Organometallics **1997,** *16,* 4041−4055

Reactivity of Lanthanide and Yttrium Hydrides and Hydrocarbyls toward Organosilicon Hydrides and Related Compounds

Alexander Z. Voskoboynikov,*[,1a] Inna N. Parshina,[1a] Alla K. Shestakova,[1a]
Kim P. Butin,[1b] Irina P. Beletskaya,[1b] Lyudmila G. Kuz'mina,[1c] and
Judith A. K. Howard[1d]

State Research Institute of Chemistry and Technology of Organoelement Compounds, sh. Entuziastov 38, Moscow 111123, Russia, Department of Chemistry, Moscow State University, V-234, Moscow, GSP 119899, Russia, N. S. Kurnakov Institute of General and Inorganic Chemistry of Russian Academy of Sciences, 31 Leninsky ave., Moscow 117907, Russia, and Department of Chemistry, Durham University, South Road, Durham DH1 3LE, U.K.

Received April 29, 1997⊗

The reaction of lanthanide and yttrium hydrocarbyls $\{Cp^*_2Ln(\mu\text{-Me})\}_2$ ($Cp^* = {}^tBuC_5H_4$ (Cp'), Ln = Y (**1**), Tb (**2**), Yb (**3**), Lu (**4**); $Cp^* = Me_3SiC_5H_4$ (Cp''), Ln = Lu (**5**)), one of which, **2,** has been characterized by X-ray crystal analysis, with various organosilicon, -germanium, and -tin hydrides (as well as some organoaluminum and -gallium hydrides) in hydrocarbon solution was found to yield the corresponding unsolvated dimeric lanthanide and yttrium hydrides $\{Cp^*_2Ln(\mu\text{-H})\}_2$ rather than compounds with lanthanide−element (Si, Ge, Sn) bonding. Thus, the reaction involves hydride transfer to Ln rather than the silyl transfer studied earlier for pentamethylcyclopentadienyllanthanide hydrocarbyls. Dimeric compounds $Cp^*_2Ln(\mu\text{-H})(\mu\text{-Me})LnCp^*_2$ with different bridging ligands were isolated; they are intermediates in this reaction. Dimeric lanthanide and yttrium hydrides catalyze the H/D exchange in silanes. This catalytic reaction is most correctly described by a mechanism involving nucleophilic substitution at the silicon atom. Yttrium and lutetium hydrocarbyls **1** and **4** react with various alkoxysilanes to produce the dimeric alkoxides $\{Cp'_2Ln(\mu\text{-OR})\}_2$ or the hydrocarbyl alkoxides $Cp'_2Ln(\mu\text{-Me})(\mu\text{-OR})LnCp'_2$ (R = Me, Et), depending on the reaction conditions. The reaction of **4** with $(MeO)_4Si$ provided $Cp'_2Lu(\mu\text{-Me})(\mu\text{-OMe})LuCp'_2$, which has been characterized by X-ray crystal analysis. This compound contains one methyl bridge (Lu−C 2.57(2) and 2.58(2) Å) and nonsymmetrically bonded μ-OMe ligand (Lu−O 2.20(2) and 2.12(2) Å). The reaction of **1** and **4** with Me_3SiCl leads to the corresponding dimeric chlorides $\{Cp'_2Ln(\mu\text{-Cl})\}_2$ only. Thus, the reaction of lanthanide and yttrium hydrocarbyls with various heterosubstituted organosilanes R_3SiX, where X = H, OR, or Cl, is a selective and convenient synthetic method in the chemistry of the group 3 elements. Complexes with $Ln(\mu\text{-H})(\mu\text{-Me})Ln$ and $Ln(\mu\text{-H})(\mu\text{-Cl})Ln$ bridging were prepared in high yield by the exchange reactions between the corresponding dimeric compounds $\{Cp^*_2Ln(\mu\text{-X})\}_2$ (X = H, Me, Cl) in a hydrocarbon solution. The capacities of various bridging fragments to undergo reversible cleavage (dissociation) in the hydrocarbon solution increase in the sequence $Ln{-}O(Me){-}Ln \ll Ln{-}Cl{-}Ln < Ln{-}H{-}Ln < Ln{-}Me{-}Ln$.

Introduction

Bis(cyclopentadienyl)lanthanide hydrides and hydrocarbyls, Cp_2LnH and Cp_2LnR, play a significant role in the chemistry of organolanthanides,[2] particularly due to their peculiar catalytic properties.[3] Therefore, these complexes were investigated in detail. Nevertheless, further studies can bring about the development of both new synthetic methods and novel reactivity of the compounds. In this work, we found a convenient and effective method for the synthesis of bis(cyclopentadienyl)lanthanide hydrides. This method involves reaction of the corresponding lanthanide hydrocarbyls with silanes (eq 1, Cp = C_5H_5, Cp', Cp'') or with organohydrides of some nontransition metals. This reaction was

$$Cp_2Ln{-}R + R'_3SiH \rightarrow Cp_2Ln{-}H + 2R'_3SiR \quad (1)$$

suggested by this group[4,5] and Marks[6] to be a key stage

⊗ Abstract published in *Advance ACS Abstracts,* August 1, 1997.

(1) (a) State Research Institute of Chemistry and Technology of Organoelement Compounds. (b) Moscow State University. (c) N. S. Kurnakov Institute of General and Inorganic Chemistry of Russian Academy of Sciences. (d) Durham University.

(2) To simplify the discussion the term lanthanide means both lanthanides and yttrium because of similar properties of their compounds.[3]

(3) (a) Marks, T. D.; Ernst, R. D. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 3, p 173. Edelmann, F. T. In *Comprehensive Organometallic Chemistry II: A review of the literature 1982−1994*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Exeter, 1995; Vol. 4, p 11. (b) Bochkarev, M. E.; Zacharov, L. N.; Kalinina, G. S. *Organoderivatives of Rare Earth Elements*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1995.

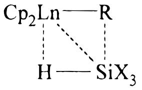
(4) Beletskaya, I. P.; Voskoboynikov, A. Z.; Parshina, I. N.; Magomedov, G. K.-I. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1990**, *39*, 613−614.

(5) Beletskaya, I. P.; Magomedov, G. K.-I.; Voskoboynikov, A. Z.; Parshina, I. N. *Abstracts of Posters*; XXVIII International Conference on Coordination Chemistry, Gera, GDR, August 13−18, 1990, Vol. 2, pp 3−67.

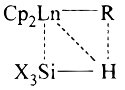
S0276-7333(97)00363-4 CCC: $14.00

of the catalytic cycle of olefin hydrosilylation catalyzed by organolanthanides.

The interaction between molecules of alkyl (aryl) lanthanide complexes with silane can be described as proceeding via either a four-centered transition state **A** or the alternative **B** state. Transition state **A** implies hydride transfer to the lanthanide atom and alkylation of the silane. On the contrary, structure **B** corresponds to the transfer of the silyl group to the metal atom, leading to the formation of a compound with Ln−Si bonding[7] and the corresponding hydrocarbon (pathway b). This structure corresponds to the transition state of σ-bond metathesis, which was studied earlier for early transition metal complexes and silanes (as well as H_2 or hydrocarbons).[10−13] As this duality evoked some discussion,[4−6,8] we have performed MO calculations for the alternative reaction pathways involving transformations of several simple molecules. The calculations indicate a silyl group transfer to the metal atom, i.e., formation of methane and the corresponding compound with Ln−Si bonding, is preferred over the hydride transfer (like eq 1) found in the reaction of $(C_5H_5)_2YMe$ with SiH_4 in the gas phase.

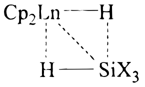


A

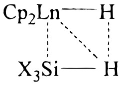


B

On the other hand, the reaction of silanes with less sterically hindered lanthanide hydrides Cp_2LnH was recently shown by Marks[15b] and Tilly[8] for complexes containing C_5Me_5 ligands to proceed via a four-centered transition state **B′** and form H_2 and compounds with Ln−Si bonding. This fact correlates well with our calculation results (see below). Apparently, the dehydrogenative coupling of silanes catalyzed by organolanthanides,[15] a mechanism studied by Marks[15b] (see also the results of Ziegler's MO calculation[14]), includes a similar Ln−Si bond formation stage. In this paper, we have shown that the reaction of lanthanide hydrides with silanes can proceed in a different manner. This reaction between R'_3SiD and lanthanide hydrides that involves monosubstituted cyclopentadienyl ligands can be used for the preparation of the corresponding lanthanide deuterides. In a catalytic manner, this reaction causes an isotope exchange between various silanes (R'_3SiH and R''_3SiD) (see below). Certainly, this isotope exchange could include the stage of silane metalation. However, we obtained some data which favors a direct participation of the lanthanide hydride intermediates in the degenerative exchange between Cp_2LnH and $R'_3SiH(D)$ proceeding via a four-centered transition state type **A′**.



A'



B'

In the absence of suitable salts (e.g., LiCl) or donating molecules (e.g., THF, Et_2O), organolanthanides are known to form stable associated complexes, particularly dimers that contain various bridging ligands.[3] We found that various dimeric complexes can take part in exchange reactions to form new dimers either with different bridging ligands (eq 2) or with different metals (eq 3). These stable dimers could be good models for

$$\{Cp_2Ln(\mu\text{-}L)\}_2 + \{Cp_2Ln(\mu\text{-}L')\}_2 \xrightarrow{C_6H_6} Cp_2Ln(\mu\text{-}L)(\mu\text{-}L')LnCp_2 \quad (2)$$

$$\{Cp_2Lu(\mu\text{-}L)\}_2 + \{Cp_2Y(\mu\text{-}L)\}_2 \xrightarrow{C_6H_6} Cp_2Lu(\mu\text{-}L)_2YCp_2 \quad (3)$$

the transition state of type **A** or **A′**. Reaction 2 was found to proceed readily for those compounds that include alkyl, hydride, and chloride bridging ligands. However, this reaction does not take place for alkoxy derivatives of lanthanides. Dimeric complexes with Ln(μ-Me)(μ-OR)Ln bridging can be synthesized by an alternative reaction between the corresponding alkoxysilanes and complexes with Ln(μ-Me)$_2$Ln bridging (a reaction like eq 1). The study of various equilibrium processes makes it possible to obtain the relative

---

(6) Fu, P.-F.; Brard, L.; Li, Y.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 7157−7168.

(7) A number of compounds both with lanthanide−silicon[8,9a,b] and with lanthanide−germanium, lanthanide−tin bonding[9b−e] have been synthesized and characterized.

(8) (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.

(9) (a) Schumann, H.; Nickel, S.; Hahn, E. *Organometallics* **1985**, *4*, 800−801. Schumann, H.; Nickei, S.; Loebel, J.; Pickardt, J. *Organometallics* **1988**, *7*, 2004−2009. Schumann, H.; Meese-Marktscheffel, J. A.; Hahn, E. *J. Organomet. Chem.* **1990**, *390*, 301−308. Campion, B. K.; Heyn, R. H.; Tilley, T. D. *Organometallics* **1993**, *12*, 2584−2590. (b) Bochkarev, L. N.; Makarov, V. N.; Hrzhanovskaya, Y. N.; Zakharov, L. N.; Fukin, G. K.; Yanovsky, A. I.; Struchkov, Y.-T. *J. Organomet. Chem.* **1994**, *467*, C3−C5. (c) Schumann, H.; Cygon, M. *J. Organomet. Chem.* **1978**, *144*, C43−C45. (d) Razuvaev, G. A.; Kalinina, G. S.; Fedorova, E. A. *J. Organomet. Chem.* **1980**, *190*, 157−165. Fedorova, E. A.; Kalinina, G. S.; Bochkarev, M. N.; Razuvaev, G. A. *Zh. Obshch. Khim. (USSR)* **1982**, *52*, 1187−1190. (e) Bochkarev, L. N.; Cholodilova, M. N.; Zhil'tsov, S. F.; Guseva, T. V.; Bochkarev, M. N.; Razuvaev, G. A. *Zh. Obshch. Khim. (USSR)* **1986**, *56*, 723−724. Bochkarev, L. N.; Fedyushkin, I. L.; Cholodilova, M. N.; Zhil'tsov, S. F.; Bochkarev, M. N.; Razuvaev, G. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1987**, 658−659. Bochkarev, M. N.; Khramenkov, V. V.; Rad'kov, Y.-F.; Zakharov, L. N.; Struchkov, Y.-T. *J. Organomet. Chem.* **1991**, *408*, 329−334. Bochkarev, M. N.; Khramenkov, V. V.; Rad'kov, Y.-F.; Zakharov, L. N.; Struchkov, Y.-T. *J. Organomet. Chem.* **1991**, *421*, 29−38. Cloke, F. G. N.; Dalby, C. I.; Hitchcock, P. B.; Karamallakis, H.; Lawless, G. A. *J. Chem. Soc., Chem. Commun.* **1991**, 779−781. Bochkarev, L. N.; Grachev, O. V.; Molosnova, N. E.; Zhiltsov, S. F.; Zakharov, L. N.; Fukin, G. K.; Yanovsky, A. I.; Struchkov, Y.-T. *J. Organomet. Chem.* **1993**, *443*, C26−C28. Bochkarev, L. N.; Makarov, V. M.; Zakharov, L. N.; Fukin, G. K.; Yanovsky, A. I.; Struchkov, Y.-T. *J. Organomet. Chem.* **1995**, *490*, C29−C31.

(10) (a) Woo, H. G.; Tilley, T. D. *J. Am. Chem. Soc.* **1989**, *111*, 3757−3758 and references therein. (b) Woo, H. G.; Tilley, T. D. *J. Am. Chem. Soc.* **1989**, *111*, 8043−8044. (c) Tilley, T. D.; Woo, H. G. *Polym. Prepr.* **1990**, *31*, 228−229. (d) Tilley, T. D. *Comm. Inorg. Chem.* **1990**, *10*, 37−51. (e) Woo, H. G.; Tilley, T. D. in *Inorganic and Organometallic Oligomers and Polymers*; Laine, R. M., Harrod, J. F., Eds.; Kluwer Publishers: Amsterdam, 1991; p 3. Tilley, T. D.; Radu, N. S.; Walzer, J. F.; Woo, H.-G. *Polym. Prepr.* **1992**, *33*, 1237. (f) Woo, H. G.; Waltzer, J. F.; Tilley, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 7047−7055. (g) Tilley, T. D. *Acc. Chem. Res.* **1993**, *26*, 22−29.

(11) Woo, H. G.; Heyn, R. H.; Tilley, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 5698−5707.

(12) (a) Walzer, J. F.; Woo, H. G.; Tilley, T. D. *Polym. Prepr.* **1991**, *32*, 441−442. Ziegler, T.; Folga, E.; Berces, A. *J. Am. Chem. Soc.* **1993**, *115*, 636−646 and references therein. (b) Nolan, S. P.; Porchia, M.; Marks, T. J. *Organometallics* **1991**, *10*, 1450−1457.

(13) Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 789−805.

(14) Ziegler, T.; Folga, E. *J. Organomet. Chem.* **1994**, *478*, 57−65.

(15) (a) Watson, P. L.; Tebbe, F. N. U.S. Patent 4,965,386, Oct. 23, 1990 (March 26, 1990). (b) Forsyth, C. M.; Nolan, S. P.; Marks, T. J. *Organometallics* **1991**, *10*, 2543−2545. (c) Sakakura, T.; Lautenschlager, H. J.; Nakajima, M.; Tanaka, M. *Chem. Lett.* **1991**, 913−916.

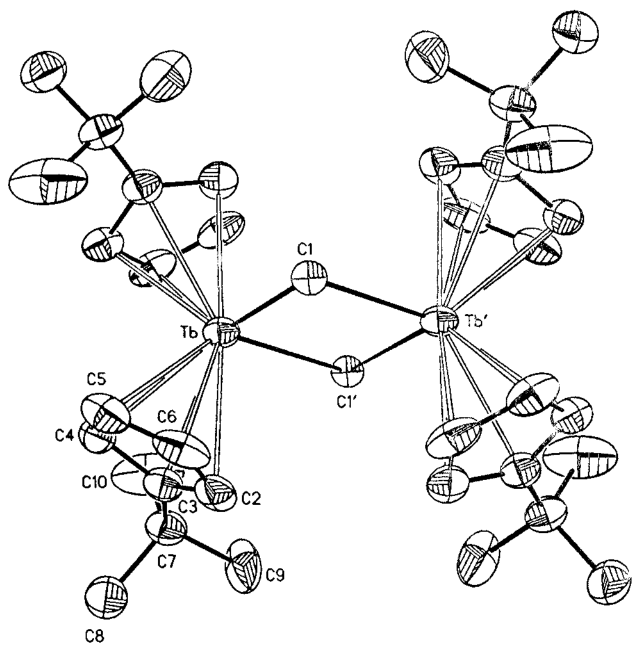
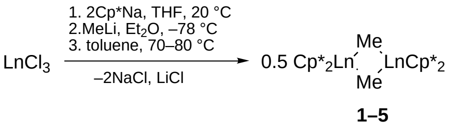


Figure 1. ORTEP view of {(^{t}BuC$_5$H$_4$)$_2$Tb(μ-Me)}$_2$ (**2**).

capacity of various bridgings Ln(μ-X)Ln, where X = Me, H, Cl, OMe, to cleave in hydrocarbon solution. Alternatively, this investigation brings about a development of several convenient synthetic methods for nonesymmetrical dimeric lanthanide complexes.

Results

Synthesis and Structural Characterization of Dimeric (μ-Methyl)bis(cyclopentadienyl)lanthanides. Dimeric methyl complexes of lanthanides **1**−**5** were prepared as shown in eq 4. The compounds were



$$\mathrm{LnCl_3}\xrightarrow[\text{−2NaCl, LiCl}]{\text{1. 2Cp*Na, THF, 20 °C; 2. MeLi, Et}_2\text{O, −78 °C; 3. toluene, 70–80 °C}} 0.5\ \mathrm{Cp^*_2Ln}\begin{smallmatrix}\mathrm{Me}\\ \\ \mathrm{Me}\end{smallmatrix}\mathrm{LnCp^*_2} \qquad (4)$$

1–5

Cp* = Cp′; Ln = Y(**1**), Tb(**2**), Yb(**3**), Lu(Me) = CH(**4**);Me = CD$_3$(**4-*d***)

Cp* = Cp″; Ln = Lu(**5**)

isolated as extremely air- and moisture-sensitive solids in high yield after decomposition of the intermediate *ate* complexes Cp*$_2$Ln(μ-Cl)(μ-Me)M(THF)$_n$, where M = Li or Na, by treatment with hot toluene. Complexes **1**−**5** were characterized by standard analytical and spectroscopic techniques (see Experimental Section). The ^{1}H NMR spectra of **1**, **4**, and **5** in C$_6$D$_6$ are consistent with C_{2v} dimeric structures characterized by two Cp*−H signals, the appropriate AA′BB′ patterns being observed. The Ln−CH$_3$ resonances occur at a relatively high field (e.g., δ −0.47 ppm for **1**, −0.01 ppm for **4**), which is typical for lanthanide hydrocarbyls.[16,17] The ^{89}Y−^{1}H coupling pattern in **1** (triplet, $^2J_{\mathrm{Y-H}} = 3.1$ Hz) is consistent with the symmetrical Y(μ-Me)$_2$Y bridging (cf., {(C$_5$H$_5$)$_2$Y(μ-Me)}$_2$ where $^2J_{\mathrm{Y-H}} = 3.6$ Hz[16]).

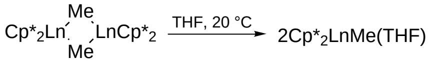
The structure of the terbium complex **2** with the ^{t}BuC$_5$H$_4$ ligands was determined by X-ray diffraction analysis (Figure 1). The bond lengths and selected bond angles are given in Table 1. The compound under study turned out to have a dimeric structure (C_{2h} symmetry) with two Me bridges. The terbium atoms symmetrically coordinate both methyl bridges.[18]

Table 1. Selected Bond Distances (Å) and Angles (deg) for {(^{t}BuC$_5$H$_4$)$_2$Tb(μ-Me)}$_2$ (2)

Bond Distances			
Tb···Tb′	3.629(3)	Tb−C(2)	2.716(7)
Tb−C(1)	2.573(6)	Tb−C(4)	2.678(7)
Tb−C(3)	2.771(9)	Tb−C(6)	2.654(8)
Tb−C(5)	2.63(1)	C(1)−H(2)	1.068(5)
C(1)−H(1)	0.570(8)	C(2)−C(6)	1.40(2)
C(2)−C(3)	1.42(2)	C(3)−C(7)	1.53(1)
C(3)−C(4)	1.41(1)	C(5)−C(6)	1.38(2)
C(4)−C(5)	1.42(2)		

Angles			
C(1)−Tb−C(1′)	90.3(2)	Tb−C(1)−Tb′	89.7(2)
H(1)−C(1)−H(2)	71.1	H(2)−C(1)−H(2′)	100.2
C(3)−C(2)−C(6)	109.6(9)	C(2)−C(3)−C(4)	104.9(8)
C(2)−C(3)−C(7)	129.3(8)	C(4)−C(3)−C(7)	125.1(8)
C(3)−C(4)−C(5)	109.7(9)	C(4)−C(5)−C(6)	107.5(9)
C(2)−C(6)−C(5)	108.2(9)		

Dimeric hydrocarbyls **1**−**5** completely dissociate into monomeric solvates **6**−**10** in THF solution (eq 5) (see also ref 20). The Y−Me resonance of **6** occurs at δ −0.99



$$\mathrm{Cp^*_2Ln}\begin{smallmatrix}\mathrm{Me}\\ \\ \mathrm{Me}\end{smallmatrix}\mathrm{LnCp^*_2}\xrightarrow{\text{THF, 20 °C}} 2\mathrm{Cp^*_2LnMe(THF)} \qquad (5)$$

6–10

Cp* = Cp′; Ln = Y(**6**), Tb(**7**), Yb(**8**), Lu(**9**)

Cp* = Cp″; Ln = Lu(**10**)

ppm, and the ^{89}Y−^{1}H coupling pattern (doublet, $^2J_{\mathrm{Y-H}}$ = 2.1 Hz) is consistent with a monomeric structure. Even under vacuum at ambient temperature solids **6**−**10** were found to lose coordinated THF to form the corresponding dimeric hydrocarbyls.

Reactivity of Lanthanide and Yttrium Hydrocarbyls toward Organosilicon and Organoelement Hydrides. Recently, we described the synthesis of lutetium hydride {(C$_5$H$_5$)$_2$Lu(μ-H)(THF)}$_2$ upon treatment of (C$_5$H$_5$)$_2$LuC$_6$H$_4$Me-4(THF) with PhMeSiH$_2$ in benzene at ambient temperature.[4] Here, we have found that a similar reaction readily proceeds with various unsolvated dimeric hydrocarbyls **1**−**5**. In an excess amount of organosilicon hydride, compounds **1**−**5** form the corresponding dimeric hydrides **11**−**15** in quantitative yield (eq 6).[21] Deuterium-labeled yttrium hydride

$$\{\mathrm{Cp^*_2Ln(\mu\text{-}Me)}\}_2 + 2\mathrm{PhMeSiH_2} \xrightarrow{\mathrm{C_6H_6},\ 20\ °\mathrm{C}} \{\mathrm{Cp^*_2Ln(\mu\text{-}H)}\}_2 + 2\mathrm{PhMe_2SiH} \qquad (6)$$

11–15

Cp* = Cp′; Ln = Y(**11**), Tb(**12**), Yb(**13**), Lu(**14**)

Cp* = Cp″; Ln = Lu(**15**)

---

(16) Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Rearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 54−61.

(17) Schumann, H.; Genthe, W.; Bruncks, N.; Pickardt, J. *Organometallics* **1982**, *1*, 1194−1200.

(18) A number of unsolvated dimeric (methyl)bis(cyclopentadienyl)lanthanides have been characterized by structural analysis. Some of them, as well as **2**, contain symmetrically coordinated methyl fragments;[16,19a,b] the other compounds possess two nonequivalent hydrocarbyl ligands.[19c,d]

(19) (a) Evans, W. J.; Drummond, D. K.; Hanusa, T. P.; Doedens, R. J. *Organometallics* **1987**, *6*, 2279−2285. (b) Stults, S. D.; Andersen, R. A.; Zalkin, A. *J. Organomet. Chem.* **1993**, *462*, 175−182. (c) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51−56. (d) Shen, Q.; Cheng, Y.; Lin, Y. *J. Organomet. Chem.* **1991**, *419*, 293−298.

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

(21) Lutetium hydrocarbyl {(C$_5$H$_5$)$_2$Lu(μ-Me)}$_2$ also forms the corresponding hydride {(C$_5$H$_5$)$_2$Lu}$_3$(μ-H)$_2$(μ^3-H) in quantitative yield under treatment with PhMeSiH$_2$ or PhSiH$_3$ in benzene or toluene solution.

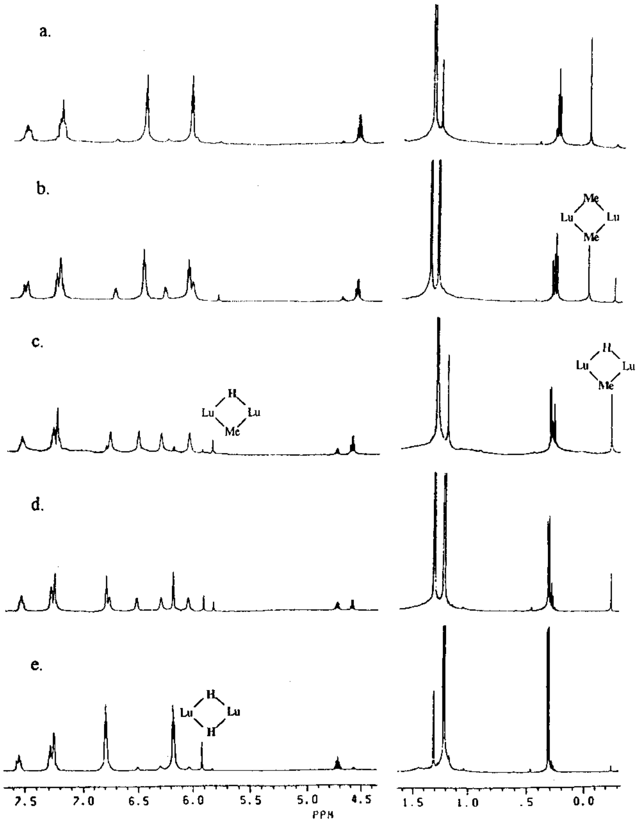


Figure 2. ^{1}H NMR spectrum of the reaction mixture of **4** and PhMeSiH$_2$ in benzene-d_6 at 20 °C: (a) 0.5 h; (b) 6 h; (c) 21 h; (d) 48 h; (e) 2 weeks.

{Cp′$_2$Y(μ-D)}$_2$ (**11-*d***) was prepared in quantitative yield in a similar manner starting from **1** and PhMeSiD$_2$. The ^{1}H NMR spectra of the diamagnetic compounds **11**, **11-*d***, **14**, and **15** are consistent with C_{2v} dimeric structures, characterized by two Cp*−H resonances (AA′BB′). The Ln−H resonances occur at a relatively low field (e.g., δ 3.09 ppm for **11** and δ 5.91 ppm for **14**), which is typical for unsolvated organolanthanide hydrides.[22,23] In compound **11**, the ^{89}Y−^{1}H coupling pattern (triplet, $^1J_{Y-H}$ = 32.8 Hz) is consistent with symmetrical Y(μ-H)$_2$Y bridging (cf. $^1J_{Y-H}$ = 35.3 Hz for {Et$_2$Si(C$_5$H$_4$)(C$_5$Me$_4$)Y(μ-H)}$_2$[23]).

Monitoring the reaction of **4** with PhMeSiH$_2$ (eq 6) with the use of ^{1}H NMR reveals the formation of an intermediate. This intermediate has one μ-methyl (δ −0.26 ppm) and one μ-hydride (δ 5.82 ppm) ligand (Figure 2). The quantitative conversion of **4** into the intermediate complex requires only an equivalent of the organosilicon hydride and takes several hours at ambient temperature. The ^{1}H NMR data for the intermediate are consistent with the C_s dimeric structure **17** with two different ligands (H and Me) and four equivalent ^{t}BuC$_5$H$_4$ ligands in the vicinity of two lanthanide atoms. In particular, the occurrence of four Cp′−H signals was attributed to the nonequivalent protons of the Cp′ ring, which constitute an ABCD spin system, with the *tert*-butyl substituent behaving as an anchor. In the presence of an excess amount of PhMeSiH$_2$, intermediate **17** forms lutetium hydride **14** (eq 7). The formation of intermediates **16** and **18** was also observed for dimeric hydrocarbyls **1** and **5**.

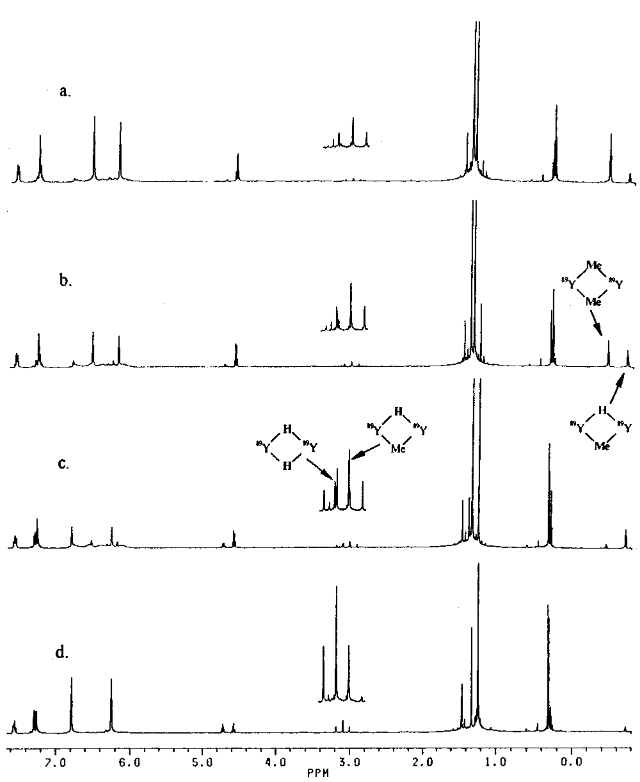
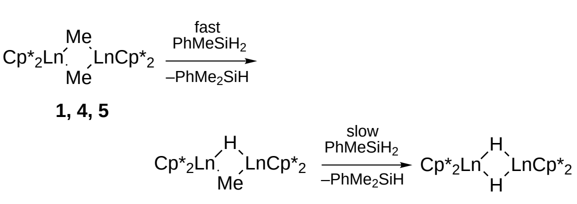


Figure 3. ^{1}H NMR spectrum of the reaction mixture of **1** and PhMeSiH$_2$ in benzene-d_6 at 20 °C: (a) 1.3 h; (b) 4.5 h; (c) 13 h; (d) 120 h.



1, 4, 5 **16-18** **11, 14, 15** (7)

Cp* = Cp′; Ln = Y(**16**), Lu(**17**)

Cp* = Cp″; Ln = Lu(**18**)

The ^{1}H NMR spectra for the reaction mixture of yttrium hydrocarbyl **1** and PhMeSiH$_2$ are presented in Figure 3. Only dimeric organoyttrium compounds were observed during the reaction. All the proton resonances of **16** assigned to methyl and hydride ligands (δ −0.73 ppm and $^2J_{Y-H}$ = 3.3 Hz for μ-Me; δ 3.00 ppm and $^1J_{Y-H}$ = 36.0 Hz for μ-H) are triplets, which means that such ligands bridge two yttrium atoms. The proton resonances of the cyclopentadienyl rings in **16** are broad compared to those of **17**.

The rates of both of the steps of reaction 7 increase with an increase in the lanthanide radius and when the Me$_3$SiC$_5$H$_4$ ligand is changed to a ^{t}BuC$_5$H$_4$ ligand. Since the second step of this reaction is slow, we have isolated dimeric organolanthanides **16**−**18** and characterized them using standard analytical and spectroscopic techniques (see Experimental Section). The compounds do not disproportionate in benzene, toluene, or pentane solutions and can be purified by recrystallization.

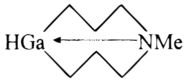
Stepwise reactions of lanthanide hydrocarbyls **1**−**5**, analogous to eq 7, proceed for various organoelement

---

[22] Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091−8103. Jeske, G.; Schock, L. E.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8103−8110.

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

hydrides, i.e., hydrides of silicon, germanium, and tin and complex hydrides of aluminium and gallium.[24] The rates of both steps of the transformation decrease in the following sequence (C_6D_6, 20 °C):



> HAlEt$_2$·NEt$_3$ > Ph$_3$SnH >

> Et$_3$SnH > PhSiH$_3$ > ^{n}C$_6$H$_{13}$SiH$_3$ > Ph$_2$SiH$_2$ >

> PhMeSiH$_2$ > ^{n}Bu$_2$GeH$_2$ > ^{n}Bu$_2$SiH$_2$ >>

>> Et$_3$GeH, Ph$_3$SiH, Ph$_2$MeSiH, PhMe$_2$SiH, Et$_3$SiH

In THF solution, the reactions with silanes are complicated by several side reactions. Thus, the total yield of the corresponding lanthanide hydrides was ca. 20−30% (with the quantitative conversion of the starting hydrocarbyls **6** and **9**). In addition to Cp′$_3$Y, yttrium hydrocarbyl **7** forms the corresponding dimeric solvate **19** after several weeks at ambient temperature (eq 8).

$$2\mathrm{Cp'_2YMe(THF)} \xrightarrow[\mathrm{THF,\ 20\ °C}]{\mathrm{PhMeSiH_2}} \underset{\mathbf{19}}{\{\mathrm{Cp'_2Y}(\mu\text{-H})(\mathrm{THF})\}_2} \qquad (8)$$

In this compound, the Y−H resonance occurs at δ 2.64 ppm, with the ^{89}Y−^{1}H coupling constant $^1J_{\mathrm{Y-H}} = 29.3$ Hz (cf. δ 2.18 ppm, $^1J_{\mathrm{Y-H}} = 20$ Hz for $\{(C_5H_5)_2Y(\mu\text{-H})(THF)\}_2$[20]). It was found that lutetium hydrocarbyl **9** does not react with PhMeSiH$_2$ in THF at ambient temperature. However, it forms ca. 30% of the dimeric *unsolvated* hydride **14** (eq 9), along with Cp′$_3$Lu, CH$_4$, and other unidentified products, after 30 h at 80 °C.

$$2\mathrm{Cp'_2LuMe(THF)} \xrightarrow[\mathrm{THF,\ 80\ °C}]{\mathrm{PhMeSiH_2}} \underset{\mathbf{14}}{\{\mathrm{Cp'_2Lu}(\mu\text{-H})\}_2} \qquad (9)$$

This result is rather unusual (cf., for instance, ref 28). We performed an additional study and showed that yttrium hydride **11** forms solvate **19** on dissolving in THF. In contrast, lutetium hydride **14** does not react with THF.

Deuterium−Protium Exchange in Silanes Catalyzed by Lanthanide and Yttrium Hydrides. Yttrium and lanthanide hydrides **11**−**15** are efficient catalysts of the Si−H/Si−D exchange between various silanes. Treatment of a PhMeSiD$_2$ and PhEtSiH$_2$ mixture with **11** (2 mol %) at 70 °C for 1.5 h results in a complete statistical redistribution of hydrogen isotopes. Neither the formation of products with deuterium in their Ph, Et, and Me fragments nor that of compounds with Si−Si bonding was observed even when the reaction was carried out at elevated temperatures for a week.

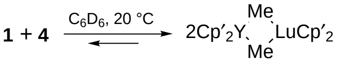
In the presence of an excess amount of PhMeSiD$_2$, yttrium hydride **11** forms the corresponding yttrium deuteride **11-*d***, which has a high content of deuterium in the bridging fragments, after several hours at ambient temperature (eq 10). No formation of products

$$\{\mathrm{Cp'_2Y}(\mu\text{-H})\}_2 \xrightarrow[\mathrm{C_6H_6}]{\mathrm{PhMeSiD_2}} \underset{\mathbf{11\text{-}\mathit{d}}}{\{\mathrm{Cp'_2Y}(\mu\text{-D})\}_2} \qquad (10)$$

with lanthanide−silicon bonding was observed in benzene solution either at ambient or at elevated temperatures.

Dehydrogenative Coupling of Organotin Hydrides Catalyzed by Lanthanide and Yttrium Hydrides. Lanthanide hydrides **11**−**14** were found to catalyze the dehydrogenative coupling of tin hydrides at elevated temperature. For instance, both Et$_3$SnH and ^{n}Bu$_3$SnH give the corresponding distannanes X$_3$SnSnX$_3$, where X = Et or ^{n}Bu, in quantitative yield and molecular hydrogen in the presence of 1−3 mol % of **11**−**14** at 70 °C for several minutes. This reaction does not take place at room temperature. In the absence of the lanthanide compounds, these organotin hydrides give the corresponding distannanes (probably via a free radical pathway[29]) in 5−10% yield after 0.5 h at 70 °C.

Exchange Reactions of Dimeric Lanthanide and Yttrium Compounds with Various Bridging Ligands. We observed an equilibrium between yttrium and lutetium hydrocarbyl complexes **1** and **4** (eq 11), in which, according to the NMR data, up to 70% of heterometallic compound **20** is present after several minutes at ambient temperature. The upfield region



$$\mathbf{1} + \mathbf{4} \underset{}{\overset{\mathrm{C_6D_6,\ 20\ °C}}{\rightleftharpoons}} 2\mathrm{Cp'_2Y}\overset{\mathrm{Me}}{\underset{\mathrm{Me}}{\cdot\cdot}}\mathrm{LuCp'_2} \qquad (11)$$

20

of the NMR spectrum of the reaction mixture is shown in Figure 4. Since the yttrium-89 nucleus has a spin equal to $^1/_2$, the central doublet resonance (δ −0.26 ppm; $^2J_{\mathrm{Y-H}}$ = 3.8 Hz) corresponds to the heterometallic compound **20**, which contains both yttrium and lutetium atoms. The ^{13}C{^{1}H} NMR spectrum exhibits a resonance at δ 27.56 ppm (d, $^1J_{\mathrm{Y-C}}$ = 22.9 Hz) corresponding to the Y−Me−Lu bridging.[30] No monomeric particles were detected by NMR spectroscopy.

In contrast, dimeric hydrides **11** and **14** require 2 weeks to equilibrate in benzene at ambient temperature

---

(24) When uncomplexed organoaluminium and organogallium compounds are used, heterometallic lanthanide−aluminum complexes are formed.[25,26] For instance, we found that yttrium hydrocarbyl **1** reacts with $\{Et_2Al(\mu\text{-H})\}_2$ in benzene at ambient temperature to form the $Cp'_2Y(\mu\text{-H})(\mu\text{-alkyl})Al(alkyl)_2$ heterometallic complex, in which the Y−H resonance occurs at δ 2.64 ppm with ^{89}Y−^{1}H coupling constant $^1J_{\mathrm{Y-H}}$ = 30.2 Hz (doublet) (cf. δ 2.88 ppm for μ-H in $\{Et_2Al(\mu\text{-H})\}_2$ in C_6D_6). Such heterobimetallic compounds decompose in the presence of various bases to form homometallic lanthanide complexes.[16,27]

(25) Rabaâ, H.; Saillard, J.-Y.; Hoffmann, R. *J. Am. Chem. Soc.* **1986**, *108*, 4327−4333.

(26) (a) Ballard, D. G. H.; Pearse, R. *J. Chem. Soc., Chem. Commun.* **1975**, 621. (b) Holton, J.; Lappert, M. F.; Scollary, G. R.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Chem. Commun.* **1976**, 425−426. Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 54−61. (c) Watson, P. L. *J. Am. Chem. Soc.* **1982**, *104*, 337−339. (d) Evans, W. J.; Chamberlain, L. R.; Ziller, J. W. *J. Am. Chem. Soc.* **1987**, *109*, 7209−7211.

(27) Gun'ko, Y.-K.; Bulychev, B. M.; Soloveichik, G. L.; Belsky, V. K. *J. Organomet. Chem.* **1992**, *424*, 289−300.

(28) Evans, W. J.; Meadows, J. H.; Wayda, A. L.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 2008−2014.

(29) 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; and references therein.

(30) **$(^t\mathrm{BuC_5H_4})_2\mathrm{Y}(\mu\text{-Me})_2\mathrm{Lu}(\mathrm{C_5H_4}{}^t\mathrm{Bu})_2$ (20).** ^{1}H NMR (benzene-*d*$_6$): δ −0.26 (d, 6H, $^2J_{\mathrm{Y-H}}$ = 3.8 Hz, μ-Me), 1.35 (s, 18H, ^{t}*Bu*C$_5$H$_4$Y), 1.38 (s, 18H, ^{t}*Bu*C$_5$H$_4$Lu), 6.08 (t, 4H, J = 2.7 Hz, H2,5 in C$_5$H$_4$Lu), 6.15 (t, 4H, J = 2.8 Hz, H2,5 in C$_5$H$_4$Y), 6.46 (t, 4H, J = 2.7 Hz, H3,4 in C$_5$H$_4$Lu), 6.54 (t, 4H, J = 2.7 Hz, H3,4 in C$_5$H$_4$Y). ^{13}C NMR (benzene-*d*$_6$): δ 27.56 (d, $^1J_{\mathrm{Y-C}}$ = 22.9 Hz, μ-Me), 29.02 (*C*Me$_3$), 32.44 (C*Me*$_3$), 108.76 (C2,5 in C$_5$H$_4$Lu), 108.76 (C3,4 in C$_5$H$_4$Lu), 110.39 (C2,5 in C$_5$H$_4$Y), 111.18 (C3,4 in C$_5$H$_4$Y), 135.35 (C1 in C$_5$H$_4$Lu), 137.37 (C1 in C$_5$H$_4$Y).

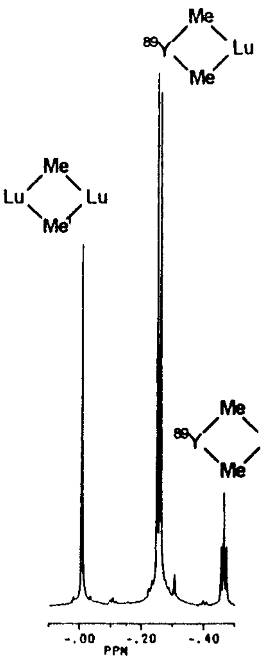


Figure 4. The upfield region of ^{1}H NMR spectrum of the equimolar mixture of **1** and **4** in benzene-d_6.

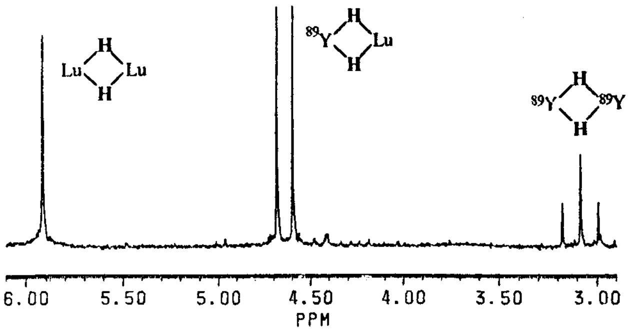
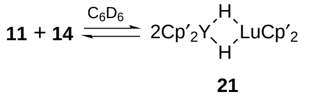


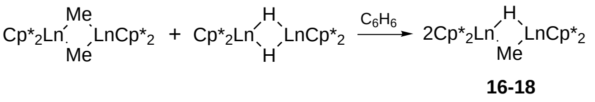
Figure 5. The region of the μ-H resonances of the ^{1}H NMR spectrum of an equimolar mixture of **11** and **14** in benzene-d_6.

(eq 12). According to the NMR spectra, the equilibrium mixture contains ca. 50% of heterometallic compound **21**. The region of the μ-H resonances in the NMR spectrum of this mixture is shown in Figure 5. The central doublet (δ 4.64 ppm, $^{1}J_{Y-H}$ = 30.5 Hz) corresponds to heterometallic compound **21**.[31]

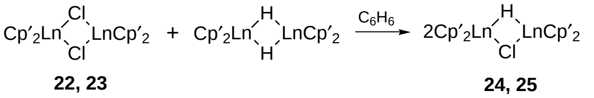


$$\mathbf{11} + \mathbf{14} \overset{C_6D_6}{\rightleftharpoons} \underset{\mathbf{21}}{2Cp'_2Y(\mu\text{-}H)_2LuCp'_2} \qquad (12)$$

The exchange between dimeric hydrides and hydrocarbyls of the same metal (eq 13) proceeds rather slowly in benzene at ambient temperature. This reaction yields complexes **16**−**18**. A similar reaction between dimeric complexes **22** and **23** with the μ-Cl ligands[32] and the corresponding dimeric hydrides **11** and **14** proceeds very slowly at ambient temperature and gives rise to the dimeric hydridochloro complexes **24** and **25** in quantitative yield after ca. 1 h at 70 °C (eq 14) (see also ref 33).



$$Cp^*_2Ln(\mu\text{-}Me)_2LnCp^*_2 + Cp^*_2Ln(\mu\text{-}H)_2LnCp^*_2 \xrightarrow{C_6H_6} \underset{\mathbf{16\text{-}18}}{2Cp^*_2Ln(\mu\text{-}H)(\mu\text{-}Me)LnCp^*_2} \qquad (13)$$



$$\underset{\mathbf{22,\,23}}{Cp'_2Ln(\mu\text{-}Cl)_2LnCp'_2} + Cp'_2Ln(\mu\text{-}H)_2LnCp'_2 \xrightarrow{C_6H_6} \underset{\mathbf{24,\,25}}{2Cp'_2Ln(\mu\text{-}H)(\mu\text{-}Cl)LnCp'_2} \qquad (14)$$

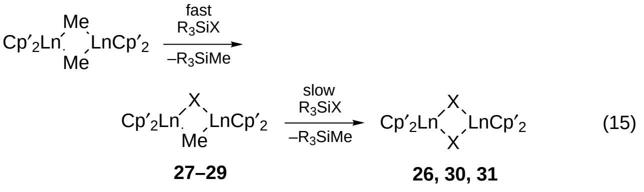
Ln = Y(**22**, **24**), Lu(**23**, **25**)

The ^{1}H NMR spectra of **24** and **25** are consistent with C_s dimeric structures, characterized by four Cp′−H resonances (ABCD). The Y−H resonance for **24** occurs at δ 2.95 ppm, with the $^{89}Y-^{1}H$ coupling pattern (triplet, $^{1}J_{Y-H}$ = 33.5 Hz) consistent with symmetrical Y(μ-H)Y bridging.

Our attempts to synthesize compounds with both Ln(μ-H)(μ-OMe)Ln and Ln(μ-Me)(μ-OMe)Ln bridging using the same strategy failed. Binary lutetium alkoxide $\{Cp'_2Lu(\mu\text{-}OMe)\}_2$ (**26**), which is prepared by alcoholysis of **4** (see also ref 34), turned out to react with neither hydrocarbyl **4** nor hydride **14** either at ambient or elevated temperatures.

Reactions of Lanthanide Hydrocarbyls with Alkoxy- and Chlorosilanes. Not much is known about the reactivity of organolanthanides toward chloro- and alkoxysilanes.[35,36] We have found that the reaction of these or similar heterosubstituted silanes with lanthanide complexes is a convenient route for the preparation of various compounds with both Ln(μ-R)(μ-X)Ln and Ln(μ-X)$_2$Ln bridging (R = H, Me; X = OR, SR, NR$_2$, PR$_2$, etc.).

Lanthanide hydrocarbyls **1** and **4** react readily with various alkoxysilanes to yield the corresponding dimeric compounds with different bridging fragments ((μ-Me)(μ-OMe) (**27** and **28**), (μ-Me)(μ-OEt) (**29**)) and with an excess amount of the organosilicon compound to yield the respective dimeric alkoxides **26**, **30**, and **31** (eq 15).[37] Compounds **26**−**28** and **30** have been isolated in high yield and characterized by standard analytical and



$$Cp'_2Ln(\mu\text{-}Me)_2LnCp'_2 \xrightarrow[-R_3SiMe]{\text{fast } R_3SiX} \underset{\mathbf{27\text{–}29}}{Cp'_2Ln(\mu\text{-}X)(\mu\text{-}Me)LnCp'_2} \xrightarrow[-R_3SiMe]{\text{slow } R_3SiX} \underset{\mathbf{26,\,30,\,31}}{Cp'_2Ln(\mu\text{-}X)_2LnCp'_2} \qquad (15)$$

X = OMe; Ln = Y(**27**, **30**), Lu(**26**, **28**)
X = OEt; Ln = Lu(**29**, **31**)

---

[31] **(^{t}BuC$_5$H$_4$)$_2$Y(μ-H)$_2$Lu(C$_5$H$_4$^{t}Bu)$_2$ (21).** ^{1}H NMR (benzene-d_6): δ 1.22 (s, 36H, ^{t}Bu), 4.64 (d, 2H, $^{1}J_{Y-H}$ = 30.5 Hz, μ-H), 6.17 (t, 4H, J = 2.3 Hz, H2,5 in C$_5$H$_4$Lu), 6.21 (t, 4H, J = 2.6 Hz, H2,5 in C$_5$H$_4$Y), 6.78 (t, 8H, J = 2.8 Hz, H3,4 in C$_5$H$_4$). ^{13}C NMR (benzene-d_6): δ 30.16 (*C*Me$_3$), 31.35 (C*Me*$_3$), 107.69 (C2,5 in C$_5$H$_4$Lu), 108.65 (C2,5 in C$_5$H$_4$Y), 109.24 (C3,4 in C$_5$H$_4$Lu), 109.46 (C3,4 in C$_5$H$_4$Y), 136.98 (C1 in C$_5$H$_4$-Lu), 138.54 (C1 in C$_5$H$_4$Y).

[32] Shen, Q.; Qi, M.; Guan, J.; Lin, Y. *J. Organomet. Chem.* **1991**, *406*, 353−361.

[33] Qiao, K.; Fischer, R. D.; Paolueci, G. *J. Organomet. Chem.* **1993**, *456*, 185−194.

[34] Stults, S. D.; Andersen, R. A.; Zalkin, A. *Organometallics* **1990**, *9*, 1623−1629.

[35] Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *Organometallics* **1991**, *10*, 134−132.

[36] Yasuda, H.; Yamamoto, H.; Yokota, K.; Nakamura, A. *Chem. Lett.* **1989**, 1309−1312. Magomedov, G. K.-I.; Voskoboynikov, A. Z.; Kirillova, N. I.; Gusev, A.I.; Parshina, I. N.; Beletskaya, I. P. *Metalloorgan. Khim. (USSR)* **1992**, *5*, 679−683.

[37] Evans, W. J.; Sollberger, M. S.; Khan, S. I.; Bau, R. *J. Am. Chem. Soc.* **1988**, *110*, 439−446.

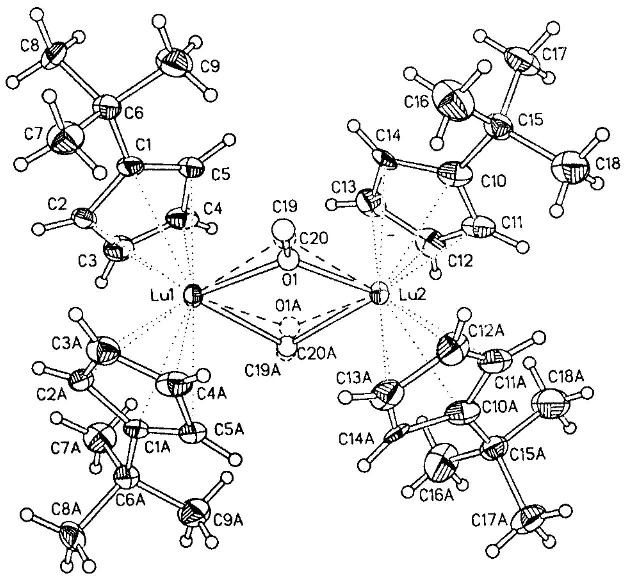
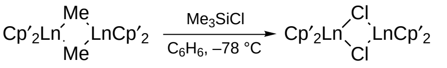


Figure 6. ORTEP view of $(^tBuC_5H_4)_2Lu(\mu\text{-}Me)(\mu\text{-}OMe)Lu(C_5H_4{}^tBu)_2$ (**28**).

spectroscopic techniques (see Experimental Section). Compounds **29** and **31** were detected by NMR spectroscopy. The ^1H NMR spectra of **27**−**29** correspond to C_s dimeric structures, which are characterized by four Cp′−H resonances (ABCD). The Y−Me resonance for **27** occurs at δ −0.42 ppm, and the $^{89}Y-{}^1H$ coupling pattern (triplet, $^2J_{Y-H}$ = 3.4 Hz) is consistent with symmetrical Y(μ-Me)Y bridging. Reaction 15 proceeds easily for tri- and tetrasubstituted alkoxysilanes, such as $(RO)_4Si$ and $(RO)_3SiMe$ (R = Me, Et). Mono- and disubstituted alkoxysilanes are rather inactive, and only traces of the products were observed in the reaction with $MeOSiMe_3$, $(MeO)_2SiMe_2$, and $EtOSiMe_3$. However, the rate of this reaction increases considerably at elevated temperature. No cleavage of the Cp′−Ln bonds was observed at ambient temperature in excess amounts of alkoxysilanes.

The structure of the lutetium complex **28** was determined by X-ray diffraction analysis (Figure 6). The bond lengths and selected bond angles are given in Table 2. The molecule represents a binuclear complex. Two (η^5-Cp′)$_2$Lu fragments are linked through a couple of bridges, Me and OMe. Some differences in the similar geometrical parameters of the OMe bridge (the Lu−O distances are 2.20(2) and 2.12(2) Å and the Lu−O−C angles are 122(1) and 129(1)°) are observed.

The reactivity of lanthanide hydrocarbyls toward chlorosilanes turned out to be quite different. Complexes **1** and **4** react with various chlorosilanes to form halogenide complexes **22** and **23**, respectively (eq 16), but do not form compounds with Ln(μ-Me)(μ-Cl)Ln bridging. The latter compounds also cannot be prepared by the exchange reaction between the corresponding dimeric hydrocarbyls **1** and **4** and chlorides **22** and **23**.



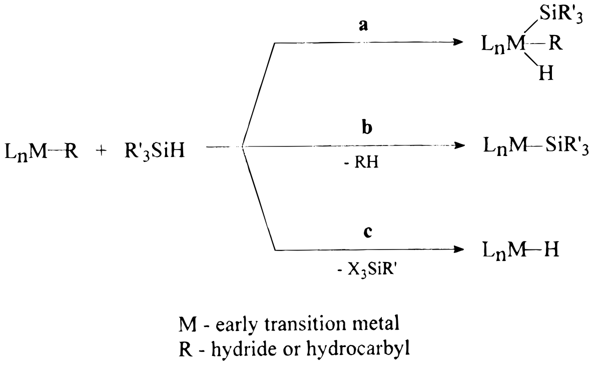
$$Cp'_2Ln(\mu\text{-}Me)_2LnCp'_2 \xrightarrow[C_6H_6,\ -78\ °C]{Me_3SiCl} Cp'_2Ln(\mu\text{-}Cl)_2LnCp'_2 \quad (16)$$

22, 23

Table 2. Selected Bond Distances (Å) and Angles (deg) for $(^tBuC_5H_4)_2Lu(\mu\text{-}Me)(\mu\text{-}OMe)Lu(C_5H_4{}^tBu)_2$ (28)

Bond Distances			
Lu(1)···Lu(2)	3.498(1)	Lu(2)−C(13)	2.618(11)
Lu(1)−O(1)	2.201(14)	Lu(2)−C(14)	2.687(10)
Lu(1)−C(1)	2.709(10)	O(1)−C(19)	1.42(2)
Lu(1)−C(3)	2.557(11)	C(1)−C(5)	1.39(2)
Lu(1)−C(20)	2.57(2)	C(1)−C(2)	1.425(14)
Lu(1)−C(4)	2.610(11)	C(2)−C(3)	1.42(2)
Lu(1)−C(2)	2.638(10)	C(3)−C(4)	1.41(2)
Lu(1)−C(5)	2.678(10)	C(4)−C(5)	1.46(2)
Lu(2)−O(1)	2.12(2)	C(10)−C(11)	1.40(2)
Lu(2)−C(20)	2.58(2)	C(10)−C(14)	1.45(2)
Lu(2)−C(10)	2.708(11)	C(11)−C(12)	1.36(2)
Lu(2)−C(12)	2.583(11)	C(12)−C(13)	1.44(2)
Lu(2)−C(11)	2.615(11)	C(13)−C(14)	1.41(2)
Angles			
Lu(1)−C(20)−Lu(2)	85.6(8)	C(4)−C(3)−C(2)	109.7(10)
Lu(2)−O(1)−Lu(1)	108.3(7)	C(3)−C(4)−C(5)	106.1(11)
C(19)−O(1)−Lu(1)	121.1(11)	C(1)−C(5)−C(4)	108.1(10)
C(19)−O(1)−Lu(2)	129.3(11)	C(11)−C(10)−C(14)	105.3(10)
O(1)−Lu(1)−C(20)	82.3(8)	C(12)−C(11)−C(10)	111.1(11)
O(1)−Lu(2)−C(20)	83.8(7)	C(11)−C(12)−C(13)	108.7(10)
C(5)−C(1)−C(2)	109.1(10)	C(14)−C(13)−C(12)	105.9(10)
C(3)−C(2)−C(1)	106.9(10)	C(13)−C(14)−C(10)	108.9(11)

Scheme 1



Discussion

Reactions of Lanthanide Hydrocarbyls with Silanes or Organoelement Hydrides: Hydride vs Silyl Transfer. The reactions of hydrocarbyl (and hydride) complexes of various early transition metals with silanes can involve the formation of different intermediates and products, depending on the reaction mechanism. Possible reaction pathways are presented in Scheme 1.[39] Pathway a is preferable for complexes of the early transition metals that can exist in several stable oxidation states. Silyl complexes of niobium and tantalum,[41−43] as well as titanium[44] and zirconium,[45−48]

---

[38] The reaction of lutetium hydride **14** with $(MeO)_4Si$ was monitored by NMR. This reaction produced Cp′$_2$Lu(μ-H)(μ-OMe)LuCp′$_2$ and then compound **26** (see also ref 38). It is of interest that the compound with the Lu(μ-H)(μ-OMe)Lu bridging cannot be prepared upon a treatment of hydrocarbyl complex **28** with $PhMeSiH_2$ both at ambient and at elevated temperatures.

[39] Interpretation of synthetic experiments in the context of such reaction mechanisms should be made with great care because of the possibility that the reaction may occur by a multistep mechanism,[8b] even involving redox processes different from the oxidative addition[15b] and free-radical pathways.[40]

[40] (a) Harrod, J. F.; Yun, S. S. *Organometallics* **1987**, *6*, 1381−1387. (b) Aitken, C.; Barry, J.-P.; Gauvin, F.; Harrod, J. F.; Malek, A.; Rousseau, D. *Organometallics* **1989**, *8*, 1732−1736.

[41] Curtis, M. D.; Bell, L. G.; Butler, W. M. *Organometallics* **1985**, *4*, 701−707.

[42] Berry, D. H.; Jiang, Q. *J. Am. Chem. Soc.* **1989**, *111*, 8049−8051.

[43] Berry, D. H.; Koloski, T. S.; Carroll, P. J. *Organometallics* **1990**, *9*, 2952−2962.

are probably formed through the oxidative addition of organosilicon hydrides to organometallic intermediates with the metal in a low oxidation state.

Transition metal hydrides (and probably hydrocarbyls) can react with silane as a base with a "Si−H acid". Thus, silanes and d^0 metal complexes,[10a,b,d,f,11] including some lanthanide hydrides with C_5Me_5 ligands,[8,15b] have recently been shown to undergo σ-bond metathesis to form compounds with direct silicon−transition-metal bonding (pathway b).

On the other hand, in this paper we have shown that bis(cyclopentadienyl)lanthanide hydrocarbyls containing C_5H_5, $^tBuC_5H_4$, $Me_3SiC_5H_4$, and even C_5Me_5 ligands react readily with silanes to form the products of nucleophilic substitution at silicon and the corresponding lanthanide hydrides (pathway c and eq 1).[4,5,49,50] This reaction is a very convenient route for the synthesis of the corresponding lanthanide hydrides,[3] which are difficult to prepare. In regard to reaction conditions, both $\{Cp_2Ln(\mu\text{-}H)\}_2$ and $\{Cp_2LnH(THF)\}$, where Cp = C_5H_5, $^tBuC_5H_4$, or $Me_3SiC_5H_4$, were prepared in a high yield. A similar reaction is suggested to be a key stage of the catalytic cycle of olefin hydrosilylation catalyzed by organolanthanides.[4−6,15a,51−53] In contrast, complexes with permethylcyclopentadienyl ligands $(C_5Me_5)_2LnCH(SiMe_3)_2$ react with silanes in a different manner to form the corresponding compounds with Ln−Si bonds.[8a,15b] However, Tilley et al. recently showed that this reaction is not a single-step process. [8b] The compound with Ln−Si bonding is formed by the reaction of silane with the hydride $(C_5Me_5)_2LnH$, which is generated by the hydrogenolysis of the former lanthanide hydrocarbyl with traces of H_2.

Thus, a single-step reaction of alkyl (aryl) lanthanide complexes with silanes can proceed via two alternative pathways, i.e., it can include either hydride transfer to the lanthanide atom (pathway c) or transfer of a silyl group to the metal atom (pathway b). We have performed geometrical and energy calculations for the encounter complexes and transition states in the alternative model reactions of hydride and silyl transfer (eqs 17 and 18, Cp = C_5H_5 and R = Me) using the semiempirical ZINDO/1 method proposed by Zerner et al. for computation of transition metal complexes (see Supporting Information for more details).[54] Analysis of

$$Cp_2Y{-}R + SiH_4 \rightleftharpoons Cp_2Y{-}H + RSiH_3 \qquad (17)$$

$$Cp_2Y{-}R + SiH_4 \rightleftharpoons Cp_2Y{-}SiH_3 + RH \qquad (18)$$

molecular orbital plots for the encounter complexes and transition states enabled us to construct a correlation diagram for the five upper occupied molecular orbitals for the alternative reactions of hydride transfer and silyl group transfer to the yttrium atom (Figure 7).

The most significant result of these studies can be drawn: along with the additional agostic interaction, the transition states revealed are characterized by the effective interaction of yttrium with all three atoms involved in the bond transposition processes. In other words, the interaction in the transition states may be considered as occurring between the Cp_2Y^+ cation and the respective allyl-like anion.

The calculation indicates the silyl group transfer to the metal atom to be more preferable to the hydride transfer in the reaction of $(C_5H_5)_2YMe$ with SiH_4 in the gas phase. Thermodynamic parameters ΔH and $\Delta E^{\ddagger}$ (kcal/mol) were 1.4 and 24.0 for hydride transfer (eq 17), −99.5 and 2.9 for silyl transfer (eq 18). This result correlates poorly with our chemical experiments (see above). Thermochemical data obtained for bis(pentamethylcyclopentadienyl) derivatives of Sm(III) showed both of these alternative reactions to be exothermic, with ΔH equal to ca. −11 and −9 kcal mol^{-1} for the silyl and hydride transfer, respectively.[6] The comparative analysis of the geometry of the corresponding alternative intermediates, as well as the chemical experiments, demonstrated that *the steric factor plays a crucial role.* Evidence for this is the fact that trisubstituted silanes R_3SiH do not react with the yttrium and lanthanide hydrocarbyls studied. However, silanes R_2SiH_2 and $RSiH_3$ react readily in this manner (see above). The steric factor must affect the reaction of the silyl group transfer to the lanthanide atom to a greater extent than the alternative hydride transfer (see Supporting Information for more details). However, a single-step metalation of silane with lanthanide hydrocarbyl should not be excluded. The results of our investigation of olefin hydrosilylation catalyzed by organolanthanides suggest an occurrence of a slow single-step reaction of silyl group transfer for sterically unhindered monomeric lanthanide complexes Cp_2LnR that include an alkyl group R with a high basicity.[52]

Reactions of Lanthanide Hydrides with Silanes: H/D Exchange vs Metalation. The reaction of $\{Cp'_2Ln(\mu\text{-}H)\}_2$ with deuterosilanes can be used for preparation of $\{Cp'_2Ln(\mu\text{-}D)\}_2$ (eq 10) and, in a catalytic manner, for H/D scrambling between R_3SiH (or R_3SnH) and R'_3SiD. The observed H/D exchange in silanes can proceed by one of two alternative routes. The first one involves two sequential hydrogen exchanges with the participation of $Cp'_2Ln{-}H(D)$ intermediates (Scheme 2, pathway *i*). Pathway *ii* suggests the formation of intermediates with Ln−Si bonding, $Cp'_2Ln{-}SiR_3$. This situation is similar to the possibility of two alternative mechanisms for the olefin hydrosilylation catalyzed by

---

[44] Aitken, C. T.; Harrod, J. F.; Samuel, E. *J. Am. Chem. Soc.* **1986**, *108*, 4059−4066.

[45] Aitken, C. T.; Harrod, J. F.; Samuel, E. *Can. J. Chem.* **1986**, *64*, 1677−1679.

[46] Mu, Y.; Aitken, C.; Cote, B.; Harrod, J. F.; Samuel, E. *Can. J. Chem.* **1991**, *69*, 264−276.

[47] Takahashi, T.; Hasegawa, M.; Suzuki, N.; Saburi, M.; Rousset, C. J.; Fanwick, P. E.; Negishi, E.-I. *J. Am. Chem. Soc.* **1991**, *113*, 8564−8566.

[48] Corey, J. Y.; Huhmann, J. L.; Zhu, X.-H. *Organometallics* **1993**, *12*, 1121−1130.

[49] Beletskaya, I. P.; Voskoboynikov, A. Z.; Parshina, I. N.; Magomedov, G. K.-I. USSR Patent 1,745,727, March 8, 1992 (June 27, 1990).

[50] Beletskaya, I. P. *Proceedings of the 206th Meeting of the ACS*; Chicago, August 1993; American Chemical Society: Washington, DC, 1993; INOR 333.

[51] Beletskaya, I. P.; Voskoboynikov, A. Z.; Parshina, I. N.; Magomedov, G. K.-I. USSR Patent 1,663,832, March 15, 1991 (Nov. 17, 1989).

[52] Voskoboynikov, A. Z.; Shestakova, A. K.; Beletskaya, I. P. Unpublished results.

[53] Sakakura, T.; Lautenschlager, H. J.; Tanaka, M. *J. Chem. Soc., Chem. Commun.* **1991**, 40−41. Takahashi, T.; Hasegawa, M.; Suzuki, N.; Saburi, M.; Rousset, C. J.; Fanwick, P. E.; Negishi, E. *J. Am. Chem. Soc.* **1991**, *113*, 8564−8566. Molander, G. A.; Julius, M. *J. Org. Chem.* **1992**, *57*, 6347−6351. Kesti, M. R.; Waymouth, R. M. *Organometallics* **1992**, *11*, 1095−1103. Onozawa, S.-Y.; Sakakura, T.; Tanaka, M. *Tetrahedron Lett.* **1994**, 8177−8180. Molander, G. A.; Retsch, W. H. *Organometallics* **1995**, *14*, 4570−4575.

[54] Bacon, A. D.; Zerner, M. C. *Theor. Chim. Acta* **1979**, *53*, 21−54. Anderson, W. P.; Edwards, W. D.; Zerner, M. C. *Inorg. Chem.* **1986**, *25*, 2728−2732.

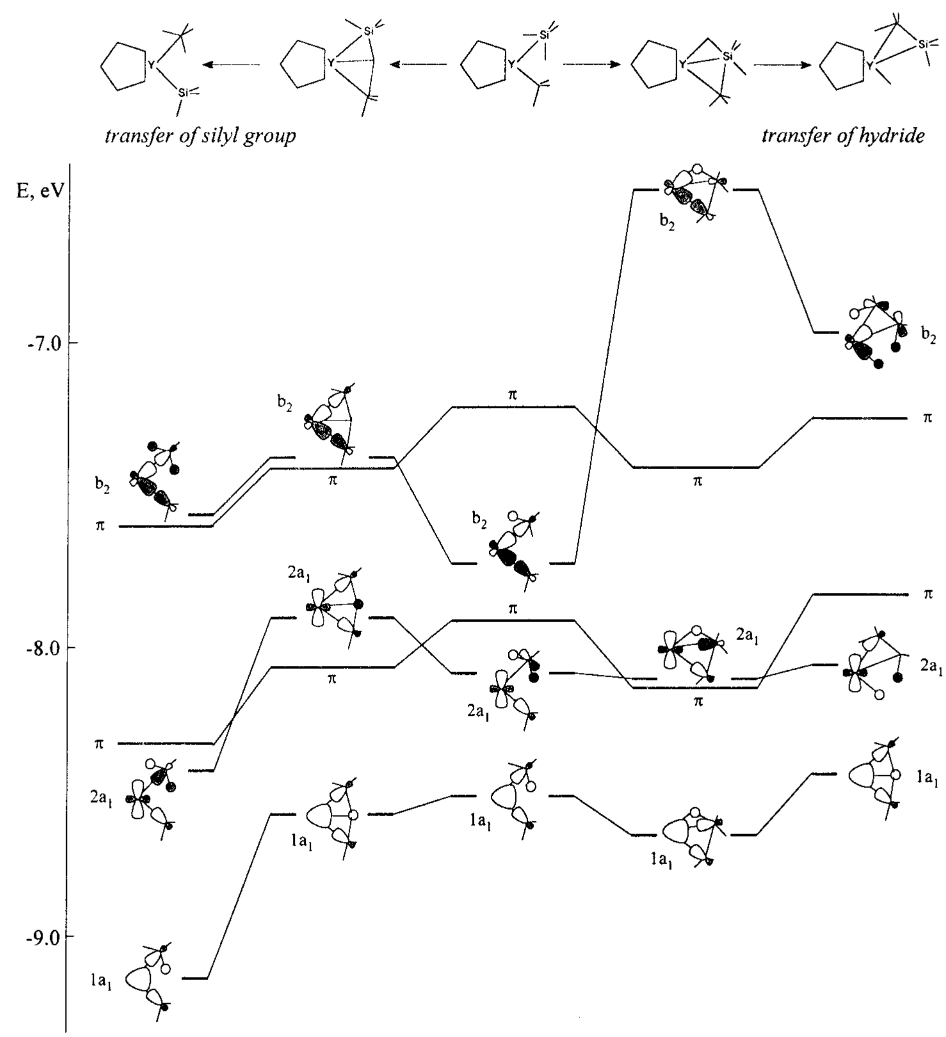
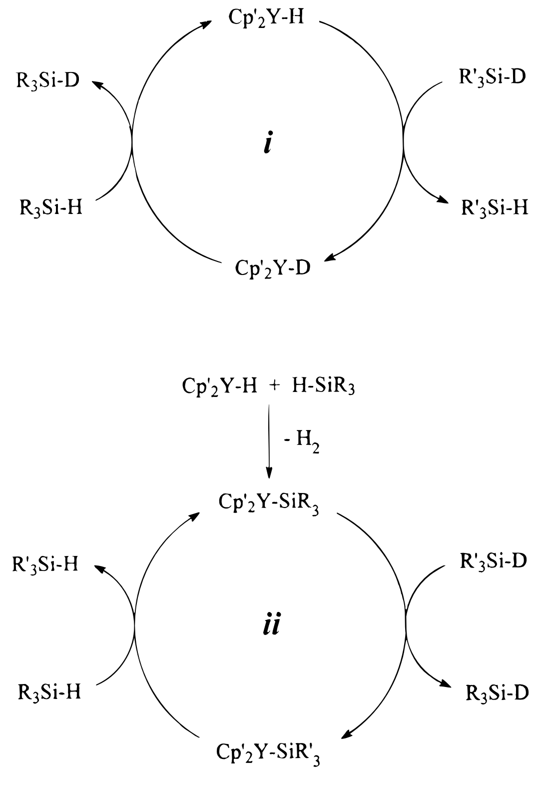


Figure 7. Schematic correlation diagram for σ-bond metathesis reactions of eqs 17 and 18 (Cp = C_5H_5 and R = Me).

organolanthanides.[6] Pathway *ii* seems to be more probable. The complexes $(C_5Me_5)_2LnH$ are known to react readily with silanes to form compounds with Ln−Si bonding.[8b,15b] Moreover, a similar H/D exchange in hydrocarbons catalyzed by lanthanide d^0 complexes proceeds via transmetalation, i.e., analogously to mechanism *ii*.[55] However, in this paper we have shown that the reaction between silanes and lanthanide hydrides with unsubstituted and monosubstituted cyclopentadienyl ligands does not give the corresponding complexes with Ln−Si bonding under different conditions. More evidence for this reactivity is the results of our recent detailed study of olefin hydrosilylation catalyzed by $\{Cp'_2Ln(\mu\text{-}H)\}_2$.[52] All of these data favor mechanism *i* for H/D exchange in silanes and tin hydrides.

Geometrical and energy calculations for the encounter complexes and transition state in the model reaction of silyl transfer (eq 18, Cp = C_5H_5 and R = H) using the semiempirical ZINDO/1 method show that the strongly exothermic ($\Delta H = -85.4$ kcal/mol) metalation reaction must proceed rapidly ($\Delta E^{\ddagger} = 3.8$ kcal/mol) (see Supporting Information for more details). This fact correlates poorly with the recent theoretical study results on the σ-bond metathesis reaction between Cl_2ScH and SiH_4,[14] but it is in a good agreement with the experimental results on the reactivity of $(C_5Me_5)_2LnH$. These

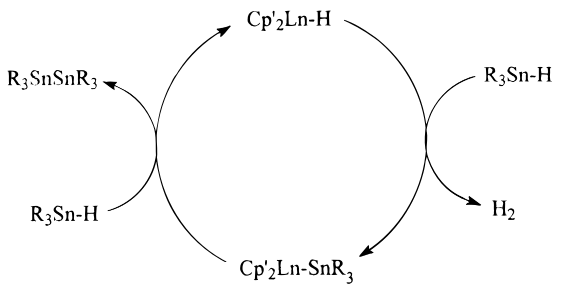
Scheme 2



---

(55) Deelman, B.-J.; Teuben, J. H.; Macgregor, S. A.; Eisenstein, O. *New J. Chem.* **1995**, *19*, 691−698.

Scheme 3



unsolvated monomeric hydride complexes react rapidly with silanes ($k_{obs} > 5.4(5) \times 10^{-2}$ M^{-1} s^{-1} at 25 °C, Ln = La). This reaction has a ΔH of ca. −4 kcal mol^{-1}.[15b] However, the computational data indicate that the silyl transfer should be strongly exothermic. This discrepancy may be explained by the influence of two donating C_5Me_5 ligands, whose introduction into the molecule brings about a large change in the electron density formally matching the decrease in the oxidation state of the metal by unit.[56]

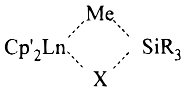
The calculations performed indicate the evolution of hydrogen to be preferable in the interaction of $(C_5H_5)_2$-YH with SiH_4 in the gas phase (eq 18, Cp = C_5H_5 and R = H). The calculated parameters for the alternative hydrogen exchange reaction (eq 17, R = H) are $\Delta H = 0$ kcal/mol and $\Delta E^{\ddagger} > 12$ kcal/mol. Even small steric problems give rise to an essentially different result. The rates of these alternative reactions become practically equal (see Supporting Information for more details). Even greater changes in the reactivity can occur in the case of substantial steric hindrances to putting the silicon atom in the coordination sphere of yttrium in the transition state. Obviously, that hydride transfer (compared to the alternative transfer of silyl group) to the lanthanide atom could include no considerable Ln···Si interaction in transition state **A′**. In this case, the structure of the transition state is likely to be similar to the structure of dimeric lanthanide hydrides that involve a silicon atom instead of one lanthanide atom in the Ln(μ-H)$_2$Ln metallocycle.

Lanthanide hydrides $\{Cp'_2Ln(\mu\text{-}H)\}_2$ catalyze a rapid isotope exchange in organotin hydrides at ambient temperature. Alternatively, organolanthanides catalyze dehydrogenative coupling of stannanes at elevated temperatures. Most likely, the latter reaction proceeds via a free radical pathway,[29] which is initiated by either a redox reaction between Cp'_2LnH and R_3SnH or by thermal decomposition of some intermediates with Ln−Sn bonding. It is well-known that tin hydrides are metalated more easily than the corresponding silanes.[3b,9d,57] Therefore, the formation of Ln−Sn intermediates is probable. On the other hand, if the intermediates are formed (although they were not detected by NMR spectroscopy), then the dehydrogenative coupling of stannanes could proceed via the nonhomolytic mechanism (Scheme 3). This pathway is similar to the mechanism of the dehydrogenative coupling of silanes.[15b]

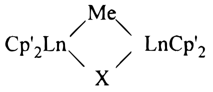
Synthesis and Dissociative Stability of Dimeric Organolanthanides. Highly associated complexes with various bridging ligands are known to have a great significance in organolanthanide chemistry.[3] In this paper, we propose two new methods for the synthesis of dimeric lanthanide compounds. The first one implies selective reaction of silane or alkoxysilane with lanthanide hydrocarbyl $\{Cp'_2Ln(\mu\text{-Me})\}_2$. Depending on the ratio of the reagents, this reaction gives either $\{Cp'_2Ln(\mu\text{-X})\}_2$ or $Cp'_2Ln(\mu\text{-Me})(\mu\text{-X})LnCp'_2$ (X = H, OR). The formation of the complexes with different bridging ligands starting from $\{Cp'_2Ln(\mu\text{-Me})\}_2$ should involve preliminary dissociation of the dimeric methyl complexes (eq 19).[52] In unsolvated media, the following

$$\{Cp'_2Ln(\mu\text{-Me})\}_2 \overset{\text{fast}}{\rightleftarrows} 2Cp'_2LnMe \qquad (19)$$

nucleophilic substitution at silicon must proceed via the four-centered transition state **C**, and therefore, the corresponding dimeric complexes with the Ln(μ-Me)(μ-X)Ln metallocycle (**D**) could be a model for the transition state of this reaction. The following reaction, i.e., the

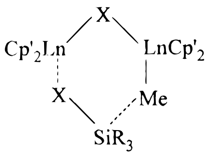


C

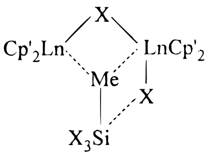


D

formation of $\{Cp'_2Ln(\mu\text{-X})\}_2$ from $Cp'_2Ln(\mu\text{-Me})(\mu\text{-X})$-$LnCp'_2$, seems to imply a cleavage of only one bridging bond Ln−Me−Ln and, probably, proceed via a bimetallic transition state,[50,52] e.g.



or



This selective method of bridging ligand substitution seems to be the general synthetic procedure and can be used for the preparation of various lanthanide complexes starting from various substituted silanes. In preliminary experiments, we showed that $\{Cp'_2Lu(\mu\text{-}H)\}_2$ reacts readily with $(MeO)_4Si$ to form $\{Cp'_2Lu(\mu\text{-OMe})\}_2$ and $Cp'_2Lu(\mu\text{-}H)(\mu\text{-OMe})LuCp'_2$. Yttrium complex $\{Cp'_2Y(\mu\text{-Me})\}_2$ reacts with $(Me_2N)_4Si$ in a similar manner to form $\{Cp'_2Y(\mu\text{-NMe}_2)\}_2$ and $Cp'_2Y(\mu\text{-Me})(\mu\text{-NMe}_2)YCp'_2$.

Another general approach studied for the synthesis of new dimeric lanthanide complexes either with different bridging ligands or with different metals is an exchange between two different starting dimeric complexes in hydrocarbon solution. Both of the above-mentioned methods are used for the synthesis of different objects and, therefore, they complete with one another. Not much is known about the dissociative stability of dimeric organolanthanides with various bridging ligands, particularly comparative data.[16,58−60]

---

(56) Kaupp, M.; Schleyer, P. v. R.; Dolg, M.; Stoll, H. *J. Am. Chem. Soc.* **1992**, *114*, 8202−8208.

(57) *Comprehensive Organic Chemistry*; Barton, D., Ollis, W. D., Eds.; Pergamon Press: Oxford, 1979; Vol. 3. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 1.

(58) Schaverien, C. J. *Organometallics* **1994**, *13*, 69−82.

(59) Watson, P. L. *J. Am. Chem. Soc.* **1983**, *105*, 6491−6493.

(60) Watson, P. L. *J. Chem. Soc., Chem. Commun.* **1980**, 652−653. Watson, P. L.; Whitney, J. F.; Harlow, R. D. *Inorg. Chem.* **1981**, *20*, 3271−3278. Evans, W. J.; Meadows, J. H.; Hanusa, T. P. *J. Am. Chem. Soc.* **1984**, *106*, 4454−4460. Jeske, G.; Lauke, H.; Mauermann, H.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8111−8118.

The above-mentioned experimental data on the relative rates of ligand exchange for the complexes $Cp'_2Ln(\mu$-$X)(\mu$-$Y)LnCp'_2$ confirm that the capacities of various bridging fragments in the vicinity of yttrium and lutetium atoms to undergo reversible cleavage in hydrocarbon solution increase in the sequence Ln–O(Me)–Ln ≪ Ln–Cl–Ln < Ln–H–Ln < Ln–Me–Ln. It is very important that this series does not correlate with the sequence of the corresponding $D(Cp^*_2Sm{-}X)$ values, where $Cp^* = C_5Me_5$, which is as follows (kcal/mol) [X]: 47.0 (1.5) $[CH(SiMe_3)_2]$, 54.2 (3.0) [H], 82.4 (3.5) $[O^tBu]$, 97.1 (3.0) [Cl].[60] Interestingly, the Ln–SR–Ln fragments dissociate relatively rapidly in hydrocarbon solution and the corresponding compounds take part in the exchange processes,[34] although the respective thermodynamic parameters $D(Cp^*_2Sm{-}X)$, where X = OR and SR, are rather close.[61] Moreover, the preceding sequence is rather imprecise because of a strong dependence of the dissociative ability of separate bridges on the structure of the second bridge in the dimeric organolanthanide compound. The discussed exchange in the series of dimeric lanthanide complexes with bridging ligands can presumably proceed without complete dissociation of these compounds in solution, as well as by the associative mechanism involving cleavage or loosening of only one bridging bond. Only in the case of the dimeric methyl complexes which enter into the rapid exchange in eq 19 does the dissociative mechanism appear to be well-grounded, although the equilibrium in this reaction is shifted toward the starting associates.

Conclusions

In this paper, we have shown that the reaction of lanthanide and yttrium hydrocarbyls with organosilicon hydrides and alkoxy- and chlorosilanes, as well as with other substituted silanes, is a very convenient and selective route for the preparation of the corresponding heterosubstituted organolanthanide and -yttrium compounds, particularly those complexes that include various bridging ligands, $Cp'_2Ln(\mu$-$L')(\mu$-$L'')LnCp'_2$. This method is important for the preparation of lanthanide hydrides, which are known to be very active catalysts for various transformations of organic and organoelement substrates. Here, we have shown that the reaction between lanthanide hydrocarbyls and silanes giving the corresponding lanthanide hydrides must be a key stage of the catalytic cycle of olefin hydrosilylation catalyzed by organolanthanides. Marks[6] and our group[4,5] suggested this previously.

We have also shown that the reaction of lanthanide hydrides with silanes that gives compounds with Ln–Si bonding has an alternative pathway, i.e., hydride exchange. Therefore, the corresponding dimeric lanthanide deuterides were prepared in the presence of deuterosilanes. In a catalytic manner, this reactivity enables carrying out H/D scrambling in silanes R_3SiH and R'_3SiD. The dual behavior of lanthanide and yttrium hydrides and hydrocarbyls toward organosilicon hydrides is a dramatic example of how a relatively small modification in the immediate metal environment can influence the reactivity of early transition metal complexes.

Another point of interest is the mobility of various ligands in the coordination sphere of the metal of lanthanide complexes in solution (see also ref 62). The study of various equilibrium processes makes it possible to obtain the relative capacity of various bridgings $Ln(\mu$-$X)Ln$, where X = Me, H, Cl, OMe, to cleave in hydrocarbon solution. These results are of significance for synthetic chemistry. They enable carrying out the synthesis of well-designed dimeric lanthanide complexes either with different bridging ligands $Ln(\mu$-$L')(\mu$-$L'')Ln$ or with different metals $Ln'(\mu$-$L)_2Ln''$. On the other hand, the information about the mobility of various bridging ligands in the vicinity of lanthanide atoms is of importance for further insight into the mechanism of some commercial-scale catalytic reactions, such as stereospecific diene polymerization catalyzed by Ziegler–Natta systems, including lanthanide compounds.[63]

Experimental Section

General Procedure. All manipulations were performed either on a high-vacuum line in an all-glass apparatus equipped with PTFE stopcocks or in an atmosphere of thoroughly purified argon using standard Schlenk techniques or in a Vacuum Atmospheres drybox. The tetrahydrofuran and ether used for synthesis (and THF-d_8 for NMR measurements) were purified by distillation over $LiAlH_4$ and kept over sodium benzophenone ketyl. Hydrocarbon solvents (including benzene-d_6 and toluene-d_8 for NMR measurements) were distilled and stored over CaH_2 or Na/K alloy. Anhydrous YCl_3, $TbCl_3$, $YbCl_3$, and $LuCl_3$ were obtained from commercially available hydrates (Reachim).[64] The organosilicon hydrides $PhSiH_3$, $^nC_6H_{13}SiH_3$, Ph_2SiH_2, $PhMeSiH_2$, $^nBu_2SiH_2$, Ph_3SiH, and Et_3SiH were prepared from commercially available organochlorosilanes by standard literature procedures.[65] $^tBuC_5H_5$,[66] $Me_3SiC_5H_5$,[67] Ph_3SnH, Et_3SnH, Bu_3SnH, $^nBu_2GeH_2$, Et_3GeH,[29] and $PhMeSiD_2$[68] were prepared by the published methods. $^tBuC_5H_4Na$ and $Me_3SiC_5H_4Na$ were prepared by the treatment of the corresponding cyclopentadienes with NaH in THF. ^1H and ^{13}C NMR spectra were recorded with a Bruker AM 360 for 3–10% solutions in deuterated solvents. The chemical shifts for the ^1H and ^{13}C NMR spectra were measured relative to TMS. MS measurements were carried out on a MX-1321 spectrometer ($E_i = 70$ eV). C,H microanalyses were done using commercial equipment for CHN microanalysis (Khimlaborpribor, Klin, Russia) or a CHN-O-Rapid analyzer (Heracus). Lanthanide contents were assayed by titration (EDTA, Xylenol Orange). Electron-probe X-ray analysis were performed with a scanning electron microscope SEM-505 (Phillips) equipped with a unit for X-ray energy dispersive analysis (Edax).

$\{(^tBuC_5H_4)_2Y(\mu$-$Me)\}_2$ (1). A mixture of 5.89 g (30 mmol) of YCl_3 with 8.68 g (60 mmol) of Cp′Na in 150 mL of THF was

---

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

[62] Beletskaya, I. P.; Voskoboynikov, A. Z.; Chuklanova, E. B.; Kirillova, N. I.; Shestakova, A. K.; Parshina, I. N.; Gusev, A. I.; Magomedov, G. K.-I. *J. Am. Chem. Soc.* **1993**, *115*, 3156–3166.

[63] Mazzei, A. In *Organometallics of the f-Elements*; Marks, T. J., Fischer, R. D., Eds.; Reidel Publishing: Dordrecht, The Netherlands, 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 Publishing: Dordrecht, The Netherlands, 1985; pp 387–400. Monakov, Y.-B.; Tolstikov, G. A. *Kataliticheskaya polimerizatsiya 1,3-dienov (Catalytic Polymerization of 1,3-dienes)*; Nauka: Moscow, 1990.

[64] *Handbuch der Praparativen Anorganischen Chemie*; Brauer, G., Ed.; Verlag: Stuttgart, 1981.

[65] Andrianov, K. A. *Metody elementoorganicheskoy khimii. Kremnij (Methods of Organo-Element Chemistry. Silicon)*; Nauka: Moscow, 1968.

[66] Reimschneider, R.; Nehring, R. *Monatsh. Chem.* **1959**, *90*, 568–570.

[67] Abel, E. W.; Dunster, M. O.; Waters, A. *J. Organomet. Chem.* **1973**, *49*, 287–321.

[68] Watanabe, H.; Ohsawa, N.; Sudo, T.; Hirakata, K.; Nagai, Y. *J Organomet. Chem.* **1977**, *128*, 27–35.

stirred for 24 h at ambient temperature. The solution formed was cooled to −78 °C and treated with 17.9 mL of a 1.68 M solution of MeLi in Et_2O. The reaction mixture was stirred for 1 h at −78 °C. After slowly warming the mixture to ambient temperature, it was evaporated to dryness. The organolanthanide was extracted by hot toluene (150 mL) using a special pressure filter (10−20 μ) funnel equipped with a thermostated (70 °C) water jacket. The extract was evaporated to dryness, and treatment with hot toluene (100 mL) was repeated until complete decomposition of the ate complexes. Then the solution was evaporated to ca. 30 mL. The crystals that precipitated at −30 °C were separated, washed with a minimal amount of cold toluene, and dried *in vacuo*. Yield: 6.95 g (67%) of colorless crystals of **1**, mp 199−202 °C (dec). The complex can be purified by recrystallization from toluene. ^{1}H NMR (benzene-d_6): δ −0.47 (t, 6H, $^2J_{Y-H}$ = 3.1 Hz, μ-Me), 1.36 (s, 36H, ^{t}Bu), 6.15 (t, 8H, J = 2.7 Hz, H2,5 in C_5H_4), 6.50 (t, 8H, J = 2.7 Hz, H3,4 in C_5H_4). ^{13}C NMR (benzene-d_6): δ 25.03 (t, $^1J_{Y-C}$ = 24.9 Hz, μ-Me), 30.17 (*C*Me$_3$), 32.52 (C*Me*$_3$), 110.04 (C2,5 in C_5H_4), 110.43 (C3,4 in C_5H_4), 137.32 (C1 in C_5H_4). MS: *m/z* 692 (M$^+$, 0.3), 331 ([0.5M − CH$_3$]$^+$, 100). Anal. Calcd for $C_{38}H_{58}Y_2$: C, 65.90; H, 8.38; Y, 25.72. Found: C, 66.07; H, 8.45; Y, 25.57.

{(^{t}BuC$_5$H$_4$)$_2$Tb(μ-Me)}$_2$ (2). The reaction was carried out similar to the preparation of compound **1**, starting from 7.20 g (27 mmol) of $TbCl_3$, 7.80 g (54 mmol) of Cp′Na in 150 mL of THF, and 16.1 mL of a 1.68 M solution of MeLi in Et_2O. Yield: 6.70 g (59%) of colorless crystals of **2**, mp 193−197 °C (dec). MS: *m/z* 832 (M$^+$, 0.7), 401 ([0.5M − CH$_3$]$^+$, 100). Anal. Calcd for $C_{38}H_{58}Tb_2$: C, 54.81; H, 6.97; Tb, 38.22. Found: C, 54.97; H, 7.08; Tb, 38.01.

{(^{t}BuC$_5$H$_4$)$_2$Yb(μ-Me)}$_2$ (3). The reaction was carried out similar to the preparation of compound **1**, starting from 5.40 g (19 mmol) of $YbCl_3$, 5.60 g (38 mmol) of Cp′Na in 150 mL of THF, and 11.3 mL of a 1.68 M solution of MeLi in Et_2O. Yield: 6.05 g (74%) of orange crystals of **3**, mp 179−182 °C (dec). MS: *m/z* 860 (M$^+$, 0.6), 415 ([0.5M − CH$_3$]$^+$, 100). Anal. Calcd for $C_{38}H_{58}Yb_2$: C, 53.02; H, 6.74; Yb, 40.23. Found: C, 53.21; H, 6.85; Yb, 40.05.

{(^{t}BuC$_5$H$_4$)$_2$Lu(μ-Me)}$_2$ (4). The reaction was carried out similar to the preparation of compound **1**, starting from 8.12 g (28 mmol) of $LuCl_3$, 8.31 g (58 mmol) of Cp′Na in 150 mL of THF, and 16.7 mL of a 1.68 M solution of MeLi in Et_2O. Yield: 9.07 g (59%) of colorless crystals of **4**, mp 188−190 °C (dec). ^{1}H NMR (benzene-d_6): δ −0.01 (s, 6H, μ-Me), 1.37 (s, 36H, ^{t}Bu), 6.08 (t, 8H, J = 2.7 Hz, H2,5 in C_5H_4), 6.50 (t, 8H, J = 2.8 Hz, H3,4 in C_5H_4). ^{13}C NMR (benzene-d_6): δ 29.02 (μ-Me), 31.18 (*C*Me$_3$), 32.48 (C*Me*$_3$), 109.08 (C2,5 in C_5H_4), 110.88 (C3,4 in C_5H_4), 135.14 (C1 in C_5H_4). MS: *m/z* 864 (M$^+$, 0.4), 417 ([0.5M − CH$_3$]$^+$, 100). Anal. Calcd for $C_{38}H_{58}Lu_2$: C, 52.78; H, 6.71; Lu, 40.51. Found: C, 52.96; H, 6.89; Lu, 40.43.

{(^{t}BuC$_5$H$_4$)$_2$Lu(μ-CD$_3$)}$_2$ (4-*d*). The reaction was carried out similar to the preparation of compound **1**, starting from 3.19 g (11 mmol) of $LuCl_3$, 3.15 g (22 mmol) of Cp′Na in 80 mL of THF, and 10.8 mL of a 1.02 M solution of CD_3Li in Et_2O. Yield: 3.14 g (66%) of colorless crystals of **4-*d***, mp 187−190 °C (dec). The ^{1}H and ^{13}C NMR spectra were the same as those of **4**, excluding the resonance attributed to the protons of the μ-Me ligands. MS: *m/z* 870 (M$^+$, 0.5), 417 ([0.5M − CH$_3$]$^+$, 100). Anal. Calcd for $C_{38}H_{52}D_6Lu_2$: C, 52.41; H/D, 7.36; Lu, 40.23. Found: C, 52.53; H/D, 7.29; Lu, 40.37.

{(Me$_3$SiC$_5$H$_4$)$_2$Lu(μ-Me)}$_2$ (5). The reaction was carried out similar to the preparation of compound **1**, starting from 3.70 g (13 mmol) of $LuCl_3$, 4.20 g (27 mmol) of Cp″Na in 70 mL of THF, and 7.7 mL of a 1.68 M solution of MeLi in Et_2O. Recrystallization of the compound was performed using hot hexane because of the high solubility of **5** in toluene. Yield: 3.64 g (63%) of colorless crystals of **5**, mp 176−178 °C (dec). ^{1}H NMR (benzene-d_6): δ −0.19 (s, 6H, μ-Me), 0.38 (s, 36H, Me$_3$Si), 6.33 (t, 8H, J = 2.3 Hz, H2,5 in C_5H_4), 6.80 (t, 8H, J = 2.3 Hz, H3,4 in C_5H_4). ^{13}C NMR (benzene-d_6): δ 0.66 (Me$_3$Si), 28.69 (μ-Me), 113.67 (C2,5 in C_5H_4), 116.94 (C1 in C_5H_4), 121.02 (C3,4 in C_5H_4). MS: *m/z* 928 (M$^+$, 1.5), 449 ([0.5M − CH$_3$]$^+$, 100). Anal. Calcd for $C_{34}H_{58}Lu_2Si_4$: C, 45.95; H, 6.53; Lu, 39.41. Found: C, 46.13; H, 6.67; Lu, 39.45. Electron probe microanalysis: Lu:Si = 1:2.

(^{t}BuC$_5$H$_4$)$_2$YMe(THF) (6). A sample of 235 mg (0.34 mmol) of **1** was dissolved in ca. 5 mL of THF. This mixture was stirred for 15 min at ambient temperature and evaporated to dryness. The residue was dried in vacuum for 2 h at ambient temperature. Yield: 241 mg (95%) of the colorless solid of **6**, mp 80−82 °C (dec). ^{1}H NMR (THF-d_8): δ −0.99 (d, 3H, $^2J_{Y-H}$ = 2.1 Hz, YMe), 1.21 (s, 18H, ^{t}Bu), 5.83 (t, 4H, J = 2.7 Hz, H2,5 in C_5H_4), 6.01 (t, 4H, J = 2.9 Hz, H3,4 in C_5H_4). ^{13}C NMR (THF-d_8): δ 14.22 (d, $^1J_{Y-C}$ = 53.3 Hz, YMe), 30.63 (*C*Me$_3$), 32.49 (C*Me*$_3$), 108.34 (C2,5 in C_5H_4), 108.59 (C3,4 in C_5H_4), 138.73 (C1 in C_5H_4). Anal. Calcd for $C_{23}H_{37}YO$: C, 66.03; H, 8.85; Y, 21.29. Found: C, 66.17; H, 8.92; Lu, 21.15.

(^{t}BuC$_5$H$_4$)$_2$TbMe(THF) (7). The synthesis was carried out similar to the preparation of compound **6**, starting from 211 mg (0.25 mmol) of **2**. Yield: 238 mg (96%) of a colorless solid of **7**, mp 76−78 °C (dec). Anal. Calcd for $C_{23}H_{37}TbO$: C, 56.55; H, 7.58; Tb, 32.58. Found: C, 56.70; H, 7.69; Tb, 32.33.

(^{t}BuC$_5$H$_4$)$_2$YbMe(THF) (8). The synthesis was carried out similar to the preparation of compound **6**, starting from 268 mg (0.31 mmol) of **3**. Yield: 291 mg (93%) of a yellow-orange solid of **8**, mp 69−70 °C (dec). Anal. Calcd for $C_{23}H_{37}YbO$: C, 54.98; H, 7.37; Yb, 34.46. Found: C, 55.14; H, 7.46; Yb, 34.20.

(^{t}BuC$_5$H$_4$)$_2$LuMe(THF) (9). The synthesis was carried out similar to the preparation of compound **6**, starting from 205 mg (0.24 mmol) of **4**. Yield: 227 mg (95%) of a colorless solid of **9**, mp 69−71 °C (dec). ^{1}H NMR (THF-d_8): δ −0.87 (s, 3H, LuMe), 1.27 (s, 18H, ^{t}Bu), 5.81 (t, 4H, J = 2.6 Hz, H2,5 in C_5H_4), 5.99 (t, 4H, J = 2.7 Hz, H3,4 in C_5H_4). ^{13}C NMR (THF-d_8): δ 19.20 (LuMe), 30.72 (*C*Me$_3$), 32.46 (C*Me*$_3$), 107.70 (C2,5 in C_5H_4), 108.29 (C3,4 in C_5H_4), 137.35 (C1 in C_5H_4). Anal. Calcd for $C_{23}H_{37}LuO$: C, 54.76; H, 7.34; Lu, 34.72. Found: C, 54.92; H, 7.40; Lu, 34.56.

(Me$_3$SiC$_5$H$_4$)$_2$LuMe(THF) (10). The synthesis was carried out similar to the preparation of compound **6**, starting from 241 mg (0.26 mmol) of **5**. Yield: 267 mg (96%) of a colorless solid of **10**, mp 68−71 °C (dec). ^{1}H NMR (THF-d_8): δ −0.94 (s, 3H, LuMe), 0.21 (s, 18H, Me$_3$Si), 6.11 (t, 4H, J = 2.5 Hz, H2,5 in C_5H_4), 6.24 (t, 4H, J = 2.5 Hz, H3,4 in C_5H_4). ^{13}C NMR (THF-d_8): δ 0.65 (SiMe$_3$), 18.67 (LuMe), 112.52 (C2,5 in C_5H_4), 118.34 (C1,3,4 in C_5H_4). Anal. Calcd for $C_{21}H_{37}LuSi_2O$: C, 47.01; H, 6.90; Lu, 32.65. Found: C, 47.20; H, 7.02; Lu, 32.53. Electron probe microanalysis: Lu:Si = 1:2.

{(^{t}BuC$_5$H$_4$)$_2$Y(μ-H)}$_2$ (11). A mixture of 7.83 g (11.3 mmol) of **1** with 4.51 g (37 mmol) of $PhMeSiH_2$ in 150 mL of toluene was stirred for 6 days at ambient temperature (or for 1 day at ca. 40 °C). Then the mixture was evaporated to dryness. The product was purified by recrystallization from hot hexane and dried in vacuum. Yield: 3.82 g (88%) of colorless crystals of **11**, mp 174−175 °C. ^{1}H NMR (benzene-d_6): δ 1.23 (s, 36H, ^{t}Bu), 3.09 (t, 2H, $^1J_{Y-H}$ = 32.8 Hz, μ-H), 6.24 (t, 8H, J = 2.7 Hz, H2,5 in C_5H_4), 6.78 (t, 8H, J = 2.7 Hz, H3,4 in C_5H_4). ^{13}C NMR (benzene-d_6): δ 30.05 (*C*Me$_3$), 31.31 (C*Me*$_3$), 108.87 (C2,5 in C_5H_4), 108.96 (C3,4 in C_5H_4), 138.64 (C1 in C_5H_4). Anal. Calcd for $C_{36}H_{54}Y_2$: C, 65.06; H, 8.13; Y, 26.81. Found: C, 65.21; H, 8.18; Y, 26.69.

{(^{t}BuC$_5$H$_4$)$_2$Y(μ-D)}$_2$ (11-*d*). The reaction was carried out similar to the preparation of compound **11**, starting from 1.31 g (1.9 mmol) of **1** and 0.94 g (7.6 mmol) of $PhMeSiH_2$ in 30 mL of toluene. The reaction mixture was stirred for 6 h at 60 °C. Yield: 0.69 g (55%) of colorless crystals of **11-*d***, mp 172−175 °C. ^{1}H and ^{13}C NMR spectra were the same as those of **11**, excluding the resonance attributed to the protons of the μ-H ligands. Anal. Calcd for $C_{36}H_{52}D_2Y_2$: C, 64.86; H/D, 8.41; Y, 26.73. Found: C, 65.02; H/D, 8.50; Y, 26.61.

{(^{t}BuC$_5$H$_4$)$_2$Tb(μ-H)}$_2$ (12). The reaction was carried out similar to the preparation of compound **11**, starting from 3.16

g (3.9 mmol) of **2** and 1.55 g (12.7 mmol) of $PhMeSiH_2$ in 50 mL of toluene. The mixture was stirred for 12 days at ambient temperature. Yield: 2.52 g (83%) of colorless crystals of **12**, mp 194−197 °C. Anal. Calcd for $C_{36}H_{54}Tb_2$: C, 53.73; H, 6.72; Tb, 39.55. Found: C, 53.86; H, 6.80; Tb, 39.41.

$\{(^tBuC_5H_4)_2Yb(\mu\text{-}H)\}_2$ (13). The reaction was carried out similar to the preparation of compound **11**, starting from 4.07 g (4.7 mmol) of **3** and 2.05 g (19 mmol) of $PhSiH_3$ in 70 mL of toluene. The mixture was stirred for 5 days at ambient temperature. Yield: 3.07 g (78%) of orange crystals of **13**, mp 214−216 °C. Anal. Calcd for $C_{36}H_{54}Yb_2$: C, 51.92; H, 6.49; Yb, 41.59. Found: C, 52.14; H, 6.56; Yb, 41.50.

$\{(^tBuC_5H_4)_2Lu(\mu\text{-}H)\}_2$ (14). The reaction was carried out similar to the preparation of compound **11**, starting from 6.78 g (7.8 mmol) of **4** and 3.35 g (31 mmol) of $PhSiH_3$ in 150 mL of toluene. The mixture was stirred for 5 days at ambient temperature. Yield: 4.88 g (74%) of colorless crystals of **14**, mp 227−229 °C. ^1H NMR (benzene-d_6): δ 1.21 (s, 36H, ^{t}Bu), 5.91 (s, 2H, μ-H), 6.17 (t, 8H, $J = 2.6$ Hz, H2,5 in C_5H_4), 6.79 (t, 8H, $J = 2.6$ Hz, H3,4 in C_5H_4). ^{13}C NMR (benzene-d_6): δ 30.03 (*C*Me₃), 31.33 (C*Me*₃), 108.04 (C2,5 in C_5H_4), 109.34 (C3,4 in C_5H_4), 136.91 (C1 in C_5H_4). Anal. Calcd for $C_{36}H_{54}Lu_2$: C, 51.67; H, 6.46; Lu, 41.87. Found: C, 51.71; H, 6.44; Lu, 41.95.

$\{(Me_3SiC_5H_4)_2Lu(\mu\text{-}H)\}_2$ (15). The reaction was carried out similar to the preparation of compound **11**, starting from 2.32 g (2.6 mmol) of **5** and 1.14 g (10.6 mmol) of $PhSiH_3$ in 50 mL of toluene. The mixture was stirred for 5 days at ambient temperature. The product was recrystallized from pentane. Yield: 1.00 g (44%) of colorless crystals of **15**, mp 219−222 °C. ^1H NMR (benzene-d_6): δ 0.25 (s, 36H, Me_3Si), 5.80 (s, 2H, μ-H), 6.47 (t, 8H, $J = 2.3$ Hz, H2,5 in C_5H_4), 7.19 (t, 8H, $J = 2.4$ Hz, H3,4 in C_5H_4). ^{13}C NMR (benzene-d_6): δ −0.31 (Me_3Si), 112.52 (C2,5 in C_5H_4), 119.57 (C3,4 in C_5H_4), 121.04 (C1 in C_5H_4). Anal. Calcd for $C_{32}H_{54}Lu_2Si_4$: C, 42.67; H, 6.00; Lu, 38.89. Found: C, 42.91; H, 6.14; Lu, 38.77. Electron probe microanalysis: Lu:Si = 1:2.

$(^tBuC_5H_4)_2Y(\mu\text{-}H)(\mu\text{-}Me)Y(C_5H_4{}^tBu)_2$ (16): Method A. A mixture of 5.20 g (7.5 mmol) of **1** with 0.92 g (7.5 mmol) of $PhMeSiH_2$ in 70 mL of toluene was stirred for 1 day at ambient temperature. Then the mixture was evaporated to dryness. The crude product was treated with 250 mL of pentane. The solution was evaporated to ca. 100 mL. The crystals that precipitated at −30 °C were separated, washed with a minimal amount of cold pentane, and dried *in vacuo*. Yield: 2.85 g (56%) of colorless crystals of **16**, mp 198−200 °C (dec). ^1H NMR (benzene-d_6):[69] δ −0.73 (t, 3H, $^2J_{Y-H} = 3.3$ Hz, μ-Me), 1.32 (s, 36H, ^{t}Bu), 3.00 (t, 1H, $^1J_{Y-H} = 36.0$ Hz, μ-H), 6.11 (s, 4H, line width (lw) = 25 Hz, H5 in C_5H_4), 6.39 (s, 4H, lw = 25 Hz, H2 in C_5H_4), 6.54 (s, 4H, lw = 25 Hz, H3 in C_5H_4), 6.76 (s, 4H, lw = 25 Hz, H4 in C_5H_4). ^{13}C NMR (benzene-d_6):[69] δ 26.34 (t, $^1J_{Y-C} = 25.8$ Hz, μ-Me), 30.18 (*C*Me₃), 32.26 (C*Me*₃), 108.66 (lw = 35 Hz, C5 in C_5H_4), 109.54 (lw = 35 Hz, C2 in C_5H_4), 110.27 (lw = 35 Hz, C3 in C_5H_4), 111.84 (lw = 35 Hz, C4 in C_5H_4), 134.40 (lw = 35 Hz, C1 in C_5H_4). Anal. Calcd for $C_{37}H_{56}Y_2$: C, 65.49; H, 8.26; Y, 26.25. Found: C, 65.57; H, 8.34; Y, 26.07.

Method B. A mixture of 1.31 g (1.89 mmol) of **1** with 1.64 g (1.90 mmol) of **11** in 50 mL of toluene was stirred for 5 days at ambient temperature. The treatment of the solution obtained was carried out similar to the procedure described in method A. Yield: 0.95 g (37%) of **16**. Anal. Found: C, 65.61; H, 8.31; Y, 26.11.

$(^tBuC_5H_4)_2Lu(\mu\text{-}H)(\mu\text{-}Me)Lu(C_5H_4{}^tBu)_2$ (17): Method A. The reaction was carried out similar to the preparation of compound **16** (method A), starting from 3.62 g (4.2 mmol) of **4** and 0.51 g (4.2 mmol) of $PhMeSiH_2$ in 100 mL of toluene. The reaction mixture was stirred for 3 days at ambient temperature. Yield: 2.88 g (81%) of colorless crystals of **17**, mp 189−190 °C (dec). ^1H NMR (benzene-d_6):[69] δ −0.25 (t, 3H, μ-Me), 1.31 (s, 36H, ^{t}Bu), 5.82 (s, 1H, μ-H), 6.03 (q, 4H, $J = 3.0$ Hz, $J = 5.6$ Hz, H5 in C_5H_4), 6.29 (q, 4H, $J = 2.8$ Hz, $J = 5.5$ Hz, H2 in C_5H_4), 6.50 (q, 4H, $J = 2.4$ Hz, $J = 5.1$ Hz, H3 in C_5H_4), 6.76 (q, 4H, $J = 2.4$ Hz, $J = 5.1$ Hz, H4 in C_5H_4). ^{13}C NMR (benzene-d_6):[69] δ 30.03 (μ-Me), 31.92 (*C*Me₃), 32.26 (C*Me*₃), 107.16 (C5 in C_5H_4), 109.00 (C2 in C_5H_4), 109.97 (C3 in C_5H_4), 110.21 (C4 in C_5H_4), 136.92 (C1 in C_5H_4). Anal. Calcd for $C_{37}H_{56}Lu_2$: C, 52.24; H, 6.59; Lu, 41.18. Found: C, 52.30; H, 6.52; Lu, 41.29.

Method B. The synthesis was carried out similar to the preparation of compound **16** (method B), starting from 1.12 g (1.30 mmol) of **4** and 1.08 g (1.30 mmol) of **14** in 50 mL of toluene. The reaction mixture was stirred for 7 days at ambient temperature. Yield: 0.97 g (44%). Anal. Found: C, 52.39; H, 6.65; Lu, 41.02.

$(Me_3SiC_5H_4)_2Lu(\mu\text{-}H)(\mu\text{-}Me)Lu(C_5H_4SiMe_3)_2$ (18): Method A. The reaction was carried out similar to the preparation of compound **16** (method A), starting from 2.85 g (3.1 mmol) of **5** and 0.37 g (3.1 mmol) of $PhMeSiH_2$ in 50 mL of toluene. The reaction mixture was stirred for 6 days at ambient temperature. Yield: 1.71 g (61%) of colorless crystals of **18**, mp 174−175 °C (dec). ^1H NMR (benzene-d_6):[69] δ −0.38 (s, 3H, μ-Me), 0.34 (s, 36H, Me_3Si), 5.65 (s, 1H, μ-H), 6.28 (q, 4H, H5 in C_5H_4), 6.58 (q, 4H, H2 in C_5H_4), 6.86 (q, 4H, H3 in C_5H_4), 7.10 (q, 4H, H4 in C_5H_4). ^{13}C NMR (benzene-d_6):[69] δ 0.42 (Me_3Si), 32.60 (μ-Me), 112.22 (C5 in C_5H_4), 113.96 (C2 in C_5H_4), 119.15 (C3 in C_5H_4), 120.31 (C4 in C_5H_4), 120.59 (C1 in C_5H_4). Anal. Calcd for $C_{31}H_{52}Lu_2Si_4$: C, 40.70; H, 5.69; Lu, 38.29. Found: C, 40.91; H, 5.80; Lu, 38.15. Electron probe microanalysis: Lu: Si = 1:2.

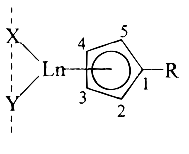
Method B. The synthesis was carried out similar to the preparation of compound **16** (method B), starting from 1.36 g (1.47 mmol) of **5** and 1.32 g (1.47 mmol) of **15** in 50 mL of toluene. The reaction mixture was stirred for 5 days at ambient temperature. Yield: 0.75 g (28%). Anal. Found: C, 40.84; H, 5.60; Lu, 38.09.

$\{(^tBuC_5H_4)_2Y(\mu\text{-}H)(THF)\}_2$ (19). A sample of 314 mg (0.47 mmol) of **11** was dissolved in 5 mL of THF and stirred for 0.5 h at ambient temperature. Then the mixture was evaporated, and the solid was dried *in vacuo* for 2 h. Yield: 337 mg (97%) of colorless crystals of **19**, mp 151−152 °C. ^1H NMR (THF-d_8): δ 1.25 (s, 36H, ^{t}Bu), 2.64 (t, 2H, $^1J_{Y-H} = 29.3$ Hz, μ-H), 6.02 (t, 8H, $J = 2.6$ Hz, H2,5 in C_5H_4), 6.34 (t, 8H, $J = 2.6$ Hz, H3,4 in C_5H_4). ^{13}C NMR (THF-d_8): δ 30.61 (*C*Me₃), 32.35 (C*Me*₃), 107.13 (C2,5 in C_5H_4), 108.93 (C3,4 in C_5H_4), 134.09 (C1 in C_5H_4). Anal. Calcd for $C_{40}H_{62}Y_2O$: C, 65.22; H, 8.42; Y, 24.18. Found: C, 65.11; H, 8.37; Y, 24.26.

$\{(^tBuC_5H_4)_2Y(\mu\text{-}Cl)\}_2$ (22): Method A. A mixture of 3.14 g (16 mmol) of YCl_3 with 4.63 g (32 mmol) of Cp′Na in 100 mL of THF was stirred for 24 h at ambient temperature. Then the mixture was evaporated to dryness. The crude product was extracted by hot toluene (100 mL) using a special pressure filter (10−20 μ) funnel equipped with a thermostated (70 °C) water jacket. The extract was evaporated to ca. 30 mL. The crystals that precipitated at −30 °C were separated, washed with a minimal amount of cold toluene, and dried *in vacuo*. Yield: 4.84 g (82%) of colorless crystals of **22**, mp 201−203 °C. The complex can be purified by the recrystallization from toluene. ^1H NMR (toluene-d_8): δ 1.38 (s, 36H, ^{t}Bu), 6.30 (t, 8H, $J = 2.5$ Hz, H2,5 in C_5H_4), 6.52 (t, 8H, $J = 2.5$ Hz, H3,4 in C_5H_4). ^{13}C NMR (toluene-d_8): δ 30.09 (*C*Me₃), 32.94 (C*Me*₃), 111.15 (C2,5 in C_5H_4), 113.70 (C3,4 in C_5H_4), 138.36 (C1 in C_5H_4). Anal. Calcd for $C_{36}H_{52}Cl_2Y_2$: C, 58.94; H, 7.09; Y, 24.28. Found: C, 59.07; H, 7.14; Y, 24.20. Electron probe microanalysis: Y:Cl = 1:1.

---

(69) The assignment of the ^1H and ^{13}C resonances of the ring nucleus of the RC_5H_4-η^5 ligands, where R = ^{t}Bu, and Me_3Si in the complexes with Ln(μ-X)(μ-Y)Ln bridging is according to the following scheme



Method B. A solution of 0.76 g (7.0 mmol) of Me_3SiCl in 10 mL of toluene was added dropwise to a solution of 2.41 g (3.5 mmol) of **1** in 50 mL of toluene at −20 °C. The reaction mixture was stirred at this temperature for 1 h. After slow warming the mixture to ambient temperature, it was stirred for 2 h and then evaporated to dryness. The product was crystallized from hot toluene. Yield: 2.31 g (90%). Anal. Found: C, 59.00; H, 7.13; Y, 24.17.

{(^{t}BuC$_5$H$_4$)$_2$Lu(μ-Cl)}$_2$ (23): Method A. The reaction was carried out similar to the preparation of compound **22** (method A), starting from 2.35 g (8.3 mmol) of $LuCl_3$ and 2.40 g (16.7 mmol) of Cp′Na in 50 mL of THF. Yield: 2.93 g (78%) of colorless crystals of **23**, mp 237−238 °C. ^{1}H NMR (benzene-*d*$_6$): δ 1.38 (s, 36H, ^{t}Bu), 6.25 (t, 8H, J = 2.7 Hz, H2,5 in C_5H_4), 6.54 (t, 8H, J = 2.7 Hz, H3,4 in C_5H_4). ^{13}C NMR (benzene-*d*$_6$): δ 29.85 (*C*Me$_3$), 32.05 (C*Me*$_3$), 110.34 (C2,5 in C_5H_4), 111.82 (C3,4 in C_5H_4), 138.81 (C1 in C_5H_4). Anal. Calcd for $C_{36}H_{52}Cl_2Lu_2$: C, 47.73; H, 5.75; Lu, 38.67. Found: C, 47.81; H, 5.79; Lu, 38.60. Electron probe microanalysis: Lu:Cl = 1:1.

Method B. The synthesis was carried out similar to the preparation of compound **22** (method B), starting from 0.33 g (3.0 mmol) of Me_3SiCl and 1.30 g (1.5 mmol) of **4** in 50 mL of toluene. Yield: 1.15 g (84%). Anal. Found: C, 47.90; H, 5.87; Lu, 38.52.

(^{t}BuC$_5$H$_4$)$_2$Y(μ-H)(μ-Cl)Y(C$_5$H$_4$^{t}Bu)$_2$ (24). A mixture of 2.07 g (3.1 mmol) of **11** with 2.28 g (3.1 mmol) of **22** in 100 mL of toluene was stirred for 2 h at 70 °C. Then the mixture was evaporated to ca. 30 mL. The crystals that precipitated at −30 °C were separated and recrystallized from a minimal amount of hot toluene. The product was dried *in vacuo*. Yield: 2.78 g (64%) of colorless crystals of **24**, mp 157−158 °C(dec). ^{1}H NMR (benzene-*d*$_6$):[69] δ 1.31 (s, 36H, ^{t}Bu), 2.95 (t, 1H,$^1J_{Y-H}$ = 33.5 Hz, μ-H), 6.17 (q, 4H, J = 3.0 Hz, J = 5.6 Hz, H5 in C_5H_4), 6.37 (q, 4H, J = 2.9 Hz, J = 5.5 Hz, H2 in C_5H_4), 6.57 (q, 4H, J = 2.4 Hz, J = 5.0 Hz, H3 in C_5H_4), 6.76 (q, 4H, J = 2.4 Hz, J = 5.1 Hz, H4 in C_5H_4). ^{13}C NMR (benzene-*d*$_6$):[69] δ 30.02 (*C*Me$_3$), 31.87 (C*Me*$_3$), 108.63 (C5 in C_5H_4), 109.50 (C2 in C_5H_4), 110.28 (C3 in C_5H_4), 111.81 (C4 in C_5H_4), 140.00 (C1 in C_5H_4). Anal. Calcd for $C_{36}H_{53}ClY_2$: C, 61.85; H, 7.59; Y, 25.48. Found: C, 61.90; H, 7.63; Y, 25.39. Electron probe microanalysis: Y:Cl = 2:1.

(^{t}BuC$_5$H$_4$)$_2$Lu(μ-H)(μ-Cl)Lu(C$_5$H$_4$^{t}Bu)$_2$ (25). The reaction was carried out similar to the preparation of compound **24**, starting from 1.89 g (2.3 mmol) of **14** and 2.05 g (2.3 mmol) of **23** in 70 mL of toluene. Yield: 2.92 g (74%) of colorless crystals of **25**, mp 210−212 °C (dec). ^{1}H NMR (benzene-*d*$_6$):[69] δ 1.30 (s, 36H, ^{t}Bu), 5.56 (s, 1H, μ-H), 6.14 (q, 4H, J = 2.9 Hz, J = 5.5 Hz, H5 in C_5H_4), 6.28 (q, 4H, J = 2.9 Hz, J = 5.5 Hz, H2 in C_5H_4), 6.56 (q, 4H, J = 2.4 Hz, J = 5.1 Hz, H3 in C_5H_4), 6.81 (q, 4H, J = 2.4 Hz, J = 5.0 Hz, H4 in C_5H_4). ^{13}C NMR (benzene-*d*$_6$):[69] δ 30.16 (*C*Me$_3$), 31.94 (C*Me*$_3$), 108.17 (C5 in C_5H_4), 108.89 (C2 in C_5H_4), 110.70 (C3 in C_5H_4), 111.32 (C4 in C_5H_4), 138.07 (C1 in C_5H_4). Anal. Calcd for $C_{36}H_{53}ClLu_2$: C, 49.63; H, 6.09; Lu, 40.21. Found: C, 49.78; H, 6.01; Lu, 40.18. Electron probe microanalysis: Lu:Cl = 2:1.

{(^{t}BuC$_5$H$_4$)$_2$Lu(μ-OMe)}$_2$ (26): Method A. A mixture of 1.17 g (1.31 mmol) of **4** and 0.40 g (2.62 mmol) of $(MeO)_4Si$ in 50 mL of toluene was stirred for 5 days at ambient temperature. The solution was evaporated to dryness. The crude product was recrystallized from hot toluene. The crystals that precipitated at 30 °C were separated, washed with cold toluene, and then dried *in vacuo*. Yield: 1.04 g (86%) of colorless crystals of **26**, mp 230−232 °C. ^{1}H NMR (benzene-*d*$_6$): δ 1.45 (s, 36H, ^{t}Bu), 3.28 (s, 6H, OMe), 6.15 (t, 8H, J = 2.8 Hz, H2,5 in C_5H_4), 6.51 (t, 8H, J = 2.7 Hz, H3,4 in C_5H_4). ^{13}C NMR (benzene-*d*$_6$): δ 29.83 (*C*Me$_3$), 32.50 (C*Me*$_3$), 54.43 (OMe), 109.78 (C2,5 in C_5H_4), 110.31 (C3,4 in C_5H_4), 136.64 (C1 in C_5H_4). Anal. Calcd for $C_{38}H_{58}Lu_2O_2$: C, 50.89; H, 6.47; Lu, 39.06. Found: C, 50.94; H, 6.51; Lu, 39.01.

Method B. A solution of 0.25 g (7.8 mmol) of MeOH in 5 mL of toluene was added dropwise to a solution of 3.40 g (3.9 mmol) of **4** in 70 mL of toluene at −78 °C. The reaction mixture was stirred at this temperature for 0.5 h. After slowly warming the mixture to ambient temperature, it was evaporated to dryness. Purification of the product was carried out as described in method A. Yield: 2.08 g (59%). Anal. Found: C, 51.03; H, 6.58; Lu, 38.89.

(^{t}BuC$_5$H$_4$)$_2$Y(μ-Me)(μ-OMe)Y(C$_5$H$_4$^{t}Bu)$_2$ (27). A mixture of 2.24 g (3.2 mmol) of **1** and 0.49 g (3.2 mmol) of $(MeO)_4Si$ in 50 mL of toluene was stirred for 30 min at ambient temperature. The solution was immediately evaporated to dryness. The residue was recrystallized with hot toluene. The crystals that precipitated at −30 °C were separated, washed with cold toluene, and then dried *in vacuo*. Yield: 1.63 g (71%) of colorless crystals of **27**, mp 181−183 °C (dec). ^{1}H NMR (benzene-*d*$_6$):[69] δ −0.42 (t, 3H, $^2J_{Y-H}$ = 3.4 Hz, μ-Me), 1.39 (s, 36H, ^{t}Bu), 3.12 (s, 3H, OMe), 6.05 (q, 4H, J = 3.0 Hz, J = 5.5 Hz, H5 in C_5H_4), 6.25 (q, 4H, J = 2.8 Hz, J = 5.6 Hz, H2 in C_5H_4), 6.39 (q, 4H, J = 2.5 Hz, J = 5.1 Hz, H3 in C_5H_4), 6.53 (q, 4H, J = 2.4 Hz, J = 5.3 Hz, H4 in C_5H_4). ^{13}C NMR (benzene-*d*$_6$):[69] δ 20.23 (t, $^1J_{Y-C}$ = 26.1 Hz, μ-Me), 30.37 (*C*Me$_3$), 32.53 (C*Me*$_3$), 53.84 (OMe), 109.47 (C5 in C_5H_4), 109.62 (C2 in C_5H_4), 110.17 (C3 in C_5H_4), 111.23 (C4 in C_5H_4), 138.10 (C1 in C_5H_4). Anal. Calcd for $C_{38}H_{58}Y_2O$: C, 64.41; H, 8.19; Y, 25.14. Found: C, 64.60; H, 8.28; Y, 24.98.

(^{t}BuC$_5$H$_4$)$_2$Lu(μ-Me)(μ-OMe)Lu(C$_5$H$_4$^{t}Bu)$_2$ (28). The reaction was carried out similar to the preparation of compound **27**, starting from 3.43 g (4.0 mmol) of **4** and 0.60 g (8.0 mmol) of $(MeO)_4Si$ in 100 mL of toluene. The solution was stirred for 6 h at ambient temperature. Yield: 2.86 g (82%) of colorless crystals of **28**, mp 228−230 °C (dec). ^{1}H NMR (benzene-*d*$_6$):[69] δ −0.02 (s, 3H, μ-Me), 1.41 (s, 36H, ^{t}Bu), 3.08 (s, 3H, OMe), 6.01 (q, 4H, J = 3.0 Hz, J = 5.6 Hz, H5 in C_5H_4), 6.22 (q, 4H, J = 2.9 Hz, J = 5.5 Hz, H2 in C_5H_4), 6.41 (q, 4H, J = 2.4 Hz, J = 5.2 Hz, H3 in C_5H_4), 6.54 (q, 4H, J = 2.5 Hz, J = 5.3 Hz, H4 in C_5H_4). ^{13}C NMR (benzene-*d*$_6$):[69] δ 23.00 (μ-Me), 31.00 (*C*Me$_3$), 32.52 (C*Me*$_3$), 54.06 (OMe), 108.54 (C5 in C_5H_4), 109.78 (C2 in C_5H_4), 110.39 (C3 in C_5H_4), 110.64 (C4 in C_5H_4), 136.38 (C1 in C_5H_4). Anal. Calcd for $C_{38}H_{58}Lu_2O$: C, 51.82; H, 6.59; Lu, 39.77. Found: C, 51.87; H, 6.48; Lu, 39.65.

{(^{t}BuC$_5$H$_4$)$_2$Y(μ-OMe)}$_2$ (30). The synthesis was carried out similar to the preparation of compound **26** (method A), starting from 1.66 g (2.3 mmol) of **1** and 0.70 g (4.6 mmol) of $(MeO)_4Si$ in 50 mL toluene. Yield: 1.44 g (83%) of colorless crystals of **30**, mp 186−187 °C. ^{1}H NMR (benzene-*d*$_6$): δ 1.43 (s, 36H, ^{t}Bu), 3.32 (s, 6H, OMe), 6.17 (t, 8H, J = 2.9 Hz, H2,5 in C_5H_4), 6.47 (t, 8H, J = 2.8 Hz, H3,4 in C_5H_4). ^{13}C NMR (benzene-*d*$_6$): δ 30.16 (*C*Me$_3$), 32.61 (C*Me*$_3$), 54.28 (OMe), 109.76 (C2,5 in C_5H_4), 110.69 (C3,4 in C_5H_4), 138.26 (C1 in C_5H_4). Anal. Calcd for $C_{38}H_{58}Y_2O_2$: C, 62.90; H, 8.01; Y, 24.59. Found: C, 63.07; H, 8.10; Y, 24.51.

Dehydrogenative Coupling of ^{n}Bu$_3$SnH. A mixture of 2.80 mL (3.03 g, 10.4 mmol) of ^{n}Bu$_3$SnH and 70 mg (0.11 mmol) of **1** in 5 mL of benzene was stirred for 0.5 h at 70 °C. Vigorous gas evolution was observed. The reaction mixture was fractionated. This procedure yielded 2.75 g (91%) of hexabutylditin, bp 136−139 °C/0.5 mmHg, $n^{20}_D = 1.5133$. ^{13}C NMR ($CDCl_3$): δ 10.04 (C1), 27.57 (C3), 29.42 (C2), 30.74 (C4). Dehydrogenative coupling of Et_3SnH was carried out in a similar manner.

X-ray Crystal Analysis of Complex 2. X-ray data acquisition was accomplished with a single crystal of **2** packed in thin-walled glass capillary under argon. Crystallographic data are given in Table 3. An empirical absorption correction based on three Ψ scans was used to fit the data. The structure was solved using the heavy-atom technique and refined by the anisotropic least-squares procedure. Hydrogen atoms were located from the difference Fourier synthesis. All computations were run with the SHELXS-86 software package[70] on an IBM PC AT.

X-ray Crystal Analysis of Complex 28. Details of the X-ray experiment and crystallographic parameters are given

---

(70) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467−473.

Table 3. Crystallographic Data for Complexes 2 and 28

	2	**28**
formula	$C_{38}H_{58}Tb_2$	$C_{38}H_{55}Lu_2O$
fw	832.73	877.76
F(000)	1664	1732
space group	B_{bam}[a]	$C2/c$
a, Å	9.414(2)	18.621(3)
b, Å	16.456(2)	23.774(2)
c, Å	23.009(3)	9.140(1)
β, deg	90	118.032(1)
Z	16	4
V, Å^3	3564(1)	3571.5(6)
d (calcd), g·cm^{-3}	1.55	1.632
diffractometer	Enraf-Nonius CAD-4	Siemens SMART
radiation	Mo Kα ($\lambda = 0.710\ 73$ Å)	
μ, cm^{-1} (Mo Kα)	40.0	55.22
T, K	296	150
scan method	$\omega - 2\theta$	ω
θ limits (deg)	$2 \leq \theta \leq 25$	$1.51 \leq \theta \leq 25.50$
no. of unique reflns; total with $I_0 > 2\sigma(I)$	1191, 825	3304, 3060
no. of params refined	93	186
R[b]	0.0211	0.0574

[a] C_{mca} space group in the standard classification.

in Table 3. The experimental reflections were collected on a Siemens three-circle diffractometer with a CCD area detector. Experimental frames were integrated using a three-dimensional Lehman–Larsen algorithm. The structure was solved by the heavy-atom method. Both Lu atoms of the molecule are situated at the 2-fold axis. In the space group found ($C2/c$), the positions of metals resulted in disorder of the CH_3 and OMe bridges between the positions occupied. As a result, in the difference Fourier synthesis, three partly overlapping peaks of electron density were found in the area of the bridging groups. These peaks were included in further calculations as corresponding to oxygen and carbon atoms of the bridging groups with site occupation factors equal to 0.5. This structural model was refined in the anisotropic approximation for all non-hydrogen atoms except for those of the bridging groups. The bridging group atoms were refined isotropically. Hydrogen atoms of non-bridging groups were calculated in their ideal positions and included in the refinement as riding on the corresponding carbon atoms with B(iso) equal to 1.5B(eq) for the corresponding carbon atoms. An alternative possibility noncentrocymmetric space group (C_c) was also checked. However, disordered positions of the two bridging groups were found in this group as well. Moreover, least-squares refinement of the structure in the C_c space group resulted in nonpositive definition for many carbon atoms. These observations show that the first model is the correct one. In the difference Fourier synthesis, the highest electron density peaks are located in the vicinity of the heavy atoms. Their rather high value (Table 3) is probably due to the poor quality of the single crystal and the disorder, which results in partial superposition of three electron density peaks corresponding to the bridge group atoms. All the calculations were performed using the SHELXS-86[70] and SHELXL-93[71] software. The SHELXTL-Plus molecular graphics program[72] was used for drawing the molecule (a thermal ellipsoid probability equal to 0.5 was taken).

Computational Details. All quantum-chemical calculations were carried out with the use of the semiempirical ZINDO/1 method[54] implemented in the program package HyperChem release 4.0.[73] Assumptions were made in all cases that the forward and reverse reactions in eqs 17 and 18 proceed via the same four-centered transition states (the microreversability principle). Every transition state was supposed to be preceded and followed along the reaction coordinate by bimolecular encounter complexes, the energies of which in the gas phase were considered to be lower than those of the free reagents for both the forward and back reactions. Geometry optimization (RHF) for the lowest states of all complexes studied in vacuum was performed using either the Polak–Ribiere algorithm down to a gradient value of 0.01 kcal Å^{-1} mol^{-1} for the encounter complexes or the steepest descent algorithm down to the 0.1 kcal Å^{-1} mol^{-1} gradient value for the transition states. The transition states were identified following the procedures described in the Supporting Information. No restrictions were imposed on the geometry of the metallocene fragment. A separate study showed that the optimization down to the gradient 0.1 kcal Å^{-1} mol^{-1} is insufficient for finding out the true conformation of the metallocene fragment, the appropriate value being 0.02–0.03 kcal Å^{-1} mol^{-1}. However, the bond lengths and angles of the moiety involved in the bond transposition process as well as the total energy of the system turned out to be affected little by the further improvement of the geometry that is machine-time consuming. The orbital sketches for molecules and their fragments were drawn employing the possibilities provided by the software package HyperChem release 4.0.[73] The computations were performed with an IBM PC AT.

Acknowledgment. This work was generously supported by the Russian Foundation for Basic Research (Grant No. 95-03-09658). The authors thank the International Science Foundation (Grant No. MRR000) and this Foundation and Russian Government (Grant No. MRR300) for their support. We thank Dr. O. Just and Prof. Dr. H. Schumann from Technische Universität Berlin who performed the synthesis and kindly supplied us with a sample of $HGa(CH_2CH_2CH_2)_2NMe$. We are also grateful to Dr. E. B. Chuklanova and Dr. A. I. Gusev who carried out the X-ray diffraction study of **2**.

Supporting Information Available: Tables of positional and thermal parameters, bond lengths, bond angles, anisotropic displacement parameters, and hydrogen coordinates for **2** and **28**, text giving computational analysis data, calculation parameters, energies and gradient, atomic orbital electron populations, and net charges and coordinates for the corresponding encounter complexes and transition states as well as for H_2, CH_4, SiH_4, H_3CSiH_3, and Si_2H_6, and energy profile diagrams (75 pages). Ordering information is given on any current masthead page.

OM970363G

---

(71) Sheldrick, G. M. *SHELX93, Program for Refinement of Crystal Structure*; University of Göttingen: Göttingen, Germany, 1993.

(72) Sheldrick, G. M. *SHELXTL-Plus*, Release 4.1; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1991.

(73) *HyperChem Release 4 for Windows, Molecular Modeling System*; Hypercube, Inc., 1994.