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Reactivity of [Sm(DippForm)$_2$(thf)$_2$] with Substrates Containing Azo Linkages

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This paper explores the interaction of divalent [Sm(DippForm)$_2$(thf)$_2$] with substrates containing azo linkages. Treatment of [Sm(DippForm)$_2$(thf)$_2$] with *trans*-azobenzene results in formation of mononuclear [Sm^{III}(DippForm)$_2$(Ph$_2$N$_2$)(thf)]$\cdot$3THF (**1**) or dinuclear [Sm^{III}(DippForm)(Ph$_2$N$_2$)(thf)]$_2\cdot$4THF (**2**) and [Sm(DippForm)$_3$] depending on the reaction stoichiometry, where azobenzene has undergone either a one or two electron reduction. These reactions parallel the corresponding reactions of [Sm(C$_5$Me$_5$)$_2$(thf)$_2$], but the coordination of [N$_2$Ph$_2$]$^-$ in **1** differs significantly from that of {Sm(C$_5$Me$_5$)$_2$(Ph$_2$N$_2$)(thf)}. On the other hand, the structure of **2** is similar to that of the pentamethylcyclopentadienyl analogue. The reaction of [Sm(DippForm)$_2$(thf)$_2$] with 1*H*-1,2,3-benzotriazole also yielded a trivalent samarium complex containing benzotriazolate (btz), [Sm^{III}(DippForm)$_2$(btz)(thf)]$\cdot$THF (**3**), and suggests more utilization of 1*H*-1,2,3-benzotriazole in divalent lanthanoid reduction chemistry is possible.

Introduction

The impact of divalent samarium complexes in the field of reduction chemistry has been exceptional owing to their high reduction potentials and their interaction with unsaturated substrates resulting in impressive and unprecedented outcomes.[1] Among those highly reactive complexes, bis(pentamethylcyclopentadienyl)samarium(II) [SmCp*$_2$] and its solvated analogue [SmCp*$_2$(thf)$_2$] stand on a pedestal as they give rise to a range of intriguing trivalent samarium complexes by utilizing their tremendous reducing power.[2] They have been used to reduce and trap a variety of ligands, resulting in a wide spectrum of spectacular complexes which include [(C$_5$Me$_5$)$_2$Sm]$_2$(N$_2$),[3a] [(C$_5$Me$_5$)$_2$Sm]$_2$Bi$_2$,[3b] [(C$_5$Me$_5$)$_2$Sm]$_3$(Sb$_3$)(thf),[3c] [(C$_5$Me$_5$)$_4$Sm$_2$(O$_2$CCCO)(thf)]$_2$,[3d] samarium polyphosphides,[4a] polyantimonides,[4b] polyarsenides,[4c] iron carbonyl sulfide clusters,[4d] and arsenic sulfide species.[4e] Later the emphasis has shifted to find N- donor alternatives[5] for this remarkable cyclopentadienyl ligand. [Sm(DippForm)$_2$(thf)$_2$] (DippForm = N,N′– bis(2,6-diisopropylphenyl)formamidinate) is one of such divalent lanthanoid complexes which exhibit promising reaction chemistry sometimes similar to that of [SmCp*$_2$] and [SmCp*$_2$(thf)$_2$].[6]

[Sm(DippForm)$_2$(thf)$_2$] has enforced some effective reductive trapping reactions, which includes the formation of interesting and unexpected products upon reaction with benzophenone and carbon disulfide.[7] Treatment with metal carbonyls[8a] and reduction of polypnictogenides[8b,c] led to the synthesis of polynucleated complexes with unusual trapped fragments such as [{(DippForm)$_2$Sm(thf)}$_2${(μ-CO)$_2$Co(CO)$_2$}$_2$],[8a] [{(DippForm)$_2$Sm}$_2${(μ_3-CO)$_2$Fe$_3$(CO)$_9$}],[8a] [(DippForm)$_2$Sm(Cp*Fe)E$_5${(CH$_2$)$_4$O}{(DippForm)$_2$Sm(thf)}] (E = P, As),[8b] [{(DippForm)$_2$Sm}$_2$(μ^2-η^4:η^4-E$_4$)] (E = P, As)[8c] and [{(DippForm)(DippForm-AsS$_2$)}Sm(thf)].[8c] Moreover, its reductive action towards phosphine chalcogenides was reported recently, giving trivalent samarium complexes [{(DippForm)$_2$Sm}$_2$(μ-E$_n$)] (E = S, Se; n = 1, 2).[8d]

We have already reported that [Sm(DippForm)$_2$(thf)$_2$] shows both similar and different reactivity to [SmCp*$_2$] upon treatment with 1,3,5,7-cyclooctatetraene (COT).[9] Azo compounds (containing NN linkages) are further interesting reactants as the behaviour of the N=N double bond with divalent lanthanoid complexes usually leads to novel outcomes. This is evident from previously reported examples,[10,11] including the remarkable discovery of dinitrogen trapping by [SmCp*$_2$].[3a] *Trans*-azobenzene is an interesting candidate in this area as it delivers different structural and reactivity factors in the reduction chemistry.[11] Interaction of [SmCp*$_2$(thf)$_2$] with *trans*-azobenzene resulted in reductive trapping of mono- and dianionic azobenzene moieties in which it displayed different binding modes (Scheme 1a).[11a] Here we report the reactions of N- donor alternative reductant [Sm(DippForm)$_2$(thf)$_2$] with *trans*-azobenzene and 1*H*-1,2,3-benzotriazole.

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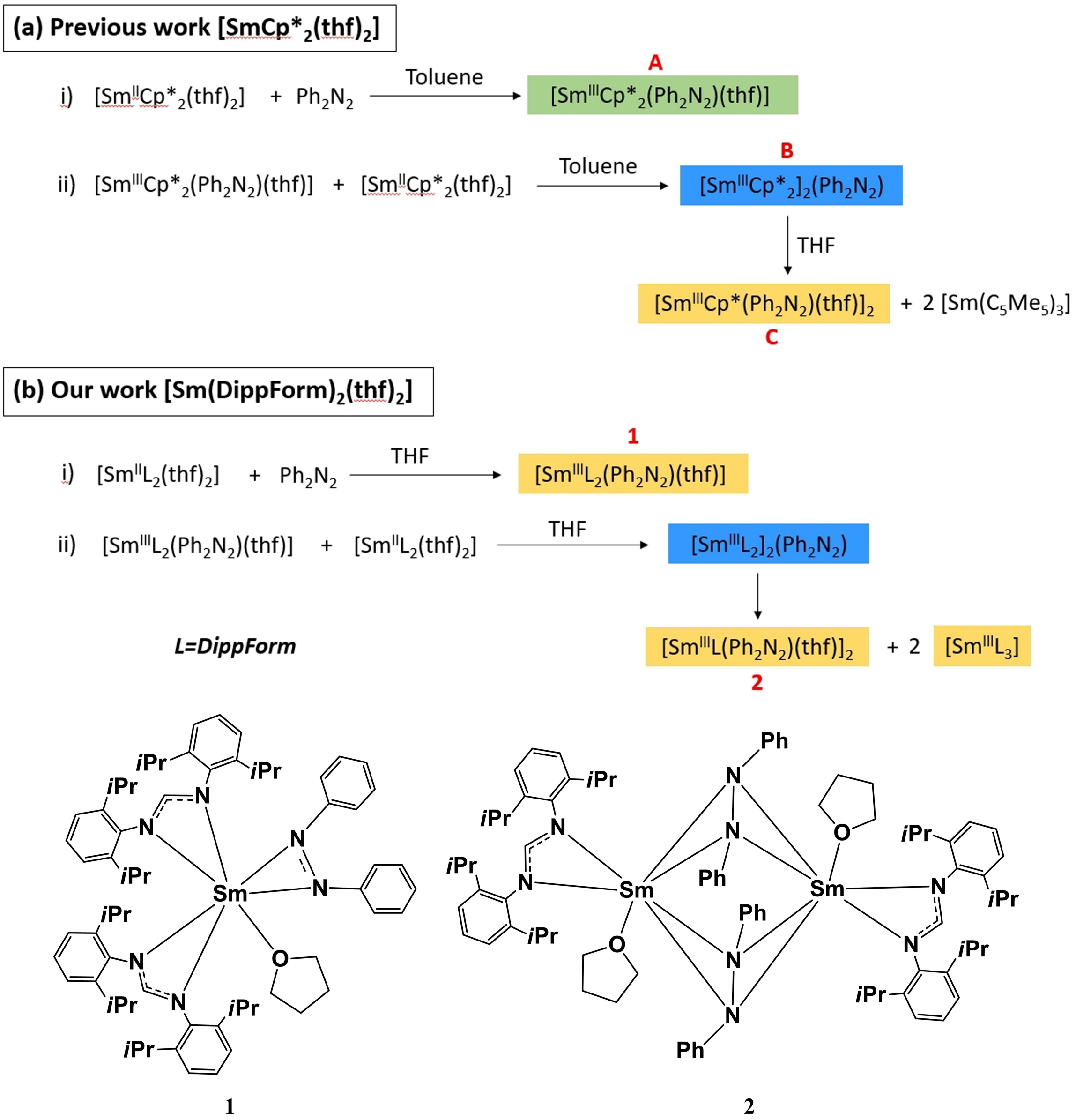
Results and Discussion

Reactions of [Sm(DippForm)$_2$(thf)$_2$] with *trans*-azobenzene

Reactions between [Sm(DippForm)$_2$(thf)$_2$] and *trans*-azobenzene were carried out in two different stoichiometries. Complex [Sm^{III}(DippForm)$_2$(Ph$_2$N$_2$)(thf)]·3THF **(1)** was obtained when the mole ratio was 1:1, while when the ratio was changed to 2:1, yellow crystals of [Sm^{III}(DippForm)(Ph$_2$N$_2$)(thf)]$_2$·2THF **(2)** and [Sm(DippForm)$_3$] were obtained (Scheme 1). When [Sm(DippForm)$_2$(thf)$_2$] and *trans*-azobenzene (1:1) were mixed in THF a dark blue solution was obtained. Yellow crystals of [Sm^{III}(DippForm)$_2$(Ph$_2$N$_2$)(thf)]·3THF **(1)** were obtained from THF by storing the concentrated solution at −18 °C for several weeks. The complex without THF of crystallization was identified when the synthesis was performed in toluene. Alternatively, addition of DME allowed more rapid crystallization since crystals of complex **1** formed within 3 days at −18 °C, but these contained some DME in place of THF (see below). Complex **1** is highly air and moisture sensitive, and minor exposure of the initial solution to the atmosphere results in a colour change from dark blue to orange due to decomposition.

The reaction of [Sm(DippForm)$_2$(thf)$_2$] and *trans*-azobenzene in a 2:1 stoichiometric ratio gave a dark blue colour, which gradually changed to yellowish green after stirring for two days, and eventually became an orange/yellow solution after a week. Yellow crystals of [Sm^{III}(DippForm)(Ph$_2$N$_2$)(thf)]$_2$·4THF (**2**) and [Sm(DippForm)$_3$] (Scheme 1) were obtained from THF by keeping the concentrated solution at −18 °C for several weeks. Crystallization of [Sm(DippForm)$_3$] along with complex **2** is a



Scheme 1. (a) The reaction of *trans*-azobenzene with [SmCp*$_2$] *(Previous work)*,[11a] (b) The reaction of *trans*-azobenzene with [Sm(DippForm)$_2$(thf)$_2$] (*Our work*). Colours of the new complexes are matched with the shading used in the Scheme 1.

barrier in obtaining pure crystals, as both have a similar colour and shape. Adding a minimal amount of hexane to the solid product after removal of the THF allows partial separation of **2** from [Sm(DippForm)$_3$] since the latter has lower solubility in hexane. This gave a green solution of compound **2** with a lot of yellow solid material, but complete separation still could not be achieved. The products were identified by X-ray crystallography of arbitrarily chosen single crystals.

Complex **1** was characterized by ^{1}H NMR, ^{13}C NMR, IR, and elemental analysis. ^{1}H NMR data were obtained using the crystals formed in toluene (a toluene resonance can be seen at $\delta = 2.11$ ppm (CH_3)). Even though the broadening of signals due to paramagnetic trivalent samarium can be seen, the data are interpretable and are consistent with the X-ray crystal structure. The NC*H*N (DippForm) proton (Figure S1) appears as a singlet at $\delta = 10.51$ ppm with an integration value of 2, and is shifted from 8.19 ppm in diamagnetic [Yb(DippForm)$_2$(thf)$_2$].[12] Aromatic protons from both ligands coincide with solvent and toluene resonances. Thf resonances can be located at $\delta =$ 1.37 ppm and $\delta = 3.39$ ppm, where the latter signal is slightly broadened. A broad resonance at $\delta = 2.66$ ppm is attributed to C*H* protons of the isopropyl groups (DippForm). Complex **1** obtained from DME was used for the ^{13}C NMR spectrum (Figure S2), where partial DME substitution of the coordinated THF molecules was evident from the two additional DME signals at $\delta = 72.26$ ppm (**C**H$_2$) and $\delta = 58.74$ ppm (**C**H$_3$). The DippForm backbone NCHN resonance was not observed in the spectrum. The IR spectrum and the elemental analysis are also consistent with the crystal structure result (below). In the IR spectrum, several intense bands at 1700–700 cm^{-1} are typical for anionic formamidinate ligands.[7,9] For example, a strong absorption at 1667 cm^{-1} is attributed to a stretching mode of a delocalized NCN group.

Complex **1** is analogous stoichiometrically to the trivalent samarium pentamethylcyclopentadienyl complex [Cp*$_2$Sm(N$_2$Ph$_2$)(thf)] (Complex **A** in Scheme 1),[11a] but there are significant structural differences (below). In the reaction on a 2:1 stoichiometry, the outcome (**2** and [Sm(DippForm)$_3$]) parallels the ultimate outcome (**C** + [SmCp*$_3$]) of the corresponding reaction of [SmCp*$_2$(thf)$_2$].[11a] ([SmCp*$_3$] was not proposed as the co-product in the initial report, as at that stage it was believed the compound could not be prepared owing to steric constraints.) Attempts to isolate an analogue of Complex **B** (Scheme 1) were not successful, despite solvent variation. This intermediate complex containing a dianionic azobenzene species is not regarded as being favoured thermodynamically and, while it was observed in the case of complex **B**, mild conditions such as adding THF triggered the formation of complex **C** through ligand redistribution.[11a]

Initially, when the reaction was carried out in a 1:1 stoichiometric ratio, the solution immediately changed to dark blue, but isolated **1** is yellow, suggesting a further reaction *in situ* (see below). The Cp* analogue **A** (Scheme 1) is green.[11a] Addition of 1 mole of *trans*-azobenzene per 2 moles of [Sm(DippForm)$_2$(thf)$_2$] also results in an initial dark blue colour of the reaction mixture before changing to the yellow of **2** and [Sm(DippForm)$_3$]. The blue colour resembles that of [(SmCp*$_2$)$_2$N$_2$Ph$_2$] **B**,[11a] containing [Ph$_2$N$_2$]$^{2-}$. The transitory colour can be understood if it is from [{Sm(DippForm)$_2$}$_2$(Ph$_2$N$_2$)] **2a** (the DippForm analogue of complex **B** in Scheme 1), which could not be isolated. It forms initially on both 1:1 and 1:2 mole ratios. In the former case, it then reacts with the additional Ph$_2$N$_2$ present to give **1**, whilst in the latter it undergoes rearrangement analogous to **B** to give **2** and [Sm(DippFom)$_3$].

The reaction of [Sm(DippForm)$_2$(thf)$_2$] with 1H-1,2,3-benzotriazole

The reaction was performed using an equimolar mixture of [Sm(DippForm)$_2$(thf)$_2$] and 1*H*-1,2,3-benzotriazole in THF. The colour of the solution changed from dark green to yellowish green after stirring for three days. Off-white crystals of [Sm^{III}(DippForm)$_2$(btz)(thf)]·thf **(3)** were isolated after keeping the concentrated solution at 4 °C overnight (Scheme 2). The formation of hydrogen gas as a co-product was confirmed by an NMR scale repeat reaction in d_8-THF. A small resonance at $\delta =$ 4.72 ppm was detected (Figure S3), which is attributable to H$_2$.[13] The identity of **3** was established by X-ray crystallography (below), but the bulk product was somewhat impure as evident from a low carbon analysis, though this is not uncommon for lanthanoid complexes owing to ease of metal carbide formation during combustion.[14] In the ^{1}H NMR spectrum, satisfactory integrations could not be obtained, as the effects of paramagnetism were more evident than in the case of **1**. Thus, the backbone NCHN resonance was further shifted to 12.85 ppm (Figure S4), the aromatic hydrogens of Hbtz at 7.7–8.3 ppm were shifted to an AB doublet at 6.66–6.64 ppm, the CH and CH$_3$ resonances of DippForm were considerably broadened, as was the shifted thf resonance. In the ^{13}C NMR spectrum **(Figure S5)** the resonance at $\delta = 192.29$ ppm is assigned to the NCHN formamidinate backbone carbon atom, contrasting the failure to locate this for **1.**

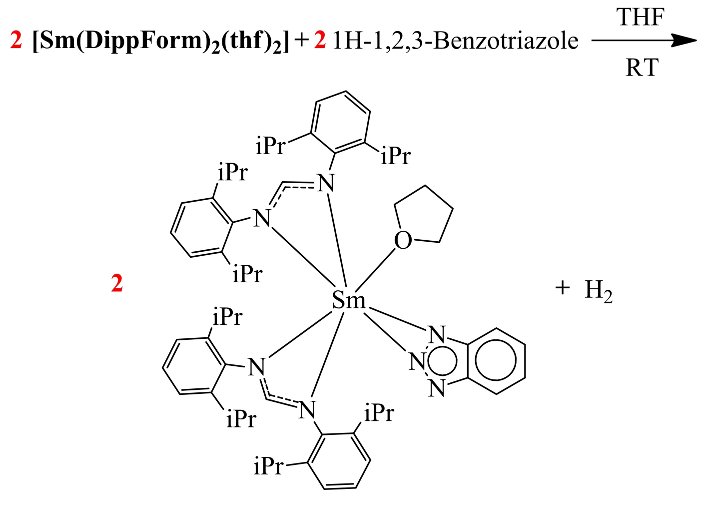
No structurally characterized samarium benzotriazolate complexes are in the CCDC data base. A range of elegant lanthanoid trisbenzotriazolates have been prepared by Mueller-Buschbaum.[15] More relevant given the Cp/DippForm analogy is [DyCp$_2$(btz)]$_2$ from protolysis of [DyCp$_3$] with benzotriazole in THF.[16a] This formally nine coordinate dimer without thf coordination contrasts momomeric seven coordinate **3** with thf coordinated, both crystallized from THF. From steric coordination numbers, DippForm[16b] is bulkier than Cp[16c] and monomeric [DyCp$_2$(btz)(thf)] would not be crowded.

1 and **3** decompose on attempted melting point determination, and microanalysis shows **1** very readily loses THF of solvation.

X-ray Structures

[Sm^{III}(DippForm)$_2$(Ph$_2$N$_2$)(thf)]·3THF 1

Complex **1** crystallizes in the monoclinic space group $P2_1/n$ with three lattice THF molecules. Two DippForm ligands bind in a κ^2



3

Scheme 2. The reaction of [Sm(DippForm)$_2$(thf)$_2$] with 1*H*-1,2,3-benzotriazole.

fashion to the samarium(III) ion, along with one thf ligand (Figure 1). The $[N_2Ph_2]^-$ moiety is η^2-bonded to the samarium centre through the NN vector where the coplanarity and *trans* orientation of the phenyl rings in free N_2Ph_2 no longer exist. The *cis*-azobenzene moiety has a dihedral angle of 71.2°(C_{Ph}–NN–C_{Ph}) which is in line with the values of the analogous complex [Sm(C$_5$Me$_5$)$_2$(N$_2$Ph$_2$)(thf)] **A** (63.1° and 70.8° for two crystallographically independent molecules).[11a] **A** is formally nine-coordinate as compared with seven for **1**. However, some structural features are different from monomeric azobenzene complex **A**. The Sm–N$_{azobenzene}$ bond lengths show two disparate values, namely 2.267(2) Å and 2.586(2) Å.

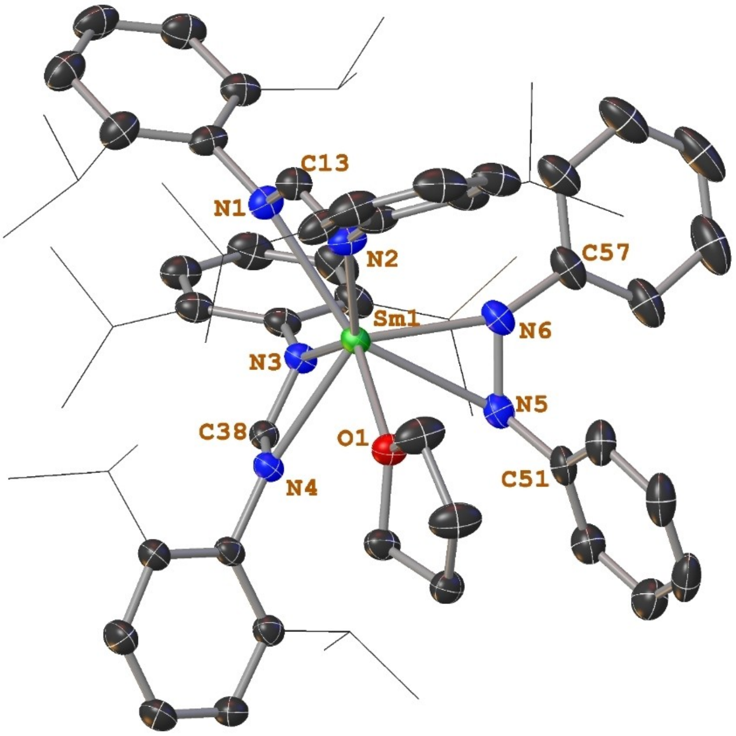


Figure 1. ORTEP diagram of complex **1** in which relevant atoms are labelled. Thermal ellipsoids are drawn at a 50 % probability level. Isopropyl groups of DippForm are shown as lines and hydrogen atoms along with three lattice THF molecules are omitted for clarity. Selected bond lengths (Å) and angles (°): Sm1–O1 2.4973(16), Sm1–N6 2.267(2), Sm1–N5 2.586(2), Sm1–N1 2.479(2), Sm1–N2 2.503(2), Sm1–N3 2.5301(19), Sm1–N4 2.4754(19), N5–N6 1.438(3), N5–C51 1.427(3), N6–C57 1.397(3), N1–C13 1.323(3), N2–C13 1.323(3), N3–C38 1.320(3), N4–C38 1.323(3), N6–Sm1–N5 33.66(7), N5–N6–Sm1 85.41(12), C57–N6–Sm1 154.42(19), C57–N6–N5 116. 2(2), N6–N5–Sm1 60.93(11), C51–N5–Sm1 130.67(15), C51–N5–N6 118.47(19), N3–C38–N4 120.2(2), N2–C13–N1 118.8(2).

The first value is close to the typical $Sm^{3+}–NR_2$ σ bond length (2.284 Å),[17] while the latter falls in the range of conventional $R_3N:\rightarrow Sm^{3+}$ donor bond lengths (2.53–2.77 Å),[18] suggesting that the N_2Ph_2 ligand is involved in one single σ bond and one donor bond to the samarium atom. This contrasts the bonding in $[SmCp^*_2(N_2Ph_2)(thf)]$ **A** in which the Sm–N bonds are much closer (2.390(10)-2.450(10) Å for two independent molecules) and lie midway between the values of **1**, but is similar to $Sm–N(N_2Ph_2)$ of **2** and **C** (below). The N–N bond length in the trapped azobenzene ligand is 1.438(3) Å which is significantly longer relative to the NN double bond length in free azobenzene (1.25 Å) and is similar a typical N–N single bond length (1.45 Å).[19] The substantial elongation in the N–N bond implies the reduction of the ligand which is consistent with oxidation of Sm to the trivalent state. The average N–C(Ph) bond distance of *cis*-oriented C_6H_5 rings of azobenzene in **1** is 1.412 Å, which is marginally shorter compared with 1.433 Å of free *trans*-azobenzene. All these structural dimensions indicate the presence of significant electron delocalization in the azobenzene ligand. Moreover, the $Sm–N_{DippForm}$ bond lengths are shorter [2.475(19)–2.530(19) Å] compared with the divalent starting material $[Sm(DippForm)_2(thf)_2]$ [2.529(4) Å and 2.617(4) Å] and the same trend can be observed in the case of the Sm–O(thf) bond length [2.4973(16) Å compared to 2.560(3) Å and 2.599(3) Å of the starting material].[6] The ionic radius of Sm^{3+} is smaller than Sm^{2+}.[20] Although the steric coordination numbers of Cp*[16c] and DippForm[16b] are similar, the ligands have a different shape and this may contribute to the bonding difference between **1** and isostoichiometric **A**.

$[Sm^{III}(DippForm)(Ph_2N_2)(thf)]_2\cdot 4THF$ 2

The X-ray crystal structure of complex **2** was solved and refined in the triclinic space group *P*-1 with four lattice THF molecules per dimer. One DippForm ligand is κ^2 coordinated to each samarium atom. Two dianionic azobenzene units act as a bridge between two samarium ions by using μ-η^2:η^2 binding modes, with one thf ligand on each metal (Figure 2). Again, a considerable difference is evident regarding the shape of coordinated N_2Ph_2 moieties compared to free azobenzene. The phenyl rings in the bridged azobenzene molecules are oriented in a *cis* fashion having a dihedral angle of 81.1°, which is comparable to that of the analogous Cp* complex $[Sm(C_5Me_5)(thf)]_2[\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2Ph_2]_2$ **C** (76°).[11a] The N–N bond length in the bridged azobenzene ligand is 1.456(3) Å which is clearly elongated compared to the typical NN double bond in free azobenzene (1.25 Å) and similar to the normal N–N single bond length (1.45 Å), indicating the formation of an N–N single bond.[19] The $Sm–N_{azobenzene}$ bond lengths on each metal atom are 2.2815(19) Å (Sm1–N3), 2.3256(19) Å (Sm1–N4*), 2.6165(19) Å (Sm1–N4) and 2.600(2) Å (Sm1–N3*) displaying two distinct ranges of bond length values. Here again, the first two values are close to the typical Sm–N sigma bond length (2.284 Å),[17] while the latter two fall in the range of conventional Sm–N donor bond length (2.41-2.65 Å).[21] This indicates that each samarium atom is forming two different types of bonds with each bridged $[N_2Ph_2]^{2-}$ unit: one single bond and a donor bond. These structural features imply the existence of two completely reduced $[N_2Ph_2]^{2-}$ moieties which are com-

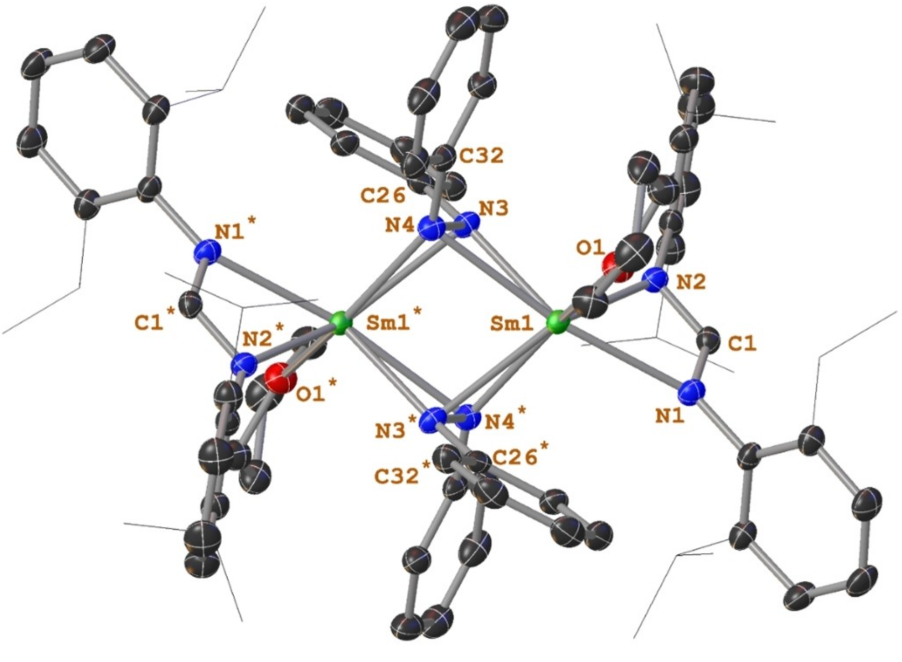


Figure 2. ORTEP diagram of complex **2** in which relevant atoms are labelled. Thermal ellipsoids are drawn at a 50% probability level. Isopropyl groups of DippForm are shown as lines and hydrogen atoms along with two lattice THF molecules are omitted for clarity. Selected bond lengths (Å) and angles (°): Sm1–N3 2.2815(19), Sm1–N3* 2.600(2), Sm1–N4 2.6165(19), Sm1–N4* 2.3256(19), Sm1–N1 2.500(2), Sm1–O1 2.4759(17), Sm1–N2 2.482(2), N2–C1 1.329(3), N2–C2 1.427(3), N1–C1 1.316(3), N1–C14 1.430(3), N3–N4 1.456(3), N3–C26 1.390(3), N4–C32 1.397(3), N3–Sm1–N4 33.70(6), N4*–Sm1–N3* 33.79(6), N4–N3–Sm1* 62.70(10), N4–N3–Sm1 85.87(11), N3–N4–Sm1* 83.51(11), N3–N4–Sm1 60.43(10), C26–N3–N4 118.03(18), C32–N4–N3 116.94(19), N3–Sm1–N3* 87.97(7), N4*–Sm1–N4 89.37(6), Sm1–N3–Sm1* 92.03(7), Sm1*–N4–Sm1 90.63(6), C26–N3–Sm1* 89.97(13), C26–N3–Sm1 153.69(16), C32–N4–Sm1* 148.71(15), C32–N4–Sm1 119.66(14), N1–C1–N2 118.4(2).

plexed by two trivalent samarium ions. All these bond parameters discussed above and especially the Sm–N bond disparity, along with a few significant bond angles are comparable to those of $[Sm(C_5Me_5)(thf)]_2[\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2Ph_2]_2$ **C**. As in $[Sm(C_5Me_5)(thf)]_2[\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2Ph_2]_2$, here also two samarium ions are relatively close (3.519 Å) [*cf.* 3.491(2) Å for the Cp* analogue].[11a] This close DippForm/Cp* relationship occurs despite the difference 7/9 in formal coordination numbers. The trivalent state of the samarium ions can also be confirmed by comparison with the $Sm–N_{DippForm}$ and Sm–O(THF) bond lengths of the divalent starting material $[Sm(DippForm)_2(thf)_2]$. The $Sm–N_{DippForm}$ bond lengths are shorter [2.482(2) Å and 2.531(4) Å] compared with the divalent starting material $[Sm(DippForm)_2(thf)_2]$ [2.529(4) Å and 2.617(4)] reflecting the smaller size of Sm^{3+} compared with Sm^{2+}.[20] Likewise, a similar result can also be noticed in the case of Sm–O(thf) bond length, which is 2.4759(17) Å compared to 2.560(3) Å and 2.599(3) Å of the starting material.[6]

$[Sm^{III}(DippForm)_2(btz)(thf)]\cdot THF$ 3

Complex **3** crystallizes in the monoclinic space group $P2_1/n$ with one lattice THF molecule. The samarium atom is ligated by two DippForm moieties in a κ^2 fashion along with one coordinating thf molecule (Figure 3). The benzotriazolate moiety is η^2-bonded to the samarium centre through two nitrogen atoms. The $Sm–N_{Btz}$ bond lengths (Sm–N1 2.422(3) Å) and (Sm–N2 2.460(3) Å) are longer than the typical Sm–N sigma bond length (2.284 Å),[17] but are close to Sm–N donor bond lengths (2.390(19)–2.450(19) Å) of **A** The two N–N bond lengths are approximately equal, which are 1.342(4) Å for N1–N2 and 1.322(5) Å for N2–N3. These values are intermediate between the value for N–N double bond in free azobenzene (1.25 Å) and the normal N–N single bond length (1.45 Å).[19] The $N_{Btz}–C_{Btz}$ bond lengths for trapped benzotriazolate are 1.354(4) Å (N1–C1) and 1.363(4) Å (N3–C6). Delocalization of π electron density of the N=N double bond owing to the deprotonation is clear from these structural features. In addition, these N–N and N–C bond distances are comparable to the previously reported bond length ranges of rare earth benzotriazolates.[15a–c,16a] Similar to the two previous structures (**1** & **2**), the $Sm–N_{DippForm}$ bond lengths are shorter [2.423(3) Å and 2.471(3) Å] than those (above) of the divalent reactant $[Sm(DippForm)_2(thf)_2]$ and the same trend can be observed in the case of Sm–O(thf) bond lengths.

Conclusions

The hypothesis that $[Sm(DippForm)_2(thf)_2]$ is an *N*-donor supported alternative to $[Sm(C_5Me_5)_2(thf)_2]$ in reduction chemistry gains traction from reactions of the former with azobenzene. On a 1:1 stoichiometry, [Sm-

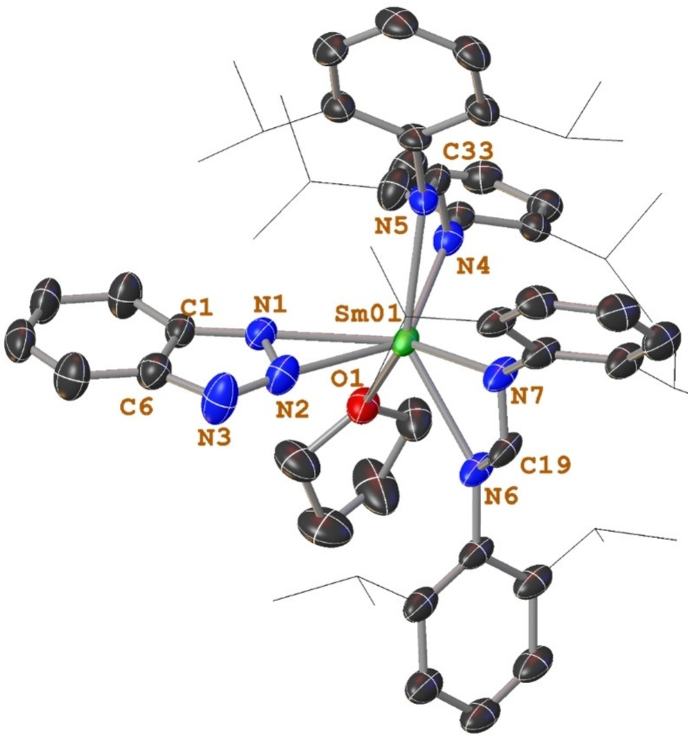


Figure 3. ORTEP diagram of complex **3** in which relevant atoms are labelled. Thermal ellipsoids are drawn at a 50 % probability level. Isopropyl groups of DippForm are shown as lines and hydrogen atoms along with one lattice THF molecule are omitted for clarity. Selected bond lengths (Å) and angles (°): Sm01–N1 2.422(3), Sm01–N2 2.460(3), N1–N2 1.342(4), N1–C1 1.354(4), N2–N3 1.322(5), N3–C6 1.363(4), Sm01-O1 2.452(2), Sm01–N4 2.423(3), Sm01–N5 2.471(3), Sm01–N7 2.440(3), Sm01–N6 2.457(3), N1-Sm01–N2 31.90(10), N2–N1- Sm01 75.59(19), C1–N1–Sm01 176.8(2), N1–N2- Sm01 72.51(19), N3–N2–Sm01 174.6(3), N2–N1–C1 106.6(3), N3–C6–C1 107.9(3), N3–N2–N1 112.5(3), N2–N3–C6 106.1(3), N4–Sm01–N5 55.46(9), N7–Sm01–N6 55.34(9), N5–C33–N4 118.4(3), N7–C19–N6 118.4(3).

(DippForm)$_2$(N$_2$Ph$_2$)(thf)) (**1**) is obtained, which is the stoichiometric analogue of the product by reduction with [Sm(C$_5$Me$_5$)$_2$(thf)$_2$]. However, the bonding of [Ph$_2$N$_2$]$^-$ in **1** is an unsymmetrical Sm–N$_{amide}$/Sm–N$_{amine}$ in contrast to the near symmetrical π-bonding in the Cp* analogue. The reaction of [Sm(DippForm)$_2$(thf)$_2$] with azobenzene on a 2:1 stoichiometry yields [Sm^{III}(DippForm)(Ph$_2$N$_2$)(thf)]$_2$·4THF (**2**) (with a dianionic reduced azobenzene) and [Sm(DippForm)$_3$] in parallel with the [SmCp*$_2$(thf)$_2$] reaction, and in this case, the structure of **2** is similar to that of the Cp* analogue with amide/amine binding of [Ph$_2$N$_2$]$^{2-}$. The reaction of [Sm(DippForm)$_2$(thf)$_2$] with 1*H*-1,2,3-benzotriazole (Hbtz) yields the samarium(III) triazolate complex [Sm(DippForm)$_2$(btz)(thf)] encouraging greater use of this reagent in lanthanoid reduction chemistry.

Experimental Section

General: The samarium compounds described here are highly air and moisture sensitive, and were prepared and handled with vacuum-nitrogen line techniques and in a dry box in an atmosphere of purified nitrogen. [Sm(DippForm)$_2$(thf)$_2$] was prepared by the literature method.[6] Samarium metal was from Eutectix. Large chunks were filed in the drybox before use. Solvents (thf, DME, C$_6$D$_6$, toluene and hexane) were pre-dried by distillation over sodium or sodium benzophenone ketyl before being stored under an atmosphere of nitrogen. *Trans*-azobenzene and 1*H*-1,2,3-benzotriazole were purchased from Sigma Aldrich and dried under vacuum prior to use. IR spectra were recorded as Nujol mulls between NaCl plates using an Agilent Technologies Cary 630 FTIR instrument within the range 4000–700 cm^{-1}. ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker 400 MHz instrument. Chemical shifts were referenced to the residual ^{1}H and ^{13}C resonances of the deuterated solvents. Microanalyses were determined by the Chemical Analysis Facility, Macquarie University, and all the samples were sealed in tubes under nitrogen. Crystals were immersed in crystallography oil and were measured on a Rigaku SynergyS diffractometer or the MX1 beamline at the Australian Synchrotron. Crystal data and refinement details are given in Table S1.

Deposition Numbers 2297133 for [Sm^{III}-(DippForm)$_2$(Ph$_2$N$_2$)(thf)]·3THF (**1**), 2297134 for [Sm^{III}-(DippForm)(Ph$_2$N$_2$)(thf)]$_2$·2THF (**2**), and 2297135 for [Sm^{III}-(DippForm)$_2$(btz)(thf)]·THF (**3**) contain 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.

Syntheses: [Sm^{III}(DippForm)$_2$(Ph$_2$N$_2$)(thf)]·3THF (**1**): Separate solutions of [Sm(DippForm)$_2$(thf)$_2$] (0.23 g, 0.2 mmol) and N$_2$Ph$_2$ (0.036 g, 0.2 mmol) in 5 mL THF were mixed and stirred for 24 hours giving initially a dark blue solution. Adding N$_2$Ph$_2$ in excess is advantageous. Complex **1** was obtained from THF by storing the concentrated solution at −18 °C for several weeks, yellow crystals (0.573 g, 42.5 %). Found: C, 69.88; H, 8.39; N, 7.64; C$_{78}$H$_{112}$N$_6$O$_4$Sm (1348.08) requires C, 69.49; H, 8.37; N, 6.23 %, loss of three thf of crystallization, C$_{66}$H$_{88}$N$_6$OSm (1131.80) requires C, 70.04; H, 7.84; N, 7.43 %. IR (Nujol): 1667 s, 1587w, 1521 m, 1334 m,1295 m, 1260 m, 1235w, 1189w, 1098w, 1014w, 934w, 799 m, 766w, 755 m, 722w, 690w cm^{-1}. After a similar preparation in toluene, crystals of [Sm^{III}(DippForm)$_2$(Ph$_2$N$_2$)(thf)] were obtained and were transferred to an NMR tube for identification. ^{1}H NMR (C$_6$D$_6$, 300 MHz, 10.51 (s, 2H, NC***H***N), 8.03,m, trace, *trans*-azobenzene impurity), 7.2–6.9 (m, aromatic Hs including from toluene and C$_6$D$_6$), 3.39 (4H, THF: 2,5-C$\boldsymbol{H}_2$), 2.66 (m,8H, Dipp-C***H***), 2.11 (s, 3H, Toluene-C$\boldsymbol{H}_3$) 1.37 (4H, THF: 3,4-C$\boldsymbol{H}_2$), 1.18 (m, 48H, Dipp-C$\boldsymbol{H}_3$). A resonance at 8.03 ppm (Ph$_2$N$_2$) is indicative of slight decomposition of the product on manipulation for NMR measurements. Alternatively, DME was added and the solution was concentrated in vacuo before storing the solution at −18 °C for 3 days to afford yellow/colourless crystals Complex **1** obtained from DME was used for the ^{13}C NMR spectrum, ^{13}C NMR (75.5 MHz, C$_6$D$_6$, 296 K): 22.90 (Dipp-**C**H$_3$), 23.85 (Dipp-**C**H$_3$), 24.61 (Dipp-**C**H$_3$), 25.77 (THF: 3,4-**C**H$_2$), 28.34 (Dipp-**C**H), 28.63 (Dipp-**C**H), 58.74 (DME: **C**H$_3$), 68.14 (THF: 2,5-**C**H$_2$), 72.26 (DME: **C**H$_2$), 123.36, 123.48, 123.77, 125.05, 128.70, 129.30, 131.13, 138.90, 143.41, 145.66, 146.10, 146.73, 153.28, 167.82 (aromatic C resonances).

[Sm^{III}(DippForm)(Ph$_2$N$_2$)(thf)]$_2$·4THF (**2**): Separate solutions of [Sm(DippForm)$_2$(thf)$_2$] (0.23 g, 0.2 mmol) and N$_2$Ph$_2$ (0.018 g, 0.1 mmol) in 5 mL THF were mixed and stirred for one week, causing a colour change to yellow/orange from initial dark blue. Addition of DME, concentration *in vacuo* and storing the solution at −18 °C for 3–4 days gave yellow crystals of a mixture of **2** and [Sm(DippForm)$_3$], which could not be visually distinguished. This makes obtaining significant amounts of pure crystals of **2** extremely difficult and impedes its purification and characterization. Adding a minimal amount of hexane to the solid product (after removal of the THF) is a method to separate product **2** from [Sm(DippForm)$_3$] to a limited extent since the latter has low solubility in hexane. This gave a green solution of compound **2** with a lot of yellow solid material, but complete separation was still not possible. Thus, **2** was identified from a crystal structure of a hand picked crystal, and [Sm(DippForm)$_3$] by a unit cell $a=13.143$, $b=38.000$, $c=16.400$, $\beta=96.25$, which is similar to the reported unit cell $a=13.166$, $b=37.913$, $c=16.499$, $\beta=96.11$[6] of a hand picked crystal.

[Sm^{III}(DippForm)$_2$(btz)(thf)]·THF (**3**): 10 mL of THF was added to a Schlenk flask charged with [Sm(DippForm)$_2$(thf)$_2$] (0.23 g, 0.2 mmol) and 1*H*-1,2,3-benzotriazole (0.024 g, 0.2 mmol) and was stirred for three days causing a colour change from dark green to yellowish green. The solution was concentrated *in vacuo* and stored at 4 °C overnight to afford off-white crystals of **3** (0.605 g, 53 %). Although identifiable crystals of **3** were obtained, the bulk product was not pure. Found: C, 63.65; H, 8.12; N, 8.97; C$_{64}$H$_{90}$N$_7$O$_2$Sm (1139.77) requires C, 67.44; H, 7.96; N, 8.60 %. IR (Nujol): 3061 m, 1666 m, 1593 m, 1522 s, 1361 m, 1318 s, 1278 s, 1233 s, 1190s, 1138w, 1107 m, 1070 s, 1044 m, 1021 m, 972w, 942 m, 911 m, 867 m, 802 m, 776 m, 758 m, 748 s, 629 m cm^{-1}. ^{1}H NMR (C$_6$D$_6$, 300 MHz): Satisfactory integrations could not be obtained (see Fig S4). 12.85 (s, NC***H***N), 7.4–6.9 (m, aromatic Hs overlapped by solvent resonances), 6.66-6.64, dd(AB), 6.659, J$_{AB}$ 3,2 Hz. H$_A$ (*o*-H of btz), 6.645, J$_{AB}$ 3.2 Hz, H$_{B,}$(*m*-H of btz) 3.37-3.15, br, Dipp-CH, 1.52-1.05, complex m, Dipp-CH$_3$, O.05, vbr, thf (with sp silicone grease impurity). ^{13}C NMR (75.5 MHz, C$_6$D$_6$, 296 K): 22.47 (Dipp-**C**H$_3$), 23.94 (Dipp-**C**H$_3$), 25.45 (Dipp-**C**H$_3$), 26.59 (THF: 3,4-**C**H$_2$), 28.36 (Dipp-**C**H), 29.07 (Dipp-**C**H), 68.71 (THF: 2,5-**C**H$_2$), 116.36, 123.49, 123.89, 124.46, 124.73, 128.69, 140.34, 143.69, 146.87 (aromatic **C** resonances), 192.29 (Dipp-N**C**HN).

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Conflict of Interests

There are no conflicts of interest to declare.

Data Availability Statement

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

Keywords: lanthanoid complexes · one- and two-electron reduction · reductive trapping · samarium · *trans*-azobenzene

[1] a) M. Bochkarev, L. Zakharov, G. Kalimina, *Organoderivatives of rare earth elements*, Kluwer Academic Publishers, Dordrecht, **1995**; b) *Lanthanides: Chemistry and Use in Organic Synthesis. In Topics in Organometallic Chemistry* (Ed.: S. Kobayashi), Springer, Berlin, **1999**; Vol. 2; c) C. Huang, *Rare earth coordination chemistry*, Wiley-Blackwell, Oxford, **2010**; d) L. R. Morss, *Chem. Rev.* **1976**, *76*, 827–841; e) F. Ortu, *Chem. Rev.* **2022**, *122*, 6040–6116; f) K. Gopalaiah, H. B. Kagan, *Chem. Rec.* **2013**, *13*, 187–208; g) K. Gopalaiah, H. B. Kagan, *New J. Chem.* **2008**, *32*, 607–637, and references therein; h) M. Szostak, N. J. Fazakerley, D. Parmar, D. J. Procter, *Chem. Rev.* **2014**, *114*, 5959–6039.

[2] W. J. Evans, I. Bloom, W. E. Hunter, J. L. Atwood, *J. Am. Chem. Soc.* **1981**, *103*, 6507–6508.

[3] a) W. J. Evans, T. A. Ulibarri, J. W. Ziller, *J. Am. Chem. Soc.* **1988**, *110*, 6877–6879; b) W. J. Evans, S. L. Gonzales, J. W. Ziller, *J. Am. Chem. Soc.* **1991**, *113*, 9880–9882; c) W. J. Evans, S. L. Gonzales, J. W. Ziller, *J. Chem. Soc. Chem. Commun.* **1992**, 1138–1139; d) W. J. Evans, J. W. Grate, L. A. Hughes, H. Zhang, J. L. Atwood, *J. Am. Chem. Soc.* **1985**, *107*, 3728–3730.

[4] a) S. N. Konchenko, N. A. Pushkarevsky, M. T. Gamer, R. Köppe, H. Schnöckel, P. W. Roesky, *J. Am. Chem. Soc.* **2009**, *131*, 5740–5741; b) C. Schoo, S. Bestgen, A. Egeberg, S. Klementyeva, C. Feldmann, S. N. Konchenko, P. W. Roesky, *Angew. Chem. Int. Ed.* **2018**, *57*, 5912–5916; c) C. Schoo, S. Bestgen, A. Egeberg, J. Seibert, S. N. Konchenko, C. Feldmann, P. W. Roesky, *Angew. Chem. Int. Ed.* **2019**, *58*, 4386–4389; d) S. N. Konchenko, T. Sanden, N. A. Pushkarevsky, R. Köppe, P. W. Roesky, *Chem. Eur. J.* **2010**, *16*, 14278–14280; e) N. Arleth, S. Bestgen, M. Gamer, P. W. Roesky, *J. Am. Chem. Soc.* **2014**, *136*, 14023–14026.

[5] a) F. T. Edelmann, *Chem. Soc. Rev.* **2012**, *41*, 7657–7672; b) F. T. Edelmann, *Chem. Soc. Rev.* **2009**, *38*, 2253–2268.

[6] M. L. Cole, P. C. Junk, *Chem. Commun.* **2005**, 2695–2697.

[7] a) G. B. Deacon, P. C. Junk, J. Wang, D. Werner, *Inorg. Chem.* **2014**, *53*, 12553–12563; b) D. Wener, G. B. Deacon, P. C. Junk, *Inorg. Chem.* **2019**, *58*, 1912–1918.

[8] a) R. Yadav, M. E. Hossain, R. Peedika Paramban, T. Simler, C. Schoo, J. Wang, G. B. Deacon, P. C. Junk, P. W. Roesky, *Dalton Trans.* **2020**, *49*, 7701–7707; b) C. Schoo, S. Bestgen, M. Schmidt, S. N. Konchenko, M. Scheer, P. W. Roesky, *Chem. Commun.* **2016**, *52*, 13217–13220; c) C. Schoo, S. Bestgen, R. Köppe, S. N. Konchenko, P. W. Roesky, *Chem. Commun.* **2018**, *54*, 4770–4773; d) B. Y. Savkov, T. S. Sukhikh, S. N. Konchenko, N. A. Pushkarevsky, *Aust. J. Chem.* **2022**, *75*, 732–745.

[9] a) R. Peedika Paramban, Z. Guo, G. B. Deacon, P. C. Junk, *Dalton Trans.* **2023**, *52*, 3563–3566; b) R. Peedika Paramban, *PhD Thesis*, James Cook University, **2022**.

[10] W. J. Evans, D. K. Drummond, *J. Am. Chem. Soc.* **1989**, *111*, 3329–3335.

[11] a) W. J. Evans, D. K. Drummond, L. R. Chamberlain, R. J. Doedens, S. G. Bott, H. Zhang, J. L. Atwood, *J. Am. Chem. Soc.* **1988**, *110*, 4983–4994; b) E. D. Brady, D. L. Clark, D. W. Keogh, B. L. Scott, J. G. Watkin, *J. Am. Chem. Soc.* **2002**, *124*, 7007–7015; c) J. Takats, X. W. Zhang, V. W. Day, T. A. Eberspacher, *Organometallics* **1993**, *12*, 4286–4288; d) W. J. Evans, *Coord. Chem. Rev.* **2000**, *206–207*, 263–283; e) C. A. P. Goodwin, N. F. Chilton, G. F. Vettese, E. Moreno Pineda, I. F. Crowe, J. W. Ziller, R. E. P. Winpenny, W. J. Evans, D. P. Mills, *Inorg. Chem.* **2016**, *55*, 10057–10067; f) Z. Hou, T.-a. Koizumi, M. Nishiura, Y. Wakatsuki, *Organometallics* **2001**, *20*, 3323–3328; g) A. R. Willauer, A. M. Dabrowska, R. Scopelliti, M. Mazzanti, *Chem. Commun.* **2020**, *56*, 8936–8939.

[12] M. L. Cole, G. B. Deacon, C. M. Forsyth, P. C. Junk, K. Konstas, J. Wang, H. Bittig, D. Werner, *Chem. Eur. J.* **2013**, *19*, 1410–1420.

[13] a) S. Hamidi, G. B. Deacon, P. C. Junk, P. Neumann, *Dalton Trans.* **2012**, *41*, 3541–3552; b) G. R. Fulmer, A. J. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* **2010**, *29*, 2176–2179; c) Z. Guo, V. Blair, G. B. Deacon, P. C. Junk, *Chem. Commun.* **2021**, *57*, 11513–11516; d) T. Pery, K. Pelzer, G. Buntkowsky, K. Philippot, H. H. Limbach, B. Chaudret, *ChemPhysChem* **2005**, *6*, 605–607.

[14] M. Salehisaki, N. E. Rad, G. B. Deacon, J. Wang, Z. Guo, P. C. Junk, *Inorg. Chim. Acta.* **2022**, *539*, 120997.

[15] a) K. Mueller-Buschbaum, Y. Mokaddem, *Eur. J. Inorg. Chem.* **2006**, 2000–2010; b) K. Mueller-Buschbaum, Y. Mokaddem, *Z. Anorg. Allg. Chem.* **2007**, *633*, 521–523; c) K. Mueller-Buschbaum, Y. Mokaddem, *Z. Anorg. Allg. Chem.* **2008**, *634*, 2360–2366; d) J. C. Rybak, K. Mueller-Buschbaum, *Z. Anorg. Allg. Chem.* **2010**, *636*, 126–131; e) J. C. Rybak, I. Schellenberg, R. Pottgen, K. Mueller-Buschbaum, *Z. Anorg. Allg. Chem.* **2010**, *636*, 1720–1725.

[16] a) R. A. Layfield, J. J. W. McDouall, S. A. Sulway, F. Tuna, D. Collison, R. E. P. Winpenny, *Chem. Eur. J.* **2010**, *16*, 4442–4446; b) Z. Guo, V. L. Blair, G. B. Deacon, P. C. Junk, *Dalton Trans.* **2020**, *49*, 13588–13600; c) J. Marcalo, A. Pires de Matos, *Polyhedron* **1989**, *8*, 2431–2437.

[17] H.-X. Li, Q.-F. Xu, J.-X. Chen, M.-L. Cheng, Y. Zhang, W.-H. Zhang, J.-P. Lang, Q. Shen, *J. Organomet. Chem.* **2004**, *689*, 3438–3448.

[18] W. J. Evans, T. P. Hanusa, J. H. Meadows, W. E. Hunter, J. L. Atwood, *Organometallics* **1987**, *6*, 295–301.

[19] C. Brown, *Acta Crystallogr.* **1966**, *21*, 146–152.

[20] R. D. Shannon, *Acta Crystallogr. Sect. A.* **1976**, *32*, 751–767.

[21] F. Yuan, Q. Shena, J. Sun, *Polyhedron* **1998**, *17*, 2009–2012.

[22] N. P. Cowieson, D. Aragao, M. Clift, D. J. Ericsson, C. Gee, S. J. Harrop, N. Mudie, S. Panjikar, J. R. Price, A. Riboldi-Tunnicliffe, R. Williamson, T. Caradoc-Davies, *J. Synchrotron Radiat.* **2015**, *22*, 187–190.

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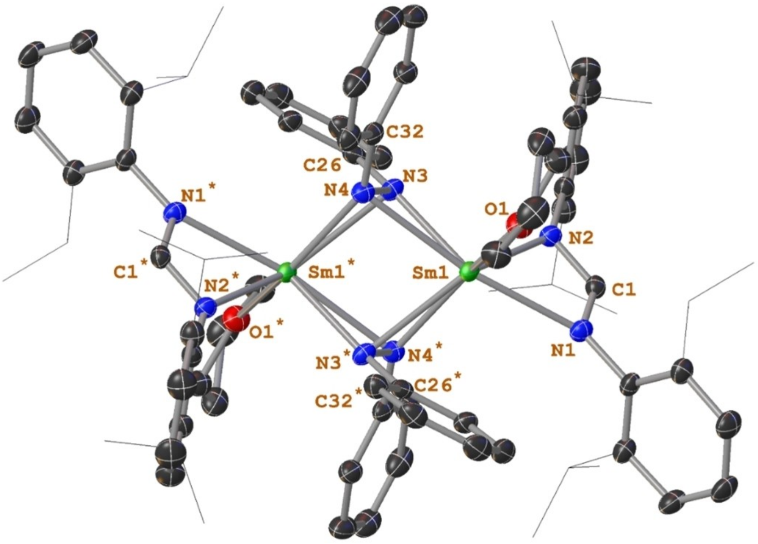
RESEARCH ARTICLE



Treatment of $[Sm(DippForm)_2(thf)_2]$ with *trans*-azobenzene results in formation of mononuclear $[Sm^{III}(DippForm)_2(Ph_2N_2)(thf)]\cdot 3THF$ (**1**) and dinuclear $[Sm^{III}(DippForm)(Ph_2N_2)(thf)]_2\cdot 4THF$ (**2**) with $[Sm(DippForm)_3]$ respectively, where azobenzene has undergone either one or two electron reduction. The reaction with 1*H*-1,2,3-benzotriazole also yielded a trivalent samarium complex containing benzotriazolate (btz), $[Sm^{III}(DippForm)_2(btz)(thf)]\cdot THF$ (**3**).

*Dr. R. Peedika Paramban, Dr. Z. Guo, Prof. Dr. G. B. Deacon, Prof. Dr. P. C. Junk**

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Reactivity of $[Sm(DippForm)_2(thf)_2]$ with Substrates Containing Azo Linkages