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# Monomeric f-element chemistry with sterically encumbered allyl ligands

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## Abstract

A new class of allyl-lanthanide salts of the type  $[\text{K}(\text{thf})_4][(\text{C}_3\text{H}_3(\text{SiMe}_3)_2)_3\text{LnI}]$  ( $\text{Ln} = \text{Ce}, \text{Pr}, \text{Nd}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Er}$ ) have been prepared and isolated by reaction of three equivalents of the 1,3-bis(trimethylsilyl)allyl anion with  $\text{LnI}_3$ . The neutral complex  $[\text{C}_3\text{H}_3(\text{SiMe}_3)_2]_3\text{Nd}(\text{thf})$  has been isolated from the reaction of the triflate complex  $\text{Nd}(\text{O}_3\text{SCF}_3)_3$  with three equivalents of the 1,3-bis(trimethylsilyl)allyl anion. These complexes have been structurally characterized using single crystal X-ray diffraction.

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**Keywords:** Allyl; Lanthanide; Tetrahydrofuran; Complex; Crystal structure; Bulky ligands

## 1. Introduction

Several examples of homoleptic and pseudo-homoleptic allyl-lanthanide complexes have recently been prepared and shown to be catalytically active [1–10]. For instance,  $\text{Nd}(\text{allyl})_3(\text{solvent})_x$  has been employed as a catalyst for stereospecific butadiene polymerization [4]. However, the allyl moiety undergoes insertion, becoming incorporated into the growing chain, and the fate of the catalyst thereafter is not well understood. Our hope is to gain better control of the activity of these complexes by protecting the allyl moiety using bulky end groups that will hinder insertion. Extremely bulky cyclopentadienyl ligands have been used effectively to improve the stability of base-free metallocenes of the divalent lanthanides [11–13], but this strategy has not generally been applied to allyl-lanthanide compounds with the exception of the preparation of the divalent samarium species  $(\text{C}_3\text{H}_3(\text{SiMe}_3)_2)_2\text{Sm}(\text{thf})_2$  [14].

The work presented here was initiated in an attempt to expand upon the number of complexes employing the bulky 1,3-bis(trimethylsilyl)allyl ligand toward the lanthanide elements. Previous studies [15,16] demonstrated that the application of this ligand imparts additional thermal stability relative to the parent complexes for transition metals. Furthermore, we and others have observed the potential for  $\sigma$ – $\pi$  interconversions of the parent allyl moiety to open up coordination sites for catalytic reactions [17–21]. The ability of 1,3-bis(trimethylsilyl)allyl to adopt a  $\sigma$  geometry has recently been confirmed based on the structure of a Mn-complex [22]. Such  $\sigma$ – $\pi$  fluxionality would be problematic for the parent allyl-lanthanide complexes due to the aforementioned propensity of these systems to undergo insertion.

Herein we report that the reaction of three equivalents of the 1,3-bis(trimethylsilyl)allyl anion with lanthanide(III) iodides in tetrahydrofuran (THF) generates crystalline salts of the general formula  $[\text{K}(\text{thf})_4][(\text{C}_3\text{H}_3(\text{SiMe}_3)_2)_3\text{LnI}]$ , as was confirmed by X-ray structures of the Ce, Er and Tb congeners. Included in our report is a discussion of our attempts to form strictly homoleptic allyl species.

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## 2. Experimental

### 2.1. General

All manipulations were performed under inert atmosphere using standard glovebox and Schlenk techniques. Solvents were dried by elution from columns of activated alumina and copper oxide catalyst according to the procedure described by Grubbs and co-workers [23] or dried over potassium benzophenone ketyl and distilled under nitrogen. Toluene-*d*<sub>8</sub> and THF-*d*<sub>8</sub> were stirred over Na/K alloy and vacuum transferred prior to use.  $K[C_3H_3(SiMe_3)_2]$  was prepared as previously described [24]. Anhydrous lanthanide iodides were used as received from Aldrich. Nominally anhydrous lanthanide triflates (Aldrich) were dried under vacuum for 12 h between 100 and 120 °C prior to use. NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer at room temperature (r.t.). Magnetic moments ( $\mu_{\text{eff}}$ ) were determined by the Evans method in toluene-*d*<sub>8</sub> [25,26]. Calculated moments were taken from the literature for  $Ln^{3+}$  hydrated salts [27].

### 2.2. Preparation of complexes

#### 2.2.1. Synthesis of $[K(thf)_4][C_3H_3(SiMe_3)_2]_3CeI$ (**1**)

Inside an inert atmosphere glovebox,  $K[C_3H_3(SiMe_3)_2]$  (0.200 g, 0.891 mmol) was dissolved in 10 ml of THF in a 20 ml scintillation vial.  $CeI_3$  (0.156 g, 0.299 mmol) and 2 ml of THF were placed in another 20 ml scintillation vial equipped with a stirring bar. Both vials were placed in the glovebox freezer (−35 °C) for 1 h. The  $K[C_3H_3(SiMe_3)_2]/THF$  solution was added dropwise to the  $CeI_3$  slurry with stirring. The reaction was allowed to warm to r.t. overnight with stirring. The solvent was removed in vacuo and ca. 10 ml of hexanes was added to the residue and the resulting solution was filtered over a medium-porosity glass frit to yield a bright orange filtrate. This filtrate was concentrated to ca. 3 ml and returned to the freezer to yield  $[K(thf)_4][C_3H_3(SiMe_3)_2]_3CeI$  as small, orange–red crystals (0.15 g, 0.366 mmol, 41.1%). Attempts to obtain reliable elemental analyses were unsuccessful presumably due to the propensity of these salts to lose coordinated thf at elevated temperatures.

<sup>1</sup>H-NMR (THF-*d*<sub>8</sub>, 25 °C):  $\delta$  10.23 (6H,  $\nu_{1/2}$  = 140 Hz, *anti*), 3.62 ( $\nu_{1/2}$  = 11 Hz, coord. thf), 1.98 (3H,  $\nu_{1/2}$  = 51 Hz, *meso*), 1.80 ( $\nu_{1/2}$  = 7 Hz, coord. thf), 0.89 (54H,  $\nu_{1/2}$  = 17 Hz,  $SiMe_3$ ).  $\mu_{\text{eff}}$ : calculated: 2.54 BM, experiment: 2.7 BM.

#### 2.2.2. Synthesis of $[K(thf)_4][C_3H_3(SiMe_3)_2]_3LnI$ ( $Ln = Tb$ (**2**), $Er$ (**3**))

The syntheses of **2** and **3** were carried out in the same manner as described for **1** and both complexes were

isolated as bright yellow blocks in ca. 75% yield. Magnetic data for **2**:  $\mu_{\text{eff}}$ : calculated: 9.72 BM, experiment: 9.0 BM. Magnetic data for **3**:  $\mu_{\text{eff}}$ : calculated: 9.58 BM, experiment: 9.9 BM.

#### 2.2.3. Syntheses of $[K(thf)_4][C_3H_3(SiMe_3)_2]_3LnI$

$Ln = Pr$  (yellow),  $Nd$  (green),  $Gd$  (yellow orange),  $Dy$  (orange) reactions were carried out in the same manner as described for **1**. In all cases crystallization occurred; however, the crystals were not suitable for X-ray crystallography.

#### 2.2.4. Synthesis of $[C_3H_3(SiMe_3)_2]_3Nd(thf)$ (**4**)

A slurry of  $Nd(O_3SCF_3)_3$  (0.496 g, 0.839 mmol) was prepared by adding 20 ml of THF to the solid in a 125-ml Erlenmeyer flask. To this slurry was added dropwise, a THF (15 ml) solution of  $K[C_3H_3(SiMe_3)_2]$  (0.565 g, 2.52 mmol) at r.t. resulting in a green coloration of the reaction mixture. The resulting solution was then allowed to stir overnight after which the solvent was removed under vacuum and 10 ml of hexanes was added to the residue. The resulting mixture was filtered through a glass frit to give a green filtrate that has an orange–red color when illuminated by a white light source. The solvent was evaporated to yield 0.373 g of a sticky, green solid. Hexanes (2 ml) was then added to the resulting solid, and green crystals (0.365 g, 0.469 mmol, 56% yield) were produced via slow evaporation at r.t. Elemental analysis of this complex provides a formulation consistent with a fractional amount of thf suggesting that the coordinated thf is labile.

<sup>1</sup>H-NMR (THF-*d*<sub>8</sub>, 25 °C):  $\delta$  11.34 ( $\nu_{1/2}$  = 259 Hz, allylic), 10.46 ( $\nu_{1/2}$  = 68 Hz, allylic), 3.58 (broad shoulder, coord. thf), 1.78 ( $\nu_{1/2}$  = 15 Hz, coord. thf), 0.91 (54H,  $\nu_{1/2}$  = 33 Hz,  $SiMe_3$ ).  $\mu_{\text{eff}}$ : calculated: 3.62 BM, experiment: 3.8 BM.

### 2.3. Single-crystal X-ray diffraction studies

Single-crystal X-ray diffraction experiments were performed on a Bruker P4/CCD/PC diffractometer with graphite-monochromated  $Mo-K_{\alpha}$  radiation ( $\lambda = 0.71073$  Å). Diffraction data were refined using SHELXTL PC [28]. Single crystals of **1**, **2**, **3** and **4** were grown from concentrated hexanes solutions at −35 °C inside the glovebox freezer. Crystals were coated in mineral oil and mounted on a glass fiber at −70 °C.

A hemisphere of data was collected using a combination of  $\phi$  and  $\omega$  scans, with 30-s frame exposures and 0.3° frame widths. Data collection and initial indexing and cell refinement was performed using SMART [29] software. Frame integration and final cell parameter calculation were carried out using SAINT [30] software. The data were corrected for absorption using the SADABS [31] program. Decay of reflection intensity was not observed. The crystal and refinement para-

Table 1  
Crystal data and data collection and refinement parameters for Ln(C<sub>3</sub>H<sub>3</sub>(SiMe<sub>3</sub>)<sub>2</sub>) complexes

	1	2	3	4
Empirical formula	C <sub>43</sub> H <sub>95</sub> O <sub>4</sub> Si <sub>6</sub> CeIK	C <sub>43</sub> H <sub>95</sub> O <sub>4</sub> Si <sub>6</sub> TbIK	C <sub>43</sub> H <sub>95</sub> O <sub>4</sub> Si <sub>6</sub> ErIK	C <sub>31</sub> H <sub>71</sub> OSi <sub>6</sub> Nd
Formula weight	1150.8	1169.6	1178.0	772.6
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>Pca</i> 2 <sub>1</sub>
<i>a</i> (Å)	17.570(4)	17.420(9)	17.14(6)	20.859(6)
<i>b</i> (Å)	19.348(5)	19.37(1)	19.30(6)	10.551(3)
<i>c</i> (Å)	18.747(4)	18.74(1)	18.60(7)	20.406(6)
$\alpha$ (°)	90	90	90	90
$\beta$ (°)	96.207(6)	96.06(1)	95.6(1)	90
$\gamma$ (°)	90	90	90	90
<i>V</i> (Å <sup>3</sup> )	6336(2)	6285(6)	6123(38)	4491(2)
$\rho_{\text{calc}}$ (g cm <sup>-3</sup> )	1.207	1.194	1.243	1.143
$\mu$ (mm <sup>-1</sup> )	1.416	1.761	2.024	1.335
$\lambda$ (Mo–K $\alpha$ ) (Å)	0.71073	0.71073	0.71073	0.71073
<i>T</i> (K)	203(2)	203(2)	203(2)	203(2)
Goof <sup>a</sup>	1.067	1.315	1.212	1.105
<i>R</i> <sub>1</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] (%) <sup>b</sup>	7.42	15.47	13.63	3.68
<i>wR</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] (%) <sup>c</sup>	16.25	26.35	23.96	8.09
<i>R</i> <sub>1</sub> (all data) (%) <sup>b</sup>	11.97	19.92	20.57	4.42
<i>wR</i> <sub>2</sub> (all data) (%) <sup>c</sup>	18.20	28.03	26.48	8.39
Largest diff. peak/hole (e Å <sup>-3</sup> )	1.276 and –0.450	1.757 and –1.284	2.173 and –0.893	0.559 and –0.367

<sup>a</sup> Goof =  $[\sum[w(F_o^2 - F_c^2)]^2 / (n - p)]^{1/2}$ ; *n*, number of reflections, *p*, total number of parameters refined.

<sup>b</sup> *R*<sub>1</sub> =  $\sum|F_o| - |F_c| / \sum|F_o|$ .

<sup>c</sup> *wR*<sub>2</sub> =  $[\sum[w(F_o^2 - F_c^2)]^2 / \sum[w(F_o^2)]^{1/2}]^{1/2}$ .

Parameters are listed in Table 1. Selected bond distances and angles are provided in Table 2. The structures were solved using difference Fourier techniques. The initial solutions revealed the metal center and the majority of other non-hydrogen positions. The remaining atomic positions were determined from subsequent Fourier syntheses. All hydrogen atoms were placed in ideal positions, with C–H distances held at 0.93 (aromatic), 0.96 (methine), 0.97 (methylene) and 0.98 Å (methyl). The hydrogen atoms were refined using a riding model, with their isotropic temperature factors set to 1.2 (aromatic, methine, methylene) or 1.5 (methyl) times the isotropic *U* of the attached carbon atom.

Table 2  
Average bond distances (Å) and angles (°) for Ln(C<sub>3</sub>H<sub>3</sub>(SiMe<sub>3</sub>)<sub>2</sub>) complexes

Nuclei	1	2	3	4
<i>Bond length</i>				
M–C <sub>methylene</sub>	2.749[9]	2.66[2]	2.61[2]	2.709[7]
M–C <sub>methine</sub>	2.810[9]	2.71[2]	2.64[2]	2.761[6]
M–X	3.146(1)	3.041(2)	2.979(8)	2.484(5)
<i>Bond angles</i>				
C–C–C	128[1]	128[2]	129[2]	128.2[8]
C–M–C <sup>a</sup>	171.8(3)	171.4(6)	171.7(6)	165.5(2)
C–C–C–Si	171.6	171.1	169.1	167.3

Esd's (standard deviations) are given in parentheses. Values in square brackets are arithmetic means of esd's.

<sup>a</sup> This value represents the angle for the methylene carbons trans to one another.

Crystals of **1** and **4** were refined in a straightforward manner. Crystals of **2** and **3** suffered from severe absorption issues (owing perhaps to poor crystal quality) that made refinement difficult. Crystals of **3** also displayed rotational disorder of the solvent molecules surrounding the potassium cation as evidenced by large thermal parameters. Attempts were made to model the rotational disorder, however, these led to unstable refinements.

### 3. Results and discussion

Treating a cold THF slurry of LnI<sub>3</sub> (Ln = Ce, Pr, Nd, Gd, Tb, Dy, Er) with three equivalents of K[C<sub>3</sub>H<sub>3</sub>(SiMe<sub>3</sub>)<sub>2</sub>] followed by warming to room temperature results in gradual transfer of three bulky allyl anions to the trivalent metal center with concomitant loss of two equivalents of potassium iodide. All reactions afforded highly colored anionic complexes of the general formula [K(thf)<sub>4</sub>][(C<sub>3</sub>H<sub>3</sub>(SiMe<sub>3</sub>)<sub>2</sub>)<sub>3</sub>LnI], the majority of which are a shade of orange, but also include green (Nd). Despite being salts, all [K(thf)<sub>4</sub>][(C<sub>3</sub>H<sub>3</sub>(SiMe<sub>3</sub>)<sub>2</sub>)<sub>3</sub>LnI] complexes are highly soluble in ethers and both aliphatic and aromatic hydrocarbons. They can be readily recrystallized from hexanes resulting in respectable purified yields. The complexes are air and water sensitive but are thermally stable crystalline materials under an inert atmosphere. We have attempted to obtain suitable elemental analyses of all complexes but have found that the experimental data indicate a

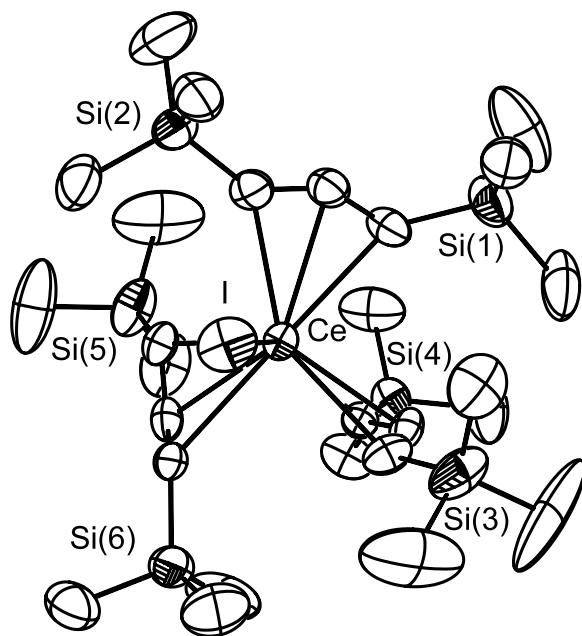


Fig. 1. Thermal ellipsoid representation of **1** shown at the 35% probability level. Hydrogen atoms and the  $\text{K}(\text{thf})_4$  cation have been omitted for clarity.

fractional occupation of thf suggesting, that the coordinated solvent is labile.

The solid-state structures for the Ce, Er, and Tb congeners were obtained by X-ray crystallography. The red–orange Ce complex crystallized as a monomer from a saturated hexanes solution at  $-35^\circ\text{C}$ . All three allyl ligands were found bonded to the Ce metal center in a *trihapto*, slightly asymmetric fashion, with Ce–C dis-

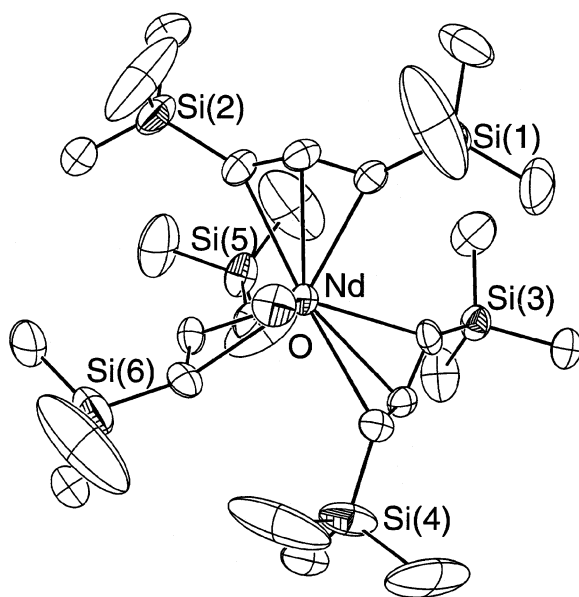


Fig. 2. Thermal ellipsoid representation of **4** shown at the 35% probability level. Hydrogen atoms have been omitted for clarity. Only the oxygen atom of the coordinated thf molecule is shown.

tances ranging from 2.67 to 2.86 Å (Fig. 1). The two longest Ce–C<sub>methylene</sub> bond distances (2.790(9) and 2.859(9) Å) are likely a result of their mutual trans influence [ $\text{C}–\text{Ce}–\text{C} = 171.8(3)^\circ$ ]. The average  $\angle \text{CCC}$  of  $128[1]^\circ$  is in close agreement with the value predicted for free  $[\text{C}_3\text{H}_3(\text{SiMe}_3)_2]^-$  [15]. The  $\text{SiMe}_3$  groups from all three allyl ligands are in a *syn, syn* configuration. The complex as a whole has no crystallographically imposed symmetry, but a pseudo-threefold rotation axis can be roughly identified to run through the Ce–I bond. The plane defined by the three allyl centroids is 0.56 Å below the Ce center. The Ce–I distance is 3.146(1) Å.

Yellow block-shaped crystals of both the Tb and Er complexes were obtained from a saturated hexanes solution left overnight in the freezer. The overall structures are isomorphous relative to the Ce analog, but with slight decreases in bond distances that follow the trend of decreasing ionic radii in moving across the lanthanide series from Ce(III) to Lu(III) (1.034–0.85 Å) [32]. The structural data are summarized in Table 2.

The anions are surprisingly halophilic and we have not succeeded in removing the iodide ligands using a variety of reagents or physical methods (e.g.  $\text{Ag}^+$ ,  $\text{BR}_3$ , excess  $[\text{C}_3\text{H}_3(\text{SiMe}_3)_2]^-$ , sublimation). We subsequently discovered that a neutral, halide-free neodymium complex,  $[\text{C}_3\text{H}_3(\text{SiMe}_3)_2]_3\text{Nd}(\text{thf})$ , can be prepared in moderate yield from rigorously anhydrous  $\text{Nd}(\text{O}_3\text{SCF}_3)_3$  and three equivalents of the 1,3-bis(trimethylsilyl)allyl anion in THF. The related  $\text{Nd}(\text{C}_3\text{H}_5)_3$  solvato complex has been prepared by Taube et al. either by allyllithium abstraction of  $\text{Li}[\text{Nd}(\text{C}_3\text{H}_5)_4] \cdot 1.5\text{dioxane}$  with  $\text{BEt}_3$  or by reacting  $\text{NdI}_3 \cdot 3.5\text{THF}$  with allyl magnesium iodide [4]. These two methods are not applicable in preparing homoleptic 1,3-bis(trimethylsilyl)allyl lanthanide complexes. The reaction of four equivalents of  $[\text{K}(\text{thf})_x][(\text{C}_3\text{H}_3(\text{SiMe}_3)_2)_4\text{Ln}]$  but only  $[\text{K}(\text{thf})_4][(\text{C}_3\text{H}_3(\text{SiMe}_3)_2)_3\text{LnI}]$  and excess  $[\text{C}_3\text{H}_3(\text{SiMe}_3)_2]^-$  are observed. Further, the preparation of the corresponding Grignard salt of  $[\text{C}_3\text{H}_3(\text{SiMe}_3)_2]^-$  has not been realized. Hence, utilizing the triflate salts of the lanthanides as starting materials should facilitate the synthesis of other homoleptic 1,3-bis(trimethylsilyl)allyl complexes.

The green Nd complex crystallizes as a monomer via slow evaporation of a saturated hexanes solution at room temperature. The complex has been structurally characterized and is illustrated in Fig. 2. Similar to the ‘ate’ complexes (vide supra), the allyl ligands were found bonded to the Nd metal center in a *trihapto*, slightly asymmetric fashion, with Nd–C distances ranging from 2.64 to 2.78 Å and an average  $\angle \text{CCC}$  of  $128.2[8]^\circ$ . The two longest Nd–C<sub>methylene</sub> bond distances (2.774(9) and 2.786(6) Å) are a result of nearly linear trans bonding ( $165.2(2)^\circ$ ) across the Nd center. The  $\text{SiMe}_3$  groups from all three allyl ligands are in a *syn, syn* configuration. The complex as a whole has no crystallographically

imposed symmetry, but a pseudo-threefold rotation axis can be roughly identified to run through the Nd–O bond. The plane defined by the three allyl centroids is 0.45 Å below the Nd center. The Nd–O distance is 2.484(5) Å. The ‘parent’ complex  $[\text{Nd}(\eta^3\text{-allyl})_3(\mu\text{-C}_4\text{H}_8\text{O}_2)]_n$  possess Nd–C distances ranging from 2.699 to 2.771 Å [4]. Therefore it would appear that the  $\text{SiMe}_3$  groups have little effect on the bonding of the  $\text{C}_3$  ‘core’. The Nd–O bond distance of 2.609[3] Å seen for the complex  $[\text{Nd}(\eta^3\text{-allyl})_3(\mu\text{-C}_4\text{H}_8\text{O}_2)]_n$  is significantly longer than that observed for **4** [2.484(5) Å], perhaps owing to the trans arrangement of the dioxane ligands.

#### 4. Conclusions

A new class of allyl-lanthanide salts of the type  $[\text{K}(\text{thf})_4][(\text{C}_3\text{H}_3(\text{SiMe}_3)_2)_3\text{LnI}]$  (Ln = Ce, Pr, Nd, Gd, Tb, Dy, Er) has been prepared by reaction of three equivalents of 1,3-bis(trimethylsilyl)allyl anion with  $\text{LnI}_3$ . The neutral complex  $[\text{C}_3\text{H}_3(\text{SiMe}_3)_2)_3\text{Nd}(\text{thf})$  has been isolated through reaction of  $\text{Nd}(\text{O}_3\text{SCF}_3)_3$  with three equivalents of the 1,3-bis(trimethylsilyl)allyl anion. These compounds were prepared with the aim of exploring their potential as catalysts or catalyst precursors with a variety of unsaturated substrates. We are currently assessing the catalytic activity of these complexes in addition to exploring the utility of added steric bulk to the allyl ligand as a means to tune base coordination.

#### 5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 205430-205433 for compounds **1–4**. Copies of this information may be obtained free of charge from The Director CCDC, 12 Union Road, Cambridge, CB2 1 EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or at <http://www.ccdc.cam.ac.uk/index.html>).

#### 6. Note added in proof

Prior to publication of this paper, the reactivity and structural details of the product of reacting  $\text{SmI}_2(\text{thf})_2$  with  $[1,3\text{-C}_3\text{H}_3(\text{SiMe}_3)_2]$  are reported. T.J. Woodman, M. Schormann, D.L. Hughes, M. Bochmann, *Organometallics*, in press.

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