Investigation of the “bent sandwich-like” divalent lanthanide hydro-tris(pyrazolyl)borates \( \text{Ln(Tp}^\text{iPr}_2)_2 \) (\( \text{Ln} = \text{Sm, Eu, Tm, Yb} \))

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The discovery of the divalent lanthanide sandwich complexes \( \text{Ln(Tp}^\text{iPr}_2)_2 \) (\( \text{Ln} = \text{Sm, Eu, Tm, Yb} \)) has been completed by the synthesis of the hitherto unknown europium and ytterbium derivatives 2 and 4. Both compounds were prepared in high yields by treatment of \( \text{LnI}_2(\text{THF})_2 \) (\( \text{Ln} = \text{Eu, Yb} \)) with 2 equiv. of \( \text{KTP}^\text{iPr}_2 \) in a THF solution. Although the molecules are sterically highly congested, an X-ray diffraction study of bright red 4 revealed a similar bent B–Yb–B arrangement (151.1° and 153.9°), two independent molecules as in the previously investigated Sm(s) and Tm(s) complexes 1 and 3. An initial reactivity study showed a very different behavior with acetonitrile. While 2 and 4 proved to be unreactive toward acetonitrile, the more strongly reducing Sm(s) complex 1 yielded two new products. The major product was the dark green-black acetonitrile solvate \( \text{Sm}(\text{TP}^\text{iPr}_2)_2(\text{CH}_3\text{CN})_2 \) (5), while the second product, the colorless \( \text{TP}^\text{iPr}_2\text{Sm}(3,5\text{-diisopropylpyrazolate})_2(\text{NCCH}_3)_2 \) (6) with two 3,5-diisopropylpyrazolate ligands, resulted from oxidation of samarium to the trivalent state and degradation of a \( \text{TP}^\text{iPr}_2 \) ligand. Disappointingly, from the most reducing \( \text{Sm(s)} \) complex 3 only the ligand fragmentation product pyrazabole, \([\text{HB}(3,5\text{-iPr}_2\text{pz})_2]^-\) could be isolated and the fate of the Tm containing by-product(s) remains unknown. The new compounds 4–6 were structurally authenticated through single-crystal X-ray diffraction. The europium compound 2 shows an extremely bright yellow emission in solution, which can be observed also at daylight excitation, as well as in the solid state. The high intensity is even remarkable when compared to other Eu(s) containing materials. The photoluminescence was investigated with the conclusion that the rigidity of this complex is responsible for these outstanding luminescence properties.

1. Introduction

The discovery of the divalent lanthanide sandwich complexes \( \text{Ln(C}_5\text{Me}_5)_2 \) (\( \text{Ln} = \text{Sm, Eu, Yb} \); \( \text{C}_5\text{Me}_5 = \eta^5\text{-pentamethylycyclopentadienyl} \)) ca. 30 years ago sparked a firework of unprecedented reactivity and structures in organolanthanide chemistry.\(^{1,2}\) The exceptionally high reactivity of decamethylsamarocene, \( \text{Sm(C}_5\text{Me}_5)_2 \), even allowed the isolation of the first dinitrogen complex of an f-element, \( \text{[N}_2\text{]_2[Sm(C}_5\text{Me}_5)_2]_2 \),\(^{3}\) and still today novel reactions of decamethylsamarocene are being uncovered.\(^{4}\) A fascinating structural feature of the unsolvated lanthanide sandwich complexes \( \text{Ln(C}_5\text{Me}_5)_2 \) (\( \text{Ln} = \text{Sm, Eu, Yb} \)) is their bent metalocene structure in the solid state. This opens up the coordination sphere of the central lanthanide(s) ions and accounts for the high reactivity of these compounds. Various theoretical and spectroscopic studies have been carried out to fully understand the nature of this unexpected deviation from the normal linear sandwich structure (Scheme 1(a)). It is now generally accepted, based on computational studies, that the unusual bent sandwich structure of \( \text{Ln(C}_5\text{Me}_5)_2 \) (\( \text{Ln} = \text{Sm, Eu, Yb} \)) is the result of attractive dispersion/van der Waals interactions.\(^{5}\)

Trofimenko’s hydro-tris(pyrazolyl)borate ligands (“scorpionates”) have proven to be useful alternatives to the omnipresent cyclopentadienyl ligands.\(^{6,7}\) Like the cyclopentadienyls, these tridentate, monoanionic ligands can also be greatly varied in their steric bulk...
by changing the substituents in the 3- and 5-positions of the pyrazolyl rings. According to Trofimenko’s nomenclature, the abbreviation Tp stands for the ring-unsubstituted hydro-tris-(pyrazolyl)borate, whereas e.g. TpMe2 denotes the sterically more demanding hydro-tris(3,5-dimethylpyrazolyl)borate. The homoletic divalent lanthanide complexes Ln(TpMe2)2 (Ln = Sm, Eu, Yb) have been found to adopt a highly symmetrical, trigonal antiprismic molecular structure comprising a linear B...Ln...B arrangement (Scheme 1(b)).8–11 Apparently, this “sandwich-like” structure of Ln(C5Me5)2 is the result of the much larger cone angle of TpMe2 (239°) as compared to the C5Me5 ligand with 142°.12 Most recently, these studies have been extended to the even larger hydro-tris-(3,5-diisopropylpyrazolyl)borate ligand (TpIPr)13 It was possible to isolate homoletic complexes of this ligand with divalent samarium and thulium.14 Rather surprisingly, crystal structure determinations revealed a “bent sandwich-like” molecular structure like Ln(C5Me5)2 as shown in Scheme 1(c). Computational studies indicated that steric repulsion between the isopropyl groups forces the TpIPr ligands apart and permits the formation of unusual interligand C-H...N hydrogen-bonding interactions that help stabilizing the structure.14

Among the “classical” divalent lanthanide ions (Sm2+, Eu2+, Yb2+) only the homoletic samarium(II) TpIPr complex Sm(TpIPr)2 (1) has previously been prepared and fully characterized.14 In this article we report the synthesis and characterization of the corresponding divalent europium and ytterbium species Eu(TpIPr)2 (2) and Yb(TpIPr)2 (3) as well as the behavior of the full series of Ln(TpIPr)2 complexes toward acetonitrile, and the first results on the photoluminescence of compound 2.

2. Results and discussion

2.1 Synthesis and reactivity

The title compounds were prepared following the synthetic route outlined in Scheme 2. Similar to the recently reported preparation of the samarium(II) and thulium(II) congeners 1 and 3,14 reactions of EuI2(THF)2 and YbI2(THF)2 with 2 equiv. of KTpIPr were carried out in THF solutions at room temperature. Both reactions were accompanied by striking color changes to “neon-yellow” (Eu) or bright red (Yb), respectively, and formation of a white precipitate (KI). After removal of the potassium iodide by-product through filtration, the products could be readily extracted with n-pentane. Recrystallization from very concentrated solutions in n-pentane at −20 °C for 24 h afforded yellow Eu(TpIPr)2 (2) and bright red Yb(TpIPr)2 (4) in high yields (2: 83%, 4: 77%). Both new compounds were fully characterized by the usual combination of spectroscopic data and elemental analyses. While the 1H NMR spectrum of diamagnetic 4 showed the expected number of resonances for the TpIPr ligands, meaningful 1H and 13C NMR data for paramagnetic 2 could not be obtained, as noted also for Eu(C5Me5)2 and its derivatives,2e,9 and Eu(TpMe2,Et)2.10 In both cases, the 11B NMR spectra showed a single broad resonance (2: δ = −7 ppm (very broad), 4: δ = −6.2 ppm). Moreover, Yb(TpIPr)2 (4) was characterized by its 171Yb NMR spectrum. High-resolution 171Yb NMR spectroscopy is well established as a valuable tool for characterizing divalent (diamagnetic) ytterbium complexes in solution and in the solid state.15,16 171Yb resonances have been reported to encompass a chemical shift dispersion of some 3000 ppm (from ca. 6 to +2500 to −500 ppm).15c The 171Yb spectrum of 4 comprises a singlet at δ = 619.1 ppm. An almost identical value (δ = 614 ppm) has previously been reported for the ytterbium(n) bis(trimethylsilyl)amide complex Yb[N(SiMe3)2]2(OEt)2.15a

The recent structural characterization of 1 and its thulium congener 3 had already shown that these “bent sandwich-like” molecules are sterically highly congested. Thus for an initial reactivity study, the reagent acetonitrile was chosen in order to find out if a small, rod-like molecule such as CH3CN could enter the coordination sphere and bind to the central Ln2+ ions in 1–4. Surprisingly, no reaction with acetonitrile was observed.
for the europium and ytterbium complexes 2 and 4 even upon slight warming. Both complexes produced clear solutions in dry acetonitrile, from which they could be recovered unchanged by evaporation or cooling. In fact, acetonitrile appears to be a suitable solvent for recrystallizing bulk samples of 2 and 4. This is not the case for the Sm(II) and Tm(II) complexes 1 and 3. Unexpectedly, and curiously the Sm(II) complex is virtually insoluble in acetonitrile. Addition of acetonitrile to solid 1 produces an almost colorless supernatant and a very dark green, almost black solid. The latter was shown to be unchanged Sm(TpPr2)2 by 1H NMR spectroscopy. To study the behavior of Sm(TpPr2)2 toward acetonitrile, acetonitrile was added to a dark green solution of 1 in diethyl ether. Concentration of the solution by slow evaporation at RT in the dry-box resulted in the formation of two types of crystals, dark green and colorless; the former was shown to be SmII(TpPr2)2·CH3CN (5), with a solvate molecule of CH3CN in the lattice, while the latter proved to be the partially ligand fragmented Sm(III) complex, (TpPr2)·SmIII(3,5-iPr2pz)2(NCCH3) (6), with a coordinated NCCH3 ligand. The most reducing Tm(II) complex 3 dissolved in acetonitrile and gave a dark, plum-red solution which slowly bleached with time, indicating oxidation of Tm(II) to Tm(III). Multiple attempts to grow crystals from various solvent mixtures only resulted in the formation of colorless blocks which were shown, by X-ray diffraction,
to be the pyrazabole derivative [HB(3,5-iPr2Pz)]2 (7). No thulium-containing product could be isolated. Scheme 3 summarizes the results of this initial reactivity study of 1–4 toward acetonitrile.

2.2 X-ray crystallography

The new compounds 4–6 were structurally authenticated through single-crystal X-ray diffraction. Bright red X-ray quality single-crystals of 4 were obtained by cooling a very concentrated solution in n-pentane to −20 °C, whereas single crystals of both 5 (green) and 6 (colorless) were obtained from the reaction of 1 with acetonitrile in diethyl ether according to Scheme 3. The single-crystals of 4 were found to contain one molecule of n-pentane per formula unit. Crystallographic data of 4–6 are listed in Table 1. The molecular structure of the Yb complex, with numbering scheme, is shown in Fig. 1. Just like the Sm and Tm compounds 1 and 3, the ytterbium(II) complex Yb(Tp-iPr2)2 also exhibits the “bent sandwich-like” geometry, and indeed the compound is isomorphous with the Tm analogue and contains two independent molecules per asymmetric unit. The B–Yb–N angles in the two independent molecules are 151.1° and 153.9°, respectively. This can be favorably compared to the B–Ln–B angles of 150.1° in the samarium(II) analogue 1 and 152.2° in Tm(Tp-iPr2)2 (3).14 As expected from the nearly identically sized Yb(II) and Tm(II) ions,17 the Ln–N distances in 3 and 4 are nearly identical and the bond angles and torsional angles are similar as well (cf. Table S1 in the ESI†).

The structure of the Sm(II) compound Sm(II)(Tp-iPr2)2(CH3CN)5, obtained by crystallization from CH3CN/Et2O, is shown in Fig. 2, and Fig. 3 shows the packing diagram. The lattice acetonitrile is just a solvate as the distance between Sm and N15 is over 6 Å, thus this is no bonding contact between Sm and NCCH3 molecule. As opposed to the crystals obtained from pentane, in this case there is only one molecule per asymmetric unit. Nevertheless, the geometry is still “bent sandwich-like” and the B1–Sm–B2 angle of 151.19(5)° is very similar to the 150.1° in the previously reported structure of Sm(II)(Tp-iPr2)2,14 demonstrating once again that the bent geometry is an inherent molecular feature of all divalent Ln(Tp-iPr2)2 complexes and is not due to crystal packing effects. However, the latter may have some subtle effect since the Sm–N32 distance of 2.735(2) Å is longer that the 2.655(6) Å seen before and the torsion angle of this pyrazolyl moiety is also large, Sm–N32–N31–B1 = 62.4(2)°, as opposed to the 20° average observed before.14

The molecular structure of the oxidized product (Tp-iPr2)Sm-(3,5-iPr2Pz)2(NCCH3) (6) is shown in Fig. 4, with important bond distances and angles also listed in the figure caption.

![Fig. 1. Molecular structure of Yb(Tp-iPr2)2 (4). Selected bond lengths (Å) and angles (°), molecule 1: Yb1–N12 2.528(2), Yb1–N22 2.530(2), Yb1–N32 2.550(2), Yb1–N42 2.487(2), Yb1–N52 2.589(2), Yb1–N62 2.478(2), B1–Yb1–B2 151.1. Molecule 2: Yb2–N12 2.525(2), Yb2–N22 2.522(2), Yb2–N32 2.528(2), Yb2–N42 2.498(2), Yb2–N52 2.540(2), Yb2–N62 2.502(2), B3–Yb2–B4 153.9.](#)

![Fig. 2. Molecular structure of Sm(II)(Tp-iPr2)2(CH3CN)5 (5). Color code: Sm red, Tp-iPr2 dark blue, CH3CN green.](#)

![Fig. 3. Packing diagram of Sm(II)(Tp-iPr2)2(CH3CN)5 (5).](#)

![Fig. 4. Molecular structure of (Tp-iPr2)Sm-(3,5-iPr2Pz)2(NCCH3) (6). Color code: Sm red, Tp-iPr2 dark blue, NCCH3 green.](#)

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**Table 1** Crystallographic data for 4–6

|    | 4                                      | 5                                      | 6                                      |
|----|----------------------------------------|----------------------------------------|----------------------------------------|
| **Empirical formula** | C59H104B2N12Yb                          | C56H95B2N13Sm                          | C58H98BN11Sm                           |
| **a (Å)** | 13.44670 (10)                           | 12.9942 (10)                           | 13.9188 (9)                            |
| **b (Å)** | 20.6731 (2)                             | 20.9744 (16)                           | 21.9614 (15)                           |
| **c (Å)** | 25.1841 (2)                             | 21.9614 (15)                           | 20.6731 (2)                            |
| **α (°)** | 83.2050 (10)                            | 90                                     | 104.2666 (8)                           |
| **β (°)** | 74.7430 (10)                            | 175.6405 (7)                           | 94.8690 (8)                            |
| **γ (°)** | 77.6100 (10)                            | 115.6405 (7)                           | 116.5405 (7)                           |
| **V (Å³)** | 6582.53 (10)                            | 3167.5 (4)                             | 3167.5 (4)                             |
| **Z** | 4                                      | 2                                      | 2                                      |
| **Formula weight** | 1176.20                                 | 1122.41                                | 959.37                                 |
| **Space group** | P1                                      | P1                                      | P21/n                                  |
| **T (°C)** | −173                                    | −100                                    | −80                                     |
| **μ (mm⁻¹)** | 1.187                                   | 1.177                                   | 1.239                                   |
| **Dcalcd (g cm⁻³)** | 0.71073                                 | 0.71073                                 | 0.71073                                 |
| **Data/restraints/parameters** | 39 188/0/1345                           | 14 330/0/658                           | 12 276/0/542                           |
| **Goodness-of-fit on F²** | 1.028                                    | 1.051                                   | 1.024                                   |
| **R (F₀ or Fm)²** | 0.0363                                  | 0.0271                                  | 0.0287                                  |
| **Rw (F₀ or Fm)²** | 0.0689                                  | 0.0678                                  | 0.0715                                  |
The coordination sphere of the Sm(III) center is defined by a classical \( \kappa^3\)-TpiPr\(_2\) ligand, two almost symmetrically bonded \( \kappa^2\)-pyrazolides and N1-bound acetonitrile. The coordination geometry can be roughly described as distorted octahedral, with N12, N22 and mid-points of N41N42 and N51N52 occupying the equatorial and N32 and N1 the axial positions (N32–Sm–N1 = 143.20(6)). As expected, the Sm–N distances to the anionic \( \kappa^2\)-pyrazolides (2.40 Å ave) are shorter than those to the \( \kappa^3\)-TpiPr\(_2\) ligand (2.560 Å ave), which in turn is shorter than the Sm–NCCCH\(_3\) distance of 2.601 Å. The Sm–N(\( \kappa^3\)-TpiPr\(_2\)) distances are shorter than those in Sm(\( \kappa^3\)-TpiPr\(_2\))(1), reflecting the smaller size of Sm(III) compared to Sm(II) and also the more congested nature of the latter complex. That steric still have an influence on the arrangement of the ligands in complex 6 is shown by the less than 180° of the Sm–N1–C1 angle (159.2(2)), the bending being away from the iPr substituent of the two \( \kappa^2\)-pyrazolide ligands.

2.3 Luminescence study of Eu(\( \kappa^3\)-TpiPr\(_2\))(2)

In general, the luminescence behaviour of divalent lanthanides is very different compared to that of the trivalent ones due to two main reasons. On the one hand, the position of the excited \( 4f^{n-1}5d^1 \) states relative to the \( 4f^n \) ground state is strongly influenced by the environment and, thus, variable over a wide spectral range. On the other hand, the respective \( 4f^n \rightarrow 4f^{n-1}5d^1 \) transitions are parity allowed leading to an intense emission in the most cases.\(^{18}\) Due to these advantages the most stable divalent ion, Eu\(^{2+}\), is mostly used in modern materials for applications, like LED phosphors, displays and medical markers.\(^{19}\) While the luminescence properties of Eu\(^{2+}\) ions doped in ionic compounds, especially the structure–luminescence-relationship, is well investigated,\(^{20}\) such investigations of molecular complexes are rather scarce. A notable example is the strong luminescence exhibited by Eu(Cp\(_{BnG}\))\(_2\) (Cp\(_{BnG}\) = C\(_5\)(C\(_6\)H\(_4\)Bu-4))\(_2\).\(^{21}\) In this contribution we present first results on the photoluminescence behavior of compound 2. It was found that Eu(\( \kappa^3\)-TpiPr\(_2\))(2) shows extremely bright yellowish-green luminescence upon UV irradiation at room temperature in the solid state as well as in n-pentane solution, which can be also observed by daylight-excitation (Fig. 5). Fig. 6 shows the luminescence of solid 2 under UV light.

The photoluminescence emission and excitation spectra of this compound are depicted in Fig. 7. The shape and position are typical for Eu(n) photoluminescence, so that it is obvious that Eu\(^{2+}\) is the only emitting species. The broad (FWHM = 2245 cm\(^{-1}\)) slightly asymmetric emission band

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Fig. 2 Molecular structure of Sm\( ^{II} \)(TpiPr\(_2\))\(_2\)-CH\(_3\)CN (5). Selected bond lengths (Å) and angle (°): Sm–N12 2.642(2), Sm–N22 2.638(2), Sm–N32 2.735(2), Sm–N42 2.631(2), Sm–N52 2.661(2), B1–Sm–B2 151.2.

Fig. 3 Crystal packing diagram of Sm\( ^{II} \)(TpiPr\(_2\))\(_2\)-CH\(_3\)CN (5).

Fig. 4 Molecular structure of (TpiPr\(_2\))Sm\( ^{III} \)(3,5-iPr\(_2\)pz)(NCCCH\(_3\)) (6). Selected bond lengths (Å) and angles (°): Sm–N1 2.601(2), Sm–N12 2.574(2), Sm–N22 2.571(2), Sm–N32 2.536(2), Sm–N41 2.379(2), Sm–N42 2.420(2), Sm–N51 2.384(2), Sm–N52 2.409(2), N1–Sm–N32 143.20(6), Sm–N1–C1 159.2(2).
peaking at 552 nm (18 120 cm⁻¹) can be assigned to the parity-allowed 4f⁶5d¹ → 4f⁷ transition of Eu(II). Its position is in very good agreement with the emissions reported for EuTp₂, and Eu(II)-activated nitridosilicates, in which Eu(II) is also coordinated by N-based ligands in its first coordination sphere. A ligand-to-metal charge transfer (LMCT) induced luminescence as suggested for EuTp₂ is excluded due to the high excitation wavelength of 450 nm (22 220 cm⁻¹) used for the detection of the emission spectrum of Eu(Tp iPr₂)₂ (2). The π → π* transitions of the pyrazole units leading to a LMCT are typically located in the range of 220 nm and thus beyond the range of measurable wavelengths of the used spectrometer.

The photoluminescence excitation spectrum reveals the presence of a raw fine structure that is characteristic for the ⁷F_J levels arising from the 4f⁶ core of the excited 4f⁶5d¹ configuration assuming a weak Coulomb interaction between the 4f and 5d electrons and rarely observed. This feature is another evidence for the presence of Eu(II) in the compound and justifies the assignment of the respective emissive transition. Moreover, the emission does not change with different excitation energies (320–480 nm), which is another evidence that the whole excitation band is originated by Eu(II). From the photoluminescence spectra of compound (2), the Stokes shift was estimated with 2830 cm⁻¹. Both the Stokes shift and the FWHM of the emission band are relatively low for a molecular compound and close to values known for Eu(II)-activated ionic compounds. This can be explained by the rigidity of the very bulky tripodal Tp iPr₂ ligands that do not allow a large change in metal–ligand distances upon excitation of the complex. An indication that this argument is correct is the even smaller Stokes Shift of Eu(CpBIG)₂ (2140 cm⁻¹), where a large degree of rigidity can be assumed too.

3. Conclusions

In summarizing the work reported here, the series of homoleptic lanthanide(II) hydro-tris(pyrazolyl)borate complexes Ln(Tp iPr₂)₂ (Ln = Sm (1), Eu (2), Tm (3), Yb (4); Tp iPr₂ = hydro-tris(3,5-diisopropylpyrazolyl)borate) has been completed by the high-yield synthesis of the hitherto unknown europium and ytterbium derivatives 2 and 4. A single crystal X-ray diffraction study of the ytterbium derivative 4 revealed the same "bent sandwich-like" structure as was previously found for the Sm and Tm compounds 1 and 3. This finding confirmed that the bent geometry is an inherent structural feature of the Ln(Tp iPr₂)₂ complexes. An initial reactivity study toward acetonitrile revealed a significant increase in reactivity in the sequence Eu < Yb < Sm < Tm. The Eu (2) and Yb (4) compounds did not react with acetonitrile even upon heating. The Sm(II) complex 1 afforded the dark green acetonitrile solvate SmII(Tp iPr₂)₂(CH₃CN) (5) in addition to the partially ligand fragmented Sm(II) complex, (Tp iPr₂)SmIII(3,5-iPr₂pz)(NCCH₃) (6). The most reducing thulium(II) complex 3 only yielded ligand fragmented pyrazabole and unidentified Tm(II) species. Despite the opening of the coordination sphere in the "bent sandwich-like" Ln(Tp iPr₂)₂ complexes, apparently not even rod-like donor ligands such as CH₃CN are able to enter the coordination sphere of the central Ln²⁺ ions. Together with the previous studies on the "linear" homoleptic Ln(II) complexes Ln(TpMe₂)₂ these results clearly
demonstrate that there is an intricate balance between stability and reactivity of such homoleptic lanthanide(II) tris(pyrazolyl)borate complexes. While the smaller Tp(Me2) provided versatile reactivity to the Sm(Tp(Me2))3 complex, it could only produce a thermally very sensitive Tm(Tp(Me2))2. In contrast, the very bulky Tp(iPr2) ligand stabilizes Tm(iPr2), but hinders reactivity. Photoluminescence studies on Eu(Tp(iPr2))2 at room temperature revealed an exceptionally intense yellow emission at 552 nm (18120 cm⁻¹, FWHM = 2245 cm⁻¹, Stokes shift = 2830 cm⁻¹) under excitation at 450 nm that can be assigned to a parity-allowed 4f⁵5d¹ → 4f⁻⁵ transition of Eu(iPr2) in the complex, supporting the sole presence of the divalent lanthanide. An intense emission is also observable at sunlight excitation. The luminescence characteristics are comparable to the values known from N-coordinated Eu(iPr2) in ionic compounds, and indicates that the Tp(iPr2) ligands provide a rigid coordination environment to the Eu(iPr2) center.

4. Experimental section
4.1 General procedures
All operations were performed with rigorous exclusion of air and water in oven-dried or flame-dried glassware under an inert atmosphere of dry argon, employing standard Schlenk, high-vacuum and glovebox techniques (MBraun MBLab: <1 ppm O₂, <1 ppm H₂O or Vacuum Atmosphere, model HE-553-2). THF, diethyl ether, and n-pentane were dried over sodium/benzophenone and freshly distilled under nitrogen atmosphere prior to use. Acetonitrile was dried over calcium hydride. All operations were performed with rigorous exclusion of air, employing standard Schlenk, high-vacuum and glovebox techniques (MBraun MBLab: <1 ppm O₂, <1 ppm H₂O or Vacuum Atmosphere, model HE-553-2).

4.2 Preparation of Eu(Tp(iPr2))2 (2)
Solid Eu₃(THF)₂ (1.73 g, 3.16 mmol) was added to a stirred solution of KTp(iPr2) (3.2 g, 6.33 mmol) in 150 ml of THF. Stirring at r.t. was continued for 24 h to give a “neon-yellow”, strongly fluorescent solution and a white precipitate (KI). After filtration and evaporation of the clear, yellow filtrate to dryness, the residue was extracted with n-pentane (80 ml) and filtered again. The filtrate was concentrated in vacuo to a total volume of ca. 25 ml. Cooling to −20 °C for 3d produced bright yellow crystals of 2. Yield: 2.84 g (83%). Decomposition range: 78−84 °C. Anal. calc. for C₅₄H₉₂B₄EuN₁₂ (1082.99 g mol⁻¹): C, 59.89; H, 8.56; N, 15.52. Found: C, 59.39; H, 8.31; N, 14.98. IR (KBr): ν_max = 3222m, 3103m, 2964vs, 2930s, 2871s, 2552w, 2471w, 2240w, 1959w, 1638m, 1567m, 1535m, 1486s, 1427m, 1381s, 1367s, 1300s, 1253m, 1174s, 1138m, 1105m, 1073m, 1050s, 1009m, 991m, 959w, 924w, 897w, 879w, 791s, 771m, 724m, 717m, 663m cm⁻¹. MS (EI): m/z 988 (7%), 935 (6), [M – px(iPr2)] 768 (100), [Tp(iPr2)Eu + px(iPr2)], 616 (88), [Tp(iPr2)Eu], 477 (40), [Tp(iPr2) + BH], 302 (23). ¹¹B NMR (300 K, C₆D₆, 128 MHz): δ = −7 (v, br).

4.3 Preparation of Yb(Tp(iPr2))2 (4)
In a similar manner as described for 2, the reaction of YbI₃(THF)₂ (1.69 g, 2.96 mmol) with KTp(iPr2) (3.0 g, 5.93 mmol) in 80 ml THF afforded, after crystallization from n-pentane and thorough drying to remove residual n-pentane, bright red crystalline 4 in 77% isolated yield (2.51 g). Mp. 99 °C (beginning dec.). Anal. calc. for C₅₃H₉₂B₂EuN₁₂ (1104.07 g mol⁻¹): C, 58.75; H, 8.40; N, 15.22. Found: C, 58.33; H, 8.10; N, 14.88. IR (KBr): ν_max = 3222m, 3092m, 2966vs, 2931s, 2870s, 2555m, 2237w, 1959w, 1638s, 1566m, 1538s, 1470s, 1426m, 1381s, 1368s, 1298s, 1237m, 1175s, 1138m, 1106m, 1053s, 1020m, 960w, 924w, 896w, 878w, 794s, 725m, 717m, 661m cm⁻¹. MS (EI): m/z 996 (7%), 968 (8), 953 (6), [M – px(iPr2)] 817 (28), 790 (100), [Tp(iPr2)Yb + px(iPr2)], 637 (6), [Tp(iPr2)Eu], 476 (9), [Tp(iPr2) + BH], 321 (14), [Yb(THF)₃], 169 (19), 147 (25). ¹H NMR (300 K, C₆D₆, 400 MHz): δ = 5.93 (s, 6H, pyrazolyl), 5.22 (s br, 2H, B–C), 3.73 ppm (d, 9H, pyrazolyl), 97.5 (C₃ pyrazolyl), 1368 (C–H iPr), 24.8 (2H, C–H iPr), 23.8 (2H, C–H iPr), 171Yb (300 K, C₆D₆, 70 MHz, relative to [Yb(η⁵-C₅Me₅)(THF)]²⁻): δ = 619.1. ¹¹B NMR (300 K, C₆D₆, 128 MHz): δ = −6.2 (v, br).

4.4 Behavior of Sm(Tp(iPr2))₃ (1) toward acetonitrile
Addition of acetonitrile (2–3 ml) to ca. 200 mg of Sm(Tp(iPr2))₃ (1) produced an almost colorless supernatant and a dark green, almost black solid (unchanged Sm(iPr2)). The supernatant was pipetted off and the solid dissolved in Et₂O to give a very dark green solution, to which acetonitrile was again added. An attempt to grow crystals by cooling at −30 °C was unsuccessful. The dark green solution was left to slowly evaporate at RT, and overnight deposited a mixture of dark green and colorless crystals. The supernatant was removed and the mixture of crystals
briefly dried. From this mixture a dark green and a colorless crystal were selected and, by X-ray diffraction, were shown to be complexes 5 and 6, respectively.

4.5 X-ray crystallographic studies of 4–6

The intensity data of 4 were registered on an Oxford Diffraction Nova A diffractometer using mirror-focussed CuKα radiation. Absorption correction was applied using the multi-scan method. The structure was solved by direct methods (SHELXS-97) and refined by full matrix least-squares methods on F² using SHELXL-97. Intensity data for 5 and 6 were collected on a Bruker D8/APEX II CCD diffractometer using graphite-monochromated MoKα radiation. Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker. Absorption corrections were applied using the Gaussian integration (face-indexed) method. The structures were solved and refined using the programs SHELXT and SHELXL-2013. Data collection parameters for 4–6 are given in Table 1.

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