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(Boratabenzene)(cyclooctatetraenyl) Lanthanide Complexes: A New Type of Organometalllic Single-Ion Magnets

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A series of new sandwich type lanthanide complexes containing both boratabenzene and cyclooctatetraenyl ligands, \{[(C_6H_5BR)(COT)] \} \{1Er: R = H, Ln = Er; 2Er: R = Me, Ln = Er; 3Er: R = NEt\textsubscript{2}, Ln = Er; 4Dy: R = H, Ln = Dy; 5Dy: R = Me, Ln = Dy; 6Dy: R = NEt\textsubscript{2}, Ln = Dy; 7Y: R = NEt\textsubscript{2}, Ln = Y\}, were synthesized. The structures of 1Er – 7Y were all characterized by single crystal X-ray diffraction. Dynamic susceptibility experiments showed that the erbium complexes 1Er – 3Er exhibited slow magnetic relaxation under zero dc field while the dysprosium complexes 4Dy – 6Dy did not. For the erbium complexes, the magnetic properties were influenced by the substituent on boron atom. 1Er exhibited a hysteresis up to 8 K, and 2Er featured the highest energy barrier (300 cm\textsuperscript{-1}) among all reported erbium single-ion magnets (SIMs). The influence of boron substituent on the magnetic properties was highlighted by \textit{ab} initio calculations.

Open the fascinating boratabenzene chemistry. In the last four decades, a large number of metal complexes bearing boratabenzene have been reported.\textsuperscript{7} \textsuperscript{8} \textsuperscript{9} However, the properties and applications of these complexes were mostly limited to their reactivity and catalytic applications in organic and polymer synthesis.\textsuperscript{10} Considering the similarity between boratabenzene and cyclopentadienyl, it is possible to construct new erbium SIMs by using boratabenzene ligands. On the other hand, the boratabenzene is a poorer electron donor in comparison with Cp\textsuperscript{a}, promoting the 4f electrons stretching along uniaxial direction. Therefore, the uniaxial magnetic anisotropy of (boratabenzene)(cyclooctatetraenyl) lanthanide might be enhanced, which may bring new opportunity in the design of erbium SIMs with high $U_{eff}$ and/or $T_0$. Furthermore, the specific electrostatic contribution of boratabenzene and electronic structure modulation on SIMs can be tuned by the choice of the exocyclic substituent on boron. Herein, we report the synthesis, characterization and magnetic properties of (boratabenzene)(cyclooctatetraenyl) lanthanide complexes. The \textit{ab} initio calculations were also performed to provide further insight into the magnetic properties of these complexes.

\textbf{Results and discussion}

\textbf{Scheme 1. Synthesis of (boratabenzene)(cyclooctatetraenyl) Lanthanide Complexes.}

\begin{align*}
\text{Li} &\rightarrow \text{B} \rightarrow \text{R} \rightarrow \text{(COT)Ln(THF)} \\
\text{R} &= \text{H, CH}_3, \text{NEt}_2 \\
\text{B} &= \text{1Er: R = H, RE = Er} \\
\text{2Er: R = CH}_3, \text{RE = Er} \\
\text{3Er: R = NEt}_2, \text{RE = Er} \\
\text{4Dy: R = H, RE = Dy} \\
\text{5Dy: R = CH}_3, \text{RE = Dy} \\
\text{6Dy: R = NEt}_2, \text{RE = Dy} \\
\text{7Y: R = NEt}_2, \text{RE = Y}
\end{align*}
Synthesis and Structural Characterization of (boratabenzene)(cyclooctatetraenyl) lanthanide complexes.

Salt elimination reactions of Li(C₆H₅BR) (R = H, Me, NEt₂) with [(COT)LnCl(THF)] (Ln = Er, Dy, Y) in THF gave the crude products, which recrystallized in toluene or hexane to provide the desired (boratabenzene)(cyclooctatetraenyl) lanthanide complexes [(C₆H₅BR)(COT)] (1Er: R = H, Ln = Er; 2Er: R = Me, Ln = Er; 3Er: R = NEt₂, Ln = Er; 4Dy: R = H, Ln = Dy; 5Dy: R = Me, Ln = Dy; 6Dy: R = NEt₂, Ln = Dy; 7Y: R = NEt₂, Ln = Y) in moderate yields (Scheme 1). Complexes 1Er–7Y were characterized by single crystal X-ray diffraction. 1Er–7Y all crystallize in the monoclinic space group P2₁/c. Molecular structures of 1Er–3Er are shown in Fig. 1, while those of 4Dy–6Dy and 7Y are present in the ESI. The structural features of 1Er–3Er and 4Dy–6Dy are very similar and 1Er–3Er were taken as the examples to analyze the structural features. 1Er–3Er are sandwich type organometallic complexes, and the erbium ion is much closer to the centroid of cyclooctatetraenyl ring (1.674 Å) than to that of boratabenzene ring (2.245 Å). The average Er–C(COT) bond lengths in 1Er, 2Er and 3Er are 2.495(8), 2.491(2) and 2.493(5) Å, respectively, which are close to that in [(Cp*)Er(COT)] (Cp* = pentamethylcyclopentadienyl) (2.513 Å). On the other hand, the average Er–C(boratabenzene) bond lengths in 1Er, 2Er and 3Er (2.661(8), 2.657(3) and 2.647(4) Å) are much longer than the average Er–C(Cp*) bond length in [(Cp*)Er(COT)] (2.573 Å) as the boratabenzene is a poorer electron donor in comparison with Cp*. The Er–C(boratabenzene) bond lengths in 1Er, 2Er and 3Er are in the ranges of 2.618(9)–2.694(9), 2.629(3)–2.678(3) and 2.603(8)–2.698(8) Å, respectively; the erbium ion is far away from the ortho carbon atoms and closer to the para carbon atom. The Er–B distances (2.76(1) Å (1Er), 2.779(3) Å (2Er) and 2.83(1) Å (3Er)) are longer than the Er–C(boratabenzene) distances. These observations revealed a slippage of erbium ion away from boron and toward para carbon. Due to the strong π-interaction between boron and the amino-substituent, the Er–B distance in 3Er is longer than those in 1Er and 2Er and the deviation of boron atom from the boratabenzene plane in 3Er (0.097 Å) is larger than those in 1Er and 2Er (0.028 and 0.059 Å, respectively). Dihedral angles between the cyclooctatetraenyl ring and the boratabenzene ring in 1Er, 2Er and 3Er are 10.6°, 5.5° and 9.3°, respectively. The nearest neighboring molecules are nearly perpendicular to each other through C–H···B interaction and edge to face π···π stacking between two aromatic rings. The nearest Er···Er distances in 1Er, 2Er and 3Er are 6.1, 6.8 and 6.3 Å, respectively (See ESI).

Magnetic Properties.

Dc magnetic measurements were conducted under 1 kOe dc field over the temperature ranging from 300 to 2 K (Fig. 2, Figure S4 in the ESI). At room temperature, the χ_mT values of 1Er, 2Er, 3Er, 4Dy, 5Dy and 6Dy are 11.01, 11.04, 11.08, 13.92, 13.94 and 14.06 emu mol⁻¹ K⁻¹, respectively, which are in good agreement with the theoretical values of ErIII (6H₁₅/₂, S = 3/2, L = 6, g = 6/5) and DyIII (6H₁₅/₂, S = 5/2, L = 5, g = 4/3). The χ_m value of 1Er decreases very slightly with decreasing temperature, but when the temperature decreases to 12 K, the χ_m value jumps to 11.32 cm³ mol⁻¹, and then decreases sharply upon further cooling. The χ_m value of 2Er also slightly upturns at about 6 K, and then drop precipitously. Similar to other reported Er²⁺ SIMs, upon decrease of the temperature, the χ_m value of 3Er decreases slightly, until about 3K where it drops drastically. The sudden drop in χ_mT observed for 1Er, 2Er and 3Er indicated their magnetizations are blocked. The sudden drop in χ_mT observed for 1Er, 2Er and 3Er may arise from antiferromagnetic coupling, saturation of the magnetization, Zeeman effect, spin-orbit coupling effect leaded change of spin population or magnetization blocking. This phenomenon is not uncommon in previous reported SIMs, the variable fields dc measurements showed that the unusual χ_mT rising observed for 1Er at 12 K is not due to the polycrystalline samples’ reorientation along the magnetic field, but related with the SIM properties (Figure S5). Further discussions on this χ_mT rising at low temperatures would be provided *vide infra*. For Dy²⁺ complexes, upon cooling, the χ_m values are nearly constant till 100 K, and then slowly decrease. Below 25 K, the χ_m values drop steeply upon further cooling. At 2 K, the values are 9.52, 10.00, 10.00 emu mol⁻¹, respectively (Figure S4). These static properties could be attributed to the typical stark sublevels depopulation.
The out-of-phase ac susceptibility of 1Er and 2Er exhibited strong frequency-dependent behaviour between 15 K and 24 K or 16 K and 25 K under zero dc field (Fig. 3(a) and 3(b), and Figures S7-S8). While below 10 K, no \( \chi'' \) peaks could be observed since the magnetic relaxation rate is so slow that it has been beyond the lowest limit of our equipment (Figure S9). The relaxation time extracted from temperature-dependent and frequency-dependent out-of-phase susceptibility gave the same results (Figures S10(a) and S10(b)). The effective energy barrier of 1Er is 371 K (259 cm\(^{-1}\)) with \( \tau_0 \) of 5.3 \( \times \) 10\(^{-1}\) s (Fig. 3(d)). The \( \chi'' \) peak of the 1Hz plot for 2Er is 17.4 K, which is higher than that for 1Er (15.8 K) (Fig. 3(a) and 3(b), Figures S7-S8). As the consequence, the effective energy barrier and \( \tau_0 \) of 2Er are 421 K (300 cm\(^{-1}\)) and 5.5 \( \times \) 10\(^{-1}\) s, respectively (Fig. 3(e)). Whereas, \( \tau \) vs. \( \tau^{-1} \) plot for 2Er at low temperature showed evident curvature, indicating a faster QTM process than that of 1Er. The energy barriers of 1Er and 2Er are higher than those of the previous reported erbium based SIMs (ranging from 15 cm\(^{-1}\) to 225 cm\(^{-1}\))\(^{4k,4l,5} \) revealing the advantage of introducing poorer electron donating boratabenzene as the ligand. Utilizing poorer electron donor decreases the electronic interaction between 4f electrons and aromatic electrons of ligands along the uniaxial direction, and enhances the uniaxial magnetic anisotropy. This experimental result is in line with the theoretical study of Rajaraman et al.\(^{12} \) It is also noteworthy that 2Er has the highest effective energy barrier among all reported Er\(^{III} \) SIMs. The out-of-phase ac susceptibility of 3Er also showed strong frequency-dependent magnetic behaviour, but which is significantly different from those observed for 1Er and 2Er. When the temperature is below 10 K, the intensity of the out-of-phase component of 3Er is distinctly larger than those of 1Er and 2Er, implying a much stronger and faster QTM process. The peaks of corresponding frequency plots are nearly unchanged until the temperature rises to 10 K, confirming the existence of temperature independent QTM process. (Fig. 3(c) and Figure S11). The effective energy barrier of 3Er is 250 K (174 cm\(^{-1}\) under zero dc field) (Fig. 3(f) and Figure S10(c)). When an optimized field 2 kOe was applied, the \( U_{\text{eff}} \) increased slightly (Fig. 3(f) and Figure S12). The lower energy barrier of 3Er compared to those of 1Er and 2Er can be attributed to two facts: a) the aminoboratabenzene is a better electron donor than the hydrogen (or methyl)-substituted one; b) the deviation of boron atom from the boratabenzene plane in 3Er is larger than those in 1Er and 2Er, which may cause more transverse components (see \( ab \) initio calculations below). Dynamic studies showed that 4Dy–6Dy only exhibited slow magnetic relaxation under applied dc field with small effective energy barriers (Figures S13-S15). Combined with the previous reports, the sandwich type geometry utilizing cyclomultiene ligands seems not suitable for dysprosium to be a good SIM.

![Fig. 3 Out-of-phase (\( \chi'' \)) signal vs. frequency (v) plots under 3 Oe ac field for 1Er (a), 2Er (b) and 3Er (c). Relaxation time (\( \tau \)) vs. inverse of temperature (1/\( T \)) plots for 1Er (d), 2Er (e) and 3Er (f). Red points were obtained under zero dc field while black points were obtained under 2 kOe dc field. The solid lines represent the fitting by applying Arrhenius law.](image3)

The hysteresis measurements showed that all Er\(^{III} \) complexes exhibited butterfly-type hysteresis loops (Figure 4). Interestingly, 1Er and 2Er have the hysteresis loops up to 8 and 6 K, respectively, which are higher than that of [(\( \text{Cp}^+ \))Er(COT)] (5 K).\(^{5a} \) So far, only two Er\(^{III} \) complexes, [K(18-crown-6)(THF)]\(_2\)[Er(COT)]\(_2\) (10 K)\(^{5b,d} \) and [Li(DME)]\(_3\)[Er(COT’’)]\(_2\) (8 K)\(^{5c} \),...
have blocking temperatures ($T_B$) up to 8 K, and both of them are ion pairs. For 3Er, the hysteresis could not be observed until the temperature was decreased to 2 K. To see whether thermal relaxation or QTM is predominant in $T_B$, we extrapolated the Arrhenius fitting and found that the blocking temperatures of $1\text{Er}-3\text{Er}$ (defined as the relaxation time of 100 s) were similar, which were 12.8, 13.7 and 10.3 K, respectively. Therefore, the hysteresis is mostly determined by QTM rate and strength at low temperatures. The differences in their hysteresis we believe are due to the QTM, which could be caused by the following reasons: 1. The differences in their local structures. 2Er has a smaller bending angle than 1Er, which may be responsible for the observed higher $U_{eff}$, but the introducing of electron-donating methyl group in 2Er enhances the electronic interaction between the Er$^{III}$ ion and the boratabenzene ligand along the uniaxial direction, leading to a more obvious QTM than that of 1Er. For 3Er, the aminoboratabenzene is a better electron donor than the hydrogen (or methyl)-substituted one due to the strong $\pi$-interaction between boron and nitrogen. The $\pi$-interaction between boron and nitrogen also causes a deviation of boron atom out from the 5 Cs plane of 0.097 Å, which is apparently larger than those in 1Er and 2Er (0.028 and 0.059Å, respectively). The unchanged maximum of the out of phase below 10 K for 3Er implies a much stronger and faster QTM process compared to QTM of 1Er and 2Er. 2. As the dipole-dipole interaction is anisotropic, the different arrangement of molecules in the lattice may also give different QTM rate for 1Er, 2Er and 3Er. Their different magnetic behaviors at low temperatures may also be caused by the different relaxation processes like Direct/Raman process. Since the QTM is more obvious in 3Er, the dilution experiment was subsequently carried out to study the role of the dipole-dipole interaction. Diluted sample of 3Er was prepared by co-crystallization of 3Er with the isostructural [(COT)Y(C$_2$H$_5$BNEt$_3$)] in a Er : Y molar ratio of 1 : 19. The co-crystallization method has been used for the magnetic dilution studies of the analogues, such as [(Cp*)Er(COT)]$^{15a}$ and [K(18-crown-6)][Er(COT)$_2$]$^{15b}$, by us and others. The ICP analysis indicated the Er : Y molar ratio in the diluted sample is 4.2 : 95.8. The ac measurement indicated that the $\chi_{ac}$ peaks occur in the range of 18 to 26 K, with $U_{eff}$ of 239 cm$^{-1}$, which is higher than that of the pure 3Er (174 cm$^{-1}$) under zero dc field (Figures S16-S17). The variable-field magnetization plots displayed a hysteresis loop up to 3 K (Figure 4(c)), which is still lower than those observed for 1Er and 2Er. The sudden magnetization lose near zero field still occurred and the coercive field was not observed. The above results indicated that the differences in the QTM of 1Er–3Er are mainly due to their local structures.

**Fig. 5** The magnetization blocking barriers in complexes 1Er–6Dy, represented by (a)–(f). The thick black lines represent the Kramers doublets as a function of their magnetic moments along the magnetic axis. The green lines correspond to diagonal quantum tunneling of magnetization (QTM), the blue lines represent off-diagonal relaxation process. The numbers at each arrow stand for the mean absolute value of the corresponding matrix element of transition magnetic moment.

**Ab Initio Calculations.**

To further elucidate the differences in their dynamic relaxations, *ab initio* CASSCF/RASSI/SINGLE_ANISO calculations with MOLCAS 7.8 package were performed to determine the low-lying energy levels and magnetic properties of molecules.$^{13}$ The calculated results showed that the ground Kramers doublets of Er$^{III}$ complexes are well separated from the excited states (Table S3). The effective $g_z$ values of 1Er–3Er are 17.87, 17.89 and 17.81, respectively, indicating their magnetically uniaxial anisotropic ground states. Correspondingly, the $g_{xy}$ value is almost negligible ($g_{xy} \approx 1 \times 10^{-4}$), except for 3Er ($g_x \approx 0.0025$, $g_y \approx 0.0028$). Even for the first excited Kramers
doubles, the transversal components still remain small values for $^{13}$Er and $^{2}$Er ($g_{xx} = 2 \times 10^{-3}$). Relatively, opposite case happens on $^{3}$Er, the $g_{xx}$ value of higher excited states increases obviously. These relatively large transverse components may promote more pronounced QTM process, which is consistent with the hysteresis measurements. The calculations also revealed that all Dy$^{III}$ complexes have small magnetic anisotropic ground Kramers doubles and low energetic first excited states (Table S4). The $g_{xx}$ values are not negligible, giving significantly large transversal magnetic moment to Dy$^{III}$ complexes. The energy gap between the ground state and the first excited state is also small. Fig. 5 indicated that the transversal diagonal magnetic moments (ca. $10^{-1}$ $\mu$B) in the ground state arising from internal magnetic fields of $^{4}$Dy-$^{6}$Dy are much larger than those (ca. $10^{-3}$-$10^{-5}$ $\mu$B) of $^{1}$Er-$^{3}$Er, therefore allowing a fast QTM. According to a recent proposal by Ungur and co-workers,$^{14}$ the relaxation path can be related to the tunneling gaps. Thus, according to the relaxation path indicated in Fig. 5, the blocking barriers of $^{1}$Er-$^{6}$Dy were deduced, which are 201.0 cm$^{-1}$ (15/2$\rightarrow$13/2$\rightarrow$5/2$\rightarrow$9/2$\rightarrow$11/2), 223.5 cm$^{-1}$ (15/2$\rightarrow$13/2$\rightarrow$9/2$\rightarrow$9/2), 158.8 cm$^{-1}$ (15/2$\rightarrow$13/2$\rightarrow$13/2$\rightarrow$13/2), 56.2 cm$^{-1}$ (15/2$\rightarrow$13/2$\rightarrow$13/2), 33.6 cm$^{-1}$ (15/2$\rightarrow$13/2) and 39.7 cm$^{-1}$ (15/2$\rightarrow$11/2), respectively. These calculated blocking barriers are in the same sequence of the experimental ones, although deviations in particular values are observed, due to the exclusion of electron dynamic correlation in the calculations. The tunneling gaps of the diagonal and off-diagonal in the ground and the first excited states of $^{3}$Er are much larger than those of $^{1}$Er and $^{2}$Er, therefore $^{3}$Er has the fastest QTM in three Er$^{III}$ complexes. This is also consistent with the ac susceptibility and hysteresis measurements. Moreover, only the magnetic relaxation in the complexes $^{1}$Er and $^{2}$Er can occur by the second excited state.$^{34,15}$ The calculated magnetic easy-axis of Er$^{III}$ complexes further confirmed that the sandwich type geometry is preferable for prolate type Er$^{III}$ ion possessing SIM properties (Figure S18). On the contrary, the easy axis of Dy$^{III}$ complexes is not perpendicular to the COT ring as Er$^{III}$ complexes (Figure S18), as the equatorial ligand field is not suitable to stabilize the Ising type oblate ground state of Dy$^{III}$ ion.

Unprecedented Frozen Magnetization.

The $\chi_{\text{m}}$-$T$ rising observed for $^{1}$Er and $^{2}$Er at 12 or 6 K has no precedent. As the rising occurs around their $T_{\text{b}}$, the magnetization may be “frozen” below certain temperature. Two independent measurements were carried out: (a) the magnetization of $^{1}$Er was measured upon cooling; (b) the sample was firstly cooled to 2 K under 1 kOe dc field, and then the magnetization was measured upon warming. At each data point, the measurement was delayed for a certain time before the data was recorded. During the cooling down experiment, the $\chi_{\text{m}}$-$T$ value decreases smoothly and no peak was observed (Figure S19). While in the warming up experiment, the $\chi_{\text{m}}$-$T$ rising was observed (Fig. 6). When the delay time is 2 s, a distinct peak was observed at about 6.3 K. The $\chi_{\text{m}}$-$T$ rising becomes less pronounced when increasing the delay time. When the delay time is up to 7200 s, the $\chi_{\text{m}}$-$T$ rising can be ignored (Fig. 6). These results indicated that a long delay time is needed to let the system relaxes to equilibrium. Indeed, the magnetization equilibrium at 2 K can only be reached by delaying as long as 10 hours (Figure S20). This is probably due to poorly coupling of the spin system and the phonon bath.$^{16}$ These results indicated that the observed $\chi_{\text{m}}$-$T$ rising is not due to the long range ordering, but the non-equilibrium of magnetization.

Conclusions

In summary, sandwich type lanthanide organometallic complexes $[(\text{C}_{5}\text{H}_{5}\text{BR})\text{Ln(COT)}]$ were successfully synthesized, the erbium complexes are SIMs while the dysprosium ones are not, and magnetic properties of the erbium complexes are strongly influenced by the substituent on boron atom. Using poorer electron donating boratabenzenes $[(\text{C}_{5}\text{H}_{5}\text{BR})]$ (R = H or Me) instead of carbon aromatic anions, such as Cp* and COT, results in the erbium SIMs with higher effective energy barrier. It is also noteworthy that the blocking temperature of $[(\text{C}_{5}\text{H}_{5}\text{BH})\text{Er(COT)}]$ is higher than that of $[(\text{Cp*})\text{Er(COT)}]$. This study experimentally demonstrated that utilizing poorer electron donors--boratabenzenes decreases the electronic interaction between 4f electrons and aromatic electrons of ligands along the uniaxial direction, and enhances the uniaxial magnetic anisotropy. Therefore, this study not only disclosed a new application of the boratabenzen metal complexes but also provided a practical guideline for the design and synthesis of erbium SIMs with better performance. Further studies following this guideline are actually ongoing.

Experimental

General Methods.

The synthesis of air and/or moisture sensitive compounds was carried out under an atmosphere of argon using Schlenk techniques or in nitrogen filled glovebox. Toluene, hexane, and THF were dried over Na/K alloy, transferred under vacuum, and stored in the glovebox. $[(\text{COT})\text{LnCl(THF)}]$ (Ln = Er, Dy, Y)$^{17}$, Li$(\text{C}_{5}\text{H}_{5}\text{BH})^{10}$, and Li$(\text{C}_{5}\text{H}_{5}\text{BNET}_{2})^{10}$ were prepared according to
literature procedures. \(^{1}\)H NMR and \(^{13}\)C NMR spectra were recorded on a VARIAN Mercury 400 MHz spectrometer at 400 MHz and 100 MHz, respectively. \(^{11}\)B NMR spectra were recorded on an Agilent 600 MHz spectrometer at 193 MHz. All chemical shifts were reported in \(\delta\) units with references to the residual solvent resonances of the deuterated solvents for proton and carbon chemical shifts, to external BF\(_3\)OEt\(_2\) for boron chemical shifts. Elemental analysis was performed by Analytical Laboratory of Shanghai Institute of Organic Chemistry. ICP analysis was performed by Analytical Instrumentation Center of Peking University.

**Li(C\(_5\)H\(_8\)BCH\(_3\)).** Li(C\(_5\)H\(_8\)BCH\(_3\)) \(^{18}\) was prepared by using Fu’s method. \(^{15}\) A solution of C\(_5\)H\(_8\)BPMMe\(_2\) (972 mg, 6.39 mmol) in 30 mL of ether was added by 3.0 M MeLi solution in DEM (DEM = diethoxymethylene) (2.1 mL, 6.30mmol) at -30 °C under stirring, and then the reaction mixture was gradually warmed to room temperature. After stirring for one hour at room temperature, the volatiles of reaction mixture were removed in vacuo. The residue was washed with 2 \(\times\) 10 mL of hexane and dried in vacuo to give Li(C\(_5\)H\(_8\)BCH\(_3\)) as a pale yellow solid (594 mg, 96% yield). \(^{1}H\) NMR (400 MHz, THF-d\(_2\)), 25 °C): \(\delta\) ppm) 7.06 (t, \(J_{CH-H} = 8.4\) Hz, 2H, 3-/5-/H), 6.25 (d, \(J_{CH-H} = 10.4\) Hz, 2H, 2-/6-/H), 5.96 (t, \(J_{CH-H} = 6.8\) Hz, 1H, 4-/H of Bz). 2.94 (bs, 4H, NC\(_2\)), 6.35 (d, \(J_{CH-H} = 7.2\) Hz, 2H, 3-/5-/H of Bz), 6.15 (s, 8H, H of COD), 5.35 (d, \(J_{CH-H} = 8.4\) Hz, 2H, 2-/6-/H of Bz), 5.02 (t, \(J_{CH-H} = 6.8\) Hz, 1H, 4-/H of Bz). 2.94 (bs, 4H, NCH\(_2\)), 1.07 (t, 3H, CH\(_3\)). \(^{11}\)B NMR (100 MHz, C\(_6\)D\(_6\)), 25 °C) : \(\delta\) = 135.3, 112.2, 100.9 (Bz-C), 94.03 (COD-C), 43.2 (NCH\(_2\)), 15.8 (NCH\(_3\)). \(^{13}\)C NMR (193 MHz, C\(_6\)D\(_6\)), 25 °C) : \(\delta\) = 30.1. Anal. Calc. (%) for C\(_{29}\)H\(_{28}\)B: C, 86.26, H, 6.80, N, 4.34. Found: C, 86.26, H, 6.80, N, 4.34.

**Li(C\(_5\)H\(_8\)BMe)Er(COT).** Li(C\(_5\)H\(_8\)BMe) (22 mg, 0.262 mmol) were mixed in 4 mL of THF at -35 °C, and the reaction mixture was stirred overnight at room temperature. The solvent was removed in vacuo, and the residue was extracted with 5 mL of toluene. The extraction was concentrated to ca. 2 mL and kept at -35 °C to give 2Er as orange crystals (52 mg, 57% yield). Anal. Calc. (%) for C\(_{34}\)H\(_{24}\)Er: C, 44.83, H, 4.05. Found: C, 44.49, H, 4.17.

**Li(C\(_5\)H\(_8\)BNe)Er(COT).** (2Er). (COT)ErCl(THF) (100 mg, 0.264 mmol) and Li(C\(_5\)H\(_8\)BMe) (26 mg, 0.265 mmol) were mixed in 4 mL of THF at -35 °C, and the reaction mixture was stirred overnight at room temperature. The solvent was removed in vacuo, and the residue was extracted with 5 mL of toluene. Evaporation of this filtrate in vacuo left an orange oil, which was extracted with 10 mL of hexane. The hexane extraction was concentrated to ca. 4 mL and kept at -35 °C to give 2Er as orange crystals (53 mg, 55% yield). Anal. Calc. (%) for C\(_{36}\)H\(_{26}\)ErN: C, 46.41, H, 4.45. Found: C, 46.23, H, 4.42.

**Li(C\(_5\)H\(_8\)BNe)Er(COT).** (3Er). Following the procedure described for 1. Reaction of (COT)ErCl(THF) (100 mg, 0.264 mmol) with Li(C\(_5\)H\(_8\)BNe) (40 mg, 0.258 mmol) gave 3Er as orange crystals (61 mg, 56% yield). Anal. Calc. (%) for C\(_{38}\)H\(_{28}\)ErN: C, 48.68, H, 5.53, N, 3.34. Found: C, 48.46, H, 5.46, N, 3.27.

**Li(C\(_5\)H\(_8\)BMe)Dy(OT).** (4Dy). Following the procedure described for 1. Reaction of [(COT)DyCl(THF)] (100 mg, 0.267 mmol) with Li(C\(_5\)H\(_8\)BMe) (23 mg, 0.274 mmol) gave 4Dy as yellow crystals (51 mg, 55% yield). Anal. Calc. (%) for C\(_{34}\)H\(_{28}\)Dy: C, 45.45, H, 4.11. Found: C, 44.91, H, 4.16.

**Li(C\(_5\)H\(_8\)BMe)Dy(OT).** (5Dy). Following the procedure described for 2. Reaction of [(COT)DyCl(THF)] (100 mg, 0.267 mmol) with Li(C\(_5\)H\(_8\)BMe) (26 mg, 0.265 mmol) gave 5Dy as yellow crystals (40 mg, 42% yield). Anal. Calc. (%) for C\(_{37}\)H\(_{30}\)Dy: C, 47.02, H, 4.51. Found: C, 46.97, H, 4.66.
The calculations employed the second order Douglas-Kroll-Hess Hamiltonian, where scalar relativistic contractions were taken into account in the basis set and the spin-orbit coupling was handled separately in the restricted active space state interaction (RASSI-SO) procedure. The active electrons in 7 active spaces include all f electrons (CAS(11 in 7) for complexes 1Er-3Er and CAS(9 in 7) for complexes 4Dy-6Dy) in the CASSCF calculation. To exclude all the doubts we calculated all the roots in the active space. We have mixed the maximum number of spin-free state which was possible with our hardware (all from 35 quadruplets and all from 112 doublets for three Er\(^{3+}\) fragments, all from 21 sextets, 128 from 224 quadruplets and 130 from 490 doublets for three Dy\(^{3+}\) fragments).

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Notes and references


