Investigation of the Regioselectivity of Alkene Hydrosilylation Catalyzed by Organolanthanide and Group 3 Metallocene Complexes

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The regioselectivity of monosubstituted alkene hydrosilylation catalyzed by organolanthanide and group 3 organometallic complexes has been studied as a function of catalyst structure. A wide variety of catalyst variations were shown to be compatible with the hydrosilylation process. Several novel complexes were synthesized to widen the scope of this investigation. The results show complexes containing larger lanthanide metal ions and reduced substitution on the cyclopentadienyl ligands produce increased yields of the secondary silane product. Several complexes were identified that are highly selective for primary silane generation.

Introduction

In recent years, organolanthanide and group 3 metallocene complexes have been the focus of numerous investigations into catalytic processes for the cyclization and functionalization of unsaturated organic molecules.[1] Originally developed as olefin polymerization catalysts,[2] their reactivity has been harnessed for the hydrogenation,[3] hydrosilylation,[4] and hydroamination[5] of substrates containing one or more double and triple bonds. In suitably arranged substrates, single[3f,4a,b,d,f,h,k] or multiple[4j,l,5e] cyclization events precede the reaction of the intermediate organometallic with the trapping reagent. To be synthetically useful, single product isomers are desired. This requires high chemo-, regio-, and diastereoselectivity in each of the olefin insertion steps.

Alkene hydrosilylation[6] is a particularly flexible route for the generation of silanes and the alcohols they mask through oxidation. A number of methods to effect this transformation have been studied including transition-metal catalysis,[7] radical-initiated processes,[8] and ionic reactions.[9] Each method is characterized by certain strengths and weaknesses, the most problematic of these being alkene isomerization and isomeric product mixtures. The cyclization/silylation of dienes leading to carbocycles[10] and silicon heterocycles[11] has also been studied but has not yet been developed into a general synthetic method for the flexible preparation of complex molecules.

The hydrosilylation of olefins by trivalent metallocene complexes is of particular interest because it allows the construction of a large number of mono- and bicyclic ring systems.[4j,l] The reactions are generally high yielding and highly selective with reliably predictable diastereomeric preferences. The synthetic utility of the silanes is expanded by oxidation protocols, allowing their conversion to alcohols under either acidic[12] or basic[13] conditions.

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(1) Molander, G. A. *Chemtracts* **1998**, *11*, 237.

(2) (a) Marks T. J.; Ernst, R. D. In *Comprehensive Organometallic Chemistry*; Wilkinson G., Stone, F. G. A., Abel E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 3, Chapter 21. (b) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51. (c) Edelmann, F. T. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, 1995; Vol. 4, Chapter 2. (d) Edelmann, F. T. *Top. Curr. Chem.* **1996**, *179*, 247.

(3) (a) Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8111. (b) Molander, G. A.; Hoberg, J. O. *J. Org. Chem.* **1992**, *57*, 3266. (c) Haar, C. M.; Stern, C. L.; Marks, T. J. *Organometallics* **1996**, *15*, 1765. (d) Roesky, P. W.; Denninger, U.; Stern, C. L.; Marks T. J. *Organometallics* **1997**, *16*, 4486. (e) Roesky, P. W.; Stern, C. L.; Marks, T. J. *Organometallics* **1997**, *16*, 4705. (f) Molander, G. A.; Hoberg, J. O. *J. Am. Chem. Soc.* **1992**, *114*, 3123.

(4) (a) Fu, P. F.; Brard, L.; Li, Y.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 7157. (b) Molander, G. A.; Nichols, P. J. *J. Am. Chem. Soc.* **1995**, *117*, 4415. (c) Molander, G. A.; Retsch, W. H. *Organometallics* **1995**, *14*, 4570. (d) Molander, G. A.; Nichols, P. J. *J. Org. Chem.* **1996**, *61*, 6040. (e) Molander, G. A.; Winterfeld, J. *J. Organomet. Chem.* **1996**, *524*, 275. (f) Molander, G. A.; Retsch, W. H. *J. Am. Chem. Soc.* **1997**, *119*, 8817. (g) Molander, G. A.; Julius, M. *J. Org. Chem.* **1992**, *57*, 6347. (h) Onozawa, S.; Sakakura, T.; Tanaka, M. *Tetrahedron Lett.* **1994**, *35*, 8177. (i) Sakakura, T.; Lautenschlager, H.; Tanaka, M. *J. Chem. Soc., Chem. Commun.* **1991**, 40. (j) Molander, G. A.; Nichols, P. J. *J. Org. Chem.* **1998**, *63*, 2292. (k) Watson, P. L.; Tebbe, F. N. U.S. Patent 4,965,386; *Chem. Abstr.* **1991**, *114*, 123331p. (l) Molander, G. A.; Dowdy, E. D.; Schumann, H. *J. Org. Chem.* **1998**, *63*, 3386.

(5) (a) Gagné, M. R.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 275. (b) Giardello, M. A.; Conticello, V. P.; Brard, L.; Gagné, M. R.; Marks T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10241. (c) Li, Y.; Marks, T. J. *Organometallics* **1996**, *15*, 3770. (d) Li, Y.; Marks, T. J. *J. Am. Chem. Soc.* **1996**, *118*, 9295. (e) Li, Y.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 1757.

(6) (a) Hiyama, T.; Kusumoto, T. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 8, Chapter 3.12. (b) Ojima, I. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons Ltd.: New York, 1989; Chapter 25.

(7) (a) Speier, J. L. In *Advances in Organometallic Chemistry*; Stone, F. G. A., West, R., Eds.; Academic Press: New York, 1979; Vol. 17. (b) Uozumi, Y.; Hayashi, T. *J. Am. Chem. Soc.* **1991**, *113*, 9887. (c) Prignano, A. L.; Trogler, W. C. *J. Am. Chem. Soc.* **1987**, *109*, 3586.

(8) (a) Choo, K. Y.; Gaspar, P. P. *J. Am. Chem. Soc.* **1974**, *96*, 1284. (b) Dang, H.-S.; Roberts, B. P. *Tetrahedron Lett.* **1995**, *36*, 2875.

(9) Nozakura, S.; Konotsune, S. *Bull. Chem. Soc. Jpn.* **1956**, *29*, 322.

(10) Widenhoefer, R. A.; DeCarli, M. A. *J. Am. Chem. Soc.* **1998**, *120*, 3805.

(11) Kobrakov, K. I.; Chernysheva, T. I.; Nametkin, N. S. *Dolk. Akad. Nauk SSSR* **1971**, *198*, 1340.

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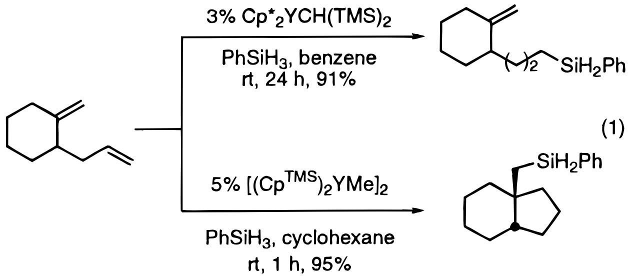
The regioselectivity of silylation of monosubstituted olefins has been found to vary considerably with the complex used to mediate the reaction. Yttrium complexes bearing pentamethylcyclopentadienyl (Cp*) ligands have been used to catalyze the selective hydrosilylation of a number of monosubstituted alkenes.[4g] The combination of a relatively small metal and hindered ligands gives complete selectivity for silylation at the terminus of the carbon chain ("1,2" addition). Cp* complexes built around larger metal ions have been used for the silylation of more hindered olefins.[4e] This enhanced reactivity is accompanied by a loss of regioselectivity in the reaction with monosubstituted olefins.[4a] Complexes with reduced substitution on the cyclopentadienyl ligands have proven useful for the insertion of 1,1-disubstituted olefins in cyclization processes.[4l] Different products may be obtained from diene substrates by judicious precatalyst selection (eq 1),[4g,l] requiring complexes with varying degrees of ligand substitution but equivalent selectivity for initial olefin insertion. The current study was undertaken to determine if synthetically useful levels of the secondary silane product would be produced by modifying the structure of the catalyst. We also sought to determine the level of regioselectivity for a large number of complexes with differing steric properties as an aid in choosing selective catalysts for future studies.



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Results and Discussion

Two mechanistic possibilities exist for the hydrosilylation reaction, involving either metal−silyl or metal−hydride intermediates. Mechanistic studies indicate that the catalytic cycle proceeds through a metal−hydride intermediate that inserts a double bond before reacting with the silane via σ-bond metathesis (Figure 1).[4a] The alkene insertion step is known to be exothermic ($\Delta H = -19$ kcal/mol)[4a] and essentially irreversible.[14] The rate law was found to be first order in lanthanide and silane and zero order in olefin,[4a] pointing to silane metathesis as the turnover-limiting step. Any mixtures of products observed, therefore, arise from nonselective olefin insertion into the metal−hydrogen bond, with the product ratios being influenced by the relative rates of σ-bond metathesis of the hydrocarbyl intermediates.

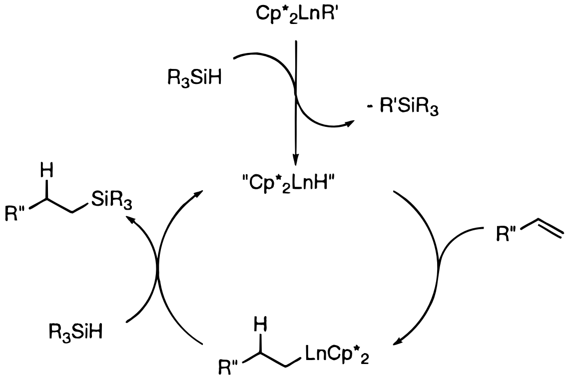


Figure 1. Catalytic cycle for the hydrosilylation of monosubstituted olefins.

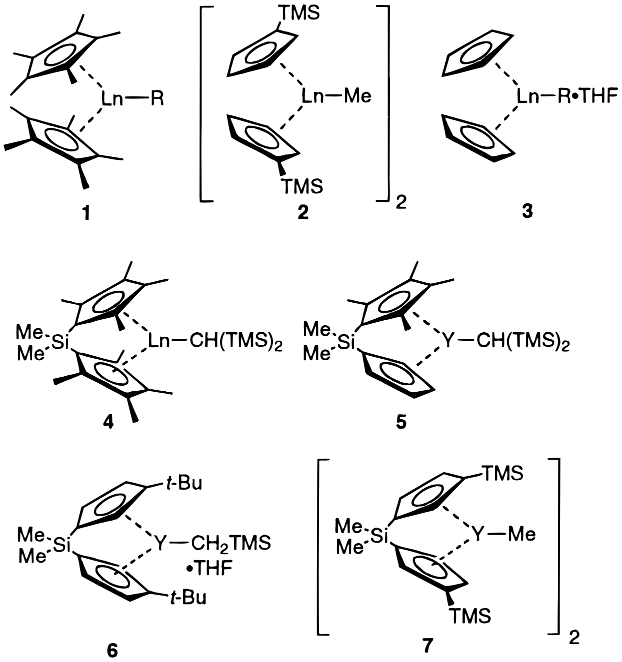
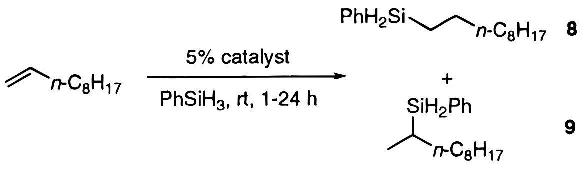


Figure 2. Complexes used for the hydrosilylation of 1-decene.

Several different ligand systems arranged around lanthanide and group 3 metals (Figure 2) were tested for reactivity in the hydrosilylation of 1-decene with phenylsilane (eq 2). The complexes were selected to provide an assortment of steric environments around the catalytic center. The number of substituents on the cyclopentadienyl ligands was varied. Silyl-bridged examples were also included, as the connection pulls the two ligands together,[15] providing more free space near



(2)

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[12] (a) Tamao, K.; Ishida, N.; Tanaka, T.; Kumada, M. *Organometallics* **1983**, *2*, 1649. (b) Bergens, S. H.; Noheda, P.; Whelan, J.; Bosnich, B. *J. Am. Chem. Soc.* **1992**, *114*, 2121. (c) Taber, D. F.; Yet, L.; Bhamidipati, R. S. *Tetrahedron Lett.* **1995**, *36*, 351. (d) Fleming, I.; Hennings, R.; Plaut, H. *J. Chem. Soc., Chem. Commun.* **1984**, 29. (e) Fleming, I.; Sanderson, P. E. J. *Tetrahedron Lett.* **1987**, *28*, 4229. (f) Fleming, I.; Winter, S. B. D. *Tetrahedron Lett.* **1993**, *34*, 7287.

[13] Smitrovich, J. H.; Woerpel, K. A. *J. Org. Chem.* **1996**, *61*, 6044.

[14] Hydrosilylation reactions of styrenes and terminal alkenes carried out with PhSiD$_3$ showed no indication of H/D scrambling, indicating the irreversible nature of the olefin insertion step. See refs 4a and 4g.

[15] X-ray crystal structures confirm the geometric effect of this structural modification. For Cp*$_2$NdCH(TMS)$_2$ the (ring centroid)−Nd−(ring centroid) angle is 134.4°,[19] and for Me$_2$SiCp''$_2$NdCH(TMS)$_2$ the (ring centroid)−Nd−(ring centroid) angle is compressed to 121.6°.[22]

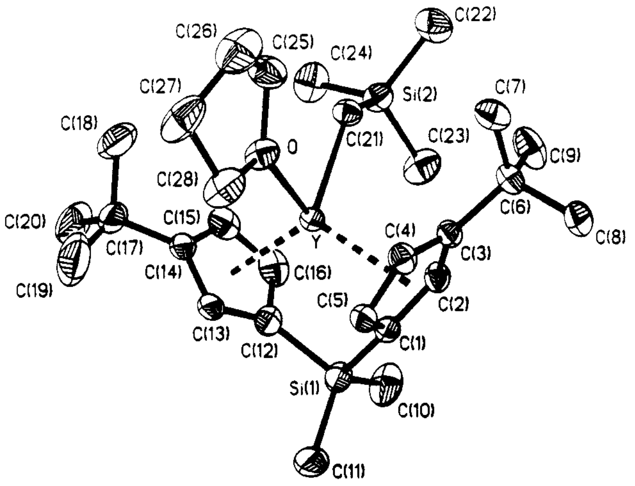


Figure 3. Thermal ellipsoid plot of $Me_2SiCp^{t-Bu}{}_2$-$YCH_2TMS{\cdot}THF$ (**6**).

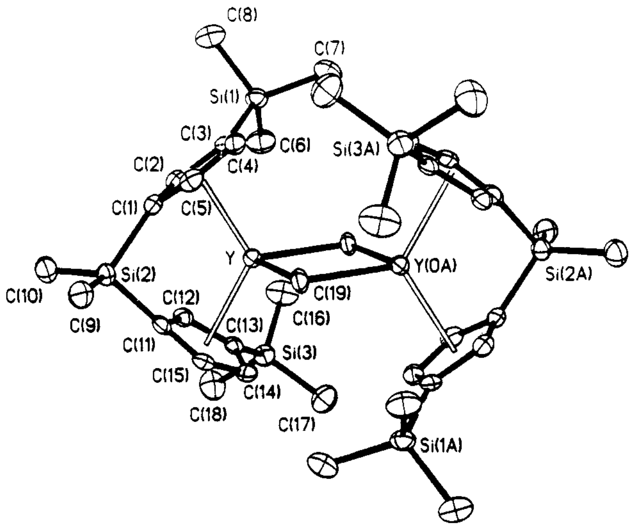
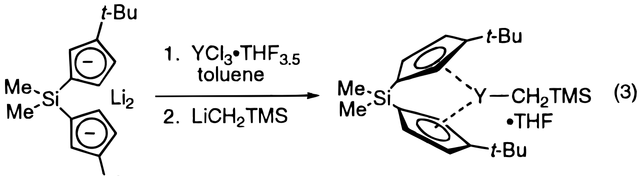


Figure 4. Thermal ellipsoid plot of $[Me_2SiCp^{TMS}{}_2YMe]_2$ (**7**).

the mouth of the catalyst for reaction. Different lanthanides were examined when possible to determine the influence of ionic radius.[16]

In the search for interesting reactivity and regioselectivity, new complexes were prepared that incorporated both a silyl bridge and reduced substitution on the cyclopentadienyl ligands. Each complex was prepared in moderate yield via sequential chelation and alkylation in a one-pot process (eqs 3 and 4). The



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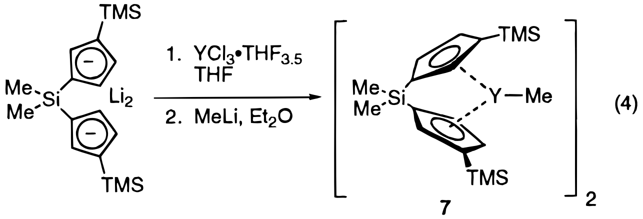

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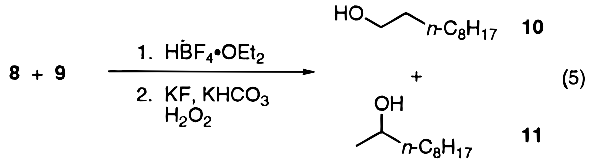
structure of each complex was elucidated by X-ray crystallography (Figures 3 and 4) and was corroborated by NMR spectroscopy.

The product yields and regioselectivity obtained in the silylation reactions are compiled in Table 1. The majority of the reactions proceeded to completion in a reasonable amount of time and provided similar yields of silylated products. The ratio of the primary and secondary silane products was determined by capillary GC analysis of reaction aliquots and confirmed by ^1H NMR of the crude product mixtures after isolation. The identity of each product was confirmed by the oxidation of the silanes to the corresponding alcohols (eq 5) and comparison of their spectral properties to literature data.[17]

Table 1. Regioselectivity of Silylation of 1-Decene with Phenylsilane

structure	precatalyst[a]	yield (% isolated)	**8**:**9**
1	$Cp^*{}_2LuMe{\cdot}THF$	98	100:0
	$Cp^*{}_2YbCH(TMS)_2$	91	100:0
	$Cp^*{}_2YMe{\cdot}THF$	84	100:0
	$Cp^*{}_2SmCH(TMS)_2$	90	11:1
	$Cp^*{}_2NdCH(TMS)_2$	85	3.2:1
	$Cp^*{}_2LaCH(TMS)_2$	90	1.9:1
2	$[Cp^{TMS}{}_2LuMe]_2$	92	100:1
	$[Cp^{TMS}{}_2YMe]_2$	97	37:1
	$[Cp^{TMS}{}_2SmMe]_2$	83[b]	6.5:1
	$[Cp^{TMS}{}_2NdMe]_2$	82	4.4:1
3	$Cp_2YCH_2TMS{\cdot}THF$	97	135:1
	$Cp_2SmCH(TMS)_2{\cdot}THF$	98	135:1
4	$Me_2SiCp''{}_2YCH(TMS)_2$	84	31:1
	$Me_2SiCp''{}_2SmCH(TMS)_2$	98	1:2
	$Me_2SiCp''{}_2NdCH(TMS)_2$	89	1:2
5	$Me_2SiCpCp''YCH(TMS)_2$	69[b]	6.4:1
6	$Me_2Si(Cp^{t-Bu})_2YCH_2TMS{\cdot}THF$	100	12.6:1
7	$[Me_2Si(Cp^{TMS})_2YMe]_2$	48	5.8:1

[a] $Cp^* = C_5Me_5$; $Cp'' = C_5Me_4$. [b] Reaction run for 4 days.



Several trends emerge when examining the regioselectivity displayed by the complexes. Within each ligand series, changing the metal to a lanthanide with a larger ionic radius[16] provides higher yields of the “2,1” product. For the Cp*-derived catalysts (**1**), the smallest metal ions were totally selective for primary silane generation but the selectivity rapidly declined when the larger lanthanides were used. A similar trend was observed for the Cp^{TMS} derivatives (**2**), but in the fully substituted bridged system (**4**), the two largest metals exhibited very similar preferences for secondary silane generation.

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[16] Eight-coordinate ionic radii: La^{3+} (1.160 Å), Nd^{3+} (1.109 Å), Sm^{3+} (1.079 Å), Yb^{3+} (0.985 Å), Lu^{3+} (0.977 Å), Y^{3+} (1.019 Å). See: Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

[17] Pouchert, C. J.; Behnke J. *The Aldrich Library of ^{13}C and ^1H FT-NMR Spectra*; Aldrich Chemical: Milwaukee, 1992.

Thus, a plateau for "2,1" selectivity was reached that other catalyst modifications did not surpass.

Organoyttrium complexes were examined for each of the ligand systems prepared. Their comparison reveals the influence of the ligands on the regioselectivity of insertion. In general, reduced substitution on the ligands and silyl bridging lead to increased yields of the secondary silane. The two effects may be cumulative as the combination of a silyl bridge and reduced substitution on the ligands (**5**, **6**, and **7**) leads to lower selectivity for the terminal silane than does either modification alone (**2** and **4**). The stark exception to these trends is the unsubstituted cyclopentadienyl derivatives (**3**), previously unexamined in catalytic hydrosilylation reactions. Both complexes showed a strong preference for the production of the primary silane. Cyclopentadienyl complexes of the lanthanides are known to form hydride-bridged dimers.[18] This hindered dimeric species is likely involved in the regioselective olefin insertion step, causing selectivity for terminal silylation.

Conclusions

The hydrosilylation of olefins may be catalyzed by a wide variety of organolanthanide and group 3 metallocene complexes. Although certain catalyst modifications provided increased yields of the secondary silane, synthetically useful selectivity was not achieved. A number of complexes were identified that are selective for terminal silylation but possess varying steric environments about the metal center.

Experimental Section

Phenylsilane, 1-decene, and cyclohexane were distilled and degassed before use. The following organometallic complexes were prepared via literature procedures: $Cp*_2LnR$ (**1**),[19] $[Cp^{TMS}{}_2LnMe]_2$ (**2**),[20] Cp_2LnR (**3**),[21] $Me_2SiCp''_2LnR$ (**4**),[22] $Me_2SiCpCp''LnR$ (**5**).[23]

$[Cp^{TMS}{}_2NdMe]_2$ (2, Ln = Nd). In a flame-dried and argon-purged Schlenk flask, $NdCl_3{\cdot}THF_3$ (4.741 g, 10.15 mmol) was suspended in 200 mL of freshly distilled THF. Next, KCp^{TMS} (3.588 g, 20.34 mmol) was added slowly. The mixture was heated at reflux for 5 h before the solvent was removed in vacuo. The blue residue was triturated 3 times with hexanes to ensure the complete removal of THF. It was then suspended in 150 mL of freshly distilled Et_2O before being cooled to −78 °C. A 1.4 M Et_2O solution of MeLi was next added via syringe, and the mixture was allowed to warm to room temperature over 1 h and stirred for an additional 4 h. The solvent was removed in vacuo, and the blue residue was extracted 2 times with a total of 250 mL of hexanes. The hexane was decanted and concentrated for crystallization at −28 °C. The supernatant was decanted from the product, and the remaining crystals were vacuum-dried (2.729 g, 3.14 mmol, 62%): ^1H NMR (300 MHz, C_6D_6) δ 17.49 (br s, 8H), 10.61 (br s, 8H), −8.26 (s, 36H), −64.84 (br s, 6H); ^{13}C NMR (75 MHz, C_6D_6) δ 255.17, 240.58, 232.59, −5.62 (μ-Me not located).

$Me_2Si(Cp^{t-Bu})_2YCH_2TMS{\cdot}THF$ (6). A 250 mL Schlenk flask was charged with 100 mL of toluene, $YCl_3{\cdot}THF_{3.5}$ (4.42 g, 10.0 mmol), and $Me_2Si(Cp^{t-Bu})_2Li_2$[24] (3.12 g, 10.0 mmol) before being heated to 80 °C for 2 days Next, the solution was cooled to −78 °C before $LiCH_2TMS$ (10 mL of a 1.0 M pentane solution) was added via syringe. The mixture was allowed to warm to room temperature overnight. The solvent was then removed in vacuo, and the residue was extracted with petroleum ether. The supernatant was decanted and concentrated to yield 1.10 g (2.01 mmol, 20%) of the product as white crystals: ^1H NMR (400 MHz, C_6D_6) δ 7.09 (br s, 1H), 6.14 (br s, 1H), 5.99 (br s, 1H), 5.92 (br s, 1H), 5.79 (br s, 1H), 5.72 (br s, 1H), 3.15−3.05 (m, 4H), 1.46 (s, 9H), 1.21 (br s, 2H), 1.14 (s, 9H), 1.02 (br s, 2H), 0.77 (s, 3H), 0.70 (s, 3H), 0.48 (s, 9H), −0.22 (m, 1H), −1.21 (m, 1H). Attempts to repeat this preparation showed it to be somewhat capricious, yielding mixtures of the desired material with an unknown isomer.

$[Me_2Si(Cp^{TMS})_2YMe]$ (7). Prepared according to the procedure given for the preparation of **2** using $YCl_3{\cdot}THF_{3.5}$ (1.23 g, 3.0 mmol), $Li_2SiMe_2(Cp^{TMS})_2$[24] (1.034 g, 3.0 mmol), and a 1.4 M solution of MeLi in Et_2O (2.14 mL, 3.0 mmol). Identical isolation yielded 0.34 g of the product as a white powder (0.39 mmol, 26%): ^1H NMR (400 MHz, C_6D_6) δ 7.04−7.03 (m, 4H), 6.64−6.63 (m, 4H), 6.23−6.22 (m, 4H), 0.75 (s, 6H), 0.36 (s, 6H), 0.35 (s, 36H), −0.58 to −0.60 (m, 6H); ^{13}C NMR (75 MHz, C_6D_6) δ 131.74, 122.31, 120.48, 119.38, 118.67, 0.37, −1.89, −5.94 (μ-Me not located).

1-(Phenylsilyl)decane (8). In a nitrogen-filled glovebox, 0.067 g (0.62 mmol) of phenylsilane was added to 0.016 g (6 mol %) of the precatalyst $Cp*_2LuMe{\cdot}THF$ dissolved in 0.5 mL of cyclohexane. Next, 0.071 g (0.51 mmol) of 1-decene was added, and the solution was stirred at ambient temperature. Small aliquots were removed periodically for GC analysis, and the reaction was found to be complete after 1 h. After being removed from the glovebox, the reaction mixture was diluted with hexanes and filtered through a plug of Florisil. The solution was concentrated by rotary evaporation and purified by Kugelrohr distillation to yield 0.123 g (0.50 mmol, 98% yield) of the title compound as a colorless oil. The spectral properties of the material obtained were identical to those reported in the literature.[4g] Anal. Calcd for $C_{16}H_{28}Si$: C, 77.34; H, 11.36. Found: C, 77.25; H, 11.61.

When performed using different precatalysts, the reactions yielded mixtures of 1-(phenylsilyl)decane and 2-(phenylsilyl)decane as indicated in Table 1. These mixtures were inseparable by column chromatography. The identity of the two products was confirmed by conversion of the silanes to the corresponding alcohols and separation by flash chromatography.

1-Decanol (10). (Representative procedure for the oxidation of silanes). 1-(Phenylsilyl)decane **(8)** (0.104 g, 0.418 mmol) was dissolved in $CHCl_3$ (5 mL) and cooled to 0 °C before the addition of $HBF_4{\cdot}OEt_2$ (0.145 g, 0.895 mmol) via pipet. The mixture was stirred for 1 h before the volatiles were removed in vacuo. The residue was dissolved in 10 mL of 1:1 MeOH: THF, and KF (0.116 g, 2.0 mmol), $KHCO_3$ (0.200 g, 2.0 mmol), and 1.0 mL of 30% H_2O_2 were added. The mixture was next heated at reflux for 12 h, during which a white precipitate formed. After cooling, the mixture was concentrated in vacuo and transferred onto 20 mL of saturated aqueous NaCl. The aqueous layer was extracted (3×) with 75 mL portions of Et_2O. The combined organic layers were dried over Na_2SO_4 and concentrated to yield a colorless oil. Purification by flash chromatography (R_f = 0.34, 20% EtOAc/hexanes) and Kugelrohr distillation yielded the title compound as a colorless oil.

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[18] Evans, W. J.; Meadows, J. H.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 1291.

[19] Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091.

[20] (a) (Ln = Lu) Voskoboynikov, A. Z.; Parshina, I. N.; Shetstakova, A. K.; Butin, K. P.; Beletskaya, I. P.; Kuz'mina, L. G.; Howard, J. A. K. *Organometallics* **1997**, *16*, 4041. (b) (Ln = Y, Sm) Keitsch, M. Unpublished results.

[21] Schumann, H.; Genthe, W.; Bruncks, N.; Pickardt, J. *Organometallics* **1982**, *1*, 1194.

[22] Jeske, G.; Schock, L. E.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8103.

[23] Stern, D.; Sabat, M.; Marks, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 9558.

[24] Bunel, E. E. Ph.D. Thesis, California Institute of Technology, 1989.

The spectral properties of this material matched literature values[17] and were consistent with the title compound. Anal. Calcd for $C_{10}H_{22}O$: C, 75.88; H, 14.01. Found: C, 75.78; H, 13.59.

2-Decanol (11). A mixture of 1-(phenylsilyl)decane and 2-(phenylsilyl)decane obtained from the hydrosilylation of 1-decene catalyzed by **4** (Ln = Sm) was subjected to the silylation conditions given above. The mixture of alcohols obtained in 71% yield was separated by flash chromatography ($R_f = 0.34$ and 0.32, 20% EtOAc/hexanes), and the components were compared to literature data.[17] Anal. Calcd for $C_{10}H_{22}O$: C, 75.88; H, 14.01. Found: C, 76.00; H, 14.18.

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Supporting Information Available: NMR spectra for compounds without reported elemental analyses as well as details of the X-ray stucture determination of **6** and **7** (27 pages). Ordering information is given on any current masthead page.

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