tween the metal atoms, as shown in Scheme I.

Acknowledgment. These studies were supported by the U.S. Department of Energy under Grant No. DEFG84ER13296.

Supplementary Material Available: Tables of crystal data, positional parameters, bond distances and angles, and anisotropic thermal parameters for the structural analyses of **2a** and **3** (16 pages); tables of structure factors (32 pages). Ordering information is given on any current masthead page.

Organolanthanide-Catalyzed Dehydrogenative Coupling of Silanes. Mechanistic Implications

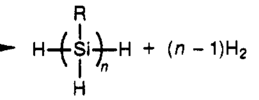
Craig M. Forsyth, Steven P. Nolan, and Tobin J. Marks*

Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3113

Received June 4, 1991

Summary: Organolanthanide complexes of the type Cp'_2LnR ($Cp' = \eta^5\text{-}Me_5C_5$; Ln = La, Nd, Sm, Y, Lu; R = H, $CH(SiMe_3)_2$), $Me_2SiCp''_2LnR$ ($Cp'' = \eta^5\text{-}Me_4C_5$; Ln = Nd; R = $CH(SiMe_3)_2$), Cp'_2Sm, and $Cp'_2Sm(THF)_2$ catalyze the rapid dehydrogenative oligomerization of $PhSiH_3$. Kinetic and mechanistic arguments exclude the importance of metal-centered redox processes in the catalytic cycle and support instead "four-center" "heterolytic" bond-scission/bond-forming sequences.

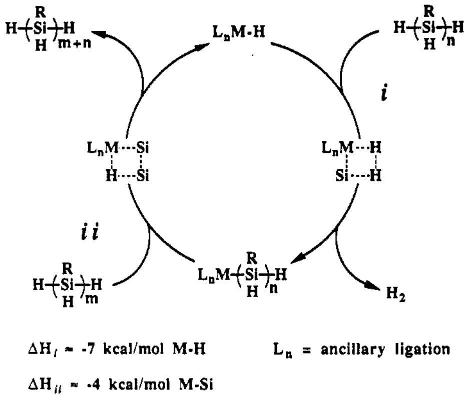
Polyorganosilanes are of considerable current interest as ceramic precursors, third-order NLO materials, deep-UV photoresists, conductive polymers, and photoconductors.[1] A major advance in polyorganosilane synthesis was Harrod's discovery of the catalytic dehydrogenative oligomerization/polymerization of organosilanes effected by organo-group 4 complexes (e.g., eq 1).[2,3] Key unresolved



$$n\mathrm{RSiH_3} \xrightarrow{\text{catalyst}} \mathrm{H}\!\left(\begin{matrix}\mathrm{R}\\ |\\ \mathrm{Si}\\ |\\ \mathrm{H}\end{matrix}\right)_{\!n}\!\mathrm{H} + (n-1)\mathrm{H_2} \tag{1}$$

mechanistic issues in such catalytic cycles concern the importance of oxidative addition/reductive elimination sequences,[2-4] the intermediacy of silylene complexes,[2,5] the importance of free radical processes,[2f] or the dominance

Scheme I



of four-center heterolytic M–Si/M–H transposition processes (Scheme I). The latter scenario is supported by Tilley's recent characterization of several group four-centered stoichiometric model reactions[6] and thermochemical results,[7] which indicate (for closely analogous M = U) that the steps in Scheme I possess no significant thermodynamic impediments. If Scheme I were indeed valid, metal centers incapable of oxidative addition/reductive elimination sequences, which possess only one possible metal-Si/H σ functionality, and for which other four-center processes are typically facile, might be expected to be catalytically competent. We report here, in an application of this test, that electrophilic organolanthanides of the type $Cp'_2LnR/Me_2SiCp''_2LnR$ ($Cp' = \eta^5\text{-}Me_5C_5$; $Cp'' = \eta^5\text{-}Me_4C_5$; Ln = lanthanide; R = hydrocarbon, hydride)[8,9] are highly active for eq 1, some initial catalytic phenomenology, and initial kinetic/mechanistic observations.[10]

---

[1] (a) Miller, R. D. *Angew. Chem., Int. Ed. Engl. Adv. Mater.* **1989**, *28*, 1733–1740. (b) Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359–1410. (c) West, R.; Maxka, J. *ACS Symp. Ser.* **1988**, *360*, 6–20. (d) Miller, R. D.; Rabolt, J. F.; Sooriyakumaran, R.; Fleming, W.; Fickes, G. N.; Farmer, B. L.; Kuzmany, H. *ACS Symp. Ser.* **1988**, *360*, 43–60. (e) Matyjaszewski, M.; Chen, Y. L.; Kim, H. K. *ACS Symp. Ser.* **1988**, *360*, 78–88. (f) Worsfold, D. J. *ACS Symp. Ser.* **1988**, *360*, 101–111. (g) Baumert, J.-C.; Bjorklund, G. C.; Jundt, D. H.; Jurich, M. C.; Looser, H.; Miller, R. D.; Rabaolt, J.; Sooriyakumaran, R.; Swalen, J. D.; Twieg, R. *J. Appl. Phys. Lett.* **1988**, *53*, 1147–1149.

[2] (a) Gauvin, F.; Harrod, J. F. *Polym. Prepr.* **1991**, *32*, 439–440. (b) Mu, Y.; Aitken, C.; Coté, B.; Harrod, J. F.; Samuel, E. *Can. J. Chem.* **1991**, *69*, 264–276. (c) Harrod, J. F.; Mu, Y.; Coté, B. *Polym. Prepr.* **1990**, *31*, 228–229. (d) Aitken, C.; Barry, J.-P.; Gauvin, F.; Harrod, J. F.; Malek, A.; Rousseau, D. *Organometallics* **1989**, *8*, 1732–1736. (e) Harrod, J. F. *ACS Symp. Ser.* **1988**, *360*, 89–100. (f) Harrod, J. F.; Yun, S. S. *Organometallics* **1987**, *6*, 1381–1387. (g) Aitken, C. T.; Harrod, J. F.; Samuel, E. *J. Organomet. Chem.* **1985**, *279*, C11–C13. (h) Aiken, C. T.; Harrod, J. F.; Samuel, E. *J. Am. Chem. Soc.* **1986**, *108*, 4059–4066.

[3] (a) Campbell, W. H.; Hilty, T. K.; Yurga, L. *Organometallics* **1989**, *8*, 2615–2618. (b) Chang, L. S.; Corey, J. Y. *Organometallics* **1989**, *8*, 1885–1893.

[4] (a) Corey, J. Y.; Zhu, X. H.; Bedard, T. C.; Lange, L. D. *Organometallics* **1991**, *10*, 924–930. (b) Brown-Wensley, K. A. *Organometallics* **1987**, *6*, 1590–1591. (c) Corey, J. Y.; Chang, L. S.; Corey, E. R. *Organometallics* **1987**, *6*, 1595–1596. (d) Ojima, I.; Inaba, S. D.; Kogure, T.; Nagai, Y. *J. Organomet. Chem.* **1973**, *55*, C7–C8.

[5] Harrod, J. F.; Ziegler, T.; Tschinke, V. *Organometallics* **1990**, *9*, 897–902.

[6] (a) Walzer, J. F.; Woo, H. G.; Tilley, T. D. *Polym. Prepr.* **1991**, *32*, 441–442. (b) Tilley, T. D.; Woo, H.-G. *Polym. Prepr.* **1990**, *31*, 228–229. (c) Tilley, T. D. *Comments Inorg. Chem.* **1990**, *10*, 37–51. (d) Woo, H. G.; Tilley, T. D. *J. Am. Chem. Soc.* **1989**, *111*, 8043–8044.

[7] Nolan, S. P.; Porchia, M.; Marks, T. J. *Organometallics* **1991**, *10*, 1450–1457.

[8] (a) Mauermann, H.; Marks, T. J. *Organometallics* **1985**, *4*, 200–202. (b) Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091–8103. (c) Jeske, G.; Schock, L. E.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8103–8110. (d) Jeske, G.; Lauke, H.; Mauermann, H.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8111–8118.

[9] Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51–55.

[10] (a) Communicated in part: Marks, T. J. First International Conference on f-Elements, Leuven, Sept 4–7, 1990. (b) While this work was nearing completion, Cp'_2LuMe-catalyzed dehydrogenative silane polymerization was also reported by P. L. Watson: Watson, P. L., First International Conference on f-Elements, Leuven, Sept 4–7, 1990. See also: Watson, P. L.; Tebbe, F. N. U.S. Patent 4,965,386, Oct 23, 1990; *Chem. Abstr.* **1991**, *114*, 123331p.

0276-7333/91/2310-2543$02.50/0

As monitored by ^1H NMR spectroscopy and H_2 evolution, Cp'_2LnR (Ln = La, Nd, Sm, Y, Lu; R = H, $CH(SiMe_3)_2$) and $Me_2SiCp''_2LnR$ (Ln = Nd; R = $CH(SiMe_3)_2$) complexes[8a-c] react rapidly with a 10-fold molar excess of $PhSiH_3$ in hydrocarbon solvents to eliminate RH and form polysilanes (eq 2, vide infra). NMR shows the hydro-

$$Cp'_2LnR + PhSiH_3 \rightarrow RH + Cp'_2LnSiH_2Ph \rightarrow \text{etc.} \quad (2)$$

carbyls to undergo quantitative elimination of $H_2C(SiMe_3)_2$ according to the rate law of eq 3 for Ln = La. This Ln–C

$$\nu = k[Cp'_2LnCH(SiMe_3)_2][PhSiH_3]$$
$$k = 5.4\ (5) \times 10^{-2}\ M^{-1}\ s^{-1} \quad (25\ °C) \qquad (3)$$

silaneolysis leads to a slight induction period, which is not observed with hydride precatalysts. Following these initiation processes, the NMR reveals the appearance and progressive increase of small oligomeric silanes (dimers and trimers).[2b,d,f,g] This initial product mix is typical of those from group 4 catalysts[2,4] and is consistent with a step-growth polymerization process. Catalytic turnover also occurs in THF-d_8, but at a considerably diminished rate ($\lesssim 0.01\times$ for Ln = La). This inhibitory behavior has considerable precedent[8,9,12] and reasonably reflects competition for vacant sites in the catalyst coordination sphere (vide infra). The conveniently prepared divalent complexes $Cp'_2Sm(THF)_2$ and Cp'_2Sm[13] are also active precatalysts for eq 1, and thermodynamic considerations (eq 4)[7] as well as NMR line widths argue that the catalytic manifold involves trivalent lanthanides.

$$Cp'_2Sm + H_3SiR \rightarrow \tfrac{1}{2}Cp'_2Sm\text{-}SiH_2R + \tfrac{1}{2}Cp'_2Sm\text{-}H \qquad \Delta H_{calcd} \approx -11\ kcal/mol \quad (4)$$

Preparative gram-scale polymerizations have been carried out using $Cp'_2LaCH(SiMe_3)_2$ as a model precatalyst and monitoring H_2 evolution manometrically.[14] At the completion of rapid H_2 evolution, a viscous oligosilane oil is obtained. Longer conversion times accompanied by heating and evacuation afford solid oligosilanes.[14] The spectral characteristics of both these products[14] are quite similar to those obtained with group 4 catalysts.[2-4] Molecular weight data (cryoscopic, GPC) indicate degrees of polymerization on the order of 5–9.[14] No attempt has been made to optimize these values, and for the present purposes, the important point is the similarity of the products to those from group 4 catalysts.

Table I. Kinetic Data for Initial Dehydrogenative Phenylsilane Coupling Catalyzed by Various Organolanthanide Complexes[a]

catalyst	N_t,[b] h^{-1}	catalyst	N_t,[b] h^{-1}
$(Cp'_2LaH)_2$	80	$(Cp'_2YH)_2$	3310
$(Cp'_2NdH)_2$	1010	$(Cp'_2LuH)_2$	5200
$(Cp'_2SmH)_2$	2140		

[a] Conditions: [catalyst] = 0.0090 M, [$PhSiH_3$] = 2.70 M, toluene solution, T = 25.4 °C. [b] Estimated uncertainty: ±5%.

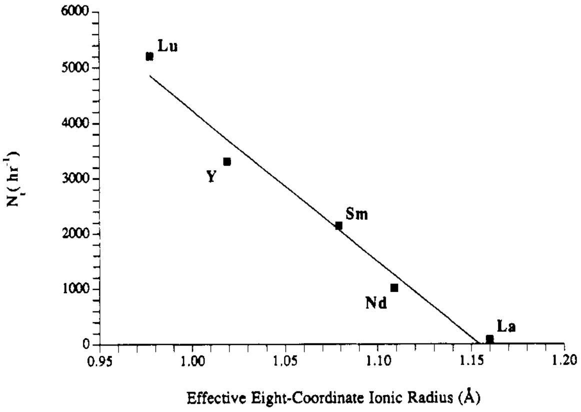
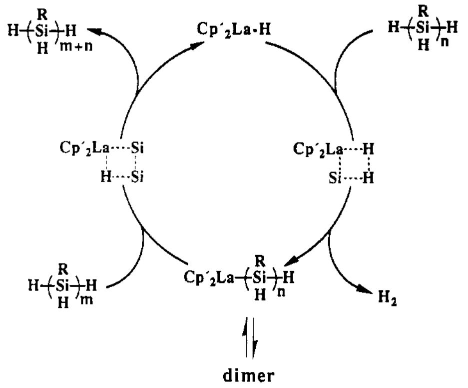


Figure 1. Turnover frequencies for initial dehydrogenative phenylsilane coupling by various $(Cp'_2LnH)_2$ catalysts plotted as a function of the Ln(III) effective eight-coordinate ionic radius.

Scheme II



In regard to the components of Scheme I, in situ NMR studies provide no evidence for lanthanide hydrides (e.g., the LaH and Cp′ signals of $(Cp'_2LaH)_2$[8b,15] are absent). However, sparingly soluble $(Me_2SiCp''_2NdH)_2$[8c] precipitates from the corresponding reaction mixture, arguing that the catalytic manifold contains a hydride or is in equilibrium with a hydride. Kinetic measurements of turnover frequency (N_t) as a function of lanthanide and other parameters were carried out manometrically by using a modified configuration of the thermostated constant-volume, pseudo-constant-pressure apparatus described previously.[8d] Typical substrate/catalyst ratios were >100:1 and reactions were monitored to ≥25% conversion. Kinetic data were taken with $(Cp'_2LnH)_2$ catalysts (in which there is no induction period) from initial rates, i.e., in the

---

(11) At longer conversions, Ph_2SiH_2 can also be detected; δ(Si–H) = 5.02, $J_{^{29}Si-H}$ = 200 Hz.

(12) (a) Gagné, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 4108–4109. (b) Gagné, M. R.; Stern, C. L.; Marks, T. J., unpublished results.

(13) (a) Evans, W. J.; Drummond, D. K.; Grate, J. W.; Zhang, H.; Atwood, J. I. *J. Am. Chem. Soc.* **1987**, *109*, 3928–3936. (b) Evans, W. J.; Grate, J. W.; Chei, H. W.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 941–946.

(14) On a preparative vacuum line, 25 mg (0.040 mmol) of $Cp'_2LaCH(SiMe_3)_2$ was stirred at 25 °C with 1.0 g (9.2 mmol) of distilled $PhSiH_3$ in 5 mL of toluene. A short (~1 min) induction period was observed followed by vigorous gas evolution. After rapid H_2 evolution ceased (~12 h), the volatiles were removed, and the residue was dissolved in toluene and filtered through a short column of silica gel, yielding the polysilane as a colorless, viscous oil following toluene evaporation. In a parallel procedure, the reaction was repeated, but after H_2 evolution had ceased, the mixture was heated to 150 °C under vacuum. This procedure resulted in the isolation after workup of a colorless solid. **Oil.** IR (neat film): 3070 s, 3050 s, 3020 m, 2120 vs, br [ν(Si–H)], 1480 s, 1339 m, 1267 m, 1196 m, 1104 vs [ν(Si–C)], 1069 m, 1040 m, 1007 s, 918 s [δ(Si–H_2)], 850 s, 770 vs, br, 720 vs, br, 610 s, 449 s cm^{-1}. M_n = 640 (cryoscopy); M_n = 506, M_w = 595 (GPC in THF versus polystyrene). **Solid.** IR (Nujol mull): 3070 w, 2110 s, br, 1590 s, 1575 w; 1430 s, 1340 w, 1310 w, 1265 w, 1200 w, 1170 w, 1107 w, 1040 w, 1010 w, 920 w, 780 s, br, 745 s, br, 705 s, br, 450 m, br. M_n = 1005 (cryoscopy) M_n = 723, M_w = 940 (GPC in THF versus polystyrene). ^1H NMR (toluene-d_8) for both materials: δ 7.4 (m, br, Ph), 7.0 (m, br, Ph), 4.75 (m, br, SiH), 4.60 (m, br, SiH). While the GPC of the oil is characteristically bimodal,[2b,6a] that of the solid is a broad envelope.

(15) Although rapid La–H/Si–H exchange might explain the absence of the La–H signal, the disappearance of the corresponding Cp′ signal upon substrate addition demonstrates that $(Cp'_2LaH)_2$ is not present in significant amonts.

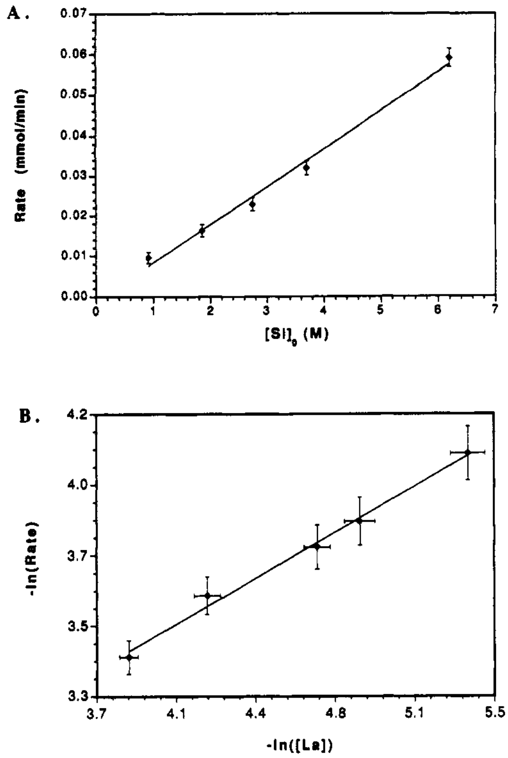


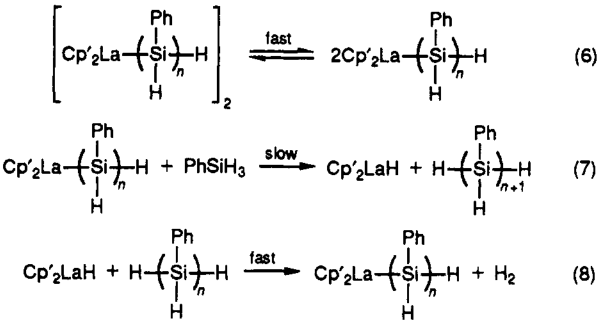
Figure 2. Kinetic data for the $(\text{Cp}'_2\text{LaH})_2$-catalyzed dehydrogenative coupling of phenylsilane in toluene. (A) Rate as a function of silane concentration for [La] = 0.0090 M. The line is a least-squares fit to the data points; k_{obs} = 9.4 (1) × 10^{-6} L min^{-1} (R = 0.99). (B) Plot to determine the reaction order in [La]. The line is a least-squares fit to the data points, yielding order = 0.4 (1) (R = 0.99).

low conversion regime (≤20 turnovers) where the reaction is essentially pseudo-zero-order in substrate. Under these conditions, NMR spectroscopy indicates only the formation of dimers and trimers, and side reactions (e.g., Ph_2SiH_2 formation) account for ≤5% of the products. For identical $(\text{Cp}'_2\text{LnH})_2$ catalyst and substrate concentrations, the relative rates vary over a wide range with La < Nd < Sm < Y < Lu (Table I). This trend reveals no parallels with lanthanide III/II redox characteristics[16] but correlates well with metal ionic radius (Figure 1).[17] Indeed, a similar kinetic trend was observed in $(\text{Cp}'_2\text{LnH})_2$-catalyzed 1-hexene hydrogenation where four-center Ln–hexyl bond hydrogenolysis is turnover-limiting.[8d] This and the present result may reflect, among other factors, charge/radius demands in the four-center transition state. Attempts to acquire accurate rate data for the $\text{Me}_2\text{SiCp}''_2\text{Nd}$ catalyst have been frustrated by the aforementioned precipitation of the corresponding hydride.

Kinetic studies of the $(\text{Cp}'_2\text{LaH})_2/\text{PhSiH}_3$ system reveal that the reaction is first-order in silane over a 7-fold concentration range (Figure 2A). Using the van't Hoff procedure,[18] the reaction is found to be approximately half-order (0.4 (1)) in La over a 5-fold concentration range (Figure 2B, eq 5).

$$\nu = k[\text{PhSiH}_3]^1[\text{La}]^{1/2} \qquad (5)$$

A minimum mechanistic scenario invokes a dimeric La–silyl species,[19] for which there is group 4 precedent,[2h] in rapid preequilibrium with a reactive monomer (eqs 6–8). The turnover-limiting step is likely to be least exothermic and sterically most demanding. Scheme I should then be modified for this catalyst (Scheme II).



In summary, these results show that organolanthanides are highly active catalysts for dehydrogenative silane oligomerization/polymerization, that one- or two-electron oxidative addition/reductive elimination sequences are not important in the catalytic cycle, and that the kinetic/mechanistic data strongly support four-center heterolytic bond-breaking/bond-forming patterns.

Acknowledgment. We are grateful to the NSF (CHE-8800813) and Akzo Corporate Research for generous support of this work. We thank Dr. E. Schomaker of Akzo for GPC measurements.

---

[16] Morss, L. R. *Chem. Rev.* **1976**, *76*, 827–841.

[17] Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *A32*, 751–767.

[18] Laidler, K. H. *Chemical Kinetics*, 2nd ed.; McGraw-Hill: New York, 1963; pp 15–17.

[19] (a) A dimeric hydridosilyl[2h] seems less likely on the basis of the aforementioned thermochemistry and in situ spectroscopy. (b) The presence of the preequilibrium must of course be considered in comparisons to the hydrogenation catalysis.[8d]