J. Am. Chem. Soc. 1995, 117, 5863−5864

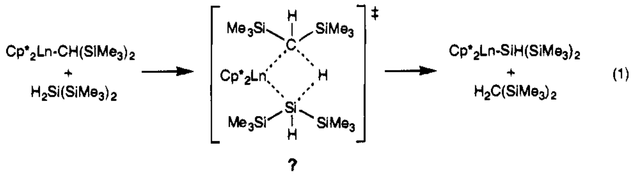
Autocatalytic Mechanism for σ-Bond Metathesis Reactions of $(\eta^5\text{-}C_5Me_5)_2SmCH(SiMe_3)_2$ with Silicon−Hydrogen Bonds†

Nora S. Radu and T. Don Tilley*

Department of Chemistry, University of California
Berkeley, California 94720-1460

Received February 15, 1995

Hydrocarbon activations by d^0 metal complexes have become well established as fundamental reaction types involving "σ-bond metathesis" steps which pass through four-center transition states.[1] In recent years, it has also been shown that related hydrosilane activations may be incorporated into dehydrocoupling cycles which produce polysilanes.[2] Organolanthanide derivatives have played a strong role in the development of C−H bond activation chemistry,[1g−m] and recent reports of dehydrocoupling[3] and hydrosilation[4] reactions catalyzed by lanthanide complexes suggest that silanes may also be activated by four-center transition states involving Ln centers. With respect to the latter issue, we have recently reported[5] the first neutral lanthanide silyl complexes, $Cp^*_2LnSiH(SiMe_3)_2$ ($Cp^* = \eta^5\text{-}C_5Me_5$; Ln = Sm, Nd), which were formed by the σ-bond metathesis reaction of $Cp^*_2LnCH(SiMe_3)_2$ with $H_2Si(SiMe_3)_2$ (eq 1). Given the apparent (but unlikely) involvement of an



(1)

exceedingly hindered four-center transition state involving bulky $CH(SiMe_3)_2$ and $SiH(SiMe_3)_2$ substituents (eq 1), we were motivated to study the mechanism of this process. Here we report initial results from this investigation, which reveal an unexpected pathway for σ-bond metathesis that may be common in reactions of this type.

Initial kinetic runs for quantitative reactions of $Cp^*_2SmCH(SiMe_3)_2$ (**1**) with $H_2Si(SiMe_3)_2$ over the temperature range 25−85 °C (benzene-d_6) provided quite reasonable second-order plots over more than 3 half-lives and data consistent with the rate law: rate = $k[\mathbf{1}][H_2Si(SiMe_3)_2]$. However, in attempting to follow the kinetics of this reaction with a sample of **1** that had been recrystallized *three times*, we found that **1** and $H_2Si(SiMe_3)_2$ do not react directly, and products formed only after a variable induction time (usually 5−20 min at 75 °C). When such induction periods are observed, the spectroscopic yield of $Cp^*_2SmSiH(SiMe_3)_2$ (**2**) is reduced to 60−75%. Figure 1 illustrates the formation of **2** as a function of time in a reaction of **1** with 5 equiv (0.48 M) of $H_2Si(SiMe_3)_2$. This "S-shaped" concentration profile is consistent with a second-order autocatalytic mechanism in which the reaction is catalyzed by a product or intermediate.[6]

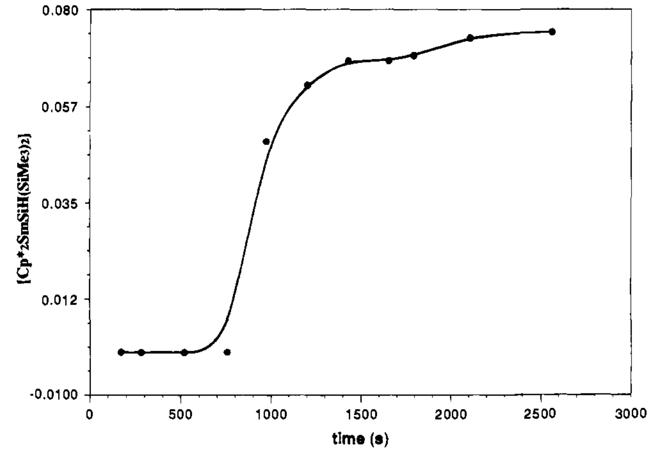
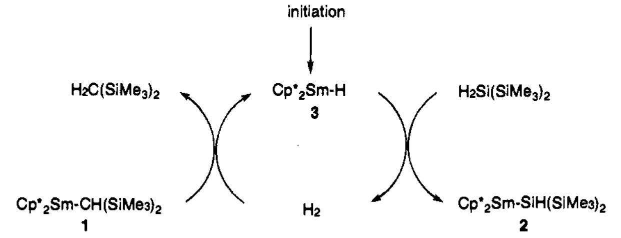


Figure 1. Kinetic profile for $Cp^*_2SmSiH(SiMe_3)_2$ formation in the reaction of $Cp^*_2SmCH(SiMe_3)_2$ with $H_2Si(SiMe_3)_2$ at 75 °C.

Scheme 1



Attempts to initiate this reaction in search of possible catalysts began with injection of various radical species. However, addition of azoisobutyronitrile, photochemically or thermally generated *tert*-butoxy radical, or AgO_3SCF_3 failed to eliminate the induction period. The induction period is eliminated by catalytic amounts of H_2 (0.15 equiv), $[Cp^*_2SmH]_2$[7] (**3**, 0.1 equiv), and $[Cp^*_2Sm(\mu\text{-}H)(\mu\text{-}CH_2C_5Me_4)SmCp^*]$ (**4**, 0.1 equiv, a decomposition product of **3**).[8] These observations led to consideration of two possible mechanisms (Schemes 1 and 2), which are based on catalysis by the samarium complexes **3** and **4**. In Scheme 1, hydride **3** catalyzes the alkyl-for-silyl exchange by directly dehydrocoupling with $H_2Si(SiMe_3)$ to produce the silyl product **2** and hydrogen, which cleaves the Sm−C bond of **1** to give the alkane product and regenerate the catalyst. The mechanism involving the hydride-bridged dimer **4** as an intermediate (Scheme 2) is based on two steps: (1) an intermolecular alkane-elimination reaction between samarium complexes **1** and **3** and (2) a σ-bond metathesis reaction of **4** with $H_2Si(SiMe_3)_2$ to produce the silyl product **2** and the hydride **3**. Consistent with both mechanisms, norbornene and 1-hexene

---

† This work was initiated at the University of California, San Diego.

[1] (a) Rothwell, I. P. *Polyhedron* **1985**, *4*, 177. (b) Steigerwald, M. L.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1984**, *106*, 308. (c) Ziegler, T.; Folga, E.; Berces, A. *J. Am. Chem. Soc.* **1993**, *115*, 636. (d) Rabaa, H.; Saillard, J. Y.; Hoffmann, R. *J. Am. Chem. Soc.* **1986**, *108*, 4327. (e) Simpson, S. J.; Andersen, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 4064. (f) Simpson, S. J.; Turner, H. W.; Andersen, R. A. *Inorg. Chem.* **1981**, *20*, 2991. (g) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51. (h) Thompson, M. E.; Bercaw, J. E. *Pure Appl. Chem.* **1984**, *56*, 1. (i) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, B. D.; Santarsiero, W. P.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203. (j) Bruno, J. W.; Smith, G. M.; Marks, T. J.; Fair, C. K.; Schultz, A. J.; Williams, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 40. (k) Evans, W. J. *Adv. Organomet. Chem.* **1985**, *24*, 131. (l) Booij, M.; Deelman, B.-J.; Duchateau, R.; Postman, D. S.; Meetsma, A.; Teuben, J. H. *Organometallics* **1993**, *12*, 3531. (m) Schaverien, C. J. *Adv. Organomet. Chem.* **1994**, *36*, 283.

[2] (a) Tilley, T. D. *Comments Inorg. Chem.* **1990**, *10*, 37. (b) Tilley, T. D. *Acc. Chem. Res.* **1993**, *26*, 22. (c) Harrod, J. F.; Mu, Y.; Samuel, E. *Polyhedron* **1991**, *10*, 1239.

[3] (a) Watson, P. L.; Tebbe, F. N. U.S. Pat 4,965,386, 1990. (b) Sakakura, T.; Lautenschlager, H.-J.; Nakajima, M.; Tanaka, M. *Chem. Lett.* **1991**, 913. (c) Forsyth, C. M.; Nolan, S. P.; Marks, T. J. *Organometallics* **1991**, *10*, 2543. (d) Tilley, T. D.; Radu, N. S.; Walzer, J. F.; Woo, H.-G. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1992**, *33(1)*, 1237.

[4] (a) Sakakura, T.; Lautenschlager, H.-J.; Tanaka, M. *J. Chem. Soc., Chem. Commun.* **1991**, *40*. (b) Molander, G. A.; Julius, M. *J. Org. Chem.* **1992**, *57*, 6347.

[5] Radu, N. S.; Tilley, T. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1992**, *114*, 8293.

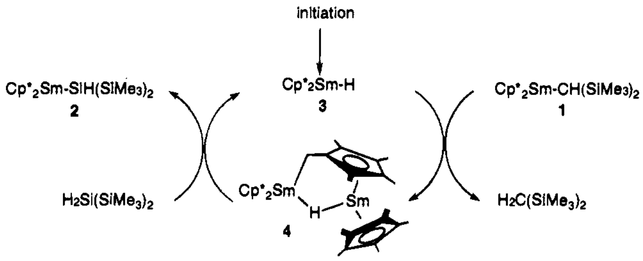
[6] Moore, J. W.; Pearson, R. G. *Kinetics and Mechanism*; John Wiley and Sons: New York, 1981; p 26.

[7] Under the experimental conditions employed ($[Cp^*_2SmH]_2 \sim 0.01$ M), a high degree of dissociation to the monomer is expected.[10]

[8] Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *Organometallics* **1991**, *10*, 134.

0002-7863/95/1517-5863$09.00/0

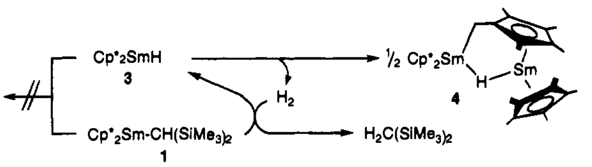
Scheme 2



inhibit the reaction of **1** with $H_2Si(SiMe_3)_2$, apparently by trapping Sm−hydride species that form.[9]

The feasibility of both mechanisms was investigated by examining the primary steps in each. The first step in the mechanism of Scheme 1, the reaction of **3** with $H_2Si(SiMe_3)_2$, quantitatively proceeds to the silyl complex **2** if a slight excess of the silane is present. Without the silane in excess, the competing decomposition of **3** to **4** (*vide infra*) leads to a decreased yield of **2**. The hydrogenolysis of **1**, in the second step, is rapid and quantitative (by ^1H NMR spectroscopy). Therefore both steps in this catalytic cycle are observable.

Evidence for the mechanism of Scheme 2 is found in the fact that complexes **1** and **3** react quantitatively to give **4** and $H_2C(SiMe_3)_2$. Closer examination of this process revealed that a concerted, bimolecular elimination is not involved since hydride **3** is consumed more rapidly than **1** during the reaction. Furthermore, a crossover experiment involving reaction of **3** with $Cp^*_2YCH(SiMe_3)_2$ revealed that the all-samarium dimer **4** is formed exclusively in the early stages of the reaction. It therefore seems clear that the reaction of **1** and **3** to give **4** involves a two-step process driven by the thermal decomposition of **3** to hydrogen and **4** (eq 2). The reaction of $H_2Si(SiMe_3)_2$ with **4** also gives the predicted products of Scheme 2, but complete conversion to **2** requires an excess (5 equiv) of silane since hydride **3** competitively dehydrocouples with the silane to also give **2**. When $H_2Si(SiMe_3)_2$ is the limiting reagent (5 equiv of **4**), significant quantitites of **3** are observed as product.



(2)

The observed reaction chemistry clearly indicates that both catalytic mechanisms (Schemes 1 and 2) are chemically possible. However, their relative importance can be judged by consideration of the reaction rates of the steps described above. In Scheme 1 the slowest step ($t_{1/2}$ ~ 50 min at 21 °C) is the formation of the silyl product **2**. The next step in this scheme is observed to be very fast, as is expected from previously reported olefin hydrogenation rates catalyzed by $[Cp^*_2LnH]_2$ complexes (e.g., $k \sim 5000\ M^{-1}\ s^{-1}$ at 25 °C for hydrogenation of $Cp^*_2Sm(hexyl)$).[10] The formation of **4** ($t_{1/2}$ ~ 30 min at 75 °C) is the rate-limiting step in Scheme 2, since the reaction of **4** with $H_2Si(SiMe_3)_2$ is faster ($t_{1/2}$ ~ 10 min at 75 °C). Taking this into consideration, it is apparent that compound **4** does not play an important role in the autocatalytic reaction of **1** and $H_2Si(SiMe_3)_2$, since both reactions in Scheme 2 are significantly slower than either step in Scheme 1.

The above results suggest that hydride **3** and $H_2Si(SiMe_3)_2$ react directly via a four-center transition state to give the observed σ-bond methathesis products. The kinetics of this reaction were followed by ^1H NMR spectroscopy (benzene-d_6 solution, 4 equiv of silane).[11] The order in Cp^*_2SmH was established as unity using the van't Hoff procedure,[12] Wilkinson plots,[13] and the linearity of $\ln[Cp^*_2SmH]$ vs time over 3 half-lives. This kinetic behavior is consistent with the samarium hydride reacting in its monomeric form, as expected.[7] The reaction was determined to be first order in silane over a four-fold concentration range (from k_{obs} vs silane concentration plots); therefore the overall rate law is

$$\text{rate} = k[Cp^*_2SmH][SiH_2(SiMe_3)_2]$$

An Eyring plot of rate data for the temperature range 21−70 °C provided the activation parameters $\Delta H^{\ddagger} = 12.6(5)$ kcal/mol and $\Delta S^{\ddagger} = -32(2)$ eu, which are consistent with what is expected for a concerted, four-center transition state.[1b,j]

This study shows that a seemingly simple σ-bond methathesis process in fact proceeds by a more complex autocatalytic mechanism mediated by a reactive hydride complex. A similar observation was recently reported by Luinstra and Teuben,[14] who determined that the thermal decomposition of $Cp^*_2Ti(alkyl)$ complexes to $Cp^*(C_5Me_4CH_2)Ti$ is not unimolecular, but is catalyzed by trace quantities of hydrogen. The mechanism reported here (Scheme 1) appears to be general, since we have observed evidence for autocatalysis (as indicated by induction periods and sigmoidal concentration profiles) in reactions of **1** with other hydrosilanes (e.g., $PhSiH_3$, $(2,4,6\text{-}Me_3C_6H_2)SiH_3$, and Ph_3SiSiH_3). Perhaps most importantly, these results emphasize the potential danger in interpreting second-order reaction kinetics for σ bond metathesis processes as involving concerted, four-center transition states. Such reactions may in fact be masked hydrogen-catalyzed processes, which may not present themselves by way of an observable induction period. This possibility seems even more likely when one considers that hydrogen forms readily by decompositions or side reactions of early- and f-metal complexes, and in addition, hydrogen is probably the most reactive substrate (compared to alkanes, silanes, etc.) for σ-bond methasis.

Acknowledgment. We thank the Divisions of Chemistry and Materials Research at the National Science Foundation and the donors of the Petroleum Research Foundation, administered by the American Chemical Society, for support of this research.

JA9505356

---

(9) Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091.

(10) Jeske, G.; Lauke, H.; Mauermann, H.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8111.

(11) Rate data: $k_{21^\circ C} = 1.9(1) \times 10^{-3}\ M^{-1}\ s^{-1}$; $k_{30^\circ C} = 4.9(1) \times 10^{-3}\ M^{-1}\ s^{-1}$; $k_{50^\circ C} = 1.2(1) \times 10^{-2}\ M^{-1}\ s^{-1}$; $k_{60^\circ C} = 2.7(4) \times 10^{-2}\ M^{-1}\ s^{-1}$; $k_{70^\circ C} = 8(2) \times 10^{-2}\ M^{-1}\ s^{-1}$.

(12) Laidler, K. H. *Chemical Kinetics*, 2nd ed.; McGraw-Hill: New York, 1963; pp 15−17.

(13) Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*; McGraw-Hill: New York, 1981; pp 33−35.

(14) Luinstra, G. A.; Teuben, J. H. *J. Am. Chem. Soc.* **1992**, *114*, 3361.