

Synthesis and Characterization of Novel Lanthanocene Complexes with Dichalcogenolate *o*-Carboranyl Ligands[†]

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Reactions of $[\text{Cp}_2\text{Ln}(\mu\text{-Cl})_2]$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$, $\text{Ln} = \text{Nd, Yb, Dy, Gd, Er}$) with an equivalent of $[(\text{THF})_3\text{LiE}_2\text{C}_2\text{B}_{10}\text{H}_{10}\text{Li}(\text{THF})_2(\text{E} = \text{S, Se})]$ in THF afforded the dinuclear sandwich complexes of formula $[\text{Cp}_2\text{LnE}_2\text{C}_2\text{B}_{10}\text{H}_{10}]_2[\text{Li}(\text{THF})_4]_2$ [$\text{E} = \text{S, Ln} = \text{Nd}$ (1a), Yb (2a), Dy (3a), Gd (4a), Er (5a); $\text{E} = \text{Se, Ln} = \text{Nd}$ (1b), Yb (2b), Dy (3b), Gd (4b), Er (5b)]. The molecular structures of complexes 1a, 2a and 2b were determined by the single crystal X-ray structure analyses. Two lanthanide atoms are connected by a pair chalcogen ($\eta^1, \eta^2\text{-E}_2\text{C}_2\text{B}_{10}\text{H}_{10}$) bridging ligands and the central Ln_2E_2 four membered ring is not planar.

Keywords lanthanocene complex, crystal structure, dichalcogenolate *o*-carborane, metathesis reaction

Introduction

Up to date considerable attention has been devoted to the metal complexes with chalcogenolate ligands.^{1,2} Recently transition metal complexes containing a chelating 1,2-dicarba-closo-dodecaborane-1,2-dichalcogenolate ligands³⁻¹⁰ have attracted a great deal of interest due to the advantage of the unique molecular structure of carborane. Organolanthanocene complexes with dichalcogenolate *o*-carboranyl ligands are expected to have interesting structures and unique properties. Although recently there were some reports of organolanthanide complexes with carbo-

ranyl ligands and its derivatives,^{11,12} comparable organolanthanide complexes with chalcogenolate carboranyl ligands were so far unknown. These prompted us to investigate the syntheses of organolanthanide complexes with dichalcogenolate *o*-carboranyl ligands.

In this paper the first examples of dinuclear sandwich lanthanide complexes containing dichalcogenolate *o*-carboranyl ligands (Scheme 1) were synthesized from the reactions of bis-cyclopentadienyl lanthanide chlorided and dilithium dichalcogenolate *o*-carborane. Among them dinuclear neodymium and ytterbium complexes were crystallographically studied.

Experimental

General considerations

All the reactions and the manipulations were routinely carried out under pure argon atmosphere using the standard Schlenk technique. The use of dry and oxygen-free solvents is necessary. Anhydrous lanthanide chlorides were obtained by heating the hydrated salt with NH_4Cl .¹³ $[(\text{THF})_3\text{LiE}_2\text{C}_2\text{B}_{10}\text{H}_{10}\text{Li}(\text{THF})_2]$ ($\text{E} = \text{S, Se}$) were synthesized according to the procedures described in a previous report of our group.¹⁴ The starting materials $[\text{Cp}_2\text{Ln}(\mu\text{-Cl})_2]$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$, $\text{Ln} = \text{Nd, Yb, Dy,}$

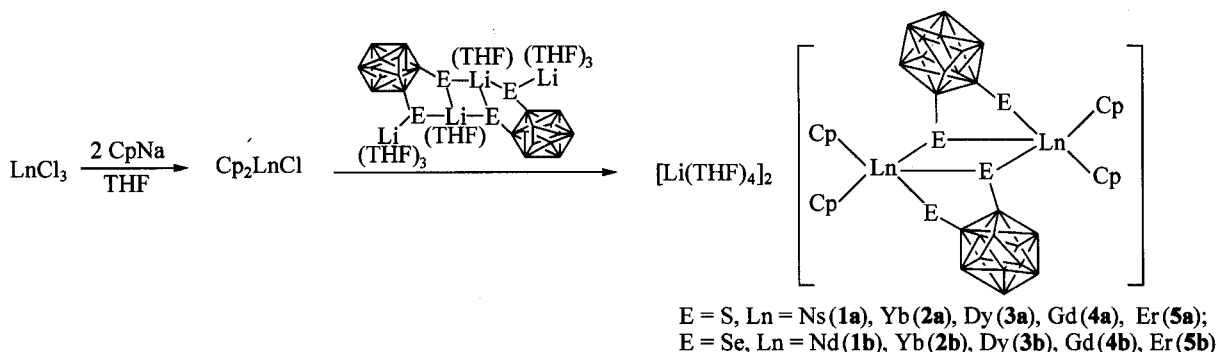
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Scheme 1



Gd, Er) were prepared according to the reported method.^{15,16} Infrared spectra were measured on a Bio-Rad FTS135 spectrometer as a KBr pellet. Elemental analyses were carried out by the Analytic Center in the Changchun Institute of Applied Chemistry.

Preparation of $[\text{Cp}_2\text{NdS}_2\text{C}_2\text{B}_{10}\text{H}_{10}]_2[\text{Li}(\text{THF})_4]_2$ (**1a**)

A solution containing $[\text{Cp}_2\text{Nd}(\mu\text{-Cl})]_2$ (0.155 g, 0.25 mmol) and $[(\text{THF})_3\text{LiS}_2\text{C}_2\text{B}_{10}\text{H}_{10}\text{Li}(\text{THF})]_2$ (0.254 g, 0.25 mmol) in 20 mL of THF was kept at r. t. with stirring for 24 h. After 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 the blue solid, which was dissolved in THF. Hexane was slowly added to top of THF solution and light blue crystals of **1a** were obtained after two days. Yield 0.303 g (79.2%); IR (KBr) ν : 3316w, 2980s, 2879s, 2573s, 2545s, 2170w, 1635w, 1486w, 1459s, 1384w, 1369s, 1244w, 1178w, 1139w, 1045s, 1010s, 968s, 889s, 840s, 775s, 752s, 727m, 670m, 413w cm^{-1} . Anal. calcd for $\text{C}_{56}\text{H}_{84}\text{B}_{20}\text{Li}_2\text{Nd}_2\text{O}_8\text{S}_4$: C 43.33, H 6.75, Nd 18.59; found C 43.82, H 6.21, Nd 18.67.

Preparation of $[\text{Cp}_2\text{NdSe}_2\text{C}_2\text{B}_{10}\text{H}_{10}]_2[\text{Li}(\text{THF})_4]_2$ (**1b**)

Complex **1b** was prepared as blue solid from $[\text{Cp}_2\text{Nd}(\mu\text{-Cl})]_2$ (0.155 g, 0.25 mmol) and $[(\text{THF})_3\text{LiSe}_2\text{C}_2\text{B}_{10}\text{H}_{10}\text{Li}(\text{THF})]_2$ (0.301 g, 0.25 mmol) in 20 mL of THF by using procedures similar to those used in the synthesis of **1a**. Yield 0.272 g (66.8%); IR (KBr) ν : 3319w, 2980s, 2879s, 2570s, 2547s, 2170w, 1635w, 1486w, 1459s, 1384w, 1369s, 1244w,

1178w, 1139w, 1045s, 1010s, 968s, 889s, 840s, 775s, 752s, 727m, 670m, 413w cm^{-1} . Anal. calcd for $\text{C}_{56}\text{H}_{84}\text{B}_{20}\text{Li}_2\text{Nd}_2\text{O}_8\text{Se}_4$: C 38.66, H 6.02, Nd 16.58; found C 39.13, H 6.55, Nd 16.88.

Preparation of $[\text{Cp}_2\text{YbS}_2\text{C}_2\text{B}_{10}\text{H}_{10}]_2[\text{Li}(\text{THF})_4]_2$ (**2a**)

Complex **2a** was prepared as red crystals from $[\text{Cp}_2\text{Yb}(\mu\text{-Cl})]_2$ (0.169 g, 0.25 mmol) and $[(\text{THF})_3\text{LiS}_2\text{C}_2\text{B}_{10}\text{H}_{10}\text{Li}(\text{THF})]_2$ (0.254 g, 0.25 mmol) in 20 mL of THF by using procedures similar to those used in the synthesis of **1a**. Yield 0.256 g (64.4%); IR (KBr) ν : 2966s, 2879s, 2588s, 2558s, 2170w, 1635w, 1486w, 1456s, 1382w, 1260s, 1098s, 1045s, 1015s, 889s, 849w, 795s, 727m, 670m cm^{-1} . Anal. calcd for $\text{C}_{56}\text{H}_{84}\text{B}_{20}\text{Li}_2\text{Yb}_2\text{O}_8\text{S}_4$: C 41.78, H 6.51, Yb 21.50; found C 41.28, H 6.87, Yb 21.98.

Preparation of $[\text{Cp}_2\text{YbSe}_2\text{C}_2\text{B}_{10}\text{H}_{10}]_2[\text{Li}(\text{THF})_4]_2$ (**2b**)

Complex **2b** was prepared as red microcrystals from $[\text{Cp}_2\text{Yb}(\mu\text{-Cl})]_2$ (0.169 g, 0.25 mmol) and $[(\text{THF})_3\text{LiSe}_2\text{C}_2\text{B}_{10}\text{H}_{10}\text{Li}(\text{THF})]_2$ (0.301 g, 0.25 mmol) in 20 mL of THF by using procedures similar to those used in the synthesis of **1a**. Yield 0.255 g (60.5%); IR (KBr) ν : 2964s, 2881s, 2584s, 2558s, 2170s, 1384s, 1262s, 1097s, 1045s, 1017s, 890s, 849w, 798s, 725m, 668w cm^{-1} . Anal. calcd for $\text{C}_{56}\text{H}_{84}\text{B}_{20}\text{Li}_2\text{Yb}_2\text{O}_8\text{Se}_4$: C 37.42; H 5.83, Yb 19.26; found C 37.77, H 6.19, Yb 19.71.

Preparation of $[\text{Cp}_2\text{DyS}_2\text{C}_2\text{B}_{10}\text{H}_{10}]_2[\text{Li}(\text{THF})_4]_2$ (**3a**)

Complex **3a** was prepared from $[\text{Cp}_2\text{Dy}(\mu\text{-Cl})]_2$

(0.164 g, 0.25 mmol) and $[(\text{THF})_3\text{LiS}_2\text{C}_2\text{B}_{10}\text{H}_{10}\text{Li} \cdot (\text{THF})_2]$ (0.254 g, 0.25 mmol) in 20 mL of THF by using procedures similar to those used in the synthesis of **1a**. Yield 0.219 g (55.8%); IR (KBr) ν : 2966s, 2879s, 2588s, 2558s, 2170w, 1635w, 1486w, 1456s, 1382w, 1260s, 1098s, 1045s, 1015s, 889s, 849w, 795s, 727m, 670m cm^{-1} . Anal. calcd for $\text{C}_{56}\text{H}_{84}\text{B}_{20}\text{Li}_2\text{Dy}_2\text{O}_8\text{S}_4$: C 42.34, H 6.60, Dy 20.46; found C 42.70, H 6.16, Dy 20.44.

*Preparation of $[\text{Cp}_2\text{DySe}_2\text{C}_2\text{B}_{10}\text{H}_{10}]_2[\text{Li}(\text{THF})_4]_2$ (**3b**)*

Complex **3b** was prepared from $[\text{Cp}_2\text{Dy}(\mu\text{-Cl})_2]$ (0.164 g, 0.25 mmol) and $[(\text{THF})_3\text{LiS}_2\text{C}_2\text{B}_{10}\text{H}_{10}\text{Li} \cdot (\text{THF})_2]$ (0.301 g, 0.25 mmol) in 20 mL of THF by using procedures similar to those used in the synthesis of **1a**. Yield 0.218 g (52.5%); IR (KBr) ν : 2964s, 2881s, 2584s, 2558s, 2170s, 1384s, 1262s, 1097s, 1045s, 1017s, 890s, 849w, 798s, 725m, 668w cm^{-1} . Anal. calcd for $\text{C}_{56}\text{H}_{84}\text{B}_{20}\text{Li}_2\text{Dy}_2\text{O}_8\text{Se}_4$: C 37.87, H 5.90, Dy 18.30; found C 37.73, H 6.22, Dy 18.75.

*Preparation of $[\text{Cp}_2\text{GdS}_2\text{C}_2\text{B}_{10}\text{H}_{10}]_2[\text{Li}(\text{THF})_4]_2$ (**4a**)*

Complex **4a** was prepared from $[\text{Cp}_2\text{Gd}(\mu\text{-Cl})_2]$ (0.161 g, 0.25 mmol) and $[(\text{THF})_3\text{LiS}_2\text{C}_2\text{B}_{10}\text{H}_{10}\text{Li} \cdot (\text{THF})_2]$ (0.254 g, 0.25 mmol) in 20 mL of THF by using procedures similar to those used in the synthesis of **1a**. Yield 0.213 g (54.7%); IR (KBr) ν : 2966s, 2879s, 2588s, 2558s, 2170w, 1635w, 1486w, 1456s, 1382w, 1260s, 1098s, 1045s, 1015s, 889s, 849w, 795s, 727m, 670m cm^{-1} . Anal. calcd for $\text{C}_{56}\text{H}_{84}\text{B}_{20}\text{Li}_2\text{Gd}_2\text{O}_8\text{S}_4$: C 42.62, H 6.64, Gd 19.93; found C 43.11, H 6.79, Gd 19.87.

*Preparation of $[\text{Cp}_2\text{GdSe}_2\text{C}_2\text{B}_{10}\text{H}_{10}]_2[\text{Li}(\text{THF})_4]_2$ (**4b**)*

Complex **4b** was prepared from $[\text{Cp}_2\text{Gd}(\mu\text{-Cl})_2]$ (0.161 g, 0.25 mmol) and $[(\text{THF})_3\text{LiS}_2\text{C}_2\text{B}_{10}\text{H}_{10}\text{Li} \cdot (\text{THF})_2]$ (0.301 g, 0.25 mmol) in 20 mL of THF by using procedures similar to those used in the synthesis of **1a**. Yield 0.229 g (55.5%); IR (KBr) ν : 2964s, 2881s, 2584s, 2558s, 2170s, 1384s, 1262s, 1097s, 1045s, 1017s, 890s, 849w, 798s, 725m, 668w cm^{-1} . Anal. calcd for $\text{C}_{56}\text{H}_{84}\text{B}_{20}\text{Li}_2\text{Gd}_2\text{O}_8\text{Se}_4$: C 38.09, H 5.94, Gd 17.81; found C 37.87, H 6.14, Gd 17.48.

*Preparation of $[\text{Cp}_2\text{ErS}_2\text{C}_2\text{B}_{10}\text{H}_{10}]_2[\text{Li}(\text{THF})_4]_2$ (**5a**)*

Complex **5a** was prepared from $[\text{Cp}_2\text{Er}(\mu\text{-Cl})_2]$ (0.166 g, 0.25 mmol) and $[(\text{THF})_3\text{LiS}_2\text{C}_2\text{B}_{10}\text{H}_{10}\text{Li} \cdot (\text{THF})_2]$ (0.254 g, 0.25 mmol) in 20 mL of THF by using procedures similar to those used in the synthesis of **1a**. Yield 0.228 g (57.7%); IR (KBr) ν : 2966s, 2879s, 2588s, 2558s, 2170w, 1635w, 1486w, 1456s, 1382w, 1260s, 1098s, 1045s, 1015s, 889s, 849w, 795s, 727m, 670m cm^{-1} . Anal. calcd for $\text{C}_{56}\text{H}_{84}\text{B}_{20}\text{Li}_2\text{Er}_2\text{O}_8\text{S}_4$: C 42.08, H 6.56, Er 20.93; found C 42.37, H 6.92, Er 21.44.

*Preparation of $[\text{Cp}_2\text{ErSe}_2\text{C}_2\text{B}_{10}\text{H}_{10}]_2[\text{Li}(\text{THF})_4]_2$ (**5b**)*

Complex **5b** was prepared from $[\text{Cp}_2\text{Er}(\mu\text{-Cl})_2]$ (0.166 g, 0.25 mmol) and $[(\text{THF})_3\text{LiS}_2\text{C}_2\text{B}_{10}\text{H}_{10}\text{Li} \cdot (\text{THF})_2]$ (0.301 g, 0.25 mmol) in 20 mL of THF by using procedures similar to those employed in the synthesis of **1a**. Yield 0.249 g (59.6%); IR (KBr) ν : 2964s, 2881s, 2584s, 2558s, 2170s, 1384s, 1262s, 1097s, 1045s, 1017s, 890s, 849w, 798s, 725m, 668w cm^{-1} . Anal. calcd for $\text{C}_{56}\text{H}_{84}\text{B}_{20}\text{Li}_2\text{Er}_2\text{O}_8\text{Se}_4$: C 37.66, H 5.87, Er 18.73; found C 37.39, H 6.16, Er 19.22.

*Structure solution and refinement for complexes **1a**, **2a** and **2b***

For complexes **1a**, **2a** and **2b**, a single crystal of each suitable for X-ray was sealed into a glass capillary respectively, and mounted on diffractometer. The intensity data of all the single crystals were collected on the CCD-Bruker Smart APEX system. All the determinations of unit cell and intensity data were performed with graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.071073$ nm). All the data were collected at room temperature using the ω scan technique. These structures were solved by the direct methods, expanded using Fourier techniques and refined on F^2 by a full-matrix least-squares method. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were included but not refined. All the calculations were carried out with Siemens SHELXTL PLUS program. Details of crystal data, selected bond distances and bond angles for complexes **1a**, **2a** and **2b** are listed in Tables 1 and 2.

Table 1 Crystallographic data for complexes **1a**, **2a** and **2b**

| Complex | 1a | 2a | 2b |
|---|---|---|--|
| Color | Light blue | red | red |
| Habit | block | block | block |
| Formula | C ₅₆ H ₈₄ B ₂₀ Li ₂ Nd ₂ O ₈ S ₄ | C ₅₆ H ₈₄ B ₂₀ Li ₂ Yb ₂ O ₈ S ₄ | C ₅₆ H ₈₄ B ₂₀ Li ₂ Yb ₂ O ₈ Se ₄ |
| Formula weight | 1532.03 | 1589.63 | 1692.56 |
| Cryst size (nm) | 0.70 × 0.30 × 0.25 | 0.70 × 0.35 × 0.25 | 0.70 × 0.25 × 0.20 |
| Cryst system | monoclinic | monoclinic | monoclinic |
| Space group | C2/c | C2/c | C2/c |
| <i>a</i> (nm) | 1.8310(7) | 1.8315(7) | 1.8508(7) |
| <i>b</i> (nm) | 2.2639(9) | 2.2498(9) | 2.2363(8) |
| <i>c</i> (nm) | 2.1496(8) | 2.1344(9) | 2.1662(8) |
| β (°) | 111.069(4) | 111.871(5) | 112.262(4) |
| <i>V</i> (nm ³) | 8.315(6) | 8.162(6) | 8.298(5) |
| <i>Z</i> | 4 | 4 | 4 |
| <i>D</i> _{calcd} (Mg/m ³) | 1.224 | 1.294 | 1.355 |
| θ _{range} (°) | 1.80—25.01 | 2.06—25.01 | 1.82—25.01 |
| μ (mm ⁻¹) | 1.377 | 2.422 | 4.034 |
| Reflections collected | 16971 | 16540 | 17119 |
| Independent reflections | 7286 (<i>R</i> _{int} = 0.0322) | 7151 (<i>R</i> _{int} = 0.0618) | 7260 (<i>R</i> _{int} = 0.0480) |
| <i>R</i> [<i>I</i> > 2 σ (<i>I</i>)] | 0.0633 | 0.0679 | 0.0688 |
| <i>R</i> _w [<i>I</i> > 2 σ (<i>I</i>)] | 0.1593 | 0.1527 | 0.1576 |
| No. of parameters | 415 | 415 | 415 |
| GOF on <i>F</i> ² | 1.094 | 1.106 | 1.084 |

Table 2 Selected bond lengths (× 10⁻¹ nm) and angles (°) for complexes **1a**, **2a** and **2b**

| Complex | 1a | 2a | 2b |
|-------------------|-----------|-----------|------------|
| Ln(1)—C(3) | 2.733(12) | 2.629(13) | 2.610(15) |
| Ln(1)—C(4) | 2.742(12) | 2.623(14) | 2.609(17) |
| Ln(1)—C(5) | 2.747(12) | 2.619(13) | 2.644(17) |
| Ln(1)—C(6) | 2.731(13) | 2.609(14) | 2.615(15) |
| Ln(1)—C(7) | 2.725(11) | 2.625(14) | 2.622(15) |
| Ln(1)—C(8) | 2.707(13) | 2.573(15) | 2.595(16) |
| Ln(1)—C(9) | 2.717(12) | 2.620(15) | 2.604(16) |
| Ln(1)—C(10) | 2.714(11) | 2.599(14) | 2.56(2) |
| Ln(1)—C(11) | 2.742(14) | 2.597(18) | 2.56(2) |
| Ln(1)—C(12) | 2.743(15) | 2.612(17) | 2.587(19) |
| Ln(1)—E(1) | 2.640(4) | 2.682(3) | 2.8716(14) |
| Ln(1)—E(2) | 2.652(3) | 2.663(3) | 2.9077(19) |
| E(1)—C(1) | 1.757(7) | 1.753(9) | 1.933(11) |
| E(2)—C(2) | 1.733(8) | 1.726(10) | 1.889(11) |
| Ln(1)-E(1)-Ln(1A) | 113.05(7) | 113.78(8) | 115.87(5) |
| E(1)-Ln(1A)-E(2) | 72.57(7) | 74.79(9) | 76.31(4) |
| C(1)-E(1)-Ln(1) | 125.3(2) | 125.8(3) | 124.1(3) |
| C(1)-E(1)-Ln(1A) | 114.6(2) | 113.9(3) | 112.4(3) |
| C(2)-E(2)-Ln(1A) | 113.1(3) | 112.3(4) | 111.3(4) |

Results and discussion

The reactions of lanthanide chlorides with sodium salts of cyclopentadiene are known as a main method, giving the useful precursor of sandwich lanthanocene complexes $[\text{Cp}_2\text{Ln}(\mu\text{-Cl})_2]$.^{15,16} Reactions of $[\text{Cp}_2\text{Ln}(\mu\text{-Cl})_2]$ with an equimolar amount of $[(\text{THF})_3\text{-LiE}_2\text{C}_2\text{B}_{10}\text{H}_{10}\text{Li}(\text{THF})_2]$ in THF at room temperature gave the organolanthanide compounds of formula $[\text{Cp}_2\text{LnE}_2\text{C}_2\text{B}_{10}\text{H}_{10}]_2[\text{Li}(\text{THF})_4]_2$ ($\text{E} = \text{S}$; $\text{Ln} = \text{Nd}$ (**1a**), Yb (**2a**), Dy (**3a**), Gd (**4a**), Er (**5a**); $\text{E} = \text{Se}$; $\text{Ln} = \text{Nd}$ (**1b**), Yb (**2b**), Dy (**3b**), Gd (**4b**), Er (**5b**)), after removal of the solvent, extraction with toluene, and recrystallization from a THF/hexane solution. These complexes 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 2570 cm^{-1} , which is consistent with the previous reported complexes with carboranyl ligands.¹¹⁻¹⁴

Recrystallization of **1a** from a THF/hexane solution resulted in the isolation of some blue crystals which were identified as $[\text{Cp}_2\text{NdS}_2\text{C}_2\text{B}_{10}\text{H}_{10}]_2[\text{Li}(\text{THF})_4]_2$ by X-ray analysis. The dianionic moiety of complex **1a** is shown in Fig. 1, together with the atomic labeling scheme. Complex **1a** has a center of symmetry at the midpoint of two neodymium atoms. The molecular structure of complex **1a** consists of a dianion $[\text{Cp}_2\text{NdS}_2\text{C}_2\text{B}_{10}\text{H}_{10}]^{2-}$ and two well-separated, alternating layers of the discrete tetrahedral cations $[\text{Li}(\text{THF})_4]^+$. The complex anion is composed of two $[\text{Cp}_2\text{NdS}_2\text{C}_2\text{B}_{10}\text{H}_{10}]^-$ units. In each of the units, the Nd^{3+} ion is η^5 -bound to two cyclopentadienyl rings and σ -bound to two μ_3 -sulfur atoms of two dithio-carboranes and to one μ_2 -sulfur atom of dithio-carborane in a distorted pentahedron arrangement. The two neodymium(III) atoms are bridged by two μ_3 -sulfur atoms of two dithio-carboranes to afford a dinuclear structure. The bridging sulfur atom is bonded to the carbon atom of the carboranyl ligand and to two neodymium metals in a slightly distorted trigonal atmosphere. The central four membered ring of two neodymium atoms and two bridging sulfur atoms is not planar. In complex **1a**, the bond distance of $\text{Nd}(1)\text{—S}(1)$ between the neodymium atom and the bridging μ_3 -sulfur atom is $0.28876(19)\text{ nm}$, similar to the bond distance of $\text{Nd}(1)\text{—S}(2\text{A})$ [$0.2898(3)\text{ nm}$] between the neodymium atom and the

μ_2 -sulfur atom. The bond length of $\text{S}(1)\text{—C}(1)$ [$0.1757(7)\text{ nm}$] is slightly longer than the bond length of $\text{S}(2)\text{—C}(2)$ [$0.1733(8)\text{ nm}$]. The average distances of Nd—C [$\text{C}(3)\text{—C}(7)$ ring and $\text{C}(8)\text{—C}(12)$ ring] [$0.2736(12)$ and $0.2725(13)\text{ nm}$, respectively], are comparable to those normally observed for organoneodymium compounds.^{17,18} The angles of $\text{Nd}(1)\text{—S}(1)\text{—Nd}(1\text{A})$ and $\text{S}(1)\text{—Nd}(1\text{A})\text{—S}(2)$ are $113.05(7)^\circ$ and $72.57(7)^\circ$, respectively.

Fig. 2 exhibits the dianionic moiety structure of complex **2a**. The solid structure of complex **2a** is isomorphous to that of complex **1a**. In complex **2a**, the bond distance of $\text{Yb}(1)\text{—S}(1)$ between the ytterbium atom and the bridging μ_3 -sulfur atom is $0.2769(2)\text{ nm}$, a little longer than the bond distance of $\text{Yb}(1)\text{—S}(2\text{A})$ [$0.2791(3)\text{ nm}$] between the ytterbium atom and the μ_2 -sulfur atom and shorter than the corresponding ones in complex **1a**. The bond length of $\text{S}(1)\text{—C}(1)$ [$0.1753(9)\text{ nm}$] is slightly longer than the bond length of $\text{S}(2)\text{—C}(2)$ [$0.1726(10)\text{ nm}$] and comparable to those in complex **1a**. The average distances of Yb—C [$\text{C}(3)\text{—C}(7)$ ring and $\text{C}(8)\text{—C}(12)$ ring] [$0.2621(14)$ and $0.2600(16)\text{ nm}$, respectively], are in line with those for other organoytterbium compounds.^{17,18} The angles of $\text{Yb}(1)\text{—S}(1)\text{—Yb}(1\text{A})$ and $\text{S}(1)\text{—Yb}(1\text{A})\text{—S}(2)$ are $113.78(8)^\circ$ and $74.79(9)^\circ$, respectively.

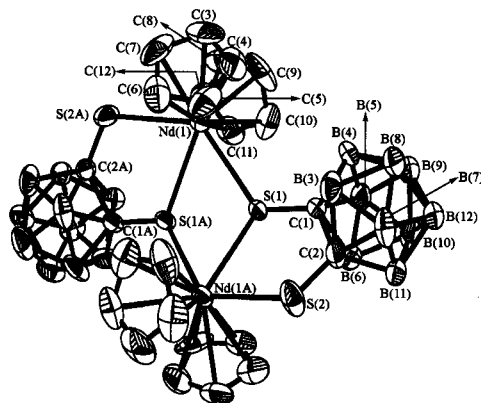


Fig. 1 Dianionic moiety of complex $[(\eta^5\text{-C}_5\text{H}_5)_2\text{NdS}_2\text{C}_2\text{B}_{10}\text{H}_{10}]_2[\text{Li}(\text{THF})_4]_2$ (**1a**) (the hydrogen atoms are omitted for clarity).

Fig. 3 illustrates the dianionic structure of complex $[\text{Cp}_2\text{YbSe}_2\text{C}_2\text{B}_{10}\text{H}_{10}]_2[\text{Li}(\text{THF})_4]_2$ (**2b**), which is coordinatively analogous to those of **1a** and **2a**. Two ytterbium atoms are connected by a pair chalcogen

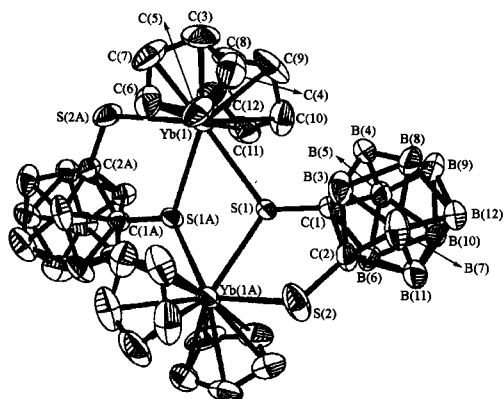


Fig. 2 Dianionic moiety of complex $[(\eta^5\text{-C}_5\text{H}_5)_2\text{YbS}_2\text{C}_2\text{B}_{10}\text{-H}_{10}]_2[\text{Li}(\text{THF})_4]_2$ (**2a**) (the hydrogen atoms are omitted for clarity).

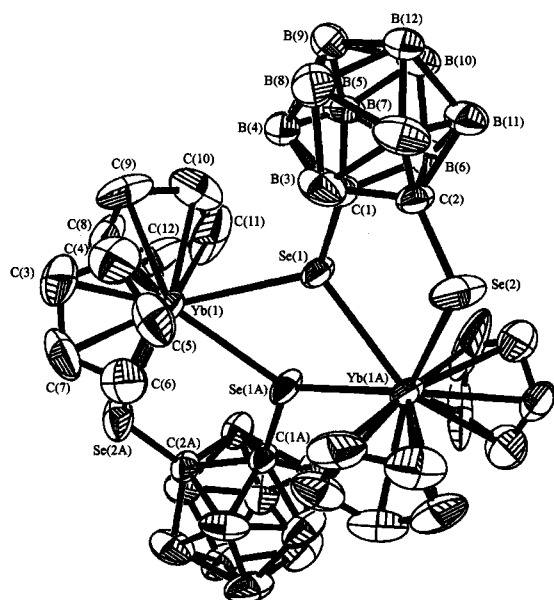


Fig. 3 Dianionic structure of complex $[\text{Cp}_2\text{YbSe}_2\text{C}_2\text{B}_{10}\text{H}_{10}]_2\cdot[\text{Li}(\text{THF})_4]_2$ (**2b**) (the hydrogen atoms are omitted for clarity).

($\eta^1, \eta^2\text{-E}_2\text{C}_2\text{B}_{10}\text{H}_{10}$) bridging ligands and the central Yb_2Se_2 four membered ring is not a planar. The bond distances of $\text{Yb}(1)\text{-Se}(1)$ and $\text{Yb}(1)\text{-Se}(2\text{A})$ are 0.28716 (14) and 0.29077 (19) nm, respectively, longer than the corresponding ones in complex **1a** or **2a**. The bond length of $\text{Se}(1)\text{-C}(1)$ [0.1933(11) nm] is slightly longer than the bond length of $\text{Se}(2)\text{-C}(2)$ [0.1889(11) nm], comparable to the case in complex

1a or **2a**. The average distances of $\text{Yb}\text{-C}$ (Cp_1 ring and Cp_2 ring) [0.2620(16) and 0.2581(18) nm], respectively, are not beyond the range for organoytterbium compounds.^{17,18} The angles of $\text{Yb}(1)\text{-Se}(1)\text{-Yb}(1\text{A})$ and $\text{S}(1)\text{-Yb}(1\text{A})\text{-S}(2)$ are $115.87(5)^\circ$ and $76.31(4)^\circ$, respectively, slightly larger than those in the isomorphous complex of **2a**.

Conclusion

Dinuclear organolanthanocene compounds with dichalcogenolate *o*-carboranyl ligands were systematically synthesized from lanthanocene complexes and dilithium dichalcogenolate *o*-carborane and structurally characterized by single crystal X-ray analyses. As far as we know, dinuclear lanthanocene complexes with dichalcogenolate *o*-carboranyl ligands are unique in organolanthanide chemistry.

References

- (a) Jin, G.-X.; Cheng, Y.-X.; Lin, Y.-H. *Organometallics* **1999**, *18*, 947.
(b) Cheng, Y.-X.; Jin, G.-X. *Chin. J. Inorg. Chem.* **1999**, *15*, 8 (in Chinese).
- Cheng, Y.-X.; Jin, G.-X.; Shen, Q.; Lin, Y.-H. *J. Organomet. Chem.* **2001**, *631*, 94.
- Herberhold, M.; Jin, G.-X.; Yan, H.; Milius, W.; Wrackmeyer, B. *Eur. J. Inorg. Chem.* **1999**, 873.
- Herberhold, M.; Jin, G.-X.; Yan, H.; Milius, W.; Wrackmeyer, B. *J. Organomet. Chem.* **1999**, *587*, 252.
- Herberhold, M.; Yan, H.; Milius, W.; Wrackmeyer, B. *J. Organomet. Chem.* **2000**, *604*, 170.
- Bae, J. Y.; Lee, Y. J.; Kim, S. J.; Ko, J.; Cho, S.; Kang, S. O. *Organometallics* **2000**, *19*, 1514.
- Kim, D. H.; Ko, J.; Park, K.; Cho, S.; Kang, S. O. *Organometallics* **1999**, *18*, 2738.
- Jin, G.-X. In *The Proceedings of the 19th International Conference on Organometallic Chemistry* S. O. 30, Shanghai, **2000**.
- Herberhold, M.; Yan, H.; Milius, W.; Wrackmeyer, B. *Angew. Chem., Int. Ed.* **1999**, *38*, 3689.
- Hawthorne, M. F.; Zheng, Z. P. *Acc. Chem. Res.* **1997**, *30*, 267.
- Zi, G.; Yang, Q.; Mak, T. C. W.; Xie, Z. *Organometallics* **2001**, *20*, 2359.
- Wang, S.; Li, H.-W.; Xie, Z. *Organometallics* **2001**, *20*, 3624.
- Taylor, M. D.; Carter, P. C. *J. Inorg. Nucl. Chem.*

- 1962, 24, 387.
- 14 Yu, X.-Y.; Jin, G.-X.; Hu, N.-H.; Wong, L.-H. *Organometallics* **2002**, 21, 2533.
- 15 Marginn, R. E.; Manastyrsky, S.; Dubeck, M. J. *Am. Chem. Soc.* **1963**, 85, 672.
- 16 Gomez-Beltran, F.; Oro, L. A.; Ibanez, F. J. *Inorg. Nucl. Chem.* **1975**, 37, 1541.
- 17 Schumann, H.; Messe-Markscheffel, J. A.; Esser, L. *Chem. Rev.* **1995**, 95, 865.
- 18 Edelmann, F. T. In *Comprehensive Organometallic Chemistry II*, Vol. 4, Eds.: Abel, E. W.; Stone, F. G. A.; Wilkinsom, G., Pergamon, New York, **1995**, p. 11.

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