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Articles

Dimeric Hydrido Complexes of Rare-Earth Metals Containing a Linked Amido−Cyclopentadienyl Ligand: Synthesis, Characterization, and Monomer−Dimer Equilibrium

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Dimeric hydrido complexes of lutetium, ytterbium, and yttrium containing a linked amido−cyclopentadienyl ligand, $[Ln(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCMe_2R)(L)(\mu\text{-}H)]_2$ (Ln = Lu, Yb, Y; R = Me, Et; L = THF, PMe_3), were synthesized and characterized by elemental analysis and ^1H, ^{13}C ^{29}Si, and ^{31}P NMR spectroscopy. A single-crystal X-ray diffraction study of $[Yb(\eta^5:\eta^1\text{-}C_5Me_4\text{-}SiMe_2NCMe_2Et)(THF)(\mu\text{-}H)]_2$ showed a homochiral dimeric structure with a trans configuration of the ancillary ligands, in analogy to the related yttrium complex. The PMe_3 adducts of lutetium and yttrium $[Ln(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(PMe_3)(\mu\text{-}H)]_2$ (Ln = Lu, Y) were prepared in low yields by substitution of THF with a large excess of PMe_3. Their crystal structures were determined and revealed a cisoid configuration of the linked amido−cyclopentadienyl ligands, isotypic with the scandium analogue previously described by Bercaw et al. On the NMR time scale fast dissociation of the Lewis base L is observed. Scrambling of the yttrium and lutetium hydrido complexes $[Ln(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(THF)(\mu\text{-}H)]_2$ (Ln = Lu, Y) in C_6D_6 gave a mixture containing the heterobimetallic species $[LuY(\eta^5:\eta^1\text{-}C_5\text{-}Me_4SiMe_2NCMe_3)_2(THF)_2(\mu\text{-}H)_2]$ within 5 min, indicating the presence of monomeric species in solution. Chloro hydrido complexes of yttrium, $[\{Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCMe_2R)(THF)\}_2\text{-}(\mu\text{-}H)(\mu\text{-}Cl)]$, were formed by scrambling the chloro complex with the hydrido complex for 3 h. The dimeric chloro complexes $[Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCMe_2R)(THF)(\mu\text{-}Cl)]_2$ could be synthesized by reacting in situ formed "$Y(CH_2SiMe_3)_2Cl(THF)_n$" with the amino−cyclopentadiene $(C_5Me_4H)SiMe_2NHCMe_2R$ in a σ-bond metathesis. Single-crystal X-ray diffraction studies showed the chloro complex $[Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCMe_2Et)(THF)(\mu\text{-}Cl)]_2$ to adopt a trans configuration of the ancillary ligands as a heterochiral dimer, whereas the chloro hydrido $[\{Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCMe_2Et)(THF)\}_2(\mu\text{-}H)(\mu\text{-}Cl)]$ was found to be a homochiral dimer.

Introduction

In contrast to the well-developed chemistry of rare-earth metallocene hydrides,[1,2] the development of mono(cyclopentadienyl)lanthanide hydrido complexes has been relatively slow, despite their relevance to polymerization catalysis.[3,4] The few reports in the literature, however, hint at their potential: Schaverien described the mono(pentamethylcyclopentadienyl)yttrium complexes $[Y(\eta^5\text{-}C_5Me_5)(OC_6H_3{}^tBu_2\text{-}2,6)(\mu\text{-}H)]_2$ as ethylene polymerization catalysts,[3,5] while Bercaw et al. reported living α-olefin polymerization catalysts based on a scandium hydrido complex supported by a linked amido−cyclopentadienyl ligand $[Sc(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)\text{-}(PMe_3)(\mu\text{-}H)]_2$.[6] We have been investigating the possibility of utilizing the latter type of ancillary ligand[7] to other rare-earth elements[8] and found that the yttrium hydrido complexes $[Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCMe_2R)(THF)\text{-}(\mu\text{-}H)]_2$ (R = Me, Et) can be prepared rather straightforwardly by hydrogenolysis of the alkyl complex $[Y(\eta^5\text{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_2R)(CH_2SiMe_3)(THF)]$.[9] More recently, Piers et al.[10] and Marks et al.[11] have described the synthesis of a limited number of alkyl and amido complexes $[Ln(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)X]$ (X = $N(SiMe_3)_2$, M = Y, Nd, Sm, Lu; X = $CH(SiMe_3)_2$ M = Yb, Lu). Some of them exhibit high catalytic activity in the intramolecular hydroamination reaction of α,ω-ami-

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noolefins. We describe here further extension of our work on the use of linked amido–cyclopentadienyl ligands to lutetium and ytterbium as well as structural studies on new hydrido complexes of yttrium.

Results and Discussion

Hydrido Complexes of Lutetium and Ytterbium. When the tris((trimethylsilyl)methyl) complexes of lutetium and ytterbium [Ln(CH_2SiMe_3)$_3$(THF)$_2$] (Ln = Lu, Yb)[12] were treated in pentane solution with 1 equiv of (C_5Me_4H)$SiMe_2NHCMe_2R$ (R = Me, Et) at 0 °C, the new complexes [Ln(η^5:η^1-$C_5Me_4SiMe_2NCMe_2R$)(CH_2SiMe_3)(THF)] were formed and the *tert*-butyl amido derivatives (R = Me: Ln = Lu, **1a**; Ln = Yb, **2a**) were isolated as colorless (**1a**) and orange crystals (**2a**) in good yields (Scheme 1). The lutetium complex **1a** was fully characterized, and its variable-temperature ^1H NMR spectra were analyzed with respect to the dissociation of THF. As was found for the crystallographically characterized yttrium complex [Y(η^5:η^1-$C_5Me_4SiMe_2NCMe_2Et$)(CH_2SiMe_3)(THF)],[9b] the compound is engaged in a fast dissociative equilibrium with the pseudo-three-coordinate, THF-free system. This behavior results in the apparent C_s symmetry above 25 °C, whereas at the low-temperature limit a chiral structure is observed. Thus, the ^1H NMR spectrum at −80 °C exhibits an AB spin pattern at −1.02 ppm with $^2J_{HH} = 16$ Hz for the CH_2 group, two singlets for the $SiMe_2$ group, and four singlets for the C_5Me_4 group. The thermodynamic parameters $\Delta H_r = 26 \pm 1$ kJ mol^{-1} and $\Delta S_r = 57 \pm 4$ J K^{-1} mol^{-1} were determined for the lutetium complex **1a** from the plot of ln K_{diss} versus $1/T$. The equilibrium constants K_{diss} were obtained from the temperature-dependent chemical shifts of the α- and β-CH_2 groups on the THF ligand. Although the thermodynamic parameters are similar to those of the analogous yttrium complex ($\Delta H_r = 24 \pm 3$ kJ mol^{-1} and $\Delta S_r = 61 \pm 12$ J K^{-1}mol^{-1}),[9b] the coalescence behavior of the ^1H NMR signals is significantly different. The activation energy was found to be $\Delta G^{\ddagger} = 62.32$ kJ mol^{-1} ($\Delta\nu = 19.96$ Hz,

Scheme 1

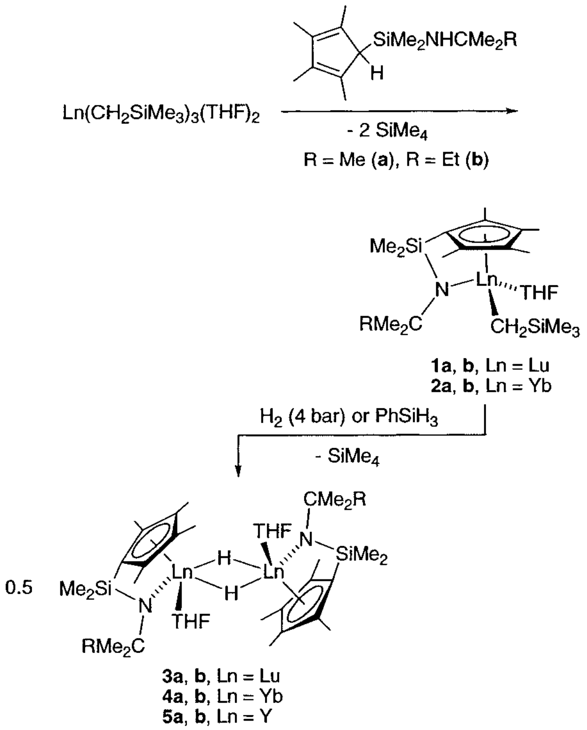

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Table 1. Experimental Data for the Crystal Structure Determination of the Complexes 4b, 6a, 7a, and 8b

	4b	**6a**	**7a**	**8b**
		Crystal Data		
empirical formula	$C_{40}H_{76}N_2O_2Si_2Yb_2$	$C_{36}H_{74}N_2P_2Si_2Lu_2\cdot C_5H_{12}$	$C_{36}H_{74}N_2P_2Si_2Y_2\cdot 0.5C_6H_6\cdot 0.5C_5H_{12}$	$C_{40}H_{74}Cl_2N_2O_2Si_2Y_2$
fw	1019.29	1075.18	906.04	919.91
cryst color	red	colorless	colorless	colorless
cryst size, mm	1.05 × 0.75 × 0.30	0.67 × 0.57 × 0.43	0.68 × 0.63 × 0.28	0.58 × 0.32 × 0.29
cryst system	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/n$ (No. 14)	$C2/c$ (No. 15)	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)
a ,Å	14.319(2)	22.652(2)	23.046(4)	11.113(3)
b, Å	16.672(2)	11.4742(9)	11.446(2)	15.464(4)
c, Å	20.414 (4)	21.641(2)	24.107(6)	15.720(3)
α, deg	90	90	90	61.43(2)
β, deg	109.21(1)	114.90(1)	125.09(1)	81.28(2)
γ, deg	90	90	90	89.07(2)
V, Å^3	4602(1)	5101.9(8)	5203(2)	2340(1)
Z	4	8/2	8/2	2
ρ_{calcd}, g cm^{-3}	1.471	1.400	1.157	1.305
μ, mm^{-1}	4.123	3.983	2.353	2.665
$F(000)$	2056	2184	1928	968
		Data Collection		
$2\theta_{max}$, deg	60	56	54	56
index ranges				
h	0−20	−30 to +30	−22 to +29	−14 to +10
k	−23 to +23	−15 to +15	0−14	−20 to +20
l	−28 to +26	−28 to +28	−30 to +25	−20 to +20
		Solution and Refinement		
no. of rflns measd	27 113	22 725	7734	16 933
no. of indep rflns	13 304 (R_{int} = 0.045)	6293 (R_{int} = 0.051)	5678 (R_{int} = 0.056)	11 246 (R_{int} = 0.034)
no. of obsd rflns	8153 ($I > 2\sigma(I)$)	4888 ($I > 2\sigma(I)$)	3107 ($I > 2\sigma(I)$)	6313 ($I > 2\sigma(I)$)
no. of parameters	459	232	244	469
GOF	1.052	1.088	1.141	1.141
final R indices R1/wR2 (obsd data)	0.0553/0.1236	0.0347/0.0796	0.0669/0.1317	0.0644/0.1083
final R indices R1/wR2 (all data)	0.1042/0.1615	0.0518/0.0881	0.1545/0.1838	0.1512/0.1505
largest e(max)/e(min), e Å^{-3}	3.474/−2.354	1.307/−1.022	1.124/−0.566	0.895/−0.463

T_c = 20 °C for the $SiMe_2$ signals) for **1a**, whereas for the yttrium analogue of **1a** [Y(η^5:η^1-$C_5Me_4SiMe_2NCMe_3$)(CH_2SiMe_3)(THF)] a value of $\Delta G^{\ddagger} = 40.50$ kJ mol^{-1} ($\Delta\nu = 69.24$ Hz, $T_c = -70$ °C) can be estimated.[13] The thermal instability of the lutetium complex is similar to that of the yttrium complex.

Both the lutetium and ytterbium alkyl complexes **1** and **2** were subjected to hydrogenolysis with dihydrogen (4 bar) or with phenylsilane[14] (which is more convenient on smaller scales) in pentane at room temperature to give the dimeric hydrides [Ln(η^5:η^1-$C_5Me_4SiMe_2NCMe_2R$)(THF)(μ-H)]$_2$ (Ln = Lu, **3a**,**b**; Ln = Yb, **4a**,**b**) in good yields. Because of the thermal instability of the alkyl complexes **1** and **2**, it proved advantageous to prepare the hydride complexes in a one-pot procedure without isolating the alkyl complexes. The hydrido complexes are sparingly soluble in saturated hydrocarbons but are soluble in aromatic and ethereal solvents. The structure of the paramagnetic ytterbium complex **4b** was studied by single-crystal X-ray diffraction (Table 1) and shown to be similar to the yttrium complex **5a** reported previously.[9] Figure 1 shows an ORTEP diagram of the ytterbium complex **4b** in the solid state. The crystal contains racemic pairs of the C_2-symmetric homochiral dimers, which appear to crystallize preferably over the other possible configurations shown in Chart 1.[15] Thus, the two linked amido−cyclopentadienyl ytterbium fragments are connected by a Yb_2H_2 core in a trans fashion. The bond distances,[16] except those for the ytterbium hydrogen bonds, are slightly shorter than those in the yttrium complex **5a**, reflecting the decrease by 4% in the ionic radii.[17] The metal-to-metal distance of 3.5927(7) Å in **4b** is significantly shorter than that in **5a** (3.672(1) Å).

The variable-temperature NMR spectra of the lutetium complex **3a** reveal a signal for the hydride ligand at 9.90 ppm (60 °C, toluene-d_8). No coupling to the lutetium ($I = {}^7/_2$) is observed, in agreement with the

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[13] For Y(η^5:η^1-$C_5Me_4SiMe_2NCMe_3$)(CH_2SiMe_3)(THF) decoalescence can be only observed for the $SiMe_2$ signals.

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[15] The dimers can be regarded as generated by dimerization of chiral square-pyramidal half-sandwich complexes of the general type $M(C_5R_5)XX'_2L$; see: von Zelewsky, A. *Stereochemistry of Coordination Compounds*; Wiley: Chichester, U.K., 1996; p 78.

[16] (a) [Yb_2{μ-(C_5H_4)$SiMe_2$(C_5H_4)}$_2$(μ-Cl)(μ-H)(THF)$_2$]: Yb−H = 1.90, 2.10 Å, Yb−O = 2.423, 2.432 Å. See: Qiao, K.; Fischer, R. D.; Paolucci, G. *J. Organomet. Chem.* **1993**, *456*, 185. (b) [Yb{$NHC_6H_3{}^i$-Pr_2}(THF)$_2$]: Yb−N = 2.171, 2.200, 2.141 Å, Yb−O = 2.354, 2.320 Å. See: Evans, W. J.; Ansari, M. A.; Ziller, J. W.; Khan, S. I. *Inorg. Chem.* **1996**, *35*, 5435. (c) [Yb(bipy)$_2$(DME)$_2$I]: Yb−N = 2.44, 2.45 Å. See: Petrovskaya, T. V.; Fedushkin, I. L.; Nevodchikov, V. I.; Bochkarev, M. N.; Borodina, N. V.; Eremenko, I. L.; Nefedov, S. E. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1998**, 2341. (d) [Yb{CH(NC_6H_{11})$_2$(N($SiMe_3$)$_2$)}$_2$-{N($SiMe_3$)$_2$}]: Yb−N = 2.329, 2.312, 2.343, 2.301, 2.329 Å. See: Zhou, Y.; Yap, G. P. A.; Richeson, D. S. *Organometallics* **1998**, *17*, 4387. (e) [Yb{N($SiMe_3$)$_2$}$_2$(THF)(μ-Cl)]$_2$: Yb−N = 2.198, 2.174 Å, Yb−O = 2.351 Å. See: Aspinall, H. C.; Bradley, D. C.; Hursthouse, M. B.; Sales, K. D.; Walker, N. P. C.; Hussain, B. *J. Chem. Soc., Dalton Trans.* **1989**, 626. (f) [Yb(C_5H_4Me)$_2$(μ-NH_2)]$_2$: Yb−N = 2.322, 2.286 Å. See: Hammel, A.; Weidlein, J. *J. Organomet. Chem.* **1990**, *388*, 75. (g) [Yb(C_5H_5)Br_2-(THF)$_3$]: Yb−O = 2.336, 2.427, 2.348 Å. See: Deacon, G. B.; Fallon, G. D.; Wilkinson, D. L. *J. Organomet. Chem.* **1985**, *293*, 45. (h) [Yb-(C_5H_5)$_2$(Me)(THF)]: Yb−O = 2.311 Å. See: Evans, W. J.; Dominguez, R.; Hanusa, T. P. *Organometallics* **1986**, *5*, 263.

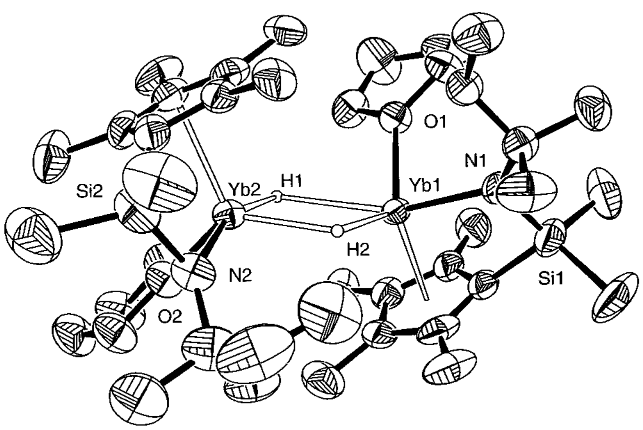
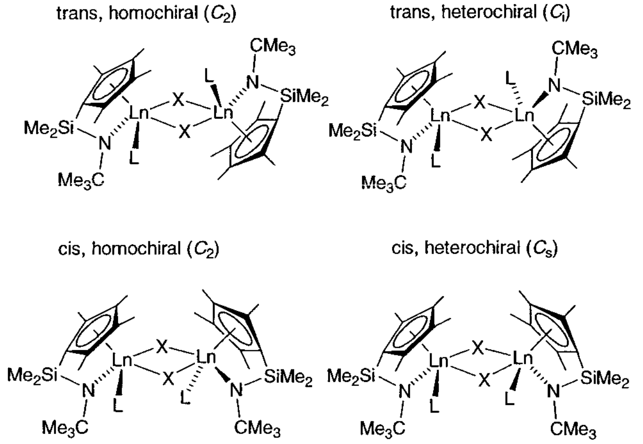


Figure 1. ORTEP diagram of the molecular structure of **4b**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms, except for the two bridging hydrides, are omitted for the sake of clarity. Selected bond lengths (Å) and bond angles (deg): Yb1−H1 = 2.57(5), Yb1−H2 = 2.16(9), Yb2−H1 = 2.50(5), Yb2−H2 = 2.13(9), $\mathrm{Cp_{Cent}}$1−Yb1 = 2.33(1), $\mathrm{Cp_{Cent}}$2−Yb2 = 2.32(1), Yb1−N1 = 2.231(7), Yb2−N2 = 2.197(8), Yb1−O1 = 2.323(6), Yb2−O2 = 2.357(6), Yb1···Yb2 = 3.5927(7); Yb1−H1−Yb2 = 90(1), Yb1−H2−Yb2 = 114(4), H1−Yb1−H2 = 77(3), H1−Yb2−H2 = 79(3), $\mathrm{Cp_{Cent}}$1−Yb1−N1 = 99(1), $\mathrm{Cp_{Cent}}$1−Yb1−O1 = 111(1), $\mathrm{Cp_{Cent}}$1−Yb1−H1 = 101(2), $\mathrm{Cp_{Cent}}$1−Yb1−H2 = 117(2), N1−Yb1−O1 = 94.1(3), N1−Yb1−H1 = 159(1), N1−Yb1−H2 = 98(2), $\mathrm{Cp_{Cent}}$2−Yb2−N2 = 99(1), $\mathrm{Cp_{Cent}}$2−Yb2−O2 = 113(1), $\mathrm{Cp_{Cent}}$2−Yb2−H1 = 101(2), $\mathrm{Cp_{Cent}}$2−Yb2−H2 = 120(2), N2−Yb2−O2 = 95.4(3), N2−Yb2−H1 = 160(1), N2−Yb2−H2 = 94(2).

Chart 1



literature on lutetium hydrides.[18] These chemical shift values are shifted to remarkably lower field. Resonances for other lutetium hydrides are reported in the region of 5−6 ppm, except when base-free or mononuclear compounds are studied (Table 2).

As was described for the yttrium complex **5a**,[9] a relatively complicated dynamic behavior is observed for the lutetium analogue **3a** which includes the fast dissociation of the THF ligands, possibly from both the dimer and the monomer.[19] Furthermore, a second isomer is observed at lower temperatures (Lu−H resonances at 9.63 and 10.01 ppm for the major and minor diastereomers, respectively). We suspect that the THF dissociation is sufficiently slowed below −40 °C. This leads to the formation of either the C_i-symmetric heterochiral diastereomer or a structure with linked amido−cyclopentadienyl ligands that have a cisoidal arrangement. Presumably the major isomer has the same structure as that in the crystalline state. From the temperature-dependent values of the equilibrium constants, thermodynamic parameters for the interchange can be estimated as $\Delta H_r = 10 \pm 1$ kJ mol^{-1} and $\Delta S_r = 23 \pm 4$ J K^{-1} mol^{-1}.

When the dimeric lutetium and yttrium hydrides **3a** and **5a** are treated with excess PMe_3, exchange against THF occurs (Scheme 2). The adduct can only be isolated in a pure state (by crystallization) when solutions containing at least a 30-fold excess of PMe_3 are used. It appears that the equilibrium constant at room temperature is close to unity. For the lutetium complex **6a** (but not for the yttrium derivative **7a**) hydrogenolysis of the alkyl **1a** in the presence of PMe_3 was also feasible. The X-ray crystallography showed that both the lutetium and yttrium complexes **6a** and **7a** adopt the C_2-symmetric homochiral structure with a cisoid arrangement of the ancillary ligands which crystallize in arrangements isotypic with that observed for the scandium complex.[6] Figure 2 shows an ORTEP diagram of the lutetium complex **6a**. It seems that at least within this series containing the metals scandium, lutetium, and yttrium it is the nature of the Lewis base rather than the size of the metal center (ionic radii[17] for coordination number 8: Sc, 0.870; Lu, 0.977; Y, 1.019) that determines the configuration. Table 3 summarizes the pertinent metrical parameters for the three analogous hydrides $[\mathrm{Ln}(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(PMe_3)(\mu\text{-}H)]_2$ (Ln = Sc, Lu (**6a**), Y (**7a**)). Most notably, the metal−phosphorus bond distance is larger than expected for the smallest metal scandium within this series, indicative of a significant metal−ligand repulsion. The NMR spectroscopic features for the PMe_3 adducts are consistent with this finding. Whereas $[\mathrm{Sc}(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(PMe_3)(\mu\text{-}H)]_2$ was reported to be a single species over the temperature range of −80 to 25 °C according to ^1H NMR spectroscopy (although the ^{31}P NMR spectrum showed two signals at −66 °C in a 4:1 ratio),[6] the PMe_3 ligands in the lutetium and yttrium complexes **6a** and **7a** are tightly bonded to the metal on the ^1H NMR time scale below −40 and −30 °C, respectively. The hydride resonance appears as a singlet at 10.44 ppm at −60 °C for **6a**; the corresponding resonance for **7a** is observed at 5.59 ppm as a higher order spin pattern. In the ^{31}P NMR spectrum at −60 °C the lutetium complex **6a** gives rise to a signal at −28.1 ppm, whereas

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(17) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *32*, 751. For coordination number 8: Sc, 0.870 Å, Lu, 0.977 Å, Y, 1.019 Å Yb, 0.985 Å. For coordination number 6: Sc, 0.745 Å, Lu, 0.861 Å, Y, 0.900 Å, Yb, 0.868 Å.

(18) (a) Xie, Z.; Qian, C.; Huang, Y. *J. Organomet. Chem.* **1991**, *412*, 61. (b) Stern, D.; Sabat, M.; Marks, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 9558. (c) Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091. (d) Roesky, P. W.; Denninger, U.; Stern, C. L.; Marks, T. J. *Organometallics* **1997**, *16*, 4486. (e) Jeske, G.; Schock, L. E.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8103. (f) Moussavi, M.; De Cian, A.; Fischer, J.; Weiss, R. *Inorg. Chem.* **1988**, *27*, 1287.

(19) (a) A rotationally flexible singly hydride bridged intermediate is also conceivable, as in the decamethyllutetocene hydride.[2d] (b) In principle the bridging hydrides in the dimers with the trans homochiral and cis heterochiral configuration are inequivalent. However, we have not been able to observe this inequivalency in the ^1H NMR spectra (or in the ^{89}Y NMR spectra for the yttrium analog) down to −80 °C. This observation may indicate the presence of only trans heterochiral and cis homochiral dimers with equivalent hydrides in solution, or what is more likely, there is an additional fluxional process which results in the exchange of the hydrides with a low activation barrier.

Table 2. Chemical Shifts of Dimeric Lutetium Hydrido Complexes in ^{1}H NMR Spectra at Room Temperature

compd	δ (ppm)	ref
$[Lu(\eta^5\text{-}C_5H_4{}^tBu)_2(\mu\text{-}H)]_2$	5.91[a]	14
$[Lu(\eta^5\text{-}C_5H_4SiMe_3)_2(\mu\text{-}H)]_2$	5.80[a]	14
$[Lu(\eta^5\text{-}C_5H_5)_2(THF)(\mu\text{-}H)]_2$	4.72[b]	2i
$[Lu\{(\eta^5\text{-}C_5H_4)(CH_2)_3(\eta^5\text{-}C_5H_4)\}(THF)(\mu\text{-}H)]_2$	4.02[b]	2p
$[Lu\{(\eta^5\text{-}C_5H_4)(CH_2)_2O(CH_2)_2(\eta^5\text{-}C_5H_4)\}(\mu\text{-}H)]_2$	4.50[b]	18a
$[Lu\{\mu\text{-}(\eta^5\text{-}C_5Me_4)SiMe_2(\eta^5\text{-}C_5H_4)\}(\mu\text{-}H)]_2$	5.92[a]	18b
$[Lu\{\mu\text{-}(\eta^5\text{-}C_5Me_4)SiEt_2(\eta^5\text{-}C_5H_4)\}(\mu\text{-}H)]_2$	5.87[a]	18c
$[(R,S)\text{-}Me_2Si(\eta^5\text{-}C_5H_3{}^tBu)\{(+)\text{-}\eta^5\text{-}C_5H_3(neomenthyl)\}LuH]_2$	6.89[a]	18d
$[Lu(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}H)]_2$	9.11[c]	2i
$Lu(pc)_2H$[f]	9.0[d]	18f
$[Lu(\eta^5\text{-}C_5Me_4)SiMe_2(\eta^5\text{-}C_5Me_4)(\mu\text{-}H)]_2$	9.25[e]	18e
3a	9.63[e] (−60 °C) 9.90[e] (60 °C)	this work
3b	9.66[e]	this work
5a	10.48[a]	this work
$[LuY(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)_2(THF)_2(\mu\text{-}H)_2]$	8.00[a] (60 °C)	this work

[a] In C_6D_6. [b] In THF-d_8. [c] In cyclohexane-d_{12}. [d] In DMSO-d_6. [e] In toluene-d_8. [f] Pc = phthalocyaninato-N,N',N'',N'''.

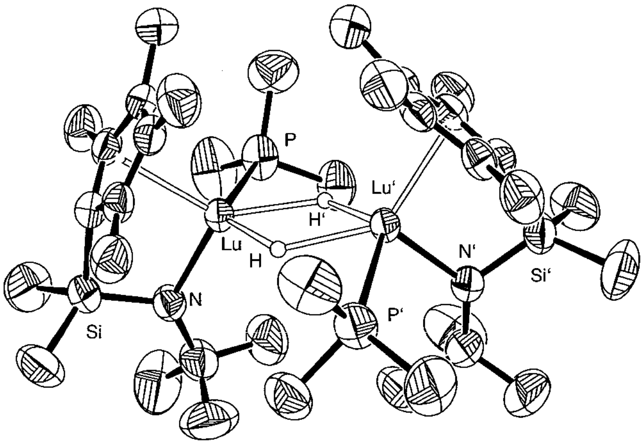

Figure 2. ORTEP diagram of the molecular structure of **6a**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms, except for the two bridging hydrides, are omitted for the sake of clarity. Selected bond lengths (Å) and bond angles (deg): Lu−H = 1.93(6), Lu−H′ = 2.10(6), Cp_{Cent}−Lu = 2.321(4), Lu−N = 2.177(4), Lu−P = 2.928(1), Lu···Lu′ = 3.5859(5); Lu−H−Lu′ = 125(3), H−Lu−H′ = 54(3), Cp_{Cent}−Lu−N = 98.8(2), Cp_{Cent}−Lu−P = 111.9(1), Cp_{Cent}−Lu−H = 134(2), Cp_{Cent}−Lu−H′ = 109(2), N−Lu−P = 97.7(1), N−Lu−H = 126(1), N−Lu−H′ = 106(1).

Scheme 2

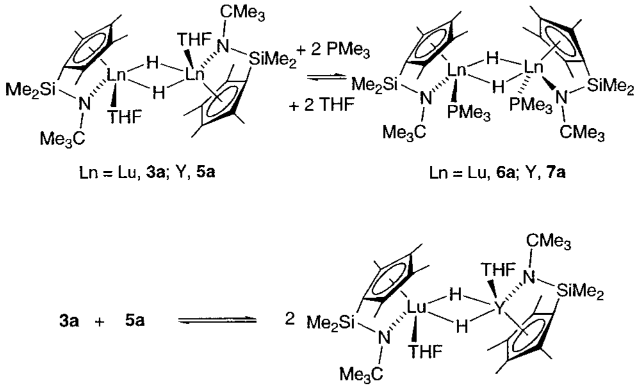

Table 3. Geometrical Parameters (Å or deg) for the Three Isotypical Hydride Complexes $[Ln(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(PMe_3)(\mu\text{-}H)]_2$ (Ln = Sc, Lu, Y)

Ln	Sc[a]	Lu (**6a**)	Y (**7a**)
Ln−Ln	3.315	3.5859(5)	3.703(1)
Ln−H	1.97(3), 1.98(3)	1.93(6), 2.10(6)	2.25(6), 2.28(6)
Ln−N	2.058(3)	2.177(4)	2.221(5)
Ln−Cp_{cent}	2.216(3)	2.321(4)	2.358(4)
Ln−P	2.996(1)	2.928(1)	2.996(2)
Cp_{cent}−Ln−Ln′−Cp_{cent}′	54	56	56
P−Ln−Ln−P	165	166	167

[a] Reference 6.

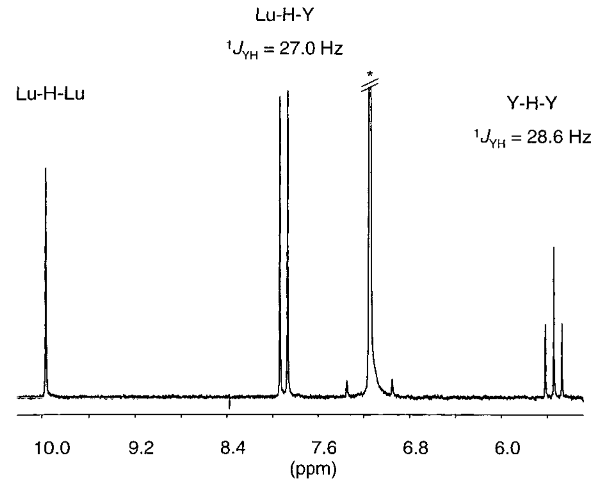

Figure 3. ^{1}H NMR spectrum of a 1:1 reaction mixture of **3a** with **5a** in C_6D_6 at 60 °C after 5 min (the asterisk denotes C_6D_5H).

two doublets in a 2:3 ratio at −42.5 ppm ($^1J_{YP}$ = 85.2 Hz) and −42.4 ppm ($^1J_{YP}$ = 64.3 Hz)[20] are recorded for the yttrium complex **7a**, consistent with the presence of two diastereomers at lower temperatures.

The presence of a monomer−dimer equilibrium on the chemical time scale could be corroborated by mixing equimolar amounts of the lutetium and yttrium hydrido complexes **3a** and **5a** in C_6D_6. Within 5 min after mixing, the formation of a statistical 1:2:1 mixture containing the three complexes **3a**, **5a**, and $[LuY(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)_2(THF)_2(\mu\text{-}H)_2]$ is observed (Figure 3). The heterobimetallic complex shows a diagnostic doublet for the hydride at δ 7.80 ppm with $^1J_{YH}$ = 27.0

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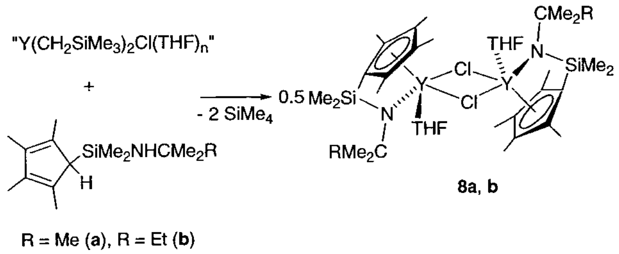
(20) For rare examples of $^1J_{YP}$ values, see: (a) Fryzuk, M. D.; Haddad, T. S.; Rettig, S. J. *Organometallics* **1991**, *10*, 2026. (b) Fryzuk, M. D.; Haddad, T. S.; Rettig, S. J. *Organometallics* **1992**, *11*, 2967.

Scheme 3



8a, b

Hz, whereas the lutetium hydride shows a singlet and the yttrium hydride is revealed as a triplet ($^1J_{\mathrm{YH}} = 28.6$ Hz).[21] The high rate of scrambling observed here is in stark contrast to that reported (weeks at 25 °C in C_6D_6) for the metallocenes $[\mathrm{Ln}(\eta^5\text{-}C_5R_5)_2(\mu\text{-H})_2]_2$ (Ln = Lu, Y).[14a]

Chloro-Bridged Complexes of Yttrium. In the course of upscaling the synthesis of the yttrium hydrido complex **5a**,**b**, we occasionally observed the presence of another dimeric yttrium hydride with a diagnostic triplet at around 4.8 ppm with $^1J_{\mathrm{YH}} = 32$ Hz. Initially we ascribed this species to a μ-hydroxo complex which would be formed by hydrolysis due to the possible influence of adventitious moisture. However, careful experimentation showed that this new hydride is the μ-chloro μ-hydrido complex $[\{\mathrm{Y}(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_2R)(THF)\}_2(\mu\text{-H})(\mu\text{-Cl})]$ (**9a**,**b**) which is formed by ligand comproportionation of the hydrido complexes **5a**,**b** with the chloro complexes **8a**,**b**. The chloro complexes **8a**,**b** were found to form when the tris((trimethylsilyl)methyl) complex is contaminated by what appears to be a mixed alkyl chloro complex of formal composition "$\mathrm{YCl(CH_2SiMe_3)_2(THF)}_n$". When the reaction of $\mathrm{YCl_3(THF)_{3.5}}$ with $\mathrm{LiCH_2SiMe_3}$ is performed in a stoichiometric ratio of 1:2 instead of 1:3, this species appears to be formed virtually exclusively.[22] It readily undergoes σ-bond metathesis with the amino–cyclopentadiene $\mathrm{(C_5Me_4H)SiMe_2NHCMe_2R}$ to give the chloro complex **8a**,**b** in good, reproducible yields (Scheme 3). We subsequently found that the reaction of the hydrides with *p*-chlorostyrene gives the chloro complexes.[23] ^{1}H and ^{13}C NMR spectroscopic data as well as elemental analysis confirm the structure. The THF ligands are labile, as can be judged from the strongly temperature-dependent signals for the α- and β-CH_2 groups. Below −45 °C, the expected loss of an apparent plane of symmetry is observed. Single-crystal X-ray structure analysis of the *tert*-pentyl amido derivative **8b** revealed a C_i-symmetric structure (Figure 4), which can be regarded as the heterochiral dimer, according to the classification in Chart 1. The metrical features of the Y_2Cl_2 core (Y1−Cl1 = 2.713(2) Å, Y1−Cl1′ = 2.760(2) Å; Y1−Cl1−Y1′ = 105.33(6)°, Cl1−Y1−Cl1′ = 74.67(6)°) are within the expected range of other chloro-bridged yttrium complexes,[24] as are the yttrium−nitrogen (Y1−N1 = 2.238(4) Å)[9,10a,25] and oxygen (Y1−O1 = 2.414(4) Å)[9,26] bond distances.

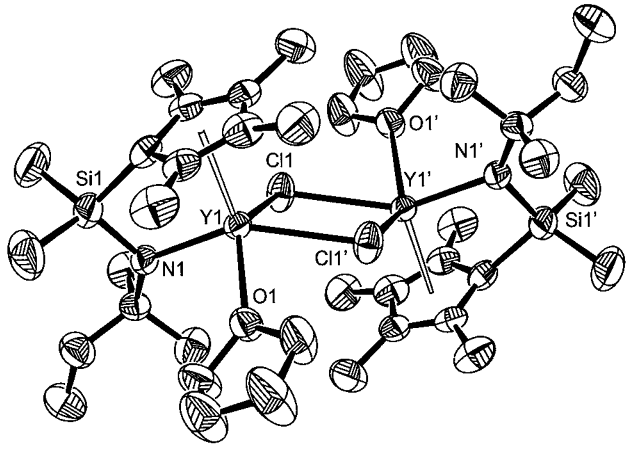


Figure 4. ORTEP diagram of the molecular structure of **8b**. One of the two independent molecules is shown. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for the sake of clarity. Selected bond lengths (Å) and bond angles (deg): Y1−Cl1 = 2.713(2), Y1−Cl1′ = 2.760(2), Y1−N1 = 2.238(4), Y1−O1 = 2.414(4), $\mathrm{Cp_{Cent}}$1−Y1 = 2.327(6), Y1···Y1′ = 4.352(2); Y1−Cl1−Y1′ = 105.33(6), Cl1−Y1−Cl1′ = 74.67(6), N1−Y1−Cl1 = 95.4(1), O1−Y1−N1 = 91.5(2), $\mathrm{Cp_{Cent}}$1−Y1−N1 = 97.3(2), $\mathrm{Cp_{Cent}}$1−Y1−O1 = 109.7(2), $\mathrm{Cp_{Cent}}$1−Y1−Cl1 = 111.4(2), $\mathrm{Cp_{Cent}}$1−Y1−Cl1′ = 113.1(2), O1−Y1−Cl1 = 137.0(1).

When a double-crossover experiment involving mixing the hydride **5a** and the chloro complex **8b** was per-

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[21] In the absence of kinetic studies, we cannot exclude the possibility that scrambling occurs via the dimers themselves without complete dissociation into mononuclear units.

[22] The reaction of $\mathrm{LiCH_2SiMe_3}$ with lanthanide trichloride is further complicated by ate complex formation: Evans, W. E.; Shreeve, J. L.; Broomhall-Dillard, R. N. R.; Ziller, J. W. *J. Organomet. Chem.* **1995**, *501*, 7.

[23] The inability of chlorobenzene to react with the hydrides **5a**,**b** makes us believe that the intermediate styrene insertion product $[\mathrm{Y}(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_2R)(THF)\{CH(CH_3)C_6H_4Cl\text{-}4]$ undergoes chlorination.[9b]

[24] (a) $[(C_5H_4SiMe_3)_2Y(\mu\text{-Cl})]_2$: Y−Cl = 2.684(1), 2.704(1) Å. See: Evans, W. J.; Sollberger, M. S.; Shreeve, J. L.; Olofson, J. M.; Hain, J. H. J.; Ziller, J. W. *Inorg. Chem.* **1992**, *31*, 2492. (b) $[(C_5H_4PPh_2)_2Y(\mu\text{-Cl})]_2$: Y−Cl = 2.655(2), 2.699(2) Å. See: Broussier, R.; Delmas, G.; Perron, P.; Gautheron, B.; Petersen, J. L. *J. Organomet. Chem.* **1996**, *511*, 185. (c) $\mathrm{Cp^*_2Y(\mu\text{-Cl})YClCp^*_2}$: Y−Cl = 2.620(3) Å, Y−Cl(terminal) = 2.575(3) Å. See: Evans, W. J.; Peterson, T. T.; Rausch, M. D.; Hunter, W. E.; Zhang, H.; Atwood, J. L. *Organometallics* **1985**, *4*, 554. (d) $[\mathrm{Y\{N(SiMe_2CH_2PMe_2)_2\}(\eta^3\text{-}C_3H_5)(\mu\text{-Cl})}]_2$: Y−Cl = 2.746(1), 2.795(1) Å. See ref 20b. (e) $\mathrm{YCl_3(THF)_2}$: Y−Cl = 2.718(2), 2.739(2) Å, Y−Cl(terminal) = 2.579(6) Å. See: Sobota, P.; Utko, J.; Szafert, S. *Inorg. Chem.* **1994**, *33*, 5203. (f) $\{[(^i\mathrm{Pr})_2\mathrm{ATI}]\mathrm{YCl_2}\}_2$: Y−Cl = 2.783(2) Å, Y−Cl(terminal) = 2.610(1) Å. See: Roesky, P. W. *Chem. Ber./Recl.* **1997**, *130*, 859. (g) $\mathrm{Cp^*_2YCl(THF)}$: Y−Cl = 2.577(3), 2.579(3) Å. See: Evans, W. J.; Grate, J. W.; Levan, K. R.; Bloom, I.; Peterson, T. T.; Doedens, R. J.; Zhang, H.; Atwood, J. L. *Inorg. Chem.* **1986**, *25*, 3614. (h) $\mathrm{CpYCl_2(THF)_3}$: Y−Cl = 2.625(7), 2.630(8) Å. See: Zhou, X.; Wu, Z.; Ma, H.; Xu, Z.; You, X. *Polyhedron* **1994**, *13*, 375.

[25] (a) $\mathrm{Cp^*_2YN(SiMe_3)_2}$: Y−N = 2.274(5), 2.253(5) Å. See: den Haan, K. H.; de Boer, J. L.; Teuben, J. H.; Spek, A. L.; Kojic-Prodic, B.; Hays, G. R.; Huis, R. *Organometallics* **1986**, *5*, 1726. (b) $(\eta^5\text{-}C_5Me_4Et)_2YN(SiMe_3)_2$: Y−N = 2.276(3) Å. See: Schumann, H.; Rosenthal, E. C. E.; Kociok-Köhn, G.; Molander, G. A.; Winterfeld, J. *J. Organomet. Chem.* **1995**, *496*, 233. (c) (*R*)-$\{\mathrm{Me_2Si(C_5Me_4)}[(-)\text{-menthylCp}]\}\mathrm{YN(SiMe_3)_2}$: Y−N = 2.281(8), 2.211(8) Å. See: Giardello, M. A.; Conticello, V. P.; Brard, L.; Sabat, M.; Rheingold, A. L.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10212. (d) *rac*-$\{(\eta^5\text{-}C_9H_5\text{-2-Me})_2SiMe_2\}YN(SiHMe_2)_2$: Y−N = 2.237(4) Å. See: Herrmann, W. A.; Eppinger, J.; Spiegel, M.; Runte, O.; Anwander, R. *Organometallics* **1997**, *9*, 11813.

[26] (a) $[(C_5H_4Me)_2Y(THF)(\mu\text{-H})]_2$: Y−O = 2.460(8) Å. See: Evans, W. J.; Meadows, J. H.; Wayda, A. L.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 2008. (b) $[(C_5H_3Me_2)_2Y(THF)(\mu\text{-H})]_2$: Y−O = 2.491(5) Å. See: Evans, W. J.; Drummond, D. K.; Hanusa, T. P.; Doedens, R. J. *Organometallics* **1987**, *6*, 2279. (c) $\mathrm{Y_2(OC_6H_3Me_2\text{-}2,6)_6(THF)_2}$: Y−O = 2.348(6) Å. See: Evans, W. J.; Olofson, J. M.; Ziller, J. W. *Inorg. Chem.* **1989**, *28*, 4308. (d) $[\mathrm{Y_3(OCMe_3)_7Cl(THF)_3}][\mathrm{BPh_4}]$: Y−O = 2.35(1)−2.37(1) Å. See: Evans, W. J.; Olofson, J. M.; Ziller, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 2308. (e) $\mathrm{Cp^*_2Y(CH_2Ph)(THF)}$: Y−O = 2.398(4) Å. See: Mandel, A.; Magull, J. *Z. Anorg. Allg. Chem.* **1996**, *622*, 1913. (f) $\mathrm{CpYCl_2(THF)_3}$: Y−O = 2.34(2)−2.50(2) Å. See: Zhou, X.; Wu, Z.; Ma, H.; Xu, Z.; You, X. *Polyhedron* **1994**, *13*, 375. (g) $\mathrm{Cp^*_2YMe(THF)}$: Y−O = 2.379(8) Å. See: den Haan, K. H.; de Boer, J. L.; Teuben, J. H.; Smeets, W. J. J.; Spek, A. L. *J. Organomet. Chem.* **1987**, *327*, 31.

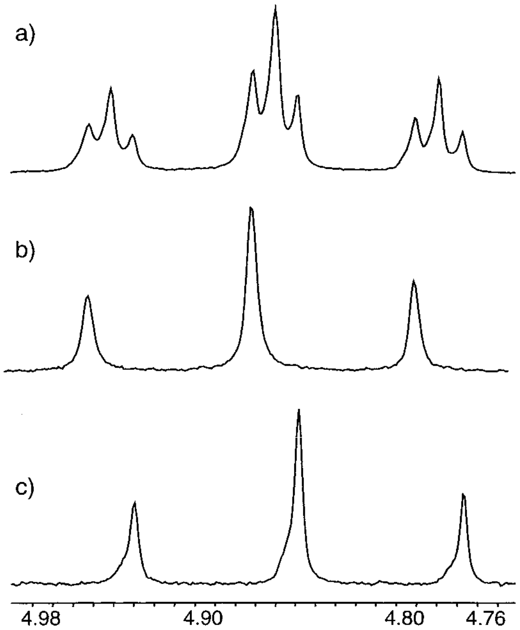
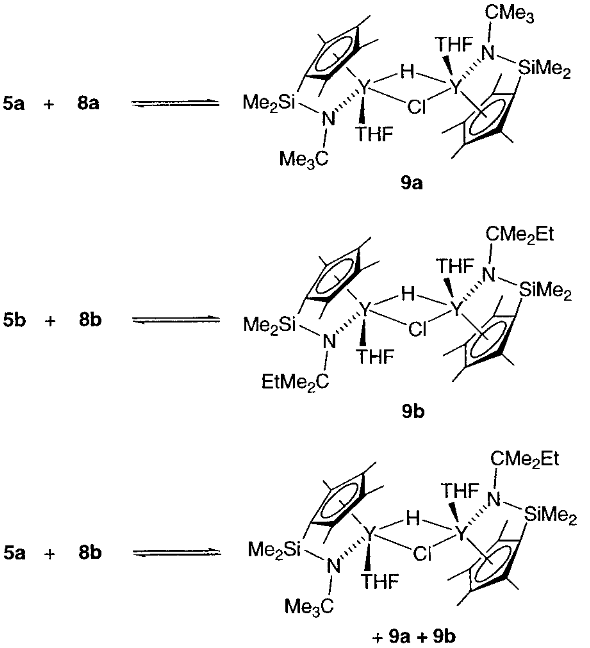


Figure 5. Hydride region of the ^{1}H NMR spectra of (a) a 1:1 reaction mixture of **5a** and **8b** (25 °C, 3 h), (b) pure complex **9a**, and (c) pure complex **9b**. All spectra were recorded in C_6D_6 at 25 °C.

Scheme 4



formed, the formation of a mixture of three distinct μ-chloro μ-hydrido complexes, [{Y(η^5:η^1-$C_5Me_4SiMe_2NCMe_2R$)(THF)}$_2$(μ-H)(μ-Cl)], was observed after 3 h at room temperature. They can be easily distinguished by the hydride triplets, which are sufficiently different at 400 MHz (Figure 5). The "symmetrical" complexes **9a**,**b** could be isolated virtually quantitatively from the scrambling reactions using the appropriate precursors **5a**,**b** and **8a**,**b**, respectively (Scheme 4). In the ^{89}Y NMR DEPTND spectrum of **9a** in toluene-d_8 at room temperature a doublet at 229.9 ppm with $^{1}J_{YH}$ = 32.5 Hz is observed, whereas the hydride **5a** displays a triplet at 334.7 ppm with $^{1}J_{YH}$ = 28.6 Hz (C_6D_6, 50 °C).[8b] According to ^{1}H and ^{13}C NMR spectra the labile THF molecule results in an apparent mirror plane at higher temperatures. Temperature-dependent measurements for **9a** reveal the expected unsymmetrical structure (C_2 or C_s symmetry) at lower temperatures. Similar to the hydrido complex **5a** the presence of two isomers below −40 °C in a 2:3 ratio can be observed, as the NMR spectra display two triplets at 4.70 and 4.86 ppm with $^{1}J_{YH}$ = 30.4 and 36.0 Hz, respectively. A single crystal of the μ-chloro μ-hydrido complex **9b** was obtained by recrystallization from toluene, and X-ray diffraction showed cell parameters[27] that are close to those of the μ-hydrido complex **5b** (which has a homochiral dimeric arrangement and a trans disposition of the supporting ligands).[9] The structure could be solved in the same space group as **4b** and **5b** ($P2_1/n$) by isotypic replacement using the atom positions of **5b** (and omitting the positions for the hydrogen atoms). The solution and initial refinement clearly showed strong electron densities in positions where a chlorine atom is expected. However, disorder between two possible positions for the chlorine atom is also indicated. Due to the low quality of the structure solution, the data will not be discussed further and have not been deposited. It is interesting to note, however, that the presence of one hydrido bridge determines the overall structure of the μ-chloro μ-hydrido dimer.[28]

Conclusion

By extending the C−H activation method to the late lanthanides ytterbium and lutetium, we have synthesized the dinuclear hydrido complexes [Ln(η^5:η^1-$C_5Me_4SiMe_2NCMe_2R$)(L)(μ-H)]$_2$ by starting with Ln(CH_2SiMe_3)$_3$(THF)$_2$ and the amino−cyclopentadiene. The gradual difference between the structures of the Sc, Lu, and Y complexes in the solid state and solution can be explained by their different ionic radii. One consequence is the way styrene undergoes insertion into the metal−hydride bond: whereas the scandium complex [Sc(η^5:η^1-$C_5Me_4SiMe_2NCMe_3$)(PMe_3)(μ-H)]$_2$ gives the bis-insertion product [Sc(η^5:η^1-$C_5Me_4SiMe_2NCMe_3$)(PMe_3)($CMePhCH_2CH_2Ph$)], formed by a 1,2-insertion followed by a 2,1-insertion,[6c,d] all other hydrides, including the complexes **6a** and **7a**, so far lead to the mono-insertion product [Ln(η^5:η^1-$C_5Me_4SiMe_2NCMe_3$)(L)(CHMePh)] through 2,1-insertion.[29] Again, as noticed earlier for the chemistry of yttrium complexes featuring the linked amido−cyclopentadienyl ligand,[8,9] C−H activation processes[30] are not predominant for the lutetium complexes. Likewise, in contrast to ytterbocene hydrides reported,[16h] the ytterbium hydrido complexes **4a**,**b** are not susceptible to reduction.[31] We ascribe this difference to the permethylated lanthanocene hydride derivatives[1] to the pronounced π-donor interaction of the amido

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(27) Cell parameters for **9b**: a = 14.819(2) Å, b = 16.340(2) Å, c = 20.381(2) Å, β = 111.246(2)°, V = 4600(1) Å^3.

(28) For a review on half-sandwich halide complexes, see: Poli, R. *Chem. Rev.* **1991**, *91*, 509.

(29) Arndt, S.; Okuda, J. Unpublished results.

(30) (a) Watson, P. L. *J. Am. Chem. Soc.* **1983**, *105*, 6491. (b) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, B. D.; Santarsiero, W.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203.

(31) Divalent ytterbium complexes such as [Yb(η^5:η^1-$C_5Me_4SiMe_2NCMe_3$)(THF)] are accessible: Trifonov, A.; Spaniol, T. P.; Okuda, J. Unpublished results. For ytterbium amides, see: Tilley, T. D.; Zalkin, A.; Andersen, R. A.; Templeton, D. H. *Inorg. Chem.* **1981**, *20*, 551. Tilley, T. D.; Andersen, R. A.; Zalkin, A. *J. Am. Chem. Soc.* **1982**, *104*, 3725. Tilley, T. D.; Andersen, R. A.; Zalkin, A. *Inorg. Chem.* **1984**, *23*, 2271. Andersen, R. A.; Boncella, J. M. *Organometallics* **1985**, *4*, 205.

function.[7,32] It appears that lanthanide hydrides supported by amido ligands are generally less electrophilic.[33]

Experimental Section

General Considerations. All operations were performed under an inert atmosphere of argon using standard Schlenk-line or glovebox techniques. After drying over KOH, THF was distilled from sodium benzophenone ketyl. Hexane and toluene were purified by distillation from sodium/triglyme benzophenone ketyl. Anhydrous trichlorides of lutetium, ytterbium, and yttrium (ALFA or Strem) were used as received. The linked amino−cyclopentadienes $\mathrm{(C_5Me_4H)SiMe_2NHCMe_2R}$ ($\mathrm{R = Me, Et}$) and the yttrium hydride complexes **5a**,**b** were prepared according to published procedures.[8] All other chemicals were commercially available and used as received unless otherwise stated. NMR spectra were recorded on a Bruker DRX 400 spectrometer (^{1}H, 400 MHz; ^{13}C, 101 MHz; ^{89}Y, 19.6 MHz; ^{29}Si, 79.5 MHz; ^{31}P, 162 MHz) in $\mathrm{C_6D_6}$ at 25 °C, unless otherwise stated. Chemical shifts for ^{1}H and ^{13}C spectra were referenced internally using the residual solvent resonances and reported relative to tetramethylsilane. ^{89}Y spectra were referenced externally to a 1 M solution of $\mathrm{YCl_3}$ in $\mathrm{D_2O}$, ^{29}Si spectra to tetramethylsilane, and ^{31}P spectra to 85% $\mathrm{H_3PO_4}$. Elemental analyses were performed by the Microanalytical Laboratory of this department. In many cases the results were not satisfactory and the best values from repeated runs were given. Moreover, the results were inconsistent from run to run and therefore not reproducible. We ascribe this difficulty, observed also by other workers for similar compound classes,[2t] to the extreme sensitivity of the material.

$\mathbf{Lu(CH_2SiMe_3)_3(THF)_2}$. Anhydrous lutetium trichloride (710 mg, 2.52 mmol) was slurried in THF (60 mL) and stirred at 60 °C for 30 min. The solvent was removed in vacuo, and the solid residue was suspended in pentane (40 mL). The suspension was cooled to −78 °C, and a solution of $\mathrm{LiCH_2SiMe_3}$ (727 mg, 7.72 mmol) in pentane (10 mL) was added. The mixture was stirred at 0 °C for 2 h and filtered, and the colorless solid was extracted with an additional 2 × 10 mL of pentane. LiCl was filtered off, and the solvent was removed from the filtrate in vacuo to give 910 mg (63%) of colorless microcrystals. ^{1}H NMR: δ −0.93 (s, 6 H, $\mathrm{LuCH_2}$), 0.26 (s, 27 H, $\mathrm{SiCH_3}$), 1.32 (m, 8 H, β-$\mathrm{CH_2}$, THF), 3.92 (m, 8 H, α-$\mathrm{CH_2}$, THF). ^{13}C{^{1}H} NMR: δ 4.3 ($\mathrm{SiCH_3}$), 24.6 (β-$\mathrm{CH_2}$, THF), 41.3 ($\mathrm{LuCH_2}$), 70.6 (α-$\mathrm{CH_2}$, THF). ^{29}Si{^{1}H} NMR: δ −2.3.

$\mathbf{Lu(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(CH_2SiMe_3)(THF)}$ (1a). To a solution of $\mathrm{Lu(CH_2SiMe_3)_3(THF)_2}$ (1.000 g, 1.74 mmol) in pentane (40 mL) was added a solution of $\mathrm{(C_5Me_4H)SiMe_2NHCMe_3}$ (438 mg, 1.74 mmol) in pentane (5 mL) at 0 °C. After it was stirred for 2 h at this temperature, the reaction mixture was decanted from an oily byproduct and concentrated in vacuo. The crude product was recrystallized from pentane at −30 °C to give 780 mg (77%) of colorless microcrystals. ^{1}H NMR (toluene-d_8, 60 °C): δ −1.09 (s, 2 H, $\mathrm{LuCH_2}$), 0.19 (s, 9 H, $\mathrm{CH_2SiC}\mathit{H}_3$), 0.67 (br s, 6 H, $\mathrm{SiCH_3}$), 1.27 (m, 4 H, β-$\mathrm{CH_2}$, THF), 1.32 (s, 9 H, $\mathrm{C(CH_3)_3}$), 1.70−2.40 (br m, 12 H, ring $\mathrm{CH_3}$), 3.53 (br s, 4 H, α-$\mathrm{CH_2}$, THF). ^{1}H NMR: δ −1.01 (s, 2 H, $\mathrm{LuCH_2}$), 0.28 (s, 9 H, $\mathrm{CH_2SiC}\mathit{H}_3$), 0.79 (br m, 6 H, $\mathrm{SiCH_3}$), 1.04 (br m, 4 H, β-$\mathrm{CH_2}$, THF), 1.35 (s, 9 H, $\mathrm{C(CH_3)_3}$), 1.80, 2.04, 2.26, 2.39 (br s, 3 H, ring $\mathrm{CH_3}$), 3.35 (br m, 4 H, α-$\mathrm{CH_2}$, THF). ^{13}C{^{1}H} NMR: δ 4.9 ($\mathrm{CH_2Si}\mathit{C}\mathrm{H_3}$), 8.3 ($\mathrm{NSiCH_3}$), 11.4, 15.0 (ring $\mathrm{CH_3}$), 24.6 (β-$\mathrm{CH_2}$, THF), 32.4 ($\mathrm{LuCH_2}$), 36.3 ($\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$), 53.7 ($\mathit{C}\mathrm{(CH_3)_3}$), 71.3 (α-$\mathrm{CH_2}$, THF), 106.0 (ring C attached to $\mathrm{SiMe_2}$), 120.5, 124.7 (ring C). ^{29}Si{^{1}H} NMR: δ −25.0 ($\mathrm{NSi(CH_3)_2}$), 0.2 ($\mathrm{CH_2Si(CH_3)_3}$). ^{1}H NMR (toluene-d_8, −80 °C): δ −1.02 (AB, $^2J_{\mathrm{HH}} = 16.4$ Hz, 2 H, $\mathrm{LuCH_2}$), 0.39 (s, 9 H, $\mathrm{CH_2SiC}\mathit{H}_3$), 0.73 (m, 4 H, β-$\mathrm{CH_2}$, THF), 0.78, 0.89 (s, 3 H, $\mathrm{SiCH_3}$), 1.36 (s, 9 H, $\mathrm{C(CH_3)_3}$), 1.68, 1.97, 2.29, 2.47 (s, 3 H, ring $\mathrm{CH_3}$), 2.88, 3.00 (br m, 2 H, α-$\mathrm{CH_2}$, THF). ^{13}C{^{1}H} NMR (toluene-d_8, −80 °C): δ 4.8 ($\mathrm{CH_2Si}\mathit{C}\mathrm{H_3}$), 8.0, 8.6 ($\mathrm{NSiCH_3}$), 10.7, 12.0, 13.5, 14.3 (ring $\mathrm{CH_3}$), 24.0 (β-$\mathrm{CH_2}$, THF), 31.7 ($\mathrm{LuCH_2}$), 35.7 ($\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$), 53.4 ($\mathit{C}\mathrm{(CH_3)_3}$, 70.8 (α-$\mathrm{CH_2}$, THF), 104.5 (ring C attached to $\mathrm{SiMe_2}$), 119.8, 122.7 (ring C). Anal. Calcd for $\mathrm{C_{23}H_{46}NOSi_2Lu}$: C, 47.32; H, 7.94; N, 2.39. Found: C, 46.48; H, 8.68; N, 3.40.

$\mathbf{Yb(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(CH_2SiMe_3)(THF)}$ (2a). Anhydrous ytterbium trichloride (1.000 g, 3.58 mmol) was slurried in THF (40 mL) and stirred at 60 °C for 30 min. The solvent was removed in vacuo, the solid residue was suspended in pentane (40 mL), and the suspension was cooled to −78 °C. The reaction mixture was treated with a solution of $\mathrm{LiCH_2SiMe_3}$ (1030 mg, 10.90 mmol) in pentane (10 mL) and stirred at 0 °C for 2 h. The reaction mixture was filtered, and the solid was extracted with an additional 2 × 10 mL of pentane. After filtration of LiCl, the solvent was removed from the filtrate in vacuo to give 750 mg (1.30 mmol) of yellow microcrystals. These were dissolved in 40 mL of pentane and treated with a solution of $\mathrm{(C_5Me_4H)SiMe_2NHCMe_3}$ (327 mg, 1.30 mmol) in pentane (5 mL) at 0 °C. After it was stirred at this temperature for 2 h, the solution was decanted and concentrated in vacuo. The crude product was recrystallized from pentane at −30 °C to give 700 mg (93%) of orange microcrystals. Anal. Calcd for $\mathrm{C_{23}H_{46}NOSi_2Yb}$: C, 47.48; H, 7.97; N, 2.41. Found: C, 46.05; H, 7.06; N, 3.40.

$\mathbf{[Lu(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(THF)(\mu\text{-}H)]_2}$ (3a). Method A. A solution of **1a** (50 mg, 86 μmol) in pentane (2 mL) was treated with phenylsilane (56 μL, 0.45 mmol) at 25 °C. After the mixture was stirred for 2 h at this temperature, the supernatant was decanted from the colorless precipitate, which was washed with 2 × 0.2 mL of pentane. Drying in vacuo gave 25 mg (59%) of a colorless powder.

Method B. A solution of **1a** (470 mg, 0.81 mmol) in pentane (10 mL) was loaded in a thick-walled 100 mL glass vessel. Dihydrogen (4 bar) was charged at room temperature, and the reaction mixture was stirred vigorously. After this mixture was stirred for 16 h, the colorless precipitate was collected by decanting the solution and dried in vacuo to afford 270 mg (67%) of a colorless powder.

Method C. Anhydrous lutetium trichloride (844 mg, 3.00 mmol) was slurried in THF (40 mL), stirred at 60 °C for 30 min, and dried in vacuo and the solid suspended in hexane (24 mL). The suspension was treated at −78 °C with a solution of $\mathrm{LiCH_2SiMe_3}$ (866 mg, 9.2 mmol) in hexane (24 mL) and stirred at 0 °C for 1 h and at 25 °C for 40 min. The reaction mixture was filtered, and the colorless solid was extracted with 2 × 10 mL of hexane. LiCl was filtered off from the extracts, and $\mathrm{(C_5Me_4H)SiMe_2NHCMe_3}$ (715 mg, 2.84 mmol) was added at 0 °C. After it was stirred for 45 min at this temperature and 60 min at 25 °C, the reaction mixture was filtered and the filtrate treated with phenylsilane (1.5 mL, 12 mmol). After it was stirred for 3.5 h at 0 °C, the mixture was cooled to −78 °C and the supernatant decanted off. The remaining colorless solid was washed with 2 × 20 mL of cold hexane and dried in vacuo to give 650 mg (44%) of a colorless powder. ^{1}H NMR (toluene-d_8, 60 °C): δ 0.70 (s, 6 H, $\mathrm{SiCH_3}$), 1.38 (s, 9 H, $\mathrm{C(CH_3)_3}$), 1.48 (m, 4 H, β-$\mathrm{CH_2}$, THF), 2.03, 2.22 (s, 6 H, ring $\mathrm{CH_3}$), 3.86 (m, 4 H, α-$\mathrm{CH_2}$, THF), 9.90 (s, 1 H, $\mathrm{Lu_2H_2}$). ^{13}C{^{1}H} NMR (toluene-d_8, 60 °C): δ 7.9 ($\mathrm{SiCH_3}$), 11.5, 13.6 (ring $\mathrm{CH_3}$), 24.7 (β-$\mathrm{CH_2}$, THF), 36.3 ($\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$), 54.1 ($\mathit{C}\mathrm{(CH_3)_3}$), 71.8 (α-$\mathrm{CH_2}$, THF), 107.1 (ring C attached to $\mathrm{SiMe_2}$); two signals for the ring carbon atoms are obscured by the solvent signal. ^{29}Si{^{1}H} NMR (toluene-d_8, 60 °C): δ −25.4. *Major isomer:* ^{1}H

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(32) For example, in group 4 metal chemistry see: (a) Okuda, J.; Schattenmann, F. J.; Wocadlo, S.; Massa, W. *Organometallics* **1995**, *14*, 789. (b) du Plooy, K. E.; Moll, U.; Wocadlo, S.; Massa, W.; Okuda, J. *Organometallics* **1995**, *14*, 3129. (c) Amor, F.; Spaniol, T. P.; Okuda, J. *Organometallics* **1997**, *16*, 4765. (d) Amor, F.; Butt, A.; du Plooy, K. E.; Spaniol, T. P.; Okuda, J. *Organometallics* **1998**, *17*, 5836.

(33) (a) Duchateau, R.; van Wee, C. T.; Meetsma, A.; van Duijnen, P. T.; Teuben, J. H. *Organometallics* **1996**, *15*, 2279. (b) Duchateau, R.; Tuinstra, T.; Brussee, E. A. C.; Meetsma, A.; van Duijnen, P. T.; Teuben, J. H. *Organometallics* **1997**, *16*, 3511. (c) Gountchev, T. I.; Tilley, T. D. *Organometallics* **1999**, *18*, 2896.

NMR (toluene-d_8, −60 °C) δ 0.83, 1.00 (s, 3 H, $SiCH_3$), 1.16 (br m, 4 H, β-CH_2, THF), 1.53 (s, 9 H, $C(CH_3)_3$), 1.93, 2.00, 2.10, 2.58 (s, 3 H, ring CH_3), 3.49, 3.96 (m, 2 H, α-CH_2, THF), 9.63 (s, 1 H, Lu_2H_2); $^{13}C\{^1H\}$ NMR (toluene-d_8, −60 °C) δ 7.7, 8.8 ($SiCH_3$), 11.5, 11.9, 13.5, 14.5 (ring CH_3), 24.9 (β-CH_2, THF), 36.1 ($C(CH_3)_3$), 54.0 ($C(CH_3)_3$), 105.8 (ring C attached to $SiMe_2$), 118.4, 122.1 (ring C); the signal for the α-CH_2 group was not detected; $^{29}Si\{^1H\}$ NMR (toluene-d_8, −60 °C) δ −25.5. *Minor isomer:* ^1H NMR (toluene-d_8, −60 °C) δ 2.16, 2.61 (s, 3 H, ring CH_3), 3.38, 3.76 (m, 2 H, α-CH_2, THF), 10.01 (s, 1 H, Lu_2H_2); $^{29}Si\{^1H\}$ NMR (toluene-d_8, −60 °C) δ −20.6. Anal. Calcd for $C_{38}H_{72}N_2O_2Si_2Lu_2$: C, 45.87; H, 7.29; N, 2.81. Found: C, 45.28; H, 7.88; N, 4.15.

[Lu(η^5:η^1-$C_5Me_4SiMe_2NCMe_2Et$)(THF)(μ-H)]$_2$ (3b). Starting from anhydrous lutetium trichloride (1.00 g, 3.55 mmol), this compound was prepared in a manner analogous to that described for the synthesis of **3a** (method C) and isolated as colorless microcrystals; yield 500 mg (28%). ^1H NMR (toluene-d_8, 25 °C): δ 0.70, 0.80 (s, 3 H, $SiCH_3$), 1.08 (t, $^3J_{HH}$ = 6.9 Hz, 3H, $N(CH_3)_2CH_2CH_3$), 1.35 (s, 6 H, $N(CH_3)_2CH_2CH_3$), 1.41 (br m, 4 H, β-CH_2, THF), 1.69 (br m, 2 H, $N(CH_3)_2CH_2CH_3$), 1.99 (s, 6 H, ring CH_3), 2.07, 2.41 (s, 3 H, ring CH_3), 3.74, 4.07 (br s, 2 H, α-CH_2, THF), 9.66 (s, 1 H, Lu_2H_2). $^{13}C\{^1H\}$ NMR (toluene-d_8, 25 °C): δ 8.8 ($SiCH_3$), 10.4 ($NC(CH_3)_2CH_2CH_3$), 11.5, 13.8 (ring CH_3), 24.8 (β-CH_2, THF), 32.9 ($NC(CH_3)_2CH_2CH_3$), 40.6 ($NC(CH_3)_2CH_2CH_3$), 56.8 ($NC(CH_3)_2CH_2CH_3$), 73.1 (α-CH_2, THF), 106.6 (ring C attached to $SiMe_2$); two signals for the ring carbon atoms are obscured by the solvent signal. $^{29}Si\{^1H\}$ NMR (toluene-d_8, 25 °C): δ −25.8. Anal. Calcd for $Lu_2C_{40}H_{76}N_2O_2Si_2$: C, 46.96; H, 7.49; N, 2.74. Found: C, 45.95; H, 7.96; N, 2.90.

[Yb(η^5:η^1-$C_5Me_4SiMe_2NCMe_3$)(THF)(μ-H)]$_2$ (4a). A solution of **2a** (284 mg, 0.49 mmol) in pentane (10 mL) was loaded in a thick-walled 100 mL glass vessel. Dihydrogen (4 bar) was charged at room temperature, and the reaction mixture was stirred vigorously. After the mixture was stirred for 16 h, the precipitate was collected by decanting the solution to yield 125 mg (52%) of an orange powder. ^1H NMR: δ −90.1, −57.9−54.9, −48.8, −37.7, −32.7, −24.8, −21.5, −15.0, −11.1, −10.8 (br), 21.0, 23.4, 26.3, 29.5, 36.1, 44.7, 53.9, 69.8, 71.6, 102.3, 120.3. Anal. Calcd for $C_{38}H_{72}N_2O_2Si_2Yb_2$: C, 46.04; H, 7.32; N, 2.83. Found: C, 45.15; H, 7.09; N, 3.52.

[Yb(η^5:η^1-$C_5Me_4SiMe_2NCMe_2Et$)(THF)(μ-H)]$_2$ (4b). Anhydrous $YbCl_3(THF)_3$ (1.98 g, 3.98 mmol) was suspended in pentane (40 mL). The suspension was cooled to −78 °C, and a solution of $LiCH_2SiMe_3$ (1.10 g, 11.70 mmol) in pentane (20 mL) was added. The suspension was stirred at 0 °C for 2 h. The mixture was filtered, and the solid was extracted with an additional 2 × 10 mL of pentane. LiCl was filtered off, and a solution of $(C_5Me_4H)SiMe_2NHCMe_2Et$ (989 mg, 3.71 mmol) in pentane (10 mL) was added at 0 °C. After it was stirred for 2 h at 25 °C, the mixture was filtered and phenylsilane (2.6 mL, 19 mmol) was added to the filtrate. After this mixture was stirred for 16 h at 25 °C, the solid was collected by decanting the solution. After extraction with 2 × 10 mL of pentane, the solvent was removed in vacuo to give 650 mg (35%) of an orange powder. ^1H NMR: δ −58.5, −56.6, −38.6, −32.9, −31.2, −23.4, −21.0, −17.8, −8.8, −4.8, 19.6, 20.3, 21.7, 36.4, 71.0, 72.0, 108.0, 124.5. Anal. Calcd for $C_{40}H_{76}N_2O_2Si_2Yb_2$: C, 47.13; H, 7.51; N, 2.75. Found: C, 46.02; H, 7.16; N, 3.11.

[Lu(η^5:η^1-$C_5Me_4SiMe_2NCMe_3$)(PMe_3)(μ-H)]$_2$ (6a). Method A. The hydride **3a** (40 mg, 0.04 mmol) was dissolved in a mixture of benzene (1 mL) and trimethylphosphine (1.6 mL, 14 mmol) and left standing for 14 days at −30 °C to afford colorless crystals (25 mg, 62%).

Method B. A solution of the alkyl **1a** (700 mg, 1.20 mmol) in pentane (40 mL) and trimethylphosphine (2.1 mL, 20 mmol) was loaded in a thick-walled glass vessel. Dihydrogen (4 bar) was charged at room temperature, and the reaction mixture was stirred vigorously. After the mixture was stirred for 16 h, the colorless precipitate was collected by decanting the solution. The solid was washed with 2 × 20 mL of pentane to give 181 mg (30%) of a colorless powder.

Method C. A solution of the alkyl **1a** (100 mg, 100 μmol) in a mixture of trimethylphosphine (300 μL, 2.9 mmol) and pentane (3.5 mL) was treated with phenylsilane (120 μL, 0.96 mmol) and the reaction mixture vigorously stirred for 16 h at room temperature. The colorless precipitate was collected by decanting the solution, and the solid was washed with 3 × 4 mL of pentane; yield 16 mg (32%). ^1H NMR: δ 0.84 (s, 6 H, $SiCH_3$), 1.05 (d, $^2J_{PH}$ = 4.4 Hz,9 H, PCH_3), 1.38 (s, 9 H, $C(CH_3)_3$), 2.11, 2.23, 2.39, 2.45 (br s, 3 H, ring CH_3), 10.48 (s, 1 H, Lu_2H_2). ^{13}C NMR: δ 13.8 ($SiCH_3$), 14.9 (d, $^1J_{PC}$ = 8 Hz, PCH_3), 22.3, 34.0 (ring CH_3), 37.4 ($C(CH_3)_3$), 55.0 ($C(CH_3)_3$), 107.2 (ring C attached to $SiMe_2$), 121.7, 128.9 (ring C). $^{29}Si\{^1H\}$ NMR: δ −25.8. ^1H NMR (toluene-d_8, −60 °C): δ 0.78 (d, $^2J_{PH}$ = 2.4 Hz, PCH_3), 0.83 (s, 3 H, $SiCH_3$), 0.90 (d, $^2J_{PH}$ = 3.9 Hz, 9 H, $LuPCH_3$), 0.92 (s, 3 H, $SiCH_3$), 1.34 (s, 9 H, $C(CH_3)_3$), 2.03, 2.16, 2.29, 2.48 (s, 3 H, ring CH_3), 10.44 (s, 1 H, Lu_2H_2). $^{31}P\{^1H\}$ NMR (toluene-d_8, −60 °C): δ −58.9 (PCH_3), −28.1 ($LuPCH_3$). Anal. Calcd for $C_{36}H_{74}N_2P_2Si_2Lu_2$: C, 43.11; H, 7.38; N, 2.79. Found: C, 43.45; H, 7.87; N, 2.29.

[Y(η^5:η^1-$C_5Me_4SiMe_2NCMe_3$)(PMe_3)(μ-H)]$_2$ (7a). The hydride **5a** (80 mg, 0.09 mmol) was dissolved in a mixture of benzene (200 μL), pentane (2 mL), and trimethylphosphine (1.6 mL, 14 mmol). After the mixture stood for 14 days at −30 °C, colorless crystals were obtained (15 mg, 20%). ^1H NMR (toluene-d_8, 25 °C): δ 0.70 (br s, 6 H, $SiCH_3$), 0.88 (d, $^2J_{PH}$ = 6.6 Hz, 9 H, $YPCH_3$), 1.29 (s, 9 H, $C(CH_3)_3$), 1.9−2.6 (br, 12 H, ring CH_3), 5.56 (t, $^2J_{YH}$ = 27.8 Hz,1 H, Y_2H_2). $^{13}C\{^1H\}$ NMR (toluene-d_8, 25 °C): δ 13.7 ($SiCH_3$), 14−15 (br, PCH_3), 22.2, 33.9 (ring CH_3), 36.7 ($C(CH_3)_3$), 54.9 ($C(CH_3)_3$), 107.51 (ring C attached to $SiMe_2$); two signals for ring carbon atoms are obscured by the solvent signal. ^{31}P NMR (toluene-d_8, 25 °C): δ −58.5 (br, PCH_3), −43.9 (br, $YPCH_3$). ^1H NMR (toluene-d_8, 0 °C): δ 0.71, 0.78 (s, 3 H, $SiCH_3$), 0.81 (br s, PCH_3), 0.92 (d, $^2J_{PH}$ = 3.5 Hz, 9 H, $YPCH_3$), 1.31 (s, 9 H, $C(CH_3)_3$), 2.03, 2.21, 2.22, 2.37 (s, 3 H, ring CH_3), 5.56 (t, $^2J_{YH}$ = 27.6 Hz,1 H, Y_2H_2). $^{31}P\{^1H\}$ NMR (toluene-d_8, 0 °C): δ: −59.2 (br, $P(CH_3)_3$), −43.6 (d, $^1J_{YP}$ = 82.8 Hz, $YPCH_3$). ^1H NMR (toluene-d_8, −60 °C): δ 0.78 (d, $^2J_{PH}$ = 2.0 Hz, PCH_3), 0.82 (d, $^2J_{PH}$ = 3.9 Hz, 9 H, $YPCH_3$), 0.85, 0.94 (s, 3 H, $SiCH_3$), 1.37 (s, 9 H, $C(CH_3)_3$), 2.04, 2.21, 2.26, 2.49 (s, 3 H, ring CH_3), 5.59 (m, 1 H, Y_2H_2). $^{31}P\{^1H\}$ NMR (toluene-d_8, −60 °C): δ −59.0 (PCH_3), −42.5 (d, $^1J_{YP}$ = 85.2 Hz, $YPCH_3$), −42.4 (d, $^1J_{YP}$ = 64.3 Hz, $YPCH_3$). Anal. Calcd for $C_{36}H_{74}N_2P_2Si_2Y_2$: C, 52.04; H, 8.98; N, 3.37. Found: C, 53.05; H, 8.79; N, 3.89.

[Y(η^5:η^1-$C_5Me_4SiMe_2NCMe_3$)(THF)(μ-Cl)]$_2$ (8a). Method A. Anhydrous yttrium trichloride (589 mg, 3.02 mmol) was slurried in THF (20 mL) and stirred at 60 °C for 30 min. The solvent was removed in vacuo, and the solid residue was suspended in pentane (30 mL). The suspension was cooled to −78 °C, a solution of $LiCH_2SiMe_3$ (572 mg, 6.10 mmol) in pentane (20 mL) was added, and the suspension was stirred at 0 °C for 3 h. The suspension was filtered, and the white solid was extracted with pentane twice. At 0 °C $(C_5Me_4H)SiMe_2NHCMe_3$ (804 mg, 3.85 mmol) was added and the solution was stirred for 2 h at this temperature. The reaction mixture was concentrated in vacuo and cooled to −30 °C. The crude product was recrystallized from toluene at −30 °C to give 695 mg (52%) of colorless microcrystals.

Method B. To a solution of [Y(η^5:η^1-$C_5Me_4SiMe_2NCMe_3$)(THF)(μ-H)]$_2$ (87 mg, 105 μmol) in benzene (3 mL) was added *p*-chlorostyrene (25 μL, 208 μmol) at room temperature. After it was stirred overnight, the solution was concentrated in vacuo and cooled to −30 °C. The crude product was recrystallized from toluene at −30 °C to give 61 mg (65%) of colorless crystals. ^1H NMR: δ 0.79 (s, 6 H, $SiCH_3$), 1.29 (br s, 4 H, β-CH_2, THF), 1.43 (s, 9 H, $C(CH_3)_3$), 2.12, 2.31 (s, 6 H, ring CH_3), 3.77 (br s, 4 H, α-CH_2, THF). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 8.4 ($SiCH_3$), 11.8, 14.8 (ring CH_3), 25.7 (br, β-CH_2, THF), 35.1 ($C(CH_3)_3$), 54.4 ($NC(CH_3)_3$), 71.3 (br, α-CH_2, THF), 108.7 (ring

C attached to $SiMe_2$), 125.7, 129.3 (ring C). ^1H NMR (−45 °C, toluene-d_8): δ 0.68, 0.72 (s, 3 H, $SiCH_3$), 0.90, 1.06 (m, 2 H, β-CH_2, THF), 1.33 (s, 9 H, $C(CH_3)_3$), 2.09, 2.13, 2.52, 2.56 (s, 3 H, ring CH_3), 3.90, 3.44 (br s, 2 H, α-CH_2, THF). Anal. Calcd for $C_{38}H_{70}Cl_2N_2O_2Si_2Y_2$: C, 51.17; H, 7.91; N, 3.14. Found: C, 51.24; H, 8.06; N, 3.42.

[Y(η^5:η^1-$C_5Me_4SiMe_2NCMe_2Et$)(THF)(μ-Cl)]$_2$ (8b). Method A. Anhydrous yttrium trichloride (753 mg, 3.85 mmol) was slurried in THF (20 mL) and stirred at 60 °C for 30 min. The solvent was removed in vacuo, and the solid residue was suspended in pentane (40 mL). The suspension was cooled to −78 °C, a solution of $LiCH_2SiMe_3$ (740 mg, 7.90 mmol) in pentane (20 mL) was added, and the suspension was stirred at 0 °C for 4 h. The suspension was filtered, and the white solid was extracted with pentane twice. At 0 °C (C_5Me_4H)$SiMe_2$-$NHCMe_2Et$ (1.03 g, 3.85 mmol) was added and the solution was stirred for 2 h at this temperature. The reaction mixture was concentrated in vacuo and cooled to −30 °C. The crude product was recrystallized from toluene at −30 °C to give 650 mg (37%) of colorless microcrystals.

Method B. To a solution of [Y(η^5:η^1-$C_5Me_4SiMe_2NCMe_2Et$)(THF)(μ-H)]$_2$ (79 mg, 87 μmol) in benzene (3 mL) was added *p*-chlorostyrene (27 μL, 225 μmol) at room temperature. After it was stirred overnight, the solution was concentrated in vacuo and cooled to −30 °C. The crude product was recrystallized from toluene at −30 °C to give 55 mg (69%) of colorless crystals. ^1H NMR: δ 0.79 (s, 6 H, $SiCH_3$), 1.02 (t, $^3J_{HH} = 7.4$ Hz, 3 H, CH_2CH_3), 1.26 (s, 4 H, β-CH_2, THF), 1.34 (s, 6 H, $C(CH_3)_2$), 1.73 (q, $^3J_{HH} = 7.4$ Hz, 2 H, CCH_2CH_3), 2.13, 2.31 (s, 6 H, ring CH_3), 3.83 (br s, 4 H, α-CH_2, THF). $^{13}C\{^1H\}$ NMR: δ 8.9 ($SiCH_3$), 11.3 ($NC(CH_3)_2CH_2CH_3$), 12.1, 15.0 (ring CH_3), 25.3 (β-CH_2, THF), 31.2 ($NC(CH_3)_2CH_2CH_3$), 40.7 ($NC(CH_3)_2CH_2CH_3$), 57.5 ($NC(CH_3)_2CH_2CH_3$), 72.3 (α-CH_2, THF), 108.4 (ring C attached to $SiMe_2$), 123.9, (ring *C*), one signal for the ring C could not be detected. ^1H NMR (toluene-d_8): δ 0.73 (s, 6 H, $SiCH_3$), 1.00 (t, $^3J_{HH} = 7.4$ Hz, 3 H, CH_2CH_3), 1.31 (s, 6 H, $C(CH_3)_2$), 1.34 (s, 4 H, β-CH_2, THF), 1.70 (q, $^3J_{HH} = 7.4$ Hz, 2 H, CCH_2CH_3), 2.10, 2.25 (s, 6 H, ring CH_3), 3.85 (br s, 4 H, α-CH_2, THF). $^{13}C\{^1H\}$ NMR (toluene-d_8): δ 8.4 ($SiCH_3$), 10.7 ($NC(CH_3)_2CH_2CH_3$), 11.6, 14.4 (ring CH_3), 24.7 (β-CH_2, THF), 30.8 ($NC(CH_3)_2CH_2CH_3$), 40.2 ($NC(CH_3)_2CH_2CH_3$), 57.1 ($NC(CH_3)_2CH_2CH_3$), 72.7 (α-CH_2, THF), 108.0 (ring C attached to $SiMe_2$), 123.6 (ring C); one signal for the ring C is obscured by the solvent signal. $^{29}Si\{^1H\}$ NMR (toluene-d_8): δ −25.5. Anal. Calcd for $C_{40}H_{74}Cl_2N_2O_2Si_2Y_2$: C, 52.23; H, 8.11; N, 3.05. Found: C, 50.86; H, 7.65; N, 3.28.

[{Y(η^5:η^1-$C_5Me_4SiMe_2NCMe_3$)(THF)}$_2$(μ-H)(μ-Cl)] (9a). To a solution of **8a** (12 mg, 14 μmol) in benzene (2 mL) was added **5a** (11 mg, 14 μmol). After 3 h the solvent was removed to give **9a** as a colorless powder in quantitative yield. ^1H NMR: δ 0.80, 0.81 (s, 6 H, $SiCH_3$), 1.27 (br s, 8 H, β-CH_2, THF), 1.43 (s, 18 H, $C(CH_3)_3$), 2.09, 2.30 (s, 12 H, ring CH_3), 3.82 (br s, 8 H, α-CH_2, THF), 4.87 (t, $^1J_{YH} = 32.4$ Hz, 1 H, YHY). $^{13}C\{^1H\}$ NMR: δ 8.5 ($SiCH_3$), 12.2, 14.7 (ring CH_3), 25.0 (β-CH_2, THF), 35.0 ($C(CH_3)_3$), 54.4 ($C(CH_3)_3$), 72.8 (α-CH_2, THF), 108.1 (ring C attached to $SiMe_2$), 123.7, 126.5 (ring C). $^{29}Si\{^1H\}$ NMR (toluene-d_8): δ −25.3. ^{89}Y NMR (toluene-d_8): δ 229.9 (d, $^1J_{YH} = 32.5$ Hz). ^1H NMR (60 °C, toluene-d_8): δ 0.57 (s, 12 H, $SiCH_3$), 1.26 (s, 18 H, $C(CH_3)_3$), 1.39 (m, 8 H, β-CH_2, THF), 1.95, 2.09 (s, 12 H, ring CH_3), 3.78 (m, 8 H, α-CH_2, THF), 4.76 (br t, $^1J_{YH} = 32.4$ Hz, 1 H, YHY). Isomer A: ^1H NMR (−60 °C, toluene-d_8) δ 0.77, 0.91 (s, 6 H, $SiCH_3$), 1.00 (br, 8 H, β-CH_2, THF), 1.39 (s, 18 H, $C(CH_3)_3$), 1.96, 2.00, 2.01, 2.54 (s, 6 H, ring CH_3), 3.38, 3.89 (m, 4 H, α-CH_2, THF), 4.70 (t, $^1J_{YH} = 30.4$ Hz, 1 H, YHY). Isomer B: ^1H NMR (−60 °C, toluene-d_8) δ 0.74, 0.94 (s, 6 H, $SiCH_3$), 1.00 (br, 8 H, β-CH_2, THF), 1.44 (s, 18 H, $C(CH_3)_3$), 1.97, 2.02, 2.03, 2.06 (s, 6 H, ring CH_3), 3.38, 3.89 (m, 4 H, α-CH_2, THF), 4.86 (t, $^1J_{YH} = 36.0$ Hz, 1 H, YHY). Anal. Calcd for $C_{38}H_{71}ClN_2O_2Si_2Y_2$: C, 53.23; H, 8.35; N, 3.27. Found: C, 53.21; H, 8.32; N, 3.20.

[{Y(η^5:η^1-$C_5Me_4SiMe_2NCMe_2Et$)(THF)}$_2$(μ-H)(μ-Cl)] (9b). Method A. Anhydrous yttrium trichloride (773 mg, 3.96 mmol) was slurried in THF (20 mL) and stirred at 60 °C for 30 min. The solvent was removed in vacuo, and the solid residue was suspended in pentane (40 mL). The suspension was cooled to −78 °C, a solution of $LiCH_2SiMe_3$ (927 mg, 9.90 mmol) in pentane (20 mL) was added, and the suspension was stirred at 0 °C for 2 h. The suspension was filtered, and the white solid was extracted with pentane twice. At 0 °C (C_5Me_4H)$SiMe_2$-$NHCMe_2Et$ (1.06 g, 3.96 mmol) was added and the solution was stirred for 2 h at this temperature. The volume of the solution was reduced to 20 mL and the solution loaded in a thick-walled 100 mL glass vessel. Dihydrogen (4.5 bar) was charged at room temperature, and the reaction mixture was stirred vigorously. After the mixture was stirred for 16 h, the white precipitate was collected by decanting the solution. The crude product was recrystallized from toluene at −30 °C to give 317 mg (18%) of colorless microcrystals.

Method B. To a solution of **8b** (14 mg, 15 μmol) in 2 mL benzene was added **5b** (13 mg, 15 μmol). After 3 h the solvent was removed to give **9b** as a colorless powder in quantitative yield. ^1H NMR: δ 0.80 (s, 12 H, $SiCH_3$), 1.05 (t, $^3J_{HH} = 7.4$ Hz, 6 H, CH_2CH_3), 1.27 (s, 8 H, β-CH_2, THF), 1.36 (s, 12 H, $C(CH_3)_2$), 1.69 (q, $^3J_{HH} = 7.4$ Hz, 4 H, CCH_2CH_3), 2.09, 2.31 (s, 12 H, ring CH_3), 3.83 (br s, 8 H, α-CH_2, THF), 4.85 (t, $^1J_{YH} = 32.6$ Hz, 1 H, YHY). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 8.7, 8.8 ($SiCH_3$), 10.9, 11.0 ($NC(CH_3)_2CH_2CH_3$), 11.8, 12.0, 14.5, 14.7 (ring CH_3), 24.9 (β-CH_2, THF), 31.0, 32.3 ($NC(CH_3)_2CH_2CH_3$), 40.4, 41.0 ($NC(CH_3)_2CH_2CH_3$), 57.3, 57.4 ($NC(CH_3)_2CH_2CH_3$), 72.9 (α-CH_2, THF), 108.2 (ring C attached to $SiMe_2$), 123.3, 126.5 (ring C). Anal. Calcd for $C_{40}H_{75}ClN_2O_2Si_2Y_2$: C, 54.26; H, 8.54; N, 3.16. Found: C, 53.34; H, 8.16; N, 5.59.

Scrambling Reaction of 8b with 5a. To a solution of **8b** (14 mg, 15 μmol) in benzene (2 mL) was added **5a** (13 mg, 15 μmol). After 3 h the solvent was removed and the colorless powder was dissolved in C_6D_6. Except for the hydride resonances, overlap of the signals precluded complete assignments. ^1H NMR: δ 0.80, 0.81 (s, $SiCH_3$), 1.07 (t, $^3J_{HH} = 7.4$ Hz, CH_2CH_3), 1.27 (s, β-CH_2, THF), 1.35 (s, $C(CH_3)_2$), 1.43 (s, $C(CH_3)_3$), 1.69 (q, $^3J_{HH} = 7.4$ Hz, CCH_2CH_3), 2.09, 2.13, 2.31 (overlap s, ring CH_3), 3.82 (br s, α-CH_2, THF), 4.85 (t, $^1J_{YH} = 32.6$ Hz, YHY, **9a**), 4.86 (t, $^1J_{YH} = 32.6$ Hz, YHY, [Y_2(η^5:η^1-$C_5Me_4SiMe_2NCMe_2Et$)(η^5:η^1-$C_5Me_4SiMe_2NCMe_3$)(μ-H)(μ-Cl)(THF)$_2$]), 4.87 (t, $^1J_{YH} = 32.6$ Hz, YHY, **9b**).

Crystal Structure Analysis of 4b, 6a, 7a, and 8b. Relevant crystallographic data for **4b**, **6a**, **7a**, and **8b** are summarized in Table 1. Single crystals suitable for X-ray crystal structure analysis were obtained by cooling concentrated benzene solutions of **4b** and **8b** to 5 °C and from benzene/PMe_3/pentane mixtures of **3a** and **5a** to give **6a** and **7a**, respectively. Data collections for **4b**, **7a**, and **8b** were performed using ω scans on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation at 296(2) K. Data correction for Lorentz polarization and absorption (empirically using ψ scans) was carried out using the program system MolEN.[34a] For **6a**, the data collection was carried out with a Bruker AXS diffractometer, and the data collection as well as the data reduction and correction for absorption was carried out using the program system SMART.[34b] The structure of **4b** was solved by isotypic replacement using the atom positions of **5b**. The structure of **6a** could also be solved by isotypic replacement by using the atom positions of the scandium complex [Sc(η^5:η^1-$C_5Me_4SiMe_2$-

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(34) (a) Fair, C. K. MolEN, An Interactive Structure Solution Procedure: Enraf-Nonius, Delft, The Netherlands, 1990. (b) Siemens. ASTRO, SAINT and SADABS: Data Collection and Processing Software for the SMART System; Siemens Analytical X-ray Instruments Inc., Madison, WI, 1996. (c) Sheldrick, G. M. SHELXS-86: Program for Crystal Structure Solution; University of Göttingen, Göttingen, Germany, 1986. (d) Sheldrick, G. M. SHELXL-93: Program for Crystal Structure Refinement; University of Göttingen, Göttingen, Germany, 1993.

$NCMe_3)(PMe_3)(\mu\text{-}H)]_2$.[6d] The structures of **7a** and **8b** were solved by Patterson and difference Fourier synthesis (SHELXS-86).[34c] From the measured reflections, all independent reflections were used and the parameters were refined by full-matrix least squares against all F_o^2 data (SHELXL-93)[34d] and refined with anisotropic thermal parameters. Hydrogen atoms were included into calculated positions. Only the hydrogen atoms that are bridging the metal atoms in **4b**, **6a**, and **7a** were refined in their position with isotropic thermal parameters. The crystals of **6a** and **7a** contain solvent molecules (pentane and benzene/pentane) in disordered positions.

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Supporting Information Available: Tables of all crystal data and refinement parameters, atomic parameters including hydrogen atoms, thermal parameters, and bond lengths and angles for **4b**, **6a**, **7a**, and **8b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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