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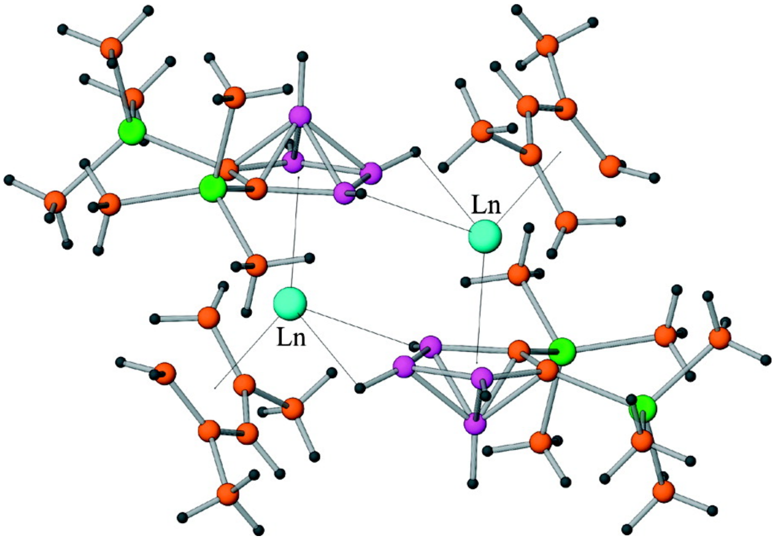

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Novel Sandwich Complexes of Terbium and Erbium Metals Derived from Mixed η^5 Open-Pentadienyl and C_2B_4 Carborane Ligands: A Synthetic and Structural Investigation

Ang Li,† Jianhui Wang,†,‡ Chong Zheng,† John A. Maguire,‡ and Narayan S. Hosmane*,†

Department of Chemistry and Biochemistry, Northern Illinois University, DeKalb, Illinois 60115-2862, and Department of Chemistry, Southern Methodist University, Dallas, Texas 75275-0314

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Summary: Mixed-ligand dimeric lanthanacarboranes of the type $[(\eta^5\text{-}2,4\text{-}(Me)_2C_5H_5)(\eta^5\text{-}2,3\text{-}(Me_3Si)_2\text{-}2,3\text{-}C_2B_4H_4)Ln]_2$ *(Ln = Tb (**2**), Er (**3**)) were prepared as orange and yellow crystalline solids in 76 and 82% yields, respectively, via the exchange reactions between* $(2,4\text{-}(Me)_2C_5H_5)_3Ln$ *and nido-*$2,3\text{-}(Me_3Si)_2\text{-}2,3\text{-}C_2B_4H_6$ *(**1**) in toluene at elevated temperature (70 °C). The compounds were characterized by IR spectra, elemental analyses, and single-crystal X-ray diffraction.*

Interest in metallacarboranes stems from the 1964 synthesis of the *nido*-$C_2B_9H_{12}^-$ anion by Hawthorne[1] and his recognition that the corresponding *nido*-$C_2B_9H_{11}^{2-}$ bears a striking similarity to the $C_5H_5^-$ ligand. This similarity was demonstrated by the syntheses of $Fe(C_2B_9H_{11})_2^{2-}$ and $Fe(C_2B_9H_{11})_2^-$, the former being an analogue of ferrocene.[2] Shortly thereafter, the synthesis and structural characterization of the mixed-ligand sandwich complex $(C_5H_5)Fe(C_2B_9H_{11})$ was reported.[3] Since then a number of mixed-ligand, half- and full-sandwich metallacarborane complexes have been described.[4] In addition to the well-studied cyclopentadienyl ligand, there is another π-electron donor, the open pentadienyl ligand, R_7C_5 (R = H or an alkyl derivative). A number of so-called "open metallocenes" where the pentadienyl group replaces one or more cyclopentadienyl ligands have been synthesized and characterized.[5] The pentadienyls have been shown to be similar to their cyclic analogues in some respects but possess a unique chemistry that has led to a number of unusual compounds, such as the metallabenzenes and their π complexes.[6,7] While both the metal−pentadienyl and metallacarborane compounds have often been compared to the metallocenes, there do not seem to have been any reports of combining open-metallocene and metallacarborane chemistry. Since such studies could produce intriguing compounds with interesting properties, we have undertaken an investigation of metallacarboranes containing pentadienyl ligands. This initial report involves the syntheses and structural determinations of two open-sandwich lanthanacarboranes, $[(\eta^5\text{-}2,4\text{-}(Me)_2C_5H_5)(\eta^5\text{-}2,3\text{-}(Me_3Si)_2\text{-}2,3\text{-}C_2B_4H_4)Ln]_2$ (Ln = Tb (**2**), Er (**3**)).

The compounds were synthesized in a two-step process, as outlined in Scheme 1.[8] The tris(pentadienyl)lanthanide complex was first synthesized by the 3:1 molar ratio reaction of $K[2,4\text{-}(Me)_2C_5H_5]$ and $LnCl_3$ (Ln = Tb, Er) in THF by following the published procedures.[9,10] The $Ln(2,4\text{-}(Me)_2C_5H_5)_3$ compounds were then treated immediately with $2,3\text{-}(SiMe_3)_2$-*nido*-$2,3\text{-}C_2B_4H_6$ in a 1:1 molar ratio in toluene to give the $[(\eta^5\text{-}2,4\text{-}(Me)_2C_5H_5)(\eta^5\text{-}2,3\text{-}(Me_3Si)_2\text{-}2,3\text{-}C_2B_4H_4)Ln]_2$ (Ln = Tb (**2**), Er (**3**)) dimers, in yields of 76 and 82%, respectively. No attempts were made to characterize the $Ln(2,4\text{-}(Me)_2C_5H_5)_3$ product of the initial $K[2,4\text{-}(Me)_2C_5H_5]$ and $LnCl_3$ reaction. Their formulations were based on the fact that KCl was a byproduct and that similar reactions produced $Ln(2,4\text{-}(Me)_2C_5H_5)_3$.[9,10] The pentadienyl group can potentially act as an η^1-, η^3-, or η^5-bonding ligand. The NMR spectra of both **2** and **3** gave no useful information from which their geometries can be elucidated. Unfortunately, while the analysis and IR spectral data of compounds **2** and **3** are consistent with their formulas, they do not offer insight into the nature of the pentadienyl−Ln interactions. Therefore, the structures of the compounds were determined unambiguously by single-crystal X-ray diffraction.[11]

Figures 1 and 2 show that each compound crystallizes as $[(\eta^5\text{-}2,4\text{-}(Me)_2C_5H_5)(\eta^5\text{-}2,3\text{-}(Me_3Si)_2\text{-}2,3\text{-}C_2B_4H_4)Ln]_2$ (Ln = Tb (**2**), Er (**3**)), a dimer in which a pentadienyl and a carborane ligand are η^5-bonded to a metal atom. In addition, each carborane is η^2-bonded to the neighboring metal in the dimer. The structures show that the

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* To whom correspondence should be addressed. E-mail: nhosmane@niu.edu.

† Northern Illinois University.

‡ Southern Methodist University.

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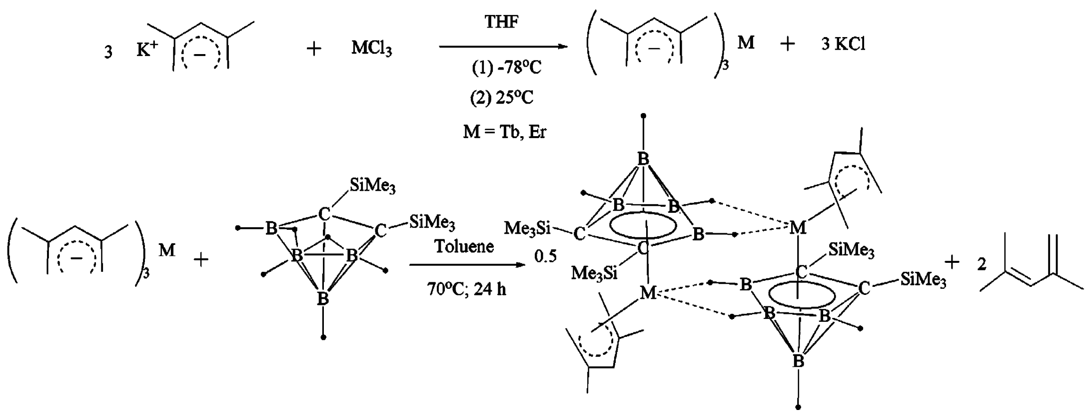
10.1021/om0497341 CCC: $27.50

Scheme 1



pentadienyl ligands are essentially planar (the C11−C14 and C12−C15 dihedral angles are 8.2 and 8.5°, respectively, in **2** and 7.7 and 7.0°, respectively, in **3**).

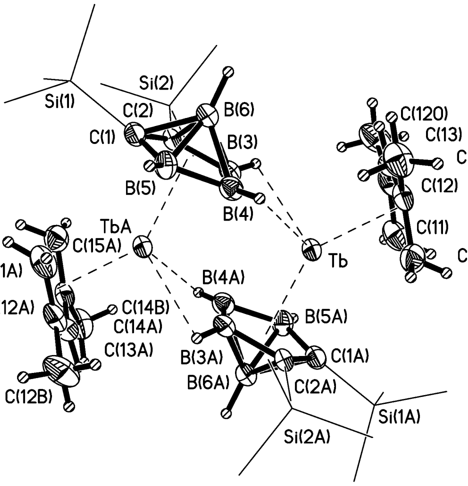


Figure 1. Molecular structure of $[(\eta^5\text{-}2,4\text{-}(Me)_2C_5H_5)(\eta^5\text{-}2,3\text{-}(Me_3Si)_2\text{-}2,3\text{-}C_2B_4H_4)Tb]_2$ (**2**) with thermal ellipsoids drawn at the 50% probability level. The exo-polyhedral $SiMe_3$ groups were drawn with thinner lines for clarity. Selected bond lengths (Å): Tb−(C_2B_3 centroid), 2.326; Tb−C(1,2), 2.660(5), 2.667(5); Tb−B(3,4,5), 2.698(6), 2.748(6), 2.682(7); Tb−C(11,12,13,14,15), 2.673(6), 2.712(5), 2.647(5), 2.714(5), 2.671(6). A full listing of bond distances and angles can be found in the Supporting Information.

The methylene carbons, C(11)−C(15), are equivalently bonded to a metal (the average Ln−(C11−C15) distance is 2.683 ± 0.024 Å in **2** and 2.631 ± 0.24 Å in **3**),[12] compared to the value of 2.778 ± 0.061 Å reported for $[(2,4\text{-}(Me)_2C_5H_5)_2ErC{\equiv}CC_6H_5]_2$.[10] The Ln−$C_2B_3$(centroid) distances are 2.326 and 2.270 Å for **2** and **3**, respectively, which are slightly smaller than the analogous distance of 2.369 Å found for the terbium trinuclear carborane cluster $\{[\eta^5\text{-}1\text{-}Tb\text{-}2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4]_3[(\mu\text{-}1\text{-}Li\text{-}2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4)_3(\mu_3\text{-}OMe)][\mu\text{-}Li(C_4H_8O)]_3(\mu_3\text{-}O)\}$[13] and 2.344 Å found in the $[1\text{-}Cl\text{-}1\text{-}(\mu\text{-}Cl)\text{-}2,2',3,3'\text{-}(SiMe_3)_4\text{-}5,6\text{-}[(\mu\text{-}H)_2Li(TMEDA)\text{-}4,4'\text{-}5'\text{-}[(\mu\text{-}H)_3Li(TMEDA)]\text{-}1,1'\text{-}$*commo*$\text{-}Er(2,3\text{-}C_2B_4H_4)_2]^-$ anion.[14] In general, the average Ln−(pentadienyl atom) and Ln−(C_2B_3 atom) distances in the Tb complex are ~0.05 Å greater than those found in the Er compound, which is consistent with the larger ionic radius of Tb compared to Er.[15]

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(8) Synthesis of $[(\eta^5\text{-}2,4\text{-}(Me)_2C_5H_5)(\eta^5\text{-}2,3\text{-}(Me_3Si)_2\text{-}2,3\text{-}C_2B_4H_4)Tb]_2$ (**2**): a 0.50 g (1.88 mmol) sample of anhydrous $TbCl_3$ was added to dry THF (20 mL) under argon, and the resulting heterogeneous mixture was stirred overnight. The mixture was then cooled to −78 °C, and a 7.29 mL THF solution of $K(2,4\text{-}(Me)_2C_5H_5)$ (5.65 mmol, 0.78 M) was added slowly with constant stirring. The resulting mixture was slowly warmed to room temperature and stirred for 72 h at this temperature, during which time the color of the heterogeneous reaction mixture changed to orange. The reaction mixture was filtered to remove KCl, and a clear filtrate was obtained. The solvent was then removed slowly from the filtrate to give a red solid. This solid was redissolved in 30 mL of toluene, to which 0.41 g (1.88 mmol) of *nido*-$2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_6$ (**1**) was slowly added at room temperature with constant stirring. After complete addition, the resulting reaction mixture was heated to 70 °C for 24 h, during which time the color of the reaction mixture changed to yellow. The solvent was then removed in vacuo to collect a yellow solid, which was repeatedly washed with hexane and then recrystallized from anhydrous toluene to give orange crystals, identified as $[(\eta^5\text{-}2,4\text{-}(Me)_2C_5H_5)(\eta^5\text{-}2,3\text{-}(Me_3Si)_2\text{-}2,3\text{-}C_2B_4H_4)Tb]_2$, in 76% yield (0.68 g, 0.72 mmol). Mp: 105−106 °C dec. Anal. Calcd (found) for $C_{30}H_{66}B_8Si_4Tb_2$ (**2**): C, 38.19 (38.40); H, 7.05 (7.43). IR (cm^{-1}, Kbr pellet): 2953 (s, s), 2916 (s, m), 2898 (s, s), 2590 (s, s), 2554 (s, s), 2540 (s, s), 2371 (s, w), 2198 (s, w), 2035 (s, w), 1945 (s, w), 1535(s, s), 1458 (s, m), 1431 (s, m), 1404 (s, m), 1247 (s, vs), 1177 (s, m), 1127 (s, w), 1059 (s, w), 973 (s, s), 858 (s, vs), 792 (s, s), 756 (s, s), 687 (s, s), 631 (s, s). Synthesis of $[(\eta^5\text{-}2,4\text{-}(Me)_2C_5H_5)(\eta^5\text{-}2,3\text{-}(Me_3Si)_2\text{-}2,3\text{-}C_2B_4H_4)Er]_2$ (**3**): in a procedure similar to that used in the synthesis of **2**, 0.50 g (1.83 mmol) of anhydrous $ErCl_3$ was stirred overnight in dry THF (20 mL), cooled to −78 °C and mixed with a 7.00 mL THF solution of $K(2,4\text{-}(Me)_2C_5H_5)$ (5.49 mmol, 0.78 M) to produce $Ln(2,4\text{-}(Me)_2C_5H_5)_3$, which was subsequently reacted with 0.40 g (1.83 mmol) of *nido*-$2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_6$ (**1**) to isolate yellow crystals, identified as $[(\eta^5\text{-}2,4\text{-}(Me)_2C_5H_5)(\eta^5\text{-}2,3\text{-}(Me_3Si)_2\text{-}2,3\text{-}C_2B_4H_4)Er]_2$, in 82% yield (0.72 g, 0.75 mmol). Mp: 80−82 °C dec. Anal. Calcd (found) for $C_{30}H_{66}B_8Si_4Er_2$ (**3**): C, 37.53 (37.65); H, 6.93 (6.75). IR (cm^{-1}, KBr pellet): 2950 (s, s), 2891 (s, m), 2587 (s, s), 2542 (s, s), 2362 (s, s), 2290 (s, w), 2259 (s, w), 2228 (s, w), 2091 (s, w), 1947 (s, w), 1531 (s, s), 1456 (s, m), 1398 (s, m), 1247 (s, vs), 1177 (s, m), 1125 (s, w), 1065 (s, w), 1023 (s, m), 929 (s, s), 832 (s, vs), 796 (s, s), 753 (s, s), 681 (s, s), 629 (s, s).

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(11) X-ray data for **2** ($C_{15}H_{33}B_4Si_2Tb$; fw 471.75; $P2_1/n$) and **3** ($C_{15}H_{33}B_4Si_2Er$; fw 474.04; $P\bar{1}$): data for **2** and **3** were collected at 208(2) K and 203(2) K, respectively, on a Bruker SMART CCD PLATFORM diffractometer with a = 15.686(4) and 8.410(2) Å, b = 8.425(2) and 11.442(3) Å, c = 16.778(4) and 14.145(4) Å, α = 90 and 73.225(4)°, β = 94.812(4) and 74.373(4)°, γ = 90 and 76.869°, V = 2209.5(9) and 1238.4(6) $Å^3$, Z = 4 and 2, D_{calcd} = 1.418 and 1.271 Mg/m^3, respectively. Of the 14 590 and 8425 reflections collected (2θ = 1.71−25° for **2** and 1.54−25° for **3**), 3850 and 4107 reflections, respectively, were independent. All reflections were corrected for Lorentz, polarization, and absorption effects (Sheldrick, G. M. SADABS, Program for Empirical Absorption Correction of Area Detector Data; University of Göttingen, Göttingen, Germany, 2003). The structures were solved by direct methods and refined by full-matrix least-squares techniques using SHELXTL (Sheldrick, G. M. SHELXTL, Version 5.1; Bruker Analytical X-ray Systems, Madison, WI, 1997). All non-H atoms were refined anisotropically. The final refinements converged at R1 = 0.0375 and 0.0660, wR2 = 0.0766 and 0.1818, and GOF = 1.335 and 1.348 for **2** and **3**, respectively.

(12) The uncertainties for average values of a parameter are the average deviations.

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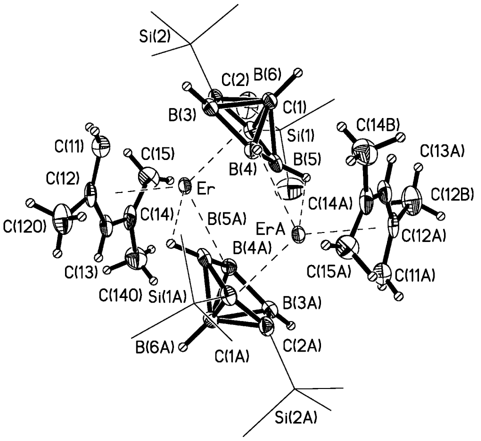

Figure 2. Perspective view of $[(\eta^5\text{-}2,4\text{-}(Me)_2C_5H_5)(\eta^5\text{-}2,3\text{-}(Me_3Si)_2\text{-}2,3\text{-}C_2B_4H_4)Er]_2$ (**3**) with thermal ellipsoids drawn at the 50% probability level. The exo-polyhedral $SiMe_3$ groups were drawn with thinner lines for clarity. Selected bond distances (Å): Er−(C_2B_3 centroid), 2.270; Er−C(1,2), 2.600(12), 2.625(13); Er−B(3,4,5), 2.650(14), 2.701(14), 2.631(13); Er−C(11,12,13,14,15), 2.617(14), 2.663(12), 2.609(13), 2.660(13), 2.607(13). A full listing of bond distances and angles along with the numbering scheme is given in the Supporting Information.

The synthesis outlined in Scheme 1 is based on the higher acidity of the bridged hydrogens in *nido*-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_6$ compared to the methylene hydrogens on the neutral pentadiene, 2,4-$(Me)_2C_5H_6$. The “diprotic” *nido*-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_6$ removes two $[2,4\text{-}(Me)_2C_5H_5]^-$ ligands by protonation on the tris(pentadienyl)lanthanide, leading to the products **2** and **3**. Since the metal plays somewhat of a passive role, it should be possible to expand the scope of these reactions to other metal−pentadienyl systems and *nido*-carboranes. Such studies are currently underway in our laboratories.

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Supporting Information Available: Tables of crystallographic data, including fractional coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom coordinates, and figures giving the structures of of **2** and **3**; crystallographic data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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