EurJIC
European Journal of Inorganic Chemistry

Research Article
doi.org/10.1002/ejic.202300731

Chemistry Europe
European Chemical Societies Publishing

www.eurjic.org

Lanthanide Amide Complexes Supported by the *Bis*-tris(pyrazolyl)borate Ligand Environment

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Synthesis of primary lanthanide amides in the *bis*-hydrotris(1-pyrazolyl)borate ligand environment has been achieved. Salt metathesis of [Dy(Tp)$_2$(OTf)] **1-Dy** (OTf = CF_3SO_3) with K(N″) (N″ = N(SiMe$_3$)$_2$) in toluene yielded the [*bis*(silyl)]amide [Dy(Tp)$_2$(N″)] **2-Dy**. Complexes **1-Ln** and **2-Ln** were both used to access primary lanthanide amides, where either metathesis of **1-Ln** with K(NHAr^{CF3}) (Ar^{CF3} = C$_6$H$_3$(CF$_3$)$_2$-3,5) or protonolysis of **2-Ln** with H$_2$NAr^{CF3} in toluene yielded [Ln(Tp)$_2$(NHAr^{CF3})] **3-Ln** (Ln = Y, Dy). The synthesis of parent amides was also attempted, but the metathesis of **1-Y** with NaNH$_2$ yielded complicated reaction mixtures, but from which the dimeric parent amide [{Y(Tp)$_2$(μ-NH$_2$)}$_2$] **4-Y** and an *'ate'*-salt [{Y(Tp)$_2$(μ_2-OTf)(μ_3-OTf)Na(THF)$_2$}$_2$] **5-Y** were isolated. Full characterisation data are presented for all complexes, including the structure determination.

1. Introduction

The first reports of the secondary lanthanide amides (Ln–NR$_2$) appeared in the 1970s.[1] The homoleptic amides [Ln(N″)$_3$] (N″ = N(SiMe$_3$)$_2$) can be synthesised by facile salt metathesis and exhibit catalytic activity in organic transformations,[2] small molecule activation,[3] and are useful precursors for Ln thin film preparation.[4] Primary lanthanide amides (Ln–NHR) are valuable synthons to access reactive lanthanide-ligand multiple-bonds in imides (Ln=NR), by deprotonation of the NHR anion.[5] Since the first report of a neutral terminal scandium imido complex in 2010,[6] the field of Ln=NR chemistry has expanded significantly.[5b] This chemistry was very recently extended to Ln=PR chemistry, with the synthesis of the first neutral terminal yttrium phosphinidine complex.[7] Although many diverse synthetic routes to Ln=NR complexes exist,[5b] the most studied approach utilises Ln–NHR complexes, where choice of ancillary ligands on the Ln metal centre is key.[5] The synthesis of molecular parent lanthanide amides, with the exception of cyclopentadienyl ligand-supported amides,[8] has remained rare. While the homoleptic amide salts [{Ln(NH$_2$)$_x$}$_n$] (x = 2, 3) and *'ate'* salts [{KLn(NH$_2$)$_3$}$_n$] have been known since the 1960s,[9] only a handful of crystallographically-characterised primary lanthanide amides supported by ancillary ligands are known, for example the dimeric amides [{Ln(Cp)$_2$(μ-NH$_2$)}$_2$] (Cp = C$_5$H$_5$)[8c] and the first ever crystallographically-characterised monomeric terminal amide [Y(Cp*)$_2$(NH$_2$)(THF)] (Cp* = C$_5$Me$_5$).[8e]

Substituted analogues of Trofimenko's scorpionate tris(1-pyrazolyl)borate (Tp^R) ligand provide a robust ancillary ligand environment for the synthesis of reactive lanthanide complexes.[10] Lanthanide [*bis*(silyl)]amide Ln(II) complexes with one Tp^R ancillary ligand, [Ln(Tp^{tBu,Me})(N″)] (Ln = Sm, Tm, Yb; Tp^{tBu,Me} = hydrotris(3-^{t}Bu-5-methyl-1-pyrazolyl)borate)[11] and the Lu(III) complex [Lu(Tp^{tBu,Me})(N(SiHMe$_2$)$_2$)(CH$_3$)] have been reported.[12] However, with two Tp^R ancillary ligands, the synthesis of such secondary lanthanide amides becomes challenging due to the steric bulk of two Tp^R ligands. Metathesis of the Ln(III) complexes [Ln(Tp*)(Cl)$_2$] (Ln = Y, Er; Tp* = hydrotris(3,5-dimethyl-1-pyrazolyl)borate) with K(N″) proved unsuccessful.[13] The only known example is with larger Nd(III) and a smaller amido R group, [Nd(Tp*)$_2$(NPh$_2$)].[14] The smaller unsubstituted hydrotris(1-pyrazolyl)borate (Tp) ligand can be utilised to overcome this steric limitation, and the Ln(III) complexes [Ln(Tp)$_2$(N″)] (Ln = Y, Yb) were reported recently.[15]

The primary lanthanide Ln(II) amide complexes with one Tp^R ancillary ligand, [Ln(Tp^{tBu,Me})(NHR)(do)$_x$] (Ln = Sm, Eu, Yb; R = Dipp or C$_6$H$_3$^{i}Pr$_2$-2,6, Ar^{Me} or C$_6$H$_3$Me$_2$-2,6, Ar^{CF3} or C$_6$H$_3$(CF$_3$)$_2$-3,5, SiPh$_3$; do = THF; x = 0, 1, or 2),[16] the Ln(III) complexes [Lu(Tp^{tBu,Me})(NHR)(CH$_3$)] (R = ^{t}Bu, adamantyl)[17] and [Y(Tp*)(NHR)(CH$_2$Ph)(THF)] (R = Ph, Dipp)[18] have been reported. In the case of the putative Tm(II) [Tm(Tp^{tBu,Me})(NHC$_6$H$_3$(2,5-^{t}Bu$_2$))], dinitrogen activation was observed.[11b] The Ln(III) amides [Ln(Tp^{tBu,Me})(NHR)(CH$_3$)] (Ln = Y, Lu; R = Ar^{Me}, Ar^{CF3}) were successfully utilised to access the imides [Ln(Tp^{tBu,Me})(=NR)(4-dimethylaminopyridine)].[19] No Ln(III) primary amides with two Tp^R ancillary ligands [Ln(Tp^R)$_2$(NHR)] have been reported to date.

Here the chemistry of Ln(III) in the [Ln(Tp)$_2$]$^+$ ligand environment has been extended to Dy(III), by the synthesis of the Ln(III) precursor complexes, [Dy(Tp)$_2$(OTf)] **1-Dy** and [Dy(Tp)$_2$(N″)] **2-Dy**. Complexes **1-Ln** and **2-Ln** (Ln = Y, Dy) enabled the

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Supporting information for this article is available on the WWW under https://doi.org/10.1002/ejic.202300731

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doi.org/10.1002/ejic.202300731

successful synthesis of the primary lanthanide amides [Ln(Tp)$_2$(NHAr^{CF3})] **3-Ln** (Ln = Y, Dy; Ar^{CF3} = C$_6$H$_3$(CF$_3$)$_2$-3,5) by metathesis of **1-Ln** with K(NHAr^{CF3}) and protonolysis of **2-Ln** with H$_2$NAr^{CF3}. Attempted synthesis of parent lanthanide amides from **1-Y** are discussed, including the isolation of [{Y(Tp)$_2$(μ-NH$_2$)}$_2$] **4-Y** and [{Y(Tp)$_2$(μ_2-OTf)(μ_3-OTf)Na(THF)$_2$}$_2$] **5-Y**.

2. Results and Discussion

2.1. Synthesis and spectroscopy of secondary lanthanide [bis(silyl)]amides

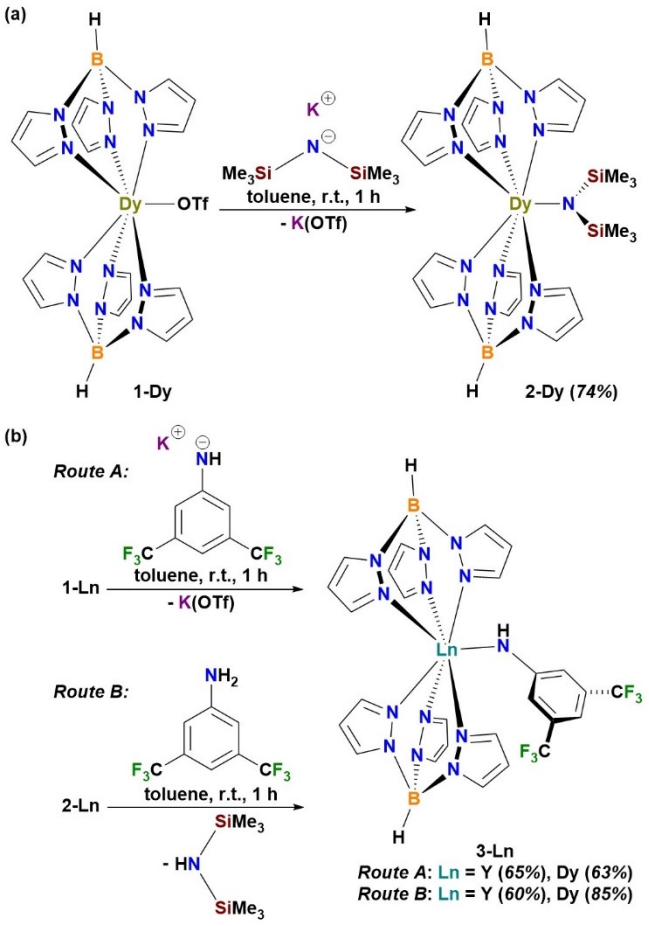
2.1.1. Synthesis of precursor complexes [Dy(Tp)$_2$(OTf)] 1-Dy and [Dy(Tp)$_2$(N″)] 2-Dy

The heteroleptic Ln(III) triflates [Ln(Tp)$_2$(OTf)] **1-Ln** (Ln = Y, Eu, Gd, Yb; Tp = hydrotris(1-pyrazolyl)borate; OTf = CF$_3$SO$_3$) and secondary Ln(III) amides [Ln(Tp)$_2$(N″)] **2-Ln** (Ln = Y, Yb; N″ = N(SiMe$_3$)$_2$) were previously reported.[15] The complex [Dy(Tp)$_2$(OTf)] **1-Dy** was synthesised analogously by salt metathesis of Dy(OTf)$_3$ with 2 equivalents of K(Tp) in THF and subsequent extraction into hot toluene (see ESI **Section A1.2** for synthetic details and **Section B3**, Figure S29 for crystallographic data). Likewise, the [*bis*(silyl)]amide complex [Dy(Tp)$_2$(N″)] **2-Dy** was synthesised analogously to **2-Y**, by metathesis of **1-Dy** with an equivalent of K(N″) in toluene. The reaction mixture was filtered to exclude K(OTf) and toluene was removed *in vacuo*. Cold (−35 °C) hexane was added to the resultant paste of **2-Dy** yielding a white powder, which was washed with further cold hexane to remove very minor HN″ impurity and subsequently dried *in vacuo* to yield **2-Dy** (74 %, Scheme 1(**a**)). This cold hexane work-up was also used to optimise the synthesis of **2-Yb**, as it proved more effective in removing the byproduct [Yb(Tp)$_3$] (see ESI **Section A2.2**),[20] than recrystallisation from toluene.[15] Elemental analyses of **1-Dy** and **2-Dy** are consistent with the [Dy(Tp)$_2$(OTf)] and [Dy(Tp)$_2$(N″)] formulations, respectively.

2.1.2. Spectroscopy of [Dy(Tp)$_2$(X)] (X = OTf, 1-Dy; N″, 2-Dy)

By ^{1}H NMR spectroscopy in d_3-MeCN, the Tp-pyrazolyl protons in **1-Dy** are observed at $\delta = -143.42$, −1.64 and 59.92 ppm and the Tp-borohydride resonance is observed at $\delta = 140.16$ ppm. In contrast to **1-Ln**,[15] **1-Dy** does not exhibit any resonances by ^{11}B NMR spectroscopy. The ^{19}F NMR spectrum of **1-Dy** exhibits a broad singlet at $\delta = -59.45$ ppm assigned to the triflate-CF$_3$ groups. The related complex [Dy(Tp*)$_2$][OTf] (Tp* = hydrotris(3,5-dimethyl-1-pyrazolyl)borate) was reported not to exhibit any resonances by multinuclear NMR spectroscopy.[21] The ATR-IR spectrum of **1-Dy** exhibits a weak absorption at 2468 cm^{-1}, assigned to the characteristic borohydride stretching frequency (υ_{BH}) for the κ^3-coordinated Tp ligands in **1-Dy**, analogous to **1-Ln** and [Ln(Tp*)$_2$(OTf)].[15,21]

In the ^{1}H NMR spectrum of **2-Dy** in d_6-benzene, the Tp-pyrazolyl protons in **2-Dy** are observed at $\delta = -54.84$, −30.12 and −5.20 ppm, the Tp-borohydride at $\delta = -70.03$ ppm, and the trimethylsilyl groups of the N″ ligand at $\delta = 69.28$ ppm, in the expected 6:6:6:2:18 ratio. Unlike **1-Dy**, the ^{11}B NMR spectrum of **2-Dy** exhibits a resonance at $\delta = -192.72$ ppm for the Tp ligands. In the ATR-IR spectrum of **2-Dy**, besides weak absorptions between 2350–2550 cm^{-1} assigned to the characteristic borohydride stretching frequencies (υ_{BH}) for the Tp ligands, weak absorptions are also observed between 2850–3000 cm^{-1}, which are assigned to the aliphatic sp^3-carbon hydrogen bond stretching frequencies ($\upsilon_{sp^3\text{-}CH}$) of the N″-methyl groups in **2-Dy**, analogous to **2-Ln**.[15]



Scheme 1. (a) Synthesis of [Dy(Tp)$_2$(N″)] **2-Dy** by metathesis of [Dy(Tp)$_2$(OTf)] **1-Dy** with K(N″); (b) Synthesis of [Ln(Tp)$_2$(NHAr^{CF3})] **3-Ln** (Ln = Y, Dy) either by metathesis (Route A) of **1-Ln** with K(NHAr^{CF3}) or by protonolysis (Route B) of **2-Ln** with H$_2$NAr^{CF3}.

2.2. Synthesis and spectroscopy of primary lanthanide amides

2.2.1. Synthesis of primary amides [Ln(Tp)$_2$(NHAr^{CF3})] 3-Ln (Ln = Y, Dy) by metathesis and protonolysis

The metathesis chemistry of **1-Ln** with M(N″) (M = group 1 metal), is known to only work with M = potassium and in toluene,[15] therefore, these conditions were explored first in the

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doi.org/10.1002/ejic.202300731

synthesis of primary Ln(III) amide [Ln(Tp)$_2$(NHR)] targets. The sterics and electronics of the R group in K(NHR) and solubility of the K(NHR) salt in toluene are important factors in the metathesis of **1-Ln** with K(NHR). The poor solubility of K(NHDipp) (Dipp = $C_6H_3{}^iPr_2$-2,6) in toluene led to very slow, and incomplete metathesis reactions. When THF was utilised instead of toluene, to overcome the solubility problems in these reactions, the reactions were faster but more complicated yielding multiple products containing [Y(Tp)$_3$].[20,22] The data for this common byproduct of failed reactions are included in the ESI (see **Section A5** for the NMR-scale synthesis of [Y(Tp)$_3$] and **Section B1.7** for ^{1}H and ^{11}B NMR data). Metathesis of **1-Ln** with the moderately toluene-soluble K(NHSiPh$_3$) in toluene also proved more complicated yielding multiple products containing [Y(Tp)$_3$], and attempts to isolate and purify the target amide proved unsuccessful. Protonolysis of **2-Ln** with H$_2$NDipp in toluene likewise led to incomplete and complicated reactions, reinforcing that careful choice of R group in H$_2$NR was required *i.e.*, the relative acidities of H$_2$NR with respect to the Ln–N″ bond (calculated pK_a values of RNH$_3{}^+$, R = Ar^{CF3}, 2.15; Dipp, 4.25; SiPh$_3$, 6.31).[5b]

Metathesis of **1-Ln** with toluene-soluble K(NHAr^{CF3}) (Ar^{CF3} = $C_6H_3(CF_3)_2$-3,5), yielded the primary amide complexes [Ln(Tp)$_2$(NHAr^{CF3})] **3-Ln** (Ln = Y, Dy). After metathesis of **1-Ln** with an equivalent of K(NHAr^{CF3}) in toluene, the reaction mixture was filtered to exclude K(OTf) and toluene was removed *in vacuo*. Extraction into hexane and recrystallisation at −37 °C (Ln = Y), or washing with hexane (Ln = Dy) and recrystallisation from the hexane washings (−37 °C), and subsequent drying *in vacuo* yielded [Ln(Tp)$_2$(NHAr^{CF3})] **3-Ln** (Ln = Y, 65 %; Dy, 63 %; Route A in Scheme 1(**b**)). Complexes **3-Ln** were also synthesised by protonolysis of **2-Ln** with H$_2$NAr^{CF3} in toluene, and with a similar hexane workup as above yielding [Ln(Tp)$_2$(NHAr^{CF3})] **3-Ln** (Ln = Y, 60 %; Dy, 85 %; Route B in Scheme 1(**b**)). Elemental analyses of **3-Ln** are consistent with the [Ln(Tp)$_2$(NHAr^{CF3})] formulation. Complex **3-Y** is soluble in both toluene and hexane. Complex **3-Dy** is soluble in toluene and has moderate solubility in hexane.

2.2.2. Spectroscopy of [Ln(Tp)$_2$(NHAr^{CF3})] 3-Ln (Ln = Y, Dy)

In the ^{1}H NMR spectrum of **3-Y** in d_6-benzene, the Tp-pyrazolyl protons in **3-Y** are observed at δ = 5.73, 7.02 and 7.46 ppm, the Tp-borohydride at δ = 4.71 ppm, consistent with **1-Y**, **2-Y**, and [Y(Tp)$_2$(hfac)] (hfac = hexafluoroacetylacetonate).[15] The pyrazolyl protons were assigned to the three individual carbon atoms of the Tp ligand and the aromatic ring protons were assigned to their respective carbon atoms by a ^{1}H-^{13}C HSQC NMR experiment (see ESI, Figure S9). The aromatic ring protons in **3-Y** are observed at δ = 5.85 and 6.99 ppm and are distinct from those observed for K(NHAr^{CF3}) (δ = 6.32 and 6.76 ppm) and the complex [Y(Cp*)(NHAr^{CF3})$_2$(THF)$_2$] (δ = 6.75 and 7.12 ppm).[23] The resonance observed at δ = 5.14 ppm is assigned as the amido proton of **3-Y** and is distinct from the amido resonances for K(NHAr^{CF3}) (δ = 3.12 ppm), and the Y(III)-NHR complexes [Y(Cp*)(NHAr^{CF3})$_2$(THF)$_2$] (δ = 4.33 ppm),[23] [Y(Tp*)(CH$_2$Ph)(NHR)(THF)] (R = Ph, δ = 4.75 ppm; Dipp, δ = 5.00 ppm), and [Y(Tp*)((DippN)$_2$CCH$_2$Ph)(NHPh)] (δ = 5.51 ppm).[18] The ratio of the pyrazolyl resonances to the amido resonances is 6:6:6:2:2:1:1 as expected. The ^{11}B NMR spectrum of **3-Y** exhibits a resonance at δ = –2.83 ppm, corresponding to the Tp ligands, consistent with [Y(Tp)$_2$]$^+$.[15] The ^{19}F NMR spectrum of **3-Y** exhibits a resonance at δ = −62.48 ppm, corresponding to the amido-CF$_3$ groups and is very similar to that observed for K(NHAr^{CF3}) (δ = −63.08 ppm), or the complexes [Y(Cp*)(NHAr^{CF3})$_2$(THF)$_2$] (δ = −62.98 ppm),[23] [Lu(Tp^{tBu,Me})(Me)(NHAr^{CF3})] (δ = −62.64 ppm),[19] and [Ce(TriNOx)(NHAr^{CF3})] (δ = −62.92 ppm, TriNOx = tris(hydroxylaminato)).[24]

In the ^{1}H NMR spectrum of **3-Dy** in d_6-benzene, five resonances instead of seven are observed at δ = −127.62, −57.76, −6.47, 1.34 and 133.73 ppm. The Tp-pyrazolyl protons in **3-Dy** are observed at δ = −57.76 and −6.47 ppm and one pyrazolyl proton resonance is not observed. The ^{11}B NMR spectrum of **3-Dy** exhibits a resonance at δ = −2.22 ppm, corresponding to the Tp ligands. Complex **3-Dy** does not exhibit any resonances by ^{19}F NMR spectroscopy. In the ATR-IR spectra of **3-Ln**, besides weak absorptions between 2330–2550 cm^{-1}, assigned to the characteristic borohydride stretching frequencies (υ_{BH}) for the Tp ligands, weak absorptions are also observed between 3280–3440 cm^{-1} (maximum at 3377 cm^{-1}). These absorptions are assigned to the amido stretching frequencies (υ_{NH}) of the amido ligands in **3-Ln**, analogous to the complexes [Y(Cp*)(NHAr^{CF3})$_2$(THF)$_2$] (υ_{NH} = 3321 cm^{-1})[23] and [Ce(TriNOx)(NHAr^{CF3})] (υ_{NH} = 3311 cm^{-1}).[24]

2.3. Attempted synthesis and spectroscopy of parent lanthanide amides

2.3.1. Isolation of the dimeric parent amide [{Y(Tp)$_2$(μ-NH$_2$)}$_2$] 4-Y

Following the synthesis of primary amides **3-Ln**, investigation of the synthetic scope was extended to target the more challenging parent Ln(III) amide [{Ln(Tp)$_2$(μ-NH$_2$)}$_2$]. Metathesis of **1-Y** with excess NaNH$_2$ in both coordinating and non-coordinating solvents always led to complicated reactions containing [Y(Tp)$_3$][20,22] and multiple byproducts with moderate to poor solubilities in non-coordinating solvents. On one occasion, the NMR-scale reaction between **1-Y** and excess NaNH$_2$ in d_6-benzene and subsequent crystallisation from a d_6-benzene: hexane mixture at −35 °C led to the isolation of a small crop of crystals of [{Y(Tp)$_2$(μ-NH$_2$)}$_2$] **4-Y** (see ESI **Section A4.1**). However, the synthetic conditions to isolate **4-Y** in non-coordinating solvents were not reproducible, and metathesis in THF led to complicated mixtures, from which an *'ate'* salt [{Y(Tp)$_2$(μ$_2$-OTf)(μ$_3$-OTf)Na(THF)$_2$}$_2$] **5-Y** was isolated on one occasion (see ESI **Section A4.2** for isolation and Figure 1 below for the crystal structure).

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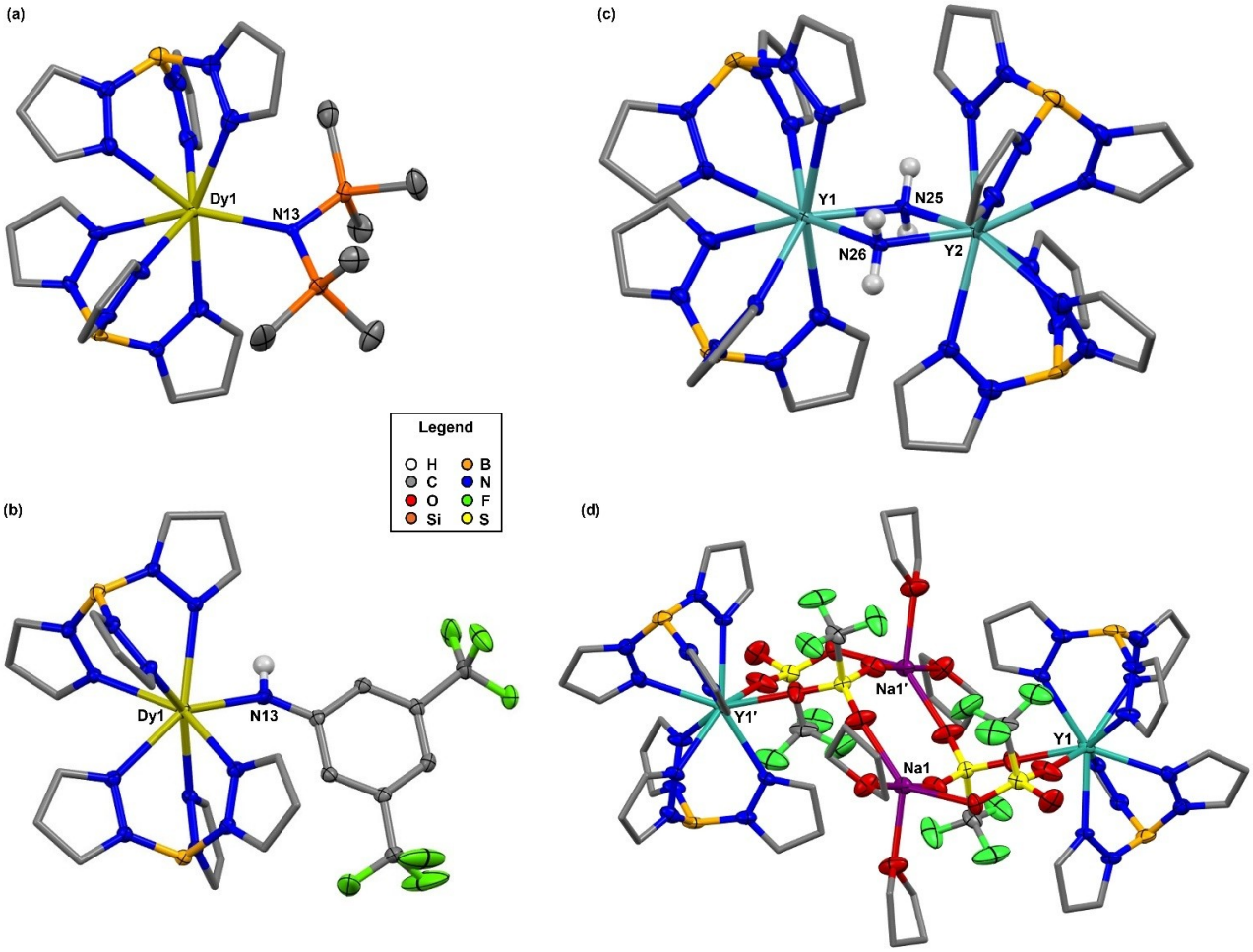

Figure 1. Crystal structures of (a) **2-Dy**, (b) **3-Dy** (see ESI **Figure S31** for the molecular structure of **3-Y**), (c) **4-Y**, and (d) **5-Y** (see ESI **Figure S34** for further views of the structure). Hydrogen atoms (except for the hydrogen atoms on the amido nitrogen atoms) and lattice solvent molecules (in c) omitted for clarity and pyrazolyl carbon atoms of Tp displayed in wireframe. Displacement ellipsoids drawn at 50% probability. Data and crystallographic information can be found in the ESI (Tables 1 and 2).

2.3.2. Spectroscopy of [{Y(Tp)$_2$(μ-NH$_2$)}$_2$] 4-Y

The Tp-pyrazolyl protons in **4-Y** are observed at $\delta = 5.73$, 7.07 and 7.49 ppm, and the Tp-borohydride at $\delta = 4.73$ ppm by ^{1}H NMR spectroscopy; these chemical shifts are essentially the same as for **3-Y**. The pyrazolyl protons were assigned to the three individual carbon atoms of the Tp ligand by a ^{1}H-^{13}C HSQC NMR experiment (see ESI, Figure S18). However, the pyrazolyl proton resonance in the ^{1}H NMR spectrum of **4-Y** at $\delta = 7.07$ ppm is significantly broadened when compared to the other pyrazolyl proton resonances in [Y(Tp)$_2$]$^+$ complexes. This broadening of a single pyrazolyl resonance was previously also observed in the dimeric complex [{Y(Tp)$_2$(μ-OH)}$_2$] and the monomeric complex [Y(Tp)$_2$(OAr)] (OAr = 2,6-^{t}Bu$_2$-4-Me-phenoxide) and attributed to steric constraints resulting in partially restricted Tp motion.[15] The resonance observed at $\delta =$ 2.16 ppm in the ^{1}H NMR spectrum of **4-Y**, is assigned as the amido proton by comparison to the complex [Y(Cp*)$_2$(NH$_2$)(THF)] ($\delta = 2.21$ ppm).[8e] However, it is of note that the resonances for amido protons in NH$_2$-bridged Y(III) clusters do not follow any diagnostic trends.[8b,d] The ratio of the pyrazolyl resonances to the amido resonance is 12:12:12:4:4 as expected. The ^{11}B NMR spectrum of **4-Y** exhibits a resonance at $\delta = -2.33$ ppm, corresponding to the Tp ligands.

2.3.3. Crystallography of amide complexes [Dy(Tp)$_2$(N″)] 2-Dy, [Ln(Tp)$_2$(NHAr^{CF3})] 3-Ln, and [{Y(Tp)$_2$(μ-NH$_2$)}$_2$] 4-Y

Colourless single crystals of the amide complexes **2-Dy**, **3-Ln** (Ln = Y, Dy) and **4-Y** suitable for X-ray diffraction were grown from cold (−35 °C or −37 °C) saturated hexane solutions. The structures of **2-Dy** and **3-Dy** (see ESI **Figure S31** for **3-Y**) are monomeric. The 7-coordinate Ln(III) ion is bound to two κ^3-coordinated Tp ligands and a monodentate amido anion (N″ in **2-Dy** or NHAr^{CF3} in **3-Ln**), in a distorted pentagonal bipyramidal geometry (Figure 1**(a)** and **(b)**). The structure of **4-Y** is dimeric, containing two 8-coordinate Y(III) ions bound to two κ^3-coordinated Tp ligands and bridged by two amido anions (Figure 1**(c)**). Important structural metrics are tabulated in the

ESI (**Section B3**, data comparison in Table S1 and crystallographic information in Table S2). The Ln–N(κ^3-Tp) distances in **2-Dy**, **3-Ln** and **4-Y** are consistent with literature.[15,25] The Ln–N(N'') distance of 2.338(11) Å in **2-Dy** is longer than those observed for the homoleptic complex [Dy(N'')$_3$] (2.213(6)-2.243(4) Å),[26] and the heteroleptic complexes [Dy(L)$_2$(N'')] (L = diazabutadiene radical, 2.260(3) Å;[27] 2-^{t}BuN=CH-5-R-C$_4$H$_2$N, R = H, 2.230(3) Å, ^{t}Bu, 2.232(3) Å).[28] The Ln–N(N'') distances in **2-Ln** (Ln = Y, Dy) are longer than those in **2-Yb** (2.2956(12) Å), and consistent with differences in size of the different Ln(III) ionic radii.[15,29] The Ln–N(NHAr^{CF3}) distances of 2.3069(12) Å in **3-Y** and 2.3019(18) Å in **3-Dy** are consistent with each other and as expected shorter than those in **2-Ln**.[15] The Ln–N(amido) distances of **2-Ln** and **3-Ln** are comparable to but shorter than the Nd–N(NPh$_2$) bond of 2.480(5) Å in [Nd(Tp*)$_2$(NPh$_2$)].[14] The Ln–N(NHAr^{CF3}) distance in **3-Y** is similar to literature Y–N(NHR) distances in the complexes [Y(Cp*)(NHAr^{CF3})$_2$(THF)$_2$] (2.293(3)-2.294(3) Å),[23] [Y(Tp*)(CH$_2$Ph)(NHDipp)(THF)] (2.242(5) Å), and [Y(Tp*)((DippN)$_2$CCH$_2$Ph)(NHPh)] (2.223(5) Å).[18] The Y–N(μ-NH$_2$) distances of 2.351(6) Å and 2.388(7) Å in **4-Y** are longer than the Ln–N(amido) bonds in **2-Y** or **3-Y**, consistent with the dimeric structure. The Y–N(μ-NH$_2$) bonds in **4-Y** are also longer than those in the monomeric complex [Y(Cp*)$_2$(NH$_2$)(THF)] (2.226(2) Å),[8e] but consistent with the clusters [{Y$_2$(η^5-C$_9$H$_6$SiMe$_2$)$_2$N)(μ-NH$_2$)(THF)$_2$}$_2$(μ_3-Cl)$_2$(μ-Cl)$_2$] (2.295(4)-2.390(5) Å),[8b] [{Y(C$_5$Me$_4$SiMe$_3$)}$_4$(μ-NH$_2$)$_6$(μ_3-NH$_2$)(μ_4-H)] (2.331(11)-2.380(10) Å, 2.568(11)-2.603(11) Å),[8d] and the dimeric Dy(III) complex [{Dy(Cp)$_2$(μ-NH$_2$)}$_2$] (2.353(4), 2.368(4) Å).[8c]

3. Conclusions

The successful syntheses of primary lanthanide amides [Ln(Tp)$_2$(NHAr^{CF3})] **3-Ln** (Ln = Y, Dy) with the *bis*-hydrotris(1-pyrazolyl)borate ligand environment have been achieved by either metathesis of [Dy(Tp)$_2$(OTf)] **1-Dy** with K(NHAr^{CF3}) or protonolysis of the secondary [*bis*(silyl)]amide amide [Dy(Tp)$_2$(N'')] **2-Dy** with H$_2$NAr^{CF3} in toluene. The metathesis chemistry of **1-Ln** is only successful when toluene is used as a reaction solvent, in combination with potassium amide salts. Likewise, the specific steric and electronics of the Ar^{CF3} R groups in K(NHR) and H$_2$NR, in the metathesis of **1-Ln** and protonolysis of **2-Ln**, respectively, are crucial to access **3-Ln**. In contrast, reactions of **1-Y** with NaNH$_2$ to access parent amides were complicated and irreproducible, but on one occasion the dimeric parent amide [{Y(Tp)$_2$(μ-NH$_2$)}$_2$] **4-Y** was isolated. We anticipate that the primary lanthanide amides **3-Ln** will be useful synthons in Ln(III) chemistry, for example in either the reaction chemistry of the Ln–N(NHAr^{CF3}) bond or in pursuit of lanthanide-imido complexes (Ln=NR).

4. Supporting Information

Supporting information for this article is given *via* a link at the end of the document. The authors have cited additional references within the Supporting Information.[30]

Acknowledgements

We acknowledge the University of Glasgow (UofG) and Eberhard Karls Universität Tübingen (EKUT) for funding, and the awards of a College of Science and Engineering (UofG) PhD Scholarship and a PhD Mobility Scholarship (UofG) to TC.

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: lanthanides · amides · pyrazoles · heteroleptic · synthesis

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[31] Deposition Numbers 2311125 (for **1-Dy**), 2311124 (for **2-Dy**), 2311129 (for **3-Y**), 2311128 (for **3-Dy**), 2311126 (for **4-Y**), 2311127 (for **5-Y**)contains; the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

Manuscript received: November 30, 2023
Revised manuscript received: December 29, 2023
Accepted manuscript online: January 12, 2024
Version of record online: February 21, 2024