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In situ Synthesis of Lanthanide Complexes Supported by a Ferrocene Diamide Ligand: Extension to Redox-Active Lanthanide Ions

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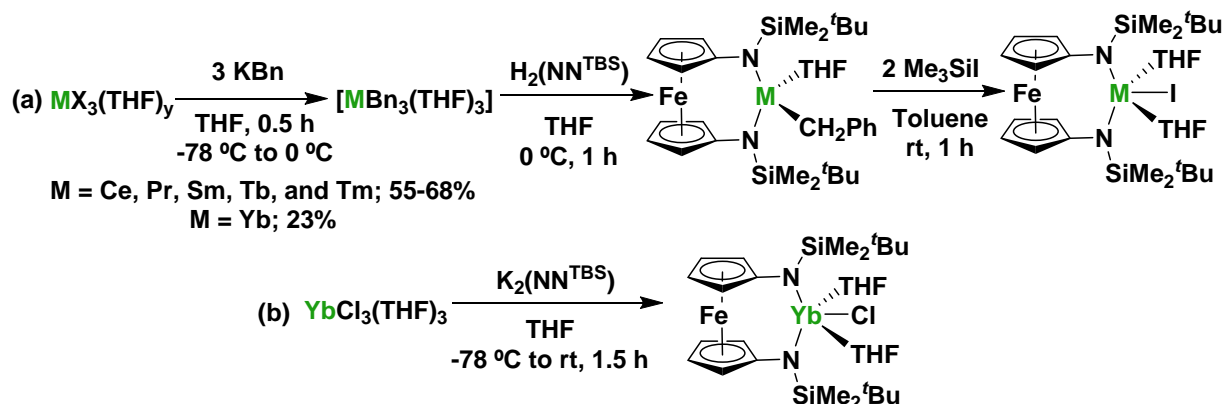
Reliable transformation of low-cost rare-earth metal oxides to organometallic rare-earth metal complexes is a prerequisite for the advancement of non-aqueous rare-earth metal chemistry. We have recently developed an *in situ* method to prepare rare-earth alkyl and halide precursors supported by a diamidoferrocene NN^{TBS} , 1,1'-*fc*($\text{NSiMe}_2^t\text{Bu}$)₂, as an ancillary ligand. Herein, we extended the scope of this method to other lanthanide ions including those that are redox active, such as cerium, praseodymium, samarium, terbium, and ytterbium. Specifically, samarium trisbenzyl could be generated *in situ* and then converted to the corresponding samarium benzyl or iodide complexes in good yield. However, it was found that ytterbium trisbenzyl could not be formed cleanly and the consequent conversion to ytterbium iodide complex was low yielding. By adapting an alternative route, the desired ytterbium chloride precursor could be obtained in good yield and purity.

Introduction

Rare-earth metals, i.e. lanthanides and group 3 metals, have been of key importance to the advancement of industry and improvement of daily life. They are widely used in fields including material science, medicinal technology, and catalysis.^{1–20} Organometallic rare-earth chemistry has seen a resurgence recently since it is essential to the development of homogenous catalysis and the discovery of new materials. The fast, efficient, and low-cost synthesis of organometallic rare-earth metal complexes paves a convenient entry to non-aqueous rare-earth metal chemistry. However, contemporary synthetic routes usually require multiple-step transformations when using the readily accessible and usually cheapest rare-earth metal source, metal oxides, and the isolation of certain intermediates can be challenging due to their instability to heat, oxygen, or moisture.^{21–23} Recently, our laboratory introduced a general method for the *in situ* generation of metal trisbenzyl species followed by an acid-base reaction with the free ligand and the consequent transformation to rare-earth metal benzyl or iodide complexes supported by a ferrocene diamide ligand, NN^{TBS} (1,1'-*fc*($\text{NSiMe}_2^t\text{Bu}$)₂).^{24–26} This method facilitates the synthesis of paramagnetic lanthanide complexes that exhibit intriguing magnetic properties.²⁷ Herein, we report the extension of this method to other lanthanide ions, including those that are redox-active such as cerium, praseodymium, samarium, terbium, and ytterbium.

Results and Discussion

In this work, we show that the commercially available metal oxides, namely CeO_2 , Pr_6O_{11} , Sm_2O_3 , Tb_4O_7 , Tm_2O_3 , and Yb_2O_3 , can be used as precursors for organometallic complexes. In the first step, we synthesize the corresponding metal trihalides (MX_3). It was found that for the early lanthanides, MBr_3 is a better precursor than MCl_3 for the subsequent reaction with KBn ($\text{Bn} = \text{CH}_2\text{Ph}$) to generate MBn_3 *in situ*.²⁶ We do not have a definitive explanation for the reasons behind it, but we hypothesize that it may be related to the kinetics of the reaction between MX_3 and KBn . For lanthanides with a larger ionic radius, the THF adducts of MCl_3 tend to be polymeric thus preventing the fast generation of a monomeric $[\text{MBn}_3]$ species; on the other hand, the THF adducts of MBr_3 are usually monomeric due to the increased Lewis acidity of the metal bromide and the larger size of bromide compared to chloride.²⁸ Therefore, we prepared $\text{MBr}_3(\text{THF})_y$ ($\text{M} = \text{Ce} / \text{Pr} / \text{Sm}$, $y = 4$; $\text{M} = \text{Tb}$, $y = 3.5$) for lanthanides larger than yttrium and $\text{MCl}_3(\text{THF})_y$ ($\text{M} = \text{Tm}$, $y = 3.5$; $\text{M} = \text{Yb}$, $y = 3$) for lanthanides smaller than yttrium following an optimized procedure from that reported in the literature (Equation 1).^{26, 29–31} For CeO_2 , Pr_6O_{11} , and Tb_4O_7 , a small amount of Br_2 was observed during the reaction since M(IV) was reduced to M(III) *in situ*. The products and yields for $\text{MX}_3(\text{THF})_y$ synthesis are summarized in Table 1.

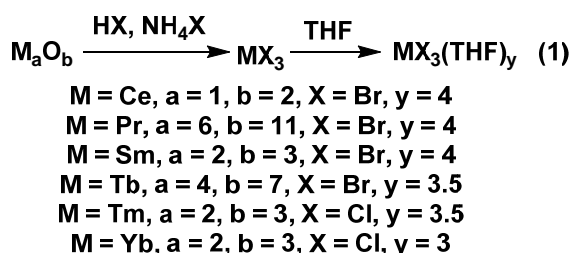


Scheme 1. (a) *in situ* synthesis of $(\text{NN}^{\text{TBS}})\text{MI}(\text{THF})_2$ from $\text{MX}_3(\text{THF})_y$; (b) salt metathesis to obtain $(\text{NN}^{\text{TBS}})\text{YbCl}(\text{THF})_2$; $\text{NN}^{\text{TBS}} = 1,1'$ - $\text{fc}(\text{NSiMe}_2^t\text{Bu})_2$, $\text{Bn} = \text{CH}_2\text{Ph}$.

Table 1. Details for the synthesis of MX_3 and $\text{MX}_3(\text{THF})_y$.

| Oxide | MX_3 | Yield (g) (Y1) | $\text{MX}_3(\text{THF})_y$ | Yield (g) (Y2) |
|------------------------------------|-----------------|-------------------|-----------------------------------|-------------------|
| CeO_2 | CeBr_3 | 18.30 (96%) | $\text{CeBr}_3(\text{THF})_4$ | 31.41 (98%) |
| Pr_6O_{11} | PrBr_3 | 17.69 (93%) | $\text{PrBr}_3(\text{THF})_4$ | 30.57 (98%) |
| Sm_2O_3 | SmBr_3 | 13.45 (69%) | $\text{SmBr}_3(\text{THF})_4$ | 22.50 (96%) |
| $\text{Tb}_4\text{O}_7^{\text{a}}$ | TbBr_3 | 6.76 (68%) | $\text{TbBr}_3(\text{THF})_{3.5}$ | 10.36 (94%) |
| Tm_2O_3 | TmCl_3 | 13.18 (96%) | $\text{TmCl}_3(\text{THF})_{3.5}$ | 24.51 (97%) |
| $\text{Yb}_2\text{O}_3^{\text{b}}$ | YbCl_3 | 24.62 (88%) | $\text{YbCl}_3(\text{THF})_3$ | 42.82 (98%) |

^a Tb_4O_7 , 25 mmol Tb; ^b Yb_2O_3 , 100 mmol Yb.



After obtaining the precursor $\text{MX}_3(\text{THF})_y$, an *in situ* method was employed to synthesize $(\text{NN}^{\text{TBS}})\text{MI}(\text{THF})_x$ without isolation of any intermediates (Scheme 1a). Namely, 3 equivalents of KBr , 1 equivalent $\text{H}_2(\text{NN}^{\text{TBS}})$, and 2 equivalents of Me_3SiI were added in order to transform $\text{MX}_3(\text{THF})_y$ to $(\text{NN}^{\text{TBS}})\text{MI}(\text{THF})_x$. Previously, we and others reported that it might be necessary to use a substoichiometric amount of KBr to avoid the formation of $\text{K}[\text{MBn}_3]$.^{22, 26, 32, 33} We later found that the slow addition of a homogenous THF solution of KBr while keeping the reaction mixture cold (-78°C) was essential to the clean formation of the $[\text{MBn}_3]$ species. Thus, there is no need to use a substoichiometric amount of KBr that would lower the yield calculated from the metal source.

For lanthanides without a stable +2 oxidation state, the *in situ* method gave a good yield of $(\text{NN}^{\text{TBS}})\text{MI}(\text{THF})_x$ (over 60%) calculated from $\text{MX}_3(\text{THF})_y$. For samarium, which has a marginally stable +2 oxidation state, this method still worked well with a yield of 55% for $(\text{NN}^{\text{TBS}})\text{SmI}(\text{THF})_2$. However, when it came to ytterbium, which has a relatively stable +2 oxidation state, the *in situ* generation of $[\text{YbBn}_3]$ was not clean and $(\text{NN}^{\text{TBS}})\text{YbI}(\text{THF})_2$ was only isolated in a low yield of 23%, while the side product $[\text{K}(\text{THF})_6][(\text{NN}^{\text{TBS}})_2\text{Yb}]$ could be separated and isolated in a 10% yield. We note that Liddle et al. also reported that by reacting $\text{YbI}_3(\text{THF})_{3.5}$ and KBr , $\text{YbBn}_3(\text{THF})_3$ was not formed, instead, a mixed valent species, $[\text{Yb}^{\text{II}}(\text{Bn})(\text{THF})_5][\text{Yb}^{\text{III}}(\text{Bn})_4(\text{THF})_2]$, was generated with the concomitant oxidation of the benzyl anion to 1,2-diphenylethane.²³ Therefore, we sought an alternative synthetic route in order to improve the yield and purity of the product.

Previously, we synthesized $[\text{K}(\text{THF})_6][(\text{NN}^{\text{TBS}})_2\text{Sc}]$ by reacting $\text{ScX}_3(\text{THF})_y$ and 2 equivalents of $\text{K}_2(\text{NN}^{\text{TBS}})$.³¹ We postulated that by carefully controlling the stoichiometry of $\text{K}_2(\text{NN}^{\text{TBS}})$ to exactly 1 equivalent and performing its slow addition to $\text{YbCl}_3(\text{THF})_3$ it would be possible to achieve the sole formation of $(\text{NN}^{\text{TBS}})\text{YbCl}(\text{THF})_2$. That hypothesis turned out to be correct: $(\text{NN}^{\text{TBS}})\text{YbCl}(\text{THF})_2$ was formed exclusively in that reaction and could be isolated in a good yield (67%) and purity (Scheme 1b).

In an attempt to apply the *in situ* synthetic method to europium(III), we prepared europium precursors from Eu_2O_3 . Following a similar preparation route, $\text{Eu}(\text{II})\text{Br}_2(\text{THF})_2$ was obtained instead of $\text{Eu}(\text{III})\text{Br}_3$ since EuBr_3 decomposed to EuBr_2 and Br_2 under the conditions used (high temperature and under vacuum).³⁴ $\text{EuBr}_2(\text{THF})_2$ could be oxidized by a half equivalent of I_2 and $\text{EuBr}_2(\text{THF})_4$ could be obtained after a usual work-up. However, $\text{EuBr}_2(\text{THF})_2$ did not react with KBr ; $\text{EuBr}_2(\text{THF})_4$ was reduced immediately by KBr to a $\text{Eu}(\text{II})$ species that remained intact after reduction. The strong oxidizing power of $\text{Eu}(\text{III})$ hindered the preparation of its organometallic complexes.

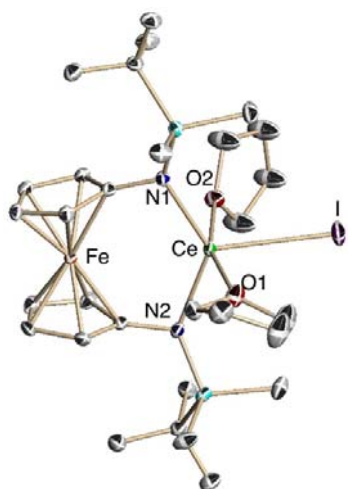


Figure 1. Molecular structure of $(\text{NN}^{\text{TBS}}\text{CeI}(\text{THF})_2)$ with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms were omitted for clarity. Selected distances [\AA] and angles [$^\circ$]: Ce-I 3.163(1), Ce-N1 2.318(3), Ce-N2 2.313(3), Ce-O1 2.535(3), Ce-O2 2.501(3), Ce-Fe 3.412(1), N1-Ce-N2 129.7(1), N1-Ce-I 115.6(1), O1-Ce-O2 163.2(1), O1-Ce-I 82.7(1), I-Ce-Fe 171.4(0.1). This structure is representative for $(\text{NN}^{\text{TBS}}\text{SmI}(\text{THF})_2)$, $(\text{NN}^{\text{TBS}}\text{TbI}(\text{THF})_2)$, $(\text{NN}^{\text{TBS}}\text{TmI}(\text{THF})_2)$, and $(\text{NN}^{\text{TBS}}\text{YbI}(\text{THF})_2)$ (see the Supporting Information for details).

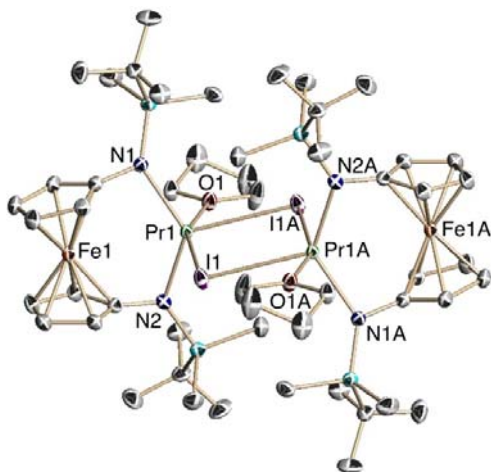


Figure 2. Molecular structure of $[(\text{NN}^{\text{TBS}}\text{Pr}(\text{THF})(\mu\text{-I}))_2]$ with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms were omitted for clarity. Selected distances [\AA] and angles [$^\circ$]: Pr1-I1 3.238(1), Pr1-I1A 3.261(1), Pr1-N1 2.281(3), Pr1-N2 2.273(3), Pr1-O1 2.494(3), Pr1-Fe1 3.364(1), I1-Pr1-I1A 78.2(0.1), N1-Pr1-N2 126.8(1), N1-Pr1-O1 88.5(1), I1-Pr1-Fe1 89.3(0.1), I1A-Pr1-Fe1 164.6(0.1).

All lanthanide complexes were characterized by X-ray crystallography. For the lanthanide iodides, both monomeric and dimeric structures were found depending on the work-up method as well as the solvents used for crystallization. Compounds $(\text{NN}^{\text{TBS}}\text{CeI}(\text{THF})_2)$ (Figure 1) and $[(\text{NN}^{\text{TBS}}\text{Pr}(\text{THF})(\mu\text{-I}))_2]$ (Figure 2) are used as representatives for monomeric and dimeric structures, respectively. Similar to $(\text{NN}^{\text{TBS}}\text{Ml}(\text{THF})_2)$

reported previously, $(\text{NN}^{\text{TBS}}\text{CeI}(\text{THF})_2)$ exhibits a pseudo-octahedral geometry with two amide donors occupying the axial positions and the two oxygen donors, one iodide, and iron of ferrocene forming the equatorial plane. The Ce-Fe distance is 3.41 \AA , slightly longer than the sum of covalent radii of Ce and Fe, at 3.36 \AA .³⁵ This is in line with our previous observations that when a strong σ donor such as THF is present, the weak interaction between the Lewis acid rare-earth metal center and the Lewis basic iron of ferrocene does not occur.^{36, 37}

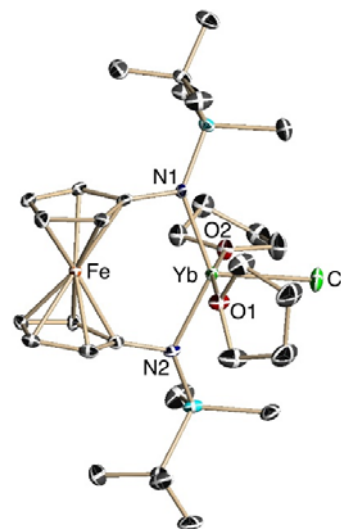


Figure 3. Molecular structure of $(\text{NN}^{\text{TBS}}\text{YbCl}(\text{THF})_2)$ with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms were omitted for clarity. Selected distances [\AA] and angles [$^\circ$]: Yb-Cl 2.534(2), Yb-N1 2.185(5), Yb-N2 2.179(5), Yb-O1 2.326(5), Yb-O2 2.340(5), Yb-Fe 3.30(1), N1-Yb-N2 134.2(2), N1-Yb-Cl 113.4(2), O1-Yb-O2 167.5(2), O1-Yb-Cl 83.6(2), Cl-Yb-Fe 171.3(1).

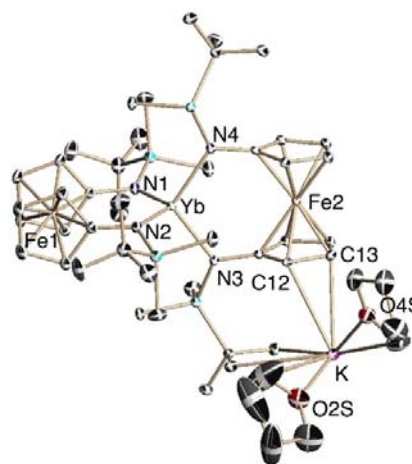


Figure 4. Molecular structure of $[\text{K}(\text{THF})_2][(\text{NN}^{\text{TBS}})_2\text{Yb}]$ with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms were omitted for clarity. Selected distances [\AA] and angles [$^\circ$]: Yb-N1 2.227(3), Yb-N2 2.229(3), Yb-N3 2.244(3), Yb-N4 2.251(3), K-C12 3.229(4), K-C13 3.190(4), K-O1S 2.661(4), K-O2S 2.707(4), N1-Yb-N2 119.1(1), N3-Yb-N4 111.1(1), N1-Yb-N3 105.8(1), N2-Yb-N4 107.0(1).

The lanthanide iodide complexes supported by NN^{TBS} can readily lose one coordinating THF molecule to form a dimeric structure when triturating with hexanes or *n*-pentane or when recrystallized from toluene / hexanes.²⁶ Figure 2 shows the molecular structure of $[(\text{NN}^{\text{TBS}}\text{Pr}(\text{THF})(\mu\text{-I}))_2]$: the molecule has an inverse center at the middle point of two praseodymium ions. The iodide ligand bridges the two praseodymium(III) centers in a symmetrical fashion with two almost equal Pr-I distances of 3.24 and 3.26 Å. The average Pr-I distance of 3.25 Å is slightly longer than the Ce-I distance of 3.16 Å in $(\text{NN}^{\text{TBS}}\text{CeI}(\text{THF})_2)$, reflecting the bridging effect of the iodide ligand. Praseodymium(III) still adopts a pseudo-octahedral geometry with a long Pr-Fe distance of 3.36 Å.

Figures 3 and 4 present the solid state molecular structures of $(\text{NN}^{\text{TBS}}\text{YbCl}(\text{THF})_2)$ and $[\text{K}(\text{THF})_2][(\text{NN}^{\text{TBS}})_2\text{Yb}]$, respectively. The structure of $(\text{NN}^{\text{TBS}}\text{YbCl}(\text{THF})_2)$ resembles that of $(\text{NN}^{\text{TBS}}\text{MI}(\text{THF})_2)$ with ytterbium(III) being in a pseudo-octahedral environment. The Yb-Cl distance of 2.534(2) Å is similar to the literature value reported for $\text{Cp}_2\text{YbCl}(\text{THF})$.³⁸ The Yb-Fe distance of 3.30(1) Å is longer than the sum of covalent radii of Yb and Fe at 3.19 Å.³⁵ Compound $[\text{K}(\text{THF})_2][(\text{NN}^{\text{TBS}})_2\text{Yb}]$ was crystallized from toluene / hexanes solution and formed a 1D chain in the solid state with a potassium ion bridging two ferrocene units of nearby molecules. Despite the disturbance caused by the bridging potassium ion, ytterbium(III) is coordinated by four amide nitrogen donors in an almost ideal tetrahedral geometry. The four Yb-N distances are identical with an average of 2.24 Å, similar to the Yb-N distance of 2.18 Å in $(\text{NN}^{\text{TBS}}\text{YbCl}(\text{THF})_2)$.

Conclusions

In summary, we showed that the *in situ* synthesis method could be expanded to most lanthanides, including those with an accessible +2 oxidation state such as ytterbium and samarium, and to those starting with a rare-earth metal oxide other than M_2O_3 such as CeO_2 . For samarium, a good yield of $(\text{NN}^{\text{TBS}}\text{SmI}(\text{THF})_2)$ could be achieved using the *in situ* method; however, for ytterbium, which has a relatively stable +2 oxidation state, $(\text{NN}^{\text{TBS}}\text{YbI}(\text{THF})_2)$ could only be obtained in a relatively low yield with significant formation of the side-product $[\text{K}(\text{THF})_2][(\text{NN}^{\text{TBS}})_2\text{Yb}]$. Therefore, an alternative route was employed to attain the synthesis of $(\text{NN}^{\text{TBS}}\text{YbCl}(\text{THF})_2)$ in good yield and purity. For the most oxidizing ion, Eu(III), the *in situ* method did not provide access to an Eu(III) organometallic precursor. The straightforward aspect and generality of the *in situ* method provide useful entries for organometallic lanthanide precursors and therefore facilitate the advancement of rare-earth metal chemistry.

Experimental Section

General Considerations. Methods and chemicals. 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 (Et_2O), tetrahydrofuran (THF), and

dichloromethane, were purified using a two-column solid-state purification system by the method of Grubbs³⁹ 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 solvent, benzene- d_6 (C_6D_6), was obtained from Cambridge Isotope Laboratories, degassed three times and stored over activated molecular sieves for at least one day prior to use. Rare earth metal oxides (cerium, praseodymium, samarium, terbium, thulium, and ytterbium, 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 (Me_3SiI) was purchased from Alfa Aesar, brought directly into the glovebox, and stored over activated molecular sieves in a -35 °C freezer 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 procedure.⁴⁰ $\text{H}_2(\text{NN}^{\text{TBS}})$ and $\text{K}_2(\text{NN}^{\text{TBS}})$ was synthesized according to literature procedure.⁴¹

Nuclear magnetic resonance (NMR) spectra. NMR spectra were recorded on Bruker AV300, Bruker DRX500, Bruker AV500, or Bruker AV600 spectrometers at 25 °C in C_6D_6 unless otherwise specified. Chemical shifts are reported with respect to internal solvent (C_6D_6 at 7.16 pPr).

CHN analyses. CHN analyses were performed in house on a CE-440 elemental analyzer manufactured by Exeter Analytical, Inc.

Synthetic details. Optimized synthesis of THF adducts of MCl_3 and MBr_3 . The optimized syntheses of MCl_3 and MBr_3 are based on previously published methods.^{26, 29-31} The metal oxide (50 mmol metal based) and 375 mmol of NH_4Cl (or NH_4Br) were weighed in a 1.0 L Erlenmeyer flask. 120 mL of concentrated HCl (or HBr) and 160 mL of H_2O were added to the flask. The flask was gently stirred (360 rPr) and heated (125 °C) on a temperature controlled magnetic hot stir plate while a gentle flow of air was directed into the flask. The excess HCl or HBr and small amount of Br_2 were absorbed into a 10% NaOH solution. Generally, after 12 to 24 hours, a heavy slurry was obtained that was transferred to a Schlenk sublimation tube and heated under reduced pressure to obtain anhydrous MCl_3 (or MBr_3). The yield and percent yield (Y1) are summarized in Table 1. The freshly synthesized grey powder of MCl_3 or MBr_3 was transferred to a Schlenk tube pre-charged with 50 mL of THF and heated at 50 °C for 2 h. The yield and percent yield (Y2) calculated based on the assigned chemical formula are summarized in Table 1.

$\text{EuBr}_2(\text{THF})_2$ and $\text{EuBr}_2(\text{THF})_4$. Following a similar procedure as for other MBr_3 , scale: Eu_2O_3 (8.80 g, 25 mmol), NH_4Br (36.73 g, 375 mmol), concentrated HBr (120 mL), and water (120 mL). Yield: EuBr_2 15.25 g, 97.8%; $\text{EuBr}_2(\text{THF})_2$ 21.04 g, 94.3%. In a 20 mL scintillation vial, $\text{EuBr}_2(\text{THF})_2$ (5.00 g, 11.6 mmol) and I_2 (1.48 g, 5.8 mmol) were dissolved in 10 mL of THF and the mixture was stirred at room temperature for 3 h. After removing

volatiles under reduced pressure, a brown powder was obtained and formulated as $\text{EuBr}_2(\text{THF})_4$. Yield: 7.97 g, 100%.

$(\text{NN}^{\text{TBS}})\text{Ce}(\text{THF})_2$. In a 20 mL scintillation vial, was placed $\text{CeBr}_3(\text{THF})_4$ (1.035 g, 1.55 mmol). THF (5 mL) was added to make a slurry. The mixture was placed in a dry ice / acetone bath for 15 min. KBr (0.605 g, 4.65 mmol) was dissolved in THF (5 mL) and placed in dry ice / acetone bath for 15 min. KBr solution was drop-wise added to $\text{CeBr}_3(\text{THF})_4$ slurry. After addition, the mixture was warmed to 0 °C and allowed to stir for 0.5 h. $\text{H}_2(\text{NN}^{\text{TBS}})$ (0.689 g, 1.55 mmol) was dissolved in 5 mL of THF and cooled down to 0 °C for 15 min. $\text{H}_2(\text{NN}^{\text{TBS}})$ was slowly added to in situ formed CeBn_3 and the mixture was allowed to stir for 1 h at 0 °C. The volatiles were removed under reduced pressure. 20 mL of toluene was used to extract the remaining solid. Me_3SiI (0.620 g, 3.10 mmol) was added drop-wise to the toluene extraction and the mixture was stirred for 1 h at room temperature. 1 mL of THF was added to quench the excess Me_3SiI and the volatiles were removed under reduced pressure. A yellow solid was collected after an extensive hexanes wash with a formula of $(\text{NN}^{\text{TBS}})\text{Ce}(\text{THF})_2$. Yield: 0.819 g, 67.6%. Single crystals were obtained from a concentrated THF solution layered with *n*-pentane in the monomeric form as $(\text{NN}^{\text{TBS}})\text{Ce}(\text{THF})_2$. Anal. (%): Calcd. for $\text{C}_{26}\text{H}_{46}\text{N}_2\text{OFeCeSi}_2$, Mw = 781.704: C, 39.95; H, 5.93; N, 3.58. Found: C, 40.58; H, 5.94; N, 3.60.

$(\text{NN}^{\text{TBS}})\text{Pr}(\text{THF})_2$. In a 20 mL scintillation vial, was placed $\text{PrBr}_3(\text{THF})_4$ (0.800 g, 1.20 mmol). THF (5 mL) was added to make a slurry. The mixture was placed in a dry ice / acetone bath for 15 min. KBr (0.467 g, 3.59 mmol) was dissolved in THF (5 mL) and placed in dry ice / acetone bath for 15 min. KBr solution was dropwisely added to $\text{PrBr}_3(\text{THF})_4$ slurry. After addition, the mixture was warmed to 0 °C and allowed to stir for 0.5 h. $\text{H}_2(\text{NN}^{\text{TBS}})$ (0.532 g, 1.20 mmol) was dissolved in 5 mL of THF and cooled down to 0 °C for 15 min. $\text{H}_2(\text{NN}^{\text{TBS}})$ was slowly added to in situ formed SmBn_3 and the mixture was allowed to stir for 1 h at 0 °C. The volatiles were removed under reduced pressure. 20 mL of toluene was used to extract the remaining solid. Me_3SiI (0.479 g, 2.39 mmol) was added drop-wise to the toluene extraction and the mixture was stirred for 1 h at room temperature. 1 mL of THF was added to quench the excess Me_3SiI and the volatiles were removed under reduced pressure. A yellow solid was collected after an extensive hexanes wash with a formula of $(\text{NN}^{\text{TBS}})\text{Pr}(\text{THF})_2$. Yield: 0.607 g, 64.9%. Single crystals were obtained from a toluene solution layered with hexanes in the dimeric form as $[(\text{NN}^{\text{TBS}})\text{Pr}(\text{THF})_2]_2$. Anal. (%): Calcd. for $\text{C}_{26}\text{H}_{46}\text{N}_2\text{OFePrSi}_2$, Mw = 782.496: C, 39.91; H, 5.93; N, 3.58. Found: C, 40.05; H, 5.87; N, 3.49.

$(\text{NN}^{\text{TBS}})\text{Sm}(\text{THF})_2$. In a 20 mL scintillation vial, was placed $\text{SmBr}_3(\text{THF})_4$ (1.000 g, 1.47 mmol). THF (5 mL) was added to make a slurry. The mixture was placed in a dry ice / acetone bath for 15 min. KBr (0.576 g, 4.42 mmol) was dissolved in THF (5 mL) and placed in dry ice / acetone bath for 15 min. KBr solution was drop-wise added to $\text{SmBr}_3(\text{THF})_4$ slurry. After addition, the mixture was warmed to 0 °C and allowed to stir for 0.5 h. $\text{H}_2(\text{NN}^{\text{TBS}})$ (0.655 g, 1.47 mmol) was dissolved in 5 mL of THF and cooled down to 0 °C for 15 min. $\text{H}_2(\text{NN}^{\text{TBS}})$ was slowly added to the in situ formed SmBn_3 and the mixture was stirred for 1 h at

0 °C. The volatiles were removed under reduced pressure. 20 mL of toluene was used to extract the remaining solid. Me_3SiI (0.590 g, 2.95 mmol) was added drop-wise to the toluene extraction and the mixture was stirred for 1 h at room temperature. 1 mL of THF was added to quench the excess Me_3SiI and the volatiles were removed under reduced pressure. The crude was dissolved in minimum amount of Et_2O layered with *n*-pentane and stored in a -35 °C freezer. Orange crystals were formed after one day with a formula of $(\text{NN}^{\text{TBS}})\text{Sm}(\text{THF})_2$. Yield: 0.638 g, 54.7%. Single crystals were obtained from an Et_2O solution layered with *n*-pentane in the monomeric form. Anal. (%): Calcd. for $\text{C}_{30}\text{H}_{54}\text{N}_2\text{O}_2\text{FeSmSi}_2$, Mw = 864.055: C, 41.70; H, 6.30; N, 3.24. Found: C, 41.26; H, 6.11; N, 3.01.

$(\text{NN}^{\text{TBS}})\text{Tb}(\text{THF})_2$. In a 20 mL scintillation vial, was placed $\text{TbBr}_3(\text{THF})_{3.5}$ (1.000 g, 1.54 mmol). THF (5 mL) was added to make a slurry. The mixture was placed in a dry ice / acetone bath for 15 min. KBr (0.600 g, 4.61 mmol) was dissolved in THF (5 mL) and placed in dry ice / acetone bath for 15 min. KBr solution was added drop-wise to $\text{TbBr}_3(\text{THF})_{3.5}$ slurry. After addition, the mixture was warmed to 0 °C and allowed to stir for 0.5 h. $\text{H}_2(\text{NN}^{\text{TBS}})$ (0.683 g, 1.54 mmol) was dissolved in 5 mL of THF and cooled down to 0 °C for 15 min. $\text{H}_2(\text{NN}^{\text{TBS}})$ was slowly added to in situ formed TmBn_3 and the mixture was allowed to stir for 1 h at 0 °C. The volatiles were removed under reduced pressure. 20 mL of toluene was used to extract the remaining solid. Me_3SiI (0.615 g, 3.07 mmol) was added drop-wise to the toluene extraction and the mixture was stirred for 1 h at room temperature. 1 mL of THF was added to quench the excess Me_3SiI and the volatiles were removed under reduced pressure. The crude was dissolved in minimum amount of Et_2O layered with *n*-pentane and stored in a -35 °C freezer. Orange crystals were formed after one week with a formula of $(\text{NN}^{\text{TBS}})\text{Tb}(\text{THF})_2$. The mother liquid was concentrated and crystallized to give a 2nd crop. Yield: 1st crop 0.626 g, 46.4%; 2nd crop 0.259 g, 19.2%; Total 65.6%. Single crystals were obtained from an Et_2O solution layered with *n*-pentane in the monomeric form. Anal. (%): Calcd. for $\text{C}_{30}\text{H}_{54}\text{N}_2\text{O}_2\text{FeTbSi}_2$, Mw = 872.620 and half molecule of *n*-pentane: C, 42.95; H, 6.66; N, 3.08. Found: C, 43.31; H, 6.68; N, 3.10.

$(\text{NN}^{\text{TBS}})\text{Tm}(\text{THF})_2$. In a 20 mL scintillation vial, was placed $\text{TmCl}_3(\text{THF})_{3.5}$ (1.000 g, 1.90 mmol). THF (5 mL) was added to make a slurry. The mixture was placed in a dry ice / acetone bath for 15 min. KBr (0.740 g, 5.68 mmol) was dissolved in THF (5 mL) and placed in dry ice / acetone bath for 15 min. KBr solution was dropwisely added to $\text{TmCl}_3(\text{THF})_{3.5}$ slurry. After addition, the mixture was warmed to 0 °C and allowed to stir for 0.5 h. $\text{H}_2(\text{NN}^{\text{TBS}})$ (0.843 g, 1.90 mmol) was dissolved in 5 mL of THF and cooled down to 0 °C for 15 min. $\text{H}_2(\text{NN}^{\text{TBS}})$ was slowly added to in situ formed TmBn_3 and the mixture was allowed to stir for 1 h at 0 °C. The volatiles were removed under reduced pressure. 20 mL of toluene was used to extract the remaining solid. Me_3SiI (0.758 g, 3.79 mmol) was added drop-wise to the toluene extraction and the mixture was stirred for 1 h at room temperature. 1 mL of THF was added to quench the excess Me_3SiI and the volatiles were removed under reduced pressure. The crude was dissolved in minimum amount of Et_2O layered with *n*-pentane and stored in a -35 °C freezer. Orange crystals

were formed after one week with a formula of $(\text{NN}^{\text{TBS}})\text{TmI}(\text{THF})_2$. The mother liquid was concentrated and crystallized to give a 2nd crop. Yield: 1st crop 0.862 g, 51.5%; 2nd crop 0.174 g, 10.4%; Total 61.9%. Single crystals were obtained from an Et₂O solution layered with *n*-pentane in the monomeric form. Anal. (%): Calcd. for C₃₀H₅₄N₂O₂FeTmSi₂, Mw = 882.629 and half molecule of *n*-pentane: C, 42.49; H, 6.58; N, 3.05. Found: C, 42.20; H, 6.39; N, 3.05.

$(\text{NN}^{\text{TBS}})\text{YbI}(\text{THF})$. In a 20 mL scintillation vial, was placed YbCl₃(THF)₃ (0.500 g, 1.01 mmol). THF (5 mL) was added to make a slurry. The mixture was placed in a dry ice / acetone bath for 15 min. K₂Bn (0.394 g, 3.03 mmol) was dissolved in THF (5 mL) and placed in dry ice / acetone bath for 15 min. K₂Bn solution was dropwisely added to YbCl₃(THF)₃ slurry. After addition, the mixture was warmed to 0 °C and allowed to stir for 0.5 h. H₂(NN^{TBS}) (0.448 g, 1.01 mmol) was dissolved in 5 mL of THF and cooled down to 0 °C for 15 min. H₂(NN^{TBS}) was slowly added to in situ formed TmBn₃ and the mixture was allowed to stir for 1 h at 0 °C. The volatiles were removed under reduced pressure. 20 mL of toluene was used to extract the remaining solid. Me₃SiI (0.404 g, 2.02 mmol) was added drop-wise to the toluene extraction and the mixture was stirred for 1 h at room temperature. 1 mL of THF was added to quench the excess Me₃SiI and the volatiles were removed under reduced pressure. The ¹H NMR spectrum of the crude reaction mixture showed that $(\text{NN}^{\text{TBS}})\text{YbI}(\text{THF})$ was the major product while $[(\text{NN}^{\text{TBS}})_2\text{Yb}][\text{K}(\text{THF})_6]$ was the minor product. The crude reaction product was dissolved in minimum amount of Et₂O layered with *n*-pentane and stored in a -35 °C freezer. Red crystals formed after one day and were confirmed to be $[\text{K}(\text{THF})_6][(\text{NN}^{\text{TBS}})_2\text{Yb}]$, yield: 0.153 g, 9.9%. Single crystals were obtained from a toluene solution layered with hexanes with a formula of $[\text{K}(\text{toluene})][(\text{NN}^{\text{TBS}})_2\text{Yb}]$. Anal. (%): Calcd. for C₆₈H₁₂₄N₄O₆Fe₂YbKSi₄, Mw = 1529.948: C, 53.38; H, 8.17; N, 3.66. Found: C, 53.92; H, 7.14; N, 3.04. The volatiles of the mother liquid were removed under reduced pressure and the remaining solid was washed with *n*-pentane to yield a green powder that was confirmed to be $(\text{NN}^{\text{TBS}})\text{YbI}(\text{THF})$, yield: 0.188 g, 22.8%. Single crystals were obtained from a concentrated Et₂O solution layered with *n*-pentane in the monomeric form. Anal. (%): Calcd. for C₂₆H₄₆N₂OFeYbSi₂, Mw = 814.642: C, 38.33; H, 5.69; N, 3.44. Found: C, 40.26, H 8.23, N 4.41. Note: several attempts of obtaining the elemental analysis for this compound failed to produce results close to the calculated values. It is likely that $(\text{NN}^{\text{TBS}})\text{YbI}(\text{THF})$ reduces quickly to a ytterbium(II) species that contaminates the samples.

$(\text{NN}^{\text{TBS}})\text{YbCl}(\text{THF})_2$. In a 20 mL scintillation vial, was placed YbCl₃(THF)₃ (0.286 g, 0.58 mmol). THF (5 mL) was added to make a slurry. The mixture was placed in a dry ice / acetone bath for 15 min. K₂(NN^{TBS}) (0.300 g, 0.58 mmol) was dissolved in THF (5 mL) and placed in dry ice / acetone bath for 15 min. K₂(NN^{TBS}) solution was dropwisely added to YbCl₃(THF)₃ slurry. After addition, the mixture was warmed to room temperature and allowed to stir for 1.5 h. The ¹H NMR spectrum of the crude showed that $(\text{NN}^{\text{TBS}})\text{YbCl}(\text{THF})_2$ was formed exclusively. The crude was dissolved in minimum amount of Et₂O layered with *n*-pentane and stored in a -35 °C freezer. Green crystals formed

after one day. Yield: 0.279 g, 66.9%. Single crystals were obtained from an Et₂O solution layered with *n*-pentane. Anal. (%): Calcd. for C₃₀H₅₄N₂O₂FeYbClSi₂, Mw = 723.174: C, 43.18; H, 6.41; N, 3.87. Found: C, 43.23; H, 6.23; N, 3.66.

X-ray crystallographic structure determinations. X-ray quality crystals were obtained from various concentrated solutions placed in a -40 °C freezer in the glove box. Inside the glove box, the crystals were coated with oil (STP Oil Treatment) on a microscope slide, which was brought outside the glove box. The X-ray data collections were carried out on a Bruker SMART 1000 single crystal X-ray diffractometer using MoK_α radiation and a SMART APEX CCD detector. The data was reduced by SAINTPLUS and an empirical absorption correction was applied using the package SADABS. The structure was solved and refined using SHELXTL (Bruker 1998, SMART, SAINT, XPREP AND SHELXTL, Bruker AXS Inc., Madison, Wisconsin, USA). Tables with atomic coordinates and equivalent isotropic displacement parameters, with all the distances and angles and with anisotropic displacement parameters are listed in the cif.

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Electronic Supplementary Information (ESI) available for X-ray crystallographic data (CCDC 1404609-1404616).

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