

Our finding that β for long-range protein electron transfers ($0.9\text{--}1.0 \text{ \AA}^{-1}$) is somewhat smaller than commonly assumed values ($1.2\text{--}1.4 \text{ \AA}^{-1}$) is supported by the observation that the three longest transfers all occur at roughly the same rate, even though d is 2–3 \AA larger for the His-12 derivative than for the other two species. Examination of $a_5\text{Ru}(\text{His-12})\text{Mb}$ with computer graphics shows that an aromatic group (Trp-14) is parallel-planar to ZnP in the medium between the porphyrin and His-12 (Figure 4), thereby raising the possibility that weak $^3\text{ZnP}^*$ (Trp-14) $a_5\text{Ru}(\text{His-12})^{3+}$ charge-transfer interactions might facilitate electron transfer.⁴⁴ However, an extensive theoretical analysis of the ZnP to $a_5\text{Ru}(\text{His-12})$ pathway by Kuki and Wolynes⁴⁵ does not support a

special role for the intervening tryptophan, and the relatively small departure of the His-12 derivative from the rate-distance correlation (eq 3) may have an entirely different origin. Hoffman, Mauk, and co-workers have found only minor effects on cytochrome *c* peroxidase ($^3\text{ZnP}^*$)|cytochrome *c*(Fe^{3+}) long-range electron-transfer rates upon changing Phe-82 of cyt *c* to other residues, although dramatic differences in the reverse-direction transfers (Fe^{2+} to ZnP^*) were observed.¹⁴ Further work on the influence of the medium in well-defined electron-transfer systems is called for, because it is apparent from these early experimental and theoretical results that many issues need to be explored in greater depth.

(43) For comparison, the β 's are 0.75 and 0.90 \AA^{-1} for the lower and upper d_m limits. The driving-force dependences of the electron-transfer rates indicate that λ is $1.90\text{--}2.45 \text{ eV}$ for $\text{Ru}(\text{His-48})\text{Mb}$ if β is 0.91 \AA^{-1} : Karas, J. L.; Lieber, C. M.; Gray, H. B. *Abstracts of Papers*, 193rd National Meeting of the American Chemical Society, Denver, CO; American Chemical Society: Washington, DC, April 1987; INOR 149, submitted for publication in *J. Am. Chem. Soc.*

(44) Calculations assuming a nearly optimal orientation indicate that Trp-14 could enhance the donor-acceptor electronic coupling: Onuchic, J. N.; Beratan, D. N. *J. Am. Chem. Soc.* **1987**, *109*, 6771-6778.

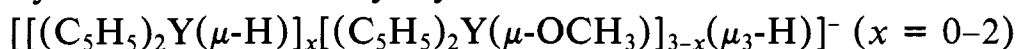
(45) Kuki, A.; Wolynes, P. G. *Science (Washington, D.C.)* **1987**, *236*, 1647-1652.

Acknowledgment. We thank Charlie Lieber, Jenny Karas, Walther Ellis, Lorne Reid, Jose Onuchic, David Beratan, A. Kuki, Harvey Schugar, R. A. Marcus, and Jay Winkler for helpful discussions. A.W.A. acknowledges a fellowship from the Fannie and John Hertz Foundation. S.L.M. acknowledges a fellowship from AT&T Bell Laboratories. This research was supported by National Science Foundation Grants CHE85-18793 and CHE85-09637.

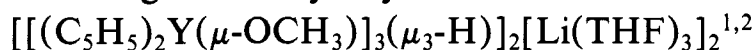
Registry No. ZnP, 14354-67-7; His, 71-00-1; Trp, 73-22-3; meso-porphyrin IX dimethyl ester, 1263-63-4.

Reactivity of Trimetallic Organoyttrium Hydride Complexes.

Synthesis of the Alkoxy Hydride Anions



Including the X-ray Crystal Structure of



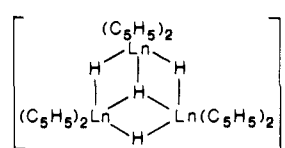
William J. Evans,*^{3a} Mark S. Sollberger,^{3a} Saeed I. Khan,^{3b} and Robert Bau*^{3b}

Contribution from the Departments of Chemistry, University of California, Irvine, Irvine, California 92717, and University of Southern California, Los Angeles, California 90089. Received February 17, 1987

Abstract: $[[(\text{C}_5\text{H}_5)_2\text{Y}(\mu\text{-H})]_3(\mu_3\text{-H})][\text{Li}(\text{THF})_4]$ (**1**) reacts with 1 equiv of CH_3OH at 0°C to form $[[(\text{C}_5\text{H}_5)_2\text{Y}(\mu\text{-OCH}_3)][(\text{C}_5\text{H}_5)_2\text{Y}(\mu\text{-H})]_2(\mu_3\text{-H})][\text{Li}(\text{THF})_4]$ (**2**). Reaction of **1** with 2 equiv of CH_3OH or **2** with 1 equiv of CH_3OH at 0°C forms $[[(\text{C}_5\text{H}_5)_2\text{Y}(\mu\text{-OCH}_3)]_2[(\text{C}_5\text{H}_5)_2\text{Y}(\mu\text{-H})](\mu_3\text{-H})][\text{Li}(\text{THF})_4]$ (**3**). $[[(\text{C}_5\text{H}_5)_2\text{Y}(\mu\text{-OCH}_3)]_3(\mu_3\text{-H})][\text{Li}(\text{THF})_4]$ (**4**) can be formed from **1**–**3** with the appropriate amount of CH_3OH at 0°C . The central $\mu_3\text{-H}$ of these trimers does not react with CH_3OH . All trimetallic species were identified by elemental analysis, hydrolytic decomposition and ^1H NMR spectroscopy. Crystallization of **4** from THF gives $[[(\text{C}_5\text{H}_5)_2\text{Y}(\mu\text{-OCH}_3)]_3(\mu_3\text{-H})]_2[\text{Li}(\text{THF})_3]_2$ (**5**) in space group $P2_1/n$ with the following unit cell dimensions: $a = 20.852$ (9), $b = 13.984$ (5), $c = 31.590$ (9) \AA ; $\beta = 92.48$ (4) $^\circ$; $V = 9203$ (7) \AA^3 , $Z = 8$; $D_{\text{calc}} = 1.81 \text{ g cm}^{-3}$. Least-squares refinement on the basis of 2987 observed reflections led to a final R value of 0.080. The structure contains an anionic $[(\text{C}_5\text{H}_5)_2\text{Y}(\mu\text{-OCH}_3)]_3(\mu_3\text{-H})^-$ unit, which has a triangular arrangement of three $(\text{C}_5\text{H}_5)_2\text{Y}$ units bridged by methoxide groups. The central hydride ligand was not located but was observable by ^1H NMR spectroscopy. The cation in **5** is comprised of a trimetallic anion like that just described, to which are attached two $(\text{THF})_3\text{Li}$ groups, i.e., $[[(\text{THF})_3\text{Li}(\mu\text{-}\eta^5\text{-C}_5\text{H}_5)(\text{C}_5\text{H}_5)_2\text{Y}(\mu\text{-OCH}_3)]_2[(\text{C}_5\text{H}_5)_2\text{Y}(\mu\text{-OCH}_3)]_3(\mu_3\text{-H})]^+$. The $(\text{THF})_3\text{Li}$ units bind on the same side of the trimetallic plane to carbon atoms in two different C_5H_5 rings with Li–C distances of 2.50 (8)–2.67 (5) \AA . The two trimetallic parts are otherwise similar, with average Y–O(OCH_3) and Y–C(C_5H_5) distances of 2.28 (2) and 2.73 (2) \AA .

In the course of studying the first crystallographically characterized molecular lanthanide hydrides,⁴ we discovered an unusual class of trimetallic hydrides, $[[(\text{C}_5\text{H}_5)_2\text{Ln}(\mu\text{-H})]_3(\mu_3\text{-H})][\text{Li}$

$(\text{THF})_4]$ ($\text{Ln} = \text{Lu}, ^5\text{Y}, ^6\text{Er}^7$), in which three $(\text{C}_5\text{H}_5)_2\text{Ln}(\mu\text{-H})$ units surround a central hydride ion:



(1) Reported in part at the 191st National Meeting of the American Chemical Society, New York, NY, April 1986, and at the 2nd International Conference on the Chemistry and Technology of the Lanthanides and Actinides, Lisbon, Portugal, April 1987; p (I)19. Organolanthanide and Organoyttrium Hydride Chemistry. 10.²

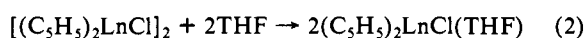
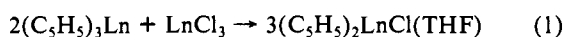
(2) Part 9: Evans, W. J.; Drummond, D. K.; Hanusa, T. P.; Doedens, R. *J. Organometallics* **1987**, *6*, 2279-2285.

(3) (a) University of California, Irvine. (b) University of Southern California.

(4) Evans, W. J.; Meadows, J. H.; Wayda, A. L.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 2008-2014.

The ^1H NMR spectra of the lutetium and yttrium derivatives and X-ray diffraction studies on the lutetium complex and the related chloro derivative $[[(\text{C}_5\text{H}_5)_2\text{Er}(\mu\text{-H})_2][(\text{C}_5\text{H}_5)_2\text{Er}(\mu\text{-Cl})](\mu_3\text{-H})][\text{Li}(\text{THF})_4]$ indicated that the $\mu_3\text{-H}$ is centrally located in the plane described by the three metal atoms. These trimetallic species were of interest because this type of metallic coordination environment had not been observed previously for hydrogen in molecular complexes.⁸

We recently have developed a high-yield synthesis of the trimetallic polyhydride complexes,⁶ which allows us to investigate their chemistry. A key question regarding the reactivity of these trimetallic complexes, as well as the reactivity of polymetallic transition-metal cluster complexes in general, is whether the polymetallic system remains intact during the reaction or whether dissociation to monometallic fragments occurs. Given the well-established tendency of organolanthanide complexes to ligand redistribute,⁹⁻¹² e.g. eq 1, and to undergo bimetallic-monometallic



interconversion,⁹⁻¹⁴ e.g. eq 2, it seemed likely that the trimetallic hydrides would dissociate and not display polymetallic chemistry. We felt it was important to determine whether this was true and to determine whether the reactivity of these trimetallic species added new insight into the principles of organolanthanide reactivity being developed from data on mono- and bimetallic lanthanide and yttrium complexes.^{12,14-23} We report here the reactivity of the trimetallic tetrahydrides as exemplified by $[(\text{C}_5\text{H}_5)_2\text{Y}(\mu\text{-H})_3(\mu_3\text{-H})][\text{Li}(\text{THF})_4]$ (1). As described earlier,^{6,24} yttrium is a particularly desirable metal for such a study because of the structural information available via coupling of hydrogen to the 100% abundant $I = 1/2$ ^{89}Y nucleus.

Experimental Section

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

tions of these compounds were conducted with rigorous exclusion of air and water with Schlenk, vacuum line, and glovebox (Vacuum Atmospheres HE-83 Dri-Lab) techniques. Methanol was dried over molecular sieves, decanted onto CaH_2 , distilled from CaH_2 , and dried with Na before use. Physical measurements and purification of the other reagents have been described previously.²⁶ The gas evolved from the methanolysis and hydrolysis reactions was identified as hydrogen by GC-mass spectrometry.

$[(\text{C}_5\text{H}_5)_2\text{Y}(\mu\text{-H})_2][(\text{C}_5\text{H}_5)_2\text{Y}(\mu\text{-OCH}_3)](\mu_3\text{-H})[\text{Li}(\text{THF})_4]$ (2). In the glovebox, $[(\text{C}_5\text{H}_5)_2\text{Y}(\mu\text{-H})_3(\mu_3\text{-H})][\text{Li}(\text{THF})_4]$ (94 mg, 0.1 mmol) was dissolved in approximately 10 mL of THF in a test tube fitted with two high-vacuum greaseless stopcocks. One stopcock was connected to a 24/40 joint, and the other was attached to an inlet sealed by a septum. The tube was attached to a high-vacuum line fitted with a Toepler pump, and the solution was degassed with four freeze-pump-thaw cycles. The tube was cooled in a liquid nitrogen bath, and CH_3OH (4 μL , 0.1 mmol) was injected with a gas-tight microliter syringe into the inlet chamber. After the CH_3OH was allowed to condense into the tube, the tube was placed in a dry ice/acetone bath and warmed to -78°C . As soon as the system started to thaw, gas evolved. After the reaction was stirred at -78°C for 1.5 h, the cold bath was removed. As the reaction warmed to room temperature and the solvent was transferred to a U-trap, 10.4 mL (0.1 \pm 0.01 mmol, 100%) of gas was collected. The somewhat oily product was taken into the glovebox, and toluene (5 mL) was added. The mixture was centrifuged and the toluene decanted off, leaving 2 as a white powder in quantitative yield. Decomposition of 2 (50 mg, 0.05 mmol) with H_2O was monitored with a Toepler pump, and 17 mL (0.12 \pm 0.01 mmol, 80%) of gas was collected. Complexometric analysis. Calcd for $\text{Y}_3\text{C}_{47}\text{H}_{68}\text{O}_3\text{Li}$: Y, 27.03. Found: Y, 27.1. NMR and IR data are given in Tables I and II.

$[(\text{C}_5\text{H}_5)_2\text{Y}(\mu\text{-H})][(\text{C}_5\text{H}_5)_2\text{Y}(\mu\text{-OCH}_3)]_2(\mu_3\text{-H})[\text{Li}(\text{THF})_4]$ (3). $[(\text{C}_5\text{H}_5)_2\text{Y}(\mu\text{-H})_3(\mu_3\text{-H})][\text{Li}(\text{THF})_4]$ (66 mg, 0.07 mmol) was treated as described above with CH_3OH (5.6 μL , 0.14 mmol). The reaction was stirred at -78°C for 2 h, and gaseous products were collected by Toepler pump. While the reaction was maintained at -78°C , 12.2 mL of gas (0.11 \pm 0.01 mmol, 80%) was collected. When the solution had warmed to 0°C , an additional amount of gas (0.05 \pm 0.01 mmol) was collected. Workup of the reaction product as described above gave 3 as a white powder in quantitative yield. Decomposition of 3 (64 mg, 0.063 mmol) with H_2O was monitored by Toepler pump and found to generate 14.2 mL (0.13 \pm 0.01 mmol, 100%) of gas. Complexometric analysis. Calcd for $\text{Y}_3\text{C}_{48}\text{H}_{70}\text{O}_6\text{Li}$: Y, 26.2. Found: Y, 26.9. NMR and IR data are given in Tables I and II.

$[(\text{C}_5\text{H}_5)_2\text{Y}(\mu\text{-OCH}_3)]_3(\mu_3\text{-H})[\text{Li}(\text{THF})_4]$ (4). **Sequential Synthesis.** $[(\text{C}_5\text{H}_5)_2\text{Y}(\mu\text{-H})_3(\mu_3\text{-H})][\text{Li}(\text{THF})_4]$ (78 mg, 0.08 mmol) was treated as described above with 1 equiv of CH_3OH (3.3 μL , 0.08 mmol) at -78°C . After the reaction was stirred for 1 h, approximately 1 equiv of gas was collected by Toepler pump. A second 1 equiv of CH_3OH was added to the reaction at -78°C and the mixture stirred for 1.5 h. Gas collection gave 0.11 mmol of gas or 70% of the amount expected for the reaction of two hydride units. The reaction was warmed to 0°C for 30 min, and additional gas was collected, giving a total of 2 equiv of gas collected since the start of the reaction. Addition of a third 1 equiv of CH_3OH to the reaction at 0°C gave additional bubbling. After the solution was stirred for 1 h, a third 1 equiv of gas was collected. Workup as described above gave 4 as a white powder. Anal. Calcd for the disolvate $\text{Y}_3\text{C}_{41}\text{H}_{56}\text{O}_3\text{Li}$: Y, 29.55. Found: Y, 29.9. Decomposition of 4 (31.4 mg, 0.030 mmol) with H_2O was monitored by Toepler pump and found to generate 0.015 mmol (50%) of gas. A more direct synthesis of 4 is given in the next section. NMR and IR data are given in Tables I and II. Integration of the resonances of the solvated THF molecules is consistent with four THF molecules of solvation.

$[(\text{C}_5\text{H}_5)_2\text{Y}(\mu\text{-OCH}_3)]_3(\mu_3\text{-H})[\text{Li}(\text{THF})_4]$ (4). **Direct Synthesis.** $[(\text{C}_5\text{H}_5)_2\text{Y}(\mu\text{-H})_3(\mu_3\text{-H})][\text{Li}(\text{THF})_4]$ (130 mg, 0.14 mmol) was treated as described above with CH_3OH (22 μL , 0.54 mmol). The reaction was stirred for 1.5 h at -78°C and an additional 1.5 h at 0°C . Workup of the reaction product as described above gave 4 as a white powder in 90% yield. The reaction of $[(\text{C}_5\text{H}_5)_2\text{Y}(\mu\text{-H})_3(\mu_3\text{-H})][\text{Li}(\text{THF})_4]$ with more than 3 equiv of CH_3OH at room temperature for more than several hours (e.g. overnight) gives insoluble products and smaller yields of 4.

Reaction of 4 and CH_3OH . Complex 4 (42 mg, 0.04 mmol) was treated as described above with CH_3OH (3.2 μL , 0.08 mmol) at 0°C . No gas evolution was observed. The reaction was allowed to warm to room temperature and stirred for 1 h; still no gaseous products were collectable by Toepler pump. The reaction was then heated at 65°C for 30 min. After this time, the system was opened to the Toepler pump, but again no gases were present. At 65°C some insoluble materials appeared in the reaction solution. Solvent was removed from the reaction, and the residue was extracted with THF. ^1H NMR analysis of the THF soluble portion showed it to be pure 4.

(5) Evans, W. J.; Meadows, J. H.; Wayda, A. L.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 2015-2017.

(6) Evans, W. J.; Meadows, J. H.; Hanusa, T. P. *J. Am. Chem. Soc.* **1984**, *106*, 4454-4460.

(7) Evans, W. J.; Meadows, J. H., unpublished results.

(8) Bau, R. *Transition Metal Hydrides*; Advances in Chemistry 167; American Chemical Society: Washington, DC, 1978.

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

(10) Evans, W. J. In *The Chemistry of The Metal-Carbon Bond*; Hartley, F. R., Patai, S., Eds.; Wiley: New York, 1982; Chapter 12.

(11) Marks, T. J.; Ernst, R. D. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Chapter 21.

(12) Schumann, H.; Genthe, W. In *Handbook on the Physics and Chemistry of Rare Earths*; Gschneidner, K. A., Jr., Eyring, L., Eds.; Elsevier: Amsterdam, 1985; Vol. 7, Chapter 53, and references therein.

(13) Ni, C.; Zhang, Z.; Deng, D.; Qian, C. *J. Organomet. Chem.* **1986**, *306*, 209-214.

(14) Evans, W. J. *Adv. Organomet. Chem.* **1985**, *24*, 131-177, and references therein.

(15) Evans, W. J. *Polyhedron* **1987**, *6*, 803-835.

(16) Evans, W. J.; Meadows, J. H.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 1291-1300.

(17) Evans, W. J.; Peterson, T. T.; Rausch, M. D.; Hunter, W. E.; Zhang, H.; Atwood, J. L. *Organometallics* **1985**, *4*, 554-559.

(18) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51-56, and references therein.

(19) Watson, P. L. *J. Chem. Soc., Chem. Commun.* **1983**, 276-277.

(20) Watson, P. L. *J. Am. Chem. Soc.* **1983**, *105*, 6491-6493.

(21) Jeske, G.; Lauke, H.; Mauermann, H.; Swebston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091-8103, and references therein.

(22) den Haan, K. H.; Teuben, J. H. *Recl.: J. R. Neth. Chem. Soc.* **1984**, *103*, 333-334.

(23) Evans, W. J.; Dominguez, R.; Hanusa, T. P. *Organometallics* **1986**, *5*, 263-270.

(24) Evans, W. J.; Hanusa, T. P.; Meadows, J. H.; Hunter, W. E.; Atwood, J. L. *Organometallics* **1987**, *6*, 295-301.

Table I. ^1H NMR Spectra (δ) of Complexes 1-4^a

complex	C_5H_5	$\mu_3\text{-H}$	$\mu\text{-H}$	$\mu\text{-OCH}_3$
1	5.93 (s, 30 H)	-1.03 (m, 1 H) $^1J_{\text{YH}} = 17.0$ Hz, $^2J_{\text{HH}} = 8.5$ Hz	0.75 (m, 3 H) $^1J_{\text{YH}} = 30.7$ Hz	
2	6.01 (s, 10 H)	-0.45 (m, 1 H) $^1J_{\text{YH}} = 18.4$ Hz, $^2J_{\text{HH}} = 8.3$ Hz	0.99 (td, 2 H) $^1J_{\text{YH}} = 28.7$ Hz	3.26 (s, 3 H)
3	5.92 (s, 20 H)	-0.46 (qd, 1 H) $^1J_{\text{YH}} = 18.4$ Hz, $^2J_{\text{HH}} = 8.1$ Hz	1.13 (td, 1 H) $^1J_{\text{YH}} = 27.2$ Hz	3.38 (s, 6 H)
4	5.88 (s, 10 H)	0.30 (q, 1 H) $^1J_{\text{YH}} = 18.4$ Hz		3.31 (s, 9 H)

^aIn THF- d_6 referenced to residual H at δ 1.79.

Table II. Infrared Spectra (KBr) of Complexes 1-4 (cm^{-1})

1	2	3	4
3090 w	3090 w	3090 w	3090 w
2970 m	2970 m		2960 m
	2940 m	2910 m	2920 m
2880 m	2880 m	2870 m	2870 m
	2790 w	2790 m	2800 m
1620 w	1620 w	1620 w	1620 w
1460 w	1460 w	1460 w	1460 w
1438 w	1440 w	1445 w	1440 w
		1355 m br	
1305 s br	1305 m br	1320 m br	1335 m br
1258 w	1250 w	1250 vw	1260 vw
1170 s br	1175 m br	1160 m	1170 w
1040 s	1040 s	1040 s br	1040 s br
1010 s	1010 s	1010 s	1010 s
	910 w		915 w
885 m	880 w	885 m	885 m
860 m			
850 m			
840 m	840 w		
770 s	770 s	767 s br	770 s br
730 m	755 s		740 m
667 m	660 w	660 w	660 vw

X-ray Data Collection, Structure Determination, and Refinement for $[(\text{C}_5\text{H}_5)_2\text{Y}(\mu\text{-OCH}_3)]_3(\mu_3\text{-H})_2[\text{Li}(\text{THF})_3]_2$ (**5**). Crystals of **5** were obtained by recrystallization of **4** from a saturated THF solution. A long needle-shaped crystal of approximate dimensions $0.6 \times 0.3 \times 0.15$ mm sealed in a glass capillary was chosen for structure analysis. A Nicolet/Syntex P_2 automated four-circle diffractometer with Mo $K\alpha$ radiation and a graphite monochromator was used for intensity data collection. Accurate unit cell parameters were obtained by carefully centering 15 high-angle reflections and are listed together with other relevant crystal data in Table III. One quadrant of data ($+h, +k, \pm l$) was collected by the 2θ scan technique, such that $3.5 < 2\theta < 45.0^\circ$. Throughout data collection 3 reflections were monitored periodically (after every 50 reflections), and no decay was observed. After the data were processed with Lorentz, polarization, and empirical absorption corrections, 2987 independent reflections with intensities greater than 3σ were retained for the structure analysis.

The initial positions of the yttrium atoms were obtained through direct methods²⁵ while the remaining non-hydrogen atoms were located in subsequent difference Fourier maps. This was followed by several cycles of full-matrix least-squares refinement.²⁶ The final agreement factors are $R = 0.080$ and $R_w = 0.087$. The relatively high R factor is undoubtedly due to the fact that the THF ligands are partially disordered. The weighting scheme was $w = 1/[\sigma(F^2) + 0.04(F^2)]^{1/2}$. The final atomic coordinates and thermal parameters are given in Table IV. Selected distances and angles are collected in Table V. Observed and calculated structure factors are available as supplementary material.

The large thermal parameters associated with many of the carbon atoms of the THF groups show that these ligands are partially disordered. This is not uncommon since, at room temperature, THF appears to be planar, in contrast to a normal puckered conformation, indicating a superposition of two or more nonplanar conformers. In fact one of the more severely disordered THF ligands (O(12), C(90), C(91), C(92), C(93)) was refined with constrained bond lengths (C-C = 1.51, C-O =

Table III. Summary of Crystal Data for $[(\text{C}_5\text{H}_5)_2\text{Y}(\mu\text{-OCH}_3)]_3(\mu_3\text{-H})_2[\text{Li}(\text{THF})_3]_2$

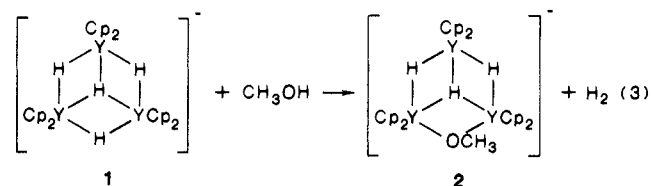
crystal type	monoclinic
space group	$P2_1/n$
unit cell param	
a , Å	20.852 (9)
b , Å	13.984 (5)
c , Å	31.590 (9)
β , deg	92.48 (4)
Z	8
V , Å ³	9203 (7)
formula wt	1949.31
D_{calcd} , g/cm ³	1.81
λ , Å	0.71069 (Mo $K\alpha$)
monochromator	graphite crystal
data limits, deg	$3.5 < 2\theta < 45$
quadrant colld	$+h, +k, \pm l$
reflens used	2987 ($I > 3\sigma(I)$)
$R(F)$	0.080
$R_w(F)$	0.087

1.43, and Li-O = 1.98 Å) during the final least-squares cycles.

Results

Reactivity. The dimeric cyclopentadienyl lanthanide hydrides $[(\text{C}_5\text{H}_5)_2\text{Ln}(\mu\text{-H})(\text{THF})_2]_2$ react with a wide range of hydrocarbons including, among others, alkenes, terminal and internal alkynes, nitriles, isocyanides, and pyridine.^{16,24} Our preliminary studies of the reactivity of such unsaturated hydrocarbon substrates with the trimeric tetrahydride complexes $[(\text{C}_5\text{H}_5)_2\text{Ln}(\mu\text{-H})]_3(\mu_3\text{-H})[\text{Li}(\text{THF})_4]$ (Ln = Lu, Y) indicated that the hydride ligands in the trimers were less reactive than those in their dimeric analogues. Consequently, a substrate more reactive than the hydrocarbons studied with the $[(\text{C}_5\text{H}_5)_2\text{Ln}(\mu\text{-H})(\text{THF})_2]_2$ complexes was needed to probe the reactivity of the hydride ligands in these trimers. Methanol was chosen since it is a small substrate with an acidic proton, which would form strong Ln-O bonds.

Addition of 1 equiv of CH_3OH to $[(\text{C}_5\text{H}_5)_2\text{Y}(\mu\text{-H})]_3(\mu_3\text{-H})[\text{Li}(\text{THF})_4]$ (**1**) at -78°C in THF in a vessel attached to a Toepler pump generated 70% of gas expected from eq 3 ($\text{Cp} =$

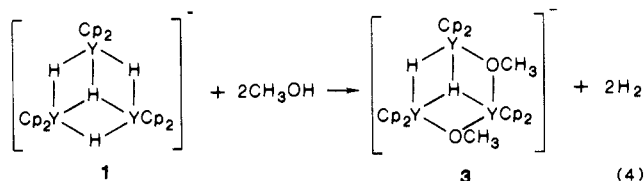


C_5H_5). If the reaction vessel was allowed to warm to room temperature, the yield of gas was 100%. The white solid product of this reaction was identified as $[(\text{C}_5\text{H}_5)_2\text{Y}(\mu\text{-H})]_3(\mu_3\text{-H})[\text{Li}(\text{THF})_4]$ (**2**) by ^1H NMR spectroscopy, complexometric metal analysis, and hydrolytic decomposition (see next section).

If an additional 1 equiv of CH_3OH is added at -78°C to the 1/ CH_3OH system described above (reaction 3) before it has been warmed to room temperature, more gas is given off. Like the 1-equiv reaction, the total amount collected was less than the theoretical yield of 2 equiv by 20–30%. When this 2-equiv reaction was warmed to 0°C , a quantitative yield of gas was obtained according to reaction 4. The white solid product of this reaction

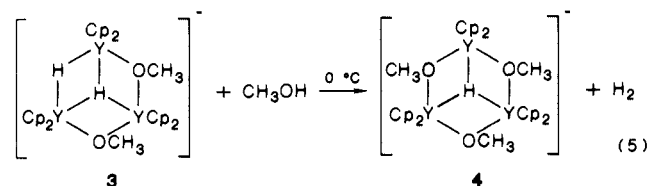
(25) MULTAN; a system of computer programs for the automatic solution of crystal structures for X-ray diffraction data: Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A: Cryst. Phys., Diff., Theor. Gen. Crystallogr.* 1971, *A27*, 368.

(26) The structural analysis was carried out with the UCLA Crystallographic Computing Package, compiled by Prof. C. E. Strouse.

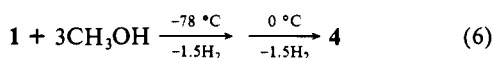


was identified as $[[(\text{C}_5\text{H}_5)_2\text{Y}(\mu\text{-H})][(\text{C}_5\text{H}_5)_2\text{Y}(\mu\text{-OCH}_3)]_2(\mu_3\text{-H})][\text{Li}(\text{THF})_4]$ (**3**) again by ^1H NMR spectroscopy, complexometric analysis, and hydrolytic decomposition. Complex **2** can also be obtained by direct addition of 2 equiv of CH_3OH to **1**. At -78°C , 70–80% of the expected gas is obtained. After the solution had warmed to 0°C , the remainder of the 2 equiv of H_2 can be collected.

All three doubly bridging hydrides in **1** can be converted to bridging methoxide ligands by reacting **1** with 3 equiv of CH_3OH under the appropriate conditions. This can be done in several ways. In one case, the previously described reaction mixture formed from 2 equiv of CH_3OH and **1** at -78 and 0°C was recooled to -78°C , and a third 1 equiv of CH_3OH was added. No reaction occurs at -78°C . After the solution had warmed to 0°C , however, 1 equiv of gas is evolved as $[[(\text{C}_5\text{H}_5)_2\text{Y}(\mu\text{-OCH}_3)]_3(\mu_3\text{-H})][\text{Li}(\text{THF})_4]$ (**4**) is formed according to eq 5. Complex **4** was characterized by the same methods used for **2** and **3** and by an X-ray crystal structure determination of a derivative (see below).



Complex **4** can also be obtained by direct reaction of **1** with 3 equiv of methanol. At -78°C , this reaction generated only 1.5 equiv of hydrogen, i.e., a 75% yield of the hydrogen expected for the formation of the dimethoxide-substituted complex **3**. Again, the third 1 equiv of methanol does not react at -78°C . After the solution was warmed to 0°C , however, a total of 3 equiv of hydrogen (identified by GC-MS) is obtained along with complex **4** (eq 6).



Neither the reaction of 4 equiv of methanol with **1** nor the reaction of methanol with **4** replaces the μ_3 -hydride in these complexes. In fact, the reaction of 4 equiv of methanol with **1** at 0°C for time periods less than 2 h gives an excellent 90% yield of **4**. On the basis of the syntheses of **4**, no reaction is expected between **4** and methanol at -78°C . No reaction was observed either at 0°C or at room temperature. To try to force the reaction of **4** with CH_3OH , higher temperatures were examined. Heating a $4/\text{CH}_3\text{OH}$ system to 65°C for 30 min generated no hydrogen gas. Some insoluble products were formed (possibly by replacement of C_5H_5 rings with OCH_3), but the major product recovered was **4**. When the reaction was run in pure methanol, the major product was insoluble.

A mixture of **1** and **4** in THF was studied by ^1H NMR to determine whether ligand redistribution reactions to form **2** and **3** would occur. After 2 h at room temperature and 1 h at 80°C , no evidence of **2** or **3** was found. Only after the sample was heated to 80°C overnight did some **2** and **3** appear in the spectrum.

Characterization. Complexes **2–4** were identified by complexometric metal analysis, hydrolysis, IR and ^1H NMR spectroscopy, and, in the case of **4**, an X-ray structure determination of a derivative. Hydrolysis of dimeric and trimeric organo-lanthanide and organoyttrium hydrides typically gives the expected hydrogen in 80–90% yield.^{4,5,27} Hydrolysis of **2**, **3**, and **4** gives

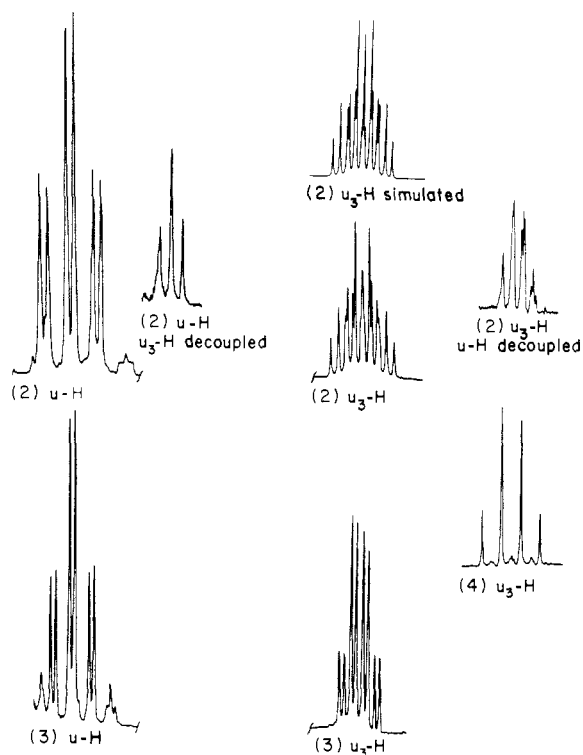


Figure 1. Representative ^1H NMR spectra and a simulation for the hydride ligands of **2–4**.

2, 4, and **0.5** equiv, respectively, of hydrogen. The yields for **2** and **3**, 80% and 100%, are near the previously observed range; for **4**, a yield of only 50% may reflect the strength of the $[\text{Y}_3(\mu\text{-OCH}_3)_3(\mu_3\text{-H})]$ linkage.²⁸

The infrared spectra of **2–4** (Table II) are in many respects similar to that of **1**. Previous studies of **1** and its deuterated analogue indicated that broad absorptions at 1305, 1170, 850, and 667 cm^{-1} were associated with the hydride ligands.⁶ As bridging hydride ligands are substituted by methoxy groups going from **1** to **4**, the absorption in the 1305-cm^{-1} region changes very little in intensity and increases slightly in frequency, moving up to 1335 cm^{-1} for **4**. The intensity of the 1170-cm^{-1} absorption, on the other hand, decreases significantly on going from **1** to **4**.

^1H NMR spectroscopy is a most informative method for identifying **2–4**. The ^1H NMR spectrum of **1** has been studied previously, and the multiplet patterns observed at 0.75 ppm for the $\mu\text{-H}$ ligands and at -1.03 ppm for the $\mu_3\text{-H}$ ligand have been successfully modeled by computer simulation.⁶ Coupling constants of 8.5 Hz (H–H), 17.0 Hz (Y–($\mu_3\text{-H}$)), and 30.7 Hz (Y–($\mu\text{-H}$)) were found. As $\mu\text{-H}$ ligands in **1** are replaced by $\mu\text{-OCH}_3$ to form **2–4**, the hydride resonances change as expected and the coupling constants are similar to those in **1**. The simplest spectrum is that of **4**, which has just one hydride resonance (Figure 1). This is split into a quartet consistent with coupling to three equivalent ^{89}Y ($I = 1/2$) nuclei ($J_{\text{YH}} = 18.4$ Hz). In **3**, the hydride resonance in the triply bridging hydride region changes to a quartet of doublets, which collapses into a broadened quartet with decoupling of the $\mu\text{-H}$ ligand. The spectrum is consistent with an 8.1-Hz ($\mu\text{-H}$)–($\mu_3\text{-H}$) coupling added to an 18.4-Hz J_{YH} coupling between

(28) Decomposition of the hydrides **1–4** with CHCl_3 rather than H_2O resulted in spectacular color changes. These changes were accompanied by chloride substitution of the doubly bridging hydrides in **1–3**, a reaction monitored by ^1H NMR spectroscopy. No correlation between the degree of chloride substitution or the extent of decomposition and color change could be made. Typically the addition of excess CHCl_3 to **1–4**, in neat form or in THF, resulted in the originally colorless solutions turning yellow and then gradually darkening to orange and red. The solutions subsequently turned purple and then green. Eventually the solutions became yellow again (several weeks at 25°C). The colored solutions of **1–4** could be maintained at the different stages without further decomposition by storing the solutions in the dark. The addition of CHCl_3 to NaC_2H_5 dissolved in THF under the same conditions resulted in a reddish brown color only.

Table IV. Listing of the Positional and Thermal Parameters for $\{[(C_5H_5)_2Y(\mu-OCH_3)]_3(\mu_3-H)\}_2Li(THF)_3\}_2$ (5)

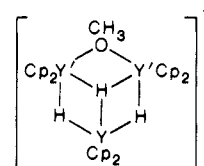
atom	X/A	Y/B	Z/C	U(11)	atom	X/A	Y/B	Z/C	U(11)
Y(1)	0.2492 (2)	0.1893 (3)	0.3353 (1)	0.040 (2)	C(41)	0.165 (1)	1.151 (2)	0.556 (1)	0.06 (1)
Y(2)	0.3727 (2)	0.1226 (3)	0.4208 (1)	0.050 (2)	C(42)	0.144 (2)	1.212 (3)	0.584 (1)	0.09 (1)
Y(3)	0.4212 (2)	0.2584 (3)	0.3237 (1)	0.042 (2)	C(43)	0.077 (2)	1.230 (3)	0.582 (1)	0.10 (1)
Y(4)	0.0897 (2)	1.0486 (3)	0.6109 (1)	0.046 (2)	C(44)	0.055 (1)	1.169 (3)	0.546 (1)	0.09 (1)
Y(5)	0.1865 (2)	0.8263 (3)	0.5959 (2)	0.056 (2)	C(45)	-0.021 (1)	1.099 (2)	0.644 (1)	0.06 (1)
Y(6)	0.2309 (2)	0.9949 (3)	0.6853 (1)	0.049 (2)	C(46)	0.006 (1)	1.041 (3)	0.675 (1)	0.07 (1)
O(1)	0.3208 (9)	0.272 (1)	0.2956 (6)	0.05 (1)	C(47)	0.007 (1)	0.947 (3)	0.659 (1)	0.08 (1)
O(2)	0.2676 (9)	0.118 (1)	0.3986 (6)	0.04 (1)	C(48)	-0.023 (1)	0.948 (2)	0.619 (1)	0.06 (1)
O(3)	0.455 (1)	0.192 (1)	0.3869 (6)	0.06 (1)	C(49)	-0.040 (1)	1.040 (3)	0.607 (1)	0.08 (1)
O(4)	0.103 (1)	0.915 (1)	0.5694 (7)	0.04 (1)	C(50)	0.169 (2)	0.665 (3)	0.644 (1)	0.11 (1)
O(5)	0.148 (1)	1.099 (1)	0.6690 (6)	0.06 (1)	C(51)	0.111 (2)	0.720 (3)	0.647 (1)	0.10 (1)
O(6)	0.255 (1)	0.852 (1)	0.6534 (6)	0.05 (1)	C(52)	0.073 (2)	0.723 (3)	0.610 (1)	0.11 (1)
O(7)	0.114 (1)	0.469 (1)	0.4418 (7)	0.08 (1)	C(53)	0.111 (2)	0.670 (3)	0.580 (1)	0.08 (1)
O(8)	0.043 (1)	0.493 (2)	0.3529 (8)	0.09 (1)	C(54)	0.170 (2)	0.636 (3)	0.601 (1)	0.10 (1)
O(9)	0.176 (6)	0.601 (2)	0.3765 (9)	0.11 (1)	C(55)	0.276 (2)	0.906 (3)	0.547 (1)	0.08 (1)
O(10)	0.593 (1)	0.574 (2)	0.3935 (8)	0.09 (1)	C(56)	0.303 (1)	0.821 (3)	0.560 (1)	0.09 (1)
O(11)	0.454 (1)	0.619 (2)	0.4237 (8)	0.07 (1)	C(57)	0.267 (2)	0.740 (3)	0.543 (1)	0.10 (1)
O(12)	0.485 (1)	0.679 (2)	0.3326 (8)	0.10 (1)	C(58)	0.220 (2)	0.781 (3)	0.517 (1)	0.11 (1)
C(1)	0.304 (1)	0.315 (2)	0.256 (1)	0.05 (1)	C(59)	0.223 (2)	0.889 (3)	0.517 (1)	0.12 (1)
C(2)	0.215 (1)	0.068 (2)	0.4218 (9)	0.06 (1)	C(60)	0.356 (1)	1.038 (3)	0.695 (1)	0.09 (1)
C(3)	0.521 (1)	0.187 (2)	0.4017 (9)	0.05 (1)	C(61)	0.322 (1)	1.126 (2)	0.706 (1)	0.07 (1)
C(4)	0.062 (1)	0.891 (2)	0.533 (1)	0.09 (1)	C(62)	0.294 (1)	1.161 (2)	0.668 (1)	0.08 (1)
C(5)	0.137 (1)	1.188 (2)	0.692 (1)	0.08 (1)	C(63)	0.310 (1)	1.102 (3)	0.632 (1)	0.09 (1)
C(6)	0.307 (1)	0.792 (2)	0.666 (1)	0.06 (1)	C(64)	0.348 (1)	1.028 (2)	0.650 (1)	0.05 (1)
C(10)	0.224 (1)	0.367 (2)	0.373 (1)	0.08 (1)	C(65)	0.234 (2)	0.868 (3)	0.751 (1)	0.09 (1)
C(11)	0.205 (1)	0.378 (2)	0.331 (1)	0.07 (1)	C(66)	0.170 (2)	0.878 (3)	0.741 (1)	0.12 (1)
C(12)	0.151 (1)	0.317 (3)	0.322 (1)	0.08 (1)	C(67)	0.148 (2)	0.973 (3)	0.750 (1)	0.09 (1)
C(13)	0.141 (1)	0.270 (2)	0.360 (1)	0.09 (1)	C(68)	0.202 (2)	1.024 (3)	0.768 (1)	0.09 (1)
C(14)	0.184 (1)	0.299 (2)	0.392 (1)	0.07 (1)	C(69)	0.253 (2)	0.957 (3)	0.769 (1)	0.09 (1)
C(15)	0.190 (2)	0.110 (3)	0.265 (1)	0.09 (1)	C(70)	0.170 (2)	0.489 (3)	0.475 (1)	0.13 (1)
C(16)	0.253 (2)	0.083 (2)	0.262 (1)	0.08 (1)	C(71)	0.143 (3)	0.425 (4)	0.508 (1)	0.18 (2)
C(17)	0.267 (1)	0.019 (2)	0.295 (1)	0.07 (1)	C(72)	0.079 (3)	0.405 (5)	0.505 (2)	0.24 (3)
C(18)	0.207 (1)	0.009 (2)	0.320 (1)	0.08 (1)	C(73)	0.066 (2)	0.409 (3)	0.455 (1)	0.12 (1)
C(19)	0.161 (1)	0.066 (3)	0.300 (1)	0.09 (1)	C(74)	0.019 (1)	0.447 (2)	0.314 (1)	0.06 (1)
C(20)	0.395 (1)	0.453 (2)	0.321 (1)	0.07 (1)	C(75)	-0.046 (1)	0.498 (2)	0.304 (1)	0.07 (1)
C(21)	0.443 (2)	0.441 (2)	0.298 (1)	0.09 (1)	C(76)	-0.057 (3)	0.558 (3)	0.342 (1)	0.10 (1)
C(22)	0.497 (1)	0.413 (2)	0.323 (1)	0.07 (1)	C(77)	-0.008 (2)	0.552 (3)	0.370 (1)	0.14 (2)
C(23)	0.482 (1)	0.406 (2)	0.369 (1)	0.05 (1)	C(78)	0.140 (3)	0.689 (6)	0.382 (2)	0.23 (3)
C(24)	0.411 (1)	0.433 (2)	0.364 (1)	0.07 (1)	C(79)	0.188 (3)	0.758 (4)	0.390 (1)	0.16 (2)
C(25)	0.350 (1)	0.289 (2)	0.463 (1)	0.05 (1)	C(80)	0.236 (2)	0.735 (4)	0.363 (1)	0.17 (2)
C(26)	0.310 (1)	0.217 (2)	0.482 (1)	0.06 (1)	C(81)	0.237 (2)	0.624 (4)	0.358 (1)	0.12 (1)
C(27)	0.358 (1)	0.154 (2)	0.504 (1)	0.05 (1)	C(82)	0.626 (2)	0.644 (3)	0.422 (1)	0.15 (2)
C(28)	0.418 (1)	0.187 (2)	0.495 (1)	0.06 (1)	C(83)	0.691 (2)	0.627 (3)	0.421 (1)	0.13 (2)
C(29)	0.417 (1)	0.274 (2)	0.471 (1)	0.06 (1)	C(84)	0.702 (2)	0.578 (3)	0.385 (1)	0.13 (2)
C(30)	0.456 (2)	-0.024 (2)	0.437 (1)	0.10 (1)	C(85)	0.644 (3)	0.523 (4)	0.374 (1)	0.16 (2)
C(31)	0.400 (1)	-0.046 (2)	0.459 (1)	0.07 (1)	C(86)	0.459 (2)	0.565 (3)	0.463 (1)	0.14 (2)
C(32)	0.350 (1)	-0.066 (2)	0.430 (1)	0.09 (1)	C(87)	0.405 (2)	0.610 (4)	0.486 (1)	0.15 (2)
C(33)	0.372 (1)	-0.052 (2)	0.387 (1)	0.05 (1)	C(88)	0.387 (3)	0.684 (5)	0.469 (2)	0.20 (2)
C(34)	0.436 (1)	-0.033 (2)	0.391 (1)	0.09 (1)	C(89)	0.420 (2)	0.700 (4)	0.425 (1)	0.14 (2)
C(35)	0.442 (1)	0.092 (2)	0.283 (1)	0.06 (1)	C(90)	0.518 (1)	0.767 (2)	0.326 (1)	0.10 (1)
C(36)	0.504 (1)	0.119 (2)	0.298 (1)	0.05 (1)	C(91)	0.459 (1)	0.793 (3)	0.298 (1)	0.10 (1)
C(37)	0.525 (1)	0.202 (2)	0.279 (1)	0.07 (1)	C(92)	0.508 (1)	0.768 (2)	0.266 (1)	0.10 (1)
C(38)	0.468 (1)	0.226 (2)	0.247 (1)	0.04 (1)	C(93)	0.496 (1)	0.673 (2)	0.288 (1)	0.10 (1)
C(39)	0.421 (1)	0.154 (2)	0.248 (1)	0.06 (1)	Li(1)	0.129 (3)	0.472 (6)	0.383 (2)	0.10 (2)
C(40)	0.110 (2)	1.123 (2)	0.530 (1)	0.08 (1)	Li(2)	0.508 (3)	0.582 (3)	0.376 (1)	0.07 (2)

atom	U(22)	U(33)	U(23)	U(13)	U(12)	atom	U(22)	U(33)	U(23)	U(13)	U(12)
Y(1)	0.037 (2)	0.053 (2)	-0.006 (2)	-0.005 (2)	0.001 (2)	O(1)	0.02 (1)	0.05 (1)	-0.007 (1)	0.01 (1)	-0.005 (1)
Y(2)	0.033 (2)	0.042 (2)	0.001 (2)	0.004 (2)	0.004 (2)	O(2)	0.04 (1)	0.05 (1)	-0.007 (1)	0.006 (1)	-0.005 (1)
Y(3)	0.031 (2)	0.048 (2)	-0.005 (2)	0.001 (1)	-0.004 (2)	O(3)	0.04 (1)	0.06 (1)	0.007 (1)	-0.001 (1)	-0.01 (1)
Y(4)	0.048 (3)	0.061 (2)	0.001 (2)	-0.007 (2)	0.008 (2)	O(4)	0.05 (2)	0.08 (1)	-0.006 (1)	-0.008 (1)	-0.002 (1)
Y(5)	0.038 (2)	0.068 (2)	-0.007 (2)	0.009 (2)	-0.003 (2)	O(5)	0.07 (2)	0.04 (1)	-0.01 (1)	-0.002 (1)	0.04 (1)
Y(6)	0.046 (3)	0.046 (2)	0.001 (2)	-0.003 (2)	-0.002 (2)	O(6)	0.03 (1)	0.06 (1)	-0.004 (1)	-0.01 (1)	-0.007 (1)

the μ_3 -H and the three yttrium nuclei. The differences in Y-(μ_3 -H) coupling for the two different types of yttrium in **3** are not resolved in this spectrum. The doubly bridging hydride in **3** is split into a triplet of doublets by its two equivalent yttrium neighbors ($J_{YH} = 27.2$ Hz) and the central hydride ($J_{HH} = 8.1$). Decoupling of the central hydride resulted in a simplified triplet pattern. Y-(μ -H) coupling from the nonadjacent yttrium atom is not resolved in this spectrum. The cyclopentadienyl resonances in **3** are split into a 2:1 pattern consistent with the proposed structure.

In complex **2**, the μ_3 -hydride resonance is a multiplet due to splitting to two μ -H ligands and the three yttrium atoms. Computer simulation²⁹ of this spectrum (Figure 1) gave a best fit for

the following coupling constants:



$$\begin{aligned}
 &^2J(\mu_3\text{-H}, \mu\text{-H}) = 8.30 \\
 &^1J(\mu_3\text{-H}, Y) = 17.0 \\
 &^1J(\mu_3\text{-H}, Y') = 19.0 \\
 &^2J(\mu\text{-H}, \mu\text{-H}) = 4.0 \\
 &^1J(\mu\text{-H}, Y) = 30.0 \\
 &^1J(\mu\text{-H}, Y') = 28.0 \\
 &^3J(\mu\text{-H}, Y) = 1.0 \\
 &^2J(Y, Y') = 4.0 \\
 &^2J(Y', Y') = 3.0
 \end{aligned}$$

Decoupling of the μ -H resonance resulted in a quartet for the μ_3 -H ligand. The μ -H resonance in **2** is a triplet of doublets similar to that found in **3**, which also collapses into a triplet with homonuclear decoupling. The cyclopentadienyl resonances are split into a 1:2 pattern consistent with the proposed structure.

Crystal Structure. Recrystallization of **4** from a concentrated THF solution gave crystals suitable for an X-ray structure determination. The structural study showed that the crystallized complex $[[(\text{C}_5\text{H}_5)_2\text{Y}(\mu\text{-OMe})]_3(\mu_3\text{-H})]_2[\text{Li}(\text{THF})_3]_2$ (**5**) was a derivative of **4**, differing in that three not four THF molecules of solvation were present per lithium cation.

In the unit cell of **5**, there are two independent species containing the trimetallic $\text{Y}_3(\mu\text{-OCH}_3)_3(\mu_3\text{-H})$ core. One is simply the $[[(\text{C}_5\text{H}_5)_2\text{Y}(\mu\text{-OCH}_3)]_3(\mu_3\text{-H})]^-$ anion (Figure 2). This anion has a structure similar to that found for the anions in $[[(\text{C}_5\text{H}_5)_2\text{Er}(\mu\text{-H})]_2[(\text{C}_5\text{H}_5)_2\text{Er}(\mu\text{-Cl})]_2(\mu_3\text{-H})][\text{Li}(\text{THF})_4]$ (**6**) and $[[(\text{C}_5\text{H}_5)_2\text{Lu}(\mu\text{-H})]_3(\mu_3\text{-H})][\text{Li}(\text{THF})_4]$ (**7**)⁵ except that methoxide groups are the doubly bridging ligands. Each yttrium is formally nine-coordinate and has a local geometry typical for a bent metallocene with three additional ligands.

The other structural unit in **5** consists of an anion of the type just described plus two $\text{Li}(\text{THF})_3$ moieties attached to two different C_5H_5 rings to form an unusual $[[(\text{THF})_3\text{Li}]_2[(\text{C}_5\text{H}_5)_2\text{Y}(\mu\text{-OCH}_3)]_3(\mu_3\text{-H})]^+$ cation (Figure 3). The $(\text{THF})_3\text{Li}$ moieties are both on the same side of the $\text{Y}_3(\mu_3\text{-OCH}_3)_3(\mu_3\text{-H})$ plane but are attached to the C_5H_5 rings in different ways. Li(2) appears to interact with just one carbon atom of a C_5H_5 ring via a Li(2)–C(23) distance of 2.54 (4) Å (Table V). All other Li(2)–C distances are in the range 2.88 (5)–3.38 (6) Å. On the other hand, Li(1) appears to interact with its C_5H_5 more in a π -allylic fashion: the Li(1)–C(10), Li(1)–C(11), and Li(1)–C(14) distances are 2.50 (5), 2.67 (5), and 2.67 (5) Å, respectively, while the other two Li(1)–C distances are substantially longer (2.92 (6) and 2.93 (4) Å).

The 2.50 (8) and 2.54 (6) Å Li–C distances in **5** can be compared to the Li–C(ring) distances observed in $[(\text{C}_5\text{H}_5)_2\text{Y}(\text{CH}_2\text{SiMe}_3)_2]_2\text{Li}_2(\text{MeOCH}_2\text{CH}_2\text{OMe})_2(\text{C}_4\text{H}_8\text{O}_2)$ (**8**)³⁰. In that structure, each lithium ion in a (DME)Li(μ -dioxane)Li(DME) unit (in which each lithium is coordinated by three oxygen atoms) interacts with a C_5H_5 ring with distances of 2.407 (12), 2.413 (13), 2.529 (12), 2.531 (13), and 2.618 (13) Å. The closest Li–C distances in **5** are significantly longer than the two short distances in **8** and are much longer than the lithium–ring carbon distances in $(\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2)\text{LiC}_5\text{H}_4\text{SiMe}_3$ ³¹ and $[(\text{Me}_2\text{NCH}_2\text{CH}_2)_2\text{NMe}]\text{LiC}_5\text{H}_2(\text{SiMe}_3)_3$ ³² which are in the 2.257 (10)–2.350 (6) Å range. The long Li–C distances in **5** suggest that this coordination is weak. Consistent with this, no evidence for this coordination has been observed in solution, and the bond distances and angles in the $[(\text{C}_5\text{H}_5)_2\text{Y}(\mu\text{-OCH}_3)]_3(\mu_3\text{-H})$ part of the cation are like those in the anion.

The Y–C(ring) distances in **5** range from 2.65 (3) to 2.82 (3) Å with an overall average of 2.73 (2) Å (Table V). The average Y–C(ring) distances for each of the 12 rings in **5** vary between 2.71 (3) and 2.75 (5) Å. The average Y–C(ring) distance in the anion is the same as that in the cation, 2.73 (2) Å. Carbon atoms C(10) and C(23), which are also attached to lithium, have two of the longest Y–C distances, and their rings have two of the three high 2.75 (5) Å average values. Longer bond distances are generally found for bridging ligands in organolanthanide complexes.^{33,34} In **5**, this lengthening is slight, which is again consistent with a weak Li–C interaction.

The Y–C(ring) average distance of **5** is unusual in that it is substantially longer than the average distance in other previously

Table V. Selected Distances (Å) and Angles (deg) in $[[(\text{C}_5\text{H}_5)_2\text{Y}(\mu\text{-OCH}_3)]_3(\mu_3\text{-H})]_2[\text{Li}(\text{THF})_3]_2$

(A) Selected Distances and Angles			
	cation	anion	
Y(1)–O(1)	2.30 (1)	Y(4)–O(4)	2.29 (2)
Y(1)–O(2)	2.25 (1)	Y(4)–O(5)	2.27 (1)
Y(2)–O(2)	2.27 (1)	Y(5)–O(4)	2.27 (2)
Y(2)–O(3)	2.29 (2)	Y(5)–O(6)	2.29 (2)
Y(3)–O(1)	2.24 (1)	Y(6)–O(5)	2.29 (2)
Y(3)–O(3)	2.29 (1)	Y(6)–O(6)	2.29 (2)
O(2)–Y(1)–O(1)	128.1 (7)	O(5)–Y(4)–O(4)	129.7 (8)
O(3)–Y(2)–O(2)	127.4 (7)	O(6)–Y(5)–O(4)	130.2 (8)
O(3)–Y(3)–O(1)	129.3 (7)	O(6)–Y(6)–O(5)	129.1 (7)
Y(3)–O(1)–Y(1)	110.8 (8)	Y(5)–O(4)–Y(4)	110.1 (9)
Y(2)–O(2)–Y(1)	112.7 (8)	Y(6)–O(5)–Y(4)	110.7 (9)
Y(3)–O(3)–Y(2)	111.1 (9)	Y(6)–O(6)–Y(5)	110.0 (9)
Y(1)···Y(2)	3.77 (1)	Y(4)···Y(5)	3.75 (1)
Y(1)···Y(3)	3.75 (1)	Y(4)···Y(6)	3.76 (1)
Y(2)···Y(3)	3.78 (1)	Y(5)···Y(6)	3.77 (1)
(B) Average Distances and Angles			
Y–C	2.73 (2)	Y–O–C	124 (1)
C–O (methoxy)	1.44 (1)	O–Li–O	107 (3)
C–C (Cp)	1.42 (1)	O–Li–C	110 (2)
Li–O	1.96 (1)		
C–O (THF)	1.44 (1)		
C–C (THF)	1.45 (1)		
(C) Li–C Distances for All C Atoms in Rings near Li			
C(10)–Li(1)	2.50 (5)	C(20)–Li(2)	3.38 (6)
C(11)–Li(1)	2.67 (5)	C(21)–Li(2)	3.35 (5)
C(12)–Li(1)	2.93 (4)	C(22)–Li(2)	2.88 (5)
C(13)–Li(1)	2.92 (6)	C(23)–Li(2)	2.54 (4)
C(14)–Li(1)	2.67 (5)	C(24)–Li(2)	2.90 (5)
(D) Yttrium–(Ring Centroid) Distances and Ring Centroid–Yttrium–Ring Centroid Angles ^a			
C(A)–Y(1)	2.52 (2)	C(A)′–Y(4)	2.47 (2)
C(B)–Y(1)	2.43 (2)	C(B)′–Y(4)	2.45 (2)
C(B)–Y(1)–C(A)	126.7 (8)	C(B)′–Y(4)–C(A)′	124.9 (7)
C(D)–Y(2)	2.44 (2)	C(C)′–Y(5)	2.45 (2)
C(E)–Y(2)	2.42 (2)	C(D)′–Y(5)	2.43 (2)
C(D)–Y(2)–C(E)	124.7 (9)	C(C)′–Y(5)–C(D)′	122.9 (8)
C(C)–Y(3)	2.47 (2)	C(E)′–Y(6)	2.46 (2)
C(F)–Y(3)	2.44 (2)	C(F)′–Y(6)	2.47 (2)
C(C)–Y(3)–C(F)	123.7 (8)	C(E)′–Y(6)–C(F)′	124.5 (8)
(E) Deviations (Å) of Y_3O_3 Units from Planarity			
Y(1)	–0.045	Y(4)	0.020
Y(2)	0.013	Y(5)	0.009
Y(3)	–0.043	Y(6)	–0.034
O(1)	0.060	O(4)	–0.028
O(2)	0.009	O(5)	0.011
O(3)	0.007	O(6)	0.021

^aC(A) is the ring centroid for the C(10)–C(14) ring, C(B) is the ring centroid for the C(16)–C(19) ring, etc.

characterized organoyttrium complexes. Previously reported Y–C(ring) distances range from 2.64 to 2.70 Å for both eight- and nine-coordinate complexes.^{4,16,17,35–41} The trimetallic erbium complex **6** also has a smaller average metal–carbon distance, 2.65 Å, despite the nearly identical radial size of Er^{3+} and Y^{3+} .⁴²

The Y–O distances in **5** fall into the 2.24 (1)–2.30 (1) Å range with an average value of 2.28 (2) Å. These distances match the

(29) GENSIM Spectrum Simulation, General Electric Co., Medical Systems Group, Fremont, CA 94539.

(30) Evans, W. J.; Dominguez, R.; Levan, K. R.; Doedens, R. J. *Organometallics* **1985**, *4*, 1836–1841.

(31) Lappert, M. F.; Singh, A.; Engelhardt, L. M.; White, A. H. *J. Organomet. Chem.* **1984**, *262*, 271–278.

(32) Jutzi, P.; Schluter, E.; Kruger, C.; Pohl, S. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 994.

(33) Zinnen, H. A.; Pluth, J. J.; Evans, W. J. *J. Chem. Soc., Chem. Commun.* **1980**, 810–812.

(34) Atwood, J. L.; Hunter, W. E.; Wayda, A. L.; Evans, W. J. *Inorg. Chem.* **1981**, *20*, 4115–4119.

(35) Evans, W. J.; Dominguez, R.; Hanusa, T. P. *Organometallics* **1986**, *5*, 1291–1296.

(36) 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.

(37) Evans, W. J.; Grate, J. W.; Levan, K. R.; Bloom, I.; Peterson, T. T.; Doedens, R. J.; Zhang, H.; Atwood, J. L. *Inorg. Chem.* **1986**, *25*, 3614–3619.

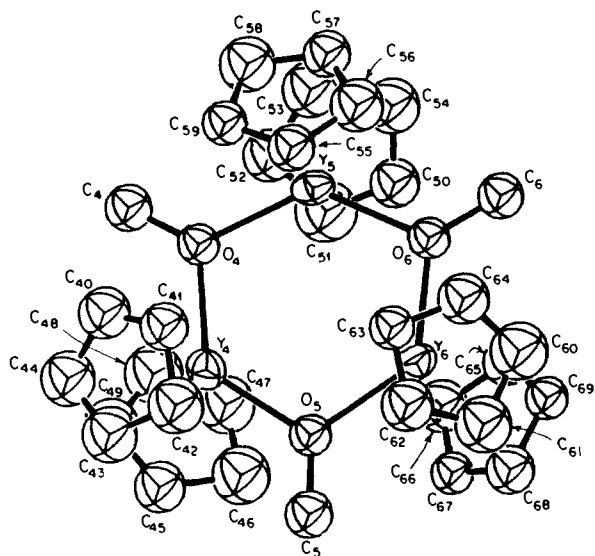


Figure 2. $[(C_5H_5)_2Y(\mu-OCH_3)]_3(\mu_3-H)^-$ anion of compound 5. (The triply bridging central H atom was not located.)

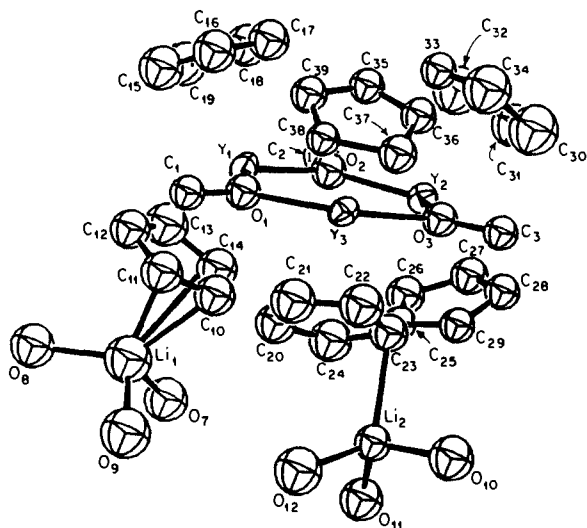


Figure 3. $[(THF)_3Li]_2[(C_5H_5)_2Y(\mu-OCH_3)]_3(\mu_3-H)^+$ cation (methylene groups of the C_4H_8O rings removed for clarity). Note that whereas the right-hand lithium, Li(2), is η^1 , the left-hand lithium, Li(1), is interacting with the C_5H_5 ring more-or-less in a π -allyl fashion (see Table V(C)). As in the anion (Figure 2), the μ_3-H atom could not be located crystallographically.

2.275 (3) and 2.290 (3) Å Y–O lengths found in the enolate-bridged structure $[(CH_3C_5H_4)_2Y(\mu-OCH=CH_2)]_2$,³⁵ and the range overlaps the 2.19 (2)–2.25 (2) Å spread of Y–O($\mu-OCH_3$) distances in $(C_5H_5)_2Y_3(\mu_3-OCH_3)_4(\mu-OCH_3)_4O$ (average 2.22 (2) Å).⁴⁰

In both the cation and the anion of 5 the six atoms comprising the Y_3O_3 ring are coplanar to within ± 0.060 Å. The central μ_3 -hydride ligands could not be located in this structure.

Discussion

Previous studies of organolanthanide or organoyttrium hydride complexes have shown that hydrogen in these systems is hydridic.^{4,16} It was expected, therefore, that the hydride ligands in 1 would react with methanol to form hydrogen and an yttrium methoxide linkage. What was unpredictable in the reaction of 1 with methanol was whether or not the trimer would remain intact. The results of this study indicate that the trimer does not dissociate under these reaction conditions. Complexes 2, 3, and 4 can be obtained cleanly in high yield by reaction of 1 with 1, 2, and 3 equiv of methanol, respectively, or by sequential conversion $1 \rightarrow 2 \rightarrow 3 \rightarrow 4$ with use of 1 equiv of methanol at a time. Ligand redistribution reactions to give mixtures of products, e.g., 1 and 3 in a reaction to form 2, apparently do not occur to any significant extent. Consistent with this, a mixture of 1 and 4 shows no sign of forming 2 or 3 under the conditions used for synthesizing 2–4. If dissociation occurred in the reaction of 1 with 1 equiv of methanol, one could expect products such as $[(C_5H_5)_2Y(\mu-H)(THF)]_2$, $(C_5H_5)_2Y(OCH_3)(THF)$, or $(C_5H_5)_2Y(OCH_3)_2^-$. None of these products have been observed.

Additional evidence on this point arises from the relative reactivities of 1–3 with methanol. Two of the doubly bridging hydride positions in 1 react with methanol under identical conditions; i.e., the $1 \rightarrow 2$ and $2 \rightarrow 3$ reactions proceed at -78 °C. However, the third doubly bridging hydride ligand is unreactive with methanol at -78 °C; i.e., 3 does not react with methanol at this temperature. If the trimer were dissociating during this reaction, the $(C_5H_5)_2YH$ or $(C_5H_5)_2YH_2^-$ fragments derived from 3 should have the same reactivity as the identical fragments formed by dissociation of 1 or 2.

The strongest evidence indicating dissociation does not occur arises from the fact that the central triply bridging hydride does not react with methanol even at 65 °C. If trimer fragmentation were occurring, this hydride would certainly react with methanol.

The variability in reactivity of the hydride ligands in 1 and 2 versus 3 versus 4 can be explained by steric factors. The μ_3-H ligand in 1–4 is obviously the most sterically inaccessible hydride in these systems. As shown in Figures 2 and 3, the μ_3-H in 5 is protected above and below the Y_3O_3H plane by the six cyclopentadienyl ligands. In the Y_3O_3H ring in 3 it is surrounded by three OCH_3 groups and three $(C_5H_5)_2Y$ moieties. Hence, the lack of reactivity of this μ_3-H ligand is consistent with its steric protection.

Steric protection may also explain why the doubly bridging hydride ligand in 3 is less reactive than the doubly bridging hydride ligands in 1 and 2. Replacement of two doubly bridging hydride groups in 1 by the larger methoxide ligands may cause the Y_3O_3H ring in 3 to distort. The $Y-(\mu-H)-Y$ part of the ring may be compressed to make more room for the two $Y-(\mu-OCH_3)-Y$ units. In support of this, the structure of 6⁵ is distorted in that the two erbium atoms bridged by chloride are 0.23 Å further apart than the pairs of erbium atoms bridged by the two doubly bridging hydride ligands. Hence, steric effects may again be used to explain differences in the reactivity of these hydride units. The importance of steric effects on the reactivity of mono- and bimetallic organoyttrium and organolanthanide complexes has previously been demonstrated.^{14,15,23}

The difference in reactivity of the $\mu-H$ position in 3 versus 1 or 2 is significant in another sense. It shows that modification done in one part of the trimer can affect reactivity in another part. This is truly polymetallic chemistry. These results suggest that the reactivity of trimetallic organoyttrium complexes of this type can be manipulated in a manner not possible with lower nuclearity systems.

The X-ray crystallographic study on 5 provides another example of the trimetallic $[(C_5H_5)_2Ln(\mu-Z)]_3(\mu_3-H)^-$ unit ($Z = H, OR, Cl$) seen previously in the structures of 6 and 7.⁵ The structure of 5 is fully consistent with the ¹H NMR data on 4 and provides additional support for the NMR assignments made for these trimetallic species.⁶ The structure of 5 also shows one way in which structures containing a lithium cation can accommodate less than four ethers of solvation. Samples of 1, 6, and 7 sent for elemental analysis all analyzed for less than four molecules of THF per

(38) den Haan, K. H.; de Boer, J. L.; Teuben, J. H.; Spek, A. L.; Kojic-Prodic, B.; Hays, G. R.; Huis, R. *Organometallics* **1986**, *5*, 1726–1733.

(39) Evans, W. J.; Meadows, J. H.; Hunter, W. E.; Atwood, J. L. *Organometallics* **1983**, *2*, 1252–1254.

(40) Evans, W. J.; Sollberger, M. S. *J. Am. Chem. Soc.* **1986**, *108*, 6095–6096.

(41) Rogers, R. D.; Atwood, J. L.; Enad, A.; Sikora, D. J.; Rausch, M. D. *J. Organomet. Chem.* **1981**, *216*, 383–392.

(42) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980.

lithium, with 7 analyzing specifically for the (THF)₃ species [(C₅H₅)₂Lu(μ-H)]₃(μ₃-H)[Li(THF)₃]. Complex **5** shows a Li(THF)₃⁺ cation can be fully coordinated in a cyclopentadienyl system.

Conclusion

The complex [(C₅H₅)₂Y(μ-H)]₃(μ₃-H)⁻ and its derivatives are ideally suited both chemically and spectroscopically to evaluate the integrity of the trimetallic unit during reactions. The reactions of these complexes with varying amounts of CH₃OH clearly demonstrate that yttrium can participate in polymetallic reaction chemistry. This is quite remarkable considering that (a) organolanthanide complexes are traditionally thought to be highly ionic and prone to ligand redistribution reactions and (b) formal metal-metal bonds are not present. In these systems, bridging hydride and alkoxide ligands hold the trinuclear array of metals intact. It is likely that the central μ₃-H ligand is most important in this regard. This result adds a new dimension to the chemistry of yttrium and related metals. By developing polymetallic derivatives of these metals, we will have new ways to precisely control reactivity.²³ Attempts to increase the number of classes of Y₃-

(μ₃-H) complexes are in progress.

Structurally, the unusual arrangement of the lithium ions in **5** emphasizes the variability possible in placing cations in these cyclopentadienyl systems. The existence of weak lithium interactions with coordinated cyclopentadienyl rings may be more prevalent than previously expected. The isolation of **5** is a rare example of a case in which this phenomenon has been directly observable.

Acknowledgment. For support of this research, we thank the Division of Chemical Sciences of the Office of Basic Energy Sciences of the Department of Energy (W.J.E.) and the National Science Foundation (R.B.).

Registry No. 1, 90762-81-5; 2, 111435-08-6; 3, 111435-10-0; 4, 111409-63-3; 5, 111409-64-4.

Supplementary Material Available: Complete tables of interatomic distances and selected angles for [(C₅H₅)₂Y(μ-OCH₃)₃(μ₃-H)]₂[Li(THF)₃]₂ (4 pages); a listing of observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

Synthesis and Spectroscopic and Structural Characterization of the Novel Lithium Borylamide Salts *trans*-[Li(Et₂O)NHBMes₂]₂, a Dimer, and the Ion Pair [Li(Et₂O)₃][Mes₂BNBMes₂] with a Linear Allene-like, [R₂B=N=BR₂]⁻, Moiety

Ruth A. Bartlett, Hong Chen, H. V. Rasika Dias, Marilyn M. Olmstead, and Philip P. Power*¹

Contribution from the Department of Chemistry, University of California, Davis, California 95616. Received May 15, 1987

Abstract: Treatment of the primary aminoborane H₂NBMes₂ (**1**) with *n*-BuLi in Et₂O/hexane gives an almost quantitative yield of the novel dimeric lithium amide [Li(Et₂O)NHBMes₂]₂ (**2**). The addition of 1 equiv of Mes₂BF to LiNHBMes₂, generated in situ, gives the recently published diborylamine HN(BMes₂)₂ (**3**). The compound **3** reacts with 1 equiv of *n*-BuLi to give the salt [Li(Et₂O)₃]⁺[Mes₂BNBMes₂]⁻ (**4**) in quantitative yield. Details of the ¹¹B NMR spectra and X-ray crystal structures of **1**, **2**, and **4** are reported. Crystal data [Mo Kα (λ = 0.71069 Å)] at 130 K (293 K for **2**) are as follows: **1**, *a* = 8.602 (3) Å, *b* = 9.637 (2) Å, *c* = 10.248 (2) Å, β = 109.38 (2)°, *Z* = 2, monoclinic, space group *P*2₁, 1505 unique data, *R*(*F*) = 0.069; **2**, *a* = 9.010 (4) Å, *b* = 9.440 (5) Å, *c* = 25.958 (12) Å, β = 97.56 (4)°, *Z* = 2, monoclinic, space group *P*2₁/*n*, 3859 unique data, *R*(*F*) = 0.063; **4**, *a* = 12.699 (3) Å, *b* = 12.889 (6) Å, *c* = 14.371 (5) Å, β = 91.87 (2)°, *Z* = 2, monoclinic, space group *P*2₁, 5645 unique data, *R*(*F*) = 0.058. The structures of the compounds are notable for a number of reasons. For example, **1** is the first primary aminoborane, i.e. R₂BNH₂ (where R = alkyl or aryl group), to be structurally characterized. It possesses a short B-N distance of 1.375 (8) Å. The X-ray crystal structure of **2** is the first for a lithium salt of a primary aminodiarylborane. The structure of the unique diborylamide anion [Mes₂B=N=BMes₂]⁻ (**4**) reveals the first example of an essentially linear 176.2 (3)° BNB system. The BN distances are 1.343 (5) and 1.348 (5) Å, and the CBC planes have a dihedral angle of 88°. Thus, it is isoelectronic to and isostructural with the corresponding allene system and the borinium cations [R₂B=N=BR₂]⁺.

Lithium amides^{2,3} have found considerable use as amide transfer agents in both inorganic and organometallic chemistry. Their structures^{3,4} are also of considerable interest from the point of view

of interest in lithium compounds in general and the comparison with their carbon analogues, the structures of which seldom follow classical bonding considerations. In this laboratory, attention on lithium compounds has been focused on their interaction with crown ethers to give separate, nonbridging, ionic species rather than the associated structures typical of many lithium salts.⁵ In general, association of lithium amides and indeed many other metal amides stems from ionic forces and the availability of a nonbonded pair of electrons on nitrogen, which may be used for bridging. The degree of association may, in principle, be reduced by increasing the size of the nitrogen substituents or by changing the electronic properties of the amide so as to reduce the availability of the

(1) Fellow of the A. P. Sloan Foundation 1985-1987.
 (2) Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. *Metal and Metalloid Amides*; Horwood: Chichester, UK, 1980.
 (3) Setzer, W. N.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1985**, *24*, 353.
 (4) Lappert, M. F.; Slade, M. J.; Singh, A.; Atwood, J. L.; Rogers, R. D. *J. Am. Chem. Soc.* **1983**, *105*, 302. Barr, D.; Clegg, W.; Mulvey, R. E.; Snaith, R. *J. Chem. Soc., Chem. Commun.* **1984**, 469. Barr, D.; Clegg, W.; Mulvey, R. E.; Snaith, R. *J. Chem. Soc., Chem. Commun.* **1984**, 285. Engelhardt, L. M.; May, A. S.; Raston, C. L.; White, A. L. *J. Chem. Soc., Dalton Trans.* **1983**, 1671. Barr, D.; Clegg, W.; Mulvey, R. E.; Smith, R.; Wright, D. S. *J. Chem. Soc., Chem. Commun.* **1987**, 716. Armstrong, D. R.; Barr, D.; Clegg, W.; Mulvey, R. E.; Reed, D.; Snarth, R.; Wade, K. *J. Chem. Soc., Chem. Commun.* **1986**, 869.

(5) Hope, H.; Olmstead, M. M.; Power, P. P.; Xu, X. *J. Am. Chem. Soc.* **1984**, *106*, 819.