scheme, requiring no reference samples, will serve as a complementary method to the standard methylation analysis.[4] Current work is directed toward studies of glycoconjugates, including sequence information obtainable from partial cleavage.

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Syntheses of Divalent Lanthanide Tetradecahydrodecaborates and Decahydrodecaborates. The X-ray Crystal Structure of $(CH_3CN)_6Yb(\mu\text{-}H)_2B_{10}H_{12}\cdot 2CH_3CN$

James P. White III, Hai-Bin Deng, and Sheldon G. Shore*

Department of Chemistry, The Ohio State University
Columbus, Ohio 43210

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The chemistry and bonding of boron hydrides to the lanthanide elements remains largely unexplored. While numerous lanthanide organometallic complexes are known,[1a,b] the only boron hydride compounds reported are the trivalent *closo*-$[B_{12}H_{12}]^{2-}$ salts[2,3] and borohydride, $[BH_4]^-$, derivatives.[4,5] No detailed structural data are available; however, the gadolinium complex $(BH_4)_3Gd(THF)_3$ has been reported to be isomorphous with the pseudo-lanthanide derivative[6] $(BH_4)_3Y(THF)_3$. Compounds containing the common divalent ions (Ln = Sm, Eu, Yb) and binary boron hydride ligands are unknown; however, carborane complexes have been reported in which the metal occupies the vertex site of an icosahedron,[7] as well as a σ-bonded carborane compound.[8] Herein we report the synthesis and the first example of a structurally characterized polyhedral boron hydride bound to a lanthanide center, $(CH_3CN)_6Yb(\mu\text{-}H)_2B_{10}H_{12}\cdot 2CH_3CN$ (I). We also report the syntheses of the divalent lanthanide decahydrodecaborate compounds $EuB_{10}H_{10}$ (II) and $YbB_{10}H_{10}$ (III).

Compounds I–III are derived from reactions of decaborane(14), $B_{10}H_{14}$, with the lanthanide metals (Ln = Eu, Yb) in liquid ammonia (Scheme I). Both europium and ytterbium dissolve in NH_3 to give deep blue, highly reducing solutions containing Ln^{2+} and solvated electrons.[9] Decaborane(14) is easily reduced in these solutions, from which several products can be isolated.

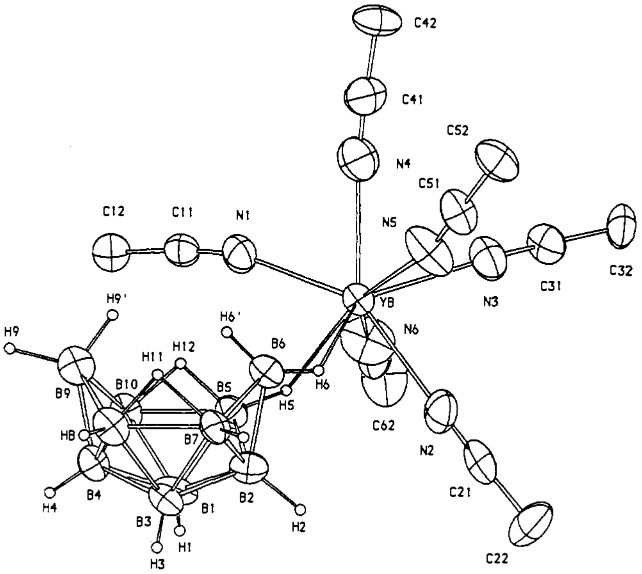
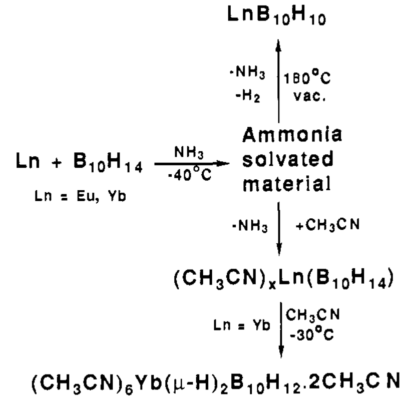
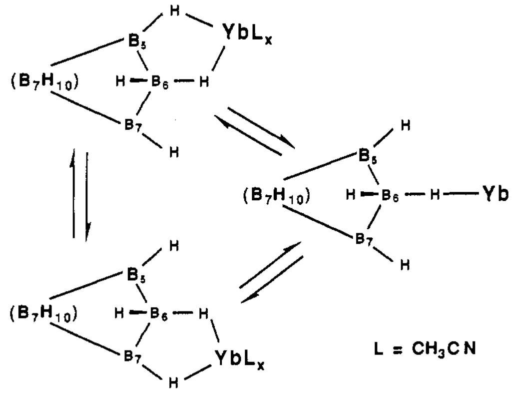


Figure 1. Molecular structure of $(CH_3CN)_6Yb(\mu\text{-}H)_2B_{10}H_{12}$ (I) (ORTEP plot with 50% probability ellipsoids). Acetonitrile hydrogens are not shown. Selected distances (Å): Yb–H(5) = 2.2 (1); Yb–H(6) = 2.4 (1); Yb–N(1) = 2.54 (1); Yb–N(2) = 2.52 (1); Yb–N(3) = 2.56 (2); Yb–N(4) = 2.53 (1); Yb–N(5) = 2.59 (2); Yb–N(6) = 2.53 (2); Yb–B(5) = 3.04 (1); Yb–B(6) = 2.83 (1). Selected bond angles (deg): H(5)–Yb–H(6) = 68 (4); B(5)–H(5)–Yb = 117 (7); B(6)–H(6)–Yb = 110 (7).

Scheme I



Scheme II



The molecular structure of I, determined from a single-crystal X-ray analysis[10] (Figure 1), reveals a $B_{10}H_{14}$ unit that is coordinated to ytterbium through two B–H–Yb bridges from adjacent $BH_2(6)$ and BH(5) positions on the boron cage. All of the hydrogen atoms on the B_{10} framework were located, and their positions were refined. Their disposition in the $B_{10}H_{14}$ unit is like that in $[B_{10}H_{14}]^{2-}$, and the structural parameters are in good agreement with those of the dianion.[11] In addition, there are six roughly linear acetonitriles bound through nitrogens to the metal center. The ytterbium is formally eight coordinate, with an ir-

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(10) Crystal data for $(CH_3CN)_6Yb(\mu\text{-}H)_2B_{10}H_{12}\cdot 2CH_3CN$ (−45 °C): space group $P\bar{1}$, $a = 8.831$ (6) Å, $b = 11.615$ (4) Å, $c = 15.568$ (6) Å; $\alpha = 104.08$ (3)°, $\beta = 97.67$ (4)°, $\gamma = 94.83$ (3)°; $V = 1523.6$ Å^3, ρ(calcd) = 1.359 g cm^{-3}, MW = 623.68, $Z = 2$, $\mu = 30.786$ cm^{-1}. Diffraction data were collected with an Enraf-Nonius CAD4 diffractometer using Mo Kα radiation. All data were corrected for Lorentz and polarization effects. An empirical absorption correction was made. Crystallographic computations were carried out on a PDP11/44 computer using the SDP (Structure Determination Package). The structure was solved by the direct method MULTAN 11/82 and difference Fourier synthesis. Full-matrix least-squares refinements were employed. $R_F = 0.052$, $R_{wF} = 0.063$, GOF = 1.88 (356 variables refined) for 2796 unique observations [$I \geq 3.0\sigma(I)$] of 4145 reflections collected over the 2θ range $4° \leq 2\theta \leq 45°$. All non-hydrogen atoms were refined anisotropically except one acetonitrile of crystallization which was disordered.

(11) Kendall, D. S.; Lipscomb, W. N. *Inorg. Chem.* **1973**, *12*, 546.

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regular coordination geometry around the metal center. The formation of I appears to involve a two-electron reduction of $B_{10}H_{14}$ by Yb to form the $[B_{10}H_{14}]^{2-}$ anion, which then back-donates four electrons to the Yb cation through two three-center two-electron bonds. Coordination of CH_3CN ligands to the ytterbium allows isolation of I as a discrete complex.

The Yb–H–B bridges in I represent the first structurally characterized example of a three-center B–H–Ln interaction. Bridging hydrogen atoms were located, and their positions were refined. The ytterbium–hydrogen distances Yb–H(5) = 2.2 (1) Å and Yb–H(6) = 2.4 (1) Å are effectively equal.

The ^{11}B NMR spectrum of I in CD_3CN indicates that the boron cage remains bonded to the metal in solution.[12] The uncomplexed $[B_{10}H_{14}]^{2-}$ ion has C_{2v} symmetry, and its ^{11}B NMR spectrum consists of four signals of intensity 2(d):4(d):2(t):2(d), corresponding to the 2,4-, 5,7,8,10-, 6,9-, and 1,3-positions, respectively.[13] Complex I has a ^{11}B NMR spectrum that is composed of six signals of intensity 1(d):1(d):4(d):1(d):1(t):2(d). A 2D-COSY ^{11}B NMR analysis showed that the resonances correspond to the 2,4-, 5,7,8,10-, 6,9-, and 1,3-borons in the cage. This spectrum is consistent with a binding of Yb^{2+} to B(6) through a single hydrogen bridge, or bidentate binding with rapid exchange between the H(5) and H(7) sites (Scheme II). Such a spectrum should exhibit seven resonances, but coincidental overlap of the 5,7 and 8,10 boron signals would yield the observed six-line pattern. Such overlap is confirmed from the NMR analysis.

In a typical synthetic procedure, a 1:1 ratio of Ln (1.0 mmol, Yb = 0.173 g, Eu = 0.150 g) to $B_{10}H_{14}$ (1.0 mmol, 0.122 g) reacts in liquid NH_3 (15 mL) at −40 °C to give an insoluble material containing ammonia-solvated Ln^{2+} and reduced B_{10} boron hydride species.[14] Extraction of the solid material with CH_3CN yields yellow (Eu) and orange (Yb) solutions consisting of acetonitrile-solvated Ln^{2+} and $[B_{10}H_{14}]^{2-}$ ions.[15] Cooling the Yb^{2+} extract to −30 °C under nitrogen causes I to form as orange crystals (0.149 g, 24% yield). The ammonia-solvated materials (Eu or Yb) decompose when heated to 180 °C in vacuum with elimination of H_2 and NH_3[16] to form the closo borane compounds, grey-green $EuB_{10}H_{10}$ (II) and pea-green $YbB_{10}H_{10}$ (III), respectively. These compounds are formed in stoichiometric yields and in relatively high (ca. 97%) purities.[17]

The closo compounds II and III are primarily ionic solids.[18] Their IR spectra resemble those of the alkali metal salts of $[B_{10}H_{10}]^{2-}$, showing only absorptions due to the boron cage.[19] They are soluble in pyridine, forming bright yellow (Eu) and deep purple (Yb) solutions. The ^{11}B NMR spectrum of III in pyridine-d_5 is very similar to the spectrum observed for free $[B_{10}H_{10}]^{2-}$ (Rb^+ salt),[18] indicating that the compound exists as solvent-separated ions in solution.

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Supplementary Material Available: Listings of bond distances, bond angles, positional parameters, and anisotropic thermal parameters for $(CH_3CN)_6Yb(\mu\text{-}H)_2B_{10}H_{12}\cdot 2CH_3CN$ (12 pages); a listing of calculated and observed structure factor amplitudes for $(CH_3CN)_6Yb(\mu\text{-}H)_2B_{10}H_{12}\cdot 2CH_3CN$ (14 pages). Ordering information is given on any current masthead page.

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[12] ^{11}B NMR data for I in CD_3CN (δ $BF_3\cdot OEt_2$ = 0.00 ppm), with coupling constants, in Hz, in parentheses, are as follows: −4.3, d (109); −7.1, d (126); −20.0, d (111); −25.6, d (113); −32.2, t (98); −40.3, d (132) ppm. Peak integration gives an intensity ratio of approximately 1:1:4:1:1:2, respectively.

[13] Lipscomb, W. N.; Wiersema, R. J.; Hawthorne, M. F. *Inorg. Chem.* **1972**, *11*, 651.

[14] The ammonia-solvated material is formed along with about 0.36 mol of H_2/mol of $B_{10}H_{14}$.

[15] On the basis of the ^{11}B NMR spectrum of the Yb^{2+} solution, there are also small amounts of the monoanions $[B_{10}H_{13}]^-$ and $[B_{10}H_{15}]^-$ present.

[16] Evolved gases were collected and measured in a calibrated toepler system. The ammonia-solvated solids released 2 mol of H_2/mole of Ln present. There were 4 mol of NH_3/mol of Eu and 2 mol of NH_3/mol of Yb given off from each solid. The evolution of H_2 from the lanthanide decaborates raises the possibility that a Ln–H intermediate is formed and assists in the transformation of *arachno*-$[B_{10}H_{14}]^{2-}$ to *closo*-$[B_{10}H_{10}]^{2-}$.

[17] Purity is based on the absence of any signals attributed to solvent in the Nujol IR spectra, and the elemental analyses for each. Calcd for $EuB_{10}H_{10}$: Eu, 56.25; B, 40.02; H, 3.73. Obsd: Eu, 55.55; B, 38.21; H, 3.46. Calcd for $YbB_{10}H_{10}$: Yb, 59.42; B, 37.12; H, 3.46. Obsd: Yb, 59.15; B, 35.73; H, 3.40. Each compound contained 0.5% residual N.

[18] Spectral data for II and III, IR (Nujol mull, NaCl plates), in cm^{-1}. $EuB_{10}H_{10}$: 2503 (s), 2456 (vs, br), 1086 (w), 1019 (mw), 974 (w). $YbB_{10}H_{10}$: 2525 (sh), 2456 (vs, br), 1076 (w), 1016 (mw), 974 (w). ^{11}B NMR data for III in pyridine-d_5 (δ $BF_3\cdot OEt_2$ = 0.00 ppm) at 353 K: +0.5, d (136); −27.5, d (102) ppm; relative intensities of 1:4, respectively. B–H coupling of the −27.5 ppm signal is not resolved at temperatures below 353 K. Eu^{2+} compounds are paramagnetic and do not give interpretable NMR spectra.

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A New Class of Room Temperature Luminescent Organometallic Complexes: Luminescence and Photophysical Properties of Permethylscandocene Chloride in Fluid Solution

Brian W. Pfennig, Mark E. Thompson,* and
Andrew B. Bocarsly*

Department of Chemistry, Frick Laboratory
Princeton University
Princeton, New Jersey 08544-1009

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The search for organometallic complexes that emit in fluid solution at room temperature has been intensely pursued for the past 35 years because of the importance of an understanding of excited-state properties to the areas of solar energy conversion and photoassisted catalysis.[1] Although extensive studies have been carried out, only complexes consisting of second- or third-row late transition metals have been identified as luminescent under the stated conditions. Usually, such luminescent complexes require the presence of an aromatic amine ligand, ruthenium tris(bipyridine) being prototypical; however, a limited number of exceptions to this observation have been recently noted.[2,3] We report here on the photophysics of the d^0 first row transition metal complex Cp^*_2ScCl (Cp^* = pentamethylcyclopentadienyl). To the best of our knowledge, this represents a new class of organometallic transition-metal complexes having no aromatic amine ligands that luminesce at room temperature in fluid solution.

The following UV–vis absorptions were found in solution (1:1 v/v mixture of isooctane and methylcyclohexane) at 298 K (see Figure 1): 39 215 cm^{-1} (255 nm, ϵ = 2500 M^{-1} cm^{-1}), 33 670 cm^{-1} (297 nm, ϵ = 2400 M^{-1} cm^{-1}), and 27 930 cm^{-1}s (358 nm, ϵ = 900 M^{-1} cm^{-1}).[4] A fourth optical transition was too weak to appear by absorption spectroscopy, but was observed in the excitation spectrum at 25 640 cm^{-1} (390 nm). Excitation into this lowest energy band produced a broad emission centered at 19 230 cm^{-1} (520 nm) with a small shoulder toward the red as shown in Figure 1 (inset). Taking inner filter effects into consideration, this emission is essentially wavelength-independent over the range in which the compound absorbs. Therefore, the lowest energy excited state is taken to be the emissive state. This conclusion is supported, as shown by the overlap between the emission and the foot of the forbidden absorption centered at 390 nm. The

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[1] See, for example: (a) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic Press, Inc.: New York, 1979. (b) Lees, A. J. *Chem. Rev.* **1987**, *87*, 711.

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[4] The solvents were obtained from Aldrich and were dried by reflux over the appropriate desiccant, followed by distillation and several freeze–pump cycles on a vacuum line. Molar absorptivities were determined by least-squares fits to Beer's law plots. Since the complex is air- and water-sensitive, all manipulations were carried out by using standard vacuum line techniques or in a glove box.

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