Organometallics **2002,** *21,* 5540−5548

Synthesis and Structural Characterization of Organolanthanide Complexes with 1,2-Dicarba-*closo*-dodecaborane-1,2-dichalcogenolate Ligands

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Received August 9, 2002

Reactions of anhydrous $LnCl_3$ (Ln = Nd, Gd, Dy, Er, Yb) with 2 equiv of LiCp′ in THF afford the lanthanocene complexes of $Cp'_2Ln(\mu\text{-}Cl)_2Li(THF)_2$ (Cp′ = η^5-t-BuC_5H_4, Ln = Nd (**1**), Gd (**2**), Dy (**3**), Er (**4**), Yb (**5**); Cp′ = 1,3-η^5-t-$Bu_2C_5H_3$, Ln = Nd (**6**), Gd (**7**), Dy (**8**), Er (**9**), Yb (**10**)). The molecular structures of **7** and **8** were characterized by X-ray crystallographic analysis. In these complexes, two Cp′ ring centroids and two μ-bridging chloride atoms around the lanthanide atoms form a distorted tetrahedron. The insertion of elemental chalcogen E (E = S, Se) into Li−C bonds of dilithium *o*-carborane in THF solution afforded dimers of dilithium dichalcogenolate carboranes, $[(THF)_3LiE_2C_2B_{10}H_{10}Li(THF)]_2$ (E = S (**12a**), Se (**12b**)), which were confirmed by a crystal structure analysis. Reactions of $Cp'_2Ln(\mu\text{-}Cl)_2Li(THF)_2$ (**1**−**10**) with **12a** or **12b** gave dinuclear complexes of the formula $[Li(THF)_4]_2[Cp'_2LnE_2C_2B_{10}H_{10}]_2$ (Cp′ = η^5-t-BuC_5H_4, E = S, Ln = Nd (**13a**), Gd (**14a**), Dy (**15a**), Er (**16a**), Yb (**17a**); E = Se, Ln = Nd (**13b**), Gd (**14b**), Dy (**15b**), Er (**16b**), Yb (**17b**); Cp′ = 1,3-η^5-t-$Bu_2C_5H_3$, E = S, Ln = Nd (**18a**), Gd (**19a**), Dy (**20a**), Er (**21a**), Yb (**22a**); E = Se, Ln = Nd (**18b**), Gd (**19b**), Dy (**20b**), Er (**21b**), Yb (**22b**)). According to the X-ray structure analyses, the dianions of **13a** and **13b** contain two *o*-carborane dichalcogenolate bridges, and each Cp'_2Ln fragment is attached to one terminal and two bridging chalcogen ligands. The central Ln_2E_2 four-membered ring is not planar, and the direct metal−metal interaction is absent.

Introduction

During the past decade considerable attention has been devoted to metal complexes with dichalcogenolate *o*-carboranyl ligands, to take the advantage of their unique molecular structure. To date, intensive studies on half-sandwich transition-metal complexes of Fe,[1] Ru,[1] Co,[2] Rh,[3,4] and Ir[2−6] containing chelating 1,2-dicarba-*closo*-dodecabarane-1,2-dichalcogenolate ligands have illustrated that these complexes serve as excellent precursors to study the insertion of alkynes into one of the metal−chalcogen bonds; this may lead to the formation of a metal-to-boron bond and/or substitution of the carborane cage in the position B(3)/B(6).[6−8] Although recently there have been some reports of organolanthanide complexes with carboranyl ligands and its derivatives,[9] comparable organolanthanide complexes with dichalcogenolate carboranyl ligands are so far unknown. This prompted us to investigate the syntheses of organolanthanide complexes with dichalcogenolate carboranyl ligands.

Since lanthanocene chlorides are important intermediates for the preparation of other organolanthanide compounds, such as hydride complexes and complexes containing chalcogen ligands,[10,11] lanthanocene chlorides have attracted a great deal of interest for several decades.[12,13] The use of the cyclopentadienyl ligand with one or two *tert*-butyl substituents is postulated to

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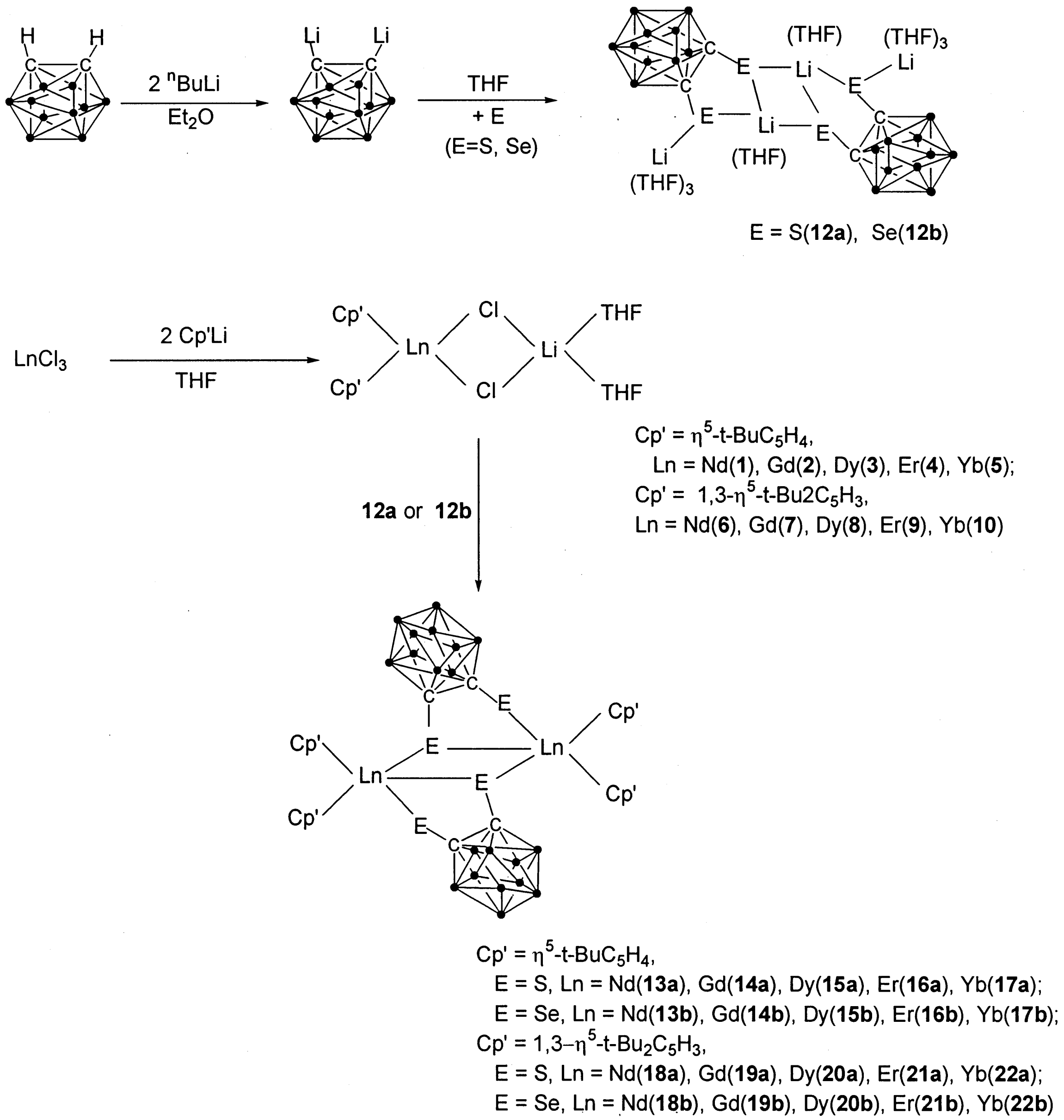
10.1021/om020647n CCC: $22.00

Scheme 1



generate a fairly considerable steric effect on the complex structures. In addition to the previously reported complexes,[14–16] here we have synthesized several other lanthanide chlorides of the formula $Cp'_2LnCl_2Li(THF)_2$ (Ln = Dy, Gd, Er, Yb, Nd), among which complexes of Gd and Dy were characterized crystallographically. Structural comparisons are made between the current and previous crystal work to describe the influence of the size of the lanthanide atom. Using the above lanthanocene complexes, further reactions were carried out to give the first example of dinuclear sandwich lanthanide complexes containing dichalcogenolate carboranyl ligands (Scheme 1). Among these dinuclear neodymium complexes **13a** and **13b** were crystallographically studied.

Experimental Section

General Considerations. All the reactions and the manipulations were routinely carried out under a pure argon atmosphere using the standard Schlenk technique. The use of dry and oxygen-free solvents is necessary. All organic solvents were distilled from sodium/benzophenone prior to use. Anhydrous lanthanide chlorides were obtained by heating the hydrated salt with NH_4Cl.[17] $Li(t\text{-}BuC_5H_4)$ and $Li(t\text{-}Bu_2C_5H_3)$ were prepared by the reactions of n-BuLi with *tert*-butylcyclopentadiene and 1,3-di-*tert*-butylcyclopentadiene, respectively, according to the procedures described in the literature.[18] Infrared spectra were measured on a Bio-Rad FTS135 spectrometer as KBr pellets. Elemental analyses were carried out at the Analytic Center of the Changchun Institute of Applied Chemistry.

Preparation of $(\eta^5\text{-t-BuC}_5H_4)_2Nd(\mu\text{-Cl})_2Li(THF)_2$ (1). A solution of $Li(t\text{-}BuC_5H_4)$ (0.24 M, 36.73 mL, 9.00 mmol) in THF was added dropwise to a solution of anhydrous $NdCl_3$ (1.13 g, 4.50 mmol) in 20 mL of THF at room temperature. The

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suspension was kept at 60 °C and stirred for 2 days. After the white precipitate was removed by centrifugation, the clear solution was evaporated under vacuum. Recrystallization from THF/hexane at −15 °C afforded light blue crystals of **1**. Yield: 1.89 g (68.8%). Anal. Calcd for $C_{26}H_{42}Cl_2LiO_2Nd$: C, 51.31; H, 6.95; Nd, 23.70; Cl, 11.65. Found: C, 51.25; H, 6.67; Nd, 23.47; Cl, 11.48; IR (KBr, cm^{-1}): 3054 w, 2954 s, 2902 m, 2865 w, 1462 m, 1390 m, 1363 m, 1295 w, 1251 m, 1228 w, 1202 m, 1165 m, 1045 s, 928 w, 896 m, 807 s, 754 m, 681 m, 665 m, 480 w.

Preparation of (η^5-t-BuC$_5$H$_4$)$_2$Gd(μ-Cl)$_2$Li(THF)$_2$ (2). Complex **2** was obtained as a light yellow precipitate from the reaction of anhydrous $GdCl_3$ (1.11 g, 4.21 mmol) in 20 mL of THF with Li(t-BuC$_5$H$_4$) (0.24 M, 34.37 mL, 8.42 mmol) in THF by the procedure described above. Yield: 1.54 g (58.8%). Anal. Calcd for $C_{26}H_{42}Cl_2LiO_2Gd$: C, 50.23; H, 6.81; Gd, 25.29; Cl, 11.41. Found: C, 50.49; H, 6.62; Gd, 24.86; Cl, 11.75; IR (KBr, cm^{-1}): 3056 w, 2960 s, 2902 m, 2869 w, 1462 m, 1390 w, 1363 m, 1295 w, 1251 m, 1228 w, 1202 m, 1165 m, 1045 s, 928 w, 896 m, 807 s, 754 m, 681 m, 665 m, 480 w.

Preparation of (η^5-t-BuC$_5$H$_4$)$_2$Dy(μ-Cl)$_2$Li(THF)$_2$ (3). Complex **3** was obtained as light yellow crystals from the reaction of anhydrous $DyCl_3$ (0.67 g, 2.50 mmol) in 20 mL of THF with Li(t-BuC$_5$H$_4$) (0.24 M, 20.40 mL, 5.00 mmol) in THF by the procedure described above. Yield: 0.86 g (55.1%). Anal. Calcd for $C_{26}H_{42}Cl_2LiO_2Dy$: C, 49.81; H, 6.75; Dy, 25.92; Cl, 11.31. Found: C, 49.75; H, 6.93; Dy, 25.28; Cl, 11.66. IR (KBr, cm^{-1}): 3056 w, 2960 s, 2902 m, 2869 w, 1462 m, 1390 w, 1363 m, 1295 w, 1251 m, 1228 w, 1202 m, 1165 m, 1045 s, 928 w, 896 m, 807 s, 754 m, 681 m, 665 m, 480 w.

Preparation of (η^5-t-BuC$_5$H$_4$)$_2$Er(μ-Cl)$_2$Li(THF)$_2$ (4). Complex **4** was obtained as a red precipitate from the reaction of anhydrous $ErCl_3$ (0.61 g, 2.23 mmol) in 20 mL of THF with Li(t-BuC$_5$H$_4$) (0.24 M, 18.20 mL, 4.46 mmol) in THF by the procedure described above. Yield: 0.89 g (63.2%). Anal. Calcd for $C_{26}H_{42}Cl_2LiO_2Er$: C, 49.44; H, 6.70; Er, 26.48; Cl, 11.22. Found: C, 49.87; H, 6.93; Er, 26.54; Cl, 11.81; IR (KBr, cm^{-1}): 3056 w, 2960 s, 2902 m, 2869 w, 1462 m, 1390 w, 1363 m, 1295 w, 1251 m, 1228 w, 1202 m, 1165 m, 1045 s, 928 w, 896 m, 807 s, 754 m, 681 m, 665 m, 480 w.

Preparation of (η^5-t-BuC$_5$H$_4$)$_2$Yb(μ-Cl)$_2$Li(THF)$_2$ (5). Complex **5** was obtained as a red precipitate from the reaction of anhydrous $YbCl_3$ (0.42 g, 1.50 mmol) in 20 mL of THF with Li(t-BuC$_5$H$_4$) (0.24 M, 12.24 mL, 3.00 mmol) in THF by the procedure described above. Yield: 0.63 g (65.9%). Anal. Calcd for $C_{26}H_{42}Cl_2LiO_2Yb$: C, 48.99; H, 6.64; Yb, 27.14; Cl, 11.12. Found: C, 48.33; H, 7.05; Yb, 26.68; Cl, 10.82; IR (KBr, cm^{-1}): 3056 w, 2960 s, 2902 m, 2869 w, 1462 m, 1390 w, 1363 m, 1295 w, 1251 m, 1228 w, 1202 m, 1165 m, 1045 s, 928 w, 896 m, 807 s, 754 m, 681 m, 665 m, 480 w.

Preparation of (η^5-t-Bu$_2$C$_5$H$_3$)$_2$Nd(μ-Cl)$_2$Li(THF)$_2$ (6). Complex **6** was obtained as light blue crystals from the reaction of anhydrous $NdCl_3$ (0.61 g, 2.45 mmol) in 20 mL of THF with Li(t-Bu$_2$C$_5$H$_3$) (0.38 M, 12.75 mL, 4.90 mmol) in THF in a manner similar to that for **1**. Yield: 1.12 g (63.9%). Anal. Calcd for $C_{34}H_{58}Cl_2LiO_2Nd$: C, 56.65; H, 8.11; Nd, 20.01; Cl, 9.84. Found: C, 56.76; H, 7.99; Nd, 19.98; Cl, 9.88; IR (KBr, cm^{-1}): 3056 w, 2960 s, 2902 m, 2869 w, 1462 m, 1390 w, 1363 m, 1295 w, 1251 m, 1228 w, 1202 m, 1165 m, 1045 s, 928 w, 896 m, 807 s, 754 m, 681 m, 665 m, 480w.

Preparation of (η^5-t-Bu$_2$C$_5$H$_3$)$_2$Gd(μ-Cl)$_2$Li(THF)$_2$ (7). Complex **7** was obtained as light yellow crystals from the reaction of anhydrous $GdCl_3$ (0.88 g, 3.34 mmol) in 20 mL of THF with Li(t-Bu$_2$C$_5$H$_3$) (0.38 M, 17.38 mL, 6.68 mmol) in THF in a manner similar to that for **1**. Yield: 1.75 g (71.4%). Anal. Calcd for $C_{34}H_{58}Cl_2LiO_2Gd$: C, 55.65; H, 7.97; Gd, 21.43; Cl, 9.66. Found: C, 55.12; H, 7.48; Gd, 21.15; Cl, 9.46; IR (KBr, cm^{-1}): 3056 w, 2960 s, 2902 m, 2869 w, 1462 m, 1390 w, 1363 m, 1295 w, 1251 m, 1228 w, 1202 m, 1165 m, 1045 s, 928 w, 896 m, 807 s, 754 m, 681 m, 665 m, 480 w.

Preparation of (η^5-t-Bu$_2$C$_5$H$_3$)$_2$Dy(μ-Cl)$_2$Li(THF)$_2$ (8). Complex **8** was obtained as light yellow crystals from the reaction of anhydrous $DyCl_3$ (0.64 g, 2.38 mmol) in 20 mL of THF with Li(t-Bu$_2$C$_5$H$_3$) (0.38 M, 12.53 mL, 4.82 mmol) in THF in a manner similar to that for **1**. Yield: 1.09 g (62.0%). Anal. Calcd for $C_{34}H_{58}Cl_2LiO_2Dy$: C, 55.25; H, 7.91; Dy, 21.99; Cl, 9.59. Found: C, 55.90; H, 8.52; Dy, 21.65; Cl, 9.25. IR (KBr, cm^{-1}): 3056 w, 2960 s, 2902 m, 2869 w, 1462 m, 1390 w, 1363 m, 1295 w, 1251 m, 1228 w, 1202 m, 1165 m, 1045 s, 928 w, 896 m, 807 s, 754 m, 681 m, 665 m, 480 w.

Preparation of (η^5-t-Bu$_2$C$_5$H$_3$)$_2$Er(μ-Cl)$_2$Li(THF)$_2$ (9). Complex **9** was obtained as a red precipitate from the reaction of anhydrous $ErCl_3$ (0.93 g, 3.40 mmol) in 20 mL of THF with Li(t-Bu$_2$C$_5$H$_3$) (0.38 M, 17.70 mL, 6.80 mmol) in THF in a manner similar to that for **1**. Yield: 1.48 g (58.5%). Anal. Calcd for $C_{34}H_{58}Cl_2LiO_2Er$: C, 54.90; H, 7.86; Er, 22.48; Cl, 9.53. Found: C, 55.23; H, 7.94; Er, 22.27; Cl, 9.43. IR (KBr, cm^{-1}): 3056 w, 2960 s, 2902 m, 2869 w, 1462 m, 1390 w, 1363 m, 1295 w, 1251 m, 1228 w, 1202 m, 1165 m, 1045 s, 928 w, 896 m, 807 s, 754 m, 681 m, 665 m, 480 w.

Preparation of (η^5-t-Bu$_2$C$_5$H$_3$)$_2$Yb(μ-Cl)$_2$Li(THF)$_2$ (10). Complex **10** was obtained as a red precipitate from the reaction of anhydrous $YbCl_3$ (0.95 g, 3.40 mmol) in 20 mL of THF with Li(t-Bu$_2$C$_5$H$_3$) (0.38 M, 17.70 mL, 6.80 mmol) in THF by the procedure described above. Yield: 1.33 g (52.2%). Anal. Calcd for $C_{34}H_{58}Cl_2LiO_2Yb$: C, 54.47; H, 7.80; Yb, 23.08; Cl, 9.46. Found: C, 54.88; H, 7.61; Yb, 22.93; Cl, 9.26. IR (KBr, cm^{-1}): 3056 w, 2960 s, 2902 m, 2869 w, 1462 m, 1390 w, 1363 m, 1295 w, 1251 m, 1228 w, 1202 m, 1165 m, 1045 s, 928 w, 896 m, 807 s, 754 m, 681 m, 665 m, 480 w.

Preparation of [(THF)$_3$LiS$_2$C$_2$B$_{10}$H$_{10}$Li(THF)]$_2$ (12a). Elemental sulfur (0.032 g, 1.00 mmol) was added to a solution of $Li_2C_2B_{10}H_{10}$[5] (0.077 g, 0.49 mmol) in THF/Et$_2$O (1:1). The reaction mixture was stirred at room temperature for 2 h and evaporated under vacuum. The residue was crystallized from THF/hexane at −15 °C gave light yellow crystals (0.227 g, 91.1%). Anal. Calcd for $C_{36}H_{84}B_{20}Li_4O_8S_4$: C, 42.51; H, 8.32. Found: C, 42.29; H, 8.53. IR (KBr, cm^{-1}): 3335 w, 2980 s, 2879 s, 2572 s, 2170 w, 1633 m, 1461 m, 1384 w, 1261 w, 1178 w, 1045 s, 1010 m, 969 m, 918 m, 890 s, 801 w, 726 m, 673 m, 412 m.

Preparation of [(THF)$_3$LiSe$_2$C$_2$B$_{10}$H$_{10}$Li(THF)]$_2$ (12b). An analogous method was used to prepare for **12b** from selenium (0.079 g, 1.00 mmol) and $Li_2C_2B_{10}H_{10}$[5] (0.077 g, 0.49 mmol) in THF/Et$_2$O (1:1). **12b** was obtained as colorless crystals (0.235 g, 90.7%). Anal. Calcd for $C_{36}H_{84}B_{20}Li_4O_8Se_4$: C, 35.89; H, 7.03. Found: C, 35.85; H, 7.09. IR (KBr, cm^{-1}): 3335 w, 2980 s, 2879 s, 2571 s, 2170 w, 1633 m, 1461 m, 1384 w, 1261 w, 1178 w, 1045 s, 1010 m, 969 m, 918 m, 890 s, 801 w, 726 m, 673 m, 412 m.

Preparation of [Li(THF)$_4$]$_2$[(η^5-t-BuC$_5$H$_4$)$_2$NdS$_2$C$_2$B$_{10}$H$_{10}$]$_2$ (13a). Complex **13a** was prepared as blue crystals from **1** (0.304 g, 0.50 mmol) and **12a** (0.254 g, 0.25 mmol) in 20 mL of THF. The mixture was stirred for 24 h. After the removal of solvent under vacuum, the residue was extracted with toluene and then the white precipitate was removed by centrifugation. Removal of the solvent gave a blue solid, which was dissolved in THF. Hexane was slowly added above the clear solution, and light blue crystals were obtained over several days. Yield: 0.345 g (77.6%). Anal. Calcd for $C_{72}H_{136}B_{20}Li_2Nd_2O_8S_4$: C, 48.68; H, 7.72; Nd, 16.24. Found: C, 48.91; H, 7.32; Nd, 16.27. IR (KBr, cm^{-1}): 3313 w, 2954 s, 2881 s, 2580 s, 2556 s, 2170 w, 1635 w, 1483 w, 1458 s, 1384 w, 1360 s, 1277 w, 1202 w, 1187 w, 1156 w, 1043 s, 917 s, 887 s, 834 s, 765 s, 755 s, 727 m, 677 m, 415 w.

Preparation of [Li(THF)$_4$]$_2$[(η^5-t-BuC$_5$H$_4$)$_2$NdSe$_2$C$_2$B$_{10}$H$_{10}$]$_2$ (13b). Complex **13b** was prepared as blue crystals from **1** (0.304 g, 0.50 mmol) and **12b** (0.301 g, 0.25 mmol) in 20 mL of THF by using procedures similar to those used in the synthesis of **13a**. Yield: 0.348 g (70.9%). Anal. Calcd for $C_{72}H_{136}B_{20}Li_2Nd_2O_8Se_4$: C, 44.03; H, 6.98; Nd, 14.69. Found:

C, 43.67; H, 7.26; Nd, 14.57. IR (KBr, cm^{-1}): 3479 w, 2958 s, 2879 s, 2565 s, 2170 w, 1633 w, 1483 m, 1459 s, 1447 m, 1382 w, 1357 s, 1294 w, 1277 m, 1261 m, 1201 m, 1187 m, 1156 m, 1042 s, 916 s, 887 s, 828 s, 757 s, 725 m, 676 m, 577 w.

Preparation of $[Li(THF)_4]_2[(\eta^5$-t-BuC$_5H_4)_2GdS_2C_2B_{10}H_{10}]_2$ (14a). Complex **14a** was prepared as a light yellow precipitate from **2** (0.31 g, 0.50 mmol) and **12a** (0.25 g, 0.25 mmol) in 20 mL of THF by using procedures similar to those used in the synthesis of **13a**. Yield: 0.23 g (51.0%). Anal. Calcd for $C_{72}H_{136}B_{20}Li_2Gd_2O_8S_4$: C, 47.97; H, 7.60; Gd, 17.45. Found: C, 47.28; H, 7.83; Gd, 17.63. IR (KBr, cm^{-1}): 3479 w, 2958 s, 2879 s, 2565 s, 2170 w, 1633 w, 1483 m, 1459 s, 1447 m, 1382 w, 1357 s, 1294 w, 1277 m, 1261 m, 1201 m, 1187 m, 1156 m, 1042 s, 916 s, 887 s, 828 s, 757 s, 725 m, 676 m, 577 w.

Preparation of $[Li(THF)_4]_2[(\eta^5$-t-BuC$_5H_4)_2GdSe_2C_2B_{10}H_{10}]_2$ (14b). Complex **14b** was prepared as a light yellow precipitate from **2** (0.31 g, 0.50 mmol) and **12b** (0.30 g, 0.25 mmol) in 20 mL of THF by using procedures similar to those used in the synthesis of **13a**. Yield: 0.19 g (38.2%). Anal. Calcd for $C_{72}H_{136}B_{20}Li_2Gd_2O_8Se_4$: C, 43.45; H, 6.89; Gd, 15.80. Found: C, 43.95; H, 7.17; Gd, 16.17. IR (KBr, cm^{-1}): 3479 w, 2958 s, 2879 s, 2565 s, 2170 w, 1633 w, 1483 m, 1459 s, 1447 m, 1382 w, 1357 s, 1294 w, 1277 m, 1261 m, 1201 m, 1187 m, 1156 m, 1042 s, 916 s, 887 s, 828 s, 757 s, 725 m, 676 m, 577w.

Preparation of $[Li(THF)_4]_2[(\eta^5$-t-BuC$_5H_4)_2DyS_2C_2B_{10}H_{10}]_2$ (15a). Complex **15a** was prepared as a light yellow solid from **3** (0.31 g, 0.50 mmol) and **12a** (0.25 g, 0.25 mmol) in 20 mL of THF by using procedures similar to those used in the synthesis of **13a**. Yield: 0.22 g (48.5%). Anal. Calcd for $C_{72}H_{136}B_{20}Li_2Dy_2O_8S_4$: C, 47.70; H, 7.56; Dy, 17.92. Found: C, 47.15; H, 7.88; Dy, 17.46. IR (KBr, cm^{-1}): 3479 w, 2958 s, 2879 s, 2565 s, 2170 w, 1633 w, 1483 m, 1459 s, 1447 m, 1382 w, 1357 s, 1294 w, 1277 m, 1261 m, 1201 m, 1187 m, 1156 m, 1042 s, 916 s, 887 s, 828 s, 757 s, 725 m, 676 m, 577 w.

Preparation of $[Li(THF)_4]_2[(\eta^5$-t-BuC$_5H_4)_2DySe_2C_2B_{10}H_{10}]_2$ (15b). Complex **15b** was prepared as a light yellow precipitate from **3** (0.31 g, 0.50 mmol) and **12b** (0.30 g, 0.25 mmol) in 20 mL of THF by using procedures similar to those used in the synthesis of **13a**. Yield: 0.26 g (52.0%). Anal. Calcd for $C_{72}H_{136}B_{20}Li_2Dy_2O_8Se_4$: C, 43.22; H, 6.85; Dy, 16.24. Found: C, 43.71; H, 7.22; Dy, 15.88. IR (KBr, cm^{-1}): 3479 w, 2958 s, 2879 s, 2565 s, 2170 w, 1633 w, 1483 m, 1459 s, 1447 m, 1382 w, 1357 s, 1294 w, 1277 m, 1261 m, 1201 m, 1187 m, 1156 m, 1042 s, 916 s, 887 s, 828 s, 757 s, 725 m, 676 m, 577 w.

Preparation of $[Li(THF)_4]_2[(\eta^5$-t-BuC$_5H_4)_2ErS_2C_2B_{10}H_{10}]_2$ (16a). Complex **16a** was prepared as a red precipitate from **4** (0.32 g, 0.50 mmol) and **12a** (0.25 g, 0.25 mmol) in 20 mL of THF by using procedures similar to those used in the synthesis of **13a**. Yield: 0.21 g (46.1%). Anal. Calcd for $C_{72}H_{136}B_{20}Li_2Er_2O_8S_4$: C, 47.45; H, 7.52; Er, 18.35. Found: C, 47.89; H, 7.86; Er, 18.91. IR (KBr, cm^{-1}): 3479 w, 2958 s, 2879 s, 2565 s, 2170 w, 1633 w, 1483 m, 1459 s, 1447 m, 1382 w, 1357 s, 1294 w, 1277 m, 1261 m, 1201 m, 1187 m, 1156 m, 1042 s, 916 s, 887 s, 828 s, 757 s, 725 m, 676 m, 577 w.

Preparation of $[Li(THF)_4]_2[(\eta^5$-t-BuC$_5H_4)_2ErSe_2C_2B_{10}H_{10}]_2$ (16b). Complex **16b** was prepared as a red precipitate from **4** (0.32 g, 0.50 mmol) and **12b** (0.30 g, 0.25 mmol) in 20 mL of THF by using procedures similar to those used in the synthesis of **13a**. Yield: 0.26 g (51.7%). Anal. Calcd for $C_{72}H_{136}B_{20}Li_2Er_2O_8Se_4$: C, 43.02; H, 6.82; Er, 16.64. Found: C, 43.77; H, 7.11; Er, 16.79. IR (KBr, cm^{-1}): 3479 w, 2958 s, 2879 s, 2565 s, 2170 w, 1633 w, 1483 m, 1459 s, 1447 m, 1382 w, 1357 s, 1294 w, 1277 m, 1261 m, 1201 m, 1187 m, 1156 m, 1042 s, 916 s, 887 s, 828 s, 757 s, 725 m, 676 m, 577 w.

Preparation of $[Li(THF)_4]_2[(\eta^5$-t-BuC$_5H_4)_2YbS_2C_2B_{10}H_{10}]_2$ (17a). Complex **17a** was prepared as a red precipitate from **5** (0.32 g, 0.50 mmol) and **12a** (0.25 g, 0.25 mmol) in 20 mL of THF by using procedures similar to those used in the synthesis of **13a**. Yield: 0.28 g (61.1%). Anal. Calcd for $C_{72}H_{136}B_{20}Li_2Yb_2O_8S_4$: C, 47.15; H, 7.47; Yb, 18.87. Found: C, 47.60; H, 7.84; Yb, 18.56. IR (KBr, cm^{-1}): 3479 w, 2958 s, 2879 s, 2565 s, 2170 w, 1633 w, 1483 m, 1459 s, 1447 m, 1382 w, 1357 s, 1294 w, 1277 m, 1261 m, 1201 m, 1187 m, 1156 m, 1042 s, 916 s, 887 s, 828 s, 757 s, 725 m, 676 m, 577 w.

Preparation of $[Li(THF)_4]_2[(\eta^5$-t-BuC$_5H_4)_2YbSe_2C_2B_{10}H_{10}]_2$ (17b). Complex **17b** was prepared as a red precipitate from **5** (0.32 g, 0.50 mmol) and **12b** (0.30 g, 0.25 mmol) in 20 mL of THF by using procedures similar to those used in the synthesis of **13a**. Yield: 0.31 g (61.3%). Anal. Calcd for $C_{72}H_{136}B_{20}Li_2Yb_2O_8Se_4$: C, 42.77; H, 6.78; Yb, 17.12. Found: C, 42.13; H, 6.64; Yb, 17.51. IR (KBr, cm^{-1}): 3479 w, 2958 s, 2879 s, 2565 s, 2170 w, 1633 w, 1483 m, 1459 s, 1447 m, 1382 w, 1357 s, 1294 w, 1277 m, 1261 m, 1201 m, 1187 m, 1156 m, 1042 s, 916 s, 887 s, 828 s, 757 s, 725 m, 676 m, 577 w.

Preparation of $[Li(THF)_4]_2[(\eta^5$-t-Bu$_2C_5H_3)_2NdS_2C_2B_{10}H_{10}]_2$ (18a). Complex **18a** was prepared as a blue precipitate from **6** (0.36 g, 0.50 mmol) and **12a** (0.25 g, 0.25 mmol) in 20 mL of THF by using procedures similar to those used in the synthesis of **13a**. Yield: 0.26 g (52.0%). Anal. Calcd for $C_{88}H_{168}B_{20}Li_2Nd_2O_8S_4$: C, 52.83; H, 8.46; Nd, 14.42. Found: C, 52.12; H, 8.08; Nd, 14.59. IR (KBr, cm^{-1}): 3475 w, 2954 s, 2879 s, 2565 s, 2170 w, 1633 w, 1483 m, 1459 s, 1447 m, 1382 w, 1357 s, 1294 w, 1277 m, 1261 m, 1201 m, 1184 m, 1156 m, 1042 s, 916 s, 887 s, 828 s, 757 s, 725 m, 676 m, 577 w.

Preparation of $[Li(THF)_4]_2[(\eta^5$-t-Bu$_2C_5H_3)_2NdSe_2C_2B_{10}H_{10}]_2$ (18b). Complex **18b** was prepared as a blue solid from **6** (0.36 g, 0.50 mmol) and **12b** (0.30 g, 0.25 mmol) in 20 mL of THF by using procedures similar to those used in the synthesis of **13a**. Yield: 0.35 g (64.0%). Anal. Calcd for $C_{88}H_{168}B_{20}Li_2Nd_2O_8Se_4$: C, 48.29; H, 7.74; Nd, 13.18. Found: C, 48.76; H, 7.94; Nd, 13.46. IR (KBr, cm^{-1}): 3479 w, 2958 s, 2879 s, 2565 s, 2170 w, 1633 w, 1483 m, 1459 s, 1447 m, 1382 w, 1357 s, 1294 w, 1277 m, 1261 m, 1201 m, 1187 m, 1156 m, 1042 s, 916 s, 887 s, 828 s, 757 s, 725 m, 676 m, 577 w.

Preparation of $[Li(THF)_4]_2[(\eta^5$-t-Bu$_2C_5H_3)_2GdS_2C_2B_{10}H_{10}]_2$ (19a). Complex **19a** was prepared as a light yellow precipitate from **7** (0.37 g, 0.50 mmol) and **12a** (0.25 g, 0.25 mmol) in 20 mL of THF by using procedures similar to those used in the synthesis of **13a**. Yield: 0.33 g (65.1%). Anal. Calcd for $C_{88}H_{168}B_{20}Li_2Gd_2O_8S_4$: C, 52.14; H, 8.35; Gd, 15.52. Found: C, 52.14; H, 7.96; Gd, 15.49. IR (KBr, cm^{-1}): 3479 w, 2958 s, 2879 s, 2565 s, 2170 w, 1633 w, 1483 m, 1459 s, 1447 m, 1382 w, 1357 s, 1294 w, 1277 m, 1261 m, 1201 m, 1187 m, 1156 m, 1042 s, 916 s, 887 s, 828 s, 757 s, 725 m, 676 m, 577 w.

Preparation of $[Li(THF)_4]_2[(\eta^5$-t-Bu$_2C_5H_3)_2GdSe_2C_2B_{10}H_{10}]_2$ (19b). Complex **19b** was prepared as a light yellow precipitate from **7** (0.37 g, 0.50 mmol) and **12b** (0.30 g, 0.25 mmol) in 20 mL of THF by using procedures similar to those used in the synthesis of **13a**. Yield: 0.33 g (59.6%). Anal. Calcd for $C_{88}H_{168}B_{20}Li_2Gd_2O_8Se_4$: C, 47.73; H, 7.65; Gd, 14.20. Found: C, 47.35; H, 7.84; Gd, 14.56. IR (KBr, cm^{-1}): 3479 w, 2958 s, 2879 s, 2565 s, 2170 w, 1633 w, 1483 m, 1459 s, 1447 m, 1382 w, 1357 s, 1294 w, 1277 m, 1261 m, 1201 m, 1187 m, 1156 m, 1042 s, 916 s, 887 s, 828 s, 757 s, 725 m, 676 m, 577 w.

Preparation of $[Li(THF)_4]_2[(\eta^5$-t-Bu$_2C_5H_3)_2DyS_2C_2B_{10}H_{10}]_2$ (20a). Complex **20a** was prepared as a light yellow precipitate from **8** (0.37 g, 0.50 mmol) and **12a** (0.25 g, 0.25 mmol) in 20 mL of THF by using procedures similar to those used in the synthesis of **13a**. Yield: 0.28 g (55.0%). Anal. Calcd for $C_{88}H_{168}B_{20}Li_2Dy_2O_8S_4$: C, 51.87; H, 8.31; Dy, 15.95. Found: C, 51.85; H, 7.99; Dy, 16.19. IR (KBr, cm^{-1}): 3479 w, 2958 s, 2879 s, 2565 s, 2170 w, 1633 w, 1483 m, 1459 s, 1447 m, 1382 w, 1357 s, 1294 w, 1277 m, 1261 m, 1201 m, 1187 m, 1156 m, 1042 s, 916 s, 887 s, 828 s, 757 s, 725 m, 676 m, 577 w.

Preparation of $[Li(THF)_4]_2[(\eta^5$-t-Bu$_2C_5H_3)_2DySe_2C_2B_{10}H_{10}]_2$ (20b). Complex **20b** was prepared as a light yellow precipitate from **8** (0.37 g, 0.50 mmol) and **12b** (0.30 g, 0.25 mmol) in 20 mL of THF by using procedures similar to those used in the synthesis of **13a**. Yield: 0.33 g (59.3%). Anal. Calcd

Table 1. Crystallographic Data for Complexes 7, 8, 12a, 13a, and 13b

	7	**8**	**12a**	**13a**	**13b**
color	light yellow	light yellow	colorless	light blue	light blue
habit	block	block	block	block	block
formula	$C_{34}H_{58}Cl_2GdLiO_2$	$C_{34}H_{58}Cl_2DyLiO_2$	$C_{36}H_{84}B_{20}Li_4O_8S_4$	$C_{72}H_{136}B_{20}Li_2Nd_2O_8S_4$	$C_{72}H_{136}B_{20}Li_2Nd_2O_8Se_4$
fw	733.89	739.14	1017.23	1776.60	1964.20
cryst size, mm	0.50 × 0.38 × 0.24	0.52 × 0.42 × 0.36	0.42 × 0.38 × 0.32	0.60 × 0.55 × 0.40	0.52 × 0.26 × 0.12
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/c$
a, Å	10.618(2)	10.637(2)	9.972(3)	12.6923(17)	15.281(5)
b, Å	20.998(4)	21.010(4)	17.193(4)	26.499(4)	20.960(7)
c, Å	17.092(3)	17.065(3)	18.318(5)	14.0837(19)	15.872(7)
β, deg	93.89(3)	94.02(3)	104.24(2)	93.595(2)	110.32(3)
V, Å^3	3802.0(13)	3804.3(13)	3044.1(14)	4727.5(11)	4767(3)
Z	5	5	2	2	2
D_{calcd}, Mg/m^3	1.603	1.613	1.110	1.248	1.368
θ range, deg	1.54−23.05	1.54−25.01	1.65−26.02	2.10−26.01	1.68−25.06
μ, mm^{-1}	2.387	2.662	0.197	1.220	2.649
no. of rflns collected	10 905	6401	7786	21 345	10 325
no. of indep rflns	4416 (R_{int} = 0.0606)	5265 (R_{int} = 0.0431)	5977 (R_{int} = 0.0197)	9280 (R_{int} = 0.0328)	8420 (R_{int} = 0.0319)
R ($I > 2\sigma(I)$)	0.0422	0.0705	0.0856	0.0565	0.0520
R_w ($I > 2\sigma(I)$)	0.0703	0.1552	0.1329	0.1199	0.0700
no. of params	361	362	305	527	493
GOF on F^2	0.795	0.817	1.050	1.178	0.781

for $C_{88}H_{168}B_{20}Li_2Dy_2O_8Se_4$: C, 47.50; H, 7.61; Dy, 14.61. Found: C, 47.97; H, 7.96; Dy, 14.96. IR (KBr, cm^{-1}): 3479 w, 2958 s, 2879 s, 2565 s, 2170 w, 1633 w, 1483 m, 1459 s, 1447 m, 1382 w, 1357 s, 1294 w, 1277 m, 1261 m, 1201 m, 1187 m, 1156 m, 1042 s, 916 s, 887 s, 828 s, 757 s, 725 m, 676 m, 577 w.

Preparation of [Li(THF)$_4$]$_2$[(η^5-t-Bu$_2$C$_5$H$_3$)$_2$ErS$_2$C$_2$B$_{10}$H$_{10}$]$_2$ (21a). Complex **21a** was prepared as a red precipitate from **9** (0.37 g, 0.50 mmol) and **12a** (0.25 g, 0.25 mmol) in 20 mL of THF by using procedures similar to those used in the synthesis of **13a**. Yield: 0.29 g (56.7%). Anal. Calcd for $C_{88}H_{168}B_{20}Li_2Er_2O_8S_4$: C, 51.63; H, 8.27; Er, 16.34. Found: C, 51.22; H, 8.69; Er, 16.59. IR (KBr, cm^{-1}): 3479 w, 2958 s, 2879 s, 2565 s, 2170 w, 1633 w, 1483 m, 1459 s, 1447 m, 1382 w, 1357 s, 1294 w, 1277 m, 1261 m, 1201 m, 1187 m, 1156 m, 1042 s, 916 s, 887 s, 828 s, 757 s, 725 m, 676 m, 577 w.

Preparation of [Li(THF)$_4$]$_2$[(η^5-t-Bu$_2$C$_5$H$_3$)$_2$ErSe$_2$C$_2$B$_{10}$H$_{10}$]$_2$ (21b). Complex **21b** was prepared as a red solid from **9** (0.37 g, 0.50 mmol) and **12b** (0.30 g, 0.25 mmol) in 20 mL of THF by using procedures similar to those used in the synthesis of **13a**. Yield: 0.31 g (55.5%). Anal. Calcd for $C_{88}H_{168}B_{20}Li_2Er_2O_8Se_4$: C, 47.30; H, 7.58; Er, 14.97. Found: C, 47.67; H, 7.88; Er, 14.66. IR (KBr, cm^{-1}): 3479 w, 2958 s, 2879 s, 2565 s, 2170 w, 1633 w, 1483 m, 1459 s, 1447 m, 1382 w, 1357 s, 1294 w, 1277 m, 1261 m, 1201 m, 1187 m, 1156 m, 1042 s, 916 s, 887 s, 828 s, 757 s, 725 m, 676 m, 577 w.

Preparation of [Li(THF)$_4$]$_2$[(η^5-t-Bu$_2$C$_5$H$_3$)$_2$YbS$_2$C$_2$B$_{10}$H$_{10}$]$_2$ (22a). Complex **22a** was prepared as red crystals from **10** (0.38 g, 0.50 mmol) and **12a** (0.25 g, 0.25 mmol) in 20 mL of THF by using procedures similar to those used in the synthesis of **13a**. Yield: 0.35 g (68.0%). Anal. Calcd for $C_{88}H_{168}B_{20}Li_2Yb_2O_8S_4$: C, 51.34; H, 8.23; Yb, 16.81. Found: C, 51.64; H, 7.89; Yb, 16.59. IR (KBr, cm^{-1}): 3479 w, 2958 s, 2879 s, 2565 s, 2170 w, 1633 w, 1483 m, 1459 s, 1447 m, 1382 w, 1357 s, 1294 w, 1277 m, 1261 m, 1201 m, 1187 m, 1156 m, 1042 s, 916 s, 887 s, 828 s, 757 s, 725 m, 676 m, 577 w.

Preparation of [Li(THF)$_4$]$_2$[(η^5-t-Bu$_2$C$_5$H$_3$)$_2$YbSe$_2$C$_2$B$_{10}$H$_{10}$]$_2$ (22b). Complex **22b** was prepared as a red solid from **10** (0.38 g, 0.50 mmol) and **12b** (0.30 g, 0.25 mmol) in 20 mL of THF by using procedures similar to those used in the synthesis of **13a**. Yield: 0.38 g (67.7%). Anal. Calcd for $C_{88}H_{168}B_{20}Li_2Yb_2O_8Se_4$: C, 47.06; H, 7.54; Yb, 15.41. Found: C, 47.52; H, 7.68; Yb, 15.48. IR (KBr, cm^{-1}): 3479 w, 2958 s, 2879 s, 2565 s, 2170 w, 1633 w, 1483 m, 1459 s, 1447 m, 1382 w, 1357 s, 1294 w, 1277 m, 1261 m, 1201 m, 1187 m, 1156 m, 1042 s, 916 s, 887 s, 828 s, 757 s, 725 m, 676 m, 577 w.

Structure Solution and Refinement for Complexes 7, 8, 12a, 13a, and 13b. For complexes **7, 8**, **12a,** and **13b**, a single crystal suitable for X-ray analysis was sealed into a glass capillary and mounted on a Siemens P4 diffractometer. The intensity data of the single crystal for complex **13a** were collected on the CCD-Bruker Smart APEX system. All the determinations of unit cell and intensity data were performed with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). All the data were collected at room temperature using the ω scan technique. These structures were solved by direct methods, using Fourier techniques, and refined on F^2 by a full-matrix least-squares method. All the non-hydrogen atoms were refined anisotropically, except for the atoms C(3), C(4), C(16), and C(17) in **12a.** All the hydrogen atoms were included but not refined. All the calculations were carried out with the Siemens SHELXTL PLUS program. Crystallographic data are summarized in Table 1.

Results and Discussion

Lanthanocene Chlorides. The reactions of lanthanide chlorides with lithium salts of alkyl-substituted cyclopentadienides are known to form bimetallic chloride complexes of the formula $Cp_2LnCl_2LiL_2$ or $Cp^*{}_2LnCl_2LiL_2$ (Cp = η^5-C_5H_5; Cp* = η^5-C_5Me_5; L = THF, TMEDA).[14−16,19] Usually the substituents on the cyclopentadienyl rings would make some difference and have more or less influence on their respective derivatives. The studies of unsolvated lanthanide hydrides and $Cp\hat{}_2LnCl_2Li(TMEDA)_2$ (Cpˆ = Cp, substituted Cp; TMEDA = tetramethylethylenediamine) with different Ln atoms have been reported.[10,19] However, only a few X-ray diffraction studies of $Cp\hat{}LnCl_2L_2$ (L = solvating ligand) with different Ln atoms are available for compounds with nonidentical cyclopentadienyl or solvating ligands.[20−23] Although many organolanthanide chlorides have been synthesized and structurally characterized,[12,13] crystal structures having 1,3-di-*tert*-butylcyclopentadienes are still few.[14−16]

Complexes **1−10** were obtained from the direct synthesis method, which is the most usual and effective way

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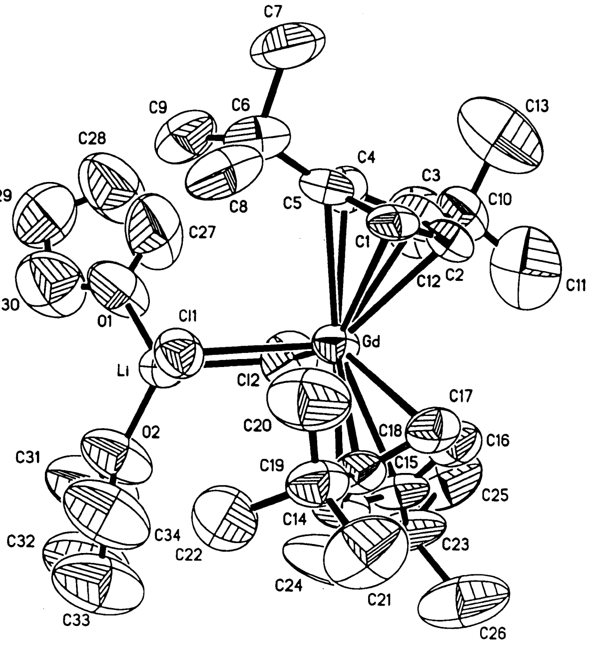

Figure 1. Molecular structure of the complex (η^5-1,3-^{t}Bu$_2$-C$_5$H$_3$)$_2$Gd(μ-Cl)$_2$Li(THF)$_2$ (**7**). Hydrogen atoms are omitted for clarity.

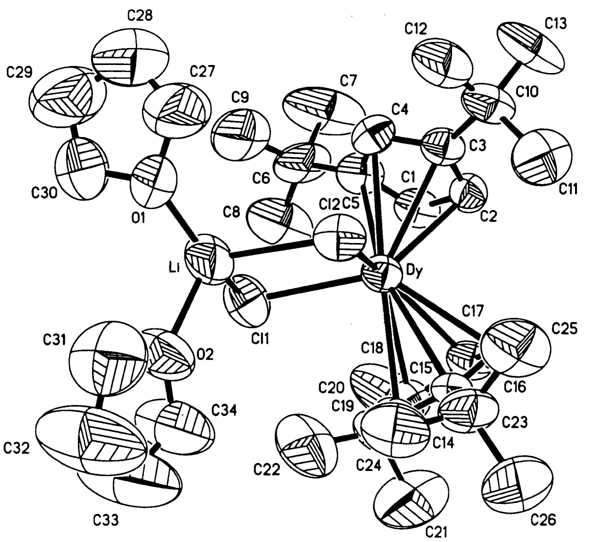

Figure 2. Molecular structure of the complex (η^5-1,3-^{t}Bu$_2$C$_5$H$_3$)$_2$Dy(μ-Cl)$_2$Li(THF)$_2$ (**8**). Hydrogen atoms are omitted for clarity.

to form organolanthanide complexes. The formulas of these complexes were confirmed by element analyses. As for their IR spectra, the absorption peaks at 3056, 2960, 1462, 1390, 1363, 1045, and 754 cm^{-1} were interpreted as the characteristic peaks of Cp′ ligands.

Figures 1 and 2 show the molecular structures of complexes **7** and **8**, respectively, together with the atomic labeling scheme. The structures of complexes **7** and **8** present analogous asymmetric dimers, consistent with reported organolanthanide chloride compounds with bulky cyclopentadienyl ligands.[19,24–25] In **7** and **8**, the lanthanide atom and the lithium atom are bridged by two chlorine atoms to form a slightly distorted square plane. The lanthanide atoms are coordinated with two Cp′ ring centroids and two μ-bridging chlorine atoms in a distorted-tetrahedral enviroment. In a similar manner, the lithium atom is bonded to two chlorine bridges and two oxygen atoms of THF.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complexes 7 and 8

	7	8		7	8
Ln−C(1)	2.653(11)	2.622(13)	Ln−C(14)	2.762(12)	2.745(13)
Ln−C(2)	2.648(10)	2.622(12)	Ln−C(15)	2.765(14)	2.754(12)
Ln−C(3)	2.731(13)	2.710(12)	Ln−C(16)	2.627(13)	2.645(11)
Ln−C(4)	2.741(11)	2.747(13)	Ln−C(17)	2.630(11)	2.634(14)
Ln−C(5)	2.768(14)	2.713(13)	Ln−C(18)	2.735(12)	2.722(12)
Ln−Cl(1)	2.682(3)	2.640(4)	Ln−Cl(2)	2.663(3)	2.652(3)
Li−Cl(1)	2.36(2)	2.34(3)	Li−Cl(2)	2.36(2)	2.41(3)
Li−O(1)	1.92(2)	1.82(3)	Li−O(2)	1.86(2)	2.02(3)
Cl(1)−Ln−Cl(2)	82.13(10)	82.20(12)	Cl(1)−Li−Cl(2)	96.1(7)	94.1(11)
O(1)−Li−O(2)	109.4(10)	111.4(16)	Li−Cl(1)−Ln	90.7(5)	92.6(7)
Li−Cl(2)−Ln	91.1(5)	90.8(8)			

Table 3. Principal Interatomic Distances (Å) in Complexes 7, 8, 11, and Other Analogous Complexes (Cp^{tt} = η^5-1,3-^{t}Bu$_2$C$_5$H$_3$)

Ln	complex	Ln−Cp^{tt}(I)	Ln−Cp^{tt}(II)	Ln−C$_{av}$	Ln−Cl$_{av}$	ref
Lu	Cp$^{tt}_2$Lu(μ-Cl)$_2$Li-(TMEDA)	2.34	2.34	2.64	2.60	24
Dy	**8**	2.42	2.41	2.691	2.646	*a*
Gd	**7**	2.43	2.42	2.706	2.673	*a*
Sm	**11**	2.46	2.45	2.732	2.848	16
Ce	[Cp$^{tt}_2$Ce(μ-Cl)$_2$]$_2$	2.52	2.52	2.79	2.868	27

[a] This paper.

Table 4. Characteristic Angles ω (deg) in Complexes 7, 8, and 11

	7	8	11
Cl(1)−Ln−Cl(2)	82.13(10)	82.20(12)	81.45(6)
Cl(1)−Li−Cl(2)	96.1(7)	94.1(11)	97.1(5)
Li−Cl(1)−Ln	90.7(5)	92.6(7)	89.8(4)
Li−Cl(2)−Ln	91.1(5)	90.8(8)	91.6(4)
O(1)−Li−O(2)	109.4(10)	111.4(16)	109.4(7)
Cp^{tt}(I)/Cp^{tt}(II)	118.4	60.4	62.7
LnCl$_2$Li/Cp^{tt}(I)	148.5	27.9	32.4
LnCl$_2$Li/Cp^{tt}(II)	30.3	32.6	30.4

Selected bond distances and bond angles for complexes **7** and **8** are listed in Table 2. The bond distances of Ln−C bond deviate from 2.622(12) to 2.754(12) Å for complex **7** and from 2.627(13) to 2.768(14) Å for complex **8**, due to the substituted bulky Cp′ ligand. The average distances of Ln−Cl, Li−Cl, and Li−O are compared to those found in other lanthanide complexes.[22−23,26]

We have reported one analogous chloride complex of samarium, (η^5-t-Bu$_2$C$_5$H$_3$)$_2$Sm(μ-Cl)$_2$Li(THF)$_2$ (**11**).[16] Tables 3 and 4 give structural comparisons of complexes **7**, **8**, **11**, and other analogous complexes (Cp^{tt} = η^5-1,3-t-Bu$_2$C$_5$H$_3$). The distances of Ln−C$_{av}$, Ln−Cl, and Ln−Cp′ increase with an increase in the metal atom size. Figure 3 shows the linear dependence of these distances on the ionic radius of the lanthanide metal, consistent with other reported lanthanide complexes.[10] The distances of each lanthanide to two Cp′ cycles slightly increase with no significant change, following the increase of the ionic radius of the lanthanide metal.

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(24) Bel'skii, V. K.; Knyazhanskii, S. Y.; Bulychev, B. M.; Soloveichik, G. L. *Organomet. Chem. USSR* **1989**, *2*, 388.

(25) Gun'ko, Y. K.; Bel'skii, V. K.; Sizov, A. I. *Organomet. Chem. USSR* **1990**, *3*, 202.

(26) Bel'skii, V. K.; Knyazhanskii, S. Ya; Bulychev, B. M.; Soloveichik, G. L. *Organomet. Chem. USSR* **1989**, *2*, 567.

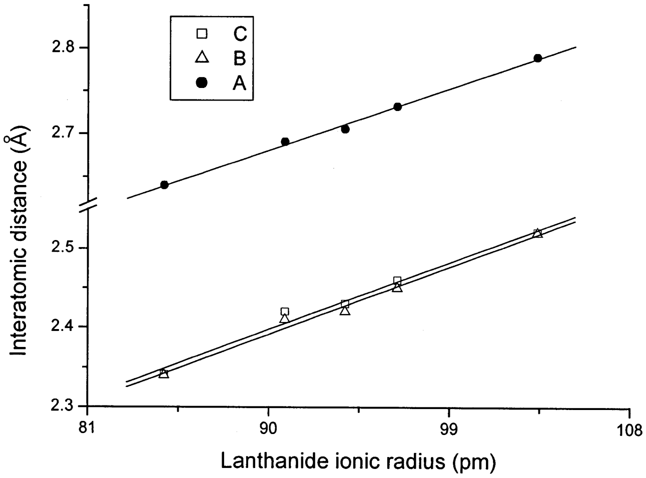
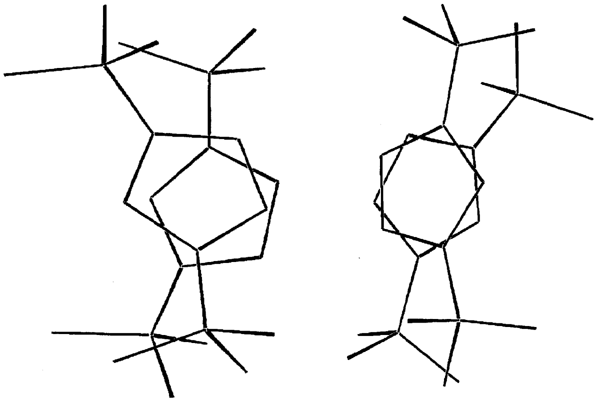


Figure 3. Plot of interatomic distances in **7**, **8**, **11**, and other previously reported complexes versus the lanthanide ionic radius (A) Ln−C$_{av}$; (B) Ln−Cp^{tt}(I); (C) Ln−Cp^{tt}(II).



(a) (b)

Figure 4. Conformation of Cp^{tt} rings in (a) complex **7** and (b) complex **8**.

However, among these complexes, the remarkably different dihedral angles between two Cp′ cycles should be noted. For complex **7**, the dihedral angle of 118.4° is significantly larger than the respective angles of 60.4 and 62.7° in complexes **8** and **11**. This can be attributed to an opposite direction of the departure of one Cp′ ligand from the gadolinium atom, compared to those of **8** and **11**. The differences in the above-mentioned angles are probably due to the characteristics of gadolinium with regard to its 4f^7 half-full electron orbital.

For both complexes **7** and **8**, the dihedral angles between the LnCl$_2$Li plane and either of the two Cp′ ligands are somewhat different, which indicates that the departure of one Cp′ ligand from the lanthanide metal is not the same as that for the other Cp′ ligand. Probably this is because of the different departure of the *tert*-butyl groups from each Cp′ ring plane, which is shown in the characteristic staggered conformation (Figure 4).[10,19,27]

Dichalcogenolate Carborane Salts. Insertion of elemental chalcogen into the Li−C bonds of dilithium carborane (Li$_2$C$_2$B$_{10}$H$_{10}$) in THF solution afforded dilithium dichalcogenolate carborane [(THF)$_3$LiS$_2$C$_2$B$_{10}$H$_{10}$-Li(THF)]$_2$ (**12a**) and [(THF)$_3$LiSe$_2$C$_2$B$_{10}$H$_{10}$Li(THF)]$_2$ (**12b**) as light yellow crystals in high yields. Both complexes **12a** and **12b** are dimers and soluble in polar organic solvents such as THF and toluene but insoluble in hexane. They can be used as chelate ligands to coordinate with transition and lanthanide metals. The IR spectra of compounds **12a** and **12b** show typical characteristic B−H absorptions of carborane at 2572 and 2571 cm^{-1}, respectively.

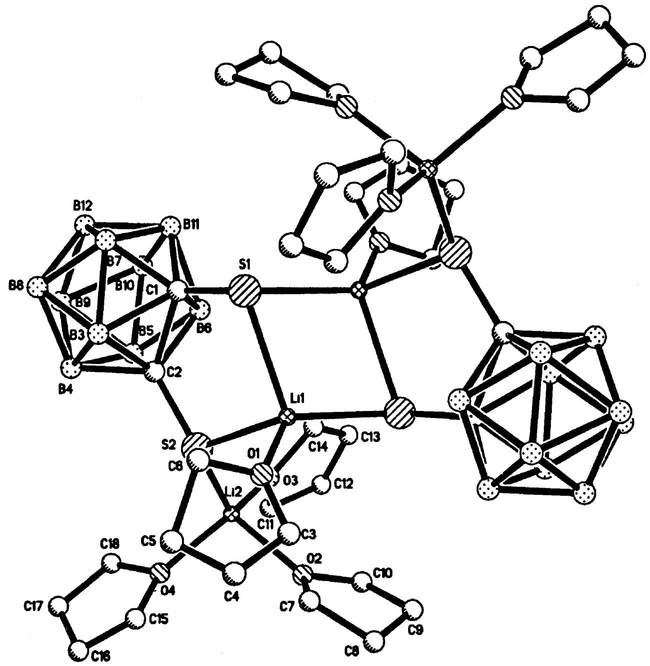


Figure 5. Molecular structure of the complex [(THF)$_3$-LiS$_2$C$_2$B$_{10}$H$_{10}$Li(THF)]$_2$ (**12a**). Hydrogen atoms are omitted for clarity.

The solid-state structure of compound **12a** was further confirmed by single-crystal X-ray analysis. This complex is composed of two [(THF)$_3$LiE$_2$C$_2$B$_{10}$H$_{10}$Li-(THF)] units with four THF molecules of solvation, the structure of which is exhibited in Figure 5. In each [(THF)$_3$LiE$_2$C$_2$B$_{10}$H$_{10}$Li(THF)] unit, one lithium atom is coordinated to two sulfur atoms of a 1,2-dithiocarboranyl ligand, one sulfur atom of another 1,2-dithiocarboranyl ligand, and the oxygen atom of a solvated THF ring in a distorted-tetragonal sphere, with the other lithium atom bonded to three solvated THF molecules and one sulfur atom of the 1,2-dithiocarboranyl ligand. In the molecular structure, each sulfur atom is bound to one carbon atom from the carboranyl ligand and two lithium atoms and is located in a trigonal arrangement. In the center part, two lithium atoms and two sulfur atoms form a distorted square plane. Selected bond distances and bond angles for complex **12a** are given in Table 5. The average S−C and S−Li distances are 1.764(3) and 2.454(6) Å, respectively. The distance between the Li(2) and Li(2′) atoms is 2.950(11) Å; this can be taken as an indication that direct lithium−lithium bonding interaction is absent. The average Li−O bond distance of 1.950(6) Å is close to those found in other compounds.[26]

Organolanthanide Compounds Derived from Dichalcogenolate Carboranyl Salts. The chlorine atoms in the lanthanocene chlorides can be easily replaced by dichalcogenolate carboranyl ligands via metathesis reactions. Reactions of Cp′$_2$Ln(μ-Cl)$_2$Li-(THF)$_2$ (Cp′ = η^5-t-BuC$_5$H$_4$, Ln = Nd (**1**), Gd (**2**), Dy (**3**),

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(27) Lobkovsky, E. B.; Gun'ko, Y. K.; Bulychev, B. M.; Belsky, V. K.; Soloveichik, G. L.; Antipin, M. Y. *J. Organomet. Chem.* **1991**, *406*, 343.

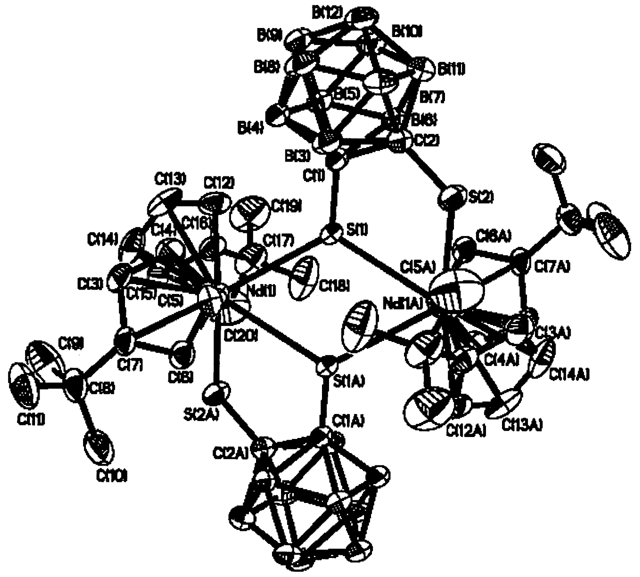

Figure 6. Anionic moiety of the complex $[Li(THF)_4]_2[(\eta^5\text{-}{}^tBuC_5H_4)_2NdS_2C_2B_{10}H_{10}]_2$ (**13a**). Hydrogen atoms are omitted for clarity.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for Complex 12a

S(1)−C(1)	1.772(6)	S(2)−C(2)	1.761(6)
S(1)−Li(1′)	2.435(12)	S(2)−Li(2)	2.421(15)
S(1)−Li(1)	2.480(10)	S(1′)−Li(1)	2.435(12)
Li(1)−O(1)	1.964(12)	Li(2)−O(2)	1.973(12)
Li(2)−O(3)	1.953(14)	Li(2)−O(4)	1.954(13)
C(1)−S(1)−Li(1′)	110.3(4)	C(1)−S(1)−Li(1)	106.5(3)
Li(1′)−S(1)−Li(1)	75.6(4)	C(2)−S(2)−Li(2)	114.8(4)
C(2)−S(2)−Li(1)	106.2(3)	Li(2)−S(2)−Li(1)	119.3(4)
S(1)−Li(1)−S(1′)	104.4(4)	S(2)−Li(1)−S(1′)	108.9(4)
S(1)−Li(1)−S(2)	89.9(3)	S(2)−Li(1)−Li(1′)	105.0(5)
S(1′)−Li(1)−Li(1′)	52.9(4)	S(1)−Li(1)−Li(1′)	51.5(3)

Er (**4**), Yb (**5**); Cp′ = 1,3-η^5-t-$Bu_2C_5H_3$, Ln = Nd (**6**), Gd (**7**), Dy (**8**), Er (**9**), Yb (**10**)) with an equimolar amount of $[(THF)_3LiE_2C_2B_{10}H_{10}Li(THF)]_2$ (E = S (**12a**), Se (**12b**)) in THF at room temperature gave organolanthanide compounds of the formula $[Li(THF)_4]_2[Cp'_2LnE_2C_2B_{10}H_{10}]_2$ (Cp′ = η^5-t-BuC_5H_4, E = S, Ln = Nd (**13a**), Gd (**14a**), Dy (**15a**), Er (**16a**), Yb (**17a**); E = Se, Ln = Nd (**13b**), Gd (**14b**), Dy (**15b**), Er (**16b**), Yb (**17b**); Cp′ = 1,3-η^5-t-$Bu_2C_5H_3$, E = S, Ln = Nd (**18a**), Gd (**19a**), Dy (**20a**), Er (**21a**), Yb (**22a**); E = Se, Ln = Nd (**18b**), Gd (**19b**), Dy (**20b**), Er (**21b**), Yb (**22b**)). These compounds are soluble in polar organic solvents such as THF and toluene but insoluble in nonpolar solvents such as hexane. Their IR spectra show a typical strong and broad characteristic B−H absorption at about 2565 cm^{-1}.

Recrystallization of **13a** and **13b** from a THF/hexane solution resulted in the isolation of blue crystals, which were identified as $[Li(THF)_4]_2[(\eta^5\text{-t-}BuC_5H_4)_2NdSe_2C_2B_{10}H_{10}]_2$ and $[Li(THF)_4]_2[(\eta^5\text{-t-}BuC_5H_4)_2NdSe_2C_2B_{10}H_{10}]_2$ by X-ray analysis, respectively. The respective dianionic moieties of complexes **13a** and **13b** are shown in Figures 6 and 7, together with the atomic labeling scheme. Both complex **13a** and complex **13b** have a central symmetry at the midpoint of two neodymium atoms. Similar to complex **13b**, complex **13a** consists of two well-separated, alternating layers of the discrete tetrahedral cations $[Li(THF)_4]^+$ and the complex anion $[(t\text{-}BuC_5H_4)_2NdS_2C_2B_{10}H_{10}]^{2-}$. The dianion of **13a** is composed of two $[(t\text{-}BuC_5H_4)_2NdS_2C_2B_{10}H_{10}]^-$ units. In each of the units, the Nd^{3+} ion is η^5-bound to two *tert*-butylcyclopentadienyl rings and σ-bound to two bridging sulfur atoms of two dithiocarboranes and to one terminal sulfur atom of dithiocarborane in a distorted-pentahedral arrangement. Each $(\eta^5\text{-t-}BuC_5H_4)_2Nd$ fragment is attached to one terminal and two bridging sulfur ligands of dithiolate carboranes. The bridging sulfur atom is bonded to the carbon atom of the carborane ligand and to two neodymium metals in a slightly distorted trigonal manner. Two neodymium atoms and two bridging sulfur atoms are not in the plane. Around one neodymium metal, the two *tert*-butyl groups on two cyclopentadienyl rings are located opposite to each other to decrease the bulky steric effect between them. In complex **13a**, the bond distances between the neodymium atoms and the bridging sulfur atom are 2.9969(14) and 3.0178(13) Å, respectively, slightly longer than the Nd(1)−S(2A) bond distance of 2.8237(15) Å between the neodymium atom and the nonbridging sulfur atom.[10] The S(1)−C(1) length of 1.775(5) Å is slightly longer than the S(2)−C(2) length of 1.754(6) Å. The average Nd−C (C(3)−C(7) ring and C(12)−C(16) ring) distances of 2.780(6) and 2.791(6) Å, respectively, are comparable to those normally observed for organoneodymium compounds.[28]

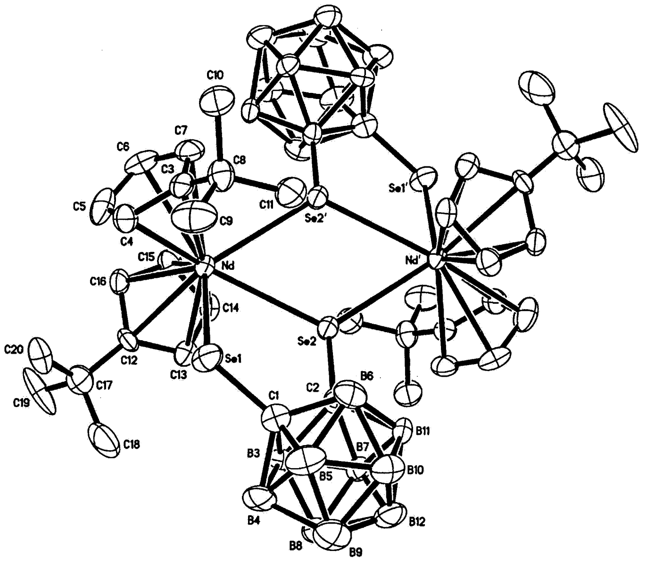

Figure 7. Anionic moiety of the complex $[Li(THF)_4]_2[(\eta^5\text{-}{}^tBuC_5H_4)_2NdSe_2C_2B_{10}H_{10}]_2$ (**13b**). Hydrogen atoms are omitted for clarity.

The solid structure of complex **13b** is isomorphous with that of complex **13a**. In complex **13b**, the bond distances between the neodymium atoms and the bridging selenium atom are 3.1065(14) and 3.1325(14) Å, respectively, slightly longer than the Nd−Se(1) bond distance of 2.9612(15) Å between the neodymium atom and the nonbridging selenium atom and those in complex **13a**. The Se(1)−C(1) length of 1.953(9) Å is slightly longer than the Se(2)−C(2) length of 1.924(7) Å and those in complex **13a**. The average Nd−C (C(3)−C(7) ring and C(12)−C(16) ring) distances of 2.787(9) and 2.772(8) Å, respectively, are in line with those for

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[28] (a) Schumann, H.; Messe-Markscheffel, J. A.; Esser, L. *Chem. Rev.* **1995**, *95*, 865. (b) Edelmann, F. T. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: New York, 1995; Vol. 4, p 11.

Table 6. Selected Bond Lengths (Å) and Angles (deg) for Complexes 13a and 13b

	13a	**13b**		**13a**	**13b**
Ln−C(3)	2.815(5)	2.887(9)	Ln−C(12)	2.780(6)	2.850(8)
Ln−C(4)	2.725(6)	2.832(8)	Ln−C(13)	2.696(6)	2.794(8)
Ln−C(5)	2.702(6)	2.716(9)	Ln−C(14)	2.727(6)	2.723(8)
Ln−C(6)	2.784(6)	2.711(9)	Ln−C(15)	2.835(6)	2.714(8)
Ln−C(7)	2.876(6)	2.790(8)	Ln−C(16)	2.915(6)	2.777(8)
Ln−E(1)	2.9969(14)	2.9612(15)	Ln−E(2)	2.8237(15)	3.1065(14)
E(1)−C(1)	1.775(5)	1.953(9)	E(2)−C(2)	1.754(6)	1.924(7)
C(2)−C(1)−E(1)	116.5(3)	120.2(6)	C(1)−C(2)−E(2)	120.1(3)	118.7(5)
C(1)−E(1)−Ln	123.72(17)	113.7(3)	C(2)−E(2)−Ln′	116.33(19)	122.0(2)
E(1)−Nd−E(2)	121.07(4)	72.78(3)	Ln−(μ-E)−Ln′	119.79(4)	121.24(3)

complex **13a** and other organoneodymium compounds.[28] The angles of Nd−Se(2)−Nd′ and Se(2)−Nd−Se(2′) are 121.24 and 58.8°, respectively. The Se(1)−Nd−Se(2) angle is 72.78(3)°. The two cyclopentadienyl rings possess a dihedral angle of 63.2° with the respective mean deviation for two planes of 0.0105 and 0.0027 Å. Selected bond distances and bond angles for complexes **13a** and **13b** are listed in Table 6.

To the best of our knowledge, these are the first structures of dinuclear lanthanocene complexes with dichalcogenolate carboranyl ligands.

Acknowledgment. Financial support from the National Natural Science Foundation of China and the Special Funds for Major State Basic Research Projects is gratefully acknowledged.

Supporting Information Available: Tables of crystallographic data and data collection details, atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates and figures giving atom-numbering schemes for complexes **7**, **8**, **12a**, **13a**, and **13b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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