ORGANOMETALLICS

Synthesis and Characterization of Paramagnetic Lanthanide Benzyl **Complexes**

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S Supporting Information



ABSTRACT: The organometallic chemistry of paramagnetic lanthanides (Ln, from Ce to Yb) is far less developed compared to that of their diamagnetic counterparts (Sc, Y, La, and Lu). Lack of available starting materials and characterization methods are the major obstacles. Herein we report the synthesis and characterization of trisbenzyl complexes of neodymium, gadolinium, holmium, and erbium. In addition, we introduce a direct procedure for the synthesis of lanthanide benzyl and iodide complexes supported by a ferrocene diamide ligand starting from the corresponding oxides. All newly synthesized compounds were characterized by X-ray crystallography, ¹H NMR spectroscopy (except for gadolinium compounds, which were NMR silent), and elemental analysis.

INTRODUCTION

The organometallic chemistry of lanthanides not only uncovers rich reactivity but also provides new opportunities for their applications ranging from catalysis to materials.¹ Among organometallic lanthanide complexes, those of scandium, yttrium, lanthanum, and lutetium are studied far more in detail than those of the other rare-earth metals due to their diamagnetic nature, which facilitates characterization by nuclear magnetic resonance (NMR) spectroscopy. All other lanthanides, except for Ce(IV) and Yb(II), have unpaired 4f electrons, which complicate the characterization of their complexes by ¹H and ¹³C NMR spectroscopy. Since the chemical properties of lanthanides depend heavily on the ionic radii of the M(III) ions, it is necessary to fill the knowledge gap between lanthanum and yttrium in order to carry out reactivity studies. Unpaired 4f electrons contribute to the interesting properties and applications of lanthanides. For example, lanthanide luminescence utilizes the 4f-4f core shell transfer and is increasingly important in various industrial and medical applications.^{2,3} The magnetic properties of paramagnetic lanthanides form another area of interest.⁴ Neodymium magnets and samarium-cobalt magnets are some of the strongest permanent magnets currently known.^{5,6} However, the lack of well defined paramagnetic lanthanide starting materials restricts the design and synthesis of new classes of metal complexes.

Lanthanide trisalkyl complexes are the most commonly used starting materials for organometallic rare-earth chemistry.7 Methyl, benzyl, and trimethylsilylmethyl are among the most commonly employed alkyl groups. The synthesis of lanthanide trisalkyl complexes is usually achieved by the salt metathesis between lanthanide halides and alkali metal alkyl reagents. Although this route has been successfully applied to various compounds, there are still some lanthanide trisalkyl complexes that have not been isolated and/or structurally characterized. This may be attributed to the Schlenk-type equilibrium occurring between the lanthanide trisalkyl complexes and the mixed alkyl halides while in the presence of an alkali metal halide in solution.⁸ By introducing N-chelating benzyl ligands, the isolation of trisalkyl complexes was possible for almost all lanthanides despite their ionic size difference.9-11 In another approach, lanthanide trisalkyl complexes were generated in situ and then protonated by amines or alcohols to form mono- or bisalkyl lanthanide complexes supported by various ancillary ligands.^{8,12-14} Herein we report the syntheses and characterization of four paramagnetic lanthanide trisbenzyl complexes (Nd,¹⁵ Gd, Ho, and Er). We also developed an *in situ* method to synthesize benzyl and iodide complexes supported by a

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ferrocene diamide ligand directly from $MX_3(THF)_y$ (X = Cl, Br) for all four metals. Further contributing to the applicability of these starting materials, all metal halides were prepared from the less expensive corresponding oxides.

RESULTS AND DISCUSSION

Our lab has focused on studying diamagnetic rare-earth metal chemistry for several years.^{16–33} We successfully introduced a series of ferrocene-based diamide ligands on scandium, yttrium, lanthanum, and lutetium by using a protonation reaction between the corresponding 1,1'-ferrocene diamine and M- $(CH_2Ar)_3(THF)_x$ (for M = Sc and Lu, Ar = 3,5-C₆H₃(CH₃)₂ and x = 2; for M = Y and La, Ar = C₆H₅ and x = 3).^{31,32} M(CH₂Ar)₃(THF)_x was synthesized from KCH₂Ar and MX₃(THF)_y (for M = Sc, X = Br, y = 2.5; for M = La, X = Br, y = 4; for Ln = Y, X = Cl, y = 3.5; for M = Lu, X = Cl, y = 3),^{31,32,34} where each metal halide was obtained from the less expensive corresponding oxide (Scheme 1).^{31,35,36} In practice, we noticed that the syntheses of M(CH₂Ar)₃(THF)_x from MX₃(THF)_y are not always successful and that they suffer from low reproducibility.



We found that the purity of $MX_3(THF)_v$ when obtained from M_2O_3 was critical to the synthesis of $M(CH_2Ar)_3(THF)_x$. In addition, the choice of halide and benzyl derivative was also important. For example, $ScCl_3(THF)_{1.5}$ is a good precursor for $Sc(CH_2Ph)_3(THF)_3$ but not for $Sc(CH_2C_6H_3Me_2-3,5)_3(THF)_2$. With the corresponding bromide the situation is reversed, where $ScBr_3(THF)_2$ is a good precursor for $Sc(CH_2C_6H_3Me_2-3,5)_3(THF)_2$ but not for $Sc-(CH_2Ph)_3(THF)_3$. The reason behind this difference is not clear to us and does not apply to all lanthanides (for example, $LaBr_3(THF)_4$ is a good precursor for $La(CH_2Ph)_3(THF)_3$). Surprisingly, despite the large difference in ionic size of the four diamagnetic lanthanides (Sc, Y, La, and Lu), a similar synthetic protocol was successfully used to isolate all $M(CH_2Ar)_3(THF)_x$ species.

Therefore, we applied the optimized protocol to four paramagnetic lanthanides, neodymium, gadolinium, holmium, and erbium, which represent large, medium, and small rareearth metals. The four lanthanides showed somewhat different behavior in the synthesis of $MX_3(THF)_y$ from the corresponding oxides. We previously noticed that the conversion of the oxide to the halide can be evaluated by transforming the solvent-free halide into its tetrahydrofuran (THF) adduct and determining the amount of THF incorporated.³¹ Following the same protocol (Scheme 1), neodymium was found to form $NdCl_3(THF)_{2.5}$, while gadolinium, holmium, and erbium were found to form $MCl_3(THF)_{3.5}$. The number of coordinating THF molecules was calculated based on the yield of the $MCl_3(THF)_y$ synthesis by assuming that the entire mass of MCl_3 was transformed into $MCl_3(THF)_y$ (see the Supporting Information for details).

The corresponding Ho and Er trisbenzyl complexes were synthesized from the THF adducts $MCl_3(THF)_{3.5}$ (eq 1).

Holmium trisalkyl complexes were previously isolated only with an N-chelating benzyl ligand,⁹ although the corresponding trisphenyl complex is known.³⁷ The erbium trisneosilyl complex was reported by two groups but without structural characterization,^{38,39} while $\text{ErPh}_3(\text{THF})_3$ was isolated and structurally characterized.⁴⁰ Both Ho and Er complexes gave pink crystals upon recrystallization. The two compounds were identified as $\text{HoBn}_3(\text{THF})_3$ and $\text{ErBn}_3(\text{THF})_2$ by X-ray crystallography (Figures 1 and 2). The erbium complex was



Figure 1. Molecular structure of $HoBn_3(THF)_3$ with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms were omitted for clarity. Selected distances [Å] and angles [deg]: Ho1–C13 2.457(2), Ho1–C20 2.443(3), Ho1–C27 2.453(2), Ho1–O1 2.410(1), Ho1–O2 2.433(2), Ho1–O3 2.401(1), C13–C14 1.470(3), C20–C21 1.465(3), C27–C28 1.470(3), O1–Ho1–O3 78.90(5), O2–Ho1–O3 77.01(5), O1–Ho1–O2 80.33(6), C13–Ho1–C20 92.71(10), C20–Ho1–C27 91.13(9), C27–Ho1–C13 96.26(8), O3–Ho1–C27 166.4(1), O1–Ho1–C20 170.1(1), O2–Ho1–C13 172.1(1).

also characterized as $\text{ErBn}_3(\text{THF})_3$, which was crystallized from a different solvent system; $\text{ErBn}_3(\text{THF})_3$ is isostructural to $\text{HoBn}_3(\text{THF})_3$ (see the Supporting Information for details).

 $HoBn_3(THF)_3$ is the first isolated and structurally characterized trisalkyl complex of holmium that does not incorporate the alkyl into a chelating ligand,⁹ while $ErBn_3(THF)_2$ is the first structurally characterized erbium trisalkyl complex.⁹ $HoBn_3(THF)_3$ is isostructural to $YBn_3(THF)_3$.⁹ The holmium atom adopts an octahedral coordination environment with a facial arrangement of the three benzyl groups and three THF



Figure 2. Molecular structure of $ErBn_3(THF)_2$ with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms were omitted for clarity. Selected distances [Å] and angles [deg]: Er1-C1 2.434(2), Er1-C2 2.902(2), Er1-C8 2.416(2), Er1-C15 2.437(2), Er1-O1 2.325(1), Er1-O2 2.311(2), C1-C2 1.461(2), C8-C9 1.468(2), C15-C16 1.472(3), O1-Er1-O2 177.51(4), O1-Er1-C1 87.27(6), O2-Er1-C1 90.82(6), C1-Er1-C8 121.34(6), C1-Er1-C15 124.48(6), C8-Er1-C15 114.12(6), Er1-C1-C2 92.9(1).

ligands, with $\angle O$ -Ho-O ranging from 77.0(1)° to 80.3(1)° and $\angle C$ -Ho-C ranging from 91.1(1)° to 96.3(1)°. The value for \angle Ho-CH₂-C_{ipso} is found from 108.5(1)° to 122.3(1)°, while the long distance of $Ho-C_{ipso}$ between 3.33(1) and 3.45(1) Å indicates that all three benzyl groups coordinate in an η^1 fashion. Single crystals of ErBn₃(THF)₂ were obtained from a toluene solution layered with hexanes, resulting in the loss of one coordinating THF molecule. A similar phenomenon (loss of one THF) was observed when triturating MBn₃(THF)₃ (M = Sc and Lu) in toluene.⁷ The erbium atom adopts a pseudotrigonal bipyramidal coordination mode with two THF ligands occupying the two axial positions and the three benzyl groups on the trigonal plane. The angle $\angle O-Er-O$ of $177.5(1)^{\circ}$ indicates linearity. The angles $\angle C-Er-C$ ranging from $114.1(1)^{\circ}$ to $124.5(1)^{\circ}$ indicate a triangular geometry, while their sum of $359.9(3)^{\circ}$ indicates the coplanarity of the three benzylic carbon atoms and the erbium atom. Due to the loss of one THF ligand, one of the benzyl groups coordinates in an η^2 fashion through both the benzylic carbon and the ipsocarbon atom. The small angle $\angle \text{Er}-\text{CH}_2-\text{C}_{ipso}$ of 92.9(1)° compared to the other two $\angle \text{Er}-\text{CH}_2-\text{C}_{ipso}$ of 111.3(1)° and 114.8(1)° and the short $Er-C_{ipso}$ distance of 2.902(2) Å compared to the other two $Er-C_{ipso}$ distances of 3.274(1) and

3.311(1) Å support the η^2 coordination mode of that benzyl group.⁴¹

When the same protocol was followed for Nd, only a dark green oil was obtained and crystals could not be isolated. For Gd, oily blocks could be isolated, but elemental analysis indicated that the solid is likely a mixture of halide-benzyl species. Recrystallization attempts did not result in isolable crystals or solid material.

Interestingly, NdBn₃(THF)₃ was previously synthesized from NdBr₃(THF)_{3.5} and structurally characterized.¹⁵ In addition, another large-lanthanide trisbenzyl complex, LaBn₃(THF)₃, was also obtained from the corresponding bromide,³⁴ so we attempted the synthesis of neodymium and gadolinium trisalkyl complexes from the metal bromides instead of the chlorides. The preparation of $NdBr_3(THF)_4$ and $GdBr_3(THF)_{3.5}$ was similar to the preparation of other lanthanide halides (Scheme 1). Applying the standard protocol and using 3 equiv of KBn, NdBn₃(THF)₃ and GdBn₃(THF)₃ were successfully synthesized in good yield, 66% and 46%, respectively. Single crystals for both compounds were obtained from a THF solution layered with hexanes. A unit cell determination for NdBn₃(THF)₃ led to the previously reported metrical parameters.¹⁵ GdBn₃(THF)₃ was found to be isostructural to $HoBn_3(THF)_3$ and $ErBn_3(THF)_3$. Both metal trisalkyl complexes were characterized by elemental analysis. NdBn₃(THF)₃ was further characterized by ¹H and ¹³C NMR spectroscopy. It is worth mentioning that, similar to holmium, GdBn₃(THF)₃ is the first isolated and structurally characterized trisalkyl complex of gadolinium that does not incorporate the alkyl into a chelating ligand.9

Since the isolation of trisbenzyl complexes may be complicated, we also looked into synthesizing these complexes *in situ*. Previous reports indicate that such compounds may be generated in this fashion and then protonated by a more acidic ligand, such as an amine or an alcohol, to form isolable monoalkyl or bisalkyl complexes.^{8,12–14} A similar method was also applied to obtain uranium bisalkyl complexes supported by a 1,1'-ferrocene diamide ligand in our lab.⁴² Therefore, we decided to employ the *in situ* method to find out whether (NN^{fc})MBn(THF) and (NN^{fc})MI(THF)_z (NN^{fc} = 1,1'-fc(NSi^tBuMe₂)₂, fc = ferrocenediyl; M = Nd, z = 1; M = Gd, Ho, and Er, z = 2) could be generated.

Starting from the THF adducts of metal chlorides and using the *in situ* procedure to generate $MBn_3(THF)_3$, 0.8 equiv (calculated based on the metal) of $H_2(NN^{fc})$ was added (Scheme 2). Following a workup procedure, $(NN^{fc})MBn-(THF)$ could be isolated in good yield (47–76%, calculated based on amine). The isolation of $(NN^{fc})MBn(THF)$, however, was not necessary in order to proceed to the synthesis of $(NN^{fc})MI(THF)_z$: a toluene solution of 1.6 equiv

Scheme 2. In Situ Synthesis of $(NN^{fc})MBn(THF)$ and $(NN^{fc})MI(THF)_z$ from $MBn_3(THF)_3$ (M = Nd, Gd, Ho, and Er)



of Me₃SiI was added to the toluene filtrate of $(NN^{fc})MBn-(THF)$ at 25 °C, and the mixture was allowed to stir for 1 h. For neodymium, $(NN^{fc})NdI(THF)$ was isolated as a green powder in high yield (70%), and its purity was confirmed by ¹H NMR spectroscopy and elemental analysis. For gadolinium, holmium, and erbium, $(NN^{fc})MI(THF)_2$ were obtained as yellow crystals in good yield (61–68%).

The *in situ* synthetic route was straightforward and expedient. The synthesis of the final product $(NN^{fc})MI(THF)_z$ could be achieved in less than one day. This is a major improvement over the stepwise synthesis since the crystallization of $MBn_3(THF)_3$ usually takes several days. More importantly, the yield of $(NN^{fc})MI(THF)_z$ is high. For instance, (NN^{fc}) -NdI(THF) was isolated in 70% yield directly from NdCl₃(THF)_{2.5}, while $(NN^{fc})HoI(THF)_2$ was isolated in 68% yield. The purity of the compounds obtained by the *in situ* method was independently confirmed by elemental analysis and ¹H NMR spectroscopy (where available, see the Supporting Information for details).

We had been employing 2.4 equiv of KBn in the synthesis of lanthanide trisbenzyl complexes in order to avoid the formation of ate complexes such as $[K(solvent)_x][MBn_4]$. However, the present study provided a better understanding of the synthesis of $MX_3(THF)_{y}$, and, as a consequence, we realized that it is not necessary to use substoichiometric amounts of KBn to avoid the formation of undesired byproducts. In addition, although no side product was observed during the synthesis of $MBn_3(THF)_3$ and *in situ* formation of $(NN^{fc})MBn(THF)$ or $(NN^{fc})MI(THF)_{z}$ when using 2.4 equiv of KBn for the small lanthanides (Ho and Er), for the large lanthanides (Nd and Gd), the synthesis of MBn₃(THF)₃ usually led to a low yield or intractable oily products when using this stoichiometry. In some instances, the side product (NN^{fc})MCl(THF) was formed while targeting (NN^{fc})MBn(THF), as evidenced by the isolation of $[(NN^{fc})Nd(THF)]_2(\mu-Cl)_2$ from the crude reaction mixture of the (NN^{fc})NdBn(THF) synthesis. The molecular structure of $[(NN^{fc})Nd(THF)]_2(\mu-Cl)_2$ was determined by X-ray diffraction (Figures SX13 and SX14). Therefore, we carried out the syntheses of MBn₃(THF)₃ and in situ syntheses of $(NN^{fc})MBn(THF)$ and $(NN^{fc})MI(THF)_z$ by using 3 equiv of KBn. In general, the yields of pure products were comparable when using 2.4 or 3 equiv of KBn if calculated based on $H_2(NN^{fc})$. However, they were about 10% higher if calculated based on metal starting materials when using 3 equiv of KBn. It is also worth mentioning that although Nd and Gd chlorides were not good starting materials for the synthesis of corresponding trisalkyl complexes, they worked as well as the bromides in the in situ syntheses of (NNfc)MBn(THF) and (NN^{fc})MI(THF).

All the (NN^{fc})MBn(THF) and (NN^{fc})MI(THF)_z complexes were characterized by X-ray crystallography. Structurally characterized organometallic complexes of holmium,^{43–46} erbium,^{45–58} and gadolinium^{46,58–61} are rare. (NN^{fc})NdBn-(THF) (Figure SX5), (NN^{fc})GdBn(THF) (Figure SX6), (NN^{fc})HoBn(THF) (Figure 3), and (TBS)ErBn(THF) (Figure SX8) are isostructural with (NN^{fc})YBn(THF).³² The benzyl group in (NN^{fc})HoBn(THF) is coordinated in an η^2 fashion, as evidenced by the short M–C2 distance of 2.695(4) Å and the small M–C1–C2 angle of 82.6(2)°. The Ho–C1 distance of 2.456(4) Å is similar to the average Ho–C distance of 2.45(1) Å in HoBn₃(THF)₃. The M–Fe distance of 3.234(1) Å is close to the Y–Fe distance of 3.240(1) Å in



Figure 3. Molecular structure of $(NN^{fc})HoBn(THF)$ with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms were omitted for clarity. Selected distances [Å] and angles [deg]: Ho1-C1 2.456(4), Ho1-C2 2.695(4), Ho1-O1 2.318(3), Ho1-N1 2.218(4), Ho1-N2 2.223(4), Ho1-Fe1 3.234(1), Ho1-C12 2.838(4), Ho1-C17 2.828(4), C1-C2 1.469(6), N1-Ho1-N2 133.4(1), O1-Ho1-C1 90.6(1), Ho1-C1-C2 82.6(2), Ho1-N1-C12 100.9(2), Ho1-N2-C17 99.7(2).

the isostructural $(NN^{fc})YBn(THF)$ and to the sum of covalent radii for iron (low spin) and holmium (3.24 Å).⁶²

Similarly, $(NN^{fc})GdI(THF)_2$ (Figure SX10), $(NN^{fc})HoI-(THF)_2$ (Figure SX11), and $(NN^{fc})ErI(THF)_2$ (Figure 4) are isostructural to $(NN^{fc})YI(THF)_2$,¹⁶ while $[(NN^{fc})Nd(THF)(\mu-I)]_2$ adopted a bridging bimetallic structural motif (Figure 5). For a reason not obvious to us, the mononuclear molecular structures show significant disorder for the iodide ligand as well as the methyl and *tert*-butyl groups on one silicon substituent. Despite the fact that gadolinium, erbium, and holmium have slightly different ionic⁶³ and covalent⁶² radii, the major diatomic distances in $(NN^{fc})MI(THF)_2$ (M = Gd, Ho, Er) are similar and also comparable to $(NN^{fc})YI(THF)_2$.¹⁶ Noteworthy, the Ho–Fe distance in $(NN^{fc})HoI(THF)$. This confirms our proposal that the metal–iron distance is flexible upon coordination changes at the metal.^{16,19,28}

CONCLUSIONS

In summary, we successfully synthesized the first gadolinium and holmium trisalkyl complexes not containing a chelating ligand and structurally characterized $\text{ErBn}_3(\text{THF})_2$ and $\text{ErBn}_3(\text{THF})_3$. For the larger lanthanides, neodymium and gadolinium, the isolation of trisbenzyl complexes was possible when using the metal bromide as a starting material but not from the corresponding metal chloride. A rather general *in situ* method was successfully applied to large, medium, and small ionic radius lanthanides (neodymium, gadolinium, holmium, and erbium), and the corresponding iodides supported by a ferrocene diamide ligand could be obtained. This method gave satisfactory yields and high-purity products, while shortening their preparation time. We are encouraged by these results and



Figure 4. Molecular structure of $(NN^{fc})ErI(THF)_2$ with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and disordered counterparts were omitted for clarity. Selected distances [Å] and angles [deg]: Er1–I1 2.998(1), Er1–N1 2.206(5), Er1–N2 2.200(4), Er1–O1 2.331(3), Er1–O2 2.359(3), Er1–Fe1 3.357(1), Er1–C1 2.897(5), Er1–C6 2.869(4), N1–Er1–N2 132.5(1), O1–Er1–O2 166.7(1).



Figure 5. Molecular structure of $[(NN^{fc})Nd(THF)(\mu-I)]_2$ with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and disordered counterparts were omitted for clarity. Selected distances [Å] and angles [deg]: Nd1–I1 3.213(1), Nd1–I1A 3.235(1), Nd1–N1 2.265(3), Nd1–N2 2.259(3), Nd1–O1 2.469(3), Nd1–Fe1 3.364(2), Nd1–C5 2.917(4), Nd1–C10 2.939(4), N1–Er1–N2 126.1(1), I1–Nd1–I1A 78.24(1), Nd1–I1– Nd1A 101.76(1).

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are currently working to complete the whole series of paramagnetic lanthanide alkyl complexes.

EXPERIMENTAL SECTION

General Considerations. All experiments were performed under a dry nitrogen atmosphere using standard Schlenk techniques or an MBraun inert-gas glovebox unless otherwise specified. Solvents, toluene, hexanes, diethyl ether (Et₂O), tetrahydrofuran (THF), and dichloromethane, were purified using a two-column solid-state purification system by the method of Grubbs⁶⁴ and transferred to the glovebox without exposure to air. n-Pentane was distilled over calcium hydride under a dinitrogen atmosphere. Methanol was distilled over calcium oxide under a dinitrogen atmosphere. All solvents were stored on activated molecular sieves for at least a day prior to use. NMR solvents, benzene- d_6 (C₆D₆) and tetrahydrofuran- d_8 (C₄D₈O), were obtained from Cambridge Isotope Laboratories, degassed three times or brought directly into the glovebox in a sealed ampule, and stored over activated molecular sieves for one week prior to use. Rare earth metal oxides (scandium, yttrium, lanthanum, neodymium, gadolinium, holmium, erbium, and lutetium, purity 99% to 99.99%) were purchased from Stanford Materials Corporation (Aliso Viejo, CA, USA) and used as received. Ammonium chloride and bromide were purchased from Alfa Aesar and used as received. Concentrated hydrochloric acid and hydrobromic acid were purchased from Fisher Scientific and used as received. Trimethylsilyl iodide (Me₃SiI) was purchased from Alfa Aesar, brought directly into the glovebox, and stored over activated molecular sieves in a -35 °C freezer prior to use. 1,3,5-Trimethylbenzene (mesitylene) was purchased from Alfa Aesar, distilled from CaH2 under reduced pressure, and brought into a glovebox to store on activated molecular sieves for a week prior to use. KO^tBu was purchased from Strem Chemicals Inc., directly brought into a glovebox without exposure to air or moisture, and used as received. KBn (benzylpotassium) was prepared according to a literature report.⁶⁵ Nuclear magnetic resonance spectra were recorded on Bruker AV300, Bruker DRX500, Bruker AV500, or Bruker AV600 spectrometers (work supported by the NSF grants CHE-9974928, CHE-0116853, and CHE-1048804) at 25 °C in C_6D_6 or C_4D_8O unless otherwise specified. Chemical shifts are reported with respect to internal solvent (C_6D_6 at 7.16 ppm or C₄D₈O at 1.73 ppm). CHN analyses were performed in house on a CE-440 elemental analyzer manufactured by Exeter Analytical. Inc.

Synthesis of NdBn₃(THF)₃ from NdBr₃(THF)₄ and 3 equiv of KBn (ref 15). Scale: 1.538 g of NdBr₃(THF)₄ (2.29 mmol) and 0.894 g of KBn (6.86 mmol, 3 equiv). The procedure was similar to that for HoBn₃(THF)₃. Crystallization was set in two vials, each with a 10 mL of THF solution layered with 10 mL of hexanes. Green needle crystals were formed after one week in a -35 °C freezer. The solution was decanted, and the crystals were washed with cold *n*-pentane. Yield: 0.927 g, 65.6%. A single crystal was used to obtain a unit cell determination to compare with literature values.¹⁵ ¹H NMR spectroscopy and elemental analysis characterization were performed since these data were not reported. ¹H NMR (500 MHz, C₄D₈O, 25 °C) δ , ppm: 5.99 (br s), and -0.31 (br s). ¹³C NMR (126 MHz, C₄D₈O, 25 °C) δ, ppm: 152.9, 148.2, and 89.4. An analytically pure sample was obtained from a THF solution layered with *n*-pentane in a -35 °C freezer after two days. Anal. Calcd for C33H45O3Nd with one molecule of *n*-pentane (C₅H₁₂), *M*_w = 706.113: C, 64.64; H, 8.14; N, 0. Found: C, 65.01; H, 7.59; N, <0.1.

Synthesis of GdBn₃(THF)₃ from GdBr₃(THF)_{3.5}. Scale: 1.587 g of GdBr₃(THF)_{3.5} (2.44 mmol) and 0.955 g of KBn (7.33 mmol, 3 equiv). The procedure was similar to that for HoBn₃(THF)₃. Crystallization was set in two vials, each with a 10 mL of a THF solution layered with 10 mL of hexanes. Colorless crystals were formed after one week in a -35 °C freezer. The solution was decanted, and the crystals were washed with cold *n*-pentane. Yield: 0.732 g, 46.3%. Single crystals suitable for single-crystal X-ray diffraction were formed from a THF solution layered with hexanes. Anal. Calcd for

 $\rm C_{33}H_{45}O_{3}Gd,\,M_w=646.970;\,C,\,61.26;\,H,\,7.01;\,N,\,0.$ Found: C, 60.23; H, 6.61; N, <0.1.

Synthesis of HoBn₃(THF)₃ by Using 2.4 equiv of KBn. To 1.500 g of HoCl₃(THF)_{3.5} (2.86 mmol) placed in a 100 mL roundbottom flask was added 80 mL of THF. The flask was placed in a -78°C dry ice/acetone or 2-propanol bath for at least 15 min. Then 0.895 g of KBn (6.87 mmol, 2.4 equivalents) was weighed in a scintillation vial, dissolved in 15 mL of THF, and cooled in a -78 °C bath. The KBn solution was added dropwise to the $HoCl_3(THF)_{3,5}$ slurry at -78°C with stirring. The red color of KBn disappeared immediately after mixing. The reaction mixture was allowed to stir in a 0 °C ice bath for 30 min and then filtered through Celite on a coarse frit. The flask and coarse frit were washed with 10 mL of THF. The volatiles were removed under reduced pressure. The resulting oily solid was dissolved in a minimum amount of THF (about 12 mL), transferred to a vial, and layered with 8 mL of hexanes. Pink crystals were formed after three days of storing in a $-35\ ^\circ C$ freezer along with some gray precipitate. The mother liquor and a gray precipitate were decanted, and the pink crystals were washed with hexanes and dried under reduced pressure. Yield: 0.552 g, 36.8% (29.4% based on Ho). $^1\mathrm{H}$ NMR (300 MHz, C₆D₆, 25 °C) δ, ppm: 39.9 (br s), 16.1 (s), 1.6 (br s), and -76.1 (br s). Peaks were too broad to get reasonable integrations and assign them. Anal. Calcd for $C_{33}H_{45}O_3H_0$, $M_w =$ 654.650: C, 60.55; H, 6.92; N, 0. Found: C, 59.86; H, 6.70; N, <0.1.

Synthesis of HoBn₃(THF)₃ by Using 3 equiv of KBn. Scale: 1.489 g of $HoCl_3(THF)_{3.5}$ (2.84 mmol) and 1.111 g of KBn (8.53 mmol). The procedure was the same as using 2.4 equiv of KBn. Yield: 1.416 g, 76.1%.

Synthesis of ErBn₃(THF)₃ by Using 2.4 equiv of KBn. To 2.000 g of ErCl₃(THF)_{3.5} (3.80 mmol) placed in a 100 mL round-bottom flask was added 80 mL of THF. The flask was placed in a -78 °C dry ice/acetone or 2-propanol bath for at least 15 min. Then 1.188 g of KBn (9.12 mmol, 2.4 equivalents) was weighed in a scintillation vial, dissolved in 15 mL of THF, and cooled in a -78 °C bath. The KBn solution was added dropwise to the ErCl₃(THF)_{3.5} slurry at -78 °C with stirring. The red color of the KBn solution disappeared shortly after mixing. The reaction mixture was allowed to stir in a 0 °C ice bath for 30 min and then filtered through Celite on a coarse frit. The flask and coarse frit were washed with 15 mL of THF. The volatiles were removed under reduced pressure. The resulting light pink solid was dissolved in a minimum amount of THF (about 12 mL), transferred to a vial, and layered with 8 mL of hexanes. Pink crystals were formed after three days' storing in a -35 °C freezer. The mother liquor was decanted, and the pink crystals were washed with hexanes and dried under reduced pressure. Yield: 1.660 g, 83.1% (66.5% based on Er). Single crystals of ErBn₃(THF)₂ were obtained by recrystallization of the aforementioned pink crystals from a toluene solution layered with *n*-pentane. Single crystals of $ErBn_3(THF)_3$ were obtained by recrystallization from a THF solution layered with hexanes. ¹H NMR (300 MHz, C₆D₆, 25 °C) δ, ppm: 41.6 (br s), 13.4 (s), 5.6 (s), and -0.2 (br s). Peaks were too broad to get reasonable integrations and assign them. Anal. Calcd for $C_{29}H_{37}O_2Er$, $M_w =$ 584.872: C, 59.55; H, 6.38; N, 0. Found: C, 59.25; H, 6.70; N, <0.1.

Synthesis of $ErBn_3(THF)_3$ by Using 3 equiv of KBn. Scale: 1.520 g of $ErCl_3(THF)_{3.5}$ (2.89 mmol) and 1.129 g of KBn (8.67 mmol). The procedure was the same as using 2.4 equiv of KBn. Yield: 1.136 g, 59.9%.

General Method for *in Situ* Synthesis of (NN^{fc})MBn(THF). Using (NN^{fc})HoBn(THF) and 2.4 equiv of KBn as an example, the protocols for the other (NN^{fc})MBn(THF) or using 3 equiv of KBn were similar unless otherwise specified. To 1.0000 g of HoCl₃(THF)_{3.5} (1.91 mmol) placed in a 100 mL round-bottom flask was added 70 mL of THF. The flask was placed in a -78 °C dry ice/acetone or 2propanol bath for at least 15 min. Then 0.5967 g of KBn (4.58 mmol, 2.4 equiv) was weighed in a scintillation vial, suspended in 10 mL of THF, and cooled in a -78 °C bath. The KBn solution was added dropwise to the HoCl₃(THF)_{3.5} slurry at -78 °C with stirring. The red color of the KBn solution disappeared shortly after mixing. The reaction mixture was allowed to stir at 0 °C in an ice bath for 30 min and then filtered through Celite on a coarse frit. The flask and coarse frit were washed with 10 mL of THF, and the washings combined with the previous filtrate. The resulting light pink solution was transferred to a clean 100 mL round-bottom flask and placed in a -78 °C dry ice/ acetone or 2-propanol bath for at least 15 min. Then 0.6792 g of $H_2(NN^{fc})$ (1.53 mmol, 0.8 equiv) was weighed in a scintillation vial, dissolved in 10 mL of THF, and cooled in a -78 °C bath for 5 min. The $H_2(NN^{fc})$ solution was added dropwise to the aforementioned light pink solution at -78 °C with stirring. The solution color turned to pale yellow upon addition. The reaction mixture was allowed to stir at -78 °C for 30 min. The volatiles were removed under reduced pressure. The resulting yellow solid was extracted with 20 mL of toluene and filtered through Celite on a coarse frit. The volatiles were removed under reduced pressure. Recrystallization from a concentrated toluene solution layered with n-pentane gave (NNfc)HoBn-(THF) as yellow crystals after three days of storing in a -35 °C freezer. Yield: 0.2093 g. The mother liquor was dried under reduced pressure to yield a yellow solid, which was washed with 15 mL of npentane and collected on a medium frit to give a second crop as a yellow powder: 0.4142 g. Total yield: 0.6235 g, 53.0% (based on H₂(NN^{fc}) and 42.4% based on Ho). ¹H NMR (300 MHz, C₆D₆, 25 °C) δ_i ppm: 299.5 and 210.1 (br s, 12H, SiCH₃), 169.6 (br s, 18H, $C(CH_3)_3$, -59.9 (br s), -71.8 (br s), -126.4 (br s), -137.1 (br s), -159.5 (br s), -171.2 (br s), -211.4 (br s), and -306.1 (br s). Peaks were too broad to get reasonable integrations and assign them. Anal. Calcd for $C_{33}H_{53}N_2$ OFeHoSi₂, $M_w = 770.747$: C, 51.43; H, 6.93; N, 3.63. Found: C, 50.91; H, 7.63; N, 4.32.

Yields for the analogous Nd, Gd, and Er syntheses: 1.0526 g, 75.6% (Nd); 0.6043 g, 51.1% (Gd); first crop 0.2475 g, second crop 0.3061 g, total 47.1% (Er).

Elemental analysis for (NN^{fc})NdBn(THF): Calcd for $C_{33}H_{53}N_2OFeNdSi_2$, $M_w = 750.059$: C, 52.84; H, 7.12; N, 3.73. Found: C, 50.10; H, 6.91; N, 3.86.

Elemental analysis for (NN^{fc})GdBn(THF): Calcd for $C_{33}H_{53}N_2OFeGdSi_2$, $M_w = 763.067$: C, 51.94; H, 7.00; N, 3.67. Found: C, 50.66; H, 6.86; N, 3.35.

Elemental analysis for (NN^{fc})ErBn(THF): Calcd for $C_{33}H_{53}N_2OErFeSi_2$, $M_w = 773.076$: C, 51.27; H, 6.91; N, 3.62. Found: C, 51.10; H, 6.82; N, 3.43.

Synthesis of (NN^{fc})HoBn(THF) Using 3 equiv of KBn and 1 equiv of $H_2(NN^{fc})$. Scale: 0.800 g of $HoCl_3(THF)_{3.5}$ (1.53 mmol), 0.597 g of KBn (4.58 mmol), and 0.679 g of $H_2(NN^{fc})$ (1.53 mmol). The procedure was the same as using 2.4 equiv of KBn. Yield: first crop, 0.258 g; second crop, 0.211 g; total 39.8%.

Yields for the analogous Nd, Gd, and Er syntheses: 0.770 g, 69.0% (Nd from NdBr₃(THF)₄); 0.280 g, 37.9% (Gd); first crop, 0.606 g; second crop, 0.127 g; total 62.4% (Gd from GdBr₃(THF)_{3.5}); first crop, 0.531 g; second crop, 0.064 g; total 50.5% (Er).

General Method for in Situ Synthesis of (NN^{tc})MI(THF)_z. Using (NN^{fc})HoI(THF)₂ as an example, the protocols for the other $(NN^{tc})MI(THF)_z$ or using 3 equiv of \overline{KBn} were similar unless otherwise specified. To 1.300 g of HoCl₃(THF)_{3.5} (2.48 mmol) placed in a 100 mL round-bottom flask was added 70 mL of THF. The flask was placed in a -78 °C dry ice/acetone or 2-propanol bath for at least 15 min. Then 0.781 g of KBn (6.00 mmol, 2.4 equiv) was weighed in a scintillation vial, dissolved in 10 mL of THF, and cooled in a -78 °C bath. The KBn solution was added dropwise to the HoCl₃(THF)_{3.5} slurry at -78 °C with stirring. The red color of the KBn solution disappeared shortly after mixing. The reaction mixture was allowed to stir at 0 °C in an ice bath for 30 min and then filtered through Celite on a coarse frit. The flask and coarse frit were washed with 10 mL of THF ,and the washings combined with the previous filtrate. The resulting light pink solution was transferred to a clean 100 mL roundbottom flask and placed in a -78 °C dry ice/acetone or 2-propanol bath for at least 15 min. Then 0.883 g of $H_2(NN^{fc})$ (1.99 mmol, 0.8 equiv) was weighed in a scintillation vial, dissolved in 10 mL of THF, and cooled in a -78 °C bath for 5 min. The H₂(NN^{fc}) solution was added dropwise to the aforementioned light pink solution at -78 °C with stirring. The solution color turned to pale yellow upon addition. The reaction mixture was allowed to stir at -78 °C for 30 min. The volatiles were removed under reduced pressure. The resulting yellow

solid was extracted with 15 mL of toluene and filtered through Celite on a coarse frit. The toluene filtrate was transferred to a scintillation vial. A 0.8559 g portion of Me₃SiI (4.28 mmol, 1.73 equiv) was added dropwise as a toluene solution (2 mL) at ambient temperature, and the reaction mixture was allowed to stir for 1 h. At the end of the reaction, 5 mL of THF was added to quench the extra Me₃SiI. The volatiles were removed under reduced pressure. The resulting yellow solid was dissolved in a minimum amount of Et₂O layered with npentane. Yellow crystals as (NN^{fc})HoI(THF)₂ formed after three days of storing in a -35 °C freezer. Yield: 0.818 g. After decanting, the mother liquor was concentrated and stored in a -35 °C freezer to give a second crop: 0.351 g. Total yield: 1.169 g, 68.4% (based on $H_2(NN^{fc})$, 54.7% based on Ho). ¹H NMR (300 MHz, C₆D₆, 25 °C) δ , ppm: 315.7 (br s, 12H, SiCH₃), 199.6 (br s, 18H, C(CH₃)₃), -137.4 (br s), -142.5 (br s), and -223.6 (br s). Peaks were too broad to get reasonable integrations and assign them. Anal. Calcd for $C_{30}H_{54}N_2O_2FeIHoSi_2$, $M_w = 878.625$, with 0.25 molecule of npentane: C, 41.86; H, 6.41; N, 3.12. Found: C, 41.75; H, 6.34; N, 3.08.

Yields for the analogous Nd, Gd, and Er syntheses: first crop, 0.507 g; second crop, 0.195 g; total 0.702 g, 69.6% (Nd); first crop, 0.524 g; second crop, 0.279 g; total 60.7% (Gd); first crop, 0.664 g; second crop, 0.165 g; total 61.9% (Er).

Elemental analysis for (NN^{fc})NdI(THF): Calcd for $C_{26}H_{46}N_2OFeINdSi_2$, $M_w = 785.830$: C, 39.74; H, 5.90; N, 3.56. Found: C, 40.21; H, 5.57; N, 4.01.

Elemental analysis for (NN^{fc})GdBn(THF)₂: Calcd for $C_{30}H_{54}N_2O_2FeGdISi_2$, $M_w = 870.945$, with half a molecule of *n*-pentane: C, 43.04; H, 6.67; N, 3.09. Found: C, 42.74; H, 6.54; N, 3.32.

Elemental analysis for (NN^{fc})ErBn(THF)₂: Calcd for $C_{30}H_{54}N_2O_2$ ErFeISi₂, $M_w = 880.954$, with half a molecule of *n*-pentane: C, 42.57; H, 6.60; N, 3.05. Found: C, 41.97; H, 6.34; N, 3.21.

Synthesis of $(NN^{fc})Hol(THF)_2$ Using 3 equiv of KBn and 1 equiv of H₂(NN^{fc}). Scale: 0.800 g of HoCl₃(THF)_{3.5} (1.53 mmol), 0.597 g of KBn (4.58 mmol), 0.679 g of H₂(NN^{fc}) (1.53 mmol), and 0.611 g of Me₃SiI (3.05 mmol). The procedure was the same as using 2.4 equiv of KBn. Yield: first crop, 0.520 g; second crop, 0.380 g; total 67.0%.

Yields for the analogous Nd, Gd, and Er syntheses: 0.772 g, 66.0% (Nd); first crop, 0.665 g; second crop, 0.185 g; total 63.4% (Gd); first crop, 0.649 g; second crop, 0.240 g; total 66.3% (Er).

ASSOCIATED CONTENT

Supporting Information

Details of synthetic procedures, NMR spectra, and the X-ray crystallographic study can be found online. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

W.H. and P.L.D. designed the experiments. W.H. performed all the syntheses and NMR spectroscopy. B.M.U. performed the elemental analysis. S.I.K. solved some molecular structures by X-ray crystallography. W.H. and P.L.D. wrote the manuscript. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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Article

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