PhMeSiD_2$, but the PhEtBuSiD formed (M = Zr, Hf) exhibits an average number of deuterium atoms nearer to 4 than 5. The oligomers show loss of deuterium, with the greatest loss exhibited with the titanium catalyst system. When the reaction of $PhEtSiD_2$ is conducted in the presence of olefin, the major product is the trisilane which contains less deuterium than the samples obtained in the absence of olefin. The ^2H NMR spectra of both oligomer mixtures and purified trisilane contain only SiD resonances.

$PhCH_2(Me)SiD_2/Cp_2ZrCl_2$/nBuLi. Extensive hydrogen (deuterium) stripping from both the parent ions and fragment ions for the oligomers precluded a determination of deuterium content. However, minor scrambling of deuterium is indicated in the ^2H NMR spectrum of isolated oligomers which shows a ratio of $SiD/CH_{2-x}D_x/CH_{3-x}D_x$ of 20/1.0/1.3 (trisilane).

Table IV. Cocondensation of $PhMeSiD_2$ and *p*-Tol(Me)SiH_2 in the Presence of Cp_2ZrCl_2/nBuLi: Deuterium Distribution in Products[a]

	D_3	D_2	D_1	D_0	av
$H(PhMeSi)_2H$	1.4	19.4	43.3	29.6[b]	0.86
H(PhMeSi)(TolMeSi)H	1.6	20.1	43.1	30.2[b]	0.88
$H(TolMeSi)_2H$	1.1	20.1	46.4	32.4[b]	0.90
$H(PhMeSi)_3H$	1.7	21.2	47.3	27.8	0.95
$H(PhMeSi)_2(TolMeSi)H$	1.6	21.9	46.5	28.2	0.95
$H(PhMeSi)(TolMeSi)_2H$	2.0	19.8	46.7	29.6	0.92
$H(TolMeSi)_3H$	1.3	22.7	45.2	29.1	0.94
$H(PhMeSi)_4H$	1.9	20.8	47.3	30.1	0.95
$H(PhMeSi)_3(TolMeSi)H$		20.8	47.4	31.8	0.89

[a] SIM data adjusted for isotopic distribution of carbon and silicon and cluster sum set to 100. [b] Remainder due to presence of ion with one less mass.

$PhMeSiD_2$/*p*-$TolMeSiH_2/Cp_2ZrCl_2$/nBuLi. The cocondensation of $PhMeSiD_2$ and *p*-$TolMeSiH_2$ produced a nearly statistical distribution of disilane, trisilane, and tetrasilane oligomers, $D(PhMeSi)_x(p\text{-}TolMeSi)_yD$ ($x + y = 2$–4; hydrogen may terminate the chain). The deuterium distribution for the oligomer products is summarized in Table IV and shows that the deuterium is scattered almost equally into all of the disilane, trisilane, and tetrasilane combinations including those derived only from the *p*-$TolMeSiH_2$.

$PhCD_3SiH_2/Cp_2ZrCl_2$/nBuLi. When the reaction of $PhCD_3SiH_2$ was conducted for 2- or 4-day periods analysis showed that no deuterium was bound to silicon. The condensation was then conducted in a sealed tube for 8 days after which time no detectable SiD was observed. The sealed tube experiment was repeated for 30 days when deuterium scrambling was evident in the mass spectra of the oligomers and the ^2H NMR spectrum exhibited a ratio of CD (methyl group only) to SiD of approximately 14:1. The MS data for these two experiments are presented in Table V.

Discussion

The condensation of $RR'SiD_2$ with the combination catalysts Cp_2MCl_2/nBuLi led to the following observations: (1) the presence of excess deuterium in the monosilane product PhMeBuSiD; (2) deuterium scrambling in the oligomer products produced from $PhMeSiD_2$ with Cp_2MCl_2/nBuLi occurs to a significant extent only when M = Zr; (3) no deuterium scrambling is observed in the oligomers produced from $PhEtSiD_2$ with all three metals, and those from $PhCH_2MeSiD_2$ contain only minor scrambling when M = Zr; (4) scrambling of CD to SiD in $PhCD_3SiH_2$ is a very slow process. The results provide support for the details of previously suggested mechanisms for silicon–silicon bond formation and indicate that an additional process occurs that appears to be specific to the zirconium catalyst system under comparable reaction conditions.

Catalyst Precursor. At low temperature the reaction of Cp_2ZrCl_2 with nBuLi generates Cp_2ZrBu_2,[8] and upon warming to room temperature elimination of butane occurs to form a zirconocene–butene complex, 1, which has been trapped with PMe_3 to give the adduct $Cp_2Zr(CH{=}CHEt)(PR_3)$, 2.[9] The butane that is eliminated has been identified in the head gases by Waymouth and coworkers,[10] and the coordinated butene in 1 can be replaced

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[9] (a) Buchwald, S. L.; Watson, B. T.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 2544. (b) Binger, P.; Muller, P.; Benn, R.; Rufinske, A.; Gabor, B.; Kruger, C.; Blitz, P. *Chem. Ber.* **1989**, *122*, 1035. (c) Negishi, Eii.; Holmes, S. J.; Tour, J. M.; Miller, J. A.; Cederbaum, F. E.; Swanson, D. R.; Takahashi, T. *J. Am. Chem. Soc.* **1989**, *111*, 3336.

[10] Kesti, M. R.; Waymouth, R. M. *Organometallics* **1992**, *11*, 1095.

Table V. Condensation of $PhCD_3SiH_2$ in the Presence of Cp_2ZrCl_2/nBuLi: Deuterium Distribution in Products

	8 days Si/Zr = 18	30 days Si/Zr = 29
$PhMe_DSiH_2$[a]		
127		1.2
126		8.5
125 (D_3) (32.5)[b]		24.8
124 (47.5)		33.7
123 (18.8)		22.3
122 (1.2)		9.5
$PhMe_DBuSiH$[c]		
182	1.0	18.3
181 (D_3)	90.0	69.8
180	9.0	11.9
av no. of D[d]	2.92	3.06
$Si_2C_{14}H_{18-x}D_x$[c]		
249	2.0	11.5
248 (D_6)	79.1	30.7
247	16.0	31.7
246	2.9	17.4
245		6.7
244		1.8
av no. of D[d]	5.80	5.18
$Si_3C_{21}H_{26-x}D_x$		
373		1.9
372	1.3	13.6
371 (D_9)	87.7	30.7
370	11.0	27.6
369		16.6
368		9.6
av no. of D	8.91	8.28

[a] SIM data with cluster sum set to 100. [b] Data for $PhMe_DSiH_2$ (unreacted). [c] SIM data adjusted for isotopic distribution of carbon and silicon and cluster sum set to 100. [d] Numbers are not corrected for the presence of P − 1 contribution.

by other olefins.[10,11] Addition of silane to **1** gives $[Cp_2Zr(H)(SiRR'R'')]_2$ or $Cp_2Zr(H)(SiRR'R'')(PMe_3)$, **3**, if phosphine is present.[12a] Reaction of **2** with $HSiPh_2R$ (R = H, Ph) has also provided the phosphine adduct, $Cp_2Zr(H)(SiPh_2R)(PMe_3)$.[12b]

The chemistry of Cp_2HfBu_2 is closely related to that of Cp_2ZrBu_2 although elimination of butane requires more rigorous conditions (~80 °C) with the former.[11b,13a] However, the isobutylene complex, $Cp_2Hf(CH_2{=}CMe_2)(PMe_3)$, **4**, is formed relatively cleanly[13] and reaction of **4** with $HSiPh_3$ provides $Cp_2Hf(H)(SiPh_3)(PMe_3)$.[13a] Although Cp_2TiBu_2 has been isolated at low temperatures, it decomposes above −50 °C to give butane and butenes (1:1)[14a] and additional minor products have also been reported.[14b] When solutions of Cp_2TiBu_2 are warmed in the presence of PMe_3, $Cp_2Ti(PMe_3)_2$ is isolated in nearly quantitative yield.[9b] Olefins also appear to stabilize Cp_2Ti.[14a] The reaction of hydrosilanes with Cp_2TiBu_2 has not been studied on a stoichiometric scale although the Ti(III)–silyl complexes $[Cp_2Ti(\mu\text{-}HSiHPh)]_2$ and $[Cp_2Ti(\mu\text{-}H)(\mu\text{-}HSiHPh)TiCp_2]$ have been isolated from the reaction of Cp_2TiMe_2 with $PhSiH_3$ and the phosphine complexes, $Cp_2Ti(SiHPhR)PMe_3$ (R = H, Me, Ph, SiH_2Ph), are formed when mixtures of silane and phosphine are added to Cp_2TiMe_2.[15] Thus the thermal decomposition of Cp_2MBu_2 appears to be similar for Ti, Zr, and Hf with formation of an olefin complex of Cp_2M although in the case of Ti the olefin complex does not appear to be stable and "Cp_2Ti" is formed. The reaction of the olefin complex with a silane results in transfer of the butyl group to silicon (hydrosilylation of the coordinated olefin) with both Zr and Hf although not cleanly in the latter case and no BuSi is formed from Ti.

Previous studies have shown that addition of Ph_3SiD to **2** results in the formation of $Cp_2Zr(SiPh_3)H(PMe_3)$ with the label transferred to the displaced butene.[12b] It should be noted that hydrosilylation of coordinated olefins is not observed with tertiary silanes.[10,12b] Addition of butene to $Cp_2Zr(SiPh_3)D(PMe_3)$ also results in transfer of the label to butene.[12b] When Ph_2SiD_2 and styrene are added to Cp_2ZrBu_2 and the reaction mixture is quenched at an early stage of the reaction, the unreacted styrene contains deuterium and unreacted silane contains SiH. Thus H/D exchange occurs much faster than hydrosilylation of the styrene and this was believed to be consistent with the presence of MH bonds.[10] Similarly, CpCp*HfHCl interacts with $PhSiD_3$ with rapid deuterium scrambling between silicon and hafnium and coupling to give $CpCp^*Hf(SiH_{2-x}D_xPh)Cl$ occurs more slowly.[16]

In the current study secondary silanes are added to $Cp_2Zr(CH_2{=}CHEt)$ in the absence of a phosphine. The coordinated butene is hydrosilylated, as indicated by the formation of RR'BuSiH. That the hydrosilylation product with $PhMeSiD_2$ is not simply the expected $CH_3CH_2CHCDCH_2SiPhMeD$ is clear from the extensive deuterium incorporation (in most cases from D_3 to D_8) with an average number of deuteriums of about 5. Samples of reaction mixtures that have been analyzed within 1 min of injection of $RR'SiH_2$ show that the butylsilane has formed and coupling of silanes to oligomers follows at a considerably slower rate.[2] Although there is no unique explanation for the formation of deuterated butylsilane, a reasonable rationale is provided in Scheme I. The reaction is initiated either by oxidative addition of silane to **1** (A) to give **2** (three isomers) or by a metathesis reaction of **1** (B) to place the silicon either at carbon as in **3A** or at Zr as in **3B**. Insertion of the olefin into either ZrSi or ZrD of **2** provides **3A** and **3B**, respectively. The multiple incorporation of deuterium suggests a rapid and ultimately reversible β-hydride elimination. A rapid exchange of ZrH with external SiD must occur to provide the additional deuterium eventually incorporated into the butyl group. The sequence outlined as **3A** → **4A** → **4B** → **4C** → **3A** (Scheme I) illustrates these steps. Although **3B** could also undergo facile β-hydride elimination, the intermediate **5** is coordinatively saturated and direct exchange with DSi should be slow. In this case, reductive elimination of silane from **5** gives labeled **1** which can recycle from **1** → **2** → **3B** → **5** → **1** to incorporate additional deuterium. Loss of butene from **5** or **2** could also occur although under the conditions of the experiment butene should be lost from

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(11) (a) Negishi, E.; Swanson, D. R.; Takahishi, T. *J. Chem. Soc., Chem. Commun.* **1990**, 1254. (b) Takashishi, T.; Murakami, M.; Kunishige, M.; Saburi, M.; Uchida, Y.; Kozawa, K.; Uchida, T.; Swanson, D. R.; Negisihi, E. *Chem. Lett.* **1989**, 761.

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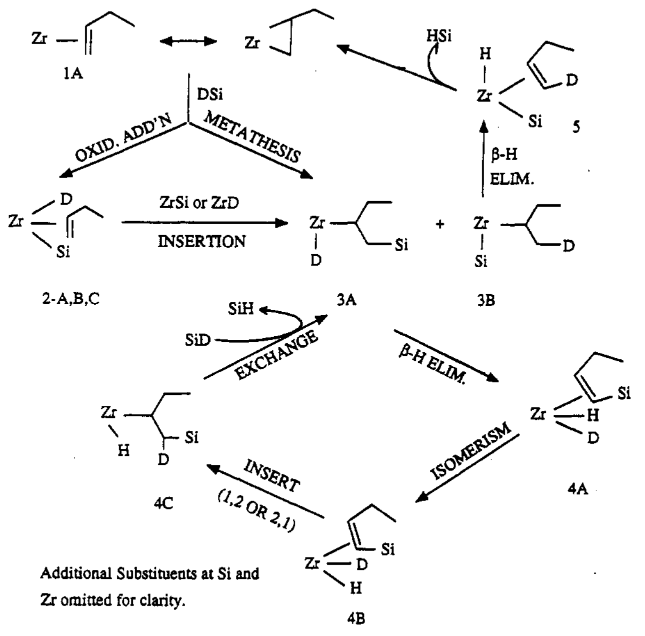
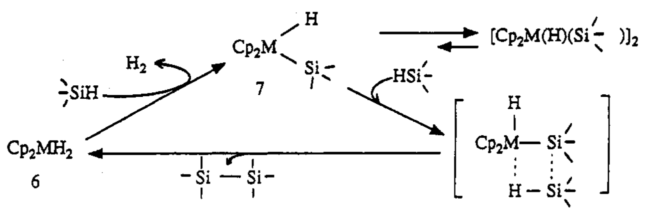
Scheme I



Additional Substituents at Si and Zr omitted for clarity.

Scheme II. Oligomerization



the reaction medium. Several cycles would result in incorporation of deuterium to a limit of 10 D (nine CD in the butyl group and a SiD). That β-hydride elimination from zirconium can be very fast and reversible was illustrated by Waymouth and co-workers in their studies of the hydrosilylation of styrene in the presence of $Cp_2MCl_2/nBuLi$.[10] In addition, β-hydride elimination can be faster than processes such as chelate ring conformational inversion, as demonstrated recently by Bosnich and co-workers in an intramolecular hydrosilylation reaction promoted by $[Rh(diphosphine)]^+$ where hydrosilylation proceeds by insertion of olefin into an RhSi bond.[17] Although the hydrosilylation reaction observed in the present study seems to be more consistent with olefin insertion into a ZrSi bond, such a process has been reported to be slow in reactions conducted on a stoichiometric scale.[18]

Two carbon examples of scrambling in the β-position with zirconium catalysts have been reported. When styrene was reacted with Cp_2ZrDCl in an effort to obtain specifically labeled phenethyl compounds, the products were shown to be isotopomers of $Cp_2(Cl)ZrCH_2CH_nD_{2-n}Ph$ (n = 0–2) and $Cp_2(Cl)ZrCHPhCH_nD_{3-n}$ and scrambling occurred without exchange with free styrene. The process appears to be catalyzed by $Cp_2(H)ZrR$ impurities, and the intermediacy of the coordinatively saturated species $Cp_2Zr(H)(D)(\eta^2\text{-}CH_2{=}CHPh)$ was proposed to account for these results.[19] The label in $Cp_2ZrD[CH_2\overline{CH(CH_2)_4CH_2}]$ is transferred to the β-carbon atom, and the intermediate $Cp_2Zr(H)(D)[\eta^2\text{-}CH_2{=}\overline{C(CH_2)_4CH_2}]$ was proposed to account for this observation.[20]

Ultimately, the silylated butene must be removed from the coordination sphere of the metal. This could occur by reductive elimination from **3** (or **4C**) to give "Cp_2Zr" which is subsequently trapped by hydrosilane to give a zirconium hydrosilyl, $Cp_2Zr(H)(SiHRR')$ (or the corresponding deuteriosilane to give the zirconium deuteriosilyl), proposed as the starting point for formation of silicon oligomers.[2] Alternatively, the same zirconium silyl may be generated from a σ-bond metathesis of **3** (or **4C**) with D_2SiRR'. The sequence of reactions for hafnium are probably similar although the decomposition of Cp_2HfBu_2 is not clean and catalysis may be less efficient in this case.[13a] The decomposition of Cp_2TiBu_2 apparently provides "Cp_2Ti"[14a] which should be trapped by D_2SiRR' to give $Cp_2Ti(D)(SiDRR')$. Thus the silicon coupling chemistry could occur through the same M(IV) species, but again a lower oxidation state of titanium cannot be precluded on the basis of observations made on stoichiometric scale reactions.[14a,15b]

Oligomer Formation and Deuterium Scrambling. We have previously proposed the mechanism outlined in Scheme II for the formation of silicon–silicon bonds.[2] The basic steps involve [2 + 2] σ-bond metathesis processes patterned after those outlined by Tilley.[1a] The metal hydride, **6**, may regenerate **7** through a metathesis reaction with hydrosilane or may eliminate H_2 and form "Cp_2M" which then inserts into an SiH bond. A variable-temperature ^1H NMR study of $[Cp_2ZrH_2]_x$ consistent with a monomer–dimer equilibrium which favors the monomer at temperatures >60 °C has been reported.[21a] The dimer $[CpCp^*ZrH_2]_2$ is a known dehydropolymerization catalyst for primary silanes.[21b] That steric restrictions exist in the silicon–silicon bond forming step are obvious from the fact that primary silanes react much faster than secondary silanes and tertiary silanes do not couple. Even within the secondary silanes $PhRSiH_2$ when R = Me is replaced by R = Et the highest oligomer observed changes from octasilane to trisilane.

The σ-bond metatheses outlined in Scheme II do not account for the deuterium scrambling that is observed in the condensation of $PhMeSiD_2$; therefore an additional process must occur at a slower rate than silicon–silicon bond formation. At least two processes could account for this scrambling, one of which is CH activation of the methyl group bound to silicon and the other is a β-hydride elimination reaction similar to that described in the case of the catalyst precursor but in this instance the α-atom is silicon and not carbon. The small deuterium incorporation into the SiMe group in the condensation of $PhCH_2(Me)SiD_2$ suggests that CH activation probably plays a minor role; therefore the discussion will focus on the possibility of β-hydride elimination as outlined in Scheme III. The sequence of steps is similar to those in Scheme I. Both butene (Scheme I) and silene (Scheme II) do not appear to be lost from the coordination sphere of

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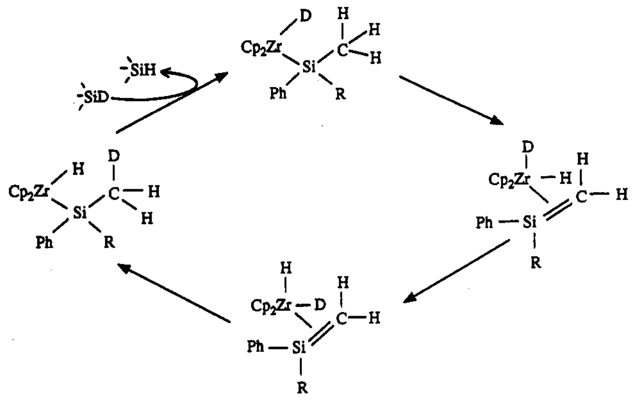
Scheme III. Deuterium Scattering



zirconium. Reactive (free) silenes form head to tail dimers (1,3-disilacyclobutane) in the absence of trapping agents. No such evidence for these dimers was obtained in the GCMS analysis of the products. The undefined R group on silicon may be –D or –$(SiPhMe)_xD$ (or H in place of either or both D atoms). If Scheme III is the explanation for the deuterium scrambling, the fact that replacing a CH bond with CMe (in $PhEtSiD_2$) shuts down the β-hydride elimination process argues that R would be the smallest possible group at silicon, that is, that this process occurs in a monosilyl substituent. Since deuterium scrambling is slower than silicon–silicon bond formation, deuterium incorporation into the oligomers should increase with time, as is observed in the case of zirconium. Continued scrambling would also occur since metathesis reactions involving silicon–silicon bond cleavage also compete with those outlined in Scheme II.[1a,2a,3]

The deuterium scrambling results outlined in this study invoke the intermediacy of a silaolefin coordinated to a metal center. Silene ligands as intermediates as well as stable silene complexes have been recently reviewed, but the examples include electron-rich metals.[22] The closest example to a silene coordinated to a titanium triad metal appears to be the cationic complex $[rac\text{-}C_2H_4(\text{indenyl})_2Zr\{CH(SiMe_2Cl)(SiMe_3)\}]^+$ where the structure appears to be intermediate between the four-membered ring $Cp'_2\overline{ZrC(H)(SiMe_3)SiMe_2Cl}$ and a silene/chloride form $Cp'_2Zr[\eta^2\text{-}H(SiMe_3)C{=}SiMe_2]Cl$.[23] An η^2-silanimine complex, $Cp_2Zr(\eta^2\text{-}Me_2Si{=}NBu^t)(PMe_3)$, has been structurally characterized.[24]

If deuterium at silicon scatters into the carbon of the methyl group, the reverse process should also occur. Initial condensation experiments of $PhCD_3SiH_2$ with Cp_2ZrCl_2/nBuLi showed that deuterium scrambling at the level detectable by ^2H NMR spectroscopy was not observed in reactions conducted for 6 days under the conditions utilized for the $PhRSiD_2$ condensations. Reactions were thus conducted in sealed tubes for 8- and 30-day periods. No detectable SiD was observed by ^2H NMR spectroscopy after 8 days, although some scrambling is indicated in the GCMS data. The sealed tube reactions involve the presence of H_2 produced from the coupling reaction, and under these conditions the buildup of oligomers is much slower, most likely due to hydrogenolysis of Zr–Si bonds. Facile hydrogenolysis of Zr–Si bonds has been demonstrated by Tilley.[1a] After longer time periods detectable deuterium is found in the SiD(H) position. The reverse reaction is kinetically slower, and there is an intrinsic isotopic preference for deuterium to be bound to carbon rather than silicon.[25]

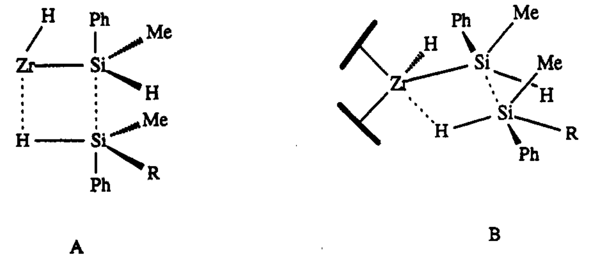


Figure 1.

In the transition state leading to silicon–silicon bond formation the coordination environment about silicon must increase from 4 to 5. If the geometry about silicon becomes approximately trigonal bipyramidal, as shown in Figure 1 (Ph groups in axial positions), then the transition states for deuterium scrambling in the catalyst precursor, deuterium scrambling in the oligomers, and also silicon–silicon bond formation are related. Just as increasing the bulk of the alkyl substituent at silicon (replacement of Me by Et) shuts down the deuterium scrambling process, increasing the bulk at silicon by replacement of Me by Et also limits the chain growth. When the R group in Figure 1 is H, coupling leads to disilane. In formation of any other chain length R must be –$(SiPhR)_xH$, a larger substituent. If the Me groups in Figure 1 are replaced by Hs, there would be less crowding in the transition state and condensation should occur more rapidly, as is observed in the reaction of a primary silane such as $PhSiH_3$.

Although it can be argued that oligomerization of silanes with Cp_2MCl_2/nBuLi involves conversion of the catalyst precursor to $Cp_2M(H)(SiHRR')$ and the oligomerization is initiated from the hydrosilyl for all three metals, the labeling results indicate that deuterium scrambling is promoted only by M = Zr. The initial decrease in deuterium content of the silicon oligomers can be rationalized from the overall "transfer" of hydrogen from the coordinated butene in $Cp_2M(\eta^2\text{-}CH_2{=}CHEt)$ to silicon during reaction with the deuteriosilane (M = Zr, Hf) (Scheme I). If subsequent β-hydride elimination–reinsertion does not occur in $Cp_2M(H)(SiMePhR)$ and no other H/D process occurs, the deuterium content should remain constant with time and be equally distributed amongst the oligomers. This appears to be the case with hafnium. Increasing the temperature of the reaction in the hafnium system from 90 to 125 °C failed to promote deuterium scrambling. The deuterium content in the oligomers obtained with the titanium system is consistently lower relative to those from zirconium and hafnium. Although BuPhMeSiH is not observed with titanium, deuterium can still be removed from the system in accord with Scheme I if butene is subsequently lost from the coordination sphere. An additional process may be required to account for the lower deuterium content, and this process may involve exchange of H/D with Cp–H. Some evidence exists

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[25] (a) From the values of the IR stretching frequencies (SiH, 2137 cm^{-1}; SiD, 1560 cm^{-1};[25b] CH, 2917 cm^{-1}; CD, 2109 cm^{-1} [25c]), the equilibrium constant calculated for the process, SiH + CD → SiD + CH, is ~0.07. (b) Experimental values for $PhMeSiH_2$ and $PhMeSiD_2$, respectively, from samples used in this study. (c) Values for CH_4 (ν_1) and CD_4 (ν_1) taken from: Shimanouchi, T. *Tables of Molecular Vibrational Frequencies*; NSRDS-NBS 39; 1972; Consolidated Vol. I.

for the addition of H_2 across M–Cp bonds to give Cp(cyclopentadiene)M^{IV} species,[26] and such a process would ultimately lead to scrambling between Cp sites and M–D(H). In the system CpCp*MHCl/$PhSiD_3$ (M = Zr, Hf) no deuterium incorporation into Cp or Cp* was observed.[16] The cationic hydride $Cp'_2Zr(H)(THF)^+$ undergoes rapid H/D exchange with D_2 at ZrH sites and slow H/D exchange at the β-Cp′H sites.[27a] Exchange between Cp hydrogens and MH in Zr(III) species has also been reported.[27b]

In the preceding discussion M(IV) species were assumed in the catalytic cycles. Under the conditions utilized for the experiments M(III) species could also be generated. As an example, the dimers $[\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2$ and $\{[SiR_2(C_5H_4)_2]ZrH(\mu\text{-}H)\}_2$ reductively eliminate H_2 at 75 °C and thermolysis of $[Cp_2ZrH(CH_2PPh_2)]_n$ gave "Cp_2ZrH" and $[Cp_2Zr(\eta^2\text{-}CH_2PPh_2)]$.[28] Although reduction of Cp_2TiCl_2 with nBuLi in the presence of PMe_3 afforded a complex of titanocene, when the reaction is conducted in the absence of phosphine the chemistry of the combination Cp_2TiCl_2/nBuLi is more consistent with the presence of Cp_2TiH.[29] Reduction of Cp_2TiCl_2 with iPrMgX has been argued to produce "Cp_2TiH"[30a] as well as "Cp_2TiCl".[30b] The reaction of Cp_2TiCl_2 with organometallic reducing agents appears to be more complicated and may also be related to the ratio of Ti/RM (M = Li or MgX).[30] In a preliminary study of the oligomer product distribution produced from $PhEtSiH_2$ and Cp_2TiCl_2/x(nBuLi) after 3 days about 50% of the starting silane has been consumed when $x = 2$ and the ratio of disilane to trisilane is 13.5. After the same time period with $x = 3$ the starting silane has been consumed and the ratio of disilane to trisilane is 1.1.[32] Harrod has also indicated that molecular weights of polyphenylsilanes produced from $PhSiH_3$ change when the ratio of Cp_2TiCl_2/MeLi is varied.[33] Excess BuLi with Cp_2ZrCl_2 did not appear to influence the oligomer product distribution in the condensation of $PhMeSiH_2$.[2a] We are currently investigating the influence of excess organometallic additives in the titanium catalyst system as well as the possibility of utilizing M(III) precursors in the dehydrocoupling of silanes. Recently, Tilley has suggested the possibility of η^1- or η^3-Cp ligands as intermediates in the photochemically induced σ-bond metathesis reactions of $CpCp^*M[Si(SiMe_3)_3]Cl$.[34]

Conclusion. Efforts to produce oligomers terminated by deuterium in the condensation of secondary silanes with Cp_2MCl_2/nBuLi were not successful as a result of processes that allowed for deuterium scrambling at various stages. The reaction of Cp_2MCl_2 with BuLi appears to form Cp_2M(butene), and removal of the coordinated butene by D_2SiRR' results in incorporation of hydrogen into the reacting silane and an unusually high amount of deuterium in the butene. The study did reveal the presence of an additional process of deuterium scrambling that is specific to the zirconium catalyst system and the condensation of $PhMeSiD_2$. Thus, it appears that the zirconium system is capable of promoting β-hydride elimination even when the α-atom is silicon. The specificity of the deuterium scrambling as well as the problems of chain growth in the oligomers may be related to the size of the cavity created by the two Cp ligands. Significant deuterium scrambling is observed only in the $PhMeSiD_2$ case, and this secondary silane is the only one that produces oligomers with chain lengths longer than the trisilane. Future directions in catalyst development will need to address the problem of steric inhibition in the condensation process.

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