Inorg. Chem. **2005**, *44*, 5820–5825

Inorganic Chemistry
Article

# Trialkylboron/Lanthanide Metallocene Hydride Chemistry: Polydentate Bridging of $(HBEt_3)^-$ to Lanthanum

**William J. Evans,* Jeremy M. Perotti, and Joseph W. Ziller**

*Department of Chemistry, University of California, Irvine, California 92697-2025*

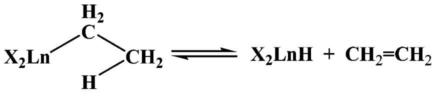
Received January 23, 2005

The reaction of $[(C_5Me_5)_2LaH]_x$ with $BEt_3$ is reported, and the solid-state structures of the lanthanum product $(C_5Me_5)_2La[(\mu\text{-}H)(\mu\text{-}Et)_2BEt]$, **1**, and its THF adduct $(C_5Me_5)_2La(THF)[(\mu\text{-}H)(\mu\text{-}Et)BEt_2]$, **2**, are compared with that of the hydride-bridged "tuckover" complex $(C_5Me_5)_2La(\mu\text{-}H)(\mu\text{-}\eta^1{:}\eta^5\text{-}CH_2C_5Me_4)La(C_5Me_5)$, **3**.

## Introduction

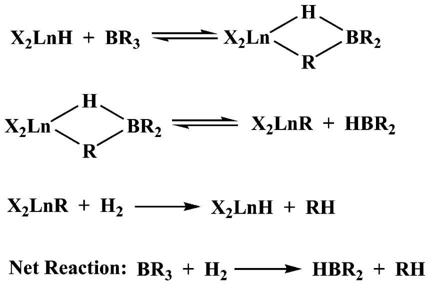
One of the several options for using hydrogen as a fuel involves the use of $NaBH_4$ as the storage material that would deliver hydrogen for use by fuel cells in battery replacement applications.[1] Recycling the boron product after hydrogen delivery may involve several stages of manipulating boron compounds back to boranes. In this connection we have begun to investigate the efficacy of lanthanide hydrides to convert trialkylboron compounds to boranes via cycles such as that shown in Scheme 1 (X = anionic ligand). Repeated movement of the $BR_{3-x}H_x$ products through the cycle would accomplish a $BR_3$ to $BH_3$ conversion.

If the alkyl group of the trialkylborane contained hydrogen on a $\beta$-carbon, an alternative pathway would be possible. $\beta$-Hydrogen elimination at the $X_2Ln{-}CH_2CH_3$ stage could occur to re-form the catalyst, $X_2LnH$, and ethylene, eq 1. However, since olefins are hydrogenated by lanthanide hydrides under hydrogen,[2,3] hydrogenolysis to form RH is likely to occur evenutally in any case.



$$X_2Ln(\mu\text{-}H)(\mu\text{-}CH_2)CH_2 \rightleftharpoons X_2LnH + CH_2{=}CH_2 \qquad (1)$$

**Scheme 1**



To test these ideas, we chose to investigate the $[(C_5Me_5)_2LnH]_x$ complexes[4,5] since these compounds have been shown to be active catalyst precursors for reactions such as hydrogenation,[2] polymerization,[5−8] hydroamination,[9] hydrosilylation,[10,11] and hydroboration.[12] Although the chemistry in Scheme 1 is reasonable based on $C_5Me_5$ lanthanide alkylaluminum derivatives,[13,14] detailed information on bridged alkylborohydride $C_5Me_5$ lanthanide complexes is not in the literature to our knowledge. Baudry and co-workers have studied monosubstituted cyclopentadienyl lanthanide chemistry with $LiBEt_3H$ as a hydride delivery reagent,[15,16]

---

* To whom correspondence should be addressed. E-mail: wevans@uci.edu.

(1) Wu, Y.; Brady, J. C.; Kelly, M. T.; Ortega, J. V.; Snover, J. L. *Prepr. Pap.*—Am. *Chem. Soc., Div. Fuel Chem.* **2003**, *48*, 938.

(2) Jeske, G.; Lauke, H.; Mauermann, H.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8111.

(3) Evans, W. J.; Engerer, S. C.; Piliero, P. A.; Wayda, A. L. *J. Chem. Soc., Chem. Commun.* **1979**, 1007.

(4) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 1401.

(5) Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091.

(6) Evans, W. J.; DeCoster, D. M.; Greaves, J. *Macromolecules* **1995**, *28*, 7929.

(7) Yasuda, H.; Furo, M.; Yamamoto, H.; Nakamura, A.; Miyake, S.; Kibino, N. *Macromolecules* **1992**, *25*, 5115.

(8) Yasuda, H.; Yamamoto, H.; Yokota, K.; Miyake, S.; Nakamura, A. *J. Am. Chem. Soc.* **1992**, *114*, 4908.

(9) Gagne, M. R.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 275.

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

(11) Koo, K.; Fu, P.-F.; Marks, T. J. *Macromolecules* **1999**, *32*, 961.

(12) Harrison, K. N.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 9220.

(13) Evans, W. J.; Chamberlain, L. R.; Ziller, J. W. *J. Am. Chem. Soc.* **1987**, *109*, 7209.

(14) Evans, W. J.; Champagne, T. M.; Giarikos, D. G.; Ziller, J. W. *Organometallics* **2005**, *24*, 570.

(15) Baudry; D.; Dormond, A.; Lachot, B.; Visseaux, M.; Zucchi, G. *J. Organomet. Chem.* **1997**, *547*, 157.

(16) Visseaux, M.; Baudry, D.; Dormond, A.; Qian, C. *J. Organomet. Chem.* **1999**, *574*, 213.

10.1021/ic0501061 CCC: $30.25

spectroscopic data are available on a $(HBEt_3)^-$ polypyrazolylborate ytterbium complex,[17] and extensive literature is available on $(BH_4)^-$ [18] and aluminum hydride bridged species,[19] but the fundamental chemistry required for Scheme 1 is not known with $C_5Me_5$-ligated complexes.

We report here on the reactivity of metallocene hydrides, $[(C_5Me_5)_2LnH]_x$, with $BEt_3$, which has generated alkylborohydride complexes that could be part of a catalytic scheme for this type of conversion and that reveal new types of lanthanide/$(HBEt_3)^-$ ligand interactions.

## Experimental Section

The syntheses and manipulations of the compounds described below were conducted under nitrogen or argon with rigorous exclusion of air and water by Schlenk, vacuum line, and glovebox techniques. The argon glovebox used in these experiments was free of coordinating solvents. Glassware was silylated with Siliclad (Gelest) before use to avoid formation of oxide decomposition products. Tetrahydrofuran, diethyl ether, toluene, hexanes, and benzene were saturated with UHP grade argon and dried by passage through Glasscontour drying columns.[20] Methylcyclohexane (99%) was purchased from Acros and distilled over NaK alloy prior to use. All deuterio solvents were dried over NaK alloy and vacuum transferred prior to use. The $[(C_5Me_5)_2LnH]_x$ (Ln = La, Sm, Y) precursors were prepared according to the literature.[21] $BEt_3$ was purchased from Aldrich and used as received. $^1H$ NMR spectra were obtained on a Bruker DRX 400 MHz or an Omega 500 MHz spectrometer at 25 °C. $^{13}C$ NMR spectra were recorded at 125 MHz on a GN 500 spectrometer. $^{11}B$ NMR spectra were obtained at 160 MHz on a GN 500 spectrometer using $BF_3{\cdot}OEt_2$ as an external reference. Infrared analyses were acquired as thin films from $C_6D_6$ solutions using an Applied Systems ReactIR 1000.[22] Elemental analyses were performed by Analytische Laboratorien (Lindlar, Germany) and complexometric titration.[23]

**$(C_5Me_5)_2La[(\mu\text{-}H)(\mu\text{-}Et)_2BEt]$, 1.** In an argon glovebox free of coordinating solvents, $BEt_3$ (10.6 $\mu$L, 0.07 mmol) was added to a colorless solution of $[(C_5Me_5)_2LaH]_x$ (30 mg, 0.036 mmol) in methylcyclohexane (5 mL) in glassware treated with Siliclad (Gelest) to avoid formation of oxide decomposition products. A pale yellow color formed within 30 min of stirring at 25 °C. Volatiles were removed in vacuo to yield **1** (34 mg, 92%) as a pale yellow solid. Anal. Calcd for $C_{26}H_{46}BLa$: C, 61.43; H, 9.12; La, 27.32. Found: C, 60.28; H, 9.11; La, 26.36. $^1H$ NMR ($C_6D_6$): $\delta$ 1.90 (s, 30H, $C_5Me_5$), 1.02 (t, $^3J_{HH}$ = 7.8 Hz, 9H, $CH_2CH_3$), 0.43 (br q, $^3J_{HH}$ = 7.8 Hz, 6H, $CH_2CH_3$). The bridging hydride resonance was not located as is sometimes the case with borohydrides bridging two quadrupolar nuclei.[24] $^{13}C\{^1H\}$ NMR ($C_6D_6$): $\delta$ 123 (s, $C_5Me_5$), 14.0 (br q, $^1J_{CB}$ = 40 Hz, $BCH_2CH_3$), 13.2 (s, $BCH_2CH_3$), 11.7 (s, $C_5Me_5$). $^{11}B$ NMR ($C_6D_6$): $\delta$ −10.1 (d, $^1J_{BH}$ = 60 Hz). IR: 2961s, 2910s, 2856s, 2725w, 2544w, 1660w, 1532w, 1444s, 1378s, 1297m, 1256m, 1166m, 1092s, 1019s, 903s, 702m cm$^{-1}$.

**$(C_5Me_5)_2La(THF)[(\mu\text{-}H)(\mu\text{-}Et)BEt_2]$, 2.** In a nitrogen glovebox, a pale yellow solution of **1** (25 mg, 0.05 mmol) in 2 mL of benzene became colorless upon addition of THF (4 $\mu$L, 0.05 mmol). Volatiles were removed in vacuo to yield **2** (22 mg, 76%) as a colorless solid. Colorless crystals suitable for X-ray diffraction were grown via slow evaporation of a $C_6D_6$ solution of **1** at 25 °C. $^1H$ NMR ($C_6D_6$): $\delta$ 1.98 (s, 30H, $C_5Me_5$), 3.58 (m, 4H, THF), 1.42 (t, $^3J_{HH}$ = 7.8 Hz, 9H, $CH_2CH_3$), 1.30 (m, 4H, THF), 0.50 (br q, $^3J_{HH}$ = 7.8 Hz, 6H, $CH_2CH_3$). The bridging hydride resonance was not located as is sometimes the case with borohydrides bridging two quadrupolar nuclei.[24] $^{13}C\{^1H\}$ NMR ($C_6D_6$): $\delta$ 121 (s, $C_5Me_5$), 70.7 (s, THF) 25.6 (s, THF), 15.0 (br q, $^1J_{CB}$ = 40 Hz, $BCH_2CH_3$), 13.2 (s, $BCH_2CH_3$), 12.1 (s, $C_5Me_5$). $^{11}B$ NMR ($C_6D_6$): $\delta$ −10.7 (d, $^1J_{BH}$ = 51 Hz). IR: 2961s, 2910s, 2856s, 2737w, 2548w, 2389w, 2281m, 1660m, 1444s, 1378s, 1258s, 1096s, 1015s, 895s, 802s, 683s cm$^{-1}$.

**$(C_5Me_5)_2La(\mu\text{-}H)(\mu\text{-}\eta^1{:}\eta^5\text{-}CH_2C_5Me_4)La(C_5Me_5)$, 3.** A colorless $C_6D_6$ solution of $[(C_5Me_5)_2LaH]_x$ (16 mg, 0.02 mmol) was allowed to stand in an NMR tube at 25 °C in an argon glovebox free of coordinating solvents. Orange crystals suitable for X-ray diffraction precipitated from the orange solution overnight and were collected via filtration (10 mg, 65% yield). Anal. Calcd for $C_{40}H_{60}La_2$: C, 58.68; H, 7.38; La, 33.93. Found: C, 57.11; H, 6.92; La, 32.62. $^1H$ NMR ($C_6D_6$): $\delta$ 2.23 (s, 1H, La−H−La), 2.07 (s, 30H, $(C_5Me_5)_2La$), 2.06 and 2.05 (both s, each 6H, $CH_2C_5Me_4$), 0.56 (s, 2H, $CH_2C_5Me_4$). IR: 2961s, 2926s, 2856s, 2737w, 1660w, 1548w, 1444s, 1378s, 1328m, 1251s, 1204m, 1162m, 1143m, 1116m, 1081s, 1058s, 1038s, 957s, 918s, 841s, 675s cm$^{-1}$.

**X-ray Data Collection, Structure Determination, and Refinement. $(C_5Me_5)_2La[(\mu\text{-}H)(\mu\text{-}Et)_2BEt]$, 1.** A pale yellow crystal of approximate dimensions 0.15 × 0.41 × 0.44 mm was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART[25] program package was used to determine the unit-cell parameters and for data collection (25 s/frame scan time for a sphere of diffraction data). The raw frame data were processed using SAINT[26] and SADABS[27] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[28] program. The diffraction symmetry was $2/m$, and the systematic absences were consistent with the centrosymmetric monoclinic space group $P2_1/n$, which was later determined to be correct.

The structure was solved by direct methods and refined on $F^2$ by full-matrix least-squares techniques. The analytical scattering factors[29] for neutral atoms were used throughout the analysis. All hydrogen atoms except those associated with C19 were located from a difference Fourier map and refined ($x$, $y$, $z$, and $U_{iso}$). The C19 hydrogen atoms were included using a riding model. At convergence, wR2 = 0.0488 and GOF = 1.055 for 425 variables refined against 6253 data. As a comparison for refinement on $F$, R1 = 0.0184 for those 5526 data with $I > 2.0\sigma(I)$. Table 1 presents the crystallographic data.

**$(C_5Me_5)_2La(THF)[(\mu\text{-}H)(\mu\text{-}Et)BEt_2]$, 2.** A pale yellow crystal of approximate dimensions 0.13 × 0.36 × 0.40 mm was mounted

---

(17) Hasinoff, L.; Takats, J.; Zhang, X. W.; Bond, A. H.; Rogers, R. D. *J. Am. Chem. Soc.* **1994**, *116*, 8833.

(18) Khvostov, A. K.; Belsky, V. K.; Sizov, A. I.; Bulychev, B. M.; Ivchenko, N. B. *J. Organomet. Chem.* **1998**, *564*, 5.

(19) Gun′ko, Y. K.; Bulychev, B. M.; Sizov, A. I.; Bel′sky, V. K.; Soloveichik, G. L. *J. Organomet. Chem.* **1990**, *390*, 153.

(20) www.glasscontour.com.

(21) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *Organometallics* **1991**, *10*, 134.

(22) Evans, W. J.; Johnston, M. A.; Clark, R. D.; Ziller, J. W. *Inorg. Chem.* **2000**, *39*, 3421.

(23) Atwood, J. L.; Hunter, W. E.; Wayda, A. L.; Evans, W. J. *Inorg. Chem.* **1981**, *20*, 4115.

(24) Basuli, F.; Tomaszewski, J.; Huffman, J. C.; Mindiola, D. J. *Organometallics* **2003**, *22*, 4705.

(25) *SMART Software Users Guide*, Version 5.1; Bruker Analytical X-Ray Systems, Inc.: Madison, WI, 1999.

(26) *SAINT Software Users Guide*, Version 6.0; Bruker Analytical X-Ray Systems, Inc.: Madison, WI, 1999.

(27) Sheldrick, G. M. *SADABS*, Version 2.05; Bruker Analytical X-Ray Systems, Inc.: Madison, WI, 2001.

(28) Sheldrick, G. M. *SHELXTL*, Version 6.12; Bruker Analytical X-Ray Systems, Inc.: Madison, WI, 2001.

(29) *International Tables for X-Ray Crystallography*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; Vol. C.

**Table 1.** Experimental Data from the X-ray Diffraction Studies of **1**−**3**

| | **1** | **2** | **3** |
|---|---|---|---|
| empirical formula | $C_{26}H_{46}BLa$ | $C_{30}H_{54}BLaO$ | $C_{40}H_{60}La_2$ |
| fw | 508.35 | 580.45 | 818.70 |
| temp (K) | 163(2) | 158(2) | 163(2) |
| cryst syst | monoclinic | monoclinic | monoclinic |
| space group | $P2_1/n$ | $P2_1/n$ | $P2_1/c$ |
| $a$ (Å) | 12.0975(14) | 11.2824(12) | 24.840(5) |
| $b$ (Å) | 14.6414(17) | 14.9424(15) | 11.226(2) |
| $c$ (Å) | 15.1196(17) | 17.7824(18) | 27.895(5) |
| α (deg) | 90 | 90 | 90 |
| $\beta$ (deg) | 104.690(2) | 90.844(2) | 105.442(3) |
| $\gamma$ (deg) | 90 | 90 | 90 |
| V (Å$^3$) | 2590.5(5) | 2997.5(5) | 7498(2) |
| $Z$ | 4 | 4 | 8 |
| $D_{calcd}$ (Mg/m$^3$) | 1.303 | 1.286 | 1.451 |
| diffractometer | Bruker CCD | Bruker CCD | Bruker CCD |
| $\mu$ (mm$^{-1}$) | 1.657 | 1.444 | 2.272 |
| wR2 (all data) | 0.0488 | 0.0751 | 0.1169 |

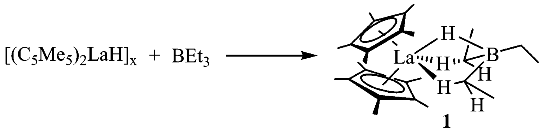
on a glass fiber and handled as in **1**. The diffraction symmetry was 2/*m*, and the systematic absences were consistent with the centrosymmetric monoclinic space group $P2_1/n$, which was later determined to be correct. All hydrogen atoms associated with carbon atoms C21−C26, in addition to H1, were located from a difference Fourier map and refined ($x$, $y$, $z$, and $U_{iso}$). Carbons atoms C28 and C29 were disordered and included using multiple components with partial site occupancy factors. At convergence, wR2 = 0.0751 and GOF = 1.070 for 350 variables refined against 7234 data. As a comparison for refinement on $F$, R1 = 0.0269 for those 6424 data with $I > 2.0\sigma(I)$.

**$(C_5Me_5)_2La(\mu\text{-}H)(\mu\text{-}\eta^1:\eta^5\text{-}CH_2C_5Me_4)La(C_5Me_5)$, 3.** An orange crystal of approximate dimensions 0.19 × 0.26 × 0.28 mm was handled as described above for **1**. The diffraction symmetry was 2/*m*, and the systematic absences were consistent with the centrosymmetric monoclinic space group $P2_1/c$, which was later determined to be correct. Hydrogen atoms were either located from a difference Fourier map and refined ($x$, $y$, $z$, and $U_{iso}$) or included using a riding model. There were two molecules of the formula unit present ($Z = 8$). The pentamethylcyclopentadienyl ring defined by atoms C61−C70B was disordered and included using multiple components with partial site occupancy factors. At convergence, wR2 = 0.1169 and GOF = 1.102 for 771 variables refined against 18264 data. As a comparison for refinement on $F$, R1 = 0.0401 for those 12870 data with $I > 2.0\sigma(I)$.

## Results and Discussion

**Synthesis.** The reactivity of $BEt_3$ with lanthanide hydride bonds was examined with three representative members of the $[(C_5Me_5)_2LnH]_x$ hydride family. The large and small diamagnetic representatives, Ln = La and Y, respectively, were chosen as well as a midsized lanthanide hydride, Ln = Sm, the first of this series to be synthesized[4] and the one for which the most chemistry is known.[7,8,21,30] Each of these hydrides reacts immediately with $BEt_3$ in benzene or cycloalkanes as evidenced by changes in solution color and NMR spectroscopy, but so far only in the Ln = La case was the product fully characterizable by X-ray crystallography. As a result, only the lanthanum system will be discussed in detail.

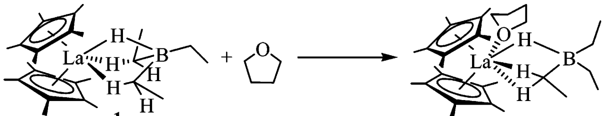
As shown in eq 2, $BEt_3$ reacts with $[(C_5Me_5)_2LaH]_x$ to make a product of composition $(C_5Me_5)_2La(HBEt_3)$, **1**. As shown in Figure 1, X-ray crystallography revealed a structure in which the $(HBEt_3)^-$ ligand approaches the trivalent $[(C_5Me_5)_2La]^+$ unit not only with the hydride attached to boron, but also with two of the ethyl groups. Since the hydrogen positions could be located and refined, closer inspection showed that one hydrogen substituent from each bridging ethyl group is oriented toward lanthanum. Although the relative amount of interaction with lanthanum of the hydrogen substituents versus the carbon atoms is difficult to estimate, the formula for **1** in the solid state could be written as $(C_5Me_5)_2La(\mu\text{-}H)[(\mu\text{-}H)CHMe]_2BEt$ to reflect the directed orientation of the hydrogen atoms. Alkylborohydrides have been observed to use alkyl hydrogen atoms to bridge to alkali metals,[31−34] alkaline-earth metals,[35] scandium,[24] and zirconium[36] but not to metals as large as lanthanum to our knowledge. For example, a similar mode of coordination for the $(HBEt_3)^-$ ligand in **1** has been observed for lithium in $(DMPE)_2H_3Ta(\mu\text{-}H)_2Li(HBEt_3)$[34] and scandium in $[CH(CMeNAr)_2]Sc(NHAr)(HBEt_3)$.[24]



**1**

(2)

Solution NMR studies of **1** show that the ethyl groups in these products are equivalent on the NMR time scale down to −90 °C, a result that is similar to that of the variable-temperature NMR study of $[CH(CMeNAr)_2]Sc(NHAr)(HBEt_3)$.[24] Infrared spectroscopy shows an absorption at 2544 cm$^{-1}$ for **1** that is consistent with a bridging B−H unit.[17]



**1** **2**

(3)

Crystallization of **1** from toluene-$d_8$ in the presence of 1 equiv of THF led to a THF adduct of formula $(C_5Me_5)_2La(HBEt_3)(THF)$, **2**, eq 3, Figure 2. In this complex the $(HBEt_3)^-$ ligand also ligates the lanthanum center with the hydride attached to boron, but in this case only one ethyl group is oriented toward the lanthanide. Once again the bridging hydrogen positions could be located and refined. These data revealed that, in contrast to that of **1**, the ethyl bridging involves both methylene hydrogen atoms of a single ethyl group. The analogous formula for **2** that emphasizes this interaction is $(C_5Me_5)_2La(\mu\text{-}H)[(\mu\text{-}H)_2CMe]BEt_2$. This mode of bridging has not been previously observed for

---

(30) Castillo, I.; Tilley, T. D. *Organometallics* **2001**, *20*, 5598.

(31) Rhine, W. E.; Stucky, G.; Peterson, S. W. *J. Am. Chem. Soc.* **1975**, *97*, 6401.

(32) Fryzuk, M. D.; Lloyd, B. R.; Clentsmith, G. K. B.; Rettig, S. J. *J. Am. Chem. Soc.* **1994**, *116*, 3804.

(33) Köster, R.; Schüssler, W.; Boese, R.; Bläser, D. *Chem. Ber.* **1991**, *124*, 2259.

(34) Dawson, D. M.; Meetsma, A.; Roedelof, J. B.; Teuben, J. H. *Inorg. Chim. Acta* **1997**, *259*, 237.

(35) Harvey, M. J.; Hanusa, T. P.; Pink, M. *Chem. Commun.* **2000**, 489.

(36) Chen, X.; Liu, S.; Plecnik, C. E.; Liu, F.-C.; Fraenkel, G.; Shore, S. G. *Organometallics* **2003**, *22*, 275.

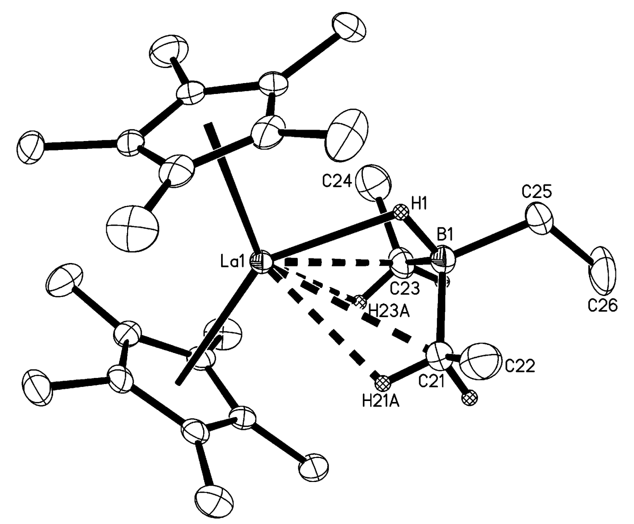


**Figure 1.** Thermal ellipsoid plot of **1** with ellipsoids drawn at the 50% probabiltity level. All hydrogen atoms shown were located and refined isotropically.

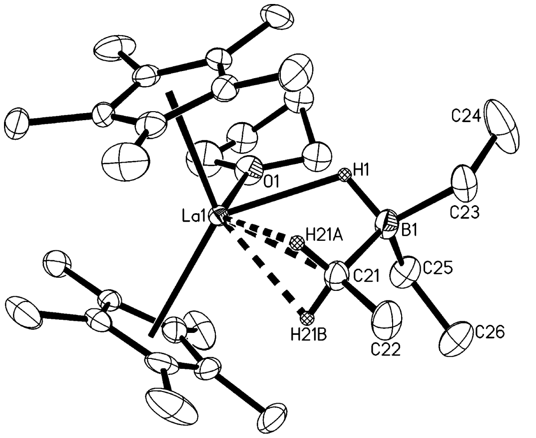
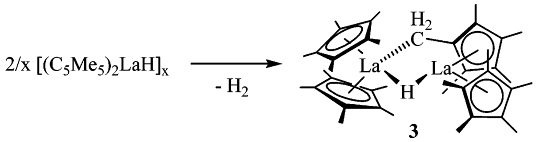


**Figure 2.** Thermal ellipsoid plot of **2** with ellipsoids shown at the 50% probability level. All hydrogen atoms shown were located and refined isotropically.

$(HBEt_3)^-$ to our knowledge. NMR studies down to −90 °C in $C_7D_8$ did not reveal the inequivalence of the hydrogen atoms observed in the solid state. An infrared stretch at 2548 $cm^{-1}$ was observed for **2** and attributed to the bridging B−H unit.

In the course of working with $[(C_5Me_5)_2La(\mu\text{-}H)]_x$, the structure of the internal C−H activation product, $(C_5Me_5)_2La(\mu\text{-}H)(\mu\text{-}\eta^1{:}\eta^5\text{-}CH_2C_5Me_4)La(C_5Me_5)$, **3**, was obtained, Figure 3, eq 4. This provides the only $(C_5Me_5)_2La-H$ bond distance in the literature to our knowledge. Samarium and yttrium analogues of **3** have previously been reported.[21,37]

 (4)

**3**

**Structural Studies.** The bis(pentamethylcyclopentadienyl) environment around La in **1** and **2** is as expected for

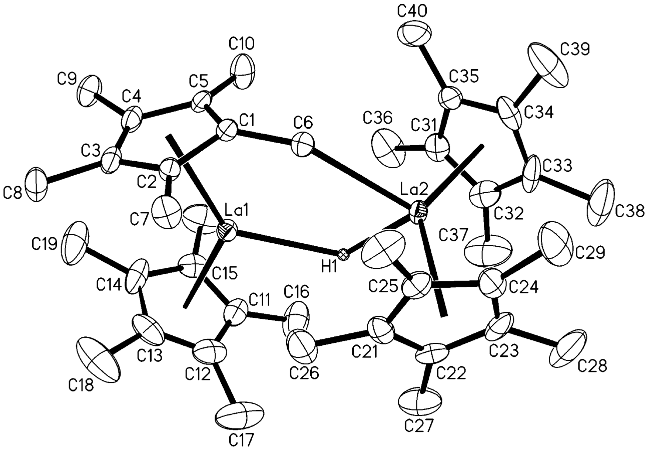
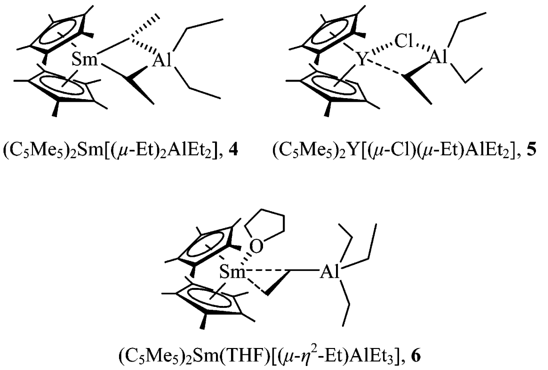


**Figure 3.** Thermal ellipsoid plot of **3** drawn at the 50% probability level.



$(C_5Me_5)_2Sm[(\mu\text{-}Et)_2AlEt_2]$, **4** $(C_5Me_5)_2Y[(\mu\text{-}Cl)(\mu\text{-}Et)AlEt_2]$, **5**

$(C_5Me_5)_2Sm(THF)[(\mu\text{-}\eta^2\text{-}Et)AlEt_3]$, **6**

**Figure 4.** Some bridging alkylaluminum lanthanide metallocene complexes.

lanthanum metallocenes. The ($C_5Me_5$ ring centroid)−La−($C_5Me_5$ ring centroid) angles in **1** and **2**, 130.3° and 129.5°, respectively, are normal for $(C_5Me_5)_2LaXL$ complexes (X = anion; L = neutral ligand)[9,38−43] as are the average La−C($C_5Me_5$) distances, 2.82(1) Å for **1** and 2.84(2) Å for **2**. The 2.540 and 2.565 Å La−($C_5Me_5$ ring centroid) distances for **1** and 2.556 and 2.540 Å lengths for **2** are also typical for lanthanum metallocenes.[9,38−43] These are longer than those in $(C_5Me_5)_2Sm[(\mu\text{-}Et)_2AlEt_2]$, **4** (2.436 and 2.445 Å),[13] and $(C_5Me_5)_2Y[(\mu\text{-}Cl)(\mu\text{-}Et)AlEt_2]$, **5** (2.345 and 2.340 Å),[14] as expected on the basis of the larger radius of La (1.160 Å) vs Sm (1.079 Å) and Y(1.019 Å).[44]

The most unusual structural aspects of **1** and **2** arise from the ethyl bridges. These are compared with those in *aluminum* complexes of trivalent lanthanide metallocenes as shown in the examples in Figure 4. Since the most reliable structural data involve the lanthanide carbon bonds and since

---

(37) Booij, M.; Deelman, B.-J.; Duchateau, R.; Postma, D. S.; Meetsma, A.; Teuben, J. T. *Organometallics* **1993**, *12*, 3531.

(38) Heeres, H. J.; Meetsma, A.; Teuben, J. H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 420.

(39) Thiele, K.-H.; Bambirra, S.; Schumann, H.; Hemling, H. *J. Organomet. Chem.* **1996**, *517*, 161.

(40) Scholz, A.; Smola, A.; Scholz, J.; Loebel, J.; Schumann, H.; Thiele, K.-H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 435.

(41) Forsyth, C. M.; Nolan, S. P.; Stern, C. L.; Marks, T. J.; Rheingold, A. L. *Organometallics* **1993**, *12*, 3618.

(42) Scholz, J.; Scholz, A.; Weimann, R.; Janiak, C.; Schumann, H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1171.

(43) Thiele, K.-H.; Bambirra, S.; Schumann, H.; Hemling, H. *J. Organomet. Chem.* **1996**, *517*, 161.

(44) For eight coordinate ions: Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

**Table 2.** Selected Bond Distances (Å) and Angles (Deg) for **1** and **2**

| | **1** | **2** |
|---|---|---|
| La−C(ring)$_{av}$ | 2.83(1), 2.81(1) | 2.82(2), 2.85(1) |
| La−Ct | 2.565, 2.540 | 2.556, 2.587 |
| La−H1 | 2.30(2) | 2.38(3) |
| La−H23A | 2.56(2) | |
| La−H21A | 2.68(2) | 2.59(4) |
| La−H21B | | 2.67(3) |
| La−C23 | 2.857(2) | |
| La−C21 | 3.118(2) | 2.853(3) |
| La−B | 2.823(2) | 3.050(3) |
| La−O | | 2.617(2) |
| Ct−La−Ct | 130.3 | 129.5 |
| H1−La−B | 23.6(5) | 21.9(7) |
| B−C21−C22 | 114.83(16) | 115.9(2) |
| La1−C21−C22 | 116.63(13) | 163.74(19) |
| La1−C21−B1 | 64.23(9) | 80.21(14) |

**Table 3.** Selected Distances (Å) and Angles (Deg) for $(C_5Me_5)_2Ln(\mu\text{-}H)(\mu\text{-}\eta^1{:}\eta^5\text{-}CH_2C_5Me_4)Ln(C_5Me_5)$ (Ln = La, **3**; Sm, **8**; Y, **9**)

| | **3** | **8** | **9** |
|---|---|---|---|
| Ln−Ct($C_5Me_5$) | | | |
| Ln1 | 2.551 | 2.452 | 2.37(1) |
| Ln2 | 2.561, 2.563 | 2.471, 2.472 | 2.39(2), 2.37(2) |
| Ln3 | 2.550 | | |
| Ln4 | 2.572, 2.561 | | |
| Ln−Ct(Fv) | | | |
| Ln1 | 2.499 | 2.408 | 2.33(1) |
| Ln3 | 2.501 | | |
| Ln−C($C_5Me_5$)$_{av}$ | | | |
| Ln1 | 2.82(2) | 2.71(2) | 2.66(2) |
| Ln2 | 2.83(2), 2.83(3) | 2.74(2), 2.74(2) | 2.67(4), 2.66(4) |
| Ln3 | 2.82(1) | | |
| Ln4 | 2.82(2), 2.83(2) | | |
| Ln−C(Fv)$_{av}$ | | | |
| Ln1 | 2.8(2) | 2.7(2) | 2.62(3) |
| Ln3 | 2.8(2) | | |
| Ln−C($CH_2$)$_{Fv}$ | | | |
| Ln2 | 2.723(5) | 2.628(7) | 2.631(9) |
| Ln4 | 2.724(5) | | |
| Ln−H | | | |
| Ln1 | 2.43(5) | 2.11(9) | 2.14(7) |
| Ln2 | 2.15(5) | 2.05(11) | 2.10(7) |
| Ln3 | 2.37(5) | | |
| Ln4 | 2.32(5) | | |
| Ln1−H1−Ln2 | 118.2 | 135.3(41) | 135(3) |
| Ln3−H2−La4 | 114.4 | | |
| Ct($C_5Me_5$)−Ln−Ct($C_5Me_5$) | | | |
| Ln2 | 136.7 | 135.4 | 133.5 |
| Ln4 | 135.1 | | |
| Ct(Fv)−Ln−Ct($C_5Me_5$) | | | |
| Ln1 | 130.8 | 131.0 | 136.3 |
| Ln3 | 129.8 | | |

the hydrogen atoms were not located in all of the aluminum examples, the differences will be discussed primarily in terms of the Ln−C bond lengths that can be established more reliably.

Table 4 shows the variation in Ln−C($\mu$-Et) bonds in **1**, **2**, **4**,[13] **5**,[14] and $(C_5Me_5)_2Sm(THF)[(\mu\text{-}\eta^2\text{-}Et)AlEt_3]$, **6**.[14] The actual distances are presented as well as the lengths adjusted for the difference in Shannon radii, so direct comparisons can be made. Examining these radius-adjusted Ln−C distances in columns 3 and 5, numbers that can be directly compared, it appears that an ethyl group can bridge lanthanides with a large range of distances.

The La−C($CH_2$) distances in **1** are in themselves disparate: 2.8572(18) Å (C23) and 3.1184(18) Å (C21). The smaller of these numbers matches the 2.853(3) Å analogue in **2** as well as the radius-adjusted distances found in **5** and **6**, 2.862(5) and 2.838(3) Å. Hence, four of these distances are similar. However, the analogous distances in **4**, 2.72(1)−2.76(1) Å, are much shorter. Overall, the distances have a spread of 0.4 Å.

**Table 4.** Lanthanide−Carbon Distances (Å) in the Ethyl-Bridged Complexes **1**, **2**, and **4**−**6**

| | Ln−C(methylene) | | Ln−C(methyl) | |
|---|---|---|---|---|
| compd | *a* | *b* | *a* | *b* |
| **1** | | 2.857(2)<br>3.118(2) | | 3.251(2)<br>4.045(2) |
| **2** | | 2.853(3) | | 4.352(3) |
| **4** | 2.64(1)−2.68(1) | 2.72(1)−2.76(1) | 4.22 | 4.30 |
| **5** | 2.721(5) | 2.862(5) | 4.184(5) | 4.325(5) |
| **6** | 2.757(3) | 2.838(3) | 2.938(4) | 3.019(4) |

[a] Ln−C distance (Å) where Ln ≠ La. [b] Ln−C distance (Å) where Ln = La or corrected to values expected for La on the basis of differences in ionic radii.

The Ln−C(Me) distances in these bridging ethyl complexes display an even larger range, 3.019(4)−4.352(3) Å, including two very different values for analogous distances in **1**, 3.251(2) and 4.045(2) Å. For comparison, the La···B distances in **1** and **2** are 2.823(2) and 3.050(3) Å, respectively; i.e., they are also dissimilar.

Like the La−C distances in **1** and **2**, the La−H lengths span a wide range. In addition, each of the measurements has a large associated error limit. The smallest of the La−H distances involves the La−($\mu$-H)B hydrogen H1: 2.30(2) and 2.38(3) Å in **1** and **2**, respectively. These lengths are within the range of the 2.15(5) and 2.45(3) Å La−H bond lengths found in **3** described below. In comparison, La−H distances in the borohydrides $[(C_{13}H_8CPh_2C_5H_4)Ln(BH_4)_2][Li(THF)_4]$ (Ln = La, Nd)[45] and $(MeOCH_2CH_2C_9H_6)_2Ln(BH_4)$ (Ln = La, Y)[46] are in the broad range of 2.37(6)−2.60(6) Å.

The La−H($\mu$-Et) distances in **1** and **2** were measured to be 2.56(2) Å (La−H23A) and 2.68(2) Å (La−H21A) in **1** and 2.59(4) Å (La−H21A) and 2.67(3) Å (La−H21B) in **2**. All are equivalent within the error limits. Considering the 0.40 Å difference in radii of hydrogen and carbon,[47] these interactions are no shorter than the La−C($CH_2$) lengths. Hence, these bridges are similar to C−H agostic interactions[48] in which both carbon and hydrogen contribute to the ligation of the metal.

The structure of complex **3** is similar to that of the samarium and yttrium analogues $(C_5Me_5)_2Ln(\mu\text{-}H)(\mu\text{-}\eta^1{:}\eta^5\text{-}CH_2C_5Me_4)Ln(C_5Me_5)$ (Ln = Sm,[21] **8**; Y,[37] **9**) previously reported. Although crystals of all three complexes were obtained from benzene, they are not isomorphous. Complex **3** is monoclinic, whereas **8** and **9** are triclinic but crystallize with different amounts of benzene in the lattice.

Bimetallic lanthanide metallocenes such as $(C_5Me_5)_2Sm(\mu\text{-}H)_2Sm(C_5Me_5)_2$[4] and $(C_5Me_5)_2Ln(\mu\text{-}O)Ln(C_5Me_5)_2$[49] typically have a tetrahedral arrangement of the four cyclopen-

---

(45) Qian, C.; Nie, W.; Sun, J. *J. Chem. Soc., Dalton Trans.* **1999**, 3283.

(46) Qian, C.-T.; Zou, G.; Nie, W.-L.; Sun, J.; Lemenovskii, D. A.; Borzov, M. V. *Polyhedron* **2000**, *19*, 1955.

(47) Pauling, L. *General Chemistry*; Dover: New York, 1988.

(48) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395.

(49) Evans, W. J.; Davis, B. L.; Nyce, G. N.; Perotti, J. M.; Ziller, J. W. *J. Organomet. Chem.* **2003**, *677*, 89.

tadienyl rings.[4,21,49−51] The dihedral angles between the two planes defined by each metal and its two ring centroids are 90°. Since **3** has two different bridging groups and one, the $(\mu\text{-}\eta^1:\eta^5\text{-}CH_2C_5Me_4)^{2-}$ ligand, involves a cyclopentadienyl ring attached to a metal, such a symmetrical structure would not be expected. Nonetheless, the angle between the plane defined by the C1−C5 tetramethylfulvene ring centroid, La1, and the C11−C15 ring centroid and the plane defined by the C21−C25 ring centroid, La2, and the C31−C35 ring centroid is relatively close to the 90° value of the more symmetrical complexes, namely, 94.4°. The analogous angles in the Sm and Y analogues are 90.3° and 97.7°, respectively.

The 2.82(2)−2.83(2) Å La−C($C_5Me_5$) average ring carbon distances in **3** are normal for lanthanum metallocene complexes and are comparable to those found for Sm (2.71(2)−2.74(2) Å)[21] and Y (2.66(4)−2.67(4) Å)[37] considering the difference in ionic radii between the three metals. The methylene carbon, C6, of the tetramethylfulvenide ligand is 2.723(5) Å from La2, a bond that is longer than the La−C single bonds in $(C_5Me_5)La[CH(SiMe_3)_2]_2$, 2.537(5) and 2.588(4) Å,[52] and La{$[CH(SiMe_3)_2]_3(\mu\text{-}Cl)Li(pmdeta)$}, which displays a mean La−C distance of 2.60(3) Å.[53] A similar situation was found in the Sm and Y examples.[21,37] The bridging hydride appears to be located asymmetrically between the La atoms, with 2.15(5) and 2.45(3) Å La−(μ-H) distances. As discussed above, the error limits on these measurements are large.

**Reactivity.** The ethyl-bridged structure $(C_5Me_5)_2La[(\mu\text{-}H)(\mu\text{-}Et)BEt_2]$ in Scheme 1 was originally proposed on the basis of ethyl aluminum lanthanide chemistry.[13,14] Since the ethyl groups of the $(HBEt_3)^-$ ligands bridged to La in the structures of **1** and **2** have considerable hydrogen involvment, it was uncertain if the dissociation of a $LaHBEt_3$ unit into LaEt and $HBEt_2$ would occur as written in Scheme 1. Indeed, in the *tert*-butylcyclopentadienyl complex "$(C_5H_4CMe_3)_2Sm(HBEt_3)$", dissociation into $[(C_5H_4CMe_3)_2SmH]_x$ and $BEt_3$ occurs in solution. To test the efficacy of Scheme 1 in light of the bridged structure observed for **1**, $(C_5Me_5)_2La(HBEt_3)$ was treated with hydrogen at 1 atm in benzene. Even up to 60 °C, no reaction was observed. However, the reaction of the analogous yttrium product, presumably $(C_5Me_5)_2Y(HBEt_3)$, with hydrogen gave the expected ethane byproduct after 24 h at room temperature. The Sm analogue under $H_2$ formed ethane after 8 h at 60 °C. This observed sensitivity of reactivity to the radial size of the lanthanide is typical of the lanthanide metals.[54] Evidently, this is a reaction system in which the relative size of the metal and the ligand set can be tuned to optimize the outcome. Further studies are in progress to determine if the reactivity observed with Y and Sm is related to a structure different from that of **1**.

## Conclusion

Reaction of the lanthanum metallocene hydride $[(C_5Me_5)_2La(\mu\text{-}H)]_x$ with triethylborane, $BEt_3$, provides the first detailed structural information on lanthanide alkylborohydride complexes **1** and **2**. The bridging nature of the $(HBEt_3)^-$ ligands in **1** and **2** is unique in organolanthanide chemistry. The effects of structure on reactivity are under study.

**Acknowledgment.** We thank the Chemical Sciences, Geosciences, and Biosciences Division of the Office of Basic Energy Sciences of the Department of Energy for support and Drs. Ying Wu and Jason Brady of Millennium Cell Inc. for helpful discussions.

**Supporting Information Available:** $^1H$ and $^{13}C$ NMR spectra, X-ray diffraction data, atomic coordinates, thermal parameters, complete bond distances and angles, and a listing of observed and calculated structure factor amplitudes for compounds **1**−**3** (PDF and CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

IC0501061

---

(50) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 6877.

(51) Evans, W. J. *J. Alloys Compd.* **1993**, *192*, 205.

(52) Van der Heijden, H.; Schaverien, C. J.; Orpen, A. G. *Organometallics* **1989**, *8*, 255.

(53) Atwood, J. L.; Lappert, M. F.; Smith, R. G.; Zhang, H. *J. Chem. Soc., Chem. Commun.* **1988**, 1308.

(54) Evans, W. J.; Davis, B. L. *Chem. Rev.* **2002**, *102*, 2119.