Chemistry–A European Journal

Research Article
doi.org/10.1002/chem.202300956

Chemistry Europe
European Chemical
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Bromobenzene Transforms Lanthanoid Pseudo-Grignard Chemistry

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Abstract: Divalent lanthanoid pseudo-Grignard reagents PhLnBr (Ln = Sm, Eu and Yb) can be easily prepared by the oxidative addition of bromobenzene (PhBr) to lanthanoid metals in tetrahydrofuran (THF). PhLnBr reacts with bulky N,N′-bis(2,6-di-*iso*propylphenyl)formamidine (DippFormH) to generate Ln^{II} complexes, namely $[Ln(DippForm)Br(thf)_3]_2 \cdot 6thf$ (**1**; **Sm**, **2**; **Eu**), and $[Yb(DippForm)Br(thf)_2]_2 \cdot 2thf$ (**3**; **Yb**). Samarium and europium (in **1** and **2**) are seven coordinate, whereas ytterbium (in **3**) is six coordinate, and all are bromine-bridged dimers. When PhLnBr reacts with 3,5-diphenylpyrazole (Ph_2pzH), both divalent (**5**; $[Eu(Ph_2pz)_2(thf)_4]$) and trivalent (**4a**; $[Sm(Ph_2pz)_3(thf)_3] \cdot 3thf$, **4b**; $[Sm-(Ph_2pz)_3(dme)_2] \cdot dme]$ complexes are obtained. In the monomeric compounds **4(a,b)**, samarium is nine coordinate but europium is eight coordinate in **5**. The use of PhLnBr in this work transforms the outcomes from earlier reactions of PhLnI.

Introduction

Pseudo-Grignard reagents of lanthanoid metals $[RLn(solv)_nX]$ (X = I mainly, Br) were discovered in the 1970s and were formed by the reaction between free metals (mainly Eu, Sm, Yb) and organic halides (Eq. (1)).[1,2]

$$Ln + RX \xrightarrow[-78 \text{ to } -50\,°C]{thf} \text{"}RLnX(thf)_n\text{"}$$

$$R = Me, Ph$$
$$Ln = Sm, Eu, Yb$$

(1)
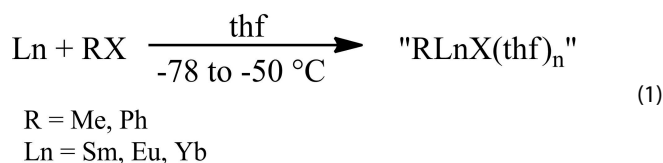
Early characterization was largely based on reaction chemistry, for example towards acids and electrophiles and similarities to the behavior of classical Grignard reagents.[1–4] However, differences in reactivity with some organic substrates also attracted attention.[5,6] Thus, with α, β- unsaturated ketones, 1,2 addition occurred by contrast with 1,4-addition by Grignard reagents[5] and reactions with esters can give ketones unlike Grignard reagents.[6] Early magnetic measurements showed that the solution species were not exclusively Ln^{II} and that significant Ln^{III} derivatives were present, especially for Ln = Sm, Yb.[2] These are formed by an oxidation reaction, (Eq. (2))

$$2\ RLnX + RX = R_2LnX + RLnX_2 \qquad (2)$$
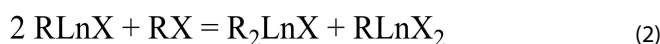
Both the Ln^{II} and Ln^{III} complexes can undergo Schlenk-type equilibria further complicating the reaction chemistry. (Scheme 1 Equations (3–5)).

In addition, the low thermal stability of the Ln–C (σ-bond) produces another challenge for the isolation of these reagents.[7] Despite these problems, organolanthanoid(II) iodides have been isolated and structurally characterized by employing bulky alkyl,[8,9] for example $[Yb\{C(SiMe_3)_2(SiMe_2R)\}I(Et_2O)]_2$ (R = Me, MeO, CH=CH$_2$) and aryl groups,[10] for example 2,6-diphenylphenyl ligands. In addition, low yields of $[Sm-(C_5Ph_5)(\mu\text{-}Br)(thf)_2]_2 \cdot 6thf$, and $[Yb(C_5Ph_4H)(\text{mu-}Br)(thf)_2]_2$ were obtained from redox transmetallation/protolysis reactions between Ln metal, PhHgBr, and C_5Ph_5H or $C_5Ph_4H_2$[11,12] and $[Sm(C_5Ph_4H)I(thf)_3]$ from a redistribution reaction.[11] If the definition of lanthanoid pseudo-Grignard compounds is extended to $Ln^{II}L(X)$ where L = N or O donor, then more known complexes fall into this category. For example, pseudo-Grignard complexes, $[Sm(dpp\text{-}Bian)(dme)Br]_2$ {dpp-Bian = 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene},[13] $[Eu(dpp\text{-}Bian)(d\text{-}me)(\mu\text{-}X)]_2$ (X = Cl, Br),[14] $[Yb(dpp\text{-}Bian)(dme)(\mu\text{-}Br)]_2$,[15a] $[Yb(dpp\text{-}Bian)I(thf)_2]_2$,[15b] $[Sm(ArO)(\mu\text{-}I)(thf)_3]_2$,[16] (Ar=C$_6H_2Bu^t_2$-2,6-Me-4), $[Sm(Ap)I(thf)_2]_2$,[17] {ApH = (2,6-diisopropylphenyl)-[6-(2,4,6-triisopropylphenyl)pyridine-2-yl]amine}, $[Yb(Ap)I(thf)_2]_2$,[17] $[YbDmp(Tph)N_3Cl(thf)]_2$, {Dmp = 2,6-Mes$_2$C$_6$H$_3$, Tph = 2′,4′,6′-triisopropylbiphenyl-2-yl},[18] have been were synthesized previously by a variety of routes.

We have been interested in exploring the simple PhLnI species prepared in situ (Scheme 2, Equation (6)) as a source of other Ln(L)X complexes by trapping reactions with LH pro-ligands. This enabled the preparation of $[Ln(Ph_2pz)I(thf)_4]$ (Ln = Eu or Yb) in high yield by reaction of PhYbI with 3,5-diphenylpyrazole (Scheme 2, Equation (7)).[19] However in reac-
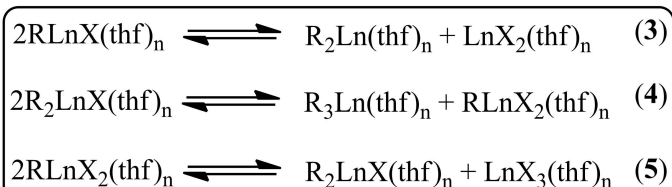
Chem. Eur. J. **2023**, *29*, e202300956 (1 of 7)

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Chemistry–A European Journal

Research Article
doi.org/10.1002/chem.202300956

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$$2RLnX(thf)_n \rightleftharpoons R_2Ln(thf)_n + LnX_2(thf)_n \quad (3)$$

$$2R_2LnX(thf)_n \rightleftharpoons R_3Ln(thf)_n + RLnX_2(thf)_n \quad (4)$$

$$2RLnX_2(thf)_n \rightleftharpoons R_2LnX(thf)_n + LnX_3(thf)_n \quad (5)$$

Scheme 1. Extended Schlenk equilibria for pseudo-Grignard reagents.

$$Ln_{(excess)} + PhI \xrightarrow[\text{sonication}]{-78°C/thf} \text{"PhLnI"} \quad (6)$$

$$\text{"PhLnI"} + Ph_2pzH \xrightarrow[\text{RT (overnight)}]{-78°C/thf} [Ln(Ph_2pz)I(thf)_4] + PhH \quad (7)$$

$$\text{"PhLnI"} + DippFormH \xrightarrow[\text{RT (overnight)}]{-78°C/thf} [Ln(DippForm)I_n(thf)_3] + PhH \quad (8)$$

$$n = 1 \text{ or } 2$$
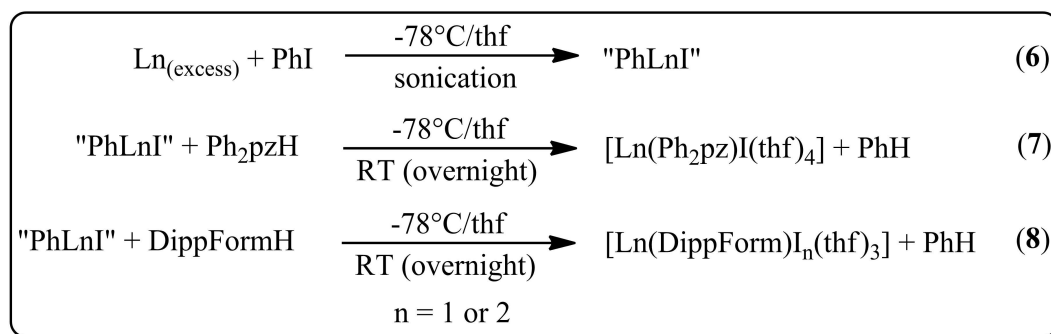
Scheme 2. Reported pseudo-Grignard reactions.

tions with formamidines, only PhEuI gave divalent complexes in some cases, whereas with ytterbium, both divalent and trivalent complexes were obtained, for example N,N'-bis(2,6-diisopropylphenyl)formamidine (DippFormH) gave a mixture of [Yb^{II}(DippForm)I(thf)$_3$] and [Yb^{III}(DippForm)I$_2$(thf)$_3$] (Scheme 2, Equation (8)).[20] Although the different oxidation state products could be separated by fractional crystallization, it took the gloss off the synthetic method and discouraged us from attempting to make Sm(Form)I by this approach as oxidation to Sm^{III} is even more likely. This led us to consider using the less investigated PhLnBr species, as, though the C–Br bond is stronger, perhaps inhibiting PhLnBr formation, greater stability of Ln–Br than Ln–I complexes might reign in oxidation. We now report that reactions of PhLnBr (Ln = Eu, Sm, Yb) with DippFormH have enabled the preparation of divalent pseudo-Grignard complexes in reasonable yields in all cases, the success with samarium being noteworthy. By contrast reactions with Ph$_2$pzH gave Eu(Ph$_2$pz)$_2$ and Sm(Ph$_2$pz)$_3$ species.

Results and Discussion

Synthesis and spectroscopic characterisation of divalent lanthanoid complexes from pseudo-Grignard reactions

Phenyllanthanoid bromides, PhLnBr (Ln = Sm, Eu, Yb) were generated in situ by reactions of an excess of Ln metal with bromobenzene in tetrahydrofuran on sonication and further stirring at room temperature for Ln = Sm. The products were treated with N,N'-bis(2,6-di-isopropylphenyl)formamidine (DippFormH) (mole ratio PhBr:DippFormH = 1:1) at 0 °C (Sm) or −78 °C (Ln = Eu, Yb) and then at room temperature to form the

pseudo-Grignard complexes [Ln^{II}(DippForm)Br(thf)$_n$]$_2$ (n = 3, Ln = Sm **1**, Eu **2**; n = 2, Ln = Yb **3**) in 45–65% crystalline yield (Scheme 3). The result for samarium is of significance as solutions of PhSmI in thf are reported to have only 50% Sm^{II},[2] whilst the outcome for ytterbium contrasts the formation of [YbI$_2$(thf)$_4$], [Yb^{II}(DippForm)I(thf)$_3$] and [Yb^{III}(DippForm)I$_2$(thf)$_3$], the last two in under 20% yield[5] from reaction of DippFormH with PhYbI.[20] The results for the DippFormH reactions are consistent with greater stability for PhLnBr than PhLnI. In addition the current complexes are isolated as bromide-bridged dimers, whereas the Yb^{II} and Yb^{III} DippForm iodides were obtained as monomers.[20] However iodide-bridged dimers were obtained with less bulky formamidines,[20] and [Yb(DippForm)I-(thf)$_2$]$_2$ was crystallized from THF/PhMe following a synthesis different from a pseudo-Grignard route.[21]

By contrast, for the Ph$_2$pzH pro-ligand, we obtained two reported compounds (Scheme 4), [Sm(Ph$_2$pz)$_3$(thf)$_3$].3thf (**4a**)[22] and [Eu(Ph$_2$pz)$_2$(thf)$_4$] (**5**)[23] in 60% yield. A new trivalent complex, [Sm(Ph$_2$pz)$_3$(dme)$_2$]·dme (**4b**) was synthesised by crystallizing **4a** from DME. No crystalline product could be obtained from the corresponding reaction of Yb. Products **5** and **4a** arise from protonation by Ph$_2$pzH of EuPh$_2$ and SmPh$_3$ respectively, which are Schlenk equilibrium products with additional oxidation for Sm (see Scheme 4).

These outcomes again contrast the behaviour of PhLnI (Ln = Eu, Yb), where the corresponding reactions yield the pseudo-Grignard reagents [Ln(Ph$_2$Pz)I(thf)$_4$] in high yield.[5,19] A similar two step experimental method was used for reactions with both PhBr and PhI, hence the differences do not arise from the procedures.

Compound **1** is green and compounds **2**, **3** and **5** are yellow, while both **4**(**a**, **b**) are colourless. The colour of **1** is
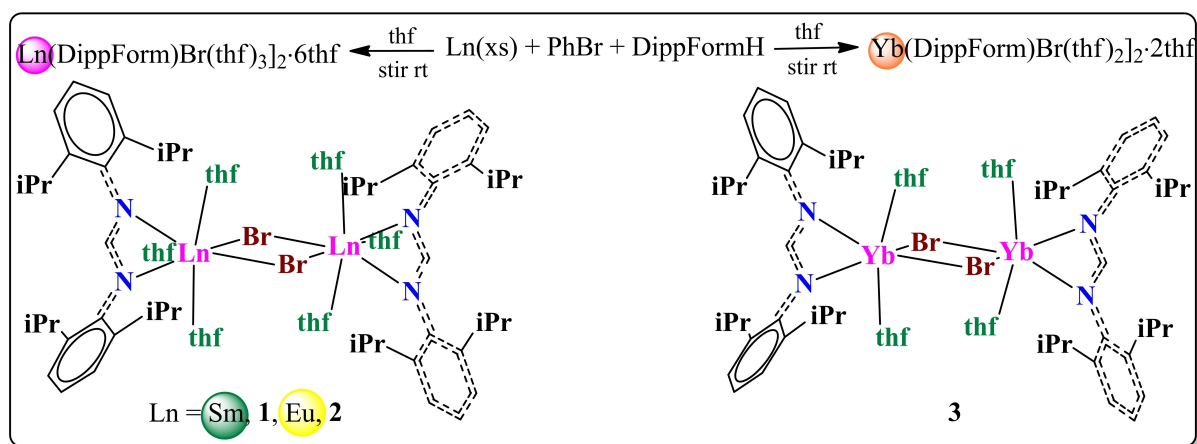
Scheme 3. Synthesis of complexes **1–3**.
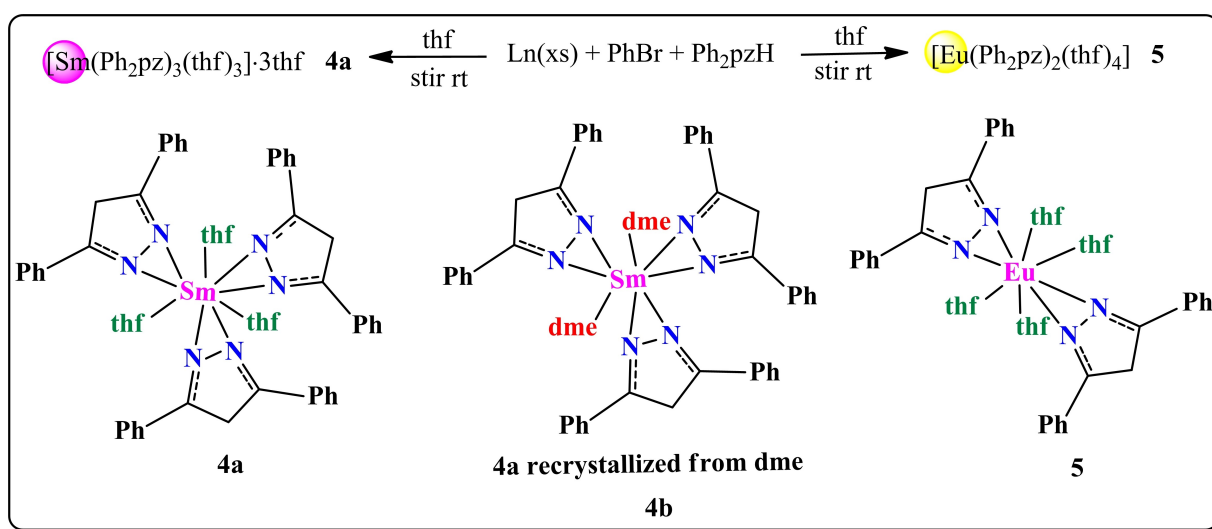
Scheme 4. Synthesis of complexes **4a**, **4b** and **5**.

associated with a broad visible band at 588 nm in the UV/vis spectrum (Figure S8), which is attributable to an f^6 to f^5d^1 transition.[24]

IR spectra showed the presence of the appropriate Dipp-Form or Ph_2pz ligand. For compounds **1–5**; the absence of (N–H) absorption (around 3300–3400 cm^{-1}) in the infrared spectrum proved the complete deprotonation of the ligands. Complexes **1**, **3** and **4**(**a**, **b**) gave satisfactory good ^1H NMR spectra in C_6H_6 (Figures S1,3,4,5), but **2** and **5** showed broad features with unsatisfactory integration owing to Eu^{II} para-magnetism (Figures S2, 6). Microanalyses or metal analysis established bulk purity, the latter being used when there were microanalysis difficulties. In some cases, analyses showed loss of solvent of crystallization from the analysis sample. The melting points indicate significant thermal stability of the new Dipp-Form compounds. Complexes **1**, **3** and **4**(**a**, **b**) gave satisfactory ^1H NMR spectra in C_6H_6 (Figure S1, 3, 4, 5), but **2** and **5** showed broad features with unsatisfactory integration owing to Eu^{II}

paramagnetism (Figure S2, 6). The NMR spectra of compound **1** indicated the loss of 3 THF of crystallization, consistent with the microanalysis, whereas **4**(**b**) had excess DME. The methine proton (NC*H*N) resonances in the ^1H NMR shifted significantly for compound **1** to lower frequencies (−10.70 ppm) comparable to paramagnetic [Sm(DippForm)$_2$(thf)$_2$] (−14.03 ppm),[25] where-as for the diamagnetic compound **3**, a higher (8.28 ppm) methine resonance than for DippFormH ($\delta = 7.50$ ppm) was observed. For compound **4a** the CH-pz resonance shifted to 9.39 ppm and for **4b** it shifted to 8.75 ppm, compared with the pro-ligand value of 6.63 ppm.

Molecular structures

Compounds **1–5** were identified and authenticated by single crystal X-ray diffraction.

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doi.org/10.1002/chem.202300956

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Complexes [Ln(DippForm)Br(thf)$_3$]$_2$·6thf (**1–2**) are isostructural having similar crystallographic and molecular parameters, and crystallise in the monoclinic *P*2$_1$/*c* space group. Compounds **1–3** (Figure 1a, b) were isolated as dimers, whereas **4a**, **4b** (Figure 2)) and **5** are monomeric. Selected bond lengths and angles of compounds **1–3**, **4**(**b**) are given with the figures and more details in the Supporting Information. The lanthanoid contraction is observed in the average Ln–N bond lengths of the complexes (**1–3**): Sm–N (2.64) > Eu–N (2.63) > Yb–N (2.46).

Compounds [Ln(DippForm)Br(thf)$_3$]$_2$·6thf (**1**, **2**) are seven coordinate Ln$_2$Br$_2$ bridged dimers with one chelating DippForm and three coordinated thf ligands bound to each Ln atom. The DippForm ligands are perpendicular to the LnBrBrLn plane, where one ligand is *cis* {C(13)-Sm(1)-Br(1) 95.06°, C(13)-Eu(1)-Br(1) 97.71°} to Br1 and *trans* {C(13)-Sm(1)-Br(2) 174.34°, C(13)-Eu(1)-Br(2) 176.92°} to Br2. The average bite angle in **1** is 51.7° and Br(1)-Sm-Br(2) is 79.48(18)° whereas in **2** the average bite angle is 0.01° larger and Br(1)-Ln-Br(2) is 0.26° smaller than in **1**

(see the Supporting Information Table S1). The stereochemistry of the seven coordinate Sm^{2+} and Eu^{2+} (**1** and **2**) ions can be described as distorted pentagonal bipyramidal. The average Sm–N bond length in [Sm(DippForm)Br(thf)$_3$]$_2$ **1** is 2.64 Å, which is longer than the average Sm–N bond length 2.59 Å in six coordinate [Sm(DippForm)$_2$(thf)$_2$].[26] This is consistent with the change in coordination number.[27] The average Sm–Br bond length in seven coordinate **1** (3.09 Å), is very comparable to the average Sm–Br bond length is 3.03 Å in seven coordinate [Sm(C$_5$Ph$_5$)(μ-Br)(thf)$_2$]$_2$.[11] It is longer than the reported average Sm–Br bond length (2.84 Å) in seven coordinate [Sm-(DippForm)Br$_2$(thf)$_3$],[28] because the latter has non-bridging Sm–Br bonds and a higher oxidation state for Sm. Again, the < Sm-O$_{(thf)}$ > bond length in **1** is 2.61 Å, which is very close to the < Sm-O$_{(thf)}$ > bond length (2.58 Å) in [Sm(C$_5$Ph$_5$)(μ-Br)(thf)$_2$]$_2$,[11] but longer than the < Sm-O$_{(thf)}$ > bond length (2.48 Å) in [Sm(DippForm)Br$_2$(thf)$_3$],[28] because of the oxidation state difference.[27] Comparisons of Eu–N, Eu-O$_{(thf)}$, and Eu–Br bond
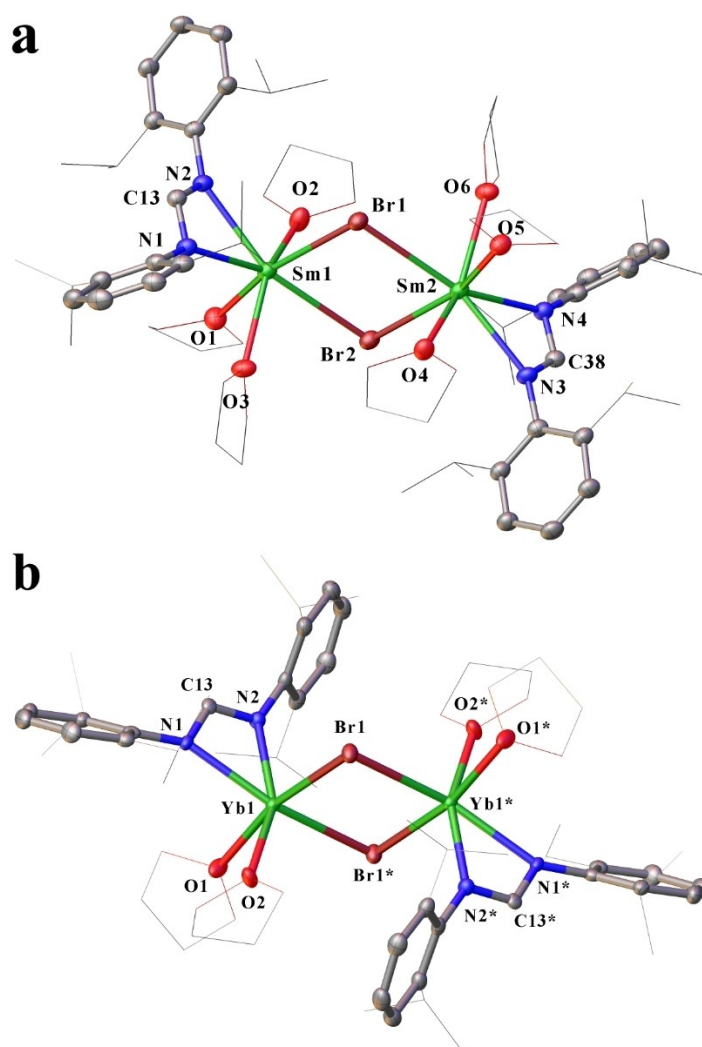

Figure 1. Molecular diagram of a) [Sm(DippForm)Br(thf)$_3$]$_2$·6thf (representative of Sm, **1**, Eu, **2**); b) [Yb(DippForm)Br(thf)$_2$]$_2$·2thf (**3**). Hydrogen atoms and lattice thf molecules are omitted and coordinated thf molecules and *i*Pr groups are drawn as wireframe for clarity and thermal ellipsoids are set to the 50% probability level. Selected bond lengths (Å): Sm(1)-N(1) 2.634(4), Sm(1)-N(2) 2.644(4), Sm(1)-Br(1) 3.0260(8); Eu(1)-N(1) 2.625(2), Eu(1)-N(2) 2.635(2), Eu(1)-Br(1) 3.1157(6); Yb(1)-N(1) 2.429(3), Yb(1)-N(2) 2.483(3), Yb(1)-Br(1) 2.892(7). More details are in the Supporting Information (Table S1).
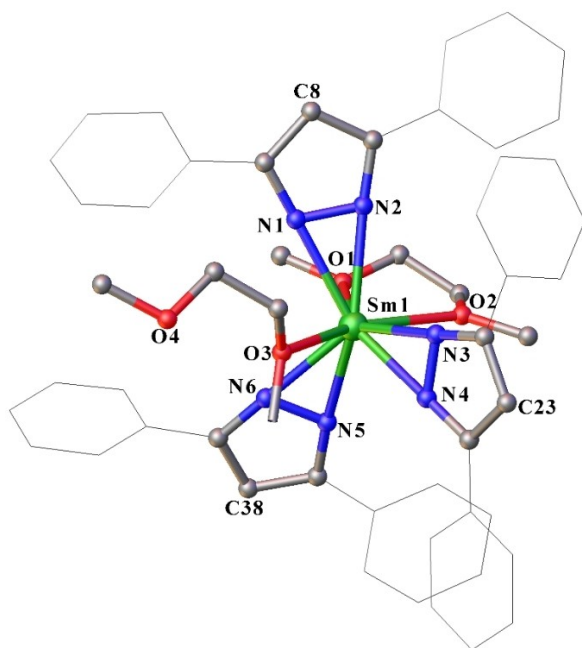
Figure 2. Molecular diagram of [Sm(Ph$_2$pz)$_3$(dme)$_2$]·dme (4b). Hydrogen atoms and lattice dme molecules are omitted, phenyl groups are drawn as wireframe for clarity and thermal ellipsoids are set to the 50% probability level. Selected bond lengths (Å): Sm(1)-N(1) 2.446(3), Sm(1)-N(2) 2.419(3), Sm(1)-N(3) 2.434(3), Sm(1)-N(4) 2.424(3), Sm(1)-N(5) 2.403(3), Sm(1)-N(6) 2.456(3). For more details, see the Supporting Information (Table S1 and associated text).

lengths of [Eu(DippForm)Br(thf)$_3$]$_2$ (**2**) with those of six coordinate [Eu(DippForm)$_2$(thf)$_2$],[29] and [(dpp-Bian)Eu(dme)(μ-Br)]$_2$,[14] show the expected relationships from the differences in coordination numbers.[27]

Compound [Yb(DippForm)Br(thf)$_2$]$_2$ (**3**) crystallises in the triclinic, space group P-1 and is a centrosymmetric dimer, where half is generated from symmetry at the midpoint of the Yb(1)···Yb(1)* vector. The six coordinate metal atom has an octahedral arrangement. The average Yb–N bond length in [Yb(DippForm)Br(thf)$_2$]$_2$ **3** is 2.45 Å, which is the same as the average Yb–N bond length (2.45 Å) of six coordinate [Yb-(DippForm)(μ-I)(thf)$_2$]$_2$[21] and nearly the same as the <Yb–N> bond length 2.47 Å of six coordinate [Yb(DippForm)$_2$(thf)$_2$].[29] The Yb–Br1 and Yb–Br1* bond lengths in **3** (2.8926(7) and 2.8979(11) Å) are comparable to the reported Yb–Br1 and Yb–Br1* bond lengths (2.8932(2) and 2.9216(3) Å) for seven coordinate [Yb(C$_5$Ph$_4$H)(μ-Br)(thf)$_2$]$_2$[12] and six coordinate [(dpp-Bian)Yb(dme)(μ-Br)]$_2$ (2.8673(9) Å and 2.9325(9) Å).[15a] The average Yb–O$_{(thf)}$ bond length in **3** is 2.42 Å, which is similar to the <Yb–O$_{(thf)}$> bond length of 2.44 Å in [Yb(C$_5$Ph$_4$H)(μ-Br)(thf)$_2$]$_2$,[12] 2.45 Å in [Yb(DippForm)(μ-I)(thf)$_2$]$_2$[21] and 2.46 Å in [Yb(DippForm)$_2$(thf)$_2$].[29]

[Sm(Ph$_2$pz)$_3$(dme)$_2$] (**4b**) crystallizes in the monoclinic space group $P2_1/c$ and has a nine coordinate trigonal prismatic structure. Three η^2-Ph$_2$pz (ligands), one chelating dme and one monodentate dme are attached to samarium. Complex (**4b**) is isostructural with [Nd(Ph$_2$pz)$_3$(dme)$_2$].[22] The average Sm–N bond length in [Sm(Ph$_2$pz)$_3$(dme)$_2$] (**4b**) is 2.44 Å, which is the

same as the average Sm–N bond length 2.44 Å in nine coordinate [Sm(Ph$_2$pz)$_3$(thf)$_3$],[22] and comparable to the <Nd–N> bond length 2.46 Å in nine coordinate [Nd-(Ph$_2$pz)$_3$(dme)$_2$].[22] The ionic radii of nine coordinate Sm^{3+} (1.132 Å) and Nd^{3+} (1.163 Å)[27] are similar. The average Sm-O$_{(dme)}$ bond length in (**4b**) is 2.53 Å, which is close to the reported <Sm–O$_{(thf)}$> bond length (2.54 Å) in [Sm-(Ph$_2$pz)$_3$(thf)$_3$],[22] and the <Nd–O$_{(dme)}$> bond length (2.55 Å) in [Nd(Ph$_2$pz)$_3$(dme)$_2$].[22]

Conclusions

The reaction of Ln^0 metals with PhBr followed by addition of DippFormH enables the synthesis of divalent dimeric pseudo-Grignard complexes, [Ln(DippForm)Br(thf)$_3$]$_2$·6thf (Ln = Sm, Eu), and [Yb(DippForm)Br(thf)$_2$]$_2$·2thf in good crystalline yields. These three compounds have a Ln$_2$Br$_2$ bridged dimer core and varying coordination numbers (Sm, Eu: 7; Yb: 6). The Ln···C$_{(backbone)}$ distances for **1**, **2** and **3** are 3.03 Å, 3.02 Å and 2.83 Å respectively. With the pro-ligand Ph$_2$pzH, we obtained nine coordinate trivalent [Sm(Ph$_2$pz)$_3$(thf)$_3$].3thf, and [Sm-(Ph$_2$pz)$_3$(dme)$_2$]·dme complexes, and the divalent compound [Eu(Ph$_2$pz)$_2$(thf)$_4$] owing to protonation of Schlenk equilibrium products with prior oxidation in the case of Sm. The outcomes differ completely from analogous reactions of PhLnI,[19,20] and the isolation of a Sm^{II} pseudo-Grignard reagent is noteworthy.

Experimental Section

General: The lanthanoid compounds described here are highly air and moisture sensitive, hence were prepared and handled using vacuum-nitrogen line techniques and a glovebox under an atmosphere of purified nitrogen. Lanthanoid metals were collected from Santoku/Molycorp/Eutectix. Large chunks were filed in the drybox before use. Ligands DippFormH[30] and Ph$_2$pzH[31] were synthesised according to the literature methods. All other chemicals were purchased from Sigma and used without purification. Solvents (THF, DME and C$_6$D$_6$) were pre-dried by distillation over sodium or sodium benzophenone ketyl before being stored under an atmosphere of nitrogen. Infrared spectra were recorded as Nujol mulls between NaCl plates using a Perkin-Elmer/Nicolet-Nexus 1600 FTIR instrument within the range 4000–650 cm^{-1}. ^{1}H NMR spectra were recorded with a Bruker 400 MHz instrument with dry perdeuterobenzene as the solvent. Satisfactory NMR spectra could not be obtained for Eu^{II} complexes due to paramagnetism. Melting points were determined in sealed glass capillaries under nitrogen. Metal analyses were carried out by complexometric titration (Xylenol orange as indicator and hexamethylenetetramine as buffer) after digesting with dilute hydrochloric acid.[32] Elemental analyses (C, H, N) were performed at the Microanalytical Laboratory, Science Centre, London Metropolitan University, England. The samples were sent in sealed glass pipettes under nitrogen. Crystals were immersed in crystallography oil and were examined using the MX1 beamline at the Australian Synchrotron. Crystal data and refinement details are given in Table S2 and associated text.

Deposition Number(s) 2248415 (**1**), 2248416 (**2**), 2248417 (**3**), 2248418 (for compound **4(b)**) contain(s) the supplementary crystallographic data for this paper. These data are provided free of

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charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

[Sm(DippForm)Br(thf)₃]₂·6thf (1): Samarium metal powder (0.225 g, 1.5 mmol) was suspended in dry THF (15 ml) under N_2, and then PhBr (0.157 g, 1.0 mmol) was added at 0 °C. The mixture was sonicated for 10 min and stirred for 24 h at room temperature, when a light brown solution formed. Solid DippFormH (0.368 g, 1.0 mmol) was added and the mixture was stirred at 0 °C for 1 h, and a green solution developed after stirring for 24 h at room temperature. The resulting mixture was filtered and concentrated to 5 mL under vacuum. Green crystals (0.656 g, 64 %) were obtained after cooling at −25 °C for 3 days. M.P. 203–205 °C. Elemental analysis: Found: C 55.83, H 7.83, N 2.90; $C_{98}H_{166}Br_2N_4O_{12}Sm_2$ (2052.86 g mol⁻¹) requires: C 57.34, H 8.15, N 2.73; loss of 3 thf of crystallization, $C_{86}H_{142}Br_2N_4O_9Sm_2$ (1836.59 g mol⁻¹) requires: C 56.24, H 7.79, N 3.05. IR (Nujol): 2724w, 1671 s, 15991 m, 1529 m, 1340w, 1274 m, 1198w, 1103w, 1074 s, 1014 s, 948 m, 915 m, 857 m, 800 m, 774w, 755 m, 722 m, 666 w cm⁻¹. ¹H NMR (C_6D_6): $\delta = $ −10.70(s, 2H, NC(H)N), 1.20(m, 8H, CH), 1.78(d, 48H, CH₃), 3.23(s, br, 36H, thf), 4.55(d, 8H, H(3,5)), 4.99(s, 36H, thf), and 6.15 ppm(t, 4H, H(4)) corresponding to loss of 3 thf of crystallization. UV: broad peak at 588 nm.

[Eu(DippForm)Br(thf)₃]₂·6thf (2): Europium metal powder (0.23 g, 1.5 mmol) was suspended in dry THF (15 ml) under N_2, and then PhBr (0.157 g, 1.0 mmol) was added at −78 °C. The mixture was sonicated for 10 min when a brown solution formed. After cooling to −78 °C, solid DippFormH (0.368 g, 1.0 mmol) was added and the mixture was stirred at −78 °C for another 3 h. A brownish-yellow solution developed after further stirring for 24 h at room temperature. The resulting mixture was filtered and concentrated to 5 mL under vacuum. Yellow crystals (0.495 g, 48 %) were obtained after cooling at −25 °C for 3 days. M.P. 186–188 °C. Elemental analysis: Found: C 53.54, H 7.08, N 3.65, Eu 20.42; $C_{98}H_{166}Br_2Eu_2N_4O_{12}$ (2056.08 g mol⁻¹) requires: C 57.25, H 8.14, N, 2.72, Eu 14.78; loss of 6 thf of crystallisation and 2 coordinated. $C_{66}H_{102}Br_2Eu_2N_4O_4$ (1479.27 g mol⁻¹) requires: C 53.59, H 6.95, N 3.79, Eu 20.55. IR (Nujol): 2724w, 1668 s, 1589w, 1345w, 1312w, 1261 m, 1170 m, 1075 m, 1010 s, 923 m, 852w, 771w, 723 s, 665 w cm⁻¹.

[Yb(DippForm)Br(thf)₂]₂·2thf (3): Ytterbium metal powder (0.26 g, 1.5 mmol) was suspended in dry THF (15 ml) under N_2, and then PhBr (0.157 g, 1.0 mmol) was added at −78 °C. The mixture was sonicated for 10 min and a dark red-brown solution formed. After cooling to −78 °C, solid DippFormH (0.368 g, 1.0 mmol) was added and the mixture was stirred for another 3 h. A red-brown solution developed after stirring for 24 h at room temperature. The resulting mixture was filtered and concentrated to 5 mL under vacuum. Yellow crystals (0.365 g, 47 %) were obtained after cooling at −25 °C for 2 days. M.P. 176–178 °C. Elemental analysis: Found: C 51.96, H 6.23, N 3.37, Yb 22.98; $C_{74}H_{118}Br_2Yb_2N_4O_6$ (1665.62 g mol⁻¹) requires: C 53.36, H 7.14, N, 3.36, Yb 20.78; loss of 2 thf of crystallization, $C_{66}H_{102}Br_2Yb_2N_4O_4$ (1521.42 g mol⁻¹) requires; C 52.10, H 6.76, N 3.68, Yb 22.75. IR (Nujol): 2723w, 1567 s, 1587 m, 1518w, 1260 m, 1235w, 1187 m, 1074 s, 1016 m, 934w, 913 m, 864w, 801 s, 756 m, 723 m, 673 s, 607 w cm⁻¹. ¹H NMR (C_6D_6): $\delta = $ 8.28(s, 2H, NC(H)N), 7.18(8H, H(3,5)), 7.05(m, 4H, H(4)), 3.85(m, 8H, CH), 3.64(s, 24H, thf), 1.34-1.19 ppm(m, 72H: 24H, thf; 48H, CH₃). ¹³C NMR (100 MHz, C_6D_6): $\delta = $ 22.74 (CH(CH₃)₂), 23.47 (CH(CH₃)₂), 24.05 (CH₂, thf), 24.40 (CH(CH₃)₂), 26.75 (CH(CH₃)₂), 27.17 (CH(CH₃)₂), 67.63 (CH₂, thf), 121.56 (Ar–C), 122.09 (Ar–C), 141.41 (Ar–C), 141.80 (Ar–C),147.28 (Ar–C), 165.80 ppm (NCN).

[Sm(Ph₂pz)₃(thf)₃]·3thf (4a): The synthesis procedure for **4(a)** was similar as described in **1**. Here, solid Ph₂pzH (0.22 g, 1.0 mmol) was added at 0 °C and a yellowish-brown solution was obtained. The resulting mixture was filtered and concentrated to 5 mL under vacuum. Colourless crystals (0.248 g, 60 %) were obtained after cooling at −25 °C for 4 days. M. P. 157–159 °C. Metal Analysis: Found: Sm 14.48%; $C_{69}H_{81}N_6O_6Sm$ (1240.75 g mol⁻¹) requires: Sm 12.12%; loss of 3 thf of crystallization, $C_{57}H_{57}N_6O_3Sm$ (1024.46 g mol⁻¹) requires: Sm,14.68%. IR (Nujol): 1605 s, 1512w, 1340w, 1297 m, 1261w, 1229 m, 1178 m, 1156w, 1073 s, 1028 s, 971 s, 915 s, 868 s, 842w, 801 m, 762 s, 724w, 697 s, 684 m, 665 w cm⁻¹. ¹H NMR (400.13 MHz, C_6D_6): $\delta = $ 0.60 (s, 24H, thf), 2.17(s, 24H, thf), 7.28 (t, 6H, H(4)), 7.58 (t, 12H, H(3,5)), 7.77 (s, 3H, CH-pz), and 9.39 ppm(s, 12H, H(2,6)). For compound **4(a)** (triclinic, P-1space group) the unit cell is; a = 13.307(3)Å, b = 18.547(4)Å, c = 25.198(5)Å, α = 76.38(3)°, β = 84.83(3)°, γ = 87.37(3)°, V = 6018(2)Å³, the reported unit cell is; a = 13.343(3), b = 18.579(4), c = 25.270(5) Å, α = 76.58(3), β = 85.19(3), γ = 87.35(3)°, V = 6070(2) Å³.[22]

[Sm(Ph₂pz)₃(dme)₂]·dme (4b): Colorless crystals (0.19 g, 53 %) from a solution of **4(a)** in DME after cooling at −25 °C for 3 days. M. P. 161–163 °C. Elemental analysis: Found: C 63.59, H 5.93, N 7.46, Sm 14.07%; $C_{57}H_{63}SmN_6O_6$ (1078.48 g mol⁻¹) requires: C 63.48, H 5.89, N 7.79, Sm 13.94%. IR (Nujol): 2722 m, 1604 s, 1513 m, 1422w, 1338w, 1306 m, 1283 m, 1246 m, 1224w, 1193 s, 1114 m, 1027w, 970s, 913 s, 864 s, 802 m, 757 s, 695 s, 682 w cm⁻¹. ¹H NMR (400.13 MHz, C_6D_6): $\delta = $ 2.82 (s, 32H, dme), 2.95 (s, 48H, dme), 7.21 (t, 6H, H(4)), 7.40 (t, 12H, H(3,5)), 7.47 (s, 3H, CH-pz), 8.75 ppm(s, 12H, H(2,6)).

[Eu(Ph₂pz)₂(thf)₄] (5): The synthesis procedure for compound **5** was as described in **2**. Here, solid Ph₂pzH (0.22 g, 1.0 mmol) was added at −78 °C, and a red brown solution formed. The resulting mixture was filtered and concentrated to 5 mL under vacuum. Yellow crystals (0.273 g, 62 %) were obtained after cooling at −25 °C for 5 days. M.P. 224–226 °C. Metal Analysis: Found Eu 17.64%; $C_{46}H_{54}EuN_4O_4$ (878.89 g mol⁻¹) requires: Eu 17.29%. IR (Nujol): 1602 s, 1524 m,1512w, 1421w, 1295w, 1259w, 1218 m, 1178w, 1042 s, 999w, 968 s, 903 s, 791w, 767 s, 753 s, 702 s, 681 s, 665 w cm⁻¹. ¹H NMR (400.13 MHz, C_6D_6): Paramagnetic. For compound **5** (triclinic, P-1space group) the unit cell is; a = 9.126(18)Å, b = 18.668(4)Å, c = 24.427(5)Å, α = 110.04(3)°, β = 91.64(3)°, γ = 90.22(3)°, V = 3907.5(16)Å³, the reported unit cell is; a = 9.27(19)Å, b = 18.952(4)Å, c = 24.803(5)Å, α = 109.99(3)°, β = 91.78(3)°, γ = 90.52(3)°, V = 4092.1(16)Å³.[23]

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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