

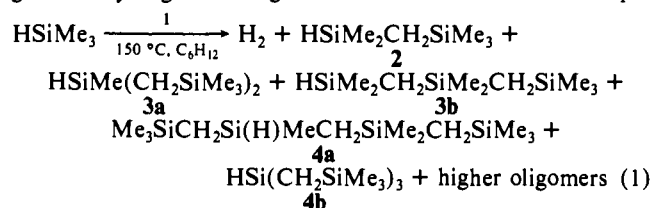
Dehydrogenative Coupling of Trialkylsilanes Mediated by Ruthenium Phosphine Complexes: Catalytic Synthesis of Carbosilanes

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Hydrosilanes, HSiR_3 , undergo a variety of both interesting and useful reactions which are catalyzed by transition-metal complexes. Common examples include the hydrosilylation of unsaturated organic molecules² and the redistribution of groups bound to silicon.³ Recently, much attention has been focused on a relatively new process, the metal-catalyzed dehydrogenative coupling of organosilanes to form oligomeric and polymeric species containing Si-Si bonds.⁴ These compounds are of interest for their unusual electronic properties as well as their intermediate role in the Yajima process for fabricating silicon carbide ceramic fibers.⁵ In the Yajima process, polysilanes are utilized as precursors for the synthesis of polycarbosilanes, compounds containing an extended backbone of alternating Si and C atoms. Polycarbosilanes are currently produced by the relatively inefficient rearrangement of polysilanes at high temperatures. We now report the direct synthesis of oligomeric carbosilanes by the dehydrogenative coupling of trialkylsilanes in the presence of a ruthenium catalyst.

The ruthenium silyl complex $\text{Ru}(\text{H})_3(\text{SiMe}_3)(\text{PMe}_3)_3$ (**1**)⁶ catalyzes the coupling of HSiMe_3 at 150 °C in cyclohexane to generate hydrogen and oligomeric carbosilanes as shown in eq 1.



The organosilicon products are the net result of activation of silane Si-H and C-H bonds and formation of new Si-C bonds. Hexamethyldisilane ($\text{Me}_3\text{SiSiMe}_3$), the expected product of Si-Si bond formation, is not observed by NMR or GC and has been shown to be stable under the experimental conditions.⁷ The structures of carbosilane products **2-4** have been confirmed by comparison with authentic samples.⁸ Although **2-4** constitute the only organosilicon products that have been conclusively

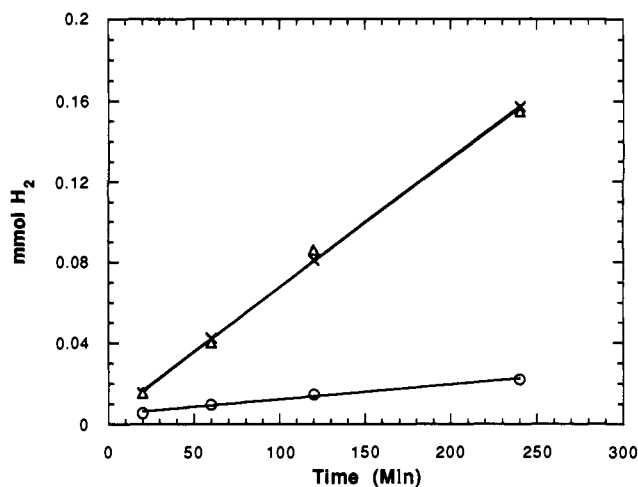


Figure 1. Evolution of H_2 vs time for dehydrogenation of HSiMe_3 catalyzed by **1**. Conditions: 150 °C, 1 mL of cyclohexane, (a) 0.74 mmol of HSiMe_3 and 2.5×10^{-3} mmol of **1** (O), (b) 0.74 mmol of HSiMe_3 and 2.5×10^{-2} mmol of **1** (X), (c) 1.48 mmol of HSiMe_3 and 2.5×10^{-2} mmol of **1** (Δ).

identified by GC, the formation of less volatile higher oligomers with the general formula $\text{H}(\text{SiMe}_2\text{CH}_2)_n\text{H}$ ($n \sim 8$)⁹ is indicated by NMR, GC, and MS analysis. As expected, the relative amounts of products **2-4** vary with reaction time. However, high conversions of HSiMe_3 to products are readily obtained. For example, in a reaction with initial concentrations of 0.74 M HSiMe_3 and 0.025 M **1** in 1 mL of cyclohexane, >95% conversion to products was observed after 425 h at 150 °C. Analysis of the final mixture by GC showed the following normalized composition of volatile components: 34% **2**, 28% **3a**, 10% **3b**, 17% **4a**, 3% **4b**, and ca. 8% higher oligomers. The latter, extremely high boiling compounds, are most likely pentamers.

The rate of catalysis in cyclohexane was determined by measuring H_2 evolution as a function of time.¹⁰ A plot of H_2 evolution vs time for three initial concentrations of **1** and HSiMe_3 at low conversions (ca. 6 turnovers) is shown in Figure 1. The catalytic coupling has been followed to ca. 60 turnovers, although there is a noticeable decrease in the rate. Under conditions of $[\text{1}] = 2.5 \times 10^{-3}$ M and $[\text{HSiMe}_3]_0 = 0.74$ M, the initial turnover rate is ca. 2 turnovers h^{-1} (mol of 1^{-1}). The initial rate is independent of initial trimethylsilane concentration over the range examined (0.74–1.48 M) and is essentially first order in catalyst ($[\text{1}] = (2.5 \times 10^{-3})$ – (2.5×10^{-2}) M). Although **1** is the only ruthenium compound observed by NMR in the reaction mixture through moderate conversions, the dihydride *cis*- $\text{Ru}(\text{H})_2(\text{PMe}_3)_4$ (**5**)¹¹ is observed later in the reaction. Other ruthenium-containing decomposition products are presumably formed concurrently, which is also suggested by the slight darkening of the reaction solution with time. Isolated **5** is approximately 2 orders of magnitude less catalytically active than **1**, and the decrease in the activity of the mixture with time suggests that the other decomposition products are not catalytically important.

Although more detailed studies are currently in progress, some comments regarding the mechanism of the catalysis are appropriate at this time. Overall, Si-H and C-H bonds must be broken and Si-C bonds must be formed during the catalytic cycle. Processes involving free Me_3Si or $\text{HMe}_2\text{SiCH}_2$ radicals are unlikely on the basis of the absence of detectable quantities of the symmetrical coupling products $\text{Me}_3\text{SiSiMe}_3$ and $(\text{HMe}_2\text{SiCH}_2)_2$.

(9) The general formula is not meant to imply the structures of the higher oligomers.

(10) The reaction can be conveniently monitored by either NMR or Toepler pump analysis of the evolved hydrogen. Products were analyzed by NMR, GC, and MS. In this instance, a turnover is defined as the number of moles of H-Si groups consumed (or alternatively, the number of moles of Si-C bonds formed) per mole of catalyst.

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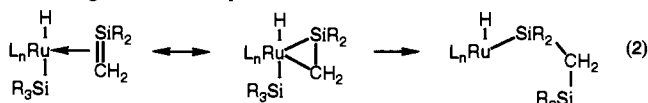
(6) Compound **1** was prepared in 89% isolated yield by the photolysis (350 nm) of $(\text{Me}_3\text{P})_3\text{Ru}(\text{H})_2$ with HSiMe_3 in cyclohexane solution. ¹H NMR (C_6D_6): δ 1.32 (m, 27 H, PMe_3), 0.30 (s, 9 H, SiMe_3), -10.34 (m, 3 H, RuH). ³¹P{¹H} NMR (C_6D_6): δ -4.5 (s). Anal. Calcd for $\text{C}_{12}\text{H}_{39}\text{P}_3\text{RuSi}$: C, 35.54; H, 9.69. Found: C, 35.36; H, 10.02.

(7) Thus, $\text{Me}_3\text{SiSiMe}_3$ is not initially formed with subsequent rearrangement to **2** under the conditions of the catalysis. However, hexamethyldisilane is known to rearrange at 450 °C to produce **2**. Sakurai, H.; Hosomi, A.; Kumada, M. *J. Chem. Soc., Chem. Commun.* 1968, 930.

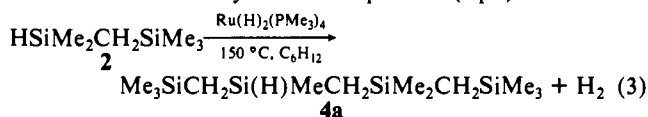
(8) Authentic samples of carbosilanes **2-4** were prepared by standard organometallic routes in analogy to literature methods: Fritz, G.; Matern, E. *Carbosilanes*; Springer-Verlag: Berlin, 1986. Details on the preparation and characterization of **2-4** are given in the supplementary material.

Cleavage of a Si-H bond can be most reasonably accomplished by oxidative addition of a hydrosilane to an unsaturated ruthenium center. Although cleavage of a C-H bond could occur by direct intermolecular addition of a free silane methyl group (e.g., H-CH₂SiMe₂H), this process appears unlikely. Catalytic coupling of HSiMe₃ in the presence of excess SiMe₄ does not yield detectable quantities of Me₃SiCH₂SiMe₃, the expected product of quaternary silane C-H activation.¹²

Recent mechanistic studies on related osmium complexes provide a simple alternative to intermolecular C-H activation in the formation of carbosilanes. The osmium silyl complex Os-(H)(SiMe₃)(PMe₃)₄ has been found to catalyze the H/D exchange between free HSiMe₃ and benzene-*d*₆ via a mechanism involving an intermediate η²-silene (η²-Me₂Si=CH₂) complex.¹³ The η²-silene ligand is generated through a novel β-hydrogen elimination from a silyl ligand, i.e., an intramolecular C-H addition. Note that stable η²-silene complexes of early and late transition metals have been isolated recently by other synthetic routes.¹⁴ Formation of an η²-silene ligand by β-hydrogen elimination from a silyl represents the dehydrogenation of a silane molecule containing adjacent Si-H and C-H bonds. The carbosilane products observed in the present study can be viewed as arising from the net addition of the Si-H bond of a free silane across the Si=C unsaturation of the coordinated η²-silene ligand as shown in eq 2. This is in direct analogy with the metal-catalyzed hydrosilylation of organic olefins.² The migration of silyls to organic olefin ligands is well preceded.¹⁵



In the present case, carbosilane dimer **2** would result from the net addition of HSiMe₃ to Me₂Si=CH₂, the complexed silene generated from a SiMe₃ ligand. Furthermore, the distribution of trimeric and tetrameric carbosilanes observed in eq 1 can be readily explained by this model. For example, the trimeric carbosilane **3a** would result from the net addition of HSiMe₃ across the silene generated from the dimeric product **2**. In a similar manner, **3b** would arise from the addition of HSiMe₂CH₂SiMe₃ (**2**) to the silene generated by dehydrogenation of HSiMe₃. Tetramer **4a** would then result from the coupling of two molecules of **2**, and **4b** would arise from the reaction of HSiMe₃ with **3a**. In fact, isolated **2** is catalytically coupled to initially yield carbosilane **4a** as the only tetrameric product (eq 3).



The first example of a homogeneous dehydrogenative coupling of hydrosilanes to directly produce oligomeric carbosilanes has been described.¹⁶ A mechanism involving the intermediacy of η²-silene ligands is most consistent with observations obtained thus far and has precedent in a related osmium system.¹³ Further exploration of this chemistry is currently in progress.

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Supplementary Material Available: Experimental procedures (including spectral and GC data) for the synthesis of **2-4** (4 pages). Ordering information is given on any current masthead page.

Microscale CD Method for Determining Absolute Configurations of Acyclic Amino Tetrols and Amino Pentols. Structures of Aminobacteriohopanepolyols from the Methylophilic Bacterium *Methylococcus luteus*

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The CD exciton chirality method¹ has been applied to numerous compounds including sugars² and acyclic polyols with up to five contiguous OH's.³ In prokaryotic membranes, hopanoids play the reinforcing role of sterols in eukaryotic membranes, and the total organic carbon in fossil hopanoids is estimated to equal the carbon in all living animals, plants, and microorganisms, ca. 10¹² tons.⁴ The CD method developed for acyclic polyols³ can be extended to amino polyols as demonstrated by its application⁵ to a bacteriohopane with an established amino triol moiety.⁶ We now extend this method to bacteriohopanoids with amino tetrol **1** and amino pentol **2** moieties of unknown stereochemistry, despite the lack of authentic hexol corresponding to **2**.

Amino tetrol **1** and amino pentol **2** were isolated as acetates from *Methylococcus luteus* (NCIMB 11914) and were identical with the corresponding triterpenoids from *Methylococcus capsulatus* and *Methylomonas methanica*.⁶ Free amino polyols **1** and **2**, as precipitates that were poorly soluble in solvents, were obtained from acetates by heating at 110 °C for 7 h in 3% KOH/*i*-PrOH.

In the bichromophoric CD method for configurational studies of acyclic polyols³ and amino polyols,⁵ the terminal OH or NH₂ is anthrolylated, the remaining OH's are *p*-methoxycinnamoylated, and the 220–340-nm CD spectra are compared with characteristic reference curves. The present improved nanomolar-scale deriv-

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