

## Dehydrogenative Coupling of Diarylsilanes

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The condensation of dihydrosilanes to disilanes and short-chain oligomers in the presence of transition-metal catalysts has been observed for a series of dibenzosilacycles that are related to  $\text{Ph}_2\text{SiH}_2$  through the joining of the phenyl rings in the ortho position by a methylene group (dihydrosilaanthracene, I), an ethano group (dihydrodibenzosilolepin, II), or a bond (silafluorene, III). The successful conversion of these secondary silanes to disilanes or short-chain oligomers was accomplished with both  $\text{ClRh}(\text{PPh}_3)_3$  and  $\text{Cp}_2\text{M}(\text{MMe}_2)$  ( $\text{M} = \text{Ti}, \text{Zr}$ ). Under the same conditions and time periods the percent conversion of starting material to condensed products with  $\text{ClRh}(\text{PPh}_3)_3$  followed the order: III (100%), I (83%),  $\text{Ph}_2\text{SiH}_2$  (59%), II (10%). The chain length of the major oligomers formed is also a function of the silacycle with at least tetrasilane formed from III, trisilane and disilane from I, and disilane from II and  $\text{Ph}_2\text{SiH}_2$ . With rhodium catalysts siloxanes are produced either on exposure of reaction mixtures to oxygen or on the silica gel columns used to remove catalyst residues. Similar oxygenation problems were not encountered with the metallocene catalysts. Possible mechanisms for dehydrogenative coupling are discussed.

## Introduction

The most common method for silicon-silicon bond formation involves the condensation of a chlorosilane with an active metal such as lithium or sodium, a reaction that is analogous to Wurtz coupling.<sup>1</sup> The potential applications of catenated silicon derivatives motivates a search for alternatives to this synthetic method. In addition to the fact that some organic substituents are not compatible with Wurtz coupling conditions there are also some classes of catenated compounds that are not directly or readily accessible through this route. These classes primarily include short chains with terminal functional groups and most 1,2-difunctional disilanes. In some cases it is possible to condense  $\text{RR}'\text{SiXCl}$  ( $\text{X} = \text{functional groups}$ ) to a disilane as is the case for  $\text{Ph}_2\text{SiHCl}$ ,<sup>2</sup> but the reaction can also lead to more complex products involving reaction of both functional groups. Although specific  $\alpha,\omega$ -functional oligomers can be obtained from cleavage of cyclopolysilanes<sup>1,3</sup> and trisilanes have been formed from the condensation of  $\text{RR}'\text{SiHCl}$  with  $\text{RR}'\text{SiCl}_2$ ,<sup>4</sup> the processes are not clean.

Hydrosilanes are attractive precursors to oligomers since these compounds are usually air-stable and may be generated easily by reduction of chlorosilanes. The coupling of secondary silanes in the presence of Wilkinson's catalyst was reported in 1973,<sup>5</sup> but, surprisingly, there was little extension of this discovery until recently. Table I sum-

marizes the coupling of acyclic arylsilanes in the presence of transition-metal catalysts. There are several important observations from this table. The metallocenes  $\text{Cp}_2\text{MMe}_2$  are effective in producing long chains from primary silanes, but coupling appears to stop at the disilane stage for secondary silanes except at a temperature in excess of 100 °C. The low-valent late transition metals Rh(I) and Pt(0) promote coupling of hydrosilanes to short chains, but disproportionation reactions can provide significant quantities of byproducts, particularly in the case of alkylarylsilanes. Although none of the catalysts listed in Table I have been reported to couple tertiary silanes,  $\text{Et}_3\text{Si}_2$  has been observed as one of the products in reaction of  $\text{Et}_3\text{SiH}$  with a few of the catalysts studied by Brown-Wensley.<sup>11</sup>

In the presence of air or water some catalysts promote the conversion of silicon-silicon bonds to siloxanes.<sup>12,13</sup> Ultimately the goal to provide an alternative to Wurtz coupling through dehydrogenative coupling will require minimization of the competitive reactions of disproportionation and oxygenation in order to obtain useable quantities of products. Our preliminary study of Rh(I)-catalyzed condensation of 9,10-dihydrosilaanthracene (Figure 1,  $\text{X} = \text{CH}_2$ ) reported conditions that demonstrated not only how isolation could be achieved but also the first trisilane produced from a diarylsilane derivative.<sup>13</sup>

Catenated derivatives in which the silicon center is part of a heterocycle are rare. Cyclopolysilanes have been obtained from the condensation of 1,1-dichlorosilacycloalkanes,<sup>14</sup> but examples that would include the equivalent of aryl groups as in the framework of Figure 1 are essentially nonexistent. Gilman and Gorsich reported the condensation of 5-chloro-5-alkyl-silafluorene to the disilane, but an attempt to generate 1,2-difunctional disilanes from reaction of *o,o'*-dilithiobiphenyl with hexachlorodisilane gave 5,5'-spiro[dibenzosilole] and biphenyl as the only isolated products.<sup>15</sup>

In this report we describe in detail reactions of secondary silanes of the type shown in Figure 1 in the presence of both Wilkinson's catalyst and  $\text{Cp}_2\text{MMe}_2$ . Our ultimate

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
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Table I. Coupling of Arylsilanes in the Presence of Transition-Metal Catalysts

cat.	silane	S/T/t			others	ref
			R	x (%)		
Cp <sub>2</sub> TiMe <sub>2</sub>	PhSiH <sub>3</sub>	C <sub>7</sub> H <sub>8</sub> /room temp/168 h	H	10 (88%) <sup>a</sup>		6
	Ph <sub>2</sub> SiH <sub>2</sub>	<i>b</i>	Ph	2		7
	PhMeSiH <sub>2</sub> <sup>c</sup>	C <sub>7</sub> D <sub>8</sub> /30 °C/ <i>b</i>	Me	2 ( <i>d</i> )		8a
Cp <sub>2</sub> TiPh <sub>2</sub>	PhMeSiH <sub>2</sub>	neat/110 °C/25 h	Me	2 (14)		8b
		<i>e</i> /110 °C/24 h	Me	3 (32)		
			Me	2 (7)		8b
Cp <sub>2</sub> ZrMe <sub>2</sub>	PhSiH <sub>3</sub>	<i>b</i>	H	20 ( <i>d</i> )		9a
	Ph <sub>2</sub> SiH <sub>2</sub>	<i>b</i> /65 °C/ <i>c</i>	Ph	2 ( <i>d</i> )		9b
ClRhL <sub>3</sub> <sup>f</sup>	PhSiH <sub>3</sub>	neat/80 °C/1 h	H	2 ( <i>d</i> )	HPh <sub>2</sub> SiSiPhH <sub>2</sub> ( <i>d</i> )	5
	Ph <sub>2</sub> SiH <sub>2</sub>	neat/80 °C/1 h	Ph	2 (38)	Ph <sub>3</sub> SiH (8%)	5
	PhMeSiH <sub>2</sub>	neat/70 °C/1 h	Me	2 (14)	Ph <sub>2</sub> MeSiH (30%)	5
				3 (30)		
PtL <sub>2</sub> C <sub>2</sub> H <sub>4</sub> <sup>f</sup>	Ph <sub>3</sub> SiH	C <sub>6</sub> H <sub>6</sub> /room temp/15 h			LRhH(SiPh <sub>3</sub> )Cl ( <i>d</i> )	10
	PhMeSiH <sub>2</sub>	neat/18 °C/75 h	Me	2 (27) <sup>g</sup>	Ph <sub>2</sub> MeSiH (52%) <sup>f</sup>	11

<sup>a</sup> Average degree of polymerization (% yield calculated on the basis of this oligomer from data given in the reference). <sup>b</sup> Condition or conditions not specified. <sup>c</sup> Olefin must be present for reaction to proceed. <sup>d</sup> Yield not specified. <sup>e</sup> Cyclooctene added. <sup>f</sup> L = PPh<sub>3</sub>. <sup>g</sup> Yields reported as percentage of total products.

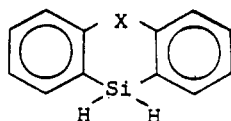
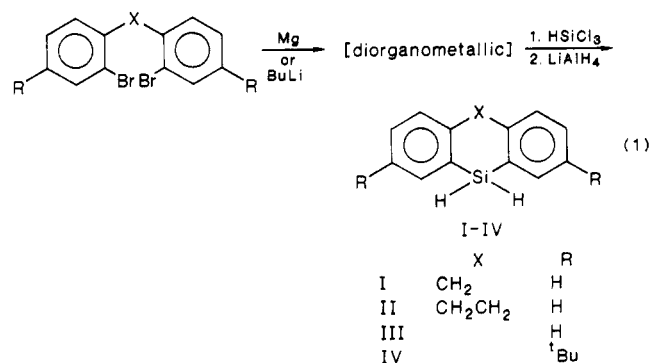


Figure 1.

objective is to prepare useful quantities of short-chain oligomers with terminal functionality as well as to develop catalyst systems useful for the condensation of diaryldihydrosilanes. The condensation of dibenzosilacycles (Figure 1) provides short chains and changes in the central ring size permit a variation in the steric requirement of the starting secondary silane.

## Results

**Synthesis of Monosilanes.** The basic route to the dihydrosilanes involves the reaction of a diorganometallic with trichlorosilane followed by reduction with lithium aluminum hydride (LAH) as shown in eq 1. Although the



formation of II has been reported previously from the dilithio reagent,<sup>12</sup> the preparation through the diGrignard provides material that is more easily purified. Heterocycles I and IV are also best prepared through the Grignard reagents. The lithium exchange and/or the coupling with the chlorosilane for II and IV are surprisingly sluggish and give substantial quantities of impurities that incorporate the butyl group from the butyllithium used for the lithium-halogen exchange with the arylbromide precursor.<sup>12,16</sup>

All the secondary silanes used in this study contained less than 10% impurities although larger quantities of impurities do not interfere with the coupling reaction.

**Coupling Reactions with Rh(I).** Reaction of I and II in toluene with Wilkinson's catalyst in the absence of air gave disilanes and trisilanes in varying ratios depending on a number of factors. Removal of the catalyst was accomplished in a drybox by filtering product mixtures through a short silica gel column. Disiloxane and trisiloxane side products were also isolated in some cases. Products were separated by preparative, centrifugally accelerated, radial, thin-layer chromatography, and the general reaction results are summarized in eq 2. The isolated oligomers except for the trisiloxanes were obtained as pure solids. Key spectroscopic data for products produced from I and II are summarized in Table II.

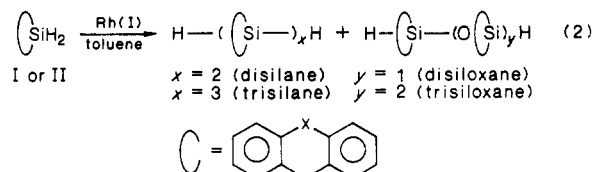


Table II shows that the SiH as well as the CH<sub>2</sub> resonances in I and its products are well separated; therefore analysis of reaction mixtures by <sup>1</sup>H NMR spectroscopy after removal of the catalyst was possible without separation of the individual products. Several factors were observed to influence the results of the coupling reaction of I, and these included concentration, catalyst/silane ratio, temperature, and scale as summarized in Table III. In the preliminary study<sup>13</sup> it was shown that when the molar ratio of Rh/SiH<sub>2</sub> exceeded about 7 × 10<sup>-3</sup>, significant reaction of the product mixture with the silica gel column occurred during the workup procedure (as an example see run 1, Table III), and when the ratio is too small (run 3, Table III), the coupling reaction proceeds slowly increasing the possibility of a slow oxygen leak. The best compromise for reaction of I occurred at a Rh/Si ratio of about 4 × 10<sup>-3</sup> and approximately 1 M silane in toluene. Higher temperatures favored the formation of trisilane as shown by comparison of run 2 with runs 4 and 7 (Table III). When the scale of the reaction is doubled, it was found necessary to conduct room-temperature reactions in sealed tubes to prevent slow reaction with oxygen. These longer reaction

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Table II. Spectroscopic Data for Secondary Silane Starting Materials and Products of Condensation Reactions

	<sup>1</sup> H NMR <sup>a</sup>		<sup>29</sup> Si NMR <sup>a</sup>	IR, <sup>b</sup> cm <sup>-1</sup>	
	SiH	X		SiH	other
I (X = CH <sub>2</sub> ) <sup>c</sup>					
I	4.80	4.08 (s)	-52.32	2120 (st) 2175 (st)	
D	5.05	3.71 (AB, q)	-53.25	2120 (st)	480 (s) <sup>d</sup>
D <sub>o</sub>	5.55	4.01 (br, s)	-31.05	2160 (st) 2180 (sh)	1030 (s, br) <sup>e</sup>
T	5.14	3.41 (s) 3.65 (AB, q)	-49.59 -60.23	2090 (st) 2120 (st)	480 (s) <sup>d</sup>
[T <sub>o</sub> ] <sup>f</sup>	5.52	3.84 (s) 3.92 (s)	-32.51 -48.50	2140 (st)	1030-1130 (br) <sup>e,g</sup>
II (X = CH <sub>2</sub> CH <sub>2</sub> ) <sup>c</sup>					
II	5.04	3.21 (s)	-36.2	2140 (st, br)	
D	5.02	2.83 (s)	-31.91	2100 (st)	470 (st) <sup>d</sup>
D <sub>o</sub>	5.66	3.17 (m) <sup>h</sup>	-19.33	2110 (st)	1100 (st) <sup>e</sup>
[T <sub>o</sub> ] <sup>f</sup>	5.60	3.04 (s) 3.09 (m)	-20.34 -43.65	2130 (st, br)	970-1100 (br) <sup>e,g</sup>

<sup>a</sup>Data determined from isolated samples in CDCl<sub>3</sub> with Me<sub>4</sub>Si as internal standard. Abbreviations: s, singlet; q, quartet; br, broad. <sup>b</sup>KBr disk, except where specified otherwise. Abbreviations: st, strong; br, broad. <sup>c</sup>Abbreviations: D, disilane; D<sub>o</sub>, disiloxane; T, trisilane; T<sub>o</sub>, trisiloxane. <sup>d</sup>Sharp bands in this region are assigned to SiSi and SiPh by analogy to Ph(Ph<sub>2</sub>Si)<sub>3-5</sub>H.<sup>17</sup> <sup>e</sup>Si-O-Si. <sup>f</sup>Tentative assignment. <sup>g</sup>Thin film. <sup>h</sup>Center of complex multiplet.

Table III. Dehydrogenative Coupling of Dibenzosilacycles

silane, g	Rh(I) <sup>a</sup>	[Si] <sup>b</sup>	time, h/temp, °C	wt % <sup>c</sup>				% recovery <sup>d</sup>
				SM	D	D <sub>o</sub>	T	
9,10-Dihydrosilaanthracene (I)								
1	0.40	0.8	16/25	9	12	24	35	82
2	0.51	0.4	10/25	17	38	3	42	100
3	0.50	0.2	20/25	65	15	10	10	100
4	0.50	0.4	1.5/82	7	17	9	66	100
5	1.03	0.4	96/25 <sup>e</sup>	19	13	3	65	100
6	1.03	0.4	1.5/85	20	36	20	20	96
7	1.00	0.4	neat	19	21	2	58	100
10,11-Dihydrodibenzo[b,f]silepin (II)								
8	0.68	0.5	37 [2]/25 <sup>f</sup>	74	26	...	...	100
9	0.46	1.3	6 [12]/25 <sup>f</sup>	35	65	...	...	100
10	0.35	2.6	6/85	34	68	...	...	100
11	0.37	0.9	neat	23	48	12	17 <sup>g</sup>	100 <sup>h</sup>
12	0.54	1.9	neat	31	56		6	93
Dihydrosilafluorene (III)								
13	0.65	0.2	1/25	66				66
14	0.58	0.4	neat	12				12

<sup>a</sup>Mole percent of ClRh(PPh<sub>3</sub>)<sub>3</sub> based on silane. <sup>b</sup>Concentration in toluene. <sup>c</sup>Based on weight of starting material. Abbreviations: SM, starting material; D, disilane; D<sub>o</sub>, disiloxane; T, trisilane. Percentages are computed from the integration of the SiH resonances in the <sup>1</sup>H NMR spectrum (300 MHz) of material obtained after removal of the catalyst. <sup>d</sup>After removal of catalyst. <sup>e</sup>Sealed tube. <sup>f</sup>Time in brackets is period under vacuum. <sup>g</sup>Product is a mixture of trisilane and trisiloxane. <sup>h</sup>product distribution determined from isolated material. <sup>i</sup>Followed by 9 h at 25 °C.

periods also favored the formation of trisilane.

To determine the effect of changing the central ring size on the condensation reaction, II and III were reacted with ClRh(PPh<sub>3</sub>)<sub>3</sub>. Although the ethano bridge proton resonances in II and the disilane product are separated, when siloxane products are produced, the spectrum is too complex and the distribution was determined from isolated products. The results under various conditions are also summarized in Table III. The major product from the reaction of the silepin is the disilane even at the higher temperatures that favored trisilane formation from I. The reactions of II were found to require higher Rh:Si ratios and higher concentrations of hydrosilane. Good results are obtained by running reactions neat under vacuum or at higher temperatures.

In contrast, when Wilkinson's catalyst is added to silafluorene rapid, evolution of hydrogen occurs and an insoluble precipitate forms within 30 min. The insoluble material, when first prepared, exhibits Si-H (2140 cm<sup>-1</sup>) and SiSi (480 cm<sup>-1</sup>) bands in the IR spectrum. On standing in air siloxane is slowly formed as evidenced by the

presence of SiOSi bands in the 1000 cm<sup>-1</sup> region. Even if the Rh:silane ratio was reduced and workup initiated at the point when insoluble material forms, the only component that was isolated was unreacted starting material (66%).

The reaction of tertiary silanes related to III with Wilkinson's catalyst was briefly examined. After 70 h at room temperature 9-hydro-9-methyl-9-silafluorene did not react and starting material was recovered. Reaction of 9-hydro-9-alkoxy-9-silafluorene occurs, but the only isolated products were 9,9-dialkoxy-9-silafluorene and the related 1,2-dialkoxydisiloxane. It appears that some disproportionation may occur in this system.

**Coupling Reactions with Other Catalysts.** The reactions of I, II, and III with Cp<sub>2</sub>MMe<sub>2</sub> and with an additional Rh(I) derivative are summarized in Table IV. No reaction of I occurs with either Cp<sub>2</sub>TiMe<sub>2</sub> or Cp<sub>2</sub>ZrMe<sub>2</sub> at room temperature. However, the zirconium derivative provided high yields of trisilane from I at 90 °C, but no reaction occurred at this temperature with II. As indicated in Table I only the disilane was obtained from the related

Table IV. Reactions of Dibenzosilacycles with Ti, Zr, and Rh Catalysts

cat.	silane	[cat.] <sup>a</sup>	T, h/t, °C	SM, %	product distributn <sup>b</sup>	
					H(-Si-) <sub>x</sub> H (%)	H(-SiO-) <sub>y</sub> H (%)
CiRhL <sub>3</sub> <sup>c</sup>	I	0.4	10/25	17	2 (38); 3 (42)	2 (3)
[Rh(COD)L <sub>2</sub> ]PF <sub>6</sub> <sup>c</sup>	I	0.4	37/25	18	...	2 (33) 3 (31) <sup>d</sup>
Cp <sub>2</sub> TiMe <sub>2</sub>	I	3.8	168/25	100		
	III	1.0	29/25	0	≥4 (100) <sup>e</sup>	
Cp <sub>2</sub> ZrMe <sub>2</sub>	I	0.6	22/25	100		
		9.0	10/90	1	2 (12); 3 (87)	
	II	6.0	100/90	100		
		8.0	72/105	27	2 (20) <sup>f</sup>	

<sup>a</sup> Mole percent of catalyst based on silane. Reactions were performed on approximately 0.5 g of starting silane in toluene. <sup>b</sup> Quantitative mass recovery except where noted. Product distribution is based on weight percent relative to the starting weight of silane. <sup>c</sup> L = PPh<sub>3</sub>. <sup>d</sup> 85% recovery based on starting silane. <sup>e</sup> Based on *m/e* data. See Experimental Section. <sup>f</sup> 52% of oligomer(s) that could not be identified.

acyclic model, Ph<sub>2</sub>SiH<sub>2</sub> with Cp<sub>2</sub>ZrMe<sub>2</sub>. After addition of Cp<sub>2</sub>TiMe<sub>2</sub> to silafluorene, a precipitate begins to form within an hour, but consumption of starting material required about 29 hours. The precipitate, insoluble in all solvents attempted, exhibited infrared bands in the region characteristic of SiH and SiSi and appears to be pentasilane (or higher) according to the mass spectrum.

### Discussion

The heterocyclic dihydrosilanes (Figure 1) are related to Ph<sub>2</sub>SiH<sub>2</sub> by connecting the two phenyl groups in the position ortho to silicon by a bond, a methylene group, or an ethano bridge to give III, I, and II, respectively. In this series the central ring size increases from five through seven and the framework structure varies from planar (III) to folded butterfly (I) to folded and twisted (II) as the central ring increases in size.<sup>18</sup> Thus, the steric requirement of these dibenzosilacycles is expected to increase through the series.

The heterocyclic secondary silanes were successfully converted to short-chain oligomers by selected transition-metal catalysts. All the new silicon-silicon bonded compounds were fully characterized except for the products obtained in the condensation of silafluorene (III and IV). The major oligomer that is formed involves a number of factors including catalyst type and the nature of X (Figure 1). Byproducts in the coupling reaction are siloxanes that can arise from reaction on the silica gel during workup or by insertion of dioxygen into the silicon-silicon bonds of the oligomers during the reaction. The disiloxanes are easily characterized crystalline solids, but the trisiloxanes were gums that could not be completely purified. The trisiloxane structure is inferred from mass spectral data as well as the following features of the <sup>1</sup>H NMR spectra: a, HSi resonances downfield of the silicon-silicon bonded oligomers and in the region associated with HSiOSi units; b, two distinct bridging methylene proton resonances in the products from I and two distinct regions for the ethano bridge in products from III, both of which are expected on the basis of the two different ring systems associated with the central silicon vs the terminal silicon. The <sup>29</sup>Si spectra exhibit two silicon resonances, one of which is closely related to that observed in the disiloxane counterparts.

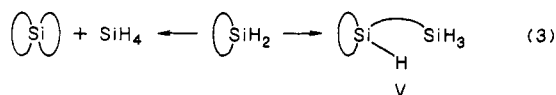
Addition of Wilkinson's catalyst to silafluorene III results in rapid evolution of hydrogen at room temperature. A precipitate forms within 30 min, and distillation pro-

vided unreacted starting material (12%) as the only volatile material. The residue exhibits infrared bands at 2140 (SiH) and 480 cm<sup>-1</sup> (Si-Si), melts higher than 400 °C, and is insoluble in all common organic solvents. On exposure to air SiOSi bands appear in the IR spectrum and the mass spectrum exhibits fragments that correspond to (C<sub>12</sub>H<sub>8</sub>-SiO)<sub>n</sub> (n = 1-4). An attempt to slow the reaction by using solvent, lowering the catalyst ratio, and filtering reaction mixtures through silica gel when the precipitate first forms resulted only in recovery of unreacted starting material. When Cp<sub>2</sub>TiMe<sub>2</sub> was used as a catalyst, a similar insoluble product was formed. The major fragments observed in the mass spectrum corresponded to (C<sub>12</sub>H<sub>8</sub>Si)<sub>x</sub> (x = 1-5). Although perphenylpolysilanes are insoluble, when alkyl substituents are present on the phenyl, solubility in common solvents is achieved. An attempt was made to incorporate substituents into III to form more soluble products. The only readily accessible dialkyl-substituted silafluorene, IV, also reacts with Wilkinson's catalyst very rapidly, and within 30 min the signals due to the starting SiH<sub>2</sub> are barely discernible. After filtering through a short silica gel column in the drybox, the mass recovery corresponded to 73% of the weight of the original starting material. The product exhibited two <sup>t</sup>Bu resonances in the <sup>1</sup>H NMR spectrum and contained a strong SiH band at 2150 cm<sup>-1</sup> but no SiOSi band in the infrared spectrum. However, during the purification step (radial chromatography) the majority of the material adhered to the silica gel and could not be eluted even when methanol.

Short-chain oligomers based on silafluorene units may have unusual properties that could not be anticipated on the basis of analogy to the disilanes and trisilanes generated from I and II; therefore attempts were made to prepare disilanes based on the silafluorene unit by Wurtz coupling routes. When 9-chlorosilafluorene was reacted with Li in THF, at least 11 products were generated that could not be separated. There is some circumstantial evidence that disilanes and trisilanes are formed on the basis of molecular ions in the mass spectra generated from solids obtained during chromatographic workup, but these materials constitute less than 10% by weight of the product mixtures. Small amounts of mixtures of disilane and disiloxane were also obtained when K in refluxing cyclohexane or Mg in refluxing THF was reacted with 9-chlorosilafluorene. The disilane, dissolved in chloroform, was easily converted to the disiloxane by bubbling air through the solution. This simple experiment demonstrates that insertion of oxygen into silicon-silicon bond occurs more readily in oligomers of III than in those formed from I and II and may account for some of the difficulty in attempts to isolate the products generated from III or IV.

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In contrast to the results observed for the reaction of acyclic secondary silanes (see Table I), the heterocyclic derivatives that are the subject of this study did not exhibit detectable redistribution reactions in the presence of  $\text{ClRh}(\text{PPh}_3)_3$ . Possible redistribution reactions include ring opening (equivalent of the exchange of one aryl group and one SiH bond) and production of an  $-\text{SiH}_3$  substituent with no loss of mass (general structure V in eq 3). A second possibility involves the formation of spiro derivatives and elimination of  $\text{SiH}_4$  in which case some silicon would be lost and mass recovery should be less than quantitative. These possibilities are summarized in eq 3. An  $\text{SiH}_3$



grouping would be expected to have a chemical shift between  $\delta$  4.0 and 4.2,<sup>19</sup> and the high melting, easily crystallized spiro derivatives<sup>20</sup> should be discernible by the NMR methods used to monitor the reactions or the products obtained during the separation procedures.

**Catalyst Systems.** Only one attempt was made to alter substituents in the Rh(I) catalyst. When  $[\text{Rh}(\text{COD})\text{L}_2]\text{PF}_6$  was used, considerable oxygenation occurred during the workup process developed for runs that employed Wilkinson's catalyst. The rhodium-carbene catalyst  $[\text{Cl}(\text{PPh}_3)_2\text{Rh}=\text{CN}(\text{Me})(\text{CH}_2)_2\text{NMe}]$ , which has been used to couple  $\text{Ph}_2\text{SiH}_2$  to the disilane also causes oxygenation of the silicon-silicon bond if air is not excluded during the workup procedure.<sup>24</sup> In a preliminary study of 11 catalysts that promoted coupling of  $\text{Et}_2\text{SiH}_2$  to the disilane side reactions with oxygen and water were also observed.<sup>11</sup>

The metallocene complexes  $\text{Cp}_2\text{MMe}_2$  ( $\text{M} = \text{Ti}, \text{Zr}$ ), which are not particularly effective for coupling acyclic secondary silanes, produced mixed results in the heterocyclic derivatives that are the subject of this report. The titanocene derivative promotes reaction with the least sterically demanding system III to provide oligomers longer than trisilanes, but the results could not be consistently reproduced. No reaction of I occurred in the presence of  $\text{Cp}_2\text{TiMe}_2$  even after 1 week. The results with I are similar to those reported for  $\text{Ph}_2\text{SiH}_2$ . The less bulky secondary silane  $\text{PhMeSiH}_2$  reacts with the titanocene catalyst only when cyclohexene is present.<sup>8</sup> However, a high conversion of I to disilane and trisilane occurred with  $\text{Cp}_2\text{ZrMe}_2$ . The surprising feature with this catalyst was the fact that the major product from I is the trisilane whereas II does not even react under similar conditions. When the temperature is increased, II forms disilane as well as other products that could not be identified.

There are two major problems in using  $\text{ClRh}(\text{PPh}_3)_3$  as a dehydrogenative coupling catalyst. The catalyst promotes oxygenation of the Si-Si bonds to siloxanes if workup is conducted in air. Although workup can be performed in a drybox, the difficulty of removing the catalyst still exists. Attempts to chemically react the

**Table V. Comparison of Dehydrogenative Coupling of Secondary Silanes with Wilkinson's Catalyst under Similar Conditions**

silane <sup>a</sup>	products, <sup>b</sup> %				other
	SM	D	D <sub>o</sub>	T	
$\text{Ph}_2\text{SiH}_2$	41	48			$\text{Ph}_3\text{SiH}$ (11%)
I	17	38	3	42	
II	90	10			
III	0				oligomer(s) <sup>c</sup>
IV	0				oligomer(s) <sup>c</sup>

<sup>a</sup> [Silane] = 1.0 M; Rh catalyst = 0.4 mol % relative to silane; T = 25 °C; t = 10 h. <sup>b</sup> Abbreviations: SM, starting material; D, disilane; D<sub>o</sub>, disiloxane; T, trisilane. <sup>c</sup> Unknown chain length but at least tetrasilane.

catalyst with either gaseous HCl or *m*-chloroperbenzoic acid, MCPBA, without destroying the oligomers were not successful. The only method that was successful, filtering reaction mixtures through short silica gel columns, can produce siloxanes if the catalyst ratios are too high. Another aspect is that conditions which maximize conversion of one secondary silane may not be favorable for another. This is demonstrated in Table V where the reactions of  $\text{Ph}_2\text{SiH}_2$ , I, II, III, and IV are compared under the same conditions. The results for  $\text{Ph}_2\text{SiH}_2$  reported in the literature were without solvent but are similar to those we obtained in toluene. Under these conditions the observed conversion of the silane is as follows: III and IV, 100%; I, 83%;  $\text{Ph}_2\text{SiH}_2$ , 59%; II, 10%. The reactivity of these five silanes at room temperature follows the order III, IV > I >  $\text{Ph}_2\text{SiH}_2$  > II. When two freely rotating phenyl groups of  $\text{Ph}_2\text{SiH}_2$  are tied in the ortho position by a bond, dehydrogenative coupling is very rapid and essentially complete within an hour. Introduction of one methylene group between the two phenyls produces a ring system that reacts more slowly than silafluorene and provides 80% of coupling product as compared to 48% for  $\text{Ph}_2\text{SiH}_2$  under the same conditions. Surprisingly, the reaction of the seven-membered ring system ( $\text{CH}_2\text{CH}_2$  links the two phenyl groups) is slower than that of I which may imply a steric requirement for II that is greater than that for  $\text{Ph}_2\text{SiH}_2$ . These results demonstrate that optimum conditions for conversion of secondary silane to dehydrogenative coupling products will most likely have to be determined for each system. The balance will require combining catalyst to silane ratio, concentration, temperature, and scale for the best conversion. Larger scale runs or slow reactions are best conducted in sealed tubes (see runs 5 and 7, Table III). The use of a hydrogen acceptor such as cyclohexene does not appear to be useful in promoting the coupling of II, but running the reaction under conditions where  $\text{H}_2$  is removed seems to be successful although this approach is certainly limited in the number of systems where this would be applicable.

**Comments on the Mechanism.** This study has demonstrated that dehydrogenative coupling can be a useful method for generating disilanes and trisilanes from secondary silanes. How the products are formed is a matter of conjecture since both oxidative addition and silylene mechanisms have been described for this reaction. In the original report of the coupling of hydrosilanes by Wilkinson's catalyst a silylene complex,  $>\text{Si}-[\text{Rh}]$  (where  $[\text{Rh}]$  may be  $\text{ClRhL}_2$ ), was proposed to deliver silylene to SiH bonds.<sup>5</sup> Presumably this process occurs successively to increase the chain length. The silylene complex is formed by oxidative addition of  $\text{R}_2\text{SiH}_2$  to  $[\text{Rh}]$  followed by elimination of dihydrogen. If the coordinatively unsaturated Rh species that undergoes the oxidative addition is formed by loss of L from  $\text{ClRhL}_3$ , then addition of L would be

(19) Model compounds  $\text{PhSiH}_3$  and *o*- $\text{PhC}_6\text{H}_4\text{SiH}_3$  have chemical shifts of  $\delta$  4.22 and 4.0, respectively.

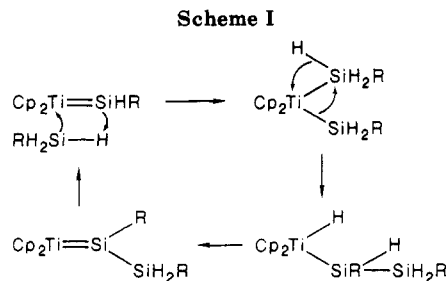
(20) Characteristics of spiro derivatives (mp;  $(\text{CH}_2)_x$  <sup>1</sup>H resonance): 5,5'-spiro[dibenzosilole] (225–227 °C; ...);<sup>21</sup> 9,9'-spirobi-9,10-dihydro-9-silaanthracene (242 °C;  $\delta$  4.15);<sup>22</sup> 5,5'-spirobi-10,11-dihydro[*b,f*]dibenzosilolepin (171 °C;  $\delta$  2.90).<sup>23</sup>

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expected to suppress the dehydrogenative coupling reaction. However, Brown-Wensley has shown that addition of  $\text{PPh}_3$  actually increases the number of moles of disilane produced.<sup>11</sup> Although features of the original mechanism may be involved in the dehydrogenative coupling, a Rh(I) derivative may not be the reactive species that undergoes the oxidative addition.<sup>25</sup>

The mechanism for the coupling of primary silanes with  $\text{Cp}_2\text{TiMe}_2$  proposed by Harrod also involves a silylene complex,  $\text{Cp}_2\text{Ti}=\text{SiRR}'$ , which could be formed by  $\alpha$ -hydride elimination from  $\text{Cp}_2\text{Ti}(\text{H})\text{SiHRR}'$ .<sup>6</sup> The steps favored by Harrod are shown in Scheme I. Since Harrod did not observe oligomers above the disilane stage from secondary silanes, such a mechanism could account for the observed results.

However, since trisilane is produced from I and  $\text{Cp}_2\text{ZrMe}_2$  and recently observed in the coupling of  $\text{PhMeSiH}_2$  with  $\text{Cp}_2\text{TiPh}_2$ , either another mechanism is operative for the zirconium system (and  $\text{Cp}_2\text{TiPh}_2$  at high temperature) or another process is required for reaction of secondary silanes. Alternatively, trisilanes may be formed from the coupling of a monosilane and a disilane (possibly through a silylene complex) or from disproportionation of the disilane in the presence of a metal species. Disproportionation of  $\text{H}(\text{SiMe}_2)_x\text{H}$  in the presence of  $(\text{Et}_3\text{P})_2\text{PtCl}_2$  at 90 °C has been reported, but the mechanistic details are unknown.<sup>26</sup> To test for the possibility of disproportionation as the source of trisilane, the disilane generated from I was heated under conditions specified in run 4, Table III. Under these conditions only 7% conversion of disilane to trisilane and I was observed. Therefore, disproportionation cannot be the only process that leads to trisilane. A similar reaction of the disilane from II showed that trisilane may be formed, but no monosilane was detected.

Silylene-metal complexes have been isolated only recently, and all have been isolated as the base complex (solvent is coordinated to the silicon center of the silylene).<sup>27</sup> No attempts to add hydrosilanes to these new complexes has yet been reported. It is entirely possible that base-free metal-silylene complexes will be required to promote the dehydrogenative coupling reaction. Harrod has also suggested that metallocenes  $\text{Cp}_2\text{M}$  are formed from  $\text{Cp}_2\text{MMe}_2$ , and it is this species that reacts with hydrosilane to initiate the dehydrogenative coupling cycle. We have begun to investigate the feasibility of generating  $\text{Cp}_2\text{Zr}$  under conditions similar to those reported by Negishi<sup>28</sup> but with toluene instead of a coordinating solvent.

Our preliminary results with  $\text{PhMeSiH}_2$  have thus far shown that disilanes through pentasilanes are formed (and possibly higher oligomers) in what appears to be a stepwise fashion, but we have been unable to determine as yet whether metal-silylenes are involved.<sup>29</sup>

**Summary.** Dehydrogenative coupling of secondary silanes can lead to small oligomers. Wilkinson's catalyst, which was the best dehydrogenative coupling catalyst of the 11 examples studied by Brown-Wensley for condensation of  $\text{Et}_2\text{SiH}_2$ , works reasonably well for diarylsilanes but promotes significant disproportionation for alkylarylsilanes. The ratio of disproportionation to coupling was about 2:1 for  $\text{PhMeSiH}_2$  with the Pt(0) catalyst listed in Table I.<sup>11</sup> The additional disadvantage of these heavy late-transition-metal catalysts is the ability to promote oxygenation of the silicon-silicon bonds which makes workup considerably more tedious. The metallocene complexes of Ti and Zr do not appear to promote either oxygenation or disproportionation side reactions and simple workup in air is possible. The disadvantage of  $\text{Cp}_2\text{ZrMe}_2$  is that it is unstable with a short shelf life and not commercially available. However, our recently reported alternative of the combination of  $\text{Cp}_2\text{ZrCl}_2/\text{BuLi}$  overcomes this disadvantage, and we are pursuing this catalyst precursor combination in current studies.<sup>29</sup>

Dehydrogenative coupling provides a good alternative to Wurtz coupling for the formation of functional disilanes and trisilanes that are currently available for only a limited number of systems. The ready availability of 1,2-difunctional disilanes may provide alternative routes to disilanes, and the possibility exists that the 1,3-functional trisilanes can be converted to cyclotrisilanes as has been demonstrated in the synthesis of  $[(^t\text{Bu})_2\text{Si}]_3$ .<sup>3</sup>

## 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 Atmosphere HE-43 drybox. Solvents were dried by using standard techniques, and all glassware was rinsed in acid and thoroughly dried in an oven at 110–120 °C prior to use. The silica gel was dried at 200 °C. The following compounds were prepared by literature methods:  $\text{ClRh}(\text{PPh}_3)_3$ ,<sup>30</sup>  $[\text{Rh}(\text{COD})(\text{PPh}_3)_2]\text{PF}_6$ ,<sup>31</sup>  $\text{Cp}_2\text{TiMe}_2$ ,<sup>32</sup> and  $\text{Cp}_2\text{ZrMe}_2$ .<sup>33</sup>

<sup>1</sup>H NMR spectra were recorded on a Varian T-60 spectrometer and <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si on a Varian XL-300 multinuclear spectrometer. The <sup>1</sup>H and <sup>29</sup>Si are summarized in Table II. The relaxation agent  $\text{Cr}(\text{acac})_3$  (10 mg) was added for <sup>29</sup>Si NMR spectra. Unless specified otherwise, data were collected in  $\text{CDCl}_3$  with TMS as the internal standard. Mass spectral data were collected at 70 eV on an AEI MS-1201B mass spectrometer. Infrared spectra were determined on a Perkin-Elmer Model 783 as KBr disks. Kugelrohr distillation was employed in all vacuum distillations. Separations were carried out on a Chromatotron (Harrison Research Model 7924T) with Kieselgel ( $\text{SiO}_2$ -60) plates, unless otherwise specified.

Analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

**Bis(o-chlorophenyl)methane.** A modification of the published procedure was used.<sup>22a</sup> The reduction of bis(o-chlorophenyl)carbinol was conducted with hydriodic acid (56%) in acetic acid/acetic anhydride mixtures. Solutions are stirred for 15 h at room temperature and then heated at reflux for 2 h after which workup was conducted as described by Jutzi. The bis(o-chloro-

(25) For example, reduction of PtCl bonds by hydrosilanes has been reported by: Lewis, L. N.; Lewis, N. *J. Am. Chem. Soc.* **1986**, *108*, 7228.

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phenyl)methane produced by this preparative modification is sometimes accompanied with varying quantities of the solid acetate, (*o*-ClC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CH(O<sub>2</sub>CCH<sub>3</sub>), mp 135–136 °C (lit.<sup>22b</sup> mp 137–138 °C). The acetate can also be reduced.

To a solution containing the acetate (29.1 g, 99 mmol) in acetic acid (85 mL) and acetic anhydride (130 mL) was added a solution of HI (56%, 54.5 g) dropwise over a 1-h period. The reaction mixture was stirred at room temperature for 0.5 h followed by reflux for 5 h after which the cooled solution was poured into aqueous sodium bisulfite. The resultant solution was extracted with ether, and after removal of ether the residue was distilled to give bis(*o*-chlorophenyl)methane (23.5 g, 100%), bp 108–118 °C (0.2 mmHg) [lit.<sup>22</sup> bp 112–115 °C (0.1 mmHg)].

**9,9-Dihydrosilafluorene (III).** Silafluorene was prepared by the literature method.<sup>16</sup> After workup, distillation of the residue provided 9,9-dihydrosilafluorene: bp 85–95 °C (0.1–0.2 mmHg); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 4.73 (s, 1.8 H, SiH), 7.07–7.63 (m, 8.2 H, Ar). A GC analysis showed that the product contained silafluorene (90%) and biphenyl (10%). The impure silafluorene was used for dehydrogenative coupling studies. Crystallization from ether provided the silafluorene: mp 36–36.5 °C (lit.<sup>34</sup> mp 36.5 °C); IR (KBr disk) 2140 cm<sup>-1</sup> (SiH, st). The pot residue was recrystallized from ethyl acetate to give 5,5'-spirobi[dibenzosilole] (1.3 g, 30%): mp 225–227 °C (lit.<sup>21</sup> mp 227–229 °C); mass spectrum, *m/e* 332 (M<sup>+</sup>).

In an effort to improve the yield of III, 2,2'-dilithiobiphenyl, prepared from 2,2'-dibromobiphenyl (10 g, 32 mmol) and *n*-BuLi (46 mL, 1.55 M), was reacted with triethoxysilane (6 mL, 32 mmol) in the same manner. A solid residue was obtained (5.0 g), mp 195–220 °C, which provided 5,5'-spiro[dibenzosilole] (3.4 g, 63%), mp 225–227 °C, on washing with ethyl acetate.

**9-Methyl-9-hydro-9-silafluorene.** A slurry of magnesium (100 mesh, 8.6 g, 0.35 mol), *o,o'*-bromochlorobiphenyl (18.9 g, 0.070 mol), and a few drops of EDB in THF (125 mL) was stirred at reflux for 46 h. At room temperature methylchlorosilane (12 mL, 0.12 mol) in THF (125 mL) was added dropwise, and then the mixture was stirred overnight. After hydrolytic workup with saturated NH<sub>4</sub>Cl, Kugelrohr distillation of the residual oil obtained from the ether layer provided a fraction, bp 89–100 °C (0.5 mmHg) (9.4 g, 68%). A GC analysis showed that the sample contained 8% biphenyl. Trituration of the oil (1.37 g) with EtOH provided clear crystals (0.97 g) of the silafluorene, mp 39.5–40.5 °C (lit.<sup>35</sup> mp 41–42 °C); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.5 (d, 2.8 H, SiMe), 4.87 (q, 0.9 H, SiH), 7.1–7.6 (m, 8.3 H, arom); mass spectrum, *m/e* 196 (M<sup>+</sup>).

**3,6-Di-*tert*-butyl-9,9-dihydrosilafluorene.** a. **From the Grignard Reagent.** The Grignard reagent was prepared by heating 2,2'-dibromo-4,4'-di-*tert*-butylbiphenyl (10.5 g, 24.8 mmol) in THF (150 mL) with Mg (100 mesh, 8.2 g) and a few crystal of iodine at reflux for 2 days and cannulated into a pressure addition funnel. A second addition funnel was charged with HSiCl<sub>3</sub> (5 mL) in the same volume of THF, and the two solutions were added simultaneously to THF (300 mL). After completion of the addition, the mixture was stirred for 24 h and LiAlH<sub>4</sub> (1.5 g) added in two portions. After being stirred overnight, the slurry was cooled to -78 °C and hydrolyzed with NH<sub>4</sub>Cl (saturated) and the organic layer dried over MgSO<sub>4</sub>. The oil that remained after removal of the volatiles was distilled to give impure silafluorene, bp 135–150 °C (0.4 mmHg) (2.2 g, 62%), which solidified on standing. Recrystallization from EtOH gave 1.5 g, mp 98–101 °C. The GC analysis showed silafluorene (82%) and 4,4'-di-*tert*-butylbiphenyl (18%). A second recrystallization (0.3 g) with EtOH provided 0.1 g of platelike crystals, mp 98–99 °C, which still contained 4,4'-di-*tert*-butylbiphenyl (3%, GC): <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.36 (s, 17.9 H), 4.75 (s, 1.9 H), 7.24–7.78 (m, 8.2 H); <sup>13</sup>C δ 31.40, 34.70, 120.64, 127.87, 131.02, 131.06, 146.91, 149.94; mass spectrum, *m/e* 294 (M<sup>+</sup>). Samples were recrystallized twice for the dehydrogenative coupling studies.

b. **From the Dilithium Reagent.** To a stirred solution of 2,2'-dibromo-4,4'-di-*tert*-butylbiphenyl (3.0 g, 7.0 mmol) in a mixture of dry ether (23 mL) and THF (23 mL) at 0 °C was added

*n*-BuLi in hexane (9.5 mL, 1.6 M, 15 mmol) dropwise over a 1-h period. The reaction mixture was stirred at 0 °C at least 3 h and then warmed to room temperature overnight. The lithium reagent was cannulated into a pressure addition funnel, and HSiCl<sub>3</sub> (1.4 mL, 14 mmol) in THF-Et<sub>2</sub>O (30 mL/30 mL) was added to another pressure addition funnel. The two solutions were added simultaneously to THF-Et<sub>2</sub>O (60 mL/60 mL) and the resultant solutions stirred for 10 h. A charge of LAH (0.7 g, 21 mmol) was added and the mixture stirred overnight, heated for 20 min, and finally cooled to room temperature. After hydrolysis with saturated ammonium chloride, the organic layer was separated and dried over sodium sulfate and the volatiles were removed to give a viscous oil (2.2 g). Distillation of the residue gave a colorless oil, bp 115–134 °C (0.07 mmHg) (1.62 g). The GC analysis indicated that the oil contained five components in a ratio of 17/23/25/22/12. The components were partially separated by preparative, centrifugally accelerated, radial, thin-layer chromatography (silica gel, hexane) and were identified as 2-silyl-4,4'-di-*tert*-butylbiphenyl, 2,2'-dibutyl-4,4'-di-*tert*-butylbiphenyl, 2-butyl-4,4'-di-*tert*-butylbiphenyl, 3,6-di-*tert*-butyl-9,9-dihydro-9-silafluorene, and 4,4'-di-*tert*-butylbiphenyl on the basis of <sup>1</sup>H NMR spectra, mass spectra, and comparison to authentic examples.

**9,10-Dihydro-9-silaanthracene.** The dihydrosilaanthracene was prepared according to the literature method.<sup>12</sup> The distilled product, bp 105–130 °C (0.3 mmHg), was recrystallized from hexane to give purified product (4.5 g), mp 75–76 °C, which contained no impurity according to GC analysis: <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 41.97, 125.77, 128.17, 128.59, 129.78, 135.01, 146.62; mass spectrum, *m/e* 196 (M<sup>+</sup>).

**10,11-Dihydro-5*H*-dibenzo[*b,f*]silepin.** A solution of *o,o'*-dibromobenzyl (7.0 g, 21 mmol) in THF (75 mL) was added to a slurry of magnesium (100 mesh, 48 mmol) in THF (15 mL) containing a few iodine crystals. After completion of the addition the reaction mixture was heated at reflux for 53 h. A hydrolyzed aliquot showed a minimum of 57% bibenzyl according to GC analysis. The diGrignard reagent was cannulated into a pressure addition funnel. A solution of HSiCl<sub>3</sub> (2.9 mL) in the same volume of THF was added to a second addition funnel, the two solutions were added to THF (100 mL), and the resultant solution was stirred for 18 h. After addition of lithium aluminum hydride (0.9 g), the slurry was stirred at room temperature for 20 h. After workup with saturated ammonium chloride solution, the organic layer was dried and the volatiles were removed. Distillation of the resultant oil gave two fractions: (1) 1.6 g, bp 90–95 °C (0.15 mmHg) (81% silepin by GC); (2) 2.0 g, bp 95 °C (0.15 mmHg) (98% by GC). The first fraction could be purified by redistillation, but an analytical sample could not be obtained: <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 36.00, 125.34, 128.42, 128.95, 130.19, 135.78, 149.30; mass spectrum, *m/e* 210 (M<sup>+</sup>); IR (thin film) 2140 cm<sup>-1</sup> (Si-H).

Samples used for dehydrogenative coupling were 93–98% (GC analysis).

**General Procedure for Dehydrogenative Coupling.** a. **With ClRh(PPh<sub>3</sub>)<sub>3</sub>.** Samples of dihydrosilanes (approximately 0.5 g) were dissolved in deoxygenated toluene, and the rhodium catalyst was added. At the end of the reaction period, the volatiles were removed under vacuum and the viscous product mixture was transferred into a drybox. The silane oligomers were separated from the catalyst residues by elution through a short silica gel column (silica gel 60, 230–400 mesh) with 45% toluene in hexanes. The semisolid obtained from removal of the solvents from the filtrate was separated on the Chromatotron (silica gel, with 1% EtOAc in hexane). Several runs are summarized in Table III. Larger scale reactions (1.0 g of dihydrosilane) were conducted in sealed tubes.

b. **With Cp<sub>2</sub>ZrMe<sub>2</sub>.** Since the catalyst is air-sensitive samples of dihydrosilane, toluene and catalyst were loaded in the drybox and stirred vigorously for 30 min, then capped with a septum, and removed from the drybox. Reaction mixtures were then either stirred at room temperature or heated under argon for the times specified in Table IV. The catalyst was removed by filtering through a short silica gel column in air (45% toluene in hexane as eluant), and the products were separated on the Chromatotron.

**Reaction of 9,10-Dihydro-9-silaanthracene with ClRh(PPh<sub>3</sub>)<sub>3</sub>.** The disilane, trisilane, and disiloxane generated from reaction of the silaanthracene I have been described.<sup>12</sup> One reaction of I (1.03 g, 5.3 mmol) in degassed toluene (2 mL) at room

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temperature with  $\text{ClRh}(\text{PPh}_3)_3$  (20 mg) was conducted in base-washed glassware for 14 h. After workup the  $^1\text{H}$  NMR spectrum was consistent with the presence of unreacted starting material (18%), disiloxane (53%), and a new siloxane component (29%). The siloxanes were separated on the Chromatotron (silica gel with 1% EtOAc in hexane), and disiloxane was isolated and purified by recrystallization from 20% toluene in hexane. The second siloxane was also separated but could not be recrystallized from  $\text{CH}_2\text{Cl}_2$ /hexane, EtOH/ $\text{CHCl}_3$ , or hexane. The new siloxane component was assigned to the trisiloxane on the basis of spectroscopic data:  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  39.95, 40.47, 125.54, 125.75, 127.96, 129.98, 130.04, 130.07, 130.12, 132.21, 132.61, 134.16, 146.12, 146.86; mass spectrum,  $m/e$  778 ( $\text{M}^+$ ).

**Reaction of 10,11-Dihydro-5H-dibenzo[*b,f*]silepin (II) with  $\text{ClRh}(\text{PPh}_3)_3$ .** In a typical reaction (run 9, Table III), II (0.46 g, 2.1 mmol) in toluene (3 mL), which had been saturated with nitrogen for 20 min, and  $\text{ClRh}(\text{PPh}_3)_3$  (25 mg,  $2.7 \times 10^{-2}$  mmol) were stirred vigorously for 6 h and then pumped dry under vacuum ( $10^{-2}$  Torr) for 12 h. The viscous product mixture was transferred into a drybox, dissolved in hexanes/toluene, and passed through a silica gel column with 45% toluene in hexane to remove the catalyst. Evaporation of the solvent gave a semisolid which was separated on the Chromatotron (silica gel, with 2% EtOAc in hexane) to provide dihydrodibenzosilepin dimer (270 mg) and starting material (190 mg). The disilane was further purified by recrystallization from 1/4 toluene/hexane to give the analytical sample:  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  36.75, 36.71 ( $\text{CH}_2$ ), 125.02, 128.85, 129.26, 130.73, 135.86, 150.18 (arom); mass spectrum,  $m/e$  418 ( $\text{M}^+$ ); mp 152 °C. Anal. Calcd for  $\text{C}_{28}\text{H}_{26}\text{Si}_2$ : C, 80.32; H, 6.26. Found: C, 80.11; H, 6.18.

When the reaction was conducted with II (0.47 g, 1.2 mmol) and  $\text{ClRh}(\text{PPh}_3)_3$  (22 mg,  $2.4 \times 10^{-2}$  mmol) in toluene (0.5 mL) for 37 h under ultrasound conditions, the products contained about 50% siloxanes. The mixture of disiloxane and trisiloxane was separated on the Chromatotron (silica gel, with 2% EtOAc in hexane). The siloxanes elute more slowly than the starting material and disilane products. The disiloxane, mp 93–94 °C, was purified by recrystallization from 1/4  $\text{CH}_2\text{Cl}_2$ /hexane:  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  35.98 ( $\text{CH}_2$ ), 125.32, 128.79, 130.42, 134.00, 135.26, 148.44 (arom); mass spectrum,  $m/e$  434 ( $\text{M}^+$ ). Anal. Calcd for  $\text{C}_{28}\text{H}_{26}\text{Si}_2\text{O}$ : C, 77.37; H, 6.03. Found: C, 77.67; H, 5.91. A slower moving siloxane could not be crystallized or purified and was tentatively assigned the trisiloxane structure on the basis of the spectroscopic data:  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  35.91, 36.68, 125.07, 125.21, 128.68, 130.23, 130.27, 134.01, 134.50, 135.38, 148.36, 148.54; mass spectrum,  $m/e$  658 ( $\text{M}^+$ ).

When the reaction of the silepin (370 mg) with  $\text{ClRh}(\text{PPh}_3)_3$  (16 mg) was conducted without solvent at 85 °C for 3 h and worked up in the usual manner, 370 mg was recovered. Recrystallization from methylene chloride/hexane provided disilane (180 mg), m.p. 143–146 °C. Material recovered from the filtrate was separated on the Chromatotron (silica gel, 2% EtOAc in hexane) and provided unreacted II (85 mg) and a mixture of three components (110 mg). Recycling the mixture on the Chromatotron gave a mixture of trisiloxane and a component which was assigned the trisilane on the basis of the following data:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  5.22 (s, SiH, trisilane) and 5.60 (s, SiH, trisiloxane); mass spectrum,  $m/e$  626 ( $\text{M}^+$ , trisilane), 658 ( $\text{M}^+$ , trisiloxane). Attempts to obtain pure trisilane from these mixtures by crystallization (EtOAc/hexane, toluene/hexane, EtOH/toluene,  $\text{CH}_2\text{Cl}_2$ /hexane) were not successful.

**Reaction of Impure II with Wilkinson's Catalyst.** A mixture of impure II (0.76 g which analyzed 64% II by GC),  $\text{ClRh}(\text{PPh}_3)_3$  (50 mg), and toluene (0.5 mL) were stirred at room temperature for 11 h followed by heating at 85 °C for 1 h. After removal of the catalyst 0.71 g of semisolid material was recovered. The semisolid was recrystallized from 1/3 toluene/hexane to give crystalline disilane, mp 150–151 °C (0.36 g, 73% based on the actual starting material).

**Reaction of Diphenylsilane with Wilkinson's Catalyst in Toluene.** To a solution of diphenylsilane (0.68 g, 3.7 mmol) in toluene (3.7 mL), degassed and saturated with argon, was added Wilkinson's catalyst (15 mg,  $1.6 \times 10^{-2}$  mmol). This mixture was stirred vigorously at room temperature for 10 h followed by the usual procedure to remove the catalyst. GC analysis indicated that the eluant contained  $\text{Ph}_2\text{SiH}_2$ ,  $\text{Ph}_3\text{SiH}$ , and  $\text{Ph}_2(\text{H})\text{SiSi}(\text{H})\text{Ph}_2$

by comparison to authentic samples in 41%, 48%, and 11%, respectively. The disilane, mp 76–77 °C (lit.<sup>24</sup> mp 79–80 °C), was separated on the Chromatotron with 1% EtOAc in hexane and exhibited spectroscopic characteristics that were identical with those of an authentic sample.

**Reaction of 9,9-Dihydrosilafluorene (III) with  $\text{ClRh}(\text{PPh}_3)_3$ .** A mixture of III (0.58 g, 3.2 mmol) and  $\text{ClRh}(\text{PPh}_3)_3$  (0.012 g, 0.013 mmol) was stirred under argon until the mixture solidified (1.5 h). A small amount of unreacted III (61 mg, bp 80–160 °C (0.08 mmHg)) was obtained on attempted distillation. The solid residue is insoluble in the usual NMR solvents and has a melting point >400 °C: IR (KBr disk) 2140  $\text{cm}^{-1}$  (SiH, weak), 480  $\text{cm}^{-1}$  (Si–Si, st).

The reaction of III (0.56 g, 3.1 mmol) and  $\text{ClRh}(\text{PPh}_3)_3$  (5 mg, 0.005 mmol) in toluene (3.6 mL) was run for 1 h until precipitation was observed and the mixture immediately filtered through a short silica gel column in the drybox. Removal of solvent from the filtrate provided III (0.37 g, 66%) as the only isolated material.

**Reaction of III with  $\text{Cp}_2\text{TiMe}_2$ .** A solution of III (0.53 g, 2.9 mmol) in toluene (0.9 mL) was saturated with argon for 20 min, and  $\text{Cp}_2\text{TiMe}_2$  (6 mg, 0.03 mmol) was added. After 5 min the solution turned green and the precipitate formed in about 1 h. A GC analysis indicated that starting material was still present. After 29 h the starting material is consumed and a solid (0.52 g) was obtained after the reaction mixture is filtered. The solid, mp >400 °C, is insoluble in toluene, benzene, ether, THF, and DMSO: IR (KBr disk) 2110  $\text{cm}^{-1}$  (SiH, weak), 480  $\text{cm}^{-1}$  (SiSi); mass spectrum,  $m/e$  (180)<sub>n</sub> ( $n = 1-5$ ).

Three additional runs gave yellow-brown solutions that contained unreacted starting material after 2 days. Distillation of reaction residues provided unreacted III (75% recovery). The residues did not contain SiH according to the IR spectra.

**Reaction of 3,7-Di-*tert*-butyl-5,5-dihydro-dibenzosilole (IV) with  $\text{ClRh}(\text{PPh}_3)_3$ .** The reaction of IV (0.39 g, 1.3 mmol) and  $\text{ClRh}(\text{PPh}_3)_3$  (4 mg) in toluene (1.5 mL) was conducted in the drybox. After 15 min the solution turned cloudy and was filtered through a short silica gel column. Removal of the volatiles provided a semi solid, 0.34 g, which exhibited a strong SiH band at 2150  $\text{cm}^{-1}$  and no SiOSi band:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.27 (s,  $^t\text{Bu}$ ), 1.35 (s,  $^t\text{Bu}$ ), 4.75 (s, SiH), with a  $^t\text{Bu}/\text{SiH}$  of 3611. An attempt to separate the products by radial chromatography (silica gel) was not successful as material could not be removed from the silica gel even with methanol.

**Reaction of 9-Hydro-9-methylsilafluorene with  $\text{ClRh}(\text{PPh}_3)_3$ .** A solution of 9-hydro-9-methylsilafluorene (1.4 g, 78% by GC analysis) in toluene (0.8 mL) was degassed and saturated with argon before addition of  $\text{ClRh}(\text{PPh}_3)_3$  (45 mg). The mixture was stirred for 70 h and worked up in the drybox as described for reaction of I. Removal of the solvents provided a solid (1.2 g) which was starting material (90% by GC analysis) as determined by retention time and spectroscopic comparison to authentic examples.

The reaction was also conducted with the silafluorene (0.40 g, 2.0 mmol) in degassed  $\text{C}_6\text{D}_6$  (0.9 mL) under argon with  $\text{ClRh}(\text{PPh}_3)_3$  (16 mg) for 48 h. After removal of the solvents and elution with 5% EtOAc in hexane on the Chromatotron, a white solid (0.32 g, 80% mass recovery) was obtained that contained 77% of one component. Recrystallization from hexane gave white crystals of the disiloxane 5,5'-oxybis[5-methylidibenzosilole]: mp 123.5–124.5 °C (lit.<sup>15</sup> mp 127–128 °C);  $^1\text{H}$  NMR  $\delta$  0.27 (s,  $\text{SiCH}_3$ ), 6.98–7.88 (m, arom); mass spectrum,  $m/e$  406 ( $\text{M}^+$ ); IR (KBr disk) SiOSi (br, 1020  $\text{cm}^{-1}$ ).

**Reaction of the Disilane of I with  $\text{ClRh}(\text{PPh}_3)_3$ .** To a stirred solution of the disilane of I (75 mg, 0.20 mmol) in toluene (0.7 mL), which had been degassed and then saturated with argon for 30 min, was added  $\text{ClRh}(\text{PPh}_3)_3$  (1.2 mg). The mixture was stirred at 82 °C under argon for 1.5 h, and the volatiles were removed under vacuum. The catalyst was removed as described in the general procedure, and the solid (74 mg) obtained after removal of the solvents contained a mixture of I (7%), disilane (86%), and trisilane (7%) as determined by  $^1\text{H}$  NMR.

**Reaction of the Disilane of II with  $\text{ClRh}(\text{PPh}_3)_3$ .** A solution of the disilane of II (32 mg) and  $\text{ClRh}(\text{PPh}_3)_3$  in degassed toluene (0.38 mL) was heated at 55 °C for 12 h. The catalyst was removed in the drybox, and 32 mg of solid was recovered. The mixture contained two components with smaller  $R_f$  values than the disilane



according to TLC (silica gel). The components could not be cleanly separated on the Chromatotron. The  $^1\text{H}$  NMR spectrum shows the presence of disilane and disiloxane, and the mass spectrum exhibits molecular ions at  $m/e$  418 (disilane), 434 (disiloxane), and 626 (trisilane). There was no evidence for the monosilane starting material.

When oxygen is bubbled through a  $\text{CH}_2\text{Cl}_2$  solution of the disilane of II for 5 h, disiloxane is produced. After 5 h the ratio between the disilane and the disiloxane is 4:1 according to  $^1\text{H}$  NMR.

#### Reaction of 9-Hydro-9-chlorosilafluorene with Metals. a.

**Lithium.** To a slurry of lithium dispersion (0.37 g, 25% in mineral oil washed with hexane, 13 mmol) in THF (20 mL) at 25 °C was added a solution of 9-hydro-9-chlorosilafluorene (silafluorene<sup>12</sup>) (1.2 g, 5.5 mmol) in THF (7 mL) dropwise over a 1-h period. After addition, the resultant mixture was heated to reflux for 22 h. The red solution was cooled to room temperature and absolute ethanol added dropwise until the exothermic reaction ceased, and then water was added. The resultant was extracted with three portions of ether and the combined ether extract dried over  $\text{Na}_2\text{SO}_4$ . Removal of the volatiles provided a solid (0.95 g). The solid did not contain any SiH resonances in the  $^1\text{H}$  NMR spectrum. An attempt was made to separate the constituents of the mixture on the Chromatotron with  $\text{CH}_2\text{Cl}_2$ /hexane (4:1). At least 11 products were present with no single product dominating. The products contained mixtures of silicon-silicon bonded materials, siloxanes, and products that incorporated butoxy groups most likely from the cleavage of THF as determined from a combination of  $^1\text{H}$  NMR, IR, and mass spectroscopy.

**b. Potassium.** A slurry of potassium (0.327 g, 8.36 mmol) in cyclohexane (12 mL) was heated with rapid stirring until the potassium melted. A solution of impure 9-hydro-9-chlorosilafluorene (2.1 g, 80% with 15% 9,9-dichlorosilafluorene and 5% III) dissolved in cyclohexane (20 mL) was added dropwise over a 5-min period and the reaction mixture heated at reflux under argon. After 19 h the mixture was cooled to room temperature and filtered under argon. The filtrate was pumped to dryness to give a viscous yellow oil (1.55 g). Distillation of the residue gave a fraction, bp 140–170 °C (0.07 mmHg), which solidified to a white solid, mp 124–130 °C, which is a mixture of disiloxane and a second component tentatively assigned to the disilane in 54% and 44% yields, respectively (GC). The  $^1\text{H}$  NMR spectrum exhibits two SiH resonances at 5.27 and 5.42 ppm, and the mass spectrum contains the molecular ions expected for disilane ( $m/e$  362) and disiloxane ( $m/e$  378). When air is bubbled through this mixture in  $\text{CDCl}_3$  for 30 min, the SiH resonance at  $\delta$  5.27 ppm disappears and the resonance at  $\delta$  5.42 ppm increases in intensity. Removal of the solvent and recrystallization of the

solid from toluene/hexane gave disiloxane, mp 131–132 °C, by comparison to an authentic sample prepared by hydrolysis of the chlorosilafluorene.

**c. Magnesium.** A mixture of 9-hydro-9-chlorosilafluorene (1.99 g, 85%) and Mg (0.45 g, 18.7 mmol) and EtI (0.020 mL) in THF (20 mL) was heated to reflux under argon for 48 h. After hydrolysis the residue was distilled and gave a fraction, bp 140–170 °C (0.05 mmHg) (0.24 g), which was a mixture of disilane and disiloxane. An attempt to separate the disilane from the disiloxane by chromatography over silica gel led to decomposition of the disilane.

**5,5'-Oxybis[5-hydrodibenzosilole].** To a solution of 9-hydro-9-chlorosilafluorene (0.5 g, 2.3 mmol) in ether (30 mL) was added water (1 mL), and the solution was stirred for 12 h. The ether layer was separated and dried over  $\text{Na}_2\text{SO}_4$ . Removal of the solvent gave a semisolid (0.4 g). An analytical sample of 5,5'-oxybis[5-hydrodibenzosilole] was obtained by recrystallization from  $\text{CHCl}_3$ /EtOH (1/4):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  5.42 (s, 1.7 H, SiH), 7.05–7.9 (m, 16.3 H, arom); IR (KBr, disk) 1050, 1070  $\text{cm}^{-1}$  (SiOSi), 2140  $\text{cm}^{-1}$  (SiH); mass spectrum,  $m/e$  378 ( $\text{M}^+$ ); mp 132–133 °C. Anal. Calcd for  $\text{C}_{24}\text{H}_{18}\text{Si}_2\text{O}$ : C, 76.17; H, 4.81. Found: C, 75.56; H, 4.97.

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**Registry No.** I, 38948-57-1; I ( $x = 2$  disilane), 109065-63-6; I ( $x = 3$  trisilane), 109065-64-7; I ( $y = 2$  disiloxane), 109065-65-8; I ( $y = 3$  trisiloxane), 121441-96-1; II, 106992-87-4; II ( $x = 2$  disilane), 121441-93-8; II ( $x = 3$  trisilane), 121471-40-7; II ( $y = 2$  disiloxane), 121441-94-9; II ( $y = 3$  trisiloxane), 121441-95-0; III, 244-96-2; III ( $x = 2$  disilane), 121441-97-2; III ( $y = 2$  disiloxane), 121441-98-3; IV, 121441-89-2; (*o*- $\text{ClC}_6\text{H}_4$ )<sub>2</sub>CH(O<sub>2</sub>CCH<sub>3</sub>), 7498-78-4;  $\text{HSiCl}_3$ , 10025-78-2;  $\text{ClRh}(\text{PPh}_3)_3$ , 14694-95-2;  $\text{Ph}_2\text{SiH}_2$ , 775-12-2;  $\text{Ph}_3\text{SiH}$ , 789-25-3;  $\text{Ph}_2(\text{H})\text{SiSi}(\text{H})\text{Ph}_2$ , 16343-18-3;  $\text{Cp}_2\text{TiMe}_2$ , 1271-66-5;  $\text{Cp}_2\text{ZrMe}_2$ , 12636-72-5;  $\text{Rh}(\text{COD})(\text{PPh}_3)_2\text{PF}_6$ , 121442-00-0; bis(*o*-chlorophenyl)carbinol, 6335-15-5; bis(*o*-chlorophenyl)methane, 32306-73-3; 5,5'-spiro[dibenzosilole], 159-68-2; 2,2'-dibromobiphenyl, 13029-09-9; triethoxysilane, 998-30-1; 9-methyl-9-hydro-9-silafluorene, 53268-89-6; *o,o'*-bromochlorobiphenyl, 107208-70-8; methylchlorosilane, 75-54-7; 2,2'-dibromo-4,4'-di-*tert*-butylbiphenyl, 70728-93-7; 2,2'-di-*tert*-butyl-4,4'-di-*tert*-butylbiphenyl, 121441-90-5; 2-butyl-4,4'-di-*tert*-butylbiphenyl, 121441-91-6; 4,4'-di-*tert*-butylbiphenyl, 1625-91-8; 2-silyl-4,4'-di-*tert*-butylbiphenyl, 121441-92-7; *o,o'*-dibromobiphenyl, 59485-34-6; 5,5'-oxybis[5-methyldibenzosilole], 18766-02-4; 9-hydro-9-chlorosilafluorene, 53268-90-9.