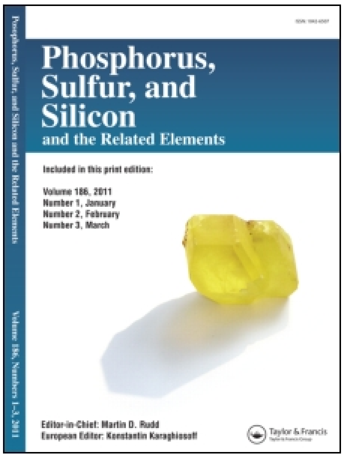


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Sigma-Bond Metathesis Reactions Involving Lanthanide-Silicon and Lanthanide-Hydrogen Bonds

N. S. Radu[a]; T. D. Tilley[a]
[a] Department of Chemistry, University of California at San Diego, CA

To cite this Article Radu, N. S. and Tilley, T. D.(1994) 'Sigma-Bond Metathesis Reactions Involving Lanthanide-Silicon and Lanthanide-Hydrogen Bonds', Phosphorus, Sulfur, and Silicon and the Related Elements, 87: 1, 209 — 218
To link to this Article: DOI: 10.1080/10426509408037454
URL: http://dx.doi.org/10.1080/10426509408037454

Phosphorus, Sulfur, and Silicon, 1994, Vol. 87, pp. 209–218
Reprints available directly from the publisher
Photocopying permitted by license only

SIGMA-BOND METATHESIS REACTIONS INVOLVING LANTHANIDE-SILICON AND LANTHANIDE-HYDROGEN BONDS

N. S. RADU and T. D. TILLEY*
Department of Chemistry, University of California at San Diego, La Jolla, CA 92093-0506

Neutral lanthanide silyl complexes $Cp^*_2LnSiH(SiMe_3)_2$ (**1**, Ln = Sm; **2**, Ln = Nd; **3**, Ln = Y; $Cp^* = \eta^5\text{-}C_5Me_5$) are synthesized by reaction of the corresponding alkyls $Cp^*_2LnCH(SiMe_3)_2$ with neat $SiH_2(SiMe_3)_2$. These complexes are monomeric in solution, but form dimers in the solid state through intermolecular Ln···CH_3-Si interactions. Mechanistic studies on this reaction indicate that it proceeds via a second-order autocatalytic process catalyzed by $[Cp^*_2LnH]_2$. Reactions of $[Cp^*_2LnH]_2$ with Cp_2WH_2 give the σ-bond metathesis products $Cp^*_2Ln(\mu\text{-}\eta^1,\eta^5\text{-}C_5H_4)(\mu\text{-}H)_2WCp$ (**5**, Ln = Sm; **6**, Ln = Y), via activation of a C-H (and not a W-H) bond of the tungsten hydride. The lanthanide borohydride complexes $Cp^*_2Ln(\eta^2\text{-}H_2BMes_2)$ (Mes = mesityl; **7**, Ln = Sm; **8**, Ln = Y) are obtained by the reaction of $[Cp^*_2LnH]_2$ with $[HBMes_2]_2$.

Key Words: Autocatalysis; borohydride; hydride; lanthanide complexes; silyl; tungsten.

INTRODUCTION

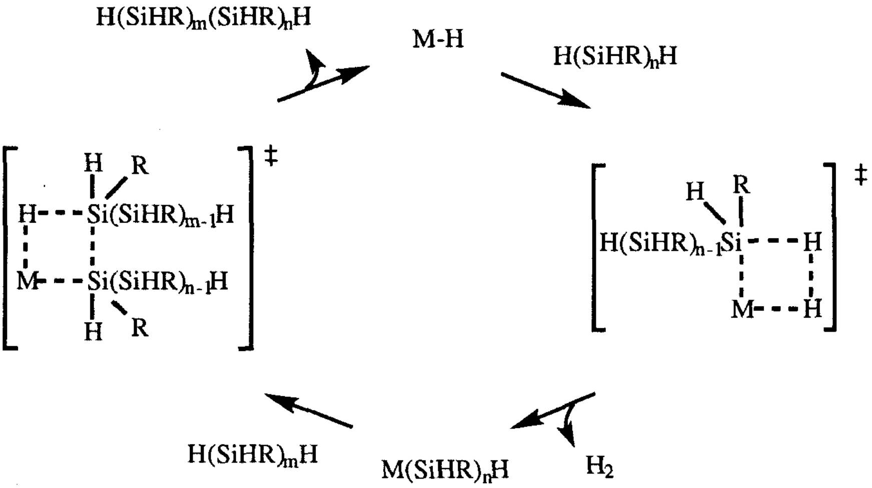
Much attention has recently been focused on production of polysilane polymers via the transition metal-catalyzed dehydrogenative coupling of silanes.[1] Interest in this approach has been stimulated by Harrod's discovery that titanocene and zirconocene complexes showed unique activity as catalysts for the dehydrocoupling of primary silanes $RSiH_3$ to oligomers of the type $H(SiHR)_nH$ (eq. 1, n = 10 - 20).

$$nRSiH_3 \xrightarrow{\text{catalyst}} (n-1)H_2 + H(SiHR)_nH \qquad (1)$$

Thus far, group 4 transition metal catalysts have shown the most promise, and currently the most active catalysts are “mixed ring” zirconocene complexes such as $CpCp^*Zr[Si(SiMe_3)_3]Me$.

Investigations of d^0 metal silyl complexes have generated a wide range of unprecedented chemical transformations.[2] These early transition-metal silyl complexes are particularly reactive toward insertions[3] and σ-bond metathesis processes,[4] which appear to involve participation of the d^0 M-Si σ-bond in 4-center, concerted transition states. In our study of early transition metal silicon compounds, we have observed all possible σ-bond metathesis reactions involving a d^0 metal center, silicon and hydrogen. These observations have led to development of a new coordination polymerization mechanism (Scheme 1) based on 4-center transition states.[5] The proposed mechanism involves two steps: the "dehydrometalation" of a hydrosilane with a metal hydride, followed by coupling of the resulting metal silyl complex with a second hydrosilane to produce a Si-Si bond and regenerate the metal hydride catalyst.

SCHEME 1

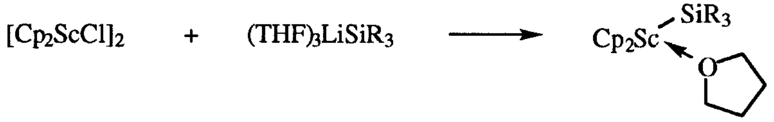


This mechanism strongly suggests that lanthanide and actinide complexes might be active dehydropolymerization catalysts, given their well known participation in related σ-bond metathesis reactions with hydrocarbons.[6] In fact, it has recently been reported that lanthanocene complexes are catalysts for the dehydrocoupling of primary silanes to polysilanes.[7] We studied the catalytic activity of $[Cp^*_2LnH]_2$ (Ln = Sm, Nd) in the dehydropolymerization of phenysilane.[8] This dehydrocoupling polymerization is very slow in comparison to the reaction catalyzed by mixed-ring zirconium complexes, and produces only small oligomers. This somewhat puzzling observation heightened our interest in the chemistry of lanthanide-silicon bonds, and motivated the investigations described here.

Of course, any thorough study of lanthanide-silicon bonded complexes requires significant quantities of isolable examples. Such compounds have proven to be synthetically illusive, and very few silyl complexes of the group 3 and lanthanide metals have been reported.[9a] The previously reported examples of lanthanide silyl complexes, of the type $[Li(DME)_3]^+[Cp_2Ln(SiMe_3)_2]^-$, were obtained by reaction of Cp_2LnCl_2- with $LiSiMe_3$.[9b-d] However, no reaction chemistry for these compounds has been described. In order to explore the potentially rich chemistry of lanthanide-silicon bonded compounds, we have developed a new synthetic route to stable lanthanide silyl derivatives which are amenable to investigation.

RESULTS AND DISCUSSION

We have recently reported the first silyl derivatives of scandium, obtained using silyl lithium reagents (eq. 2).[9a] Initial efforts to prepare lanthanide silyls by this route proved unsuccessful. For example, addition of $[Cp^*{}_2NdCl_2][Li(OEt_2)_2]$ to $(THF)_3LiSiR_3$ (R = Ph, $SiMe_3$) in toluene failed to give any isolable silyl derivatives.



(2)

A second potential route to lanthanide silyls seemed to be via σ-bond metathesis reactions involving hydrosilanes and lanthanide alkyl derivatives. We have previously shown that group 4 transition-metal silyl complexes can be prepared using a similar approach.[4a,d]

The reaction of $Cp^*{}_2YMe(THF)$ with $PhSiH_3$ yields $PhMeSiH_3$, indicating a primary σ-bond metathesis process involving a 4-center transition state that transfers the silyl group to carbon rather than to yttrium.[10] Sterically crowded alkyl derivatives, such as $Cp^*{}_2LnCH(SiMe_3)_2$ (Ln = Sm,[6c] Nd,[6c] Y[13c]), were next employed in order to direct transfer of the silyl group to the metal center. No reaction was observed between these alkyls and Ph_3SiH, Ph_2MeSiH or $^tBu_2SiH_2$ (room temperature, 8 days), probably due to severe steric constraints. These complexes do react with less hindered silanes such as $MesSiH_3$ (Mes = mesityl; over 10 min at 70 °C), to produce $CH_2(SiMe_3)_2$ (quantitatively), the corresponding hydrides $[Cp^*{}_2LnH]_2$, and $MesH_2SiSiH_2Mes$ (but no observed silyl complexes).[11] Such reactions probably proceed via the formation of intermediate silyl complexes $Cp^*{}_2LnSiHRR'$, which undergo rapid dehydrocoupling reactions which produce the observed products (e.g., eq. 3).

$$\begin{array}{c} \mathrm{Cp^*_2LnCH(SiMe_3)_2} \\ + \\ \mathrm{MesSiH_3} \end{array} \longrightarrow \left[\mathrm{Cp^*_2LnSiH_2Mes} \right] \xrightarrow{\mathrm{MesSiH_3}} \begin{array}{c} {}^1/_2\mathrm{[Cp^*_2LnH]_2} \\ + \\ \mathrm{MesH_2SiSiH_2Mes} \end{array} \qquad (3)$$

It therefore appeared that silanes with intermediate steric properties were required, and for this reason reactions with $SiH_2(SiMe_3)_2$ were examined. The alkyls $Cp^*_2LnCH(SiMe_3)_2$ (Ln = Sm, Nd, Y) react with neat $SiH_2(SiMe_3)_2$ (ca. 5 equiv) at 85 °C to give the new silyl complexes $Cp^*_2LnSiH(SiMe_3)_2$ as red (**1**, Ln = Sm), blue-green (**2**, Ln = Nd) or yellow (**3**, Ln = Y) crystals from pentane (eq. 4).[11]

$$\begin{array}{c} \mathrm{Cp^*_2LnCH(SiMe_3)_2} \\ + \\ \mathrm{SiH_2(SiMe_3)_2} \end{array} \longrightarrow \begin{array}{c} \mathrm{Cp^*_2LnSiH(SiMe_3)_2} \\ + \\ \mathrm{CH_2(SiMe_3)_2} \end{array} \qquad (4)$$

These complexes are exceedingly air- and moisture-sensitive, and show no evidence of thermal decomposition in the solid state at room temperature over several weeks. In all cases the ^1H NMR spectra show a single Cp* resonance, indicating rapid rotation about the Ln-Si bond. The Cp* resonance for **2** decoalesces into two singlets at 10 °C, which corresponds to an activation barrier of rotation about the Nd-Si bond of 13.3 (1) kcal/mol. The analogous rotational barrier for the shorter Nd-C bond in $Cp^*_2NdCH(SiMe_3)_2$ is significantly higher, at 19.9 (1) kcal/mol.

The new silyl complexes **1**-**3** are monomeric in pentane solution at room temperature (by isothermal distillation). The ^1H NMR chemical shift for **2** displays Curie-Weiss behavior, indicating that **2** is monomeric in toluene-d_8 down to -80 °C. However, the X-ray structure analysis[11] (Figure 1) reveals that **1** forms dimers in the solid state via intermolecular $Sm\cdots CH_3\text{-}Si$ interactions, which result in Sm-C(Me) distances of 2.97 (2) Å. The Sm-Si bond distance in **1**, 3.052 (8) Å, is the longest metal-silicon bond yet reported. For comparison, the Lu-Si distance in $[Cp_2Lu(SiMe_3)_2]^-$ is 2.888 (2) Å.[9d] The difference in the Ln-Si bond distance between these two complexes (0.16 Å) is somewhat greater than can be attributed to the lanthanide contraction (ca. 0.10 Å).[12] Given the essentially identical infrared spectra for **1**-**3**, we assume that all these complexes are dimeric in the solid state. However, as with other complexes that display $Ln\cdots CH_3\text{-}Si$ interactions in the solid state,[13] evidence for the interactions is not found in solution-state NMR spectra.

Several compounds containing an agostic interaction involving an $SiMe_3$ group-lanthanide interaction have been reported.[13] In particular, the compounds $Cp^*_2LnCH(SiMe_3)_2$ (Ln = Y,[13c] Ce,[13b] Nd[6c]) provide an interesting comparison.

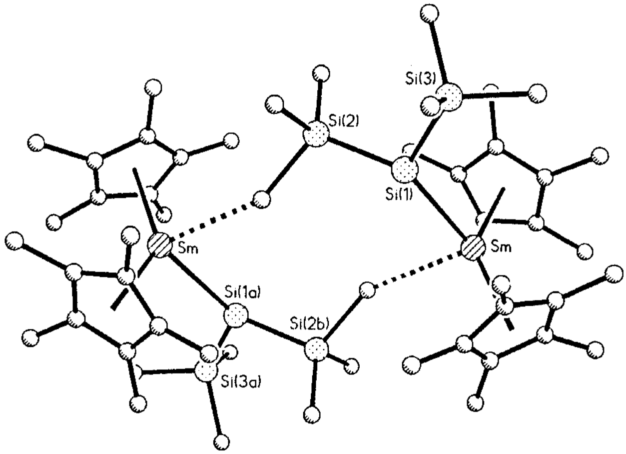
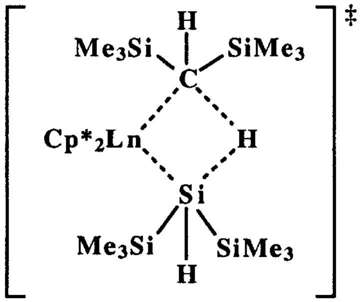


FIGURE 1 ORTEP view of the molecular structure of $Cp^*_2SmSiH(SiMe_3)_2$ (**1**).

These complexes are monomeric in the solid state and contain an *intramolecular* Ln···CH_3-Si interaction. Intermolecular methyl-coordination to a lanthanide metal has previously been found in complexes such as $Cp^*Be(\mu\text{-}Me)YbCp^*_2$.[14] These interactions have been attributed to weak electrostatic attraction between the metal and the methyl carbon atom.[13a]

The above σ-bond metathesis route to lanthanide silyl complexes appears related to analogous reactions of $CpCp^*Hf[Si(SiMe_3)_3]Cl$ with hydrosilanes.[15] However for the reactions of eq. 4, a concerted process would appear to involve an unreasonably crowded four-center transition state:

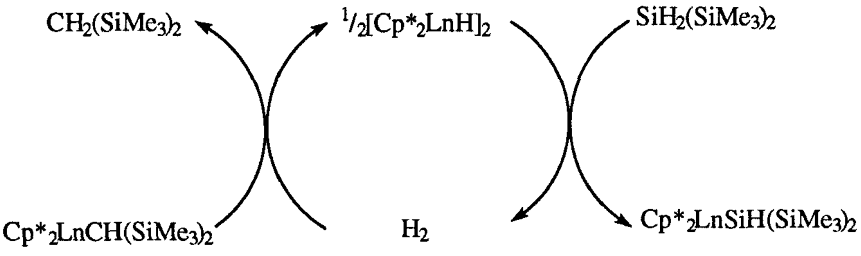


For this reason we have examined mechanistic details for this reaction.

The kinetics of the reaction of $Cp^*_2SmCH(SiMe_3)_2$ and $H_2Si(SiMe_3)_2$ were studied under second-order conditions using excess silane (5 equiv.). Initial attempts to follow the progress of the reaction revealed a variable induction time, followed by a sudden rate increase. These reactions proceed to 65-70% yields for the samarium silyl product as determined by ^1H NMR spectroscopy. The induction time is not dependent on the initial concentrations of starting materials, but does depend on the purity of the $Cp^*_2SmCH(SiMe_3)_2$ starting material. With $Cp^*_2SmCH(SiMe_3)_2$ purified by a single crystallization, the induction time is imperceptible, the rate of formation of **1** is dramatically accelerated, and the yield of **1** is increased to 90-100% (by ^1H NMR spectroscopy). Significantly, addition of $[Cp^*_2SmH]_2$ (**4**, 0.1 equiv) to the reaction mixture completely eliminates the induction period and leads to rapid formation of products.

These preliminary observations suggest that $Cp^*_2SmCH(SiMe_3)_2$ does not react directly with $H_2Si(SiMe_3)_2$, but rather secondary species arising from one or both starting materials lead to formation of the products. A possible mechanism for this reaction is given in Scheme 2. In this simple process, a direct σ-bond metathesis reaction of **4** with the silane produces the samarium silyl complex. The hydrogen produced then hydrogenates the alkyl starting material to form more hydride. Since **4** does not build up as an intermediate during the course of the reaction, it would appear that the faster reaction in the cycle involves reaction with the silane. Studies on this "modified σ-bond metathesis reaction" are underway.

SCHEME 2

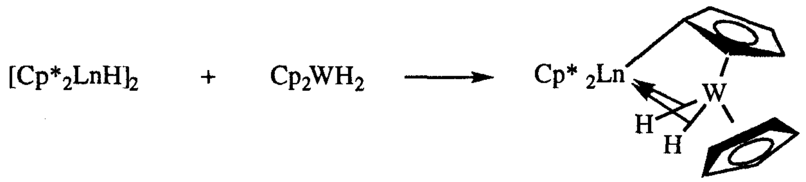


Lanthanide-silicon bonds are more reactive than analogous lanthanide-carbon bonds, as demonstrated by initial reactivity studies.[8] For example, hydrogenolysis of the silyl complexes **1-3** rapidly occurs to produce $[Cp^*_2LnH]_2$ and the corresponding silane. Also, σ-bond metathesis reactions involving Si-H bonds are more facile. Compound **1** reacts with $MesSiH_3$ (3 equiv.) over 10 min at room temperature to afford $[Cp^*_2LnH]_2$, $H_2Si(SiMe_3)_2$ and $MesH_2SiSiH_2Mes$, whereas the analogous reaction of $Cp^*_2SmCH(SiMe_3)_2$ requires 10 min at 70 °C (no induction period was observed for the latter reaction at this temperature). The complexes are also active polymerization catalysts for ethylene (by ^1H NMR spectroscopy).

Given the above results, which suggest that Ln-H bonds may be more active than Ln-Si bonds in σ-bond metathesis processes, we have explored the potential for dehydrocoupling reactions involving $[Cp^*{}_2LnH]_2$ to afford general routes to lanthanide-element bonds (eq. 5). Assuming that the best substrates for this reaction

$$\text{Ln-H} \;+\; \text{H-E} \;\longrightarrow\; H_2 \;+\; \text{Ln-E} \qquad (5)$$

would possess relatively weak bonds to hydrogen, we initially focused on a transition-metal hydride, Cp_2WH_2. However, it was found that the stronger C-H bonds of Cp_2WH_2 are selectively activated. Treatment of $[Cp^*{}_2LnH]_2$ with Cp_2WH_2 affords the complexes $Cp^*{}_2Ln(\mu\text{-}\eta^1,\eta^5\text{-}C_5H_4)(\mu\text{-}H)_2WCp$ as red (**5**, Ln = Sm) and yellow (**6**, Ln = Y) crystalline materials (eq. 6).[16]



(6)

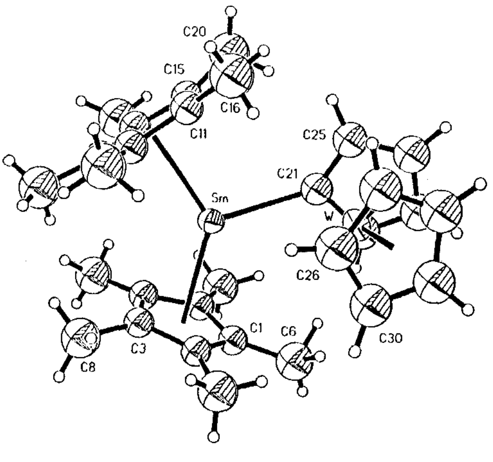
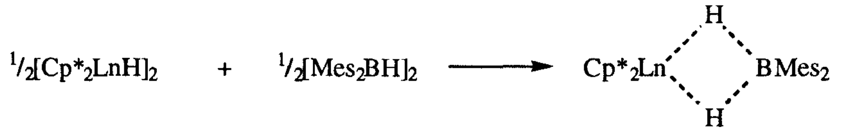


FIGURE 2 ORTEP view and atom labeling scheme for $Cp^*{}_2Sm(\mu\text{-}\eta^1,\eta^5\text{-}C_5H_4)(\mu\text{-}H)_2WCp$ (**5**).

The crystal structure of **5** reveals a new Sm-C(Cp) bond of 2.52 (2) Å (Fig. 2).[16] This bond length is significantly shorter than related ones found in $Cp^*{}_2Sm(\mu\text{-}H)(\mu\text{-}CH_2C_5Me_4)SmCp^*$[17a] (2.628 (7) Å) and $Cp^*{}_2Sm(C_5H_5)$[17b] (2.738 (4) Å).

The Sm-W distance of 3.402 (1) Å is significantly longer than the sum of the atomic radii (3.20 Å), indicating the absence of a direct Sm-W bond.[16] The tungsten hydride ligands were not located by X-ray crystallography, and proved impossible to observe by ^1H NMR spectroscopy even when the sample was cooled to - 80 °C. However, the room temperature ^1H NMR spectrum of **6** contains the hydride resonance (-14.25 ppm) as a doublet with one set of ^{183}W satellite peaks. The W-H coupling constant (J_{WH} = 34 Hz) is nearly as great as the J_{WH} coupling constant in Cp_2WH_2 (J_{WH} = 36.6 Hz).[17] In addition, coupling of the hydride ligands to ^{89}Y (J_{YH} = 6.3 Hz) is very weak (cf. $^1J_{YH}$ = 32.12 Hz for the Y-H-Y bridge in $[Cp^*{}_2YH]_2$[18]). These coupling constants suggest the presence of bridging hydrides interacting much more strongly with tungsten, as indicated by the structure in eq 6.

Hydroboranes would appear to offer substrates that behave analogously to hydrosilanes in σ-bond metathesis reactions, given the similarity in electronic properties between B-H and Si-H bonds. It was anticipated that interaction of a hydroborane HBR_2 with a d^0 M-H complex would result in BH-donation to the d^0 metal center, and subsequently stable structures with borohydride ($H_2BR_2^-$) ligands. However, if a dehydrocoupling process were kinetically accessible, then formation of a d^0 M-B bonded complex might be driven to completion by removal of hydrogen. Given the rarity of compounds with bonds between boron and an electropositive metal, we have begun an investigation into reactions of d^0 metal hydrides with boranes. Initially, we examined the reactions of $[Cp^*{}_2LnH]_2$ (Ln = Sm, Y) with $[Mes_2BH]_2$, which produce the borohydride products $Cp^*{}_2Ln(\eta^2\text{-}H_2BMes_2)$. These complexes are isolated as red (**7**, Ln = Sm) and yellow (**8**, Ln = Y) crystalline materials (eq. 7). The ^{11}B NMR spectrum for **8** (at 80 °C) exhibits a triplet (J_{BH} = 57.8 Hz), consistent with the presence of two hydrogens bonded to boron.



$$\tfrac{1}{2}[Cp^*{}_2LnH]_2 + \tfrac{1}{2}[Mes_2BH]_2 \longrightarrow Cp^*{}_2Ln(\mu\text{-}H)_2BMes_2 \qquad (7)$$

Thermolyses of these compounds have not so far resulted in isolable boryl complexes of the type $Cp^*{}_2Ln\text{-}BMes_2$. Preliminary reactivity studies have shown that **7** and **8** do not react with *trans*-stilbene or phenylpropyne, but reaction of **7** and benzaldehyde rapidly produces benzyldimesitylboronate (< 5 min, 25 °C).

CONCLUSION

A new synthetic route to lanthanide silyl compounds has been discovered, based on σ-bond metathesis reactions of a hydrosilane with lanthanide alkyl and hydride derivatives. Initial mechanistic studies on this reaction suggest that it proceeds via a second-order autocatalytic process, catalyzed by $[Cp^*{}_2LnH]_2$. In general, the σ-bond metathesis reactions of $Cp^*{}_2LnSiH(SiMe_3)_2$ and $[Cp^*{}_2LnH]_2$ appear to be quite facile. The silyl complexes readily react with hydrosilanes and hydrogen, and are good catalysts for the polymerization of ethylene. The hydrides $[Cp^*{}_2LnH]_2$ (Ln = Y, Sm) activate a C-H bond in Cp_2WH_2 (to form $Cp^*{}_2Ln(\mu\text{-}\eta^1,\eta^5\text{-}C_5H_4)(\mu\text{-}H)_2WCp$) and add to the borane $[Mes_2BH]_2$ to produce borohydride complexes. We are continuing to investigate σ-bond metathesis reactions of lanthanide-silicon and lanthanide-hydrogen bonds, as these processes show promise with respect to their synthetic utility.

ACKNOWLEDGEMENT

This work was financed by the National Science Foundation and the Petroleum Research Fund.

REFERENCES

1. (a) T. D. Tilley, *Comments in Inorg. Chem.*, **10**, 37 (1990). (b) J. F. Harrod, Y. Mu, E. Samuel, *Polyhedron*, **10**, 1239 (1990).
2. T. D. Tilley, in *The Chemistry of Organic Silicon Comopunds*, S. Patai, Z.Rappoport, Eds., Wiley: New York, 1989; Chapter 24, pp. 1415.
3. (a) B. K. Campion, R. H. Heyn, T. D. Tilley, *Inorg. Chem.*, **29**, 4355 (1990). (b) H.-G. Woo, T. D. Tilley, *J. Organomet. Chem.*, **393**, C6 (1990). (c) J. Arnold, M. P. Engler, F. H Elsner, R. H. Heyn, T. D. Tilley, *Organometallics*, **8**, 324 (1989).
4. (a) H.-G. Woo, T. D. Tilley, *J. Am. Chem. Soc.*, **111**, 3575 (1989). (b) H.-G. Woo, T. D. Tilley, *J. Am. Chem. Soc.*, **111**, 8043 (1989). (c) H.-G. Woo, T. D. Tilley, in *Inorganic and Organometallic Oligomers and Polymers,* R. M. Laine, J. F. Harrod, Eds., Kluwer Publishers: Amsterdam, 1991; pp. 3. (d) H.-G. Woo, R. H. Heyn, T. D. Tilley, *J. Am. Chem. Soc.*, **114**, 5698 (1992).
5. T. D. Tilley, *Acc. Chem. Res.*, **26**, 22 (1993).
6. (a) W. J. Evans, *Adv. Organomet. Chem.*, **24**, 131 (1985). (b) P. J. Watson, G. W. Parshall, *Acc. Chem. Res.*, **18**, 51 (1985). (c) G. Jeske, H. Lauke, H. Mauermann, P. N. Swepston, H. Schumann, T. J. Marks, *J. Am. Chem. Soc.*, **107**, 8091 (1985).
7. (a) T. Sakakura, H. J. Lautenschlager, M. Nakajima, M. Tanaka, *Chem. Lett.*, 913 (1991). (b) C. M. Forsyth, S. P. Nolan, T. J. Marks, *Organometallics*, **10**, 2543 (1991).

8. T. D. Tilley, N. S. Radu, J. F. Walzer, H.-G. Woo, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, **33**, 1237, (1992).
9. (a) B. K. Campion, R. H. Heyn, T. D. Tilley, *Organometallics*, **12**, 2584 (1993). (b) H. Schumann, S. Nickel, E. Hahn, M. J. Heeg, *Organometallics*, **4**, 800 (1985). (c) H. Schumann, S. Nickel, J. Loebel, J. Pickardt, *Organometallics*, **7**, 2004 (1988). (d) H. Schumann, J. A. Meese-Marktscheffel, F. E. Hahn, *J. Organomet. Chem.*, **390**, 301 (1990).
10. M. P. Engler, T. D. Tilley, unpublished results.
11. N. S. Radu, T. D. Tilley, A. L. Rheingold, *J. Am. Chem. Soc.*, **114**, 8293 (1992).
12. R. D. Shannon, *Acta. Crystallogr., Sect. A.*, **32**, 751 (1976).
13. (a) T. D. Tilley, R. A. Andersen, A. Zalkin, *J. Am. Chem. Soc.*, **104**, 3725 (1982). (b) H. J. Heeres, J. Renkema, M. Booij, A. Meetsma, J. H. Teuben, *Organometallics*, **7**, 2495 (1988). (c) K. H. den Haan, J. L. de Boer, J. H. Teuben, *Organometallics*, **5**, 1726 (1986). (d) H. van der Heijden, C. J. Schaverien, A. G. Orpen, *Organometallics*, **8**, 255 (1989).
14. C. J. Burns, R. A. Andersen, *J. Am. Chem. Soc.*, **109**, 5853 (1987).
15. (a) H.-G. Woo, T. D. Tilley, *J. Am. Chem. Soc.*, **111**, 3757 (1989). (b) H.-G. Woo, T. D. Tilley, *J. Am. Chem. Soc.*, **109**, 8043 (1989). (c) H.-G. Woo, Ph. D. Thesis, University of California, San Diego, 1990.
16. N. S. Radu, P. Gantzel, T. D. Tilley, submitted.
17. (a) W. J. Evans, T. A. Ulibarri, J. W. Ziller, *Organometallics*, **10**, 134 (1991). (b) W. J. Evans, T. A. Ulibarri, *J. Am. Chem. Soc.*, **109**, 4292 (1987).
18. K. H. den Haan, Y. Wielstra, J. H. Teuben, *Organometallics*, **6**, 2053 (1987).