Communications to the Editor

Organolanthanide Hydride Chemistry. 2. Synthesis and X-ray Crystallographic Characterization of a Trimetallic Organolanthanide Polyhydride Complex

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For many years, lanthanide hydride compounds were known only in interstitial metallic systems such as the binary hydrides, LnH_x,[2] and the intermetallic hydrides, e.g., $LaNi_5H_x$.[3] We recently described the synthesis of the first crystallographically characterized organolanthanide hydride complexes, $[(CH_3C_5H_4)_2LnH(THF)]_2$ (Ln = Lu, Er, Y; THF = tetrahydrofuran) via hydrogenolysis of the *tert*-butyl complexes $(CH_3C_5H_4)_2Ln(t\text{-}C_4H_9)(THF)$.[4-6] That investigation demonstrated that stable, molecular lanthanide hydride complexes could be obtained[7] and that hydrogenolysis, an organometallic reaction of general importance for most metals,[13,14] was applicable to the lanthanide metals as well.

An equally reasonable method of generating lanthanide hydrides from *tert*-butyllanthanide complexes is the β-hydrogen elimination reaction, a reaction which is also of central importance in organometallic chemistry.[14] Although *tert*-butyl transition-metal complexes are not common due to the efficacy of the β-hydrogen elimination reaction, the lanthanide metals form both homoleptic and heteroleptic *tert*-butyl complexes, $LiLn(t\text{-}C_4H_9)_4(THF)_x$[15] (Ln = Lu, Yb, Er, Sm) and $(C_5H_5)_2Ln(t\text{-}C_4H_9)(THF)$[16,17] (Ln = Lu, Er, Y), respectively. The latter complexes are particularly appropriate as organolanthanide hydride precursors via β-hydrogen elimination, since their IR spectra suggest that the alkyl C–H bonds are weakened, possibly by a C–H–Ln interaction with the lanthanide metal center.[16] We report here on the utility of these *tert*-butyl complexes in forming unprecedented trimetallic lanthanide polyhydrides via β-hydrogen elimination in the presence of LiCl.[18]

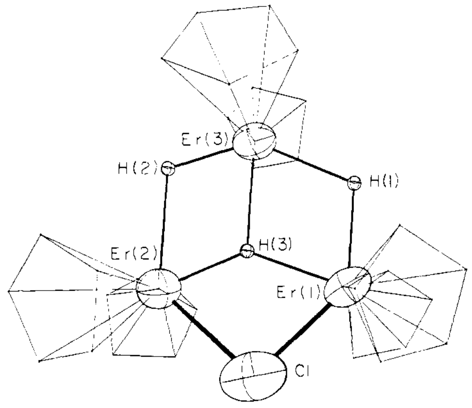

Figure 1. ORTEP plot of the structure of the $[(C_5H_5)_2ErH]_3Cl^-$ anion.

The cyclopentadienyllanthanide *tert*-butyl complexes $(C_5H_5)_2Ln(t\text{-}C_4H_9)(THF)$ (Ln = Lu, Er, Y) exhibit a range of thermal stabilities which can be correlated with metallic radius and hence coordinative saturation. Thermal decomposition of the lutetium complex requires 75 °C in toluene,[16] whereas the erbium and yttrium analogues decompose at ambient temperature overnight. For the larger metals, this instability complicates characterization and isolation of the complexes prior to β-hydrogen elimination. Complete separation of the LiCl, which is the byproduct of the synthesis of these complexes from $t\text{-}C_4H_9Li$ and $(C_5H_5)_2LnCl(THF)$, by toluene extraction is particularly difficult, and as we will show, the presence of small, nonstoichiometric amounts of LiCl during β-hydrogen elimination can have a profound effect on the chemistry which occurs.[19]

Thermal decomposition of rigorously purified, LiCl-free $(C_5H_5)_2Er(t\text{-}C_4H_9)(THF)$, **1**, generates 2-methylpropene and the same dimeric organolanthanide hydride obtained by hydrogenolysis, i.e., $[(C_5H_5)_2ErH(THF)]_2$, **2**.[4,5] The thermal reactions are considerably more complex, however, and the yields of the hydrides are generally about half those of the hydrogenolysis reactions. This is clearly an inferior synthetic route to these dimeric hydrides. However, the thermal β-hydrogen elimination reaction does provide access to other, interesting classes of hydrides in good yield when allowed to occur in the presence of LiCl.

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[1] Camille and Henry Dreyfus Teacher Scholar.

[2] Mueller, W. M.; Blackledge, J. P.; Libowitz, G. G. "Metal Hydrides"; Academic Press: New York, 1968.

[3] Van Vucht, J. H. N.; Kuijpers, F. A.; Bruning, H. C. A. M. *Philips Res. Rep.* **1970**, *25*, 133–140. Guidotti, R. A.; Atkinson, G. B.; Wong, M. M. *J. Less-Common Met.* **1977**, *52*, 13–28. Goudy, A.; Wallace, W. E.; Craig, R. S. and Takeshi, T. *Adv. Chem. Ser.* **1978**, *No. 167*, 312–326.

[4] Evans, W. J.; Wayda, A. L.; Bloom, I.; Coleson, K. M., 181st National Meeting of the American Chemical Society, Atlanta, GA, Mar 1981, INOR 219. Evans, W. J., 15th Rare Earth Research Conference, Rolla, MO, June 1981, J1.

[5] Evans, W. J.; Meadows, J. H.; Wayda, A. L.; Hunter, W. E.; Atwood, J. L., preceding article in this issue.

[6] (a) The high-pressure hydrogenolysis of $(C_5H_5)_2LuCH_2Si(CH_3)_3(THF)$ and $(C_5H_5)_2LuCH_2C_6H_5(THF)$ in THF has been recently reported,[6b] but no spectral or chemical data were reported on the product (analytical data only). (b) Schumann, H.; Genthe, W. *J. Organomet. Chem.* **1981**, *213*, C7–C9.

[7] Our earlier studies provided evidence for reactive lanthanide hydride intermediates,[8,9] unstable lanthanide hydrides,[10,11] and highly associated organolanthanide hydrides,[12] but no crystallographically characterizable species were isolated.

[8] Evans, W. J.; Engerer, S. C.; Piliero, P. A.; Wayda, A. L. *J. Chem. Soc., Chem. Commun.* **1979**, 1007–1008.

[9] Evans, W. J.; Engerer, S. C.; Piliero, P. A.; Wayda, A. L. "Fundamental Research in Homogeneous Catalysis"; Vol. 3, Tsutsui, M., Ed.; Plenum Press: New York, 1979; Vol. 3, pp 941–952.

[10] Zinnen, H. A.; Pluth, J. J.; Evans, W. J. *J. Chem. Soc., Chem. Commun.* **1980**, 810–812.

[11] Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6507–6508.

[12] Evans, W. J.; Coleson, K. M.; Engerer, S. C.; Wayda, A. L.; Zinnen, H. A., Second Chemical Congress of the North American Continent, Las Vegas, NV, Aug 1980, INOR 297. Evans, W. J.; Engerer, S. C.; Coleson, K. M. *J. Am. Chem. Soc.* **1981**, *103*, 6672–6677.

[13] Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 2488–2489.

[14] Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980 and references therein.

[15] Wayda, A. L.; Evans, W. J. *J. Am. Chem. Soc.* **1978**, *100*, 7119–7121.

[16] Evans, W. J.; Wayda, A. L.; Hunter, W. E.; Atwood, J. L. *J. Chem. Soc., Chem. Commun.* **1981**, 292–293.

[17] Schumann, H.; Genthe, W.; Bruncks, N. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 119–120.

[18] Presented in part at the meetings cited in ref 4.

[19] The importance of lithium halides in the synthesis of pentamethylcyclopentadienyl complexes has also been noted: Watson, P. L., 15th Rare Earth Research Conference, Rolla, MO, June 1981, paper J3.

0002-7863/82/1504-2015$01.25/0

Table I. Distances (Å) and Angles (Deg) in $\{[(C_5H_5)_2ErH]_3Cl\}\{Li(THF)_4\}$ with Standard Deviations in Parentheses

Er(1)-Er(2)	3.926 (2)	Cl-Er(1)-H(3)	64
Er(1)-Er(3)	3.692 (1)	H(1)-Er(1)-H(3)	75
Er(2)-Er(3)	3.684 (1)	Er(1)-H(1)-Er(3)	100
Er(1)-Cl	2.64 (1)	H(1)-Er(3)-H(3)	74
Er(2)-Cl	2.735 (9)	H(2)-Er(3)-H(3)	71
Er(1)-H(1)	2.48	Er(2)-H(2)-Er(3)	108
Er(3)-H(1)	2.33	H(2)-Er(2)-H(3)	76
Er(3)-H(2)	1.99	Cl-Er(2)-H(3)	64
Er(2)-H(2)	2.54	Er(2)-Cl-Er(1)	93.9 (3)
Er(1)-H(3)	2.18	Er(1)-H(3)-Er(2)	139
Er(2)-H(3)	2.02	Er(1)-H(3)-Er(3)	108
Er(3)-H(3)	2.39	Er(2)-H(3)-Er(3)	113

When $(C_5H_5)_2Er(t\text{-}C_4H_9)(THF)$ decomposes in toluene in the presence of LiCl at room temperature over a 10-h period, new hydride complexes are generated.[20] The IR spectrum of the pink toluene insoluble product exhibits a broad absorption with maxima at 1250 and 1200 cm^{-1} compared to ν_{ErH} at 1330 cm^{-1} for the analogous LiCl-free β-hydrogen elimination product, **2**.[4,5] Addition of toluene to a THF solution of the crude product precipitates some LiCl and ultimately a pink precipitate, which can be recrystallized to form first pink needles (25% yield) and then pink prisms, **3**[22] (25% yield). Both types of crystals are extremely air and moisture sensitive and readily desolvate, becoming opaque in the process.

The IR spectrum of crystals of **3** in a KBr pellet[23] displays absorptions characteristic of C_5H_5 (1010 and 775 cm^{-1}) and coordinated THF (1040 and 880 cm^{-1})[24] and overlapping strong and broad[26] bands with maxima at 1250 and 1200 cm^{-1} attributable to bridging erbium hydride vibrations (vide infra). Hydrolysis generates 1 mol of H_2/mol of erbium. A complete elemental analysis was not obtainable due to desolvation of the sample,[27] but an Er:Li:Cl ratio of 1:0.35:0.34 in the desolvated/decomposed sample suggested that LiCl was stoichiometrically incorporated into this possibly trimeric erbium hydride.

To structurally identify this new type of hydride, we examined a single crystal of **3** (a prism[22]) by X-ray diffraction techniques and identified it as $\{[(C_5H_5)_2ErH]_3Cl\}\{Li(THF)_4\}$. The compound exists as discrete cation and anion pairs, each with no crystallographically imposed symmetry.[28] The anion shown in Figure 1 is comprised of three dicyclopentadienylerbium units arranged in a triangular array. Two sides of the triangle are bridged by hydride ligands and the third by a chloride ion. An additional hydride resides in the interior of the triangle providing a formal coordination number of nine for each erbium atom. The hydrogen atoms in the bridging positions were located in a difference Fourier map, but their coordinates could not be refined.[29]

Several points concerning the anion deserve discussion. First, the hydrogen atoms H(1) and H(2), which bridge two erbium atoms, are located in reasonable positions with regard to the overall geometry, although nothing can be said in detail about the bond length and angles[29] (Table I). The Er(1)–Er(3) and Er(2)–Er(3) distances are 3.692 (1) and 3.684 (1) Å, respectively.[30] This compares[31] favorably with the Y–Y distance of 3.664 (1) Å for the hydrogen-bridged dimer $[(CH_3C_5H_4)_2YH(THF)]_2$.[5] Second, the central hydrogen atom, H(3), can be shown to be well placed, based not only on the difference Fourier map but also from geometrical considerations. It is needed to complete the coordination sphere of the erbium atoms (the observed coordination number with H(3) included is nine, the same as in the yttrium dimer), and it is located near the center of the triangle defined by the metal atoms. The fact that the $(C_5H_5)_2Er$ units are all oriented in a similar fashion with regard to H(3) is shown by the bond angles, H(3)–Er–bridging ligand (H or Cl), which range from 64 to 75° and by those of the C_5H_5–centroid–Er–H(3), which fall within the range 114–121°. It seems likely that H(3) may in fact be bonded preferentially to one or two of the metal atoms because of the asymmetry of the Er–Cl bond lengths, but this important point cannot be addressed at present. It should also be noted that H(3) resides only 0.06 Å out of the plane of the metal atoms.[32] Comparison of this hydride position with other examples is not possible, since no examples of μ_3-hydrides in trinuclear metal complexes are known.

The chlorine atom bridges Er(1) and Er(2) at distances of 2.64 (1) and 2.74 (1) Å, respectively, with an Er(1)–Er(2) distance of 3.926 (2) Å. Based on the Yb–Cl length of 2.64 Å in $[(CH_3C_5H_4)_2YbCl]_2$,[33] one would expect[34] the Er–Cl bond length to be 2.66 Å, a value close to the 2.69-Å average in **3**. The reason for the significant difference in the two Er–Cl distances is thought to be related to the position of the central hydrogen atom. Two other features related to the chlorine atom also bear mention. The thermal motion is much higher than anticipated and the chlorine atom lies 0.13 Å out of the plane of the metal atoms.

The average of the 30 Er–C(η^5) bond lengths, 2.65 Å, is well within the expected range. The parameters associated with the $Li(THF)_4^+$ cation are normal.

A second variant of the β-hydrogen elimination synthesis of polymetallic lanthanide polyhydrides was examined with lutetium. The lutetium complex $(C_5H_5)_2Lu(t\text{-}C_4H_9)(THF)$, requires tem-

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[20] The following typical reaction details the most efficient way to obtain these crystalline products. Sublimed $LiC(CH_3)_3$ (0.2287 g, 3.57 mmol) in pentane (20 mL) is added dropwise via an addition funnel to $(C_5H_5)_2ErCl$ (1.188 g, 3.57 mmol) in THF (20 mL) in a Schlenk flask at −78 °C. The solution is allowed to warm to room temperature overnight with stirring and is then concentrated to a pink orange paste. Addition of toluene (30 mL) forms an orange solution containing suspended LiCl. This suspension is heated to 70 °C until a pink precipitate forms and then is briefly heated to 90 °C.[21] Filtration of the solution at room temperature leaves a solid (1.09 g) which is washed with pentane and dissolved in THF (20 mL) to form a pink solution. Toluene is added slowly until a white turbidity develops. The suspension is heated to 60 °C to hasten LiCl precipitation, filtered to remove LiCl, and treated again with toluene until a pink precipitate forms. THF is added until the pink precipitate just dissolves, leaving behind a small amount of precipitated LiCl. The solution is quickly filtered while hot. The solution is taken to dryness by rotary evaporation and the pink powder redissolved in a minimum of THF. Hexane is added to saturate the solution, and crystallization is induced by slow diffusion of pentane into the solution in a specially designed H-tube apparatus maintained at −8 °C. Pink needles initially crystallize followed by pink prisms.

[21] In a separate reaction in which gaseous products were collected by Toepler pump, a 6:1 mixture of 2-methylpropene to 2-methylpropane (identified by GC) was formed.

[22] The needles have the same IR spectrum and nearly identical elemental analysis as the prisms. Attempts to obtain space group information on single crystals of the needles have failed due to desolvation.

[23] Protected from the atmosphere by 0-ring sealed salt plates.

[24] These absorptions are at higher frequencies than those from THF of the neutral dimers,[5] 1025 and 865 cm^{-1}. The higher values suggest the presence of an anionic complex.[25]

[25] Atwood, J. L.; Hunter, W. E.; Rogers, R. D.; Holton, J.; McMeeking, J.; Pearce, R.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1978**, 140–142.

[26] Overall band half width is *approximately* 250 cm^{-1}.

[27] Cf. Hodgson, K. O.; Mares, F.; Starks, D. F.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1973**, *95*, 8650–8658.

[28] The space group is the monoclinic $P2_1/c$ with a = 10.324 (5) Å, b = 28.132 (9) Å, c = 16.773 (6) Å, β = 101.00 (4)°, and D_{calcd} = 1.71 g cm^{-3} for Z = 4 cation–anion units. Least-squares refinement based on 3383 observed reflections led to a final $R = \sum(|F_o| - |F_c|)/\sum|F_o| = 0.054$. The erbium, chlorine, and cyclopentadienyl carbon atoms were refined with anisotropic thermal parameters, while isotropic ones were used for atoms of the cation.

[29] The electron density peaks corresponding to H(1), H(2), and H(3) were diffuse. However, they were the largest features of the difference Fourier map apart from ripple off the metal atoms. It was not possible to refine their coordinates. Therefore, significance should not be placed in the individual metal hydrogen bond lengths but rather on the overall geometry of the trimetallic core.

[30] This may be compared to an ionic radius of 0.881 Å for Er(3+) and a metallic radius (coordination number 12) of 1.757 Å: Moeller, T. In "Comprehensive Inorganic Chemistry"; Bailer, J. C. et al. Eds.; Pergamon Press: Oxford, 1973; Vol. 4, p 7.

[31] A direct comparison of bond lengths for yttrium and erbium complexes is possible since they have identical trivalent radii: Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980, p 982.

[32] H(1) and H(2) were found to be 0.49 and 0.14 Å out of the plane of the erbium triangle, respectively.

[33] Baker, E. C.; Brown, L. D.; Raymond, K. N. *Inorg. Chem.* **1975**, *14*, 1376–1379.

[34] Ytterbium and erbium differ by 0.02 Å in trivalent radius.[31]

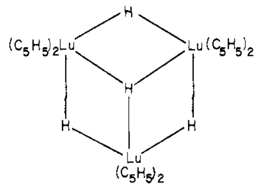

Figure 2. Proposed structure for the $[(C_5H_5)_2LuH]_3H^-$ anion.

peratures of at least 75 °C for 18 h in toluene to completely decompose, and under these conditions a complex mixture of products is formed. In order to examine a lower temperature β-hydrogen elimination reaction for lutetium, we attempted the preparation of $(C_5H_5)_2Lu(t\text{-}C_4H_9)(OEt_2)$. We anticipated that diethyl ether derivatives such as $(C_5H_5)_2Lu(t\text{-}C_4H_9)(OEt_2)$ and/or $(C_5H_5)_2Lu(t\text{-}C_4H_9)(Cl)Li(OEt_2)_2$ would be less strongly solvated and would more readily dissociate diethyl ether to provide a free coordination site for β-hydrogen elimination. Indeed, when $LiC(CH_3)_3$ is reacted with $(C_5H_5)_2LuCl$ in diethyl ether (rather than in THF), the toluene-extracted product is unstable at ambient temperature, depositing a fine white precipitate over a 24-h period.[35] The instability of the *tert*-butyl product(s) complicates characterization and precludes rigorous elimination of LiCl. Consequently, this β-hydrogen elimination also occurs in the presence of LiCl.

The toluene insoluble β-hydrogen elimination product obtained in this way, **4**, readily dissolves in THF (in contrast to the lutetium hydride formed by hydrogenolysis,[4,5] $[(C_5H_5)_2LuH(THF)]_2$, **5**, which is only sparingly soluble in hot THF) and displays a broad IR absorption at 1205 cm^{-1} (cf. ν_{Lu-H} 1350 cm^{-1} for **5**). Deuterolysis of **4** generated 0.8 mol of HD/mol of lutetium and, a CH_3I decomposition reaction generated a surprising 115% yield of CH_4 (vide infra). A complete elemental analysis was obtained on **4**, including analysis for Li and Cl since LiCl was present during the synthesis. The analytical data for Lu, C, and H were consistent with and could have been mistaken for $[(C_5H_5)_2LuH(THF)]_x$.[36] However, lithium was also found in the sample (but not chloride), suggesting a formula of the type $\{[(C_5H_5)_2LuH]_3H\}\{Li(THF)_3\}$.[37]

White needle-like crystals of **4** were obtained by slow diffusion of pentane into a hexane/THF solution and analyzed by X-ray diffraction. Although an adequate data set was obtained, structure solution has not yet been possible.

However, the ^1H NMR spectrum of **4** and the known structure of **3** allow a reasonable structure to be postulated. The 270-MHz ^1H NMR spectrum of **4** exhibits four resonances: two resonances located at δ 3.61 and 1.77 which are assigned to THF in **4**, a singlet at δ 5.83, and a doublet centered at δ 3.93 ($J = 7.8$ Hz). Although the integrated intensities of the latter two signals (10:1) are appropriate for their assignment as cyclopentadienyl and hydride resonances, respectively, the observed splitting of the hydride signal is unexplainable by Lu–H coupling (for Lu, $I = {}^7/_2$). Therefore, the splitting must be due to a magnetically inequivalent hydride which is not resolved at 270 MHz. The problem was solved by examination of the 500-MHz ^1H NMR spectrum of **4**. At the higher magnetic field, a quartet centered at δ 1.83 is resolved from the β protons of THF (resonating at δ 1.77). This signal is assigned to the postulated inequivalent hydride, based on its coupling constant ($J_{HH} = 7.8$ Hz) and proton-decoupling experiments. This information together with the knowledge that the cyclopentadienyl rings are equivalent (confirmed by ^{13}C NMR data[38]) allows the structure illustrated in Figure 2 to be proposed for **4**.

Complexes **3** and **4** represent the first trimetallic organolanthanides as well as the first organolanthanide polyhydrides. The synthesis and structural characterization of such species clearly demonstrate that a much more diverse chemistry is available to the lanthanides than has previously been known. Additional syntheses of other classes of lanthanide hydrides,[39] the reaction chemistry of these trimers and the previously reported dimers,[4,5] and the relationship, if any, of these hydrides to the interstitial metallic systems are under investigation.

Acknowledgment. For support of this research we thank the Division of Basic Energy Sciences of the Department of Energy (W.J.E., J.H.M., A.L.W.) and the National Science Foundation (J.L.A., W.E.H.). We also thank Bell Laboratories for a fellowship (A.L.W.) under the Bell Laboratories Graduate Research Program for Women and the Camille and Henry Dreyfus Foundation for a Teacher-Scholar Grant (W.J.E.). The high-field NMR instruments used in this study were funded in part by the NSF Chemical Instrumentation Program and the National Cancer Institute.

Registry No. 1, 78683-33-7; **2**, 80642-71-3; **3**, 80795-37-5; **4**, 80795-38-6; $(C_5H_5)_2LuCl$, 76207-13-1; $(C_5H_5)_2ErCl$, 53224-35-4; $LiC(CH_3)_3$, 594-19-4; LiCl, 7447-41-8; $t\text{-}C_4H_9Li$, 109-72-8.

Supplementary Material Available: Tables of bond distances and angles, final fractional coordinates, and thermal parameter (24 pages). Ordering information is given on any current masthead page.

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[35] In a typical synthesis, $LiC(CH_3)_3$ (0.1858 g, 2.9 mmol) in pentane (15 mL) was slowly dripped into a magnetically stirred solution of $(C_5H_5)_2LuCl$ (0.988 g, 2.9 mmol) in $(C_2H_5)_2O$ (40 mL) maintained at −78 °C. The solution was allowed to slowly warm to room temperature with stirring over 12 h and stirred for several additional hours. The solvent is removed in vacuo and the residue extracted with toluene to yield a clear light gold solution. If the solution is then stirred at room temperature for 24 h, a fine white precipitate deposits which can be isolated by filtration and extracted into THF. Removal of THF by rotary evaporation yields a free-flowing white microcrystalline powder (0.14 g, 0.12 mmol, 12%). At this point, the powder is often pure by ^1H NMR spectroscopy. In some cases, however, subsequent recrystallization is necessary to obtain a pure product.

[36] Anal. Calcd for $LuC_{14}H_{19}O$: Lu, 46.26; C, 44.46; H, 5.06. Found: Lu, 46.42; C, 44.19; H, 4.81.

[37] Anal. Calcd for $Lu_3C_{42}H_{58}O_3Li$: Lu, 45.99; C, 44.20; H, 5.11; Li, 0.61; O, 4.21. Found: Lu, 46.42; C, 44.19; H, 4.81; Li, 0.51; O, 4.07 (by difference). This complex also is subject to desolvation, which is perhaps why a trisolvated complex rather than the expected tetrasolvate is indicated by the elemental analysis.

[38] $^{13}C\{^1H\}$ NMR of **4** (C_4D_8O): δ 105.45 (s).

[39] The reaction of $(C_5H_5)_2LuCl$ with NaH has recently been reported to form $(C_5H_5)_2LuH(THF)$.[6] The IR and ^1H NMR spectra of the product do not agree with our data on **4** or **5**[4,5] and also do not agree with the simple structure proposed in that paper. This complex may represent yet another class of lanthanide hydrides.

[40] **Note Added in Proof**: Recent crystallographic results on **4** verify the structure shown in Figure 2.

Unsymmetrical Introduction of Two Functional Groups into Cyclodextrin. Combination Specificity by Use of *N*-Benzyl-*N*-methylaniline *N*-Oxide Cap

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In cyclodextrin chemistry several modification techniques have been exploited to introduce a substituent directly onto the primary or secondary position.[1] This direct functionalization may be extended even to disubstitution and trisubstitution,[2] although separation of the desired product from a crude mixture seems to be somewhat laborious. More recently, regiocontrol of the capping position via capped cyclodextrins[3] has also been achieved, giving

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[1] For example: (a) Emert, J.; Breslow, R. *J. Am. Chem. Soc.* **1975**, *97*, 670. (b) Iwakura, Y.; Ueno, K.; Toda, F.; Onozuka, S.; Hattori, K.; Bender, M. L. *Ibid.* **1975**, *97*, 4432. (c) Tabushi, I.; Shimidzu, N.; Sugimoto, T.; Shiodzuka, M.; Yamamura, K. *Ibid.* **1977**, *99*, 7100.

[2] (a) Boger, J.; Brenner, D. G.; Knowles, J. R. *J. Am. Chem. Soc.* **1979**, *101*, 7630. (b) Boger, J.; Knowles, J. R. *Ibid.* **1979**, *101*, 7631.

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