Amine Elimination Reactions between Homoleptic Silylamide Lanthanide Complexes and an Isopropylidene-Bridged Cyclopentadiene−Fluorene System

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This contribution describes the amine elimination process as an alternative synthetic route to traditional salt metathesis for introducing the isopropylidene-bridged unsymmetrical ligand C_5H_5-CMe_2-$C_{13}H_9$ (CpH-CMe_2-FluH) onto group III-metal centers (Y, La, Nd) to give in turn the neutral, ate-complex-free *ansa*-lanthanidocenes. The reactions of homoleptic Ln-$[N(SiMe_3)_2]_3$ (Ln = Y (**1**), La (**2**), Nd (**3**)) with CpH-CMe_2-FluH (**4**) in THF under mild conditions lead to the formation of *ansa*-complexes (η^5,η^5-Cp-CMe_2-Flu)Ln(η^5-Cp-CMe_2-FluH) (Ln = Y (**8**), La (**12**), Nd (**13**)) in 70−84% isolated yields (based on **4**). These reactions proceed via the rapidly formed bis(amido)lanthanide intermediates (η^5-Cp-CMe_2-FluH)Ln$[N(SiMe_3)_2]_2$ (Ln = Y (**5**), La (**9**)), which undergo readily disproportionation/ligand redistribution reactions at 5−23 °C to give either a mono(amido)lanthanide complex (η^5-Cp-CMe_2-FluH)$_2$Ln-$[N(SiMe_3)_2]$ (Ln = Y (**6**)) or another species assumed to be the binuclear complex (η^5-Cp-CMe_2-FluH)$_2$Ln[μ-$N(SiMe_3)_2]_2$Ln$[N(SiMe_3)_2]_2$ (Ln = La (**10**)), respectively. Complexes **6** and **10** undergo an intramolecular amine elimination reaction under THF reflux to yield the corresponding *ansa*-complexes **8** and **12**, respectively. The reversibility of the process has been investigated in the yttrium case: complex **8** converts back to **6** in the presence of $(SiMe_3)_2NH$ in toluene at 90 °C with 50% conversion after 12 h. The effect of a noncoordinating apolar solvent on the reaction outcome of tris(amido) complexes **1**−**3** with **4** has been also studied using toluene, in which the low solubility presumably shifts the disproportionation equilibria and leads to the isolation of another class of compounds Ln(η^5-Cp-CMe_2-FluH)$_3$ (Ln = Y (**7**), La (**11**)) in reasonable yields. Compounds **5**−**12** have been characterized in solution by 1D and 2D NMR techniques (^{1}H, ^{13}C, ^{1}H−^{1}H COSY, and ^{1}H−^{13}C HETCOR), and the solid state structures of **6** and of the mono(THF) adducts of *ansa*-lanthanidocenes **12** and **13** have been established by X-ray diffraction studies. The latter *ansa*-complexes feature very narrow Cp(centroid)−Ln−Flu(centroid) bite angles (Ln = La, 103.67(1)°; Ln = Nd, 105.08(1)°).

Introduction

Neutral d^0/f organolanthanide complexes[1] have attracted considerable attention in the last two decades as ethylene polymerization catalysts. Highly efficient, single-component initiators for this purpose include trivalent lanthanidocene complexes [{Cp′$_2$LnR}$_n$] (Cp′ = substituted cyclopentadienyl ligand, typically C_5Me_5 = Cp*; Ln = La, Nd, Sm, ...; R = H, Me, CH_2SiMe_3; n = 1, 2),[2] as well as divalent complexes such as [Cp′$_2$Sm-(THF)$_n$] (n = 0, 2).[2c,3] Organolanthanidocenes are known, however, to exhibit generally a much lower ability than cationic group IV-metal complexes[4] to polymerize α-ole-

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fins, especially the highly desirable propene. Two factors that have been suggested to hamper this activity are (i) the formation of stable π-allyl complexes and (ii) limited space around the metal center for access of the monomer unit.[2b,3a] Thus, while trivalent rare-earth-metal hydrides [{Cp*$_2$LnH}$_2$] and divalent [Cp*$_2$Sm-(THF)$_n$] complexes are completely inactive for the polymerization of propene and 1-hexene, *ansa*-bridged [{(Me$_2$Si(η^5-C$_5$Me$_4$)$_2$)LnH}$_2$] complexes are slightly active; this is presumably ascribed to the more open space around the metal center and also other features that have not been clearly identified so far.[2d] Improved catalytic performances toward α-olefin polymerization were obtained upon using "constrained geometry" hemimetallocene group III complexes, e.g., [{(η^5-C$_5$Me$_4$)-SiMe$_2$(η-N^{t}Bu)Sc(η-H)}$_2$],[5] and *ansa*-metallocenes such as [*rac*-{Me$_2$Si(η^5-2-Me$_3$Si-4-^{t}Bu-C$_5$H$_2$)$_2$YH}$_2$].[6] Further work has confirmed the ability of trivalent and divalent lanthanide complexes bearing related bulky *ansa*-silylene bridged bis(cyclopentadienyl) ligands to oligomerize/(co)polymerize higher α-olefins, e.g., 1-hexene and 1-octene.[3b–d,7] Although all of these catalyst systems exhibited poor performances as compared to those of group IV-metallocenes, the results established that subtle steric factors imposed by bridging of the Cp rings and substitution on the latter substantially influence the polymerization efficiency of this type of complex toward α-olefins.

On the other hand, group IV chemistry has highlighted the outstanding performances of a variety of catalyst systems having two Cp ligands connected by carbon-based units.[4] However, in contrast with the many *ansa*-lanthanidocenes based on silylene-bridged ligands,[8] only little attention has been paid to lanthanide complexes bearing one-carbon-bridged ligands.[9–11] Attempts to introduce methylene- and alkylidene-(sp^3-C$_1$)-bridged *ansa*-ligands to lanthanides using traditional salt metathesis routes proved unsuccessful in generating neutral mononuclear complexes. Instead the products obtained are either anionic or ate complexes, or the metal moiety in its reduced form with concomitant disproportionation of the ligand.[9] We report here on new *ansa*-lanthanidocene complexes with a η^5-cyclopentadienyl and a η^5-fluorenyl moiety connected through an isopropylidene bridge. In this preliminary study, the applicability of the silylamine elimination reaction between simple homoleptic silylamide complexes Ln[N(SiMe$_3$)$_2$]$_3$ (Ln = Y (**1**), La (**2**), Nd (**3**)) and the unsymmetrical free ligand CpH-CMe$_2$-FluH (Cp = C$_5$H$_4$, Flu = C$_{13}$H$_8$; **4**)[4h,12] has been envisioned as an alternative route for the synthesis of C_2-symmetric complexes[13] to overcome the problems of traditional salt metathesis reactions.

Results and Discussion

Reaction of Y[N(SiMe$_3$)$_2$]$_3$ with CpH-CMe$_2$-FluH. The acid–base reaction of homoleptic Y[N(SiMe$_3$)$_2$]$_3$ (**1**) with CpH-CMe$_2$-FluH (**4**)[14] in THF in the temperature range 5–25 °C proceeds in two stages. Complex **1** reacts first smoothly with 1 equiv of **4** to generate the bis(amido) complex (η^5-Cp-CMe$_2$-FluH)Y[N(SiMe$_3$)$_2$]$_2$ (**5**),

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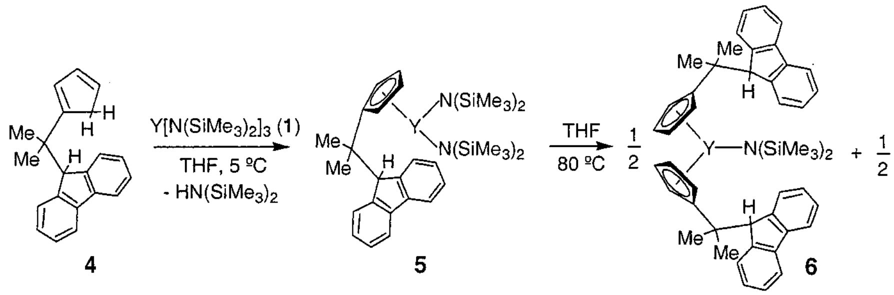
(14) The free ligand CpH-CMe$_2$-FluH exists in two isomeric forms in solution; see ref 12a.

Scheme 1



which then either disproportionates or reacts further with **4** to form the mono(amido) complex (η^5-Cp-CMe_2-FluH)$_2$Y[N($SiMe_3$)$_2$] (**6**) (Scheme 1). Monitoring the reaction by ^{1}H NMR spectroscopy in THF-d_8 showed that the amine elimination reaction occurs only at or above 5 °C. Thus, complex **5** was obtained in 50% NMR yield and 99% selectivity, along with free amine (Me_3-Si)$_2$NH, after 2 h at 5 °C. Mono(cyclopentadienyl) complex **5** transforms slowly into bis(cyclopentadienyl) complex **6** to yield a 4:1 mixture of **5**/**6** after 6 h at 5 °C with 90% conversion of **4**. Complex **5** could not be isolated and was characterized in situ by multinuclear NMR. Key NMR parameters for **5** in THF-d_8 include the presence of two virtual triplets for the protons of the cyclopentadienyl ring coordinated to the metal center, with chemical shifts (δ 6.52 and 6.35) that fall in the range observed for analogous bis(substituted Cp)-yttrium complexes.[8g] The bridged C_5−H of the pendant fluorenyl fragment appears as a singlet (δ 3.95); the latter correlates with the ^{13}C NMR signal at δ 63.0 in the ^{1}H−^{13}C HETCOR spectrum, which was confirmed to be a CH group from a ^{13}C DEPT experiment, corroborating that the fluorenyl fragment is not coordinated to the metal center.

Warming the reaction mixture to room temperature resulted in the complete consumption of **4**, and a 2:1 mixture of **5**/**6** was observed after 12 h. This ratio was unchanged at least for a period of 60 h at 20 °C. However, heating the reaction mixture to 80 °C for 2 h resulted in the complete conversion of **5** into **6** and left a final pale orange solution. Complex **6** was isolated as a pale yellow solid after workup and characterized in solution by NMR (see Supporting Information). Key ^{1}H NMR features for **6** include the presence of two virtual triplets for the coordinated Cp protons (δ 6.45 and 6.28) and a singlet resonance for the C_5-H of the pendant fluorenyl group (δ 4.03). The four well-resolved resonances for the C_6-ring protons of the fluorenyl fragment and the singlet resonances for the bridged CMe_2 and the amide protons reflect the fast motion of the ligands around the metal center and the high symmetry of **6** in solution. The ^{1}H NMR spectrum of **6** recorded in toluene-d_8 showed the absence of THF coordination to the yttrium center.

The solid state structure of **6** was further confirmed by X-ray diffraction. The molecular structure of **6** is depicted in Figure 1, and relevant structural parameters are listed in Tables 1 and 2. The geometry around the yttrium center in **6** can be described as pseudo-trigonal planar, with two η^5-coordinated cyclopentadienyl fragments of the unsymmetrical ligand (CpH-CMe_2-FluH) and one σ-bonded bis(trimethylsilyl)amide group. The

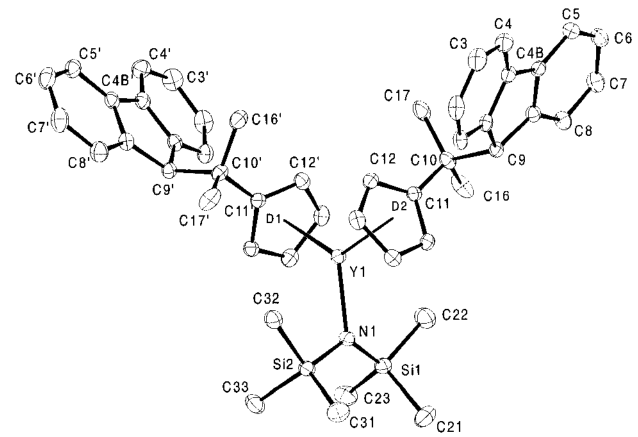


Figure 1. Molecular structure of (η^5-Cp-CMe_2-FluH)$_2$Y-[N($SiMe_3$)$_2$] (**6**) (displacement parameter ellipsoids are displayed at the 50% probability level; hydrogen atoms have been omitted for clarity).

Y−C(Cp) bond distances observed in **6** (2.608(2)−2.753-(2) Å; average 2.672 Å) compare well with values found in other η^5-yttrocene compounds, e.g., Cp*$_2$Y[N($SiMe_3$)$_2$] (2.632(7)−2.737(7) Å),[15] Cp_3Y·THF (2.65(1)−2.766(7) Å),[16] [(C_5H_4Me)$_2$Y(μ-H)·THF]$_2$ (2.67(1)−2.71(1) Å),[17] and Cp*$_2$Y(μ-Cl)YClCp*$_2$ (2.56(2)−2.69(2) Å).[18] The C−C bond parameters of the fluorenyl moiety in **6** are within the range of uncoordinated fluorenyl molecules. The Y−N bond distance in **6** (2.229(2) Å) is very similar to the one found in Y[N($SiMe_3$)$_2$]$_3$ (Y−N = 2.224(6) Å)[19] and comparable to the corresponding bond distances observed in related species, e.g., Cp*$_2$Y[N($SiMe_3$)$_2$] (2.274(5) and 2.253(5) Å for the two different molecules in the unit cell),[15] {η^5,η^5-Flu-$SiMe_2$-Cp′}Y[N($SiMe_3$)$_2$] (2.243(11) Å),[20] (η^5,η^1-C_5Me_4-$SiMe_2$-N^{t}Bu)Y[N($SiMe_3$)$_2$] (Y−N$SiMe_2$ = 2.184(7) Å, Y−N($SiMe_3$)$_2$ = 2.255(8) Å),[21] and *rac*-{Me_2Si(2-MeInd)$_2$}Y[N($SiHMe_2$)$_2$] (2-MeInd = 2-MeC_9H_5) (Y−N = 2.237(4) Å).[22] This value is consistent with a π-dative interaction between the Lewis

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Table 1. Crystal Data and Structure Refinement

	6	**12**·THF	**12**·THF(THF)$_{1.5}$	**13**·THF(THF)$_2$
formula	$C_{48}H_{56}NSi_2Y$	$C_{46}H_{46}LaO$	$C_{52}H_{57}La O_{2.50}$	$C_{54}H_{61}NdO_3$
cryst size, mm	0.14 × 0.13 × 0.02	0.29 × 0.15 × 0.12	0.76 × 0.74 × 0.28	0.29 × 0.27 × 0.11
M, g mol^{-1}	792.03	753.74	860.89	902.27
cryst syst	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a, Å	9.5915(2)	9.7148(11)	19.0242(7)	13.4280(5)
b, Å	11.3455(2)	20.524(2)	16.7576(6)	16.6206(6)
c, Å	19.6442(3)	17.1837(19)	13.3536(5)	18.9798(6)
α, deg	83.5810(10)			
β, deg	86.5210(10)	90.014(4)	90.7740(10)	91.0220(10)
γ, deg	84.3100(10)			
V, Å^3	2111.16(7)	3426.1(7)	4256.7(3)	4235.3(3)
Z	2	4	4	4
D_{calc}, Mg/m^3	1.246	1.461	1.343	1.415
θ range, deg	1.81−33.10	1.55−23.25	1.88−33.17	1.63−33.14
m, mm^{-1}	1.471	1.283	1.044	1.271
no. of measd reflns	24 361	22 989	46 450	46 569
no. of ind reflns	15 571 [R_{int} = 0.042]	4905 [R_{int} = 0.172]	15 356 [R_{int} = 0.045]	15 585 [R_{int} = 0.076]
reflns with $I > 2\sigma(I)$	12 344	3178	10 388	9030
abs corr	none	empirical	Gaussian	none
max. and min. transmn	−/−	0.896/0.819	0.69/0.38	−/−
no. of params	479	202	527	504
goodness of fit	1.145	1.026	1.055	1.001
R [$I > 2\sigma(I)$]	0.050	0.088	0.077	0.053
wR_2	0.151	0.246	0.218	0.122
lgst diff peak/hole, e Å^{-3}	0.623/−0.834	2.893/−3.082	2.531/−2.404	1.150/−1.228

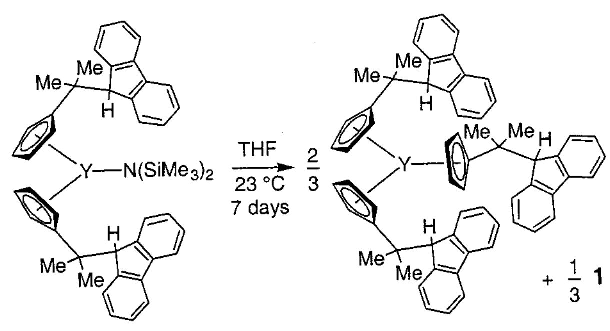
Table 2. Selected Bond Distances and Bond Angles in 6[a]

Distances (Å)			
Y(1)−C(11)	2.753(2)	Y(1)−C(11′)	2.749(2)
Y(1)−C(12)	2.694(2)	Y(1)−C(12′)	2.694(2)
Y(1)−C(13)	2.608(2)	Y(1)−C(13′)	2.611(2)
Y(1)−C(14)	2.626(2)	Y(1)−C(14′)	2.625(2)
Y(1)−C(15)	2.6813(19)	Y(1)−C(15′)	2.676(2)
Si(1)−N(1)	1.7058(19)	Si(2)−N(1)	1.7061(19)
Si(1)−C(21)	1.878(3)	Si(2)−C(31)	1.876(2)
Si(1)−C(22)	1.877(3)	Si(2)−C(32)	1.894(2)
Si(1)−C(23)	1.880(3)	Si(2)−C(33)	1.873(2)
Y(1)−N(1)	2.2294(18)	Y(1)−C(32)	3.018(2)
Y(1)−H(32A)	2.940(1)	Y(1)−H(32C)	2.629(1)
Y(1)−D(1)	2.385	Y(1)−D(2)	2.387
Angles (deg)			
N(1)−Si(1)−C(21)	112.96(12)	N(1)−Si(2)−C(31)	114.84(11)
N(1)−Si(1)−C(22)	109.23(11)	N(1)−Si(2)−C(32)	106.90(10)
N(1)−Si(1)−C(23)	114.00(11)	N(1)−Si(2)−C(33)	113.68(11)
C(21)−Si(1)−C(22)	106.70(14)	C(31)−Si(2)−C(32)	106.53(12)
C(22)−Si(1)−C(23)	107.01(13)	C(32)−Si(2)−C(33)	105.26(12)
C(23)−Si(1)−C(21)	106.53(13)	C(33)−Si(2)−C(31)	108.93(12)
Si(1)−N(1)−Y(1)	124.72(10)	Si(2)−N(1)−Y(1)	109.54(9)
Si(1)−N(1)−Si(2)	125.39(11)	D(1)−Y(1)−D(2)	130.6

[a] D1 = centroid of C(11′, 12′, 13′, 14′, 15′); D2 = centroid of C(11, 12, 13, 14, 15). Standard uncertainties involving these dummy atoms are not meaningful.

acidic yttrium center with the free electron pair on nitrogen,[23] as indicated also by the sp^2-hybridization of the N atom (sum of the bond angles around N = 359.65(10)°). There is also a *γ*-agostic interaction between the yttrium center and a methyl group (C(32)) of the silylamido moiety in **6**. The short contact distances between Y and the C or H atoms of the C(32)-methyl group (Y(1)−C(32) = 3.018(2) Å, Y(1)−H(32A) = 2.940(1) Å, Y(1)−H(32C) = 2.629(1) Å) are in the expected range for such *γ*-agostic interactions. This is also reflected by the increased bond distance of Si(2)−C(32) (1.894(2) Å) as compared to those of Si(2)−C(33) (1.873(2) Å) and Si(2)−C(31) (1.876(2) Å) as well as the smaller bond angle for Y(1)−N(1)−Si(2) (109.54(9)°) vs Y(1)−N(1)−Si(1) (124.72(10)°); also, the bond angle for N(1)−Si(2)−C(32) is ca. 8° smaller than the other two bond angles N(1)−Si(2)−C(32) and N(1)−Si(2)−C(32). Similar interactions have also been observed in $Cp^*_2Y[N(SiMe_3)_2]$,[15] $Cp^*_2Sm[N(SiMe_3)_2]$,[24] and $Cp^*La[CH(SiMe_3)_2]_2$.[25]

Scheme 2



6 **7**

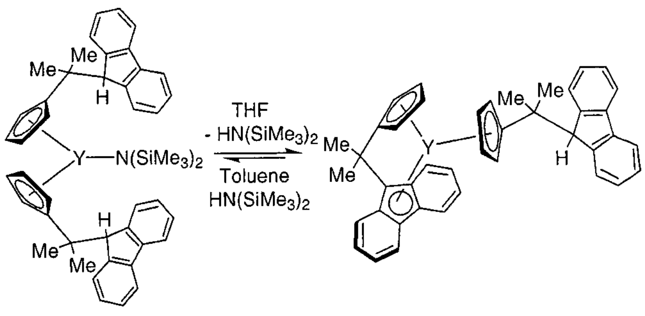
Complex **6** is stable in the solid state but undergoes slowly further disproportionation/ligand redistribution in THF solution to give the tris(cyclopentadienyl) complex Y(η^5-Cp-CMe$_2$-FluH)$_3$ (**7**, Scheme 2). A 4:1 ratio between **6** and **7** was observed in solution (NMR) after a week at room temperature, and complex **7** was isolated from this mixture as an off-white precipitate. The absence of silylamido signal in the ^{1}H and ^{13}C NMR spectra of **7** together with one set of resonances characteristic for the coordinated Cp moiety (δ ^{1}H 6.40 and 6.32, both virtual triplets) and the pendant fluorenyl moiety (δ ^{1}H C$_5$-*H* = 4.12; δ ^{1}H C(C*H*$_3$)$_2$ = 1.17) unambiguously confirm the structure. To establish whether complex **7** arises from (i) a series of dispropor-

(23) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729−1742.

(24) Evans, W. J.; Keyer, R. A.; Ziller, J. W. *Organometallics* **1993**, *12*, 2618−2633.

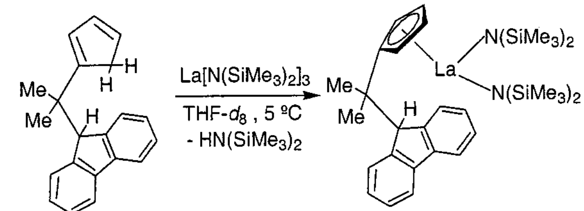
(25) (a) Klooster, W. T.; Brammer, L.; Schaverien, C. J.; Budzelaar, P. H. M. *J. Am. Chem. Soc.* **1999**, *121*, 1381−1382. (b) Van der Heijden, H.; Schaverien, C. J.; Orpen, A. G. *Organometallics* **1989**, *8*, 255−258.

Scheme 3



6 8

Scheme 4



4 9

tionation reactions of **5** and/or **6** or (ii) consecutive amine elimination reactions, i.e., the introduction of the second and third Cp fragments proceeds faster than the first one, the reaction of precursor **1** with 3 equiv of ligand **4** was carried out at room temperature. Noteworthy, the amine elimination reaction was found to proceed slowly in the presence of excess ligand; no complete consumption of the ligand was observed even after 20 days at room temperature (ca. 40% according to ^{1}H NMR), and complex **7** was isolated as an off-white solid in 22% yield. These results suggest that **7** originates from the disproportionation of **6** and not from the simultaneous protonolysis of Y−N bonds of **1** by the ligand **4**.

When complex **6** was generated in THF-d_8 as described above and heated at 80 °C in the presence of coproduct $(Me_3Si)_2NH$ for 12 h, the ^{1}H NMR spectrum showed the broadening of all of the signals; on further heating at this temperature, complex **6** started to decompose to form unidentified products. However, when the amine was completely removed from the solution and the residue was heated in THF-d_8 at 80 °C for 16 h, complex **6** underwent an intramolecular amine elimination reaction to give the *ansa*-complex (η^5,η^5-Cp-CMe$_2$-Flu)Y(η^5-Cp-CMe$_2$-FluH) (**8**) in 70% NMR yield (Scheme 3); in addition, complex **7** (18%), unreacted **6** (12%), and $(Me_3Si)_2NH$ were also present in the dark red solution.[26] Complex **8** was isolated in 45% yield as a yellow solid after workup, and its structure in solution was established by multinuclear NMR. Complete assignment of the resonances was made on the basis of 2D ^{1}H−^{1}H COSY and ^{1}H−^{13}C HETCOR experiments and by comparison to similarly chelated diamagnetic complexes, e.g., (η^5,η^5-Cp-CMe$_2$-Flu)ZrCl$_2$[12a] and (η^5,η^5-Ind-CMe$_2$-Ind)Y[N(SiHMe$_2$)$_2$] (Ind = C_9H_5).[10] The absence of silylamido resonance in the ^{1}H NMR spectrum of **8**, together with the presence of two virtual triplets for each of the two inequivalent Cp moieties (δ 6.17, 6.11, 5.72, and 3.96), one singlet resonance for the C_5-H fluorenyl (δ 3.83), and one singlet resonance for each of the two C*Me*$_2$ units (δ 1.98 and 0.95)[27] all confirm that one molecule of the ligand is coordinated to the yttrium center by *ansa*-chelation, whereas the other one is coordinated via Cp with a free fluorenyl fragment.

These results show that forcing reaction conditions is required for the proton transfer from the Cp-fluorenyl fragment to the amido moiety to occur. This can be related to the higher pK_a value of the Flu-H moiety compared to a simple Cp-H.[28] The exchange and decomposition phenomena observed in the presence of free amine $(Me_3Si)_2NH$ may reflect the reversibility of the amine elimination reaction. In fact, in an independent experiment, *ansa*-chelated complex **8** was shown to react with 3 equiv of $(Me_3Si)_2NH$ in toluene-d_8 at 90 °C to give mono(amido) complex **6** in 50% conversion after 12 h (Scheme 3). The same reaction performed in THF-d_8 yielded a mixture containing only ca. 5% of **6**.

Reactions of Ln[N(SiMe$_3$)$_2$]$_3$ (Ln = La, Nd) with CpH-CMe$_2$-FluH. To assess the effect of the ionic radius of the metal center and of its electrophilicity on the reactivity for amine elimination, the reactions of homoleptic Ln[N(SiMe$_3$)$_2$]$_3$ (Ln = La, Nd) complexes with the unsymmetrical *ansa*-ligand CpH-CMe$_2$-FluH were investigated. The NMR scale reaction of La[N(SiMe$_3$)$_2$]$_3$ (**2**) with 1 equiv of **4** in THF-d_8 at 5 °C is rapid and proceeds cleanly to give after 30 min the bis(amido) complex (η^5-Cp-CMe$_2$-FluH)La[N(SiMe$_3$)$_2$]$_2$ (**9**) in virtually quantitative yield (Scheme 4). Complex **9** is unstable and could not be isolated but was characterized in situ by multinuclear NMR. The ^{1}H NMR spectrum of **9** displays a set of signals with a pattern similar to that for the analogous yttrium compound **5**.

When spectroscopically pure **9** was generated in THF at 5 °C and warmed to room temperature for 10 min, a new set of signals appeared in the ^{1}H NMR spectrum, which was assigned to a new species (**10**). The ratio between **9** and **10** slowly increased to reach a maximum up to 2:1 after 24 h at room temperature. Species **10** is assumed to be a binuclear complex, e.g., (η^5-Cp-CMe$_2$-FluH)$_2$La[μ-N(SiMe$_3$)$_2$]$_2$La[N(SiMe$_3$)$_2$]$_2$.[29] Comparable to the transformation of **5** into **6** as described above, the formation of **10** would result from the in situ disproportionation of bis(amido) complex **9** to a 1:1 mixture of homoleptic complex precursor **2** and mono(amido) complex (η^5-Cp-CMe$_2$-FluH)$_2$La[N(SiMe$_3$)$_2$], as a non-

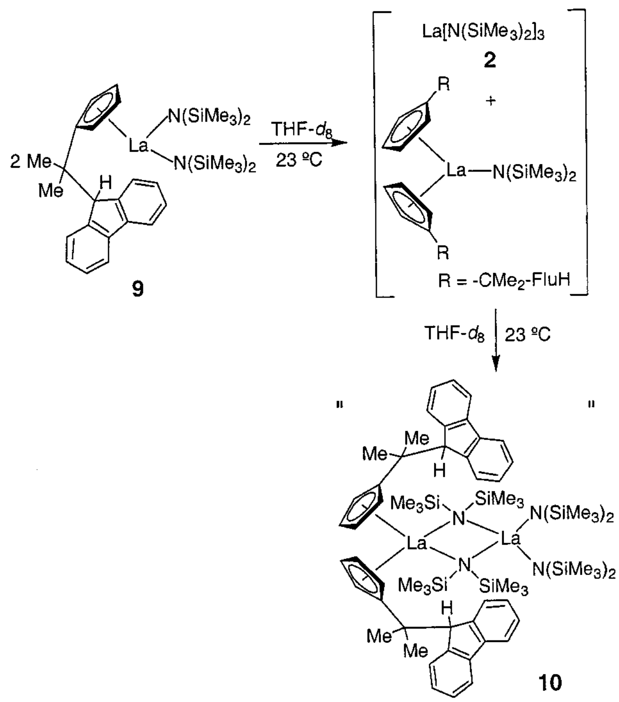
(26) Deprotonation of C_5-H of the fluorenyl moiety results into a highly conjugated system, responsible for the appearance of the red color; see ref 12a.

(27) *ansa*-{Cp-CMe$_2$-Flu}MX$_2$ type complexes (M = Zr, Ti) also feature a shielding of the C*Me*$_2$ ^{1}H resonances compared to the free ligand; see ref 12a.

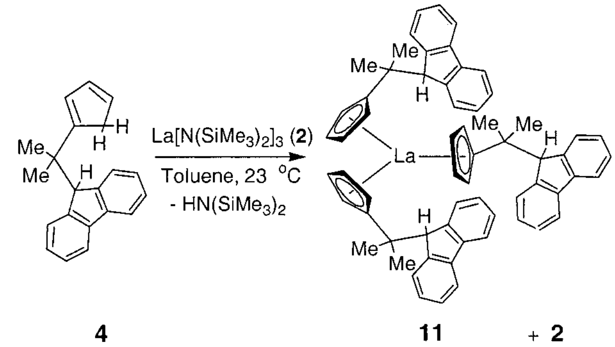
(28) pK_a of CpH = 16 and pK_a of FluH = 23; see: (a) March, J. *Advanced Organic Chemistry*, 4th ed.; John Wiley & Sons: New York, 1992; Chapter 8. (b) Bordwell, F. G.; Bausch, M. J. *J. Am. Chem. Soc.* **1983**, *105*, 6188−6189.

(29) (a) The availability of additional coordination sites was shown in Ln[N(SiMe$_3$)$_2$]$_3$ complexes by isolation of various mono and bis adducts, e.g., Y[N(SiMe$_3$)$_2$]$_3$(NCPh)$_2$; see: Anwander, R. *Top. Curr. Chem.* **1996**, *179*, 33−112, and references therein. For bridging N(SiMe$_3$)$_2$ units in lanthanide chemistry, see: (b) close Eu−C(μ^2-N(SiMe$_3$)$_2$) contacts show that the lanthanide center in NaEu[μ^2-N(SiMe$_3$)$_2$][N(SiMe$_3$)$_2$] has still some available coordination sites: Tilley, T. D.; Andersen, R. A.; Zalkin, A. *Inorg. Chem.* **1984**, *23*, 2271−2276, and references therein. (c) Yb[μ^2-N(SiMe$_3$)$_2$]$_2$[AlMe$_3$]$_2$: Boncella, J. M.; Andersen, R. A.; *Organometallics* **1985**, *4*, 205−206, and references therein. (d) [Yb(μ^2-N(SiMe$_3$)$_2$)(N(SiMe$_3$)$_2$)]$_2$: Avent, A. G.; Edelman, M. A.; Lappert, M. F.; Lawless, G. A. *J. Am. Chem. Soc.* **1989**, *111*, 3423−3425.

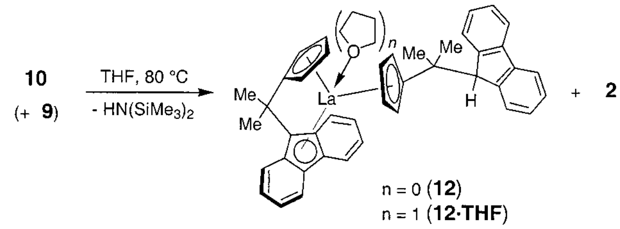
Scheme 5



Scheme 6



Scheme 7



observed transient species that would recombine to form a stable binuclear adduct via bridging amido groups (Scheme 5).[29] The proposed structure and generation scheme for **10** are supported by the following observations:

(i) The reaction of complex precursor **2** with 0.5 equiv of **4** in THF at 23 °C is rapid and resulted in the complete consumption of the ligand after 10 min. After 24 h at this temperature, complex **10** forms quantitatively, resulting in an orange solution. Attempted crystallization of **10** in different solvents and conditions failed to provide crystals suitable for X-ray diffraction, and species **10** was thus characterized in solution by multinuclear NMR. The ^{1}H NMR spectrum of **10** in THF-d_8 displays a set of signals which are very close to the resonances of **9**. The most characteristic signals of **10** are the two virtual triplets for the coordinated Cp-H (δ 6.48 and 6.30), the two singlet resonances respectively for the C_5-H of the uncoordinated fluorenyl group (δ 3.99) and the unconstrained CMe_2 bridge (δ 1.29),[27] and two singlets corresponding to two different amido groups (δ 0.19 and 0.18). The ^{13}C NMR spectrum of **10** also contains resonances consistent with one type of η^5-{Cp-CMe_2-FluH} system and two amido groups in a different environment.

(ii) The reaction of complex precursor **2** with 2 equiv of ligand **4** in THF-d_8 either at 5 °C or at room temperature failed to provide the expected mononuclear mono(amido) complex analogous to yttrium complex **6**. Instead, it formed selectively (>95%), within 10 min, the tris-Cp coordinated complex La(η^5-Cp-CMe_2-FluH)$_3$ (**11**). Monitoring the reaction by ^{1}H NMR showed that the ligand signals and those of La[N($SiMe_3$)$_2$]$_3$ disappeared completely and concomitantly to form **11**, without detecting any trace amounts of **10**. These results suggest that, in the presence of a 2-fold excess of the ligand, the protonolysis of two La−N bonds proceeds rapidly to generate a transient mono(amido) complex (η^5-Cp-CMe_2-FluH)$_2$La[N($SiMe_3$)$_2$]; unlike its yttrium analogue (**6**), the later species is unstable and, in the absence of remaining La[N($SiMe_3$)$_2$]$_3$, cannot form the stable binuclear species **10** but reacts further to yield the tris-Cp complex **11** through a series of consecutive disproportionation reactions.

Complex **11** was independently synthesized from the reaction of complex precursor **2** with 1 equiv of **4** at room temperature in toluene (Scheme 6), where its low solubility presumably shifts the disproportionation reaction and helps in isolating **11** as an off-white solid in 75% yield (based on **4**). Attempted reaction of **2** with 3 equiv of **4** showed that the amine elimination reaction proceeds slowly in the presence of excess ligand, and no complete consumption of the latter was observed. The ^{1}H NMR spectrum of **11** in THF-d_8 displays a pattern of signals similar to that of its yttrium analogue (**7**) with resonances for the Cp and C_6-fluorenyl protons shifted upfield as compared to **7**.

(iii) The reaction of spectroscopically pure bis(amido) complex **9** (vide supra) with 1 equiv of La[N($SiMe_3$)$_2$]$_3$ (**2**) in THF-d_8 at room temperature proceeded slowly to give **10** in ca. 5% yield after 5 min. The conversion of **9** into **10** was completed after 24 h, a result that compares well with those obtained from the reaction of **2** with 0.5 equiv of **4** under the same conditions. This observation confirms that compound **10** is a ligand redistribution product of **9** and rules out other alternative possible structures, e.g., a direct binuclear adduct of **9** to **2** (η^5-Cp-CMe_2-FluH)[N($SiMe_3$)$_2$]La[μ-(N($SiMe_3$)$_2$]$_2$La[N-($SiMe_3$)$_2$]$_2$.

Compound **10** is stable in solution for at least 24 h at room temperature but undergoes further reaction at higher temperatures. Heating a THF solution of either a 2:1 mixture of **9** and **10** (generated from a 1:1 reaction of **2** and **4**) or a spectroscopically pure sample of **10** (generated from a 1:0.5 reaction of **2** and **4**) at 80 °C for 72 h results in a dark red solution[26] that contains *ansa*-complex (η^5,η^5-Cp-CMe_2-Flu)La(η^5-Cp-CMe_2-FluH)(THF) (**12·**THF) (Scheme 7). The THF-free complex (η^5,η^5-Cp-CMe_2-Flu)La(η^5-Cp-CMe_2-FluH) (**12**) was isolated after workup (removal of volatiles, residue washed with

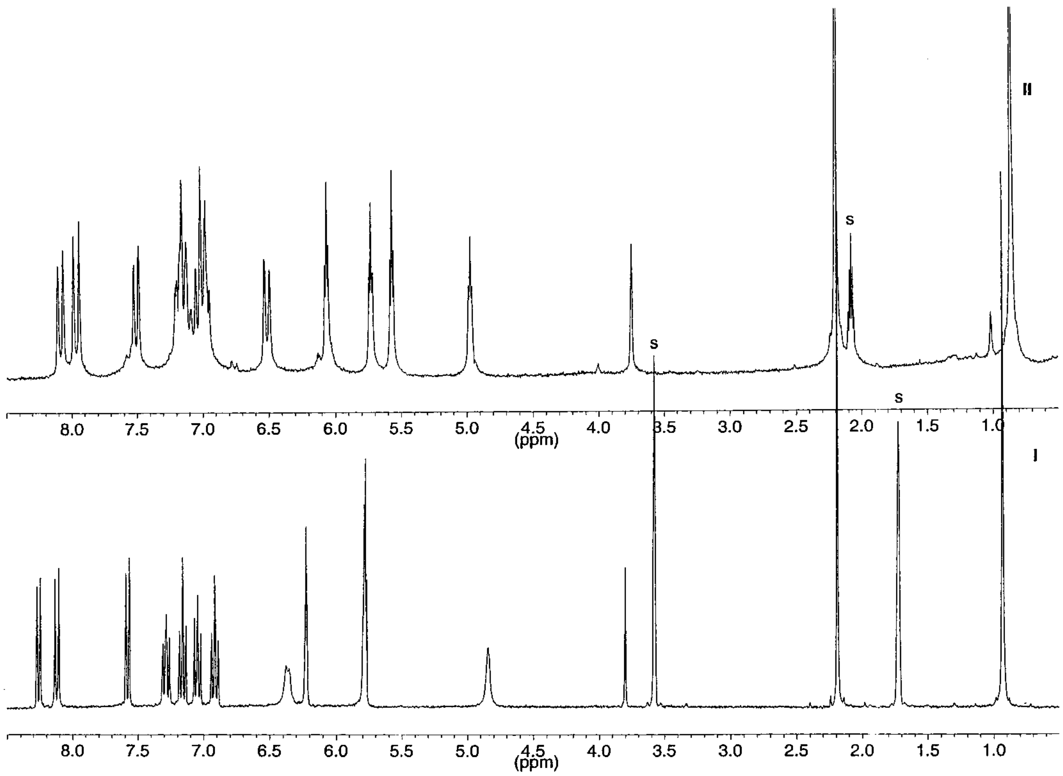
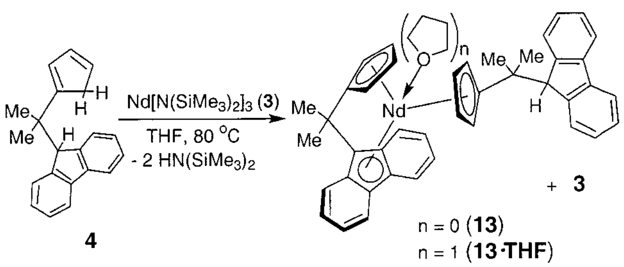


Figure 2. Comparison of the ^{1}H NMR spectrum (300 MHz, 293 K) of (η^5,η^5-Cp-CMe$_2$-Flu)La(η^5-Cp-CMe$_2$-FluH) (**12**) recorded in (I) THF-d_8; (II) toluene-d_8. The signals marked with **s** are due to solvent.

Scheme 8



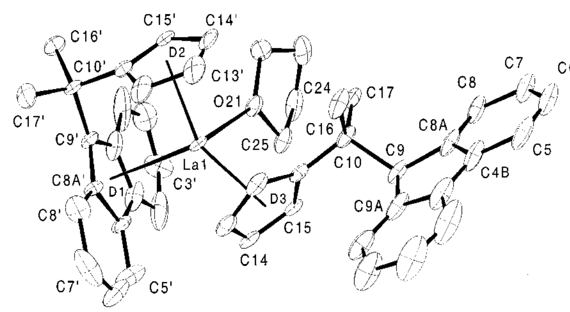


Figure 3. Molecular structure of (η^5,η^5-Cp-CMe$_2$-Flu)La(η^5-Cp-CMe$_2$-FluH)(THF) (**12**·THF) (displacement parameter ellipsoids are displayed at the 30% probability level; solvent THF molecules and hydrogen atoms have been omitted for clarity).

pentane and dried in vacuo) as an off-red solid in 42% yield. Crystallization of **12** from its saturated solution in THF at room temperature afforded red crystals of the THF adduct of **12** (**12**·THF) in 40% yield. The THF-free complex (**12**) and the THF-adduct (**12**·THF) were characterized by spectroscopic techniques, and the structure of the latter was further confirmed by X-ray diffraction studies (vide infra).

Complex **12** and its THF adduct **12**·THF are sparingly soluble in toluene-d_8 but completely soluble in THF. The ^{1}H NMR spectrum of **12** in THF-d_8 displays no silylamido resonances but a set of signals consistent with the presence of two different ligand units (Figure 2). The downfield shifts for the set of signals corresponding to the C_6-ring protons, the bridged CMe$_2$ protons (δ 2.19), and the Cp protons show that one unit of the ligand is coordinated to the La-center by *ansa*-chelation. A singlet for the C_5-H of the fluorenyl fragment (δ 3.80) together with resonances for the C_6-ring, Cp, and CMe$_2$ protons in the regions characteristic for Cp-coordinated La complex **9** all confirm that the second molecule of the ligand is coordinated to the La-center via Cp with a pendant fluorenyl moiety. The ^{1}H NMR spectra in toluene-d_8 confirm that 1 equiv of THF is coordinated in complex **12**·THF (Figure 2). The apparent symmetry suggests that rapid THF exchange takes place in this solvent on the NMR time scale.

Upon using a similar synthetic protocol, the analogous neodymium *ansa*-complex (η^5,η^5-Cp-CMe$_2$-Flu)Nd(η^5-Cp-CMe$_2$-FluH) (**13**) was obtained from the reaction of Nd[N(SiMe$_3$)$_2$]$_3$ (**3**) with 1 equiv of **4** in THF at 80 °C (Scheme 8). Due to the paramagnetic nature of Nd(III), the room-temperature ^{1}H NMR spectra of **13** in THF-d_8 and in toluene-d_8 display broad signals that could not be unambiguously assigned. The THF adduct (η^5,η^5-Cp-CMe$_2$-Flu)Nd(η^5-Cp-CMe$_2$-FluH)(THF) (**13**·THF) was isolated as red crystals from a THF-saturated solution at room temperature, and its molecular structure was established by a single-crystal X-ray diffraction study.

Figures 3 and 4 show the molecular structures of **12**·THF[30] and **13**·THF, respectively, with the atom-labeling schemes. Relevant structural parameters and selected

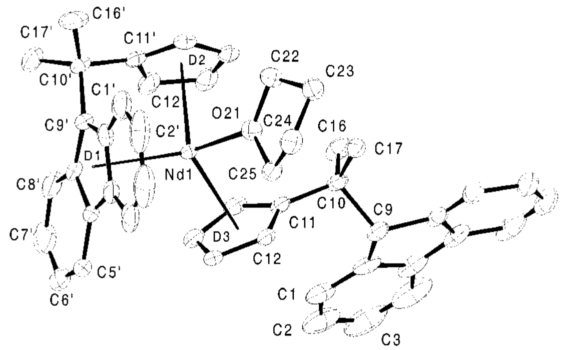


Figure 4. Molecular structure of (η^5,η^5-Cp-CMe$_2$-Flu)Nd(η^5-Cp-CMe$_2$-FluH)(THF) (**13**·THF) (displacement parameter ellipsoids are displayed at the 50% probability level; solvent THF molecules and hydrogen atoms have been omitted for clarity).

Table 3. Selected Bond Distances and Bond Angles for 12·THF (La) and 13·THF (Nd)[a]

	12·THF (La)	**13**·THF (Nd)
	Distances (Å)	
Ln(1)−C(11′)	2.755(5)	2.721(3)
Ln(1)−C(12′)	2.779(7)	2.720(3)
Ln(1)−C(13′)	2.860(7)	2.793(3)
Ln(1)−C(14′)	2.838(7)	2.787(3)
Ln(1)−C(15′)	2.784(6)	2.728(3)
Ln(1)−C(4A′)	2.997(6)	2.981(3)
Ln(1)−C(4B′)	2.994(6)	2.983(3)
Ln(1)−C(8A′)	2.867(6)	2.842(3)
Ln(1)−C(9′)	2.811(5)	2.751(3)
Ln(1)−C(9A′)	2.902(5)	2.856(3)
Ln(1)−C(11)	2.954(5)	2.901(3)
Ln(1)−C(12)	2.824(5)	2.879(3)
Ln(1)−C(13)	2.757(5)	2.763(3)
Ln(1)−C(14)	2.823(5)	2.675(3)
Ln(1)−C(15)	2.924(4)	2.762(3)
Ln(1)−O(21)	2.547(4)	2.514(2)
Ln(1)−D(1)	2.532	2.475
Ln(1)−D(2)	2.650	2.613
Ln(1)−D(3)	2.591	2.527
	Angles (deg)	
D(1)−La(1)−D(2)	103.67	105.08
D(1)−La(1)−D(3)	120.45	121.80
D(2)−La(1)−D(3)	121.21	118.94
D(1)−La(1)−O(21)	103.01	102.59
D(2)−La(1)−O(21)	104.56	104.58(5)
D(3)−La(1)−O(21)	101.27	101.07(5)
C(9′)−C(10′)−C(11′)	104.7(4)	103.3(2)
C(16′)−C(10′)−C(9′)	114.3(9)	112.9(3)
C(9′)−C(10′)−C(17′)	111.5(5)	112.4(3)
C(16′)−C(10′)−C(11′)	111.7(7)	111.7(3)
C(16′)−C(10′)−C(17′)	105.2(7)	106.5(3)
C(17′)−C(10′)−C(11′)	109.5(8)	110.1(3)

[a] D1 = centroid of C(11′, 12′, 13′, 14′, 15′); D2 = centroid of C(4A′, 4B′, 8A′, 9′, 9A′); D3 = centroid of C(11, 12, 13, 14, 15). Standard uncertainties involving these dummy atoms are not meaningful.

bond distances and bond angles for **12**·THF and **13**·THF are listed in Tables 1 and 3. In both cases, the cyclopentadienyl group and the C_5-ring of the fluorenyl fragment of one ligand molecule are coordinated to the La or Nd center by chelation, whereas the other ligand molecule is coordinated through Cp with a pendant fluorenyl moiety. In addition, the presence of one molecule of coordinated THF defines a pseudo-tetrahedral geometry around each metal center.

The La−C(Cp) bond distances in the chelated ring of **12**·THF are in the range 2.755(6)−2.860(7) Å with the *ipso*-carbon (C(11)) being the closest to the La center. The average La−C(Cp) bond distance of 2.803 Å in the chelated ring is similar to the corresponding bond distance observed in [(η^5,η^5-Cp-CPh$_2$-Flu)La(BH$_4$)$_2$][Li-(THF)$_4$] (2.792(3) Å),[9d] {Me$_2$Si(η^5-C$_5$Me$_4$)$_2$}La[N(SiHMe$_2$)$_2$] (2.800(3) Å),[10] and the nonchelated complex Cp*La[CH-(SiMe$_3$)$_2$]$_2$ (2.807(7) Å).[25a] This is consistent with an η^5-coordination mode of the chelated Cp ring to the metal center. On the other hand, this La−C(η^5-Cp) distance is longer than that of 2.686(3) Å observed in *ansa*-(η^5,η^5-Cp-Me$_2$Si-Flu)Y[N(SiMe$_3$)$_2$],[20] 2.476(7) Å in (η^5,η^5-Cp-CMe$_2$-Flu)ZrCl$_2$,[12a] and 2.30(2) Å in [*rac*-{Me$_2$C(η^5-3-(Me$_3$SiC$_5$H$_3$)}$_2$Yb(μ-Cl)$_2$Li(THF)$_2$],[9a] as expected from a major influence of effective ionic radii of the metal centers (La^{3+}, 1.17 Å; Y^{3+}, 1.04 Å; Yb^{3+}, 1.01 Å; Zr^{4+}, 0.86 Å).[31] The La−C(Flu-C$_5$) bond distances in the chelated ring (2.811(5)−2.997(6) Å) compare well to those observed in [(η^5,η^5-Cp-CPh$_2$-Flu)La(BH$_4$)$_2$][Li-(THF)$_4$] (2.788(3)−3.010(3) Å),[9d] and thus the fluorenyl moiety can be considered to be bonded to the La center in an η^5-fashion. The La−C(Cp) bond distances of the nonchelated ring are in the range 2.757(5)−2.954(5) Å, with the bridging carbon (*ipso* carbon, C(11)) being farther away from the metal center. In the absence of chelate constraints and significant substituent effects, the difference of ca. 0.2 Å between the shortest and the longest bond distances indicates that the cyclopentadienyl ring of the nonchelated ligand may be in a stage of approaching toward reduced haptacity (η^3-bonding mode). This is consistent with a total electron count on the metal complex (18e) considering two σ-electron donation from the coordinated THF. A similar trend in approaching toward an η^3-bonding mode of the fluorenyl ligand based on the difference in bond distances from the π-ring plane to the metal center is observed in (η^5,η^3-Cp-SiMe$_2$-Flu)YCl$_2$Li(OEt$_2$)$_2$,[20] (η^5,η^3)-(Flu)$_2$Sm(THF)$_2$,[32] and the group IV-metal complexes (η^5,η^3-Cp-CMe$_2$-Flu)ZrCl$_2$[12a] and (η^5,η^3)-(Flu)$_2$ZrCl$_2$.[33] This may, however, likely stem from crystal packing in the solid state.[34] The Cp-(centroid)−La−Flu(centroid) bite angle and the inner angle at the bridging carbon (C(9′)−C(10′)−C(11′)) of the chelate ring in **12**·THF are 103.67(1)° and 104.7(4)°, respectively. These very narrow angles are comparable to those observed in [(η^5,η^5-Cp-CPh$_2$-Flu)La(BH$_4$)$_2$][Li-

(30) Two types of crystals for the THF adduct of **12** were isolated, one containing just one THF molecule coordinated to the La center (**12**·THF) and a second one with additional unbound disordered THF molecules (**12**·THF(THF)$_{1.5}$). Both types of crystals showed essentially the same molecular conformation and structural features. Bond distances and angles provided in the text refer to the latter type of crystals, for which better crystallographic data were collected. Complete data for both structures are provided as Supporting Information.

(31) (a) Shannon, R. D.; Prewitt, C. T. *Acta Crystallogr., Sect. B* **1969**, *B25*, 925−946. (b) Shannon, R. D.; Prewitt, C. T. *Acta Crystallogr., Sect. B* **1970**, *B26*, 1046−1048. (c) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *A32*, 751−767.

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(34) It is difficult to establish unambiguously the formal bonding mode of the coordinated fluorenyl and Cp rings moieties in solution. The presence of high-field signals (δ 4.8−5.8) in the ^{1}H NMR spectrum of **12** (or **12**·THF), corresponding to the Cp protons of the nonchelated ligand, suggests that the latter is likely in a reduced bonding mode (allylic vs aromatic). Recently the attempted use of ^{13}C NMR data in solution to establish the bonding modes in *ansa*-Zr(fluorenyl) complexes raised many questions on the extreme situation and suggested only that both Cp and fluorenyl moieties are tending toward a reduced haptacity; see: Drago, D.; Pregosin, P. S.; Razavi, A. *Organometallics* **2000**, *19*, 1802−1805.

$(THF)_4]$ (ca. 104° and 104.1(2)°), containing similar chelate ligand environment.[9d] Other related carbon- and silicon-bridged *ansa*-lanthanidocenes display significantly larger bite angles, e.g., $\{Me_2C(\eta^5\text{-}3\text{-}^tBuC_5H_3)_2\}Yb(\mu\text{-}Cl)_2Li(OEt)_2$ (113.4(3)°),[9b] *rac*-$(CH_2)_2[\eta^5\text{-}\{4,7\text{-}(CH_3)_2\text{-}C_9H_4\}]_2Yb(THF)_2$ (118.8°),[9c] $\{Me_2Si(\eta^5\text{-}C_5Me_4)_2\}La[N(SiHMe_2)_2]\}$ (118.53(2)°),[10] and *rac*-$Me_2Si(Flu)(\eta^5\text{-}Cp)Y[N(SiMe_3)_2]$ (123.7°).[20] Also the bite angle observed in **12**·THF is much smaller as compared to group-IV metallocenes containing similar *ansa*-ligands, e.g., $(\eta^5,\eta^3\text{-}Cp\text{-}CMe_2\text{-}Flu)ZrCl_2$ (118.6°)[12a] and $(\eta^5,\eta^5\text{-}Cp\text{-}CPh_2\text{-}Flu)ZrCl_2$ (117.6°).[12e]

The structural discussion on **13**·THF is similar to that of **12**·THF. The cyclopentadienyl and the fluorenyl moieties of the chelated ring in **13**·THF are coordinated to the Nd center via an η^5-coordination mode. The average Nd−C(η^5-Cp) bond distance of 2.750 Å is similar to the corresponding bond distance observed in $Cp^*_2Nd[CH(SiMe_3)_2]$ (2.759(15) Å),[2e] $\{Me_2Si(\eta^5\text{-}C_5Me_4)_2\}Nd[CH(SiMe_3)_2]$ (2.740(6) Å),[2d] and $[(\eta^5,\eta^5\text{-}Cp\text{-}CPh_2\text{-}Flu)Nd(BH_4)_2][Li(THF)_4]$ (2.729(4) Å).[9d] Similarly, the average Nd−C(η^5-Flu) bond distance of 2.883 Å is comparable to the corresponding average bond distance of 2.845(4) Å found in $[(\eta^5,\eta^5\text{-}Cp\text{-}CPh_2\text{-}Flu)Nd(BH_4)_2][Li(THF)_4]$.[9d] The Nd−C(Cp) bond distances in the nonchelated ring are in the range 2.675(3)−2.901(3) Å, with an average distance of 2.796 Å, indicating that the cyclopentadienyl moiety may be also in a stage to approach toward an η^3-bonding mode. The Cp(centroid)−Nd−Flu(centroid) bite angle of 105.08(1)° is similar to that observed in $[(\eta^5,\eta^5\text{-}Cp\text{-}CPh_2\text{-}Flu)Nd(BH_4)_2][Li(THF)_4]$ (ca. 106°)[9d] but much smaller as compared to that observed in related silylene-bridged *ansa*-Nd systems, e.g., $\{Me_2Si(\eta^5\text{-}C_5Me_4)_2\}Nd[CH(SiMe_3)_2]$ (121.6°)[2d] and [*rac*-$\{Me_2Si(\eta^5\text{-}2\text{-}SiMe_3\text{-}4\text{-}^tBu\text{-}C_5H_4)_2\}Nd(\mu\text{-}Cl)_2Li(THF)_2]$ (118.9(11)°).[7b] The larger bite angle and the smaller average Ln−C bond distance in the chelate ring observed in **13**·THF vs **12**·THF are as expected from the ionic radii (Nd^{3+}, 1.12 Å; La^{3+}, 1.17 Å).[31]

In summary, the bridged unsymmetrical ligand CpH-CMe_2-FluH undergoes proton exchange reactions with homoleptic $Ln[N(SiMe_3)_2]_3$ complexes under smooth conditions. In contrast with the salt metathesis route in which ligand fragmentation into fulvene derivatives is observed, this amine elimination process is safe for the *ansa*-ligand. However, this process enables ligand disproportionation/redistribution reactions to occur, leading to initially undesired products such as bis(Cp-CMe_2-FluH)Ln(amido) or binuclear derivatives that further undergo intramolecular amine elimination to yield eventually neutral unsymmetrical *ansa*-isopropylidene-bridged group III metallocenes $(\eta^5,\eta^5\text{-}Cp\text{-}CMe_2\text{-}Flu)Ln(\eta^5\text{-}Cp\text{-}CMe_2\text{-}FluH)$ (Ln = Y, La, Nd). To suppress ligand redistribution reactions from the bis(amido)Ln-(Cp-CMe_2-FluH) intermediate and to find ways to stabilize it may provide an opportunity to facilitate the coordination of the fluorenyl fragments, i.e., to promote the thermodynamically favored chelation of the ligand and to obtain the desired *ansa*-complex $(\eta^5,\eta^5\text{-}C_5R_4\text{-}CR_2\text{-}Flu)Ln[NR_2]$. The issue of steric demand and acidity of the ligand vs basicity and bulkiness of the amido moiety (Anwander−Herrmann route) to reach the desired complexes and their catalytic application toward both fine chemicals and polymer synthesis are currently under investigation.

Experimental Section

General Procedures. All manipulations were performed under a purified N_2 atmosphere using standard high-vacuum Schlenk techniques or in a glovebox. Solvents were distilled from Na/benzophenone (THF) and Na/K alloy (toluene, pentane) under nitrogen, degassed thoroughly, and stored under nitrogen prior to use. Deuterated solvents (benzene-d_6, toluene-d_8, THF-d_8; >99.5% D) were vacuum-transferred from Na/K alloy into storage tubes. $LnCl_3(THF)_x$ (Ln = Y, La) salts were obtained after repeated extraction from THF as described in the literature.[15,35] $NdCl_3(THF)_2$ and ligand **4** (CpH-CMe_2-FluH) were generously provided by Rhodia and TotalFinaElf, respectively, and were used as received. $Li[N(SiMe_3)_2]$ was purchased from Aldrich and was sublimed at 70−80 °C under 10^{-2} mmHg before use. Amido precursor complexes $Ln[N(SiMe_3)_2]_3$ (Ln = Y (**1**), La (**2**), Nd (**3**)) were prepared from the room-temperature reaction of $LnCl_3(THF)_x$ and $Li[N(SiMe_3)_2]$ in toluene according to a modified literature procedure[36] as described below.

NMR spectra were recorded on a Bruker AC-200 or a AC-300 spectrometer in Teflon-valved NMR tubes at 23 °C unless otherwise indicated. ^1H (200 and 300 MHz) and ^{13}C (50 and 75 MHz) chemical shifts are reported vs $SiMe_4$ and were determined by reference to the residual solvent peaks. The assignment of the signals for spectroscopically pure compounds was made from $^1H-^1H$ COSY, $^1H-^{13}C$ HETCOR, gated-$\{^1H\}-^{13}C$ spectra, and DEPT ^{13}C NMR spectra. Coupling constants are given in hertz. Elemental analyses were performed on a LECO-CHNS 932 apparatus.

Modified Method for the Synthesis of $Ln[N(SiMe_3)_2]_3$ Precursors. The following procedure for $Nd[N(SiMe_3)_2]_3$ is representative. To a stirred suspension of anhydrous (<20 ppm H_2O) $NdCl_3(THF)_2$ (3.15 g, 7.98 mmol) in toluene (50 mL) was added freshly sublimed $Li[N(SiMe_3)_2]$ (4.0 g, 23.9 mmol) in toluene (50 mL) through a dropping funnel over a period of 30 min at 23 °C. A pale blue solution appeared at the end of the addition. The reaction mixture was stirred at 23 °C for 3 days, resulting in an intense blue solution, which was allowed to stand overnight to settle down the white solids (LiCl) at the bottom of the Schlenk flask. The solution was filtered through a frit pad of Celite. The solvent was removed under vacuum at room temperature, leaving a pale blue solid, which was shown by ^1H NMR (toluene-d_8) to contain ca. 90% of $Nd[N(SiMe_3)_2]_3$ (**3**). Pure **3** was obtained after sublimation of the crude solid at 100−105 °C under 10^{-2} mmHg as a pale blue solid (3.0 g, 60%). ^1H NMR (toluene-d_8): δ −6.30 (br s, $SiMe_3$).

$Y[N(SiMe_3)_2]_3$ (**1**) and $La[N(SiMe_3)_2]_3$ (**2**) were obtained using a similar procedure as off-white solids in 55% and 58% yields, respectively.

Generation of $(\eta^5$-Cp-CMe_2-FluH)$Y[N(SiMe_3)_2]_2$ (5). An NMR tube was charged with $Y[N(SiMe_3)_2]_3$ (**1**, 50.2 mg, 0.088 mmol) and CpH-CMe_2-FluH (**4**, 24.0 mg, 0.088 mmol), and THF-d_8 (0.6 mL) was condensed in at −196 °C. The tube was sealed, warmed to −78 °C, and vigorously agitated, resulting in a pale yellow solution. The sealed tube was placed in an NMR spectrometer probe that was precooled to 5 °C, and the progress of the reaction was monitored periodically by ^1H NMR spectroscopy. A 50% yield of the bis(amido) complex $(\eta^5$-Cp-CMe_2-FluH)$Y[N(SiMe_3)_2]_2$ (**5**) was observed after 2 h at 5 °C, along with free amine $(Me_3Si)_2NH$ and unreacted starting materials. Attempts to increase the yield of **5** either by increasing the reaction time or by warming to room temperature resulted in further reaction of **5**. Complex **5** was not

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isolated and characterized in situ by spectroscopic techniques. ^{1}H NMR (THF-d_8, 5 °C): δ 7.63 (d, J = 7.5, 2H, Flu-C$_6$$H$), 7.22 (t, J = 7.5, 2H, Flu-C$_6$$H$), 7.06−6.96 (m, 2H, Flu-C$_6$$H$), 6.58−6.55 (m, 2H, Flu-C$_6$$H$), 6.52 (virtual triplet, J = 2.7, 2H, C$_5$$H_4$), 6.35 (virtual triplet, J = 2.7, 2H, C$_5$$H_4$), 3.95 (s, 1H, Flu-C$_5$$H$), 1.27 (s, 6H, C(C$H_3$)$_2$), 0.19 (s, 36H, Si(C$H_3$)$_3$). ^{13}C NMR (THF-$d_8$, 5 °C): δ 146.2 (quat. C), 143.1 (quart. C), 143.0 (quat. C), 127.8 (CH (Flu-C$_6$H)), 127.7 (CH (Flu-C$_6$H)), 126.7 (CH (Flu-C$_6$H)), 119.8 (CH (Flu-C$_6$H)), 112.8 (CH (C$_5$H$_4$)), 111.8 (CH (C$_5$H$_4$)), 63.0 (CH (Flu-C$_5$H)), 40.6 (CMe$_2$), 26.2 (C(CH$_3$)$_2$), 6.7 (Si(CH$_3$)$_3$).

Preparation of (η^5-Cp-CMe$_2$-FluH)$_2$Y[N(SiMe$_3$)$_2$] (6). NMR Scale Generation of 6. Complex **5** was first generated in 50% yield, as described above, from the reaction of a 1:1 mixture of Y[N(SiMe$_3$)$_2$]$_3$ (**1**) and CpH-CMe$_2$-FluH (**4**) in THF-d_8 (0.6 mL) for 2 h at 5 °C. The resulting solution was kept at 5 °C, and the progress of the transformation of **5** into (η^5-Cp-CMe$_2$-FluH)$_2$Y[N(SiMe$_3$)$_2$] (**6**) was monitored by NMR. After 6 h at 5 °C, a ratio of 4:1 between **5** and **6** with 90% conversion with respect to the ligand was observed. On warming the reaction mixture to room temperature, complete consumption of the ligand and a 2:1 ratio between **5** and **6** was observed after 12 h, which was unchanged for at least 60 h at RT. Heating the reaction mixture to 80 °C for 2 h resulted in complete conversion of **5** into **6**, and the solution was orange. ^{1}H NMR (THF-d_8): δ 7.65 (d, J = 7.5, 4H, Flu-C$_6$$H$), 7.23 (t, J = 7.4, 4H, Flu-C$_6$$H$), 7.01 (dt, J = 7.5 and 1.0, 4H, Flu-C$_6$$H$), 6.54 (d, J = 7.6, 4H, Flu-C$_6$$H$), 6.45 (virtual triplet, J = 2.7, 4H, C$_5$$H_4$), 6.28 (virtual triplet, J = 2.6, 4H, C$_5$$H_4$), 4.03 (s, 2H, Flu-C$_5$$H$), 1.28 (s, 12H, C(C$H_3$)$_2$), 0.17 (s, 18H, Si(C$H_3$)$_3$). ^{13}C NMR (THF-$d_8$): δ 146.3 (quat. C), 143.2 (quat. C), 140.6 (quat. C), 127.9 (CH (Flu-C$_6$H), 127.5 (CH (Flu-C$_6$H)), 126.8 (CH (Flu-C$_6$H)), 120.0 (CH (Flu-C$_6$H)), 114.1 (CH (C$_5$H$_4$)), 113.2 (CH (C$_5$H$_4$)), 62.0 (CH (Flu-C$_5$H)), 40.4 (CMe$_2$), 26.5 (C(CH$_3$)$_2$), 4.8 (Si(CH$_3$)$_3$). In both the ^{1}H and ^{13}C NMR spectra, resonances for **1** were also observed.

Synthesis of 6. A Schlenk tube was charged with Y[N(SiMe$_3$)$_2$]$_3$ (**1**, 500 mg, 0.879 mmol) and CpH-CMe$_2$-FluH (**4**, 239 mg, 0.879 mmol), and THF (30 mL) was added via cannula transfer. A pale yellow solution was obtained, which was heated under reflux for 2 h, resulting in an orange solution. The latter was cooled to room temperature, and volatiles were removed under vacuum. The residue was washed with pentane (2 × 10 mL) and dried under vacuum to give spectroscopically pure **6** as a pale yellow solid (220 mg, 32% based on Y). Single crystals suitable for X-ray diffraction study were grown from a saturated toluene solution at −30 °C. ^{1}H NMR (toluene-d_8): δ 7.52 (d, J = 7.3, 4H, Flu-C$_6$$H$), 7.19 (virtual triplet, J = 7.2, 4H, Flu-C$_6$$H$), 7.11−7.05 (m, 4H, Flu-C$_6$$H$ overlapped with solvent signals), 6.53 (d, J = 7.6, 4H, Flu-C$_6$$H$), 6.16 (virtual triplet, J = 2.6, 4H, C$_5$$H_4$), 6.12 (virtual triplet, J = 2.6, 4H, C$_5$$H_4$), 3.74 (s, 2H, Flu-C$_5$$H$), 1.11 (s, 12H, C(C$H_3$)$_2$), 0.18 (s, 18H, Si(C$H_3$)$_3$). Anal. Calcd for C$_{48}H_{56}NSi_2$Y: C, 72.79; H, 7.12; N, 1.77. Found: C, 72.25; H, 6.92; N, 1.66.

Preparation of Y(η^5-Cp-CMe$_2$-FluH)$_3$ (7). Generation of 7 from 6. An NMR tube was charged with (η^5-Cp-CMe$_2$-FluH)$_2$Y[N(SiMe$_3$)$_2$] (**6**, 100 mg, 0.126 mmol), and THF-d_8 (0.6 mL) was condensed in at −196 °C. The tube was warmed to room temperature and monitored periodically by ^{1}H NMR. After 12 h, a new set of signals appeared that corresponds to Y(η^5-Cp-CMe$_2$-FluH)$_3$ (**7**). After 7 days, a crop of white solid precipitated out from the solution, which was collected by filtration, washed with pentane (10 mL), and dried under vacuum to afford **7** as an off-white solid (22.7 mg, 20% based on Y). ^{1}H NMR (THF-d_8): δ 7.66 (d, J = 7.5, 6H, Flu-C$_6$$H$), 7.23 (t, J = 7.4, 6H, Flu-C$_6$$H$), 7.02 (t, J = 7.5, 6H, Flu-C$_6$$H$), 6.60 (d, J = 7.6, 6H, Flu-C$_6$$H$), 6.40 (virtual triplet, J = 2.5, 6H, C$_5$$H_4$), 6.32 (virtual triplet, J = 2.5, 6H, C$_5$$H_4$), 4.12 (s, 3H, Flu-C$_5$$H$), 1.17 (s, 18H, C(C$H_3$)$_2$). ^{13}C NMR (THF-$d_8$): δ 146.4 (quat. C), 143.2 (quat. C), 138.3 (quat. C), 127.9 (CH (Flu-C$_6$H)), 127.5 (CH (Flu-C$_6$H)), 126.9 (CH (Flu-C$_6$H)), 120.0 (CH (Flu-C$_6$H)), 116.0 (CH (C$_5$H$_4$)), 112.0 (CH (C$_5$H$_4$)), 61.5 (CH (Flu-C$_5$H)), 40.3 (CMe$_2$), 26.0 (C(CH$_3$)$_2$). Anal. Calcd for C$_{63}$H$_{57}$Y: C, 83.79; H, 6.36. Found: C, 84.18; H, 5.95.

Generation of 7 from 1 and 4. An NMR tube was charged with Y[N(SiMe$_3$)$_2$]$_3$ (**1**, 50.0 mg, 0.088 mmol) and 3 equiv of CpH-CMe$_2$-FluH (**4**, 71.7 mg, 0.264 mmol), and THF-d_8 (0.6 mL) was condensed in at −196 °C. The tube was warmed to room temperature and monitored periodically by ^{1}H NMR spectroscopy. After 20 days, the solution contained ca. 60% of the ligand, and the ratio between **5** and **7** was 1:3. Complex **7** was isolated as an off-white solid after workup as described above (17.4 mg, 22% based on Y).

Preparation of Y(η^5,η^5 -Cp-CMe$_2$-Flu)(η^5-Cp-CMe$_2$-FluH) (8). NMR Scale Generation of 8. Complex **6** was generated by a heating a THF-d_8 solution of a 1:1 mixture of **1** and **4**, as described above. The solvent and volatiles were removed in vacuo, and the solid was dried overnight under vacuum. Fresh THF-d_8 (0.6 mL) was condensed in at −196 °C, warmed to room temperature, vigorously agitated, and then heated at 80 °C for 16 h. The orange color solution of **6** turned to red on heating. A ^{1}H NMR spectrum of the crude reaction mixture was recorded, which showed that complex **8** has formed in 70% yield. In addition, complex **7** (18%), unreacted **6** (12%), and free amine ((Me$_3$Si)$_2$HN) were also present in the solution.

Synthesis of 8. A Schlenk tube was charged with (η^5-Cp-CMe$_2$-FluH)$_2$Y[N(SiMe$_3$)$_2$] (**6**, 200 mg, 0.253 mmol), and THF (30 mL) was added via cannula transfer. The orange solution was refluxed for 24 h, resulting in a red solution. The latter was cooled to room temperature, and volatiles were removed in vacuo. The residue was redissolved with a minimal amount of fresh THF (ca. 5 mL) by warming to 60 °C, and crystallization was performed at room temperature to give a crop of **8** as a yellow solid (72.0 mg, 45% based on Y). ^{1}H NMR (THF-d_8): δ 8.27 (d, J = 8.3, 2H, Flu-C$_6$$H$), 7.82 (d, J = 7.9, 2H, Flu-C$_6$$H$), 7.56 (d, J = 7.6, 2H, Flu-C$_6$$H$), 7.26 (td, J = 7.5 and 1.4, 2H, Flu-C$_6$$H$), 7.14 (d, J = 7.5, 2H, Flu-C$_6$$H$), 6.97−6.84 (m, 4H, Flu-C$_6$$H$), 6.31 (br d, J = 7.0, Flu-C$_6$$H$), 6.17−6.11 (m, 4H, C$_5$$H_4$), 5.72 (virtual triplet, J = 2.7, 2H, C$_5$$H_4$), 3.96 (virtual triplet, J = 2.5, 2H, C$_5$$H_4$), 3.83 (s, 1H, Flu-C$_5$$H$), 1.98 (s, 6H, C(C$H_3$)$_2$), 0.95 (s, 6H, C(C$H_3$)$_2$). ^{13}C NMR (THF-$d_8$): δ 146.3 (quat. C), 143.0 (quat. C), 136.8 (quat. C), 130.2 (quat. C), 130.0 (quat. C), 127.7 (CH (Flu-C$_6$H)), 127.3 (CH (Flu-C$_6$H)), 126.7 (CH (Flu-C$_6$H)), 125.5 (CH (Flu-C$_6$H)), 121.4 (CH (Flu-C$_6$H)), 119.8 (CH (Flu-C$_6$H)), 115.1 (CH (Flu-C$_6$H)), 112.6 (CH (C$_5$H$_4$)), 112.2 (CH (C$_5$H$_4$)), 112.0 (CH (C$_5$H$_4$)), 105.1 (CH (C$_5$H$_4$)), 61.6 (CH (Flu-C$_5$H)), 39.7 (CMe$_2$), 39.4 (CMe$_2$), 26.2 (C(CH$_3$)$_2$), 25.4 (C(CH$_3$)$_2$). Anal. Calcd for C$_{46}$H$_{45}$OY (**8**·THF): C, 78.62; H, 6.45. Found: C, 79.02; H, 6.18.

Interconversion of (η^5-Cp-CMe$_2$-FluH)$_2$Y[N(SiMe$_3$)$_2$] (6) and Y(η^5,η^5-Cp-CMe$_2$-Flu)(η^5-Cp-CMe$_2$-FluH) (8) in the Presence of Free Amine. An NMR tube was charged with **8** (10.0 mg, 0.016 mmol), and toluene-d_8 was condensed in at −196 °C. The tube was warmed to room temperature, and free amine (Me$_3$Si)$_2$NH (10.0 μL, 3.0 equiv) was added by syringe. ^{1}H NMR spectroscopy revealed that no reaction took place after 12 h at room temperature. The tube was heated to 90 °C for 12 h, and a ^{1}H NMR spectrum was obtained, which showed 50% conversion of **8** to mono(amido) complex (**6**). A similar reaction performed in THF-d_8 produced only ca. 5% conversion to **6** after 24 h of heating at 90 °C.

Generation of (η^5-Cp-CMe$_2$-FluH)La[N(SiMe$_3$)$_2$]$_2$ (9). An NMR tube was charged with La[N(SiMe$_3$)$_2$]$_3$ (**2**, 50.0 mg, 0.081 mmol) and CpH-CMe$_2$-FluH (**4**, 22.0 mg, 0.081 mmol), and THF-d_8 (0.6 mL) was condensed in at −196 °C. The tube was sealed, warmed to −78 °C, and vigorously agitated, resulting in a pale yellow solution. The tube was placed in a NMR spectrometer probe that was precooled to 5 °C, and the progress of the reaction was monitored periodically by ^{1}H NMR spectroscopy. After 30 min at 5 °C, complete conversion of the starting materials to the bis(amido) adduct La[N(SiMe$_3$)$_2$]$_2$(η^5-

Cp-CMe_2-FluH) (**9**) and free amine $(Me_3Si)_2NH$ was observed. Complex **9** is unstable above 5 °C and could not be isolated. ^{1}H NMR (THF-d_8, 5 °C): δ 7.63 (d, J = 7.3, 2H, Flu-C_6H), 7.20 (virtual triplet, J = 7.3, 2H, Flu-C_6H), 6.99 (virtual triplet, J = 7.5, 2H, Flu-C_6H), 6.54 (d, J = 7.6, 2H, Flu-C_6H), 6.24 (s, 2H, C_5H_4), 6.11 (s, 2H, C_5H_4), 4.02 (s, 1H, Flu-C_5H), 1.28 (s, 6H, $C(CH_3)_2$), 0.19 (s, 36H, $Si(CH_3)_3$). The C_5H_4 proton signals at δ 6.24 and 6.11 feature a virtual triplet at 23 °C. ^{13}C NMR (THF-d_8, 5 °C): δ 146.6 (quat. C), 143.0 (quat. C), 139.5 (quat. C), 127.9 (CH (Flu-C_6H)), 127.6 (CH (Flu-C_6H)), 126.6 (CH (Flu-C_6H)), 119.7 (CH (Flu-C_6H)), 114.8 (CH (C_5H_4)), 111.8 (CH (C_5H_4)), 62.4 (CH (Flu-C_5H)), 40.3 (CMe$_2$), 26.2 ($C(CH_3)_2$), 5.6 ($Si(CH_3)_3$).

Generation of 10 "(η^5-Cp-CMe$_2$-FluH)$_2$La(μ-[N(SiMe$_3$)$_2$]$_2$)-La[N(SiMe$_3$)$_2$]$_2$". Generation of 10 from 9. As described above, a spectroscopically pure sample of **9** was generated at 5 °C from the reaction of a 1:1 mixture of La[N(SiMe$_3$)$_2$]$_3$ (**2**) and CpH-CMe$_2$-FluH (**4**) in THF-d_8. The tube was warmed to room temperature and subjected to ^{1}H NMR, which showed the progressive appearance of a new set of signals assigned to **10**. The ratio between **9** and **10** was 7:1 after 10 min and increased to 2:1 ratio after 24 h.

Generation of 10 from 2 and 4. An NMR tube was charged with La[N(SiMe$_3$)$_2$]$_3$ (**2**, 100 mg, 0.162 mmol) and 0.5 equiv of CpH-CMe$_2$-FluH (**4**, 22.0 mg, 0.081 mmol), and THF-d_8 (0.6 mL) was condensed in at −196 °C. The tube was sealed, warmed to room temperature, and vigorously agitated, and the resulting pale orange solution was monitored periodically by ^{1}H NMR. Complete disappearance of the ligand signals along with the formation of **9** and **10** in a 2:1 ratio was observed after 10 min. The reaction was completed after 24 h, giving **10** in virtually quantitative yield with respect to ligand **4**. ^{1}H NMR (THF-d_8): δ 7.64 (d, J = 7.32, 4H, Flu-C_6H), 7.22 (virtual triplet, J = 7.44, 4H, Flu-C_6H), 7.01 (dt, J = 7.51 and 1.13, 4H, Flu-C_6H), 6.61 (d, J = 7.56, 4H, Flu-C_6H), 6.48 (virtual triplet, J = 2.68, 4H, C_5H_4), 6.31 (virtual triplet, J = 2.80, 4H, C_5H_4), 3.99 (s, 2H, Flu-C_5H), 1.29 (s, 12H, $C(CH_3)_2$), 0.19 (s, 36H, $Si(CH_3)_3$), 0.18 (s, 36H, $Si(CH_3)_3$). ^{13}C NMR (THF-d_8): δ 146.5 (quat. C), 144.3 (quat. C), 143.1 (quat. C), 127.9 (CH (Flu-C_6H)), 127.7 (CH (Flu-C_6H)), 126.6 (CH (Flu-C_6H)), 119.8 (CH (Flu-C_6H)), 114.4 (CH (C_5H_4)), 113.5 (CH (C_5H_4)), 62.7 (CH (Flu-C_5H)), 48.6 (CMe$_2$), 26.7 ($C(CH_3)_2$), 5.6 ($Si(CH_3)_3$), 5.4 ($Si(CH_3)_3$).

Reaction of (η^5-Cp-CMe$_2$-FluH)La[N(SiMe$_3$)$_2$]$_2$ (9) with La[N(SiMe$_3$)$_2$]$_3$ (2). As described above, a spectroscopically pure sample of **9** was generated in THF-d_8 at 5 °C, and 1 equiv of La[N(SiMe$_3$)$_2$]$_3$ (**2**, 50.0 mg, 0.081 mmol) was added into it. The tube was vigorously agitated and warmed to 23 °C, and the reaction was monitored periodically by ^{1}H NMR. After 5 min only ca. 5% of **9** had reacted to produce **10**, and the complete consumption of **9** was observed after 24 h; in addition, the presence of **2** was also observed.

Synthesis of La(η^5-Cp-CMe$_2$-FluH)$_3$ (11). Preparative Scale Reaction in Toluene. A Schlenk tube was charged with La[N(SiMe$_3$)$_2$]$_3$ (**2**, 100 mg, 0.162 mmol) and CpH-CMe$_2$-FluH (**4**, 44.0 mg, 0.162 mmol), and toluene (15 mL) was added via cannula transfer. The resulting pale yellow solution was stirred at room temperature for 48 h. The solution was allowed to stand overnight, during which a white solid began to precipitate out from the solution. The solid was collected by filtration, washed with pentane (10 mL), and dried under vacuum to give pure **11** as an off-white solid (38.5 mg, 25% based on La, 75% based on **4**). ^{1}H NMR (THF-d_8): δ 7.63 (d, J = 7.38, 6H, Flu-C_6H), 7.20 (t, J = 7.5, 6H, Flu-C_6H), 6.99 (t, J = 7.5, 6H, Flu-C_6H), 6.57 (d, J = 7.6, 6H, Flu-C_6H), 6.27 (virtual triplet, J = 2.60, 6H, C_5H_4), 6.14 (virtual triplet, J = 2.60, 6H, C_5H_4), 4.04 (s, 3H, Flu-C_5H), 1.31 (s, 18H, $C(CH_3)_2$). ^{13}C NMR (THF-d_8): δ 146.7 (quat. C), 143.2 (quat. C), 139.9 (quat. C), 127.9 (CH (Flu-C_6H)), 127.6 (CH (Flu-C_6H)), 126.6 (CH (Flu-C_6H)), 119.8 (CH (Flu-C_6H)), 114.9 (CH (C_5H_4)), 112.0 (CH (C_5H_4)), 62.6 (CH (Flu-C_5H)), 40.4 (CMe$_2$), 26.3 ($C(CH_3)_3$). Anal. Calcd for $C_{63}H_{57}$La: C, 79.39; H, 6.03. Found: C, 79.21; H, 6.12.

NMR Scale Reaction in THF. An NMR tube was charged with La[N(SiMe$_3$)$_2$]$_3$ (**2**, 50.0 mg, 0.081 mmol) and 2 equiv of CpH-CMe$_2$-FluH (**4**, 44.0 mg, 0.162 mmol), and THF-d_8 (0.6 mL) (0.6 mL) was condensed in at −196 °C. The tube was sealed, warmed to room temperature, and vigorously agitated. ^{1}H NMR spectroscopy taken after 10 min revealed complete conversion of **4** to **11** along with free amine and **2**. Attempted reaction of **2** with 3 equiv of **4** in THF-d_8 resulted in poor conversion; that is, only 45% of **4** was consumed over a period of 7 days, a result that compares well with analogous yttrium experiments.

Synthesis of La(η^5,η^5-Cp-CMe$_2$-Flu)(η^5-Cp-CMe$_2$-FluH) (12) and La(η^5,η^5-Cp-CMe$_2$-Flu)(η^5-Cp-CMe$_2$-FluH)(THF) (12·THF). Preparative Scale Reaction from 2 and 4. A Schlenk tube was charged with La[N(SiMe$_3$)$_2$]$_3$ (**2**, 500 mg, 0.808 mmol) and CpH-CMe$_2$-FluH (**4**, 220 mg, 0.808 mmol), and THF (30 mL) was added via cannula transfer. A pale yellow solution was obtained, which was refluxed for 72 h, resulting in a dark red solution. The solution was cooled to room temperature, and volatiles were removed in vacuo. The residue was washed with pentane (2 × 10 mL) and dried under high vacuum to give **12** as an off-red solid (231 mg, 42% based on La). The ^{1}H NMR spectrum of this material in toluene-d_8 showed it is spectroscopically pure **12** without THF coordination. The solid was redissolved in THF (10 mL), and crystallization was performed at room temperature to give a crop of bright red crystals of La(η^5,η^5-Cp-CMe$_2$-Flu)(η^5-Cp-CMe$_2$-FluH)(THF) (**12·**THF) (240 mg). The latter contain one molecule of THF, as confirmed from ^{1}H NMR spectroscopy and an X-ray diffraction study. ^{1}H NMR (THF-d_8): δ 8.26 (d, J = 8.2, 2H, Flu-C_6H), 8.12 (d, J = 8.8, 2H, Flu-C_6H), 7.58 (d, J = 7.5, 2H, Flu-C_6H), 7.28 (td, J = 7.8 and 1.3, 2H, Flu-C_6H), 7.16 (t, J = 7.5, 2H, Flu-C_6H), 7.05 (t, J = 7.3, 2H, Flu-C_6H), 6.91 (td, J = 7.5 and 1.1, 2H, Flu-C_6H), 6.36 (br d, J = 7.0, 2H, Flu-C_6H), 6.22 (virtual triplet, J = 2.7, 2H, C_5H_4), 5.80−5.76 (m, 4H, C_5H_4), 4.84 (br s, 2H, C_5H_4), 3.80 (s, 1H, Flu-C_5H), 2.19 (s, 6H, $C(CH_3)_2$), 0.93 (s, $C(CH_3)_2$). ^{13}C NMR (THF-d_8): δ 146.5 (quat. C), 143.0 (quat. C), 140.0 (quat. C), 139.5 (quat. C), 129.7 (quat. C), 127.6 (CH (Flu-C_6H)), 127.5 (CH (Flu-C_6H)), 126.5 (CH (Flu-C_6H)), 125.1 (CH (Flu-C_6H)), 123.3 (CH (Flu-C_6H)), 121.3 (quat. C)), 120.7 (CH (Flu-C_6H)), 119.7 (CH (Flu-C_6H)), 117.1 (CH (Flu-C_6H)), 114.9 (CH (C_5H_4)), 113.3 (CH (C_5H_4)), 112.3 (CH (C_5H_4)), 106.5 (CH (C_5H_4)), 104.4 (quat. C), 61.9 (CH (Flu-C_5H)), 40.7 (CMe$_2$), 39.8 (CMe$_2$), 31.0 ($C(CH_3)_2$), 26.1 ($C(CH_3)_2$). ^{1}H NMR (THF-free complex; toluene-d_8): δ 8.09 (d, J = 7.9, 2H, Flu-C_6H), 7.97 (d, J = 8.9, 2H, Flu-C_6H), 7.51 (d, J = 7.3, 2H, Flu-C_6H), 7.23−6.92 (m, 8H, Flu-C_6H overlapped with solvent signals), 6.52 (d, J = 7.62, 2H, Flu-C_6H), 6.07 (virtual triplet, J = 2.5, 2H, C_5H_4), 5.74 (virtual triplet, J = 2.5, 2H, C_5H_4), 5.58 (virtual triplet, J = 2.7, 2H, C_5H_4), 4.98 (virtual triplet, J = 2.7, 2H, C_5H_4), 3.75 (s, 1H, Flu-C_5H), 2.20 (s, 6H, $C(CH_3)_2$), 0.86 (s, 6H, $C(CH_3)_2$). ^{1}H NMR (THF-coordinated complex; toluene-d_8): The chemical shift and pattern of the ^{1}H NMR signals for **12·**THF are similar to that of **12** (THF-free complex) except for the signals for THF, which appeared at δ 3.17 (m, 2H) and 1.29 (m, 2H). Anal. Calcd for $C_{42}H_{37}$La (THF-free **12**): C, 74.11; H, 5.48. Found: C, 74.28; H, 5.96.

NMR Scale Reaction from 10. As described above, a THF-d_8 solution of **10**, generated from the reaction of a 1:0.5 mixture of **2** and **4**, was heated to 80 °C for 3 days, resulting in a red solution. ^{1}H NMR spectroscopy (performed at room temperature) showed that **12** had formed quantitatively. Compound **12** was isolated after workup as described above in 40% yield.

Synthesis of Nd(η^5,η^5-Cp-CMe$_2$-Flu)(η^5-Cp-CMe$_2$-FluH)-(THF) (13·THF). A Schlenk tube was charged with Nd-[N(SiMe$_3$)$_2$]$_3$ (**3**, 500 mg, 0.801 mmol) and CpH-CMe$_2$-FluH (**4**, 218 mg, 0.801 mmol), and THF (30 mL) was added via cannula transfer. A green solution was obtained, which slowly changed to pale orange on refluxing and finally turned to dark red after 72 h. The solution was cooled to room temperature, and volatiles were removed under vacuum. The residue was recrystallized from THF at room temperature to give **13**·THF as red crystals (231 mg, 38%), after workup as described for the analogous lanthanum complex. Anal. Calcd for $C_{46}H_{45}$-NdO: C, 72.87; H, 5.98. Found: C, 72.36; H, 6.37.

Crystal Structure Determination of Complexes 6, 12·THF, 12·THF(THF)$_{1.5}$, and 13·THF(THF)$_2$. Suitable single crystals of all investigated compounds were mounted on glass fibers using the "oil-drop" method. All diffraction data were collected at 100 K using Mo Kα radiation (λ = 0.71073 Å) employing a sealed tube SMART area-detector diffractometer, with the exception of **6**, in which case a Kappa CCD instrument was used, located at a rotating anode. A combination of ω- and φ-scans was carried out to obtain at least a unique data set. Crystal structures were solved by means of the Patterson method, and remaining atoms were located from difference Fourier synthesis, followed by full-matrix least-squares refinement based on F^2 (programs SHELXS-97 and SHELXL-97).[37] All non-hydrogen atoms, except in **12**·THF, were refined with anisotropic displacement parameters. Hydrogen atoms were placed at calculated positions and forced to ride on the attached atom. Disordered THF molecules were included using geometry constraints. Crystal data and details of data collection and structure refinement are given in Table 1. Atomic coordinates and complete listings of bond lengths and angles are available as Supporting Information.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra for complexes **6**–**12**, as well as crystallographic data and data collection details, atomic coordinates, bond distances and angles, and anisotropic thermal parameters for complexes **6**, **12**·THF, **12**·THF(THF)$_{1.5}$, and **13**·THF(THF)$_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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