Dehydrogenative Coupling of Heterocyclic Dihydrosilanes

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*Summary:* The conditions for the conversion of secondary hydrosilanes to disilanes and trisilanes catalyzed by ClRh(PPh₃)₃ have been developed. The model system described is based on dihydrosilaanthracene. The single-crystal X-ray structural results of the trisilane are presented.

The most common route to the formation of silicon–silicon bonds involves condensation of a silicon chloride with an alkali or alkaline earth metal. Disilanes, cyclopolysilanes and linear polysilanes have all been prepared by this method.[1] Dehydrogenative coupling of SiH in the presence of transition-metal catalysts is a potential alternative for Si–Si bond formation but has been employed infrequently. The reactions of titanium,[2] zirconium,[3] and rhodium[4,5] catalysts with PhSiH₃,[2a,3,4a] Ph₂SiH₂,[3,4a,5] PhMeSiH₂,[2a,4a] and Ph₃SiH[2b,4b] have been reported. Because the majority of the studies are preliminary reports[2a,4a] or are concerned primarily with the product formed from the interaction of the catalyst with the silane,[2b,3] there is little substantive detail concerning conditions for dehydrogenative coupling of hydrosilanes, methods of isolation, and purification or of product distribution. However, there are some generalizations that can be drawn from these prior reports. Oligomers are formed from Cp₂TiR₂ and primary silanes and also from secondary silanes but only after long time periods (14 days vs. 1 day) and then only in the case of PhMeSiH₂.[2a] Disilanes are formed with rhodium catalysts, but disproportionation products produced from the starting material compete with dehydrogenative coupling[4a] in secondary silanes. Tertiary silanes do not form silicon–silicon bonded products but oxidatively add to Rh.[4b] In addition to disproportionation, oxidation of silicon–silicon bonds to siloxanes has been reported with Rh catalsysts,[5] but this problem does not appear to occur with Cp₂TiR₂.[2a]

If dehydrogenative coupling can be controlled, then secondary silanes could be the starting point for the formation of silicon chains with terminal SiH groups. In previous studies several reactions have been conducted without solvent and with silanes that are liquids at room temperature. Because arylsilanes can be solids, a more general approach should involve the use of a solvent. Other reaction variables that then need to be considered include concentration, temperature, and catalyst, as well as the

appropriate choice of a model silane system. The coupling reaction may be sensitive to the size of substituents on silicon since trisilane is formed as one of the products from PhMeSiH₂ but a disilane is the only coupling product from Ph₂SiH₂. If the two phenyl groups of Ph₂SiH₂ are tied together at the position ortho to silicon to form a heterocycle, the steric bulk of the system will be decreased. In principal, changes can be incorporated by varying the atoms or the number of atoms used to join the two phenyl groups.

The reaction of 9,10-dihydro-9-silaanthracene with ClRhL₃ (L = PPh₃) was studied at room temperature under a variety of conditions with results that are summarized in the Table I. The products obtained from the dehydrogenative coupling include disilane, trisilane, and disiloxane (eq 1).[6]
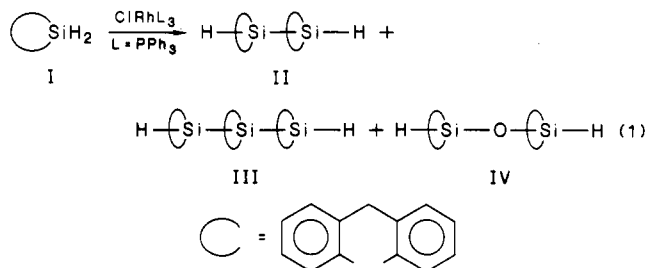
As can be seen from Table I, there are several factors that influence the distribution of products from the dehydrogenative coupling of I. Workup in this system requires elution over silica gel to remove the catalyst. This process introduces another reaction variable because the disilane that is produced reacts on the column when the concentration of catalyst is too high (compare runs 1–3 with runs 5 and 6).[10] The conditions that lead to the isolation of the highest combined yield of disilane and trisilane, and only 3% of disiloxane are summarized in run 6 of Table I. These conditions also represent the highest conversion of a secondary silane thus far reported and the first tri-

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(2) Cp₂TiMe₂ [or Cp₂Ti(CH₂Ph)₂]: (a) Aitken, C.; Harrod, J. F.; Samuel, E. *J. Organomet. Chem.* **1985,** *279,* C11. (b) Aitken, C. T.; Harrod, J. F.; Samuel, E. *J. Am. Chem. Soc.* **1986,** *108,* 4059.

(3) Cp₂ZrMe₂: Aitken, C.; Harrod, J. F.; Samuel, E. *Can. J. Chem.* **1986,** *64,* 1677.

(4) ClRh(PPh₃)₃: a. Ojima, I.; Inaba, S.-I.; Kogure, T.; Nagai, Y. *J. Organomet. Chem.* **1973,** *55,* C7. b. Haszeldine, R. N.; Parish, R. V.; Parry, D. J. *J. Chem. Soc. A* **1969,** 683.

(5) ClRh(PPh₃)₂C̄N̄(Me)(CH₂)₂NMe: Lappert, M. F.; Maskell, R. K.; *J. Organomet. Chem.* **1984,** *264,* 217.

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(8) Disilane: ¹H NMR (CDCl₃) δ 3.71 (AB quartet, J = 17 Hz, CH₂), 5.05 (s, SiH), 7.13–7.51 (m, arom); ¹³C NMR (CDCl₃) δ 41.81 (CH₂), 125.61, 128.12, 129.33, 129.59, 134.90, 146.00 (arom); mass spectrum, m/e 390 (M⁺); mp 161–162 °C. Anal. Calcd for C₂₆H₂₂Si₂: C, 79.94; H, 5.68. Found: C, 79.28; H, 5.73. Disiloxane: ¹H NMR (CDCl₃) δ 4.01 (br, CH₂), 5.55 (s, Si–H), 7.18–7.72 (m, Ar); ¹³C NMR (CDCl₃) δ 40.56 (CH₂), 125.75, 125.80, 126.01, 128.07, 128.13, 130.12, 132.32, 134.13, 146.04 (arom); mass spectrum, m/e 406 (M⁺); mp 120–121 °C. Trisilane: ¹H NMR (CDCl₃) δ 3.41 (s, CH₂), 3.65 (AB quartet, J = 17 Hz, CH₂), 5.14 (s, SiH), 6.94–7.32 (m, arom); ¹³C NMR (CDCl₃) δ 41.59 (CH₂), 42.00 (CH₂), 125.41, 125.54, 128.09, 128.87, 129.21, 129.88, 135.14, 135.18, 146.04 (arom); ²⁹Si NMR (CDCl₃) −60.23, −49.59 ppm; mass spectrum, m/e 584 (M⁺); mp 152 °C.

(9) The coupling reaction of Ph₂SiH₂ was previously performed without solvent.[4a] When the reaction is run with the conditions specified under run 6, Table I, the products are (wt % based on starting silane; the value in brackets is the related value calculated from ref 4a): Ph₂SiH₂ (41% [31%]), Ph₂SiHSiHPh₂ (48% [52%]), and Ph₃SiH (11% [8%]).

(10) The silica gel used in this study was dried at 200 °C. Reaction of II does not occur with silica gel in the absence of the catalyst. The use of gas chromatography to determine product ratios is precluded since isolated and purified samples and II and III decompose under conditions attempted.

Table I. Reaction of 9,10-Dihydro-9-silaanthracene with Catalytic Amounts of ClRh(PPh$_3$)$_3$

run	Rh/I (× 100)	[I] (toluene)	time, h/temp, °C	wt %[a] I	II	IV	III	% recovery[b]
1	2.0	0.2	6/25	12	8	27	35	82
2	0.8	0.5	16/25	9	12	24	36	81
3	0.7	0.9	24/25	4	18	13	43	78
4	0.7	0.9	48/25	4	8	18	33	63
5	0.4	0.4	9/25	36	42	7	14	100
6[c]	0.4	1.0	10/25	17	38	3	42	100
7	0.4	1.0	1.5/82	7	17	9	66	100

[a] Ratios are determined from integration ratios of the ^{1}H NMR spectrum and adjusted to the weight of starting material. [b] Based on weight of starting material. [c] Isolation of I, II, and III from this run are described in ref 6.
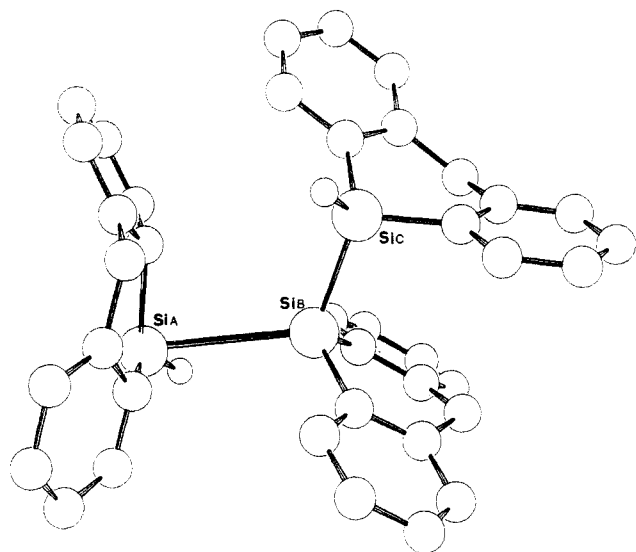

Figure 1. Molecular structure of III. Selected bond distances (Å) and angles (deg): Si(A)–Si(B) = 2.358 (2); Si(B)–Si(C) = 2.342 (2); Si(A)–Si(B)–Si(C) = 114.2 (1).

silane generated from a diarylsilane.[9] There are several other observations that are revealed from these various runs: (1) high catalyst ratios result in less recovery during the chromatography as well as formation of greater amounts of disiloxane; (2) increasing the concentration of I provides for greater recovery of disilane and trisilane and shorter reaction periods; (3) increasing the temperature favors the formation of trisilane as well as significantly decreasing the time of reaction.

The solid-state structure of III has been determined[11] and is shown in Figure 1. The structure of only one other trisilane, I–[Si(Bu-t)$_2$]$_3$–I (V), has been reported.[12] The two trisilanes exhibit about the same SiSiSi angle but distinctly different bond distances. The Si–Si bond distances reported for V are 258.1 and 264.4 pm which are consistent with bond orders of 0.41 and 0.32. These long bond distances are probably due to the steric bulk of the *tert*-butyl groups. As hypothesized earlier, the effort in this study was to minimize the size of substituents and this is reflected in the normal Si–Si bond distances observed for I. The dihedral angles down metal–metal bonds for known 1,3-difunctional trimetallanes are shown in Table

Table II. Comparison of Trimetallane Dihedral Angles (deg) Down Metal–Metal Bonds

$$X—M_1—M_2—M_3—X$$

examples	XM$_1$M$_2$M$_3$	M$_1$M$_2$M$_3$X	conformation	ref
H–[(6)Si]$_3$–H	137	58	anti-gauche	this work
I–[t-Bu$_2$Si]$_3$–I	89	165	gauche-trans	12
Cl–[Ph$_2$Ge]$_3$–Cl	140	49	anti-gauche	13
Cl–[Ph$_2$Ge]$_3$–Cl	58	49	gauche-gauche	13

II. The conformation of III closely resembles that of one of the conformers of Cl(Ph$_2$Ge)$_3$Cl.

Our preliminary work shows that dehydrogenative coupling can be a useful method for forming disilanes and trisilanes. How the products are formed is a matter of conjecture since both oxidative addition[2,3] and silylene[4a] mechanisms have been proposed for this reaction. The trisilane may be formed from coupling of a monosilane and a disilane or from disproportionation of the disilane in the presence of the catalyst.[14] When a sample of pure disilane is treated with the rhodium catalyst under the conditions specified in run 7 of Table I, the recovered disilane contains 7% of the trisilane. These results suggest that more than one reaction pathway will lead to trisilane. We are continuing to develop scaleup procedures and to access the role of temperature and ring size of the silicon heterocycle in determining product distribution. Small chain silicon derivatives with SiH terminal groups would be useful starting materials since the functionality allows the exploration of further chemistry. In particular, 1,2-dihydrosilanes may be possible precursors to disilenes[15] or to 1,4-difunctional tetrasilanes. 1,3-Dihydrosilanes could be converted to cyclotrisilanes which are precursors to both silylenes and disilenes.[16]

Supplementary Material Available: A table summarizing literature results for dehydrogenative coupling of phenylsilanes, a perspective drawing of the trisilane with atom labels, and tables of positional and thermal parameters and interatomic distances and angles (6 pages); a listing of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

(11) X-ray diffraction data for dihydrosilaanthracene trimer: C$_{39}$-H$_{32}$Si$_3$, M$_r$ 584.94, space group *Pbca*, a = 18.054 (6) Å, b = 14.402 (2) Å, c = 24.399 (3) Å, α = β = γ = 90°, V = 6344 (3) Å^3, Z = 8; D(calcd) = 1.225 g/cm^3, λ(Mo Kα) = 0.710 69 Å, μ = 1.37 cm^{-1}; scan mode ω; T = 25 °C; 2θ range = 1.0–50.0°; measured reflections 5488; observed reflections 2334 (I > 2σ (I)); all calculations with SHELX 76 system; hydrogen atoms at calculated positions; number of variables 389; R = R$_w$ = 0.054; residual electron density = 0.23 e/Å^{-3}.

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(14) Yamamoto, K.; Okinoshima, H.; Kumada, M. *J. Organomet. Chem.* **1970**, *23*, C7. We thank one of the referees for suggesting this possibility.

(15) For a review of Si=X chemistry see: Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419.

(16) Weidenbruch, M. *Comments Inorg. Chem.* **1986**, *5*, 247.