Organometallics **2001,** *20,* 2794−2801

1-Octene Hydrosilylation Catalyzed by Lanthanide and Yttrium Hydrides and Hydrocarbyls: A Mechanistic Study and the Role of Catalyst Association

Alexander Z. Voskoboynikov,* Alla K. Shestakova, and Irina P. Beletskaya

Department of Chemistry, Moscow State University, V-234, Moscow, GSP, 119899, Russia

Received January 23, 2001

Dimeric lanthanide (Tb, Yb, Lu) and yttrium hydrides, $\{Cp'_2Ln(\mu\text{-}H)\}_2$, where Cp′ = t-$BuC_5H_4$, and hydrocarbyls $\{Cp'_2Ln(\mu\text{-}Me)\}_2$, as well as compounds with different bridging, $Cp'_2Ln(\mu\text{-}H)(\mu\text{-}Me)LnCp'_2$, are efficient and selective catalysts of 1-octene hydrosilylation. *Binuclear* complexes with $Ln(\mu\text{-}H)_2Ln$ and $Ln(\mu\text{-}H)(\mu\text{-}Alkyl)Ln$ bridging fragments were found to be the key intermediates in 1-octene hydrosilylation catalyzed by both the hydrides $\{Cp'_2Ln(\mu\text{-}H)\}_2$ (Ln = Y, Tb, Yb, Lu) and the mixed compounds $Cp'_2Ln(\mu\text{-}H)(\mu\text{-}Me)LnCp'_2$ (Ln = Y, Lu) in benzene at 75 °C. Therefore, in this case, *the dissociation of the starting dimeric organolanthanide into monomeric species is not required for the catalytic reaction to proceed*. Under the conditions employed, the rate law for the hydrosilylation of 1-octene with $PhMeSiH_2$ is $V^{HS} \sim [\text{lanthanide}]^1[\text{olefin}]^1[\text{silane}]^0$, suggesting rapid hydride transfer from silane to Ln and the rate-limiting addition of Ln−H to olefin. The hydrosilylation of 1-octene with n-Bu_2SiH_2 is accompanied by olefin dimerization. In the presence of Ph_3SiH, Ph_2MeSiH, $PhMe_2SiH$, Et_3SiH, and Et_3GeH, only the dimerization of 1-octene was observed. Alternatively, the lanthanide and yttrium hydrocarbyls $\{Cp'_2Ln(\mu\text{-}Me)\}_2$ (Ln = Y, Tb, Yb, Lu) exhibit higher catalytic activity even at room temperature.The initial rate of the 1-octene hydrosilylation with $PhMeSiH_2$ was found to be $V_0 \sim [\text{lanthanide}]^{1/2}[\text{olefin}]^1[\text{silane}]^0$. In this case, the hydrosilylation seems to involve the formation of highly active *monomeric* species Cp'_2LnH. After several minutes, the hydrosilylation rate sharply decreased because of association of the catalyst.

Introduction

In 1989 we[1,2] and Watson[3a] showed that lanthanide and yttrium compounds exhibit catalytic activity in olefin hydrosilylation. Tanaka et al.,[3b,d] Molander et al.,[3c,e,g] and Schumann et al.[3h] have investigated the hydrosilylation of some novel olefin substrates. For Cp^*_2LnR complexes, where R = H or alkyl, the reaction was accompanied by side dehydrogenative coupling of silanes, which predominated in the absence of an olefin.[3a,4] In 1995 Marks et al.[3f] reported the results of their mechanistic studies on hydrosilylation and also the unexpected regio- and enantioselectivity of this reaction when catalyzed by well-designed *ansa*-complexes of samarium. The kinetic data for the reaction of styrene derivative 2-phenyl-1-butene with $PhSiH_3$ catalyzed by a Sm complex (R)-$Me_2Si(C_5Me_4\text{-}\eta^5)$-$\{[3\text{-}(-)\text{-menthyl}]C_5H_4\text{-}\eta^5\}SmCH(SiMe_3)_2$ fit a mechanism involving fast olefin insertion into the Sm−H bond, followed by a slow metathesis of the Sm−C/Si−H bonds. In 1999 Tilley and Gountchev[3k] investigated olefin hydrosilylation catalyzed by the chelating diamine yttrium complex [DADMB]YMe$(THF)_2$, where DADMB = 2,2′-bis(*tert*-butyldimethylsilylamido)-6,6′-dimethylbiphenyl. Kinetic analysis of catalytic reaction of 1-hexene with $PhMeSiH_2$ in various solvents at ambient temperature revealed a very complex mechanism. While the hydrosilylation in THF-d_8 was found to be first-order in catalyst and first-order in organosilicon hydride, suggesting a rate-limiting hydrogen transfer step involving monomeric yttrium hydrocarbyl, the catalytic reaction in C_6D_6 is approximately half-order in [DADMB]YMe$(THF)_2$. Two possible explanations of the later fact were hypothesized. At high catalyst concentrations some precipitate, presumably the less soluble yttrium hydride $\{[DADMB]YH(THF)\}_2$, was formed, which leads to a decrease of actual concentration of the

---

* Corresponding author. E-mail: voskoboy@org.chem.msu.su.

(1) (a) Beletskaya, I. P.; Voskoboynikov, A. Z.; Parshina, I. N.; Magomedov, G. K.-I. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1990**, *39*, 613−614. (b) Beletskaya, I. P.; Magomedov, G. K.-I.; Voskoboynikov, A. Z.; Parshina, I. N. *XXVIII International Conference on Coordination Chemistry*; Aug 13−18, 1990, Gera-GDR; Abstr. of posters, Vol. 2, pp 3−67. (c) Beletskaya, I. P.; Voskoboynikov, A. Z.; Parshina, I. N.; Magomedov, G. K.-I. USSR Patent 1,663,832, March 15, 1991 (November 17, 1989). (d) Voskoboynikov, A. Z.; Beletskaya, I. P. *Proceeding of 206th Meeting of the ACS*; Chicago, Aug 1993, INOR 333.

(2) Also see our recent results on olefin hydrostannylation catalyzed by organolanthanides: Voskoboynikov, A. Z.; Beletskaya, I. P. *New J. Chem.* **1995**, 217−220.

(3) (a) Watson, P. L.; Tebbe F. N. US Patent 4,965,386, October 23, 1990 (March 26, 1990). (b) Sakakura, T.; Lautenschlager, H. J.; Tanaka, M. *J. Chem. Soc., Chem. Commun.* **1991**, 40−41. (c) Molander, G. A.; Julius, M. *J. Org. Chem.* **1992**, *57*, 6347−6351. (d) Onozawa, S.-Y.; Sakakura, T.; Tanaka, M. *Tetrahedron Lett.* **1994**, 8177−8180. (e) Molander, G. A., Nichols P. J. *J. Am. Chem. Soc.* **1995**, *117*, 4415−4416. Molander, G. A.; Winterfeld, J. *J. Organomet. Chem.* **1996**, *524*, 275−279. (f) Fu P.-F.; Brard L.; Li Y.; Marks T. J. *J. Am. Chem. Soc.* **1995**, *117*, 7157−7168. (g) Molander, G. A.; Dowdy, E. D.; Schumann, H. *J. Org. Chem.* **1998**, *63*, 3386-3396. (h) Schumann, H.; Keitsch, M. R.; Demtschuk, J.; Molander G. A. *J. Organomet. Chem.* **1999**, *582*, 70−82. (i) Gountchev, T. I.; Tilley, T. D. *Organometallics* **1999**, *18*, 5661−5667.

(4) Forsyth, C. M.; Nolan, S. P.; Marks, T. J. *Organometallics* **1991**, *10*, 2543−2545.

10.1021/om010052c CCC: $20.00

Table 1. Turnover Frequencies (tof) for Catalytic Hydrosilylation of 1-Octene with $PhMeSiH_2$ ($[1\text{-octene}]_0 = [PhMeSiH_2]_0 = 1.177\ M{\cdot}L^{-1}$ in Benzene Solution)

catalyst precursor	T, °C	tof, h^{-1}			
$\{(t\text{-}BuC_5H_4)_2Ln(\mu\text{-}H)\}_2$		**1** (Ln = Y)	**2** (Tb)	**3** (Yb)	**4** (Lu)
	75	140(8)	106(8)	59(4)	51(4)
$(t\text{-}BuC_5H_4)_2Ln(\mu\text{-}H)(\mu\text{-}Me)Ln(C_5H_4Bu\text{-}t)_2$		**5** (Ln = Y)			**6** (Lu)
	75	140(8)			51(4)
$\{(t\text{-}BuC_5H_4)_2Ln(\mu\text{-}Me)\}_2$		**7** (Ln = Y)	**8** (Tb)	**9** (Yb)	**10** (Lu)
	32	260(20)	210(10)	150(9)	136(8)
$\{(C_5H_5)_2Lu(\mu\text{-}Me)\}_2$	32				1.5(1)
$\{(C_5H_5)_2Lu\}_3(\mu\text{-}H)_2(\mu_3\text{-}H)$	75				56(3)
$\{(Me_3SiC_5H_4)_2Lu(\mu\text{-}Me)\}_2$	32				96(6)
$\{(Me_3SiC_5H_4)_2Lu(\mu\text{-}H)\}_2$	75				55(3)
$(C_5Me_5)_2LuCH(SiMe_3)_2$	32				≈0
	75				0.37(3)

catalyst in solution. Alternatively, the concentration of organolanthanide intermediates can be controlled by a monomer–dimer preequilibrium.

The present paper is concentrated on the detailed study of the olefin hydrosilylation mechanism, particularly for 1-octene hydrosilylation catalyzed by organolanthanides with nonbulky monosubstituted cyclopentadienyl ligands. Our aim is to understand the role of monomeric and dimeric lanthanide intermediates in catalytic olefin hydrosilylation. Actually, a steric gap in the coordination sphere of the metal, offering free access to the metal for further coordination, and the coordinative unsaturation of the metal in the corresponding monomeric Cp''_2LnX complexes with nonbulky Cp″ ligands, such as C_5H_5, C_5H_4R, or $C_5H_3R_2$, as well as high Lewis acidity of the Ln(III) centers, lead to the extraordinary stabilization of various di- and multinuclear complexes containing bridging ligands.[5,6,7] The role of these stable associates[8] in the catalytic hydrosilylation of olefins was found to go beyond inhibition of the reaction due to slow preequilibrium involving a reactive monomer.[4,8a] We have revealed that, in several cases, dimeric lanthanide species with μ-H bridging can be intermediates in hydrosilylation; that is, *their dissociation is not required for the catalytic reaction to proceed*. Obviously, the elucidation of a special role of such binuclear intermediates is important for understanding the mechanistic aspects of some commercial-scale reactions catalyzed by organolanthanides, particularly, the stereospecific Ziegler–Natta diene polymerization.[9]

Results

Hydrosilylation of 1-Octene Catalyzed by Lanthanide Complexes with $Ln(\mu\text{-}H)_2Ln$ and $Ln(\mu\text{-}H)(\mu\text{-}Me)Ln$ Bridging. The hydrosilylation of 1-octene with $PhMeSiH_2$ in the presence of both the lanthanide hydrides $\{Cp'_2Ln(\mu\text{-}H)\}_2$, where Ln = Y (**1**), Tb (**2**), Yb (**3**), Lu (**4**), Cp′ = t-BuC_5H_4, and the lanthanide hydrocarbyls $Cp'_2Ln(\mu\text{-}H)(\mu\text{-}Me)LnCp'_2$, where Ln = Y (**5**), Lu (**6**), was found to proceed readily at 75 °C in benzene solution, to give a linear addition product, $n\text{-}C_8H_{17}\text{-}SiHMePh$. Similar regioselectivity was observed for the corresponding reactions involving $PhSiH_3$ and Ph_2SiH_2. It should be noted that the selectivity, rate law, and even the values of rate constants of the hydrosilylation catalyzed by the compounds with $Ln(\mu\text{-}H)_2Ln$ and $Ln(\mu\text{-}H)(\mu\text{-}Me)Ln$ bridging turned out to be the same for a given metal (see also Table 1).

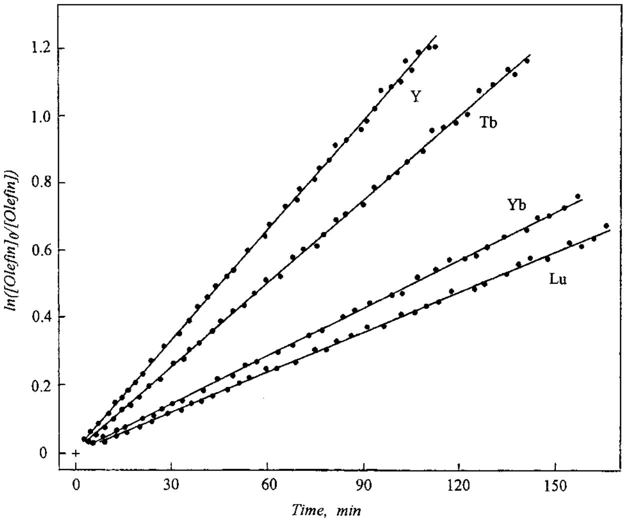


Figure 1. Olefin concentration as a function of time for the hydrosilylation of 1-octene with $PhMeSiH_2$ catalyzed by **1** (Y), **2** (Tb), **3** (Yb), and **4** (Lu) in benzene at 75 °C.

Under the conditions of this study, the hydrosilylation of 1-octene with $PhMeSiH_2$ in benzene solution at 75 °C was found to be zero-order in organosilicon hydride (in the concentration range 0.24–2.35 $M{\cdot}L^{-1}$), first-order in catalyst, and first-order in olefin. No induction period was observed. The ranges of the concentrations used are given in the representative kinetic plots in Figures 1 and 2.

---

(5) Marks, T. J.; Ernst, R. D. in *Comprehensive Organometallic Chemistry*; Wilkinson, G.. Stone, F. G. A.. Abel, E. W., Eds.; Oxford: Pergamon Press: 1982; Vol. 3, p 173. Marks, T. J., Fragala, I. L., Eds. *Fundamental and Technological Aspects of Organo-f-Element Chemistry*; D. Reidel Publ.: Dordrecht, 1985.

(6) Bochkarev, M. N.; Zakharov, L. N.; Kalinina, G. S. *Organoderivatives of Rare Earth Elements*; Kluwer: Dordrecht, 1995.

(7) Voskoboynikov, A. Z.; Parshina, I. N.; Shestakova, A. K.; Butin, K. P.; Beletskaya, I. P.; Kuz'mina, L. G.; Howard, J. A. K. *Organometallics* **1997**, *16*, 4041–4055.

(8) (a) Jeske, G.; Lauke, H.; Mauermann, H.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8111–8118. (b) Shapiro, P. J.; Cotter, W. D.; Schaefer, W. P.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 4623–4640. (c) Schaverien, C. J. *Organometallics* **1994**, *13*, 69–82.

(9) (a) Mazzei, A. In *Organometallics of the f-Elements*; Marks, T. J., Fischer, R. D., Eds.; Reidel Publ.: Dordrecht, 1979; pp 379–393. Bruzzone, M.; Carbonaro, A. In *Fundamental and Technological Aspects of Organo-f-Element Chemistry*; Marks, T. J., Fragala, I. L., Eds.; Reidel Publ.: Dordrecht, 1985; pp 387–400. Monakov, Yu. B.; Tolstikov, G. A. *Kataliticheskaya Polimerizatsiya 1,3-Dienov (Catalytic Polymerization of 1,3-Dienes)*; Nauka: Moscow, 1990. (b) Throckmorton, M. C. *Kautsch. Gummi. Kunstst. B* **1969**, *22*, 293–297. Kesuyc, Z. *Sci. Sin.* **1974**, *17*, 656. Monakov, Yu. B.; Bieshev, Ya. Ch.; Berg, A. A.; Rafikov, S. R. *Dokl. Acad. Nauk SSSR* **1977**, *234*, 1125–1127. Avdeeva, O. G.; Markevich, I. N.; Sharaev, O. K.; Bondarenko, G. N.; Tinyakova, E. I.; Dolgoplosk, B. A. *Dokl. Acad. Nauk SSSR* **1986**, *286*, 641–643.

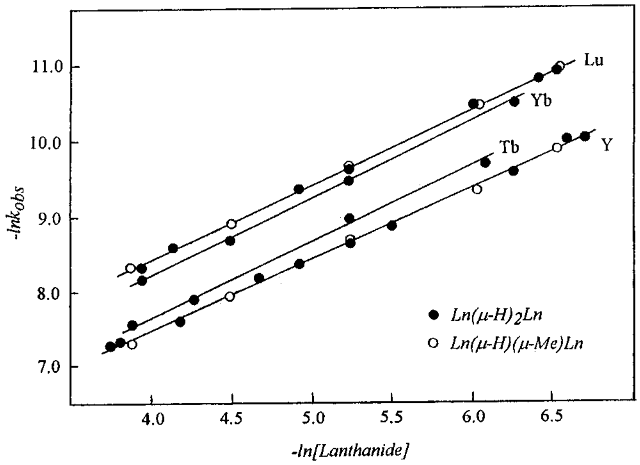
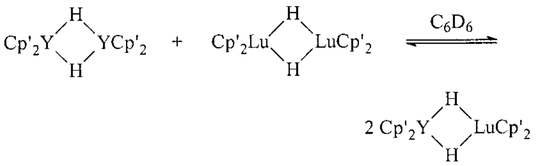


Figure 2. Hydrosilylation of 1-octene with $PhMeSiH_2$ catalyzed by **1** and **5** (Y), **2** (Tb), **3** (Yb), and **4** and **6** (Lu) in benzene at 75 °C. Plots to determine the reaction order in organolanthanide compounds ([lanthanide] refers to the concentration of the starting dimeric organolanthanide; $k_{obs} = k_1[\text{olefin}]$).

Analogous observations have been made by Marks, Schumann, et al., who studied kinetics of hydrogenation reaction catalyzed by organolanthanides.[8a] The authors found that the rate law for hydrogenation of cyclohexene with $Cp^*_2LuH(\mu\text{-}H)LuCp^*_2$ was first-order in lanthanide and first-order in olefin. They concluded that either the complex was highly dissociated under the reaction conditions or the dimer reacted directly with the olefin. In our case, on the evidence of NMR spectroscopy the equilibrium constant for the dissociation of dimeric hydrides **1**−**4** (eq 1) should be less than 10^{-2} M.[7]

$$\{Cp'_2Ln(\mu\text{-}H)\}_2 \rightleftharpoons 2\ Cp'_2Ln{-}H \qquad (1)$$

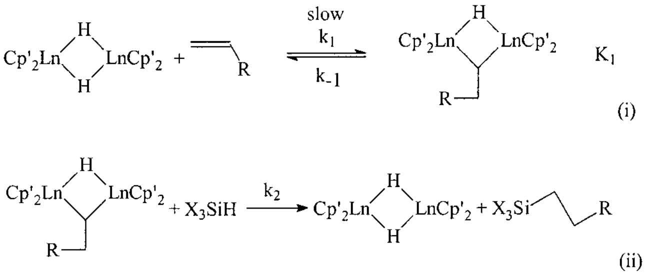
Earlier, we found that dimeric hydrides **1** and **4** take 2 weeks to equilibrate in benzene at ambient temperature or ca. 1 h at 70−75 °C (eq 2).[7] This equilibrium may be caused by slow reversible dissociation of the starting lanthanide hydrides. Another explanation is an associative mechanism, since no monomeric hydrides Cp'_2LnH were detected by NMR both at ambient and at elevated (up to 65 °C) temperatures.



(2)

In view of these data and the results on the reactivity of dimeric lanthanide hydrocarbyls toward organosilicon hydrides,[7] our kinetic observations are most simply described by the sequence of eqs i and ii (Scheme 1) involving a direct reaction of *dimeric* hydride with the olefin.[10]

Scheme 1



When $k_2[\text{silane}] \gg k_{-1} + k_1[\text{olefin}]$, the rate law reduces to eq 3 ($[Ln_2]$ denotes the concentration of the starting dimeric organolanthanide).

$$V^{HS} = k_1[Ln_2][\text{olefin}] \qquad (3)$$

In this case, the insertion of an olefin molecule into a Ln−H−Ln bridge and the formation of a dimeric lanthanide complex with hydride and hydrocarbyl bridging ligands is rate limiting. The k_1 values ($M^{-1}{\cdot}s^{-1}$) at 75 °C were obtained to be 0.033(2) for **1** and **5**, 0.025(2) for **2**, 0.014(1) for **3**, and 0.012(1) for **4** and **6** (see also Table 1). Hence, the change in relative activities occurs approximately in parallel with the change in the metal ionic radius: Y > Tb > Yb > Lu. These results correlate with the published data on the reactivity of hydride complexes of various lanthanides in the olefin insertion reactions.[8a,11a,12]

A kinetic isotope effect k_H/k_D of 5.5(2) was determined for the hydrosilylation of 1-octene with $PhMeSiH_2$/$PhMeSiD_2$ catalyzed by **1** in benzene at 75 °C. Since the rate law for hydrosilylation with $PhMeSiD_2$ is the same as that with $PhMeSiH_2$, the isotope effect studied should be attributed to the reversible insertion of an olefin into an Ln−H(D)−Ln fragment (eq i, Scheme 1). The hydrosilylation of 1-octene with $PhMeSiD_2$ yields 2-d_1-n-$C_8H_{17}SiDMePh$. According to the mass spectral investigation of reaction products, no deuterium is incorporated into the other positions of the *n*-octyl fragment. In the presence of a 2-fold excess of $PhMeSiD_2$, no decrease in deuterium content in the unreacted silane is observed. Since fast deuterium exchange in silanes is known to be catalyzed by lanthanide hydrides,[7] this result suggests that $k_2[\text{silane}] \gg k_{-1}$.

The hydrosilylation of 1-octene with n-Bu_2SiH_2 at 75 °C was considerably slower (tof (turnover frequency) 9.4(8) h^{-1} for **1**, 5.8(6) h^{-1} for **4**) than the hydrosilylation with such silanes as $PhMeSiH_2$, $PhSiH_3$, and Ph_2SiH_2, and, moreover, simultaneous 1-octene dimerization[11a,13,16] (eq 4; we did not take into consideration the actual

---

[10] Here and below the formation of η^3-allyl lanthanide complexes was not observed in both stoichiometric and catalytic reactions.[8a,11]

(11) (a) Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091−8103. (b) Jeske, G.; Schock, L. E.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8103−8110. Brunelli, M.; Poggio, S.; Pedretti, U.; Lugli, G. *Inorg. Chim. Acta* **1987**, *131*, 281−285. (c) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 2314−2324.

(12) Gagne, M. R.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114* (4), 275−294.

(13) For selective dimerization of α-olefins catalyzed by scandium compounds, see refs 8b, 14, 15.

(14) Piers, W. E.; Shapiro, P. J.; Bunel, E.; Bercaw, J. E. *Synlett* **1990**, 74−84.

(15) Hajela, S.; Bercaw, J. E. *Organometallics* **1994**, *13*, 1147−1154.

(16) Kretschmer, W. P.; Troyanov, S. I.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Organometallics* **1998**, *17*, 284−286.

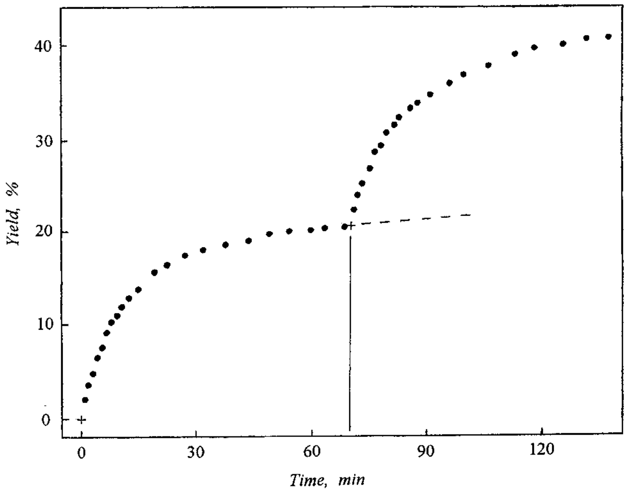
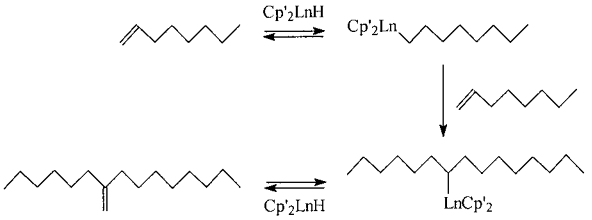


Figure 3. Yield of the product from the 1-octene hydrosilylation with $PhMeSiH_2$ catalyzed by **7** in benzene at 32 °C as a function of time. The aliquots of the catalyst solution were added at 0′00″ and 70′00″.

structure of organolanthanide intermediates) with tof 10(1) h^{-1} for **1** and 2.7(3) h^{-1} for **4** was observed.



(4)

No hydrosilylation or hydrogermylation of 1-octene was observed for silanes known as poor hydride donors,[7] such as Et_3SiH, $PhMe_2SiH$, Ph_2MeSiH, and Ph_3SiH, or germane, Et_3GeH. Only the product of the 1-octene dimerization was detected by GLC in these cases. The corresponding tof values for the dimerization were 11(1) h^{-1} for **1** and 3.0(3) h^{-1} for **4**.

Hydrosilylation of 1-Octene Catalyzed by Lanthanide Complexes with Ln(μ-Me)$_2$Ln Bridging. The lanthanide hydrocarbyls $\{Cp'_2Ln(\mu\text{-}Me)\}_2$, where Ln = Y (**7**), Tb (**8**), Yb (**9**), Lu (**10**), have been found to exhibit higher catalytic activity than the corresponding lanthanide hydrides with either Ln(μ-H)$_2$Ln or Ln(μ-H)(μ-Me)Ln bridging (see also ref 8b). The hydrocarbyls showed considerable activity even at room temperature (see Table 1). The kinetic behavior of the catalysts is fairly complicated. The hydrosilylation rate decreases sharply after several minutes, as shown in Figure 3.

Interestingly, the addition of a new portion of the catalyst causes a considerable increase in the hydrosilylation rate. Moreover, this increase was higher than the effect estimated from the account of increased concentration of the organolanthanide added.

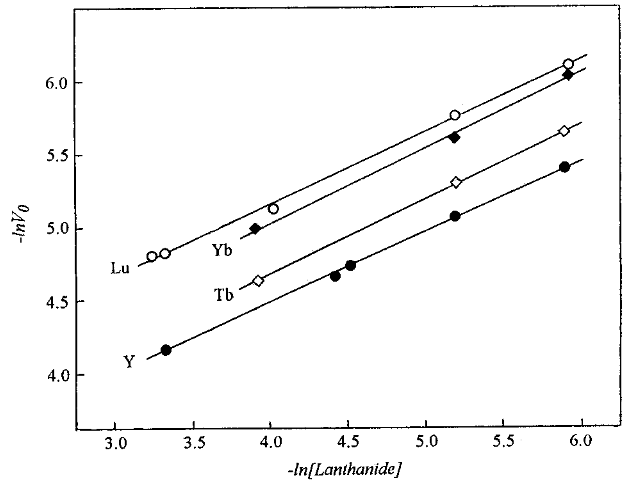


Figure 4. Hydrosilylation of 1-octene with $PhMeSiH_2$ catalyzed by **7** (Y), **8** (Tb), **9** (Yb), and **10** (Lu) in benzene at 32 °C. Initial reaction rate as a function of the catalyst concentration ($[olefin]_0 = 1.177$ M·L^{-1}; [lanthanide] refers to the concentration of the starting dimeric organolanthanide).

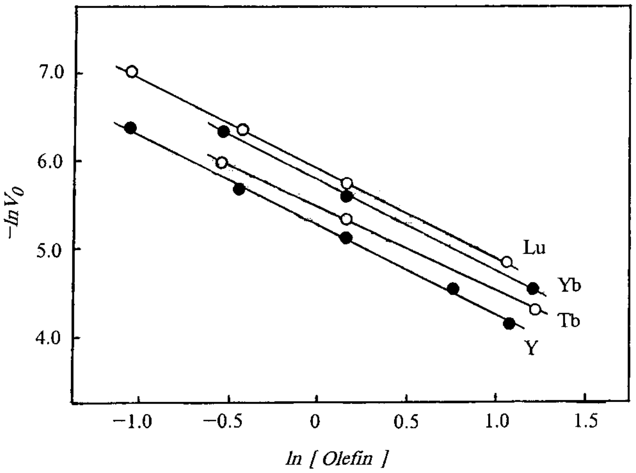


Figure 5. Hydrosilylation of 1-octene with $PhMeSiH_2$ catalyzed by **7** (Y), **8** (Tb), **9** (Yb), and **10** (Lu) in benzene at 32 °C. Initial reaction rate as a function of the olefin concentration ($[Ln_2] = 5.49 \cdot 10^{-3}$ M·L^{-1}).

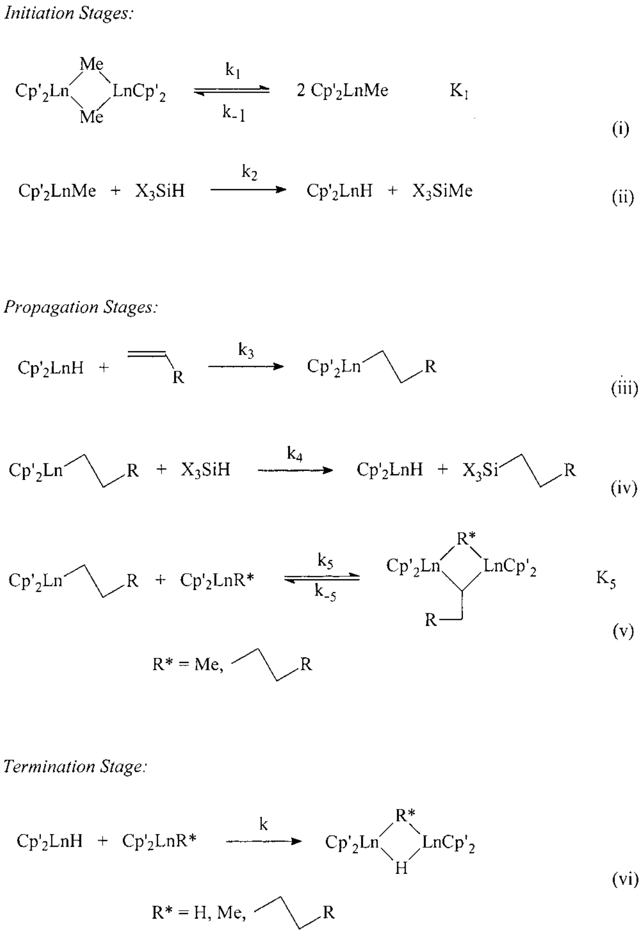
The initial rate of the hydrosilylation (V_0^{HS}) of 1-octene with $PhMeSiH_2$ catalyzed by **7**−**10** at 32 °C was found to be half-order in metal complex ($[Ln_2]$ denotes the concentration of the starting dimeric organolanthanide), first-order in olefin, and approximately zero-order in silane (in the concentration range 0.37−3.50 M·L^{-1}) (eq 5). The ranges of the concentrations used are given in the representative kinetic plots in Figures 4 and 5.

$$V_0^{HS} = k_0[Ln_2]^{1/2}[olefin] \tag{5}$$

The initial activities of **7**−**10**, k_0 (s^{-1}·M$^{-1/2}$), at 32 °C were found to be 0.0041(4) for **7**, 0.0033(2) for **8**, 0.0024(2) for **9**, and 0.0021(2) for **10,** respectively ($[olefin]_0 = [silane]_0 = 1.177$ M·L^{-1} and $[Ln_2] = 4.51$ mM·L^{-1}). Hence, the change in the relative activities occurs approximately in parallel to the change in the metal ionic radius: Y > Tb > Yb > Lu. An increase in the olefin concentration brings about a considerable increase in the lifetime of the catalyst estimated by the time interval before noticeable retardation of the hydrosilylation. In contrast, an increase in the silane concentration leads to a decrease of the catalyst activity.

Kinetic trends discussed above are consistent with the sequence shown in Scheme 2. Since $K_1 \ll 1$ at room temperature,[4,7] the reactions of eqs i−iv probably define the initial rate law. Here, the concentration of the active lanthanide species in the rate-determing step (the olefin

Scheme 2



insertion of eq iii) is controlled by an equilibrium of eq i leading to dimer formation. Thus, the hydrosilylation cycle catalyzed by the Ln(μ-Me)$_2$Ln precursor at ambient temperature appears to involve the *monomeric* lanthanide complexes rather than the dimers, in contrast to the case of the Ln(μ-H)$_2$Ln and Ln(μ-H)(μ-Me)Ln precursors. This interpretation explains a higher activity of **7**−**10** compared to that of **1**−**6**.

Influence of Bridging and Cyclopentadienyl Ligands on Catalytic Activity of Lanthanide Complexes. We performed a comparative study of the activity of Cp′$_2$Ln(μ-L′)(μ-L″)LnCp′$_2$, where Ln = Y or Lu, in the catalytic hydrosilylation of 1-octene with PhMeSiH$_2$. Lanthanide hydrocarbyls with two acetylenide bridging ligands, {(t-BuC$_5$H$_4$)$_2$Y(μ-C≡CBu-n)}$_2$, where Ln = Y, Lu, do not catalyze the reaction. Moreover, the latter compounds do not react with PhMeSiH$_2$ either at ambient or at elevated temperature. This probably results from the very high value of D(Cp′$_2$-Ln−R),[17] where R = 1-hexyn-1-yl (see also ref 18). Likewise, the compounds Cp′$_2$Ln(μ-Me)(μ-OMe)LnCp′$_2$ react neither with silanes nor even with organotin hydrides[7] and also do not catalyze the olefin hydrosilylation. The compounds Cp′$_2$Ln(μ-H)(μ-Cl)LnCp′$_2$[7] also do not catalyze the reaction. Thus, the catalytic activity of the compounds with different bridging decreases in the following series:

$$\mathrm{Ln}(\mu\text{-Me})_2\mathrm{Ln} \gg \mathrm{Ln}(\mu\text{-H})(\mu\text{-Me})\mathrm{Ln} = \mathrm{Ln}(\mu\text{-H})_2\mathrm{Ln} \gg \mathrm{Ln}(\mu\text{-H})(\mu\text{-Cl})\mathrm{Ln},\ \mathrm{Ln}(\mu\text{-Me})(\mu\text{-OMe})\mathrm{Ln},\ \text{or}\ \mathrm{Ln}(\mu\text{-C}{\equiv}\mathrm{CBu\text{-}n})_2\mathrm{Ln}$$

The catalytic activities of the lutetium hydrides with the t-BuC$_5$H$_4$, Me$_3$SiC$_5$H$_4$, and C$_5$H$_5$ ligands at 75 °C (1-octene, PhMeSiH$_2$, benzene) are similar (see Table 1). The behavior of the corresponding hydrocarbyls is quite different. Considering rather close values of rates of olefin insertion into the corresponding Lu−H bonds, it is likely that this difference results from a considerable decrease in the dissociation rate of the hydrocarbyls according to the following sequence:

$$\{(\text{t-BuC}_5\text{H}_4)_2\text{Lu}(\mu\text{-Me})\}_2 > \{(\text{Me}_3\text{SiC}_5\text{H}_4)_2\text{Lu}(\mu\text{-Me})\}_2 > \{(\text{C}_5\text{H}_5)_2\text{Lu}(\mu\text{-Me})\}_2$$

The hydrosilylations of 1-octene catalyzed by {(C$_5$H$_5$)$_2$-Lu}$_3$(μ-H)$_2$(μ_3-H) at 75 °C and {(C$_5$H$_5$)$_2$Lu(μ-Me)}$_2$ at 32 °C are likely to involve the same catalytic intermediates.

Catalytic activity of Cp*$_2$LuCH(SiMe$_3$)$_2$ (Cp* = C$_5$-Me$_5$) is unexpectedly low (Table 1). At 75 °C, the reaction mixture becomes deep yellow-orange and some precipitate forms. A relatively low catalytic activity of this lutetium hydrocarbyl might be attributed to the formation of a compound with a luthetium−silicon bond.[4,19]

Discussion

Here we have shown that olefin hydrosilylation includes a successive olefin insertion into a Ln−H bond and hydride transfer from silane to the lanthanide in the hydrocarbyl complex formed, while the intermediates with Ln−Si bonds are not involved. These mechanistic findings are in good agreement with the recent results of Marks et al.[3f] and Tilley and Gountchev.[3k] Interestingly, the catalytic activity of Cp*$_2$LuCH-(SiMe$_3$)$_2$ in 1-octene hydrosilylation was found to be unexpectedly low (Table 1), though the corresponding hydride Cp*$_2$LuH has been found to add to α-olefins very fast.[8a] This low activity might be attributed to the formation of a stable compound with a lanthanide−silicon bond.[4,19] However, Tanaka et al.[3b] and Marks et al.[3f] showed that both light lanthanide and yttrium compounds Cp*$_2$LnCH(SiMe$_3$)$_2$ exhibit high catalytic activity in olefin hydrosilylation. A dramatic difference between luthetium and other metals of the family may be due to a more open coordination shell of the latter.

Monomeric lanthanide hydrides Cp″$_2$LnH are known to be highly active catalysts of olefin transformations.[5,6] This is the result of the ability of the compounds to add olefins very fast to form the corresponding lanthanide hydrocarbyls. On the other hand, organolanthanides, if they do not involve bulky ligands, can form thermodynamically stable associates, i.e., the respective complexes with two or several metal atoms bonded with bridging ligand(s).[5−7] Here, on the evidence of kinetic experiments we have shown that 1-octene hydrosilyl-

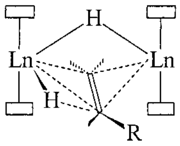
---

[17] Nolan, S. P.; Stern, D.; Marks, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 7844−7853.

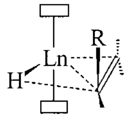
[18] den Haan, K. H.; Wielstra, Y.; Teuben, J. H. *Organometallics* **1987**, *6*, 2053−2060. Heeres, H. J.; Teuben, J. H. *Organometallics* **1991**, *10*, 1980−1986.

[19] (a) Radu, N. S.; Tilley, T. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1992**, *114*, 8293−8295. (b) Radu, N. S.; Tilley, T. D. *J. Am. Chem. Soc.* **1995**, *117*, 5863−5864.

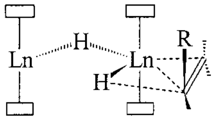
ation catalyzed by **1**−**6** includes bimetallic intermediates. In other words, this reaction does not require the preliminary dissociation of dimeric organolanthanides to the respective monomers (see Scheme 1). The rate-limiting stage of the hydrosilylation is olefin addition to dimeric lanthanide hydride $\{Cp'_2LnH\}_2$ to form the respective hydride−hydrocarbyl complex, $Cp'_2Ln(\mu\text{-}H)(\mu\text{-}n\text{-octyl})LnCp'_2$. A kinetic isotope effect of this reaction k_H/k_D of 5.5(2) was determined for the hydrosilylation of 1-octene with $PhMeSiH_2/PhMeSiD_2$ catalyzed by **1** in benzene at 75 °C. This isotope effect is much larger than that observed recently[20] for the insertion of 1-hexene into the Lu−H−Lu bridge in $\{[\mu\text{-}Et_2Si(C_5H_4)(C_5Me_4)]Lu(\mu\text{-}H)\}_2$. In the latter case, the kinetic isotope effect is 1.4(1) at 65 °C, whereas the olefin insertion process is rather slow (the rate constant of bimolecular insertion is 0.00073(1) $M^{-1}\cdot s^{-1}$ at 74.9 °C) and does not involve prior dissociation of the starting organolanthanide owing to steric reasons. Thus, the reaction rate law found, the observed values of the rate constants, and the kinetic isotope effect for the reversible insertion of the olefin molecule into the Ln−H bond are apparently consistent with a transition state that should involve, at least, a partial cleavage of the Ln−H−Ln bridge[11c,21] and a considerable degree of hydrogen transfer. It is this case in which olefin activation proceeds in the vicinity of both lanthanide atoms of the dimeric compound, i.e.,



vs. monomeric intermediate:



Alternatively, slow insertion of the olefin into the Ln−H bond may proceed in the coordination sphere of only one lanthanide atom of the partially dissociated dimer, i.e., without assistance of the second lanthanide center of this dimer, e.g.,



Actually, in this paper we do not aim to define the exact structure of the binuclear transition state. On the other hand, we aim to note that the ability of the dimeric complexes to catalyze hydrosilylation via a direct insertion of an olefin molecule, so that the prior dissociation of the dimer is not required for the reaction to occur,[22] is probably a characteristic feature of strongly associated organolanthanides. At first glance this conclusion contradicts the modern theory of olefin activation on d^0 transition metal centers. It is well recognized that a four-centered transition state of this reaction should be realized for cationic Cp''_2MR^+, where M = Ti, Zr, and Hf,[23] or electroneutral monomeric lanthanide complexes[8b,20] to carry out fast olefin insertion into the metal−carbon bond. On the other hand, the insertion into the metal−hydrogen bond was observed for $Cp^*_2ZrH_2$[24a] and other Zr complexes.[24b] Many examples of olefin hydrozirconation with $\{Cp_2Zr(H)Cl\}_n$ are described.[25] Actually, the latter zirconium complexes are isoelectronic with the above-proposed hydrosilylation intermediates, i.e., partially dissociated lanthanide complexes with one bridging ligand, $Cp'_2Ln(H)(\mu\text{-}H)M$, where M = $LnCp'_2$.

The results of the NMR spectroscopy study show that the stoichiometric reaction of **1** or **4** with 1-octene giving the corresponding lanthanide hydrocarbyls does not occur at room temperature or at elevated temperature. However, a stoichiometric olefin insertion was observed earlier for some group 3 metal hydrides.[8b,14,26] In addition, such a reaction with dimeric lanthanide hydrides can even result in the addition of an olefin only to one Ln−H−Ln fragment, to give stable compounds with $Ln(\mu\text{-}H)(\mu\text{-alkyl})Ln$ bridging.[8c,20]

The hydrosilylation of 1-octene with $PhMeSiH_2$ catalyzed by dimeric methyl complexes **7**−**10** at ambient temperature seems to involve transformations of the respective *monomeric* complexes. The complexes have a considerably higher activity in comparison with that of the corresponding *dimeric* lanthanide hydrides. Actually, both the insertion process by eq iii[20] (Scheme 2) and hydride transfer by eq iv[7] are apparently faster than similar reactions that occur with the dimeric lanthanide complexes. However, the insertion of the olefin into the monomeric lanthanide hydride seems to be the rate-limiting step for the hydrosilylation. Here, we observed half-order in the catalyst for the initial rate law of 1-octene hydrosilylation. Probably, the concentration of the reactive organolanthanide intermediate is controlled by the monomer−dimer equilibria of eq i (Scheme 2). Similar behavior was observed for olefin hydrogenation catalyzed by organolanthanides with Cp* ligands.[27] It is of interest that in our case the hydrosilylation rate decreases after several minutes because of the association of the *monomeric* intermediates. No precipitation of lanthanide complexes was observed during the catalytic reaction. After completion of the dimerization processes, the hydrosilylation rate obeys the rate law shown in eq 3. In this case, slow 1-octene hydrosilylation includes *dimeric* lanthanide intermediates (Scheme 1).

---

[20] Stern, D.; Sabat, M.; Marks, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 9558−9575.

[21] Burns, C. J.; Andersen, R. A. *J. Am. Chem. Soc.* **1987**, *109*, 915−917. Nolan, S. P.; Marks, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 8538−8540.

[22] Even though the insertion proceeds more slowly than in the case of the monomeric hydrides.

[23] Hlatky, G. G.; Turner, H. W.; Eckman, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 2728−2729. Marks, T. J. *Acc. Chem. Res.* **1992**, *25*, 57−65, and references therein. Yang, X.; King, W. A.; Sabat, M.; Marks, T. J. *Organometallics* **1993**, *12*, 4254−4258, and references therein. Bochmann, M.; Lancaster, S. J.; Hursthouse, M. B.; Malik, K. M. A. *Organometallics* **1994**, *13*, 2235−2243, and references therein.

[24] (a) Manriquez, J. M.; McAlister, D. L.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 2716. (b) Cardin, D. J.; Lappert, M. F.; Raston, C. L.; Riley, P. I. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Oxford: Pergamon Press: 1982; Vol. 3, p 559.

[25] Schwartz, J.; Labinger, J. A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 333. Schwartz, J.; Dayrit, F. T.; Temple, J. S. In *Organic Synthesis−Today and Tomorrow*; Trost, B. M.. Hutchinson, C. R., Eds.; Pergamon: Oxford, 1981. Schwartz, J. *J. Organomet. Chem.* **1976**, *1*, 461, and references therein.

[26] (a) Evans, W. J.; Meadows, J. H.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 1291−1300. (b) Shapiro, P. J.; Bunel, E.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1990**, *9*, 867−869.

[27] Giardello, M. A.; Conticello, V. P.; Brard, L.; Gagne, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10241.

Actually, a binuclear structure of the active center should result in a decrease in the activity of the catalyst in comparison to catalysts that consist of either electroneutral or cationic monometallic species. However, the application of a catalyst with bimetallic structure can provide unusual stereospecificity to the reaction (e.g., see ref 28). Moreover, a recent MO calculation has shown that the coordination of hydrocarbons to a bimetallic catalyst may result in considerable activation of C−H bonds in the substrate.[29] Thus, if the binuclear catalyst either has some coordination vacancies or forms them relatively easily, it can have rather high activity. However, in this case, not only bridging ligands but also bulky cyclopentadienyl ligands can considerably decrease the catalytic activity of organolanthanides.[8c,14,26b]

Conclusion

In this contribution the structure of organolanthanide intermediates in catalytic hydrosilylation is considered. Both our results and data of Marks et al.,[3f] as well as Tilley and Gountchev,[3k] testify that olefin hydrosilylation catalyzed by organolanthanides with both bulky and nonbulky ligands runs through a successive olefin insertion into Ln−H and hydride transfer from silane to the lanthanide in the hydrocarbyl complex formed, while the intermediates with Ln−Si bonds are not involved. We have shown that monomeric lanthanide hydrides are more efficient catalysts of the olefin hydrosilylation than the respective dimeric complexes due to a specific ability of the former to undergo a ready and fast addition to the double bond.[8a,11a] However, the association of lanthanide catalysts in solution seems to be a common phenomenon because of the extraordinary stability of bridged organolanthanides containing ligands with moderate steric demands.[6] It is essential that *the dissociation of the dimeric organolanthanide precursor is not required for olefin hydrosilylation to be effected, as the reaction can be catalyzed by organometallic intermediates with μ-H bonding*. In other words, the dissociation of the dimeric complexes is desirable to obtain a fast catalytic reaction, while if a certain organolanthanide associate fails to dissociate, the reaction can still run, though at a slower pace.

Experimental Section

General Procedures. All manipulations were performed either on a high-vacuum line in all-glass apparatus equipped with PTFE stopcocks or under an atmosphere of thoroughly purified argon using either a standard Schlenk technique or a Vacuum Atmospheres drybox. Hydrocarbon solvents (including benzene-d_6) were distilled and stored over CaH_2 or Na/K alloy. Chloroform-d_1 was purified by distillation over P_4O_{10} and kept over 4 Å molecular sieves. Complexes **1**−**10**, $Cp'_2Ln(\mu\text{-}Me)(\mu\text{-}OMe)LnCp'_2$ (Ln = Y, Lu), and $Cp'_2Ln(\mu\text{-}H)(\mu\text{-}Cl)LnCp'_2$ (Ln = Y, Lu) were prepared according to the described procedures.[7] The lutetium hydrocarbyls $Cp^*_2LuCH(SiMe_3)_2$[11a] and $\{Cp_2Lu(\mu\text{-}Me)\}_2$[30] were prepared by the published methods. The hydride $\{Cp_2Lu\}_3(\mu\text{-}H)_2(\mu^3\text{-}H)$ was prepared upon treatment of $\{Cp_2Lu(\mu\text{-}Me)\}_2$ with $PhSiH_3$ in benzene at 50 °C and recrystallized from toluene. The organosilicon hydrides $PhSiH_3$, Ph_2SiH_2, $PhMeSiH_2$, n-Bu_2SiH_2, Ph_3SiH, and Et_3SiH were obtained by reduction of commercially available organochlorosilanes with $LiAlH_4$.[31] Et_3GeH and $PhMeSiD_2$ (98% D) were prepared in a similar manner by reduction of Et_3GeCl with $LiAlH_4$[32] and $PhMeSiCl_2$ with $LiAlD_4$,[33] respectively. 1-Octene (Reachim) was distilled over CaH_2 and stored over 4 Å molecular sieves (Fluka) under argon to be vacuum-transferred into a reactor immediately before use. 1-Hexyne (Merck) was distilled and kept over 4 Å molecular sieves under argon. ^1H and ^{13}C NMR spectra were recorded with a Bruker AM 360 for 3−10% solutions in deuterated solvents. Chemical shifts for ^1H and ^{13}C resonances were measured relative to TMS. GLC analysis was performed with a Tsvet 101 (Russia) chromatograph (3 m × 3 mm column packed with 3% SP-2100 on Chromaton N-Super). The contents of the products were measured using the internal standard method. MS measurements were carried out on a MX-1321 (Russia) spectrometer (E_i = 70 eV). C, H microanalyses were carried out using a CHN-O-Rapid analyzer (Heracus). Lanthanide contents were assayed by titration (EDTA, Xylenol Orange).

Kinetic Measurements. Kinetic studies were carried out in a custom-made glass reactor (15 mL volume) equipped with a thermostated (±0.2 °C) water jacket, PTFE stopcock, Teflon stopper, a silicone membrane for run time withdrawal of samples, and a Teflon-coated magnetic stirring bar. A typical procedure for the kinetic experiment is as follows. A mixture of measured amounts of 1-octene, silane, $n\text{-}C_{12}H_{26}$ as an internal standard, and solvent benzene was prepared in a separate glass vessel equipped with PTFE stopcocks using a high-vacuum line and thoroughly purified argon. The mixture was transferred into the reaction vessel and thermostated. A measured amount of the catalyst solution was added by a syringe into the vessel. The benzene solutions of the catalysts were prepared and kept in another glass vessel equipped with PTFE stopcocks under an atmosphere of thoroughly purified argon. Samples of the reaction mixture were taken by a Hamilton syringe (10 μL). Positive pressure of argon (ca. 2 atm) was maintained in the reaction vessel during the runs to exclude the penetration of oxygen through a syringe. The time intervals were measured with an accuracy of ±5 s. The analysis of the samples was performed by GLC. The consumption of substrates and the formation of $n\text{-}C_8H_{17}SiHMePh$ were monitored by integrating their GLC picks against the internal standard. The data obtained were treated using a PC-type computer with standard kinetic software.

$\{Cp'_2Y(\mu\text{-}C{\equiv}CBu\text{-}n)\}_2$. A solution of 0.32 g (3.82 mmol) of 1-hexyne in 5 mL of toluene was added dropwise to a solution of 1.32 g (1.91 mmol) of **7** in 50 mL of toluene at room temperature.The mixture was stirred for 1 h and then evaporated to dryness. The residue was recrystallized from hexane. The crystals precipitated at −78 °C were separated, washed with a minimal amount of cold pentane, and dried in vacuo to afford 0.83 g (53%) of colorless crystals of the title compound, mp 126−128 °C. ^1H NMR (benzene-d_6): δ 0.91 (t, 6H, J = 7.2 Hz, CH_2Me), 1.37 (m, 4H, CH_2CH_2Me), 1.44 (m, 4H, $CH_2CH_2CH_2$), 1.47 (s, 36H, t-Bu), 1.97 (t, 4H, J = 7.3 Hz, CCH_2CH_2), 6.44 (t, 8H, J = 2.7 Hz, H2,5 in C_5H_4), 6.70 (t, 8H, J = 2.7 Hz,

---

(28) Choukroun, R.; Gervais, D.; Jaud, J.; Kalck, P.; Senocq, F. *Organometallics* **1986**, *5*, 67−71. Choukroun, R.; Iraqi, A.; Gervais, D.; Daran, J.-C.; Jeannin, Y. *Organometallics* **1987**, *6*, 1197−1201. Hostetler, M. J.; Butts, M. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 2743−2752, and references therein. Kalck, P.; Serra, C.; Machet, C.; Broussier, R.; Gautheron, B.; Delmas, G.; Trouve, G.; Kubicki, M. *Organometallics* **1993**, *12*, 1021−1022.

(29) Mamayev, V. M.; Gloriozov, I. P.; Ishchenko, S. Ya.; Simonyan, V. V.; Myshakin, E. M.; Prisyajnyuk, A. V.; Ustynuk, Yu. A. *Mendeleev Commun.* **1995**, 137−138.

(30) Evans, W. J.; Domingues, R.; Hanusa, T. P. *Organometallics* **1986**, *5*, 263−270.

(31) Andrianov, K. A. *Metody Elementoorganicheskoy Khimii. Kremnij* (*Methods of Organo-Element Chemistry. Silicon*); Nauka: Moscow, 1968.

(32) Kocheshkov, K. A.; Zemlyanski, N. N.; Shverdina, N. I.; Panov, E. M. *Metody Elementoorganicheskoy Khimii. Germani, Olovo, Svinets* (*Methods of Organo-Element Chemistry. Germanium, Tin, Lead*); Nauka: Moscow, 1968.

(33) Watanabe, H.; Ohsawa, N.; Sudo, T.; Hirakata, K.; Nagai, Y. *J. Organomet. Chem.* **1977**, *128*, 27−35.

H3,4 in C_5H_4). ^{13}C NMR (benzene-d_6): δ 13.62 (CH$_2$*Me*), 21.53 (CH$_2$*C*H$_2$Me), 22.52 (CH$_2$*C*H$_2$CH$_2$), 30.16 (*C*Me$_3$), 30.61 (C*C*H$_2$-CH$_2$), 32.35 (C*Me*$_3$), 108.88 (C2,5 in C_5H_4), 110.71 (C3,4 in C_5H_4), 118.65 (t, $^2J_{Y-C}$ = 3.5 Hz, C≡*C*CH$_2$), 130.10 (t, $^1J_{Y-C}$ = 27.6 Hz, *C*≡CCH$_2$), 138.56 (C1 in C_5H_4). Anal. Calcd for $C_{48}H_{70}Y_2$: C, 69.90; H, 8.50; Y, 21.60. Found: C, 69.77; H, 8.42; Y, 21.81.

{Cp′$_2$Lu(μ-C≡CBu-n)}$_2$. The synthesis was carried out similarly to the preparation of the analogous compound of yttrium starting from 0.39 g (4.8 mmol) of 1-hexyne and 2.07 g (2.4 mmol) of **10** in 60 mL of toluene. A 1.55 g (65%) sample of the title compound was obtained as colorless crystals, mp 154−157 °C. ^{1}H NMR (benzene-d_6): δ 0.90 (t, 6H, J = 7.3 Hz, CH$_2$*Me*), 1.36 (m, 4H, CH$_2$C*H*$_2$Me), 1.47 (s, 36H, t-Bu), 1.50 (m, 4H, CH$_2$C*H*$_2$CH$_2$), 2.05 (t, 4H, J = 7.5 Hz, CC*H*$_2$CH$_2$), 6.39 (t, 8H, J = 2.7 Hz, H2,5 in C_5H_4), 6.71 (t, 8H, J = 2.7 Hz, H3,4 in C_5H_4). ^{13}C NMR (benzene-d_6): δ 13.58 (CH$_2$*Me*), 21.59 (CH$_2$*C*H$_2$Me), 22.57 (CH$_2$*C*H$_2$CH$_2$), 29.86 (*C*Me$_3$), 30.54 (C*C*H$_2$-CH$_2$), 32.32 (C*Me*$_3$), 109.06 (C2,5 in C_5H_4), 109.63 (*C*≡CCH$_2$), 109.80 (C3,4 in C_5H_4), 119.80 (C≡*C*CH$_2$), 136.54 (C1 in C_5H_4). Anal. Calcd for $C_{48}H_{70}Lu_2$: C, 57.83; H, 7.03; Lu, 35.14. Found: C, 57.99; H, 7.14; Lu, 34.95.

Hydrosilylation of 1-Octene with PhMeSiH$_2$. A mixture of 4.75 mL (3.40 g, 30 mmol) of 1-octene, 4.25 mL (3.71 g, 30 mmol) of PhMeSiH$_2$, and 184 mg (0.28 mmol) of **1** in 10 mL of benzene was stirred at 70 °C for 6 h and then subjected to fractional distillation to yield 6.52 g (92%) of *n*-octylphenylmethylsilane, bp 94−96 °C/1 mm. ^{1}H NMR (CDCl$_3$): δ 0.56 (d, 3H, J = 2.1 Hz, SiMe), 1.0−1.7 (m, 17H, $^nC_8H_{17}$), 4.63 (hex, 1H, J = 2.2 Hz, SiH), 7.5−7.8 (m, 5H, Ph). ^{13}C NMR (CDCl$_3$): δ −5.63 (C1 of $^nC_8H_{17}$), 13.36 (C3 of $^nC_8H_{17}$), 14.14 (C7 of $^nC_8H_{17}$), 22.75 (C4 of $^nC_8H_{17}$), 24.42 (C2 of $^nC_8H_{17}$), 29.34 (C8 of $^nC_8H_{17}$), 32.01 (C6 of $^nC_8H_{17}$), 33.18 (C5 of $^nC_8H_{17}$), 127.83 (2,6H of Ph), 129.13 (C4 of Ph), 134.30 (3,5H of Ph), 136.74 (C1 of Ph). Anal. Calcd for $C_{15}H_{26}Si$: C, 76.84; H, 11.18. Found: C, 76.70; H, 11.07.

Dimerization of 1-Octene. A mixture of 5.50 mL (3.93 g, 35 mmol) of 1-octene and 138 mg (0.21 mmol) of **1** in 10 mL of benzene was stirred for 15 h at 70 °C. The mixture was then fractionally distilled to give 2.60 g (66%) of the olefin dimer CH$_2$═C(C$_6$H$_{13}$-n)(C$_8$H$_{17}$-n), bp 162−165 °C/28 mm. ^{1}H NMR (benzene-d_6): δ 0.85 (m, 6H, Me), 1.2−1.5 (m, 20H, CH$_2$C*H*$_2$-CH$_2$ and C*H*$_2$Me), 1.94 (m, 4H, CH$_2$═CC*H*$_2$), 4.83 (s, 2H, CH$_2$═C). ^{13}C NMR (benzene-d_6): δ 14.52, 23.36, 28.48, 29.87, 30.13, 30.21, 30.33, 32.57, 32.68, 36.73 (*n*-C$_8$H$_{17}$ and *n*-C$_6$H$_{13}$), 109.21 (*C*H$_2$═C), 149.55 (CH$_2$═*C*). Anal. Calcd for $C_{16}H_{32}$: C, 85.63; H, 14.37. Found: C, 85.59; H, 14.42.

Acknowledgment. The research described in this paper was supported in part by Grant No. MRR000 from the International Science Foundation, Grant No. MRR300 from this Foundation and the Russian Government, Grant No. 98-03-32978a from the Russian Foundation for Basic Research, Grant No. 98-15-96061 from the President of Russian Federation, and Grant No. 1036/99 from the International Science and Technology Center. We thank Prof. A. T. Lebedev (Moscow State University) for providing valuable MS data.

OM010052C