Organolanthanide Hydride Chemistry. 1. Synthesis and X-ray Crystallographic Characterization of Dimeric Organolanthanide and Organoyttrium Hydride Complexes

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Abstract: Hydrogenolysis of $(C_5H_4R)_2Ln(t\text{-}C_4H_9)(OC_4H_8)$ (R = H, CH_3; Ln = Lu, Er, Y) in toluene at room temperature and atmospheric pressure forms the dimeric hydrides $[(C_5H_4R)_2Ln(OC_4H_8)(\mu\text{-}H)]_2$, which have been characterized by IR and ^1H and ^{13}C NMR spectroscopy, complexometric analysis, quantitative deuterolysis, and X-ray crystallography. The analogous deuterides were similarly prepared and characterized. $[(CH_3C_5H_4)_2Y(OC_4H_8)(\mu\text{-}H)]_2$ crystallizes from C_4H_8O/hexane in the monoclinic space group $P2_1/c$ with $a = 8.731$ (3) Å, $b = 19.772$ (6) Å, $c = 9.054$ (3) Å, $\beta = 98.71$ (3)°, and $D_{calcd} = 1.38$ g cm^{-3} for $Z = 2$ dimers. The complex has Y–H bond lengths of 2.17 and 2.19 Å with a Y–H–Y angle of 114°. The Y–O and average Y–C(η^5) distances are 2.460 (8) and 2.69 Å, respectively.

Metal hydride complexes are fundamental components in a wide range of stoichiometric and catalytic organometallic reactions.[2–7] As stated in a recent review, their "importance in modern inorganic chemistry cannot be overemphasized."[6] However, for the lanthanide metals, hydrides have been previously described only for interstitial metallic compounds. The simple binary hydrides, LnH_x, have been known for many years.[8] Intermetallic hydrides such as $LaNi_5H_x$ are also known and are currently being intensively studied as hydrogen storage materials.[9] However, fully characterized, discrete, molecular lanthanide hydride complexes have not been previously reported in the literature.[10–12] Indeed, the group 3A metals, i.e., the lanthanides, scandium, and yttrium, constitute the last class of d or f orbital metals for which organometallic hydrides have not been crystallographically described.

Obviously, the synthesis and definitive characterization of hydride complexes of these metals is important to the advancement of the rapidly developing area of organolanthanide chemistry.

The existence of soluble, molecular samarium, erbium, and ytterbium hydrides was first suggested in 1978 by our report that organometallic complexes of these metals functioned as homogeneous catalysts for the hydrogenation of unsaturated hydrocarbons.[13–15] No hydride intermediates were isolated from these catalyses, however. We subsequently attempted to independently generate an ytterbium hydride by the well-established method of metal alkyl hydrogenolysis.[16–22] Although hydrogenolysis of $[(CH_3C_5H_4)_2YbCH_3]_2$ evidently formed a Yb(III)–H complex, this species is unstable with respect to reduction to the Yb(II) complex, $(CH_3C_5H_4)_2Yb$.[23] Recently, we have described the synthesis of soluble divalent and trivalent lanthanide hydrides by oxidative addition of terminal alkynes to zero-valent lanthanide metal atoms (generated by metal vapor techniques),[24] but the oligomeric nature of these alkynide hydrides so far has not allowed us to obtain single crystals suitable for X-ray crystallographic characterization. Evidence for divalent lanthanide hydrides has also been found in oxidative addition reactions of pentamethylcyclopentadiene to lanthanide metal vapor, but again a crystalline

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(10) The results described here were first presented in part at the 181st National Meeting, of the American Chemical Society, Atlanta, GA, Mar 1981, INOR 219, and at the 15th Rare Earth Research Conference, Rolla, MO, June 1981, Jl.

(11) While this manuscript was in preparation, the high-pressure reactions of $(C_5H_5)_2LuCH_2Si(CH_3)_3(THF)$ and $(C_5H_5)_2LuCH_2C_6H_5(THF)$ with H_2 in THF (reaction a) and the reaction of $[(C_5H_5)_2LuCl]_2$ with NaH (reaction b) were reported: Schumann, H.; Genthe, W., *J. Organomet. Chem.* **1981**, *213*, C7–C9. Two hydride products of different solubilities were claimed. Since no spectral or chemical data were reported on the product of reaction a (only analytical data), no comparison can be made with our data. The IR and ^1H NMR data on the product of reaction b do not agree with our data and also do not agree with the simple $(C_5H_5)_2LuH(THF)$ structure proposed by Schumann and Genthe. Since we have found that the presence of an alkali-metal salt can drastically change the course of a hydride forming reaction,[12] it is not unexpected that the product formed with NaH is different from the complexes we report here.

(12) The formation of lanthanide hydrides in the presence of alkali-metal salts is described in a separate paper in this issue: Evans, W. J.; Meadows, J. H.; Wayda, A. L.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.*, following in this issue.

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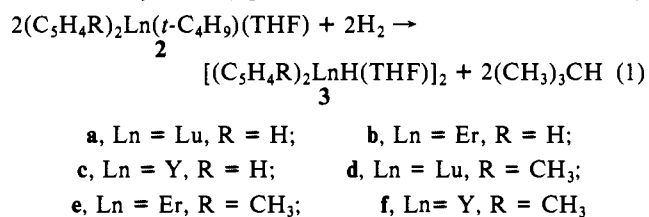
hydride has been elusive.[25] Our latest research on hydrides has focused on an extension of our earlier hydrogenolysis studies[23] to the metals lutetium, erbium and yttrium, since these elements are not readily reduced to the divalent oxidation state. We now report that this approach has led to the first successful synthesis of crystallographically characterized molecular lanthanide and yttrium hydride complexes.[26]
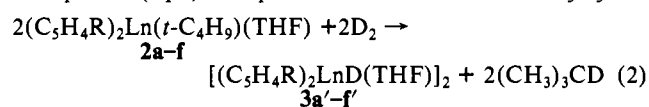
Results and Discussion

General Synthetic Method. Like much of synthetic organolanthanide chemistry,[27] the hydrogenolysis of a lanthanide carbon bond is a complex reaction which is highly dependent on the specific alkyl lanthanide substrate and the reaction conditions. Consequently, it has proven necessary to examine the reaction of hydrogen with several types of lanthanide alkyls in various solvents in order to obtain good, reproducible syntheses of fully characterizable organolanthanide hydrides. For example, hydrogenolysis of the dimeric cyclopentadienyl lanthanide methyl complexes (Ln = Yb,[23] Er,[28] Lu) at atmospheric pressure in toluene generates the expected organic product, CH_4, but the reaction is slow and requires weeks to occur. In contrast, the monomeric tert-butyl complexes $(C_5H_5)_2Ln(t\text{-}C_4H_9)(OC_4H_8)$, $\mathbf{1}$[29] (Ln = Lu, Er, Y), are much better substrates and react rapidly (in minutes) with hydrogen at atmospheric pressure in toluene at ambient temperature. In tetrahydrofuran (THF), however, no reaction is observed over a 6-h period at room temperature.[11] These results suggest that, even for metals as large as the lanthanides, access to a monomeric, unsolvated, coordinatively unsaturated complex, $(C_5H_5)_2LnR$, is critical to achieving a successful reaction between an alkyl complex and a reactive substrate which has no affinity for Ln(III) centers.[30]

Although the cyclopentadienyl *tert*-butyl complexes are good precursors to organolanthanide hydrides via hydrogenolysis,[31] complete refinement of the crystallographic data on single crystals of the erbium, lutetium, and yttrium products has proven difficult. Consequently, we have also examined the methylcyclopentadienyl derivatives, $(CH_3C_5H_4)_2Ln(t\text{-}C_4H_9)(THF)$, as hydride precursors and this has finally allowed complete crystallographic characterization of the hydride products.

The hydrogenolysis reaction has been investigated for the cyclopentadienyl and methylcyclopentadienyl derivates of lutetium, erbium, and yttrium (eq 1). This reaction was also studied by

$$2(C_5H_4R)_2Ln(t\text{-}C_4H_9)(THF) + 2H_2 \rightarrow$$
$$\mathbf{2}$$
$$[(C_5H_4R)_2LnH(THF)]_2 + 2(CH_3)_3CH \quad (1)$$
$$\mathbf{3}$$

a, Ln = Lu, R = H;   **b**, Ln = Er, R = H;

c, Ln = Y, R = H;   **d**, Ln = Lu, R = CH₃;

e, Ln = Er, R = CH₃;   **f**, Ln= Y, R = CH₃

using D_2, and the corresponding deuteride products are indicated with primes (eq 2). Representative reactions in the C_5H_5 and

$$2(C_5H_4R)_2Ln(t\text{-}C_4H_9)(THF) + 2D_2 \rightarrow$$
$$\mathbf{2a\text{-}f}$$
$$[(C_5H_4R)_2LnD(THF)]_2 + 2(CH_3)_3CD \quad (2)$$
$$\mathbf{3a'\text{-}f'}$$

Table I. Infrared Absorptions Assignable to Hydride/Deuteride Vibrations (cm^{-1})

	$[(C_5H_5)_2LnH(THF)]_2$	$[(C_5H_5)_2LnD(THF)]_2$	ratio
Lu	1350	975	1.38
Er	1330	960	1.39
Y	1315	945	1.39

	$[(CH_3C_5H_4)_2LnH(THF)]_2$	$[(CH_3C_5H_4)_2LnD(THF)]_2$	ratio
Lu	1340	960	1.40
Er	1300		
Y	1240	900^a	1.38

^{a} The maximum for this band is obscured by another absorption.

$CH_3C_5H_4$ series will be described for the case where Ln is lutetium and ancillary data from the other metals will be discussed when appropriate.[32]

Cyclopentadienyl Hydrides, $[(C_5H_5)_2LnH(THF)]_2$. In a typical cyclopentadienyl reaction (eq 1, R = H), a solution of $(C_5H_5)_2Lu(t\text{-}C_4H_9)(THF)$ (**2a**) is placed under an atmosphere of H_2 in a greaseless high vacuum reactor immersed in a −78 °C bath, and the reactor stopcock is closed. As the magnetically stirred reaction warms to room temperature, a white precipitate deposits in the flask and after 1 day at room temperature an 80–90% yield of $(CH_3)_3CH$ has formed. Although almost totally insoluble in cold THF, the crude precipitated product can be dissolved in hot THF (60 °C) and slowly cooled to yield microcrystalline $[(C_5H_5)_2LuH(THF)]_2$, **3a** (70% yield). The reaction of **2a** with D_2 proceeds analogously to form $(CH_3)_3CD$ in 90% yield and the analogous deuteride $[(C_5H_5)_2LuD(THF)]_2$, **3a′**. The complexes were identified by complexometric analyses, quantitative deuterolysis of the hydride, and hydrolysis of the deuteride, both of which form HD in good yield, and the following spectral data. The IR spectrum of **3a** contains a strong, broad[33] absorption centered at 1350 cm^{-1} in addition to absorptions assignable to C_5H_5 (1010, 775, 755 cm^{-1}) and coordinated THF (1025, 865 cm^{-1}).[34] The 1350-cm^{-1} absorption is absent in the spectrum of **3a′**, which exhibits instead a strong absorption at 975 cm^{-1}. The ratio of these absorption frequencies, 1.38, is consistent with that expected for ν_{Lu-H}/ν_{Lu-D}. Similar infrared absorptions are found for the erbium and yttrium analogues (Table I). The ^1H NMR spectra of crystalline samples of both **3a** and **3a′** contain resonances at δ 5.90 assignable to C_5H_5 and at δ 3.61 and 1.77 assignable to THF. The spectrum of **3a** also exhibits a resonance at δ 4.69, which is absent in the deuteride spectrum and is therefore assigned to Lu–*H*. The observed chemical shift is consistent with that found for other lanthanide hydrides which we have subsequently characterized by NMR (vide infra).[12] The analogous hydride resonance in the ^1H NMR spectrum of the yttrium ($I = ^1/_2$) derivative, **3c**, occurs at δ 2.02 as a triplet ($J = 27.0$ Hz) due to coupling to two equivalent yttrium atoms (vide infra).

Unfortunately, the limited solubility of complexes **3a–c** precluded characterization by some techniques (e.g., isopiestic molecular weight measurement) and made further chemical reactivity

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(30) Cf. Evans, W. J.; Wayda, A. L. *J. Organomet. Chem.*, **1980**, *202*, C6–C8 and Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 54–61.

(31) Alternative hydride syntheses including borohydride reductions and β-hydrogen eliminations have been examined. These reactions are slower, more complex and give lower yields. The latter reaction is described in ref 12.

(32) Within the C_5H_5 series and within the $CH_3C_5H_4$ series, the IR spectral properties of the complexes are very similar. Initial reactions and measurements which require large sample sizes are often conducted with the less expensive, colored erbium, but NMR measurements are not obtainable with this metal due to its large magnetic moment, 9.4–9.7 μ_b.

(33) It is difficult to measure band widths due to the shape of the hydride bands. $\Delta\nu_{1/2}$ for the hydride complexes described in this paper is 100–160 cm^{-1} with $\Delta\nu_{1/2}$ about half that, 40–75 cm^{-1}, for the corresponding deuterides. Cf. Knox, S. A. R.; Koepke, J. W.; Andrews, M. A.; Kaesz, H. C. *J. Am. Chem. Soc.* **1975**, *97*, 3942–3947.

(34) There may be an additional Lu–H absorption at 945 cm^{-1}, which shifts to 675 cm^{-1} in the deuteride, but there is too much overlap from other bands to allow a definitive assignment. The possibility that the observed broad absorption incorporates more than one Lu–H vibration also cannot be ruled out. Considerable variation in the ν_{as}/ν_s ratio for $M(\mu\text{-}X)_2M$ systems has been observed: Wing, R. M.; Callahan, K. P. *Inorg. Chem.* **1969**, *8*, 871–874. Howard, M. W.; Jayasooriya, U. A.; Kettle, S. F. A.; Powell, D. B.; Sheppard, N. *J. Chem. Soc., Chem. Commun.* **1979**, 18–20. The erbium and yttrium hydride and deuteride analogues of **3a** and **3a′** have comparable overlapped absorptions at 915 and 655 (for erbium) and 895 and 640 cm^{-1} (for yttrium), respectively.

Table II. Bond Length (Å) and Angles (Deg) for $[(CH_3C_5H_4)_2YH(THF)]_2$

Bond Lengths					
Y-Y'	3.664 (1)	Y-H(1)	2.17 (8)	Cp(6)-Cp(7)	1.42 (2)
Y-Cp(1)	2.67 (1)	Y-H(1)'	2.19 (8)	Cp(6)-Cp(10)	1.47 (2)
Y-Cp(2)	2.69 (1)	Y-Ave(1)	2.683 (9)	Cp(6)-Me(2)	1.56 (2)
Y-Cp(3)	2.69 (2)	Y-Ave(2)	2.70 (2)	Cp(7)-Cp(8)	1.38 (2)
Y-Cp(4)	2.69 (1)	Y-Cent 1	2.397	Cp(8)-Cp(9)	1.39 (2)
Y-Cp(5)	2.68 (1)	Y-Cent 2	2.414	Cp(9)-Cp(10)	1.42 (3)
Y-Cp(6)	2.70 (1)	Cp(1)-Cp(2)	1.43 (2)	O(1)-C(1)	1.43 (1)
Y-Cp(7)	2.69 (1)	Cp(1)-Cp(5)	1.48 (2)	O(1)-C(4)	1.49 (2)
Y-Cp(8)	2.66 (1)	Cp(1)-Me(1)	1.40 (2)	C(1)-C(2)	1.52 (2)
Y-Cp(9)	2.71 (2)	Cp(2)-Cp(3)	1.38 (2)	C(2)-C(3)	1.52 (2)
Y-Cp(10)	2.71 (1)	Cp(3)-Cp(4)	1.37 (2)	C(3)-C(4)	1.47 (2)
Y-O(1)	2.460 (8)	Cp(4)-Cp(5)	1.42 (2)		

Bond Angles					
Y-H(1)-Y'	114 (3)	Cp(2)-Cp(1)-Cp(5)	107 (1)	Cp(2)-Cp(1)-Me(1)	129 (2)
H(1)-Y-H(1)'	66 (3)	Cp(1)-Cp(2)-Cp(3)	107 (2)	Cp(5)-Cp(1)-Me(1)	123 (2)
O(1)-Y-H(1)'	137 (2)	Cp(2)-Cp(3)-Cp(4)	111 (2)	Cp(7)-Cp(6)-Me(2)	123 (2)
O(1)-Y-H(1)	71 (2)	Cp(3)-Cp(4)-Cp(5)	110 (2)	Cp(10)-Cp(6)-Me(2)	130 (2)
H(1)'-Y-Cent 1	101	Cp(1)-Cp(5)-Cp(4)	105 (1)	C(1)-O(1)-C(4)	109 (1)
H(1)-Y-Cent 1	112	Cp(7)-Cp(6)-Cp(10)	107 (1)	O(1)-C(1)-C(2)	108 (1)
O(1)-Y-Cent 1	98	Cp(6)-Cp(7)-Cp(8)	108 (2)	C(1)-C(2)-C(3)	104 (1)
H(1)'-Y-Cent 2	100	Cp(7)-Cp(8)-Cp(9)	110 (2)	C(2)-C(3)-C(4)	106 (1)
H(1)-Y-Cent 2	120	Cp(8)-Cp(9)-Cp(10)	108 (2)	O(1)-C(4)-C(3)	107 (1)
O(1)-Y-Cent 2	98	Cp(6)-Cp(10)-Cp(9)	106 (2)		

studies difficult. In addition, although good crystallographic data sets were obtained on single crystals of **3b** and **3c**, a structure which refined to acceptable limits has not yet been obtained.[35] Therefore, to obtain more soluble hydrides which might be crystallographically more suitable, we carried out the synthesis of the analogous methylcyclopentadienyl hydrides.

Methylcyclopentadienyl Hydrides, $[(CH_3C_5H_4)_2LnH(THF)]_2$. The methylcyclopentadienyl precursors, $(CH_3C_5H_4)_2Ln(t$-$C_4H_9)(THF)$, **2d–f** are prepared from $[(CH_3C_5H_4)_2LnCl]_2$[36] and t-C_4H_9Li in THF by methods previously described for the C_5H_5 analogues, **2a–c**.[29] Complexes **2d–f** are less thermally stable[37] and more difficult to purify than **2a–c**, and consequently, the hydrogenolysis reactions are not as clean. The reaction of H_2 with $(CH_3C_5H_4)_2Lu(t$-$C_4H_9)(THF)$, **2d**, forms 2-methylpropane in only 60% yield, and the yield of crude solid product is only 30%. The complexity of the reaction is evident from the spectral data. The ^1H NMR spectrum (THF-d_8) of the crude lutetium product indicates at least three methylcyclopentadienyl environments, as well as several resonances in the δ 3–5 region attributable to Lu–*H* moieties (confirmed by their absence in the deuteride spectrum). This crude product can be purified, however, by diffusion of pentane into a THF/hexane solution at 0 °C which provides colorless needles of the least soluble reaction product. The ^1H and ^{13}C NMR spectra of crystals of **3d** indicate a single product consistent with the formula, $[(CH_3C_5H_4)_2LuH(THF)]_2$, suggested by complexometric metal analysis. A singlet at δ 4.99 in the ^1H NMR spectrum of crystallized **3d** was assigned to Lu–*H*, since it was absent in the spectrum of crystals of the analogous deuteride, **3d'**.

The IR spectrum of the initially precipitated crude **2d** hydrogenolysis product is interesting in that the prominent hydride absorption is at 1190 cm^{-1} with only a small broad band observed at 1340 cm^{-1}. However, this 1190-cm^{-1} band is absent[38] in the purified crystals of **3d**, which exhibit instead a strong broad absorption at 1340 cm^{-1} analogous to the 1350-cm^{-1} band of **3a**. The

Table III. Final Fractional Coordinates for $[(CH_3C_5H_4)_2YH(THF)]_2$

atom	x/a	y/b	z/c
Y	0.0306 (1)	0.41701 (5)	0.9194 (1)
Cp(1)	0.318 (2)	0.411 (1)	0.854 (2)
Cp(2)	0.230 (2)	0.3651 (8)	0.751 (2)
Cp(3)	0.129 (2)	0.404 (1)	0.654 (2)
Cp(4)	0.146 (2)	0.4713 (9)	0.687 (2)
Cp(5)	0.262 (2)	0.4801 (8)	0.813 (2)
Cp(6)	0.107 (2)	0.3410 (7)	1.168 (2)
Cp(7)	0.106 (2)	0.2960 (7)	1.046 (2)
Cp(8)	-0.044 (3)	0.2898 (8)	0.975 (2)
Cp(9)	-0.144 (2)	0.327 (1)	1.049 (3)
Cp(10)	-0.054 (3)	0.3622 (8)	1.169 (2)
Me(1)	0.443 (3)	0.397 (1)	0.966 (2)
Me(2)	0.255 (3)	0.3562 (9)	1.282 (2)
O(1)	-0.202 (1)	0.4003 (4)	0.7321 (9)
C(1)	-0.306 (2)	0.4514 (7)	0.663 (1)
C(2)	-0.419 (2)	0.4174 (8)	0.542 (1)
C(3)	-0.346 (2)	0.3495 (9)	0.518 (2)
C(4)	-0.245 (2)	0.3342 (9)	0.659 (2)
H(1)	0.116 (9)	0.493 (4)	1.085 (8)

1340-cm^{-1} band is absent in the IR spectrum of crystals of the analogous deuteride, **3d'**, which contains a new band at 960 cm^{-1} assignable to ν_{Lu-D} ($\nu_{Lu-H}/\nu_{Lu-D} = 1.40$). Infrared data on erbium and yttrium analogues are presented in Table I.

Structure. In order to precisely define the coordination environment of these hydrides, complete crystallographic data sets were collected on single crystals of **3e** and **3f**.[39] The most detailed information was obtained for the yttrium derivative, **3f**, due to its smaller atomic number and more favorable absorption parameters. Figure 1 shows the molecular structure of the dimer which resides on a crystallographic center of inversion. The hydrogen atom in the bridge was located on a difference Fourier map and both the coordinates and the thermal parameters were refined to convergence. Bond distances and bond angles are presented in Table II and final fractional coordinates in Table III.

The structure of $[(CH_3C_5H_4)_2Y(THF)(\mu$-H$)]_2$, **3f**, is similar to that of $\{[C_5(CH_3)_5]_2ThH(\mu$-H$)\}_2$, **4**,[40] the only other molecular f element hydride complex for which crystallographic data is

(35) X-ray quality crystals of **3b** and **3c** were grown by slow pentane diffusion into a saturated THF solution at -8 °C. Solvent loss from crystals of **3a** has so far prevented us from crystallographically characterizing the lutetium derivative. This problem occurs even when the crystals are mounted in a glovebox saturated with THF vapor.

(36) Maginn, R. E.; Manastyrskyj, S.; Dubeck, J. *J. Am. Chem. Soc.* **1963**, *85*, 672–676.

(37) The NMR spectra of **2d** indicates observable decomposition in benzene at room temperature within 3 h, whereas **2a** is stable under these conditions for at least 1 day and requires heating to 75 °C to effect complete decomposition.

(38) The 1190-cm^{-1} IR absorption can be attributed to more highly associated hydride complexes.[12]

(39) Single crystals of **3d** have not yet given good crystallographic data due to facile desolvation.[35]

(40) Broach, R. W.; Schultz, A. J.; Williams, J. M.; Brown, G. M.; Manriquez, J. M.; Fagan, R. J.; Marks, T. J. *Science, (Washington, D.C.)* **1979**, *203*, 172–174.
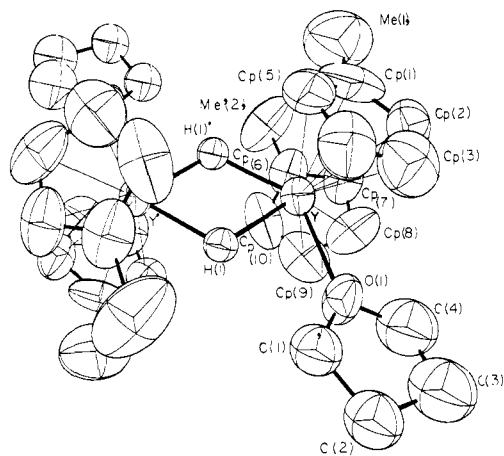
Figure 1. ORTEP plot of the molecular structure of $[(CH_3C_5H_4)_2YH-(THF)]_2$, **3f**.
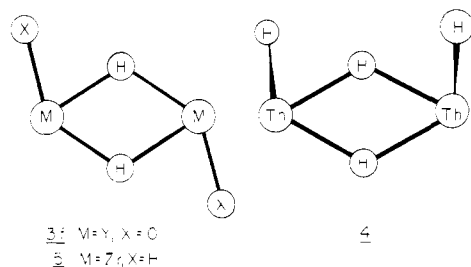
Figure 2. Central core of complexes $[(CH_3C_5R_4)_2MX(\mu-H)]_2$ where R = H for M = Zr and Y and R = CH_3 for M = Th. (View is normal to the $M_2(\mu-H)_2$ plane.)

available,[41] and the recently reported $[(CH_3C_5H_4)_2ZrH(\mu-H)]_2$, **5**.[42] In all three complexes, the metal is formally nine-coordinate due to two formally three-coordinate cyclopentadienyl rings, two bridging hydride ligands, and a monodentate ligand which is THF in **3f** and a terminal hydride in **4** and **5**. The similar geometries of the $M_2(\mu-H)_2$(terminal ligand)$_2$ central cores of **3f** and **5** are shown in Figure 2. The central core of the thorium complex, also shown in Figure 2, differs in that the terminal ligands are on the same side of the core ("cis") rather than on opposite sides ("trans"). Although the arrangement of the terminal ligands in the central cores of **3f** and **5** is similar, the orientation of the terminal ligand with respect to the methyl group of the methylcyclopentadienyl ligand differs. In **3f**, the methyl groups point away from the THF ligands; in **5**, the methyl groups point in the same direction as the terminal hydride ligands. However, in both complexes the methyl groups on rings complexed to different metal centers are oriented away from each other.[43] Comparative bond distance and bond angle data for **3f**, **4**, and **5** are presented in Table IV.

The two independent Y–H(bridge) distances in the yttrium complex, 2.17 and 2.19 Å, compare well with the average Th–H(bridge) distance in **4**, 2.29 (3) Å, and the average Zr–H(bridge) distance in **5**, 2.00 Å, taking into account the fact that Y(III) is 0.11 Å smaller than Th(IV) and 0.14 Å larger than Zr(IV).[44]

This similarity is better than one might expect considering the difference in the ligands in the system, the difference in the "cis–trans" geometry and the fact that **4** was studied by neutron rather than X-ray diffraction.[45] Indeed, comparison of the Y–H–Y angle of 114 (3)° to the Th–H–Th angle of 122 (4)° shows a greater disparity in this structural feature. Since M–H–M angles determined by X-ray diffraction are larger than those determined by neutron diffraction, this angular difference is probably even greater.[6,42,45]

The Y–O bond length, 2.460 (8) Å, is nearly equal to that found[46] in $(C_5H_5)_3Y(THF)$, 2.451 (4) Å, and is slightly larger than the distances found in $Y(\mu_3-BH_4)_2(\mu-BH_4)(THF)_3$, 2.350 (6) and 2.412 (7) Å.[26] The average Y–C(η^5) distance, 2.69 Å, is on the long end of the range for related compounds: 2.62 Å in $(C_5H_5)_2Y(CH_3)_2Al(CH_3)_2$,[47] 2.65 Å in $[\{C_5H_4Si(CH_3)_3\}_2Y-Cl]_2$,[48] 2.68 and 2.71 Å in $(C_5H_5)_3Y(THF)$.[46] The cyclopentadienyl rings are planar to within 0.01 Å, and the methyl carbon atom lies 0.12 Å out of the plane, exo to the metal.

The erbium complex, **3e**, has a molecular structure similar to that of **3f**. The two $(CH_3C_5H_4)_2(THF)Er$ units are separated by 3.616 (5) Å compared to 3.664 (1) Å in **3f** (Y and Er have nearly identical radii[44]). The hydrogen atoms were not located in **3e** but are presumed to bridge the "open" Er–Er distance as in **3f**. The symmetry of the erbium structure is such that both erbium atoms, both hydride bridges, and the oxygen atoms of the THF molecules are constrained to lie in a crystallographic mirror plane (barring disorder). In contrast, the yttrium dimer of **3f** resides on a center of inversion, and thus only the yttrium and bridging hydrogen atoms are required to be coplanar. The oxygen atom in **3f** resides 0.15 Å out of the plane.

Conclusion

The crystallographic data confirm assignments made from the spectral and chemical evidence that the crystalline products of the hydrogenolysis of $(CH_3C_5H_4)_2Ln(t-C_4H_9)(THF)$ are the dimeric lanthanide hydrides, $[(CH_3C_5H_4)_2LnH(THF)]_2$. The analogous C_5H_5 derivatives, **3a–c**, are similar based on the preliminary crystallographic data. This study demonstrates not only that stable discrete molecular lanthanide hydrides can be obtained, but also that the hydrogenolysis reaction is viable in lanthanide chemistry. This transformation constitutes another example of hydrogen activation by a d^0 metal center.[16–20,22] Furthermore, these results establish a new class of dicyclopentadienyllanthanide (anion) complexes. In addition to the solvated monomers, $(C_5H_5)_2LnX(THF)$, and the unsolvated dimers, $[(C_5H_5)_2LnX]_2$, a class of solvated dimers, $[(C_5H_5)_2LnX(THF)]_2$, is obviously accessible with the lanthanide metals if the proper Ln–X combination is found (where X is a uninegative ligand: halide, alkyl, hydride, etc.). Finally, this investigation suggests that the dimers described here are not the only type of molecular lanthanide hydrides. The complex ^1H NMR spectrum of the crude product obtained from hydrogenolysis of **2d** and the fact that the IR spectra of the crude products differ from the crystals indicate several hydride complexes are formed in this reaction.[12,38] These results suggest a diverse structural chemistry for lanthanide hydride complexes. We anticipate a correspondingly rich reaction chemistry.

Experimental Section

All of the complexes described below are extremely air and moisture sensitive. Therefore, both the syntheses and subsequent manipulations

(41) The complex $Y(\mu_3-BH_4)_2(\mu-BH_4)(THF)_3$ has Y–H distances of 2.20 (11), 2.41 (12), and 2.48 (12) Å in the μ_3-BH_4 ligand and 2.27 (9) in the $\mu-BH_4$ ligand.[26] The metal hydrogen distances in $U(BH_4)_4$ are similarly larger than those in **4** and those expected in the uranium analogue of **4**: Bernstein, E. R.; Hamilton, W. C.; Keiderling, T. A.; LaPlaca, S. J.; Lippard, S. J.; Mayerle, J. J. *Inorg. Chem.* **1972**, *11*, 3009–3016. The structure of HU[N-(SiMe$_3$)$_2$]$_3$ has also been determined, but the hydride was not located: Andersen, R. A.; Zalkin, A.; Templeton, D. H. *Inorg. Chem.*, **1981**, *20*, 622–623.
(42) Jones, S. B.; Petersen, J. L. *Inorg. Chem.* **1981**, *20*, 2889–2894.
(43) This has also been observed in $[(CH_3C_5H_4)_2TiCl]_2$: Jungst, R.; Sekutowski, D.; Davis, J.; Luly, M.; Stucky, G. *Inorg. Chem.* **1977**, *16*, 1645–1655.
(44) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980.

(45) The difference in M–H distances determined by X-ray versus neutron diffraction have been discussed: (a) Halgren, T. A.; Andersen, R. J.; Jones, D. S.; Lipscomb, W. N. *Chem. Phys. Lett.* **1971**, *8*, 547–549. (b) Beno, M. A.; Williams, J. M.; Tachikawa, M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1981**, *103*, 1485–1492. (c) Reference 6.
(46) Roger, R. D.; Atwood, J. L.; Emad, A.; Sikora, D. J.; Rausch, M. D. *J. Organomet. Chem.* **1981**, *216*, 383–392.
(47) Holton, J.; Lappert, M. F.; Scollary, G. R.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Chem. Commun.* **1976**, 425–426. Scollary, G. R. *Aust. J. Chem.* **1978**, *31*, 411–414.
(48) Shakir, R.; Atwood, J. L.; Lappert, M. F., unpublished results.

Table IV. Structural Data for Hydride-Bridged Dimers [(C₅R₅)₂MX(μ-H)]₂[a]

complex	ionic radius of the metal[b]	M–(μ-H) dist	M–(μ-H)–M angle	(μ-H)–M–X angle[c]	M–M distance
[(CH₃C₅H₄)₂Y(THF)(μ-H)]₂, **3f**	0.88	2.17 (8), 2.19 (8)	114 (3)	71 (2)	3.664 (1)
{[(CH₃)₅C₅]₂ThH(μ-H)}₂, **4**	0.99	2.29 (3)	122 (4)		4.007 (8)
[(CH₃C₅H₄)₂ZrH(μ-H)]₂, **5**	0.74	1.94 (2), 2.05 (3)	120 (1)	70 (1)	3.4599 (2)

[a] Distances in Å; angles in deg. [b] Reference 44. [c] X is the THF oxygen for **3f** and the terminal hydride for **5**.

of these compounds are conducted with rigorous exclusion of air and water using Schlenk, vacuum line, and glovebox (Vacuum/Atmospheres HE-43 Dri-Lab) techniques.

Physical Measurements. Infrared spectra are obtained as Nujol mulls on NaCl plates contained in an O-ring sealed Barnes Presslok holder or as KBr pellets prepared in the glovebox and protected from the atmosphere outside the box by attaching O-ring sealed NaCl plates to the pellet holder. The IR measurements are obtained on a Perkin-Elmer 283 spectrometer. ¹H NMR spectra are obtained on either a Bruker HX-270 or the 500-MHz DS-1000 spectrometer constructed at the University of Chicago. ¹³C NMR spectra are obtained on a Bruker HX-90E. Gas chromatographic analyses are performed on a Hewlett-Packard 5830A thermal conductivity gas chromatograph equipped with a 6 ft × ¹/₄ in. column of 4-Å molecular sieves pulverized to 40/60 mesh (used at –140°C) and a 6 ft × ¹/₄ in. column of 20% tricresyl phosphate on 60/80 Chromosorb W treated with dimethyldichlorosilane. Complete elemental analyses are obtained from Analytische Laboratorien, Engelskirchen, Germany. Complexometric analyses are obtained as previously described.²⁴

Materials. Toluene is predried with alumina and distilled from sodium. THF is distilled from potassium benzophenone ketyl. Pentane and hexane are washed with sulfuric acid, dried over MgSO₄, refluxed over finely divided LiAlH₄, and vacuum transferred. Deuterated NMR solvents are vacuum transferred from potassium benzophenone ketyl. Best results are obtained by transferring the solvent directly into the NMR tube and sealing the tube on the vacuum line. Hydrogen (Matheson, Prep grade) is purified by passage through an Alltech Oxytrap. Deuterium (Union Carbide-CP grade) is used as received. Anhydrous yttrium and lanthanide trihalides are prepared from the hydrates (Research Chemicals) by the method of Taylor and Carter.⁴⁹ *t*-C₄H₉Li is obtained from Aldrich in pentane and is purified by removal of solvent followed by sublimation at 70 °C under vacuum. NaC₅H₄R (R = H, CH₃) is prepared by the reaction of an excess of freshly cracked C₅H₅R with NaH suspended in THF at 0 °C. After evolution of H₂ ceases, the solvent is removed and the resulting white powder is desolvated by heating at 40 °C under vacuum overnight.⁵⁰ The complexes [(C₅H₄R)₂LnCl]₂ are obtained by a modification of the literature method³⁶ in which solvate-free NaC₅H₄R is reacted with LnCl₃ (1.9:1.0 molar ratio) in THF at room temperature for 24–48 h. The complexes are freed of NaCl and cyclopentadienyllanthanide side products by extraction into toluene. These complexes are usually pure at this stage by complexometric analysis and ¹H NMR spectroscopy and form in ca. 90% yield. The complexes [(CH₃C₅H₄)₂LnCl]₂ (Ln = Lu, Y) have not been described previously in the literature. Hence, their ¹H NMR spectra are included in this paper in Table V.

Since experimental details for the (C₅H₅)₂Ln(*t*-C₄H₉)(THF) complexes have not been presented and since the (CH₃C₅H₄)₂Ln(*t*-C₄H₉)-(THF) complexes are new, their syntheses will be described here. ¹H NMR data are listed in Table V.

(C₅H₅)₂Lu(*t*-C₄H₉)(THF), 2a. A pentane solution (20 mL) of *t*-C₄H₉Li (0.185 g, 2.9 mmol) is slowly added to a magnetically stirred THF solution (20 mL) of (C₅H₅)₂LuCl (1.00 g, 2.9 mmol) in a Schlenk flask cooled to –78 °C. After addition is complete, the reaction mixture is slowly warmed to ambient temperature over a 12-h period. Solvent is then removed, and the white residue is extracted with toluene. Solvent is removed from the filtrate, and the process is repeated. The resulting clear colorless toluene solution is concentrated and cooled to –78 °C until the material crystallizes as the analytically pure THF solvate (0.56 g, 45%). Rod-like crystals suitable for X-ray diffraction²⁹ are obtained by slow cooling of a toluene solution of the compound at 0 °C: ¹³C NMR (benzene-*d₆*) 110.31 (d, C₅H₅, *J* = 166 Hz), 72.85 (t, THF, *J* = 151 Hz), 37.61 (s, *C*(CH₃)₃), 35.41 (q, C(*C*H₃)₃, *J* = 120 Hz), 25.08 ppm (t, THF, *J* = 132 Hz); IR (Nujol mull, cm⁻¹) 2770 (s), 2740 (m), 2680 (w), 1770 (w, br), 1655 (w, br), 1560 (w, br), 1350 (m), 1295 (w), 1260 (w), 1250 (w), 1170 (w), 1135 (w), 1040 (w, sh), 1010 (s), 930 (w), 850 (m), 785 (s), 765 (s). Anal. Calcd for LuC₁₈H₂₇O: Lu, 40.28; C, 49.77; H,

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6.26; O, 3.68. Found: Lu, 40.68; C, 49.77; H, 6.05; O, 3.77 (by difference).

(C₅H₅)₂Er(*t*-C₄H₉)(THF), 2b. This complex is synthesized as described above for **2a**. After the second toluene extraction in the purification process, the product is isolated as an orange-pink powder in 88% yield. Anal. Calcd for ErC₁₈H₂₇O: Er, 39.20. Found: Er, 39.4. The IR spectrum of **2b** is identical with that of **2a**.

(C₅H₅)₂Y(*t*-C₄H₉)(THF), 2c. This complex is synthesized as described above for **2a**. After the second toluene extraction in the purification process, the product is isolated as a light yellow powder in 91% yield. Anal. Calcd for YC₁₈H₂₇O: Y, 25.55. Found: Y, 25.7. The IR spectrum is identical with those above.

(CH₃C₅H₄)₂Lu(*t*-C₄H₉)(THF), 2d. The complex is synthesized from (CH₃C₅H₄)₂LuCl as described above for the cyclopentadienyl analogue. Isolation of the product is more difficult, however. The solid isolated after preliminary extraction with toluene is often quite tacky and has to be extensively triturated with pentane and reextracted in order to reduce it to a pure white powder. The yield is 78%. This complex decomposes to a noticeable extent in a few days in the solid state: ¹³C NMR (THF-*d₈*) 120.26 (s, CH₃‾CCHCHCHCH), [112.21 (d, *J* = 163 Hz), 109.73 (d, *J* = 172 Hz); CH₃C‾CHCHCHCH)], 37.79 (s, *C*(CH₃)₃), 35.48 (q, C(*C*H₃)₃, *J* = 120 Hz), 15.11 (q, C₅H₄*C*H₃, *J* = 120 Hz); IR (Nujol, cm⁻¹) 2780 (s), 2740 (w), 2680 (m), 1610 (w, br), 1350 (w), 1340 (w), 1260 (w), 1240 (w), 1175 (w), 1135 (w), 1050 (m), 1035 (m), 1008 (s), 930 (m), 860 (m), 840 (s), 770 (s), 720 (w), 670 (w), 625 (w).

(CH₃C₅H₄)₂Ln(*t*-C₄H₉)(THF) (Ln = Er, Y), **2e and 2f.** Due to the larger radius of erbium and yttrium, the methylcyclopentadienyl *tert*-butyl complexes of these metals are more prone to decomposition than the lutetium complex. Consequently, care must be taken to minimize the time they are kept at room temperature, particularly when they are separated from LiCl by toluene extraction. A typical synthesis is given for the yttrium case.

A pentane solution of *t*-C₄H₉Li (0.248 g, 3.88 mmol) is added dropwise over 1 h to a magnetically stirred THF solution of (CH₃C₅H₄)₂YCl (1.125 g, 3.98 mmol) at –78 °C. The solution is stirred overnight at this temperature and then warmed to room temperature over a 3-h period. The light yellow solution is evaporated to dryness and taken into a glovebox. The solid is extracted twice with toluene and washed with pentane to give 1.30 g of a yellow powder. This powder has an infrared spectrum superimposable on that of the lutetium derivative, but its ¹H NMR spectrum in THF-*d₈* displays three distinct *t*-C₄H₉ and C*H₃*C₅H₄ resonances (some of which may arise from LiCl adducts). Some degree of decomposition is also indicated by the complexometric analysis values for the yttrium and erbium derivatives. Calcd for LnC₂₀H₃₁O: Y, 23.65; Er, 36.81. Found: Y, 24.9; Er, 37.6. However, these materials are sufficiently pure to be used as precursors to crystalline hydride complexes via hydrogenolysis (vide infra).

Synthesis of Hydride Complexes. The preparations of the six complexes [(C₅H₅)₂LnX(THF)]₂, **3a–c** and **3a′–c′**, where Ln = Lu, Er, and Y and X = H and D, are very similar and will be described in detail only for Ln = Lu and X = H. The syntheses of the complexes [(CH₃C₅H₄)₂LnH(THF)]₂, **3d–f**, where Ln = Lu, Er, and Y, and [(CH₃C₅H₄)₂LnD(THF)]₂, **3d′** and **3f′**, where Ln = Lu and Y, are also nearly identical and will be described in detail only for [(CH₃C₅H₄)₂-LuH(THF)]₂. Lanthanide hydride and deuteride stretching frequencies and ¹H NMR data are listed in Tables I and V, respectively. Attempts to obtain complete elemental analyses of [(C₅H₄R)₂LnH(THF)]₂ complexes failed due to the instability of these compounds with respect to solvent loss.³⁵

[(C₅H₅)₂LuH(THF)]₂, 3a. Freshly crystallized (C₅H₅)₂Lu(*t*-C₄H₉)-(THF) (0.2841 g, 0.654 mmol) is dissolved in toluene (10 mL) and quantitatively transferred to a tube equipped with a stir bar and an Ace Teflon stopcock. The tube is attached to a vacuum line, cooled to –78 °C, and evacuated. An atmospheric pressure of H₂ is established and the tube is closed. As the solution slowly warms, a fine white powder deposits. After the mixture was stirred for 1 day at ambient temperature, excess hydrogen is removed from the tube cooled to –196 °C. The solution is warmed to –22 °C, and the volatile gases are collected through a –78 °C U-trap by Toepler pump and analyzed by GC. An 85% yield

Table V. ^{1}H NMR Data

complex	solvent	chem shift^a	assignt
[(CH$_3$C$_5$H$_4$)$_2$LuCl]$_2$	C$_6$D$_6$	6.11 (s), 6.05 (s)	CH$_3$C$_5$H$_4$
		2.09 (s)	CH$_3$C$_5$H$_4$
[(CH$_3$C$_5$H$_4$)$_2$YCl]$_2$	C$_6$D$_6$	6.12 (s), 6.10 (s)	CH$_3$C$_5$H$_4$
		2.09 (s)	CH$_3$C$_5$H$_4$
(C$_5$H$_5$)$_2$Lu[C(CH$_3$)$_3$](THF), 2a	C$_6$D$_6$	6.02 (s)	C$_5$H$_5$
		1.30 (s)	C(CH$_3$)$_3$
		3.14, 0.96^b	C$_4$H$_8$O
	C$_4$D$_8$O	5.98 (s)	C$_5$H$_5$
		0.90 (s)	C(CH$_3$)$_3$
		3.61 (m), 1.77 (m)	C$_4$H$_8$O
(C$_5$H$_5$)$_2$Y[C(CH$_3$)$_3$](THF), 2c	C$_6$D$_6$	6.07 (s)	C$_5$H$_5$
		1.25 (s)	C(CH$_3$)$_3$
		3.12, 0.94^b	C$_4$H$_8$O
	C$_4$D$_8$O	6.02 (s)	C$_5$H$_5$
		0.83 (s)	C(CH$_3$)$_3$
		3.61 (m), 1.77 (m)	C$_4$H$_8$O
(CH$_3$C$_5$H$_4$)$_2$Lu[C(CH$_3$)$_3$](THF), 2d	C$_6$D$_6$	5.98, 5.93, 5.78^c	CH$_3$C$_5$H$_4$
		2.11 (s)	CH$_3$C$_5$H$_4$
		1.34 (s)	C(CH$_3$)$_3$
		3.18, 0.96^b	C$_4$H$_8$O
	C$_4$D$_8$O	5.88, 5.78, 5.70^c	CH$_3$C$_5$H$_4$
		2.13 (s)	CH$_3$C$_5$H$_4$
		0.91 (s)	C(CH$_3$)$_3$
		3.60 (m), 1.75 (m)	C$_4$H$_8$O
[(C$_5$H$_5$)$_2$LuH(THF)]$_2$, 3a^d	C$_4$D$_8$O	5.90 (s)	C$_5$H$_5$
		4.69 (s)	Lu–H–Lu
		3.61 (m), 1.77 (m)	C$_4$H$_8$O
[(C$_5$H$_5$)$_2$YH(THF)]$_2$, 3c^d	C$_4$D$_8$O	5.93 (s)	C$_5$H$_5$
		2.02 (t, J_{YH} = 27.0)	Y–H–Y
		3.61 (m), 1.77 (m)	C$_4$H$_8$O
[(CH$_3$C$_5$H$_4$)$_2$LuH(THF)]$_2$, 3d^d	C$_4$D$_8$O	5.84 (s), 5.75 (s)	CH$_3$C$_5$H$_4$
		2.09 (s)	CH$_3$C$_5$H$_4$
		4.99 (s)	Lu–H–Lu
		3.61 (m), 1.77 (m)	C$_4$H$_8$O
[(CH$_3$C$_5$H$_4$)$_2$YH(THF)]$_2$, 3f^d	C$_4$D$_8$O	5.91 (s), 5.81 (s)	CH$_3$C$_5$H$_4$
		2.09 (s)	CH$_3$C$_5$H$_4$
		2.31 (t, J_{YH} = 27.2)	Y–H–Y
		3.61 (m), 1.77 (m)	C$_4$H$_8$O

^{a} Chemical shifts are referenced to residual hydrogen in benzene-d_6 at δ 7.15 or THF-d_8 at δ 3.58. Chemical shifts are in δ (ppm). Coupling constants are in Hz. Integrated intensities match those expected except where noted. The CH$_3$C$_5$H$_4$ resonances often show small virtual coupling. ^{b} Broad Gaussian-shaped singlets. ^{c} Broad singlets; relative intensities 2:1:1, respectively. ^{d} The analogous deuterides have identical spectra except for the absence of the signal assigned to Ln–H–Ln.

of (CH$_3$)$_3$CH is obtained. The precipitate is separated by filtration in a glovebox (70% yield) and is extracted with hot THF to yield a clear colorless solution. Slow cooling of this solution affords small, colorless, prismatic crystals of [(C$_5$H$_5$)$_2$LuH(THF)]$_2$, 3a. The compound can also be purified by crystallization induced by slow diffusion of pentane into a THF/hexane solution at 0 °C: IR (Nujol mull, cm^{-1}) 1770 (w, br), 1640 (w, br), 1350 (s, br), 1070 (w), 1025 (s), 1010 (s), 945 (s), 920 (w), 865 (s), 800 (s), 775 (s), 755 (s), 685 (m), 670 (w). Anal. Calcd for LuC$_{14}$H$_{19}$O: Lu, 46.26. Found: 45.2. Decomposition with D$_2$O yields pure HD in quantitative yield (collected by Toepler pump and identified by GC by comparison with authentic samples[51]).

[(C$_5$H$_5$)$_2$LuD(THF)]$_2$, 3a′. The analogous reaction of (C$_5$H$_5$)$_2$Lu(t-C$_4$H$_9$)(THF) with D$_2$ generates 3a′ and (CH$_3$)$_3$CD in 90% yield, which is identified by GC-MS: IR (Nujol mull, cm^{-1}) 1770 (w, br), 1640 (w, br), 1260 (m), 1170 (w), 1070 (m), 1025 (s), 1010 (s), 975 (s, br), 930 (m), 920 (m), 865 (s), 800 (s), 775 (s), 755 (s), 675 (m), 620 (w). Decomposition of the crude deuteride product with H$_2$O yields pure HD in 75% yield. Obviously, the crude product must be recrystallized to obtain pure 3a′. The purity of the recrystallized material is readily verified by ^{1}H NMR spectroscopy.

[(C$_5$H$_5$)$_2$ErH(THF)]$_2$, 3b. This pink complex is prepared as described above for 3a. Decomposition with D$_2$O generates 0.93 mol of HD/mol of Er: IR (KBr, cm^{-1}) 3540 (w), 3085 (w), 2960 (m, br), 2880 (w), 1750 (w, br), 1625 (w, br), 1440 (w), 1360 (w), 1330 (s, br), 1260 (w), 1190 (w), 1060 (w), 1025 (m), 1010 (s), 920 (w, sh), 915 (m), 865 (m), 795 (m), 770 (s), 755 (s), 660 (m). Anal. Calcd for ErC$_{14}$H$_{19}$O: Er, 45.15. Found: 44.6.

[(C$_5$H$_5$)$_2$ErD(THF)]$_2$, 3b′. This pink complex is prepared as described above for 3a′. Hydrolysis generates 0.84 mol of HD/mol of Er: IR (KBr, cm^{-1}) 3540 (w), 3080 (w), 2940 (m, br) 2870 (w), 1750 (w, br), 1640 (w, br), 1435 (m), 1360 (w), 1255 (w), 1245 (w), 1170 (w), 1065

(w), 1025 (m), 1010 (s), 960 (m, br), 920 (w, sh), 915 (w), 865 (s), 790 (m), 755 (s), 655 (m). Anal. Calcd for ErC$_{14}$H$_{19}$O: Er, 45.01. Found: 44.0.

[(C$_5$H$_5$)$_2$YH(THF)]$_2$, 3c. This white complex is prepared as described above for 3a. Deuterolysis generates 0.91 mol of HD/mol of yttrium: IR (KBr, cm^{-1}) 3550 (w), 3090 (m), 2960 (m), 2880 (m), 1750 (w, br), 1630 (w, br), 1440 (m), 1315 (s, br), 1260 (w), 1190 (w), 1120 (w), 1065 (w), 1025 (m), 1010 (s), 925 (w, sh), 915 (w), 895 (m), 865 (m), 795 (m), 770 (s), 755 (s), 645 (m), 615 (w). Anal. Calcd for YC$_{14}$H$_{19}$O: Y, 30.45. Found: 30.0.

[(C$_5$H$_5$)$_2$YD(THF)]$_2$, 3c′. This white complex is prepared as described above for 3a′: IR (KBr, cm^{-1}, 2000–600-cm^{-1} region) 1745 (w, br), 1630 (w, br), 1440 (m), 1360 (w), 1340 (w), 1260 (w), 1250 (w), 1190 (w), 1170 (w), 1065 (w), 1025 (m), 1010 (s), 945 (m, br), 925 (w, sh), 915 (w), 865 (w), 790 (m), 770 (s), 750 (s), 665 (w), 640 (m), 620 (w).

Synthesis of [(CH$_3$C$_5$H$_4$)$_2$LuH(THF)]$_2$, 3d. (CH$_3$C$_5$H$_4$)$_2$Lu(t-C$_4$H$_9$)(THF) (0.606 g, 1.31 mmol) is extracted with 8 mL of toluene into a glass tube fitted with a Teflon stopcock (volume ≈ 88 mL). The tube is cooled to −78 °C and placed under an atmosphere of H$_2$. The solution is magnetically stirred and allowed to warm to room temperature overnight. During this time, a white precipitate deposits. The solution is filtered in the glovebox, allowing separation of a white precipitate (0.226 g, 37%). This material is dissolved in THF and brought to its solubility limit by the addition of hexane. Pentane is allowed to diffuse into this solution at 0 °C to give white needles of 3d. An additional amount of white needles of 3d can be obtained by layering pentane onto the previously separated toluene filtrate, thereby increasing the overall yield and demonstrating that 3d has partial solubility in toluene. Anal. Calcd for LuC$_{16}$H$_{23}$O: Lu, 43.09. Found: 43.2. Deuterolysis of crystals of 3d (0.046 g, 0.114 mmol) generates HD (0.11 mmol, 96%): ^{13}C{^{1}H} NMR (THF-d_8) [109.90 (s), 105.90 (s); CH$_3$CCHCHCHCH], 15.68 (s, CH$_3$C$_5$H$_4$); IR (KBr, cm^{-1}) 3530 (w), 3080 (w), 2920 (m, br), 1590 (w), 1445 (w), 1340 (s, br), 1240 (w), 1170 (w), 1035 (s), 1020 (s), 935 (m),

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Table VI. Crystal Data and Structure Refinement Parameters for
$[(CH_3C_5H_4)_2LnH(THF)]_2$

	Ln = Y	Ln = Er
mol wt	320.2	398.6
space group	$P2_1/c$	$Pnnm$
cell const		
a, Å	8.73	10.111 (5)
b, Å	19.772 (6)	12.152 (5)
c, Å	9.054 (3)	12.711 (5)
β, deg	98.71 (3)	
cell vol, Å^3	1545.0	1561.8
molecules/unit cell	2 (dimer)	2 (dimer)
D_{calcd}, g cm^{-3}	1.38	1.70
μ(calcd), cm^{-1}	38.9	55.6
radiation	Mo Kα	Mo Kα
max cryst dimens, mm	0.30 × 0.30 × 0.40	0.20 × 0.25 × 0.35
scan width	$(0.80 + 0.20 \tan \theta)°$	$(0.90 + 0.20 \tan \theta)°$
variation of stds	±2%	±3%
reflctns measd	2164	965
2θ range, deg	0–46	0–44
reflctn obsd, $I \geqslant 3\sigma(I)$	1429	571
no. of parameters varied	147	48
GOF	2.13	4.54
R	0.064	0.070
R_w	0.066	0.074

860 (m), 830 (s), 755 (s), 670 (m), 615 (m).

$[(CH_3C_5H_4)_2LuD(THF)]_2$, **3d'**. The reaction of **2d** with D_2 as described above for **3d** generates **3d'**. Hydrolysis of **3d'** forms 0.98 mol of HD/mol of Lu. Its IR spectrum is identical with that of **3d** except that the 1340-cm^{-1} absorption is absent, and an absorption at 960 cm^{-1} (m, br) is present. The absorption at 670 cm^{-1} in **3d** also appears to be absent in **3d'**, although this is more difficult to determine due to overlap of other absorptions.

$[(CH_3C_5H_4)_2ErH(THF)_2]$, **3e**. Hydrogenolysis of **2e** (0.579 g, 1.3 mmol) as described above for **3d** precipitates a pink powder (0.291 g, 50 wt%) whose IR spectrum is dominated by a band at 1180 cm^{-1} (s, br). Recrystallization of this material by pentane diffusion into a saturated THF/hexane solution at 0 °C produces pink prisms of **3e**: IR (KBr, cm^{-1}) 3060 (w), 2880 (m), 1440 (w), 1300 (s, br), 1025 (s), 930 (w), 900 (m), 870 (m), 825 (s), 750 (s), 655 (m). Isopiestic molecular weight (in THF): calculated for $Er_2C_{32}H_{46}O_2$, 797; found, 820.

$[(CH_3C_5H_4)_2YH(THF)]_2$, **3f**. The hydrogenolysis of **2f** (0.614 g, 1.6 mmol) is carried out as described above. Solvent is removed by rotary evaporation, leaving an oil which can be triturated with pentane to give a white powder (0.325 g, 53 wt %). The infrared spectrum of this material is dominated by broad absorptions having maxima at 1170 and 1250 cm^{-1}. This material is recrystallized by pentane diffusion into a THF/hexane solution at 0 °C to give colorless prisms of **3f**. The IR spectrum of **3f** is identical with that of **3e** except that the absorption at 1300 is shifted to 1240 cm^{-1}.

$[(CH_3C_5H_4)_2YD(THF)]_2$, **3f'**. Reaction of **2f** (0.270 g, 0.72 mmol) with D_2 as described above for **3f** generates a white powder (0.156 g, 58 wt %) which is recrystallized by pentane diffusion into a THF/hexane solution at 0 °C to give colorless prisms of **3f'**. The IR spectrum of **3f'** is identical with that of **3d'** except that the absorption at 960 has shifted to 900 cm^{-1}.

X-ray Data Collection and Structure Determination and Refinement for 3f, $[(CH_3C_5H_4)_2YH(THF)]_2$. Single crystals of the air-sensitive compound were sealed under N_2 in thin-walled glass capillaries. Final lattice parameters as determined from a least-squares refinement of $((\sin \theta)/\lambda)^2$ values for 15 reflections ($\theta > 20°$) accurately centered on the diffractometer are given in Table VI.

Data was collected on an Enraf-Nonius CAD-4 diffractometer by the θ-2θ scan technique. This method has been previously described.[52] A

summary of data collection parameters is given in Table VI. The intensities were corrected for Lorentz, polarization, and absorption effects. For the latter, an empirical method similar to that of Churchill was employed.[53]

Calculations were carried out with the SHELX system of computer programs.[54] Neutral atom scattering factors for Y, O, and C were taken from Cromer and Waber,[55] and the scattering for yttrium was corrected for the real and imaginary components of anomalous dispersion using the table of Cromer and Liberman.[56] Scattering factors for H were from ref 57.

The position of the yttrium atom was revealed by the inspection of a Patterson map. A difference Fourier map phased on the metal atom revealed the positions of the nonhydrogen atoms. Least-squares refinement with isotropic thermal parameters led to $R = \sum ||F_o| - |F_c||/\sum |F_o| = 0.098$. All nonhydrogen atoms except the carbons of the THF group have been refined with anisotropic thermal parameters.[58] Only the bridge hydrogen atom has been located at this stage. The final agreement factors are $R = 0.065$ and $R_w = 0.069$. A final difference Fourier showed no feature greater than 0.8 e/Å.^{3} The weighting scheme was based on unit weights; no systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin \theta)/\lambda$ was noted. The final values of the positional parameters are given in Table III.

X-ray Data Collection and Structure Determination and Refinement for 3e, $[(CH_3C_5H_4)_2ErH(THF)]_2$. Data was collected in exactly the same fashion as described above for the yttrium analogue. The structure solution proceeded in the same manner as well, except that an unresolved disorder of the THF ligand was encountered. The oxygen atom is required to lie in a crystallographic mirror plane, and at least a portion of the remainder of the ligand is disordered. The cyclopentadienyl carbon atoms also appear to suffer from high (possibly librational) thermal motion. It is therefore not surprising to note that the bridging hydrides could not be located. Final values related to the refinement are given in Table VI. The structure is of sufficient accuracy only to afford three major conclusions: (1) the molecule is a dimer, held together by hydride bridges, (2) the Er⋯Er separation is accurately defined, and (3) the molecule crystallizes in a different crystal system from the yttrium analogue.

Supplementary Material Available: A listing of structure factor amplitudes and anisotropic thermal parameters for both structures and bond distances and angles and fractional coordinates for the erbium derivative (16 pages). Ordering information is given on any current masthead page.

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(58) See paragraph at the end of paper regarding supplementary material.