

This is the author-created version of the following work:

**Salehisaki, Mehdi, Eslami Rad, Nazli E., Deacon, Glen B., Wang, Jun, Guo, Zhifang, and Junk, Peter C. (2022) *Synthesis and reactivity of rare-earth-N,N'-(diphenyl)formamidinate and rare-earth-N,N'-bis(2,4-dimethylphenyl)formamidinate complexes*. Inorganica Chimica Acta, 539 .**

Access to this file is available from:

<https://researchonline.jcu.edu.au/75370/>

Crown Copyright © 2022 Published by Elsevier B.V. All rights reserved. Accepted Version: © 2022. This manuscript version is made available under the CC-BY-NC-ND 4.0 license <http://creativecommons.org/licenses/by-nc-nd/4.0/>

Please refer to the original source for the final version of this work:

<https://doi.org/10.1016/j.ica.2022.120997>

# Synthesis and reactivity of rare-earth-*N,N'*-(diphenyl)formamidinate and rare-earth-*N,N'*-bis(2,4-dimethylphenyl)formamidinate complexes#

Mehdi Salehisaki,<sup>[a]</sup> Nazli E. Rad,<sup>[a]</sup> Glen B. Deacon,<sup>[b]</sup> Jun Wang,<sup>[a]</sup> Zhifang Guo,<sup>[a]</sup> and Peter C. Junk\*<sup>[a]</sup>

[a] College of Science & Engineering, James Cook University Townsville, QLD, 4811, Australia

[b] School of Chemistry, Monash University, Clayton, Victoria, 3800, Australia.

\* Corresponding author

Email: peter.junk@jcu.edu.au

# We dedicate this paper to Professor R. Bruce King a long time colleague and friend for his lifelong contributions to chemistry.

## Abstract

Redox transmetallation/protolysis reactions of rare earth metals,  $\text{Hg}(\text{C}_6\text{F}_5)_2$  and a formamidine ( $\text{PhFormH} = \text{N,N}'\text{-(diphenyl)formamidine}$  or  $\text{DMFormH} = \text{N,N}'\text{-bis(2,4-dimethylphenyl)formamidine}$ ) in tetrahydrofuran (thf) or 1,2-dimethoxyethane (dme) were employed to synthesize a series of the rare earth *N,N'*-bis(aryl)formamidinate complexes. Accordingly, trivalent complexes with the composition  $[\text{Ln}(\text{PhForm})_3(\text{thf})_n] \cdot (\text{solv.})_m$  [ $n = 2, m = 0$ , Ln = La (**1**), Pr (**2**);  $n = 2, m = 0.5$ , solv = thf, Sm (**3**);  $n = 2, m = 1.5$ , solv. = PhMe, Ln = Nd (**4**);  $n = 2, m = 1.5$ , solv. = thf, Ln = Gd (**5**);  $n=2, m = 3$ , solv. = thf, Ln = Tb (**6**), Dy (**7**), and Y (**8**);  $n = 1; m = 0$ , Ln = Ho (**9**), Er (**10**) and Lu (**11**)] or  $[\text{Ln}(\text{DMForm})_3(\text{solv.})]$  [Ln = Sm (**12**), Gd (**13**), solv. = dme; Ln = Pr (**14**), Ho (**15**), solv. = DMFormH; Ln = Y (**16**), Lu (**17**), solv. = thf; Ln = Er (**18**), solv. = dmf; dmf = *N,N*-dimethylformamide] were synthesized and characterized by X-ray crystallography. Complexes **1-8** have eight coordinate Ln metals with three chelating PhForm and two *transoid* thf ligands, whilst **9-11** are seven coordinate with a single thf ligand. Thus, there are **three** structural discontinuities, namely at Ho, Y, Er, the second of which occurs in defiance of a decrease in ion size. An investigation of catalytic reactivity of representative Ln complexes in the

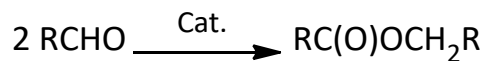
conversion of aldehydes into esters (Tishchenko reaction) revealed most have modest catalytic properties.  $[\text{Y}(\text{PhForm})_3(\text{thf})_2]\cdot 3\text{thf}$  **7** and  $[\text{Y}(\text{DMForm})_3(\text{thf})]$  **16** had the highest reactivity for their respective ligands, with **16** by far the most effective catalyst.

## Introduction

Amongst amidinate ligands [1], *N,N'*-diarylformamidinates have a special place [2]. The precursor formamidines (HForm) are readily prepared from anilines and trimethyl or triethyl orthoformate, [3] and considerable steric and electronic variation can be introduced from substituents in the anilines. They have contributed notably in rare earth chemistry [4], for example enabling steric engineering of C-F activation [5], and providing complexes of varying coordination number in both  $\text{Ln}^{\text{III}}$  [5] and  $\text{Ln}^{\text{II}}$  [6] oxidation states. In the present study we have examined the coordination chemistry of the *N,N'*-(diphenyl)formamidinate and *N,N'*-bis(2,4-dimethylphenyl)formamidinate ligands, neither of which appears to have been used previously in rare earth chemistry, where emphasis has been on bulky ligands [4]. The former is the least crowded of *N,N*-diarylformamidines, being somewhat less bulky than the previously utilised *N,N'*-di(*p*-tolyl)formamidinate (*p*-TolForm) [7-8]. The latter is a slightly bulkier proxy for *N,N'*-di(*o*-tolyl)formamidine, which is prepared from the carcinogenic *o*-toluidine.

We have also examined representative complexes as catalysts for the Tishchenko (or Claisen-Tishchenko) reaction, which is a coproportionation reaction that converts two aldehyde molecules into an ester in the presence of a metal catalyst (Scheme 1) [9]. Aluminium alkoxides are traditional catalysts for this reaction [10-11], and transition metal complexes [12], boric acid [13] and some Mg compounds [14] have been used. Rare earth complexes have also been particularly effective. Thus, a La organometallic [15], lanthanoid bistrimethylsilamides [16] and lanthanum tris(3,5-di-*t*butylpyrazolate) [17] all show excellent activity with La the preferred metal [16]. Examination of a series of lanthanum formamidinates showed that the tris(*N,N'*-di(*o*-tolyl)formamidinate) (*o*-TolForm) was the *most active* known catalyst, and was the least bulky of the compounds examined [18]. However the carcinogenic precursor encourages a search for alternatives. Thus derivatives of PhForm which is less bulky than *o*-TolForm and DMForm, slightly

more bulky than *o*-TolForm, but with a less toxic aniline precursor, are attractive candidates and have been examined.



**Scheme 1.** The Tishchenko reaction

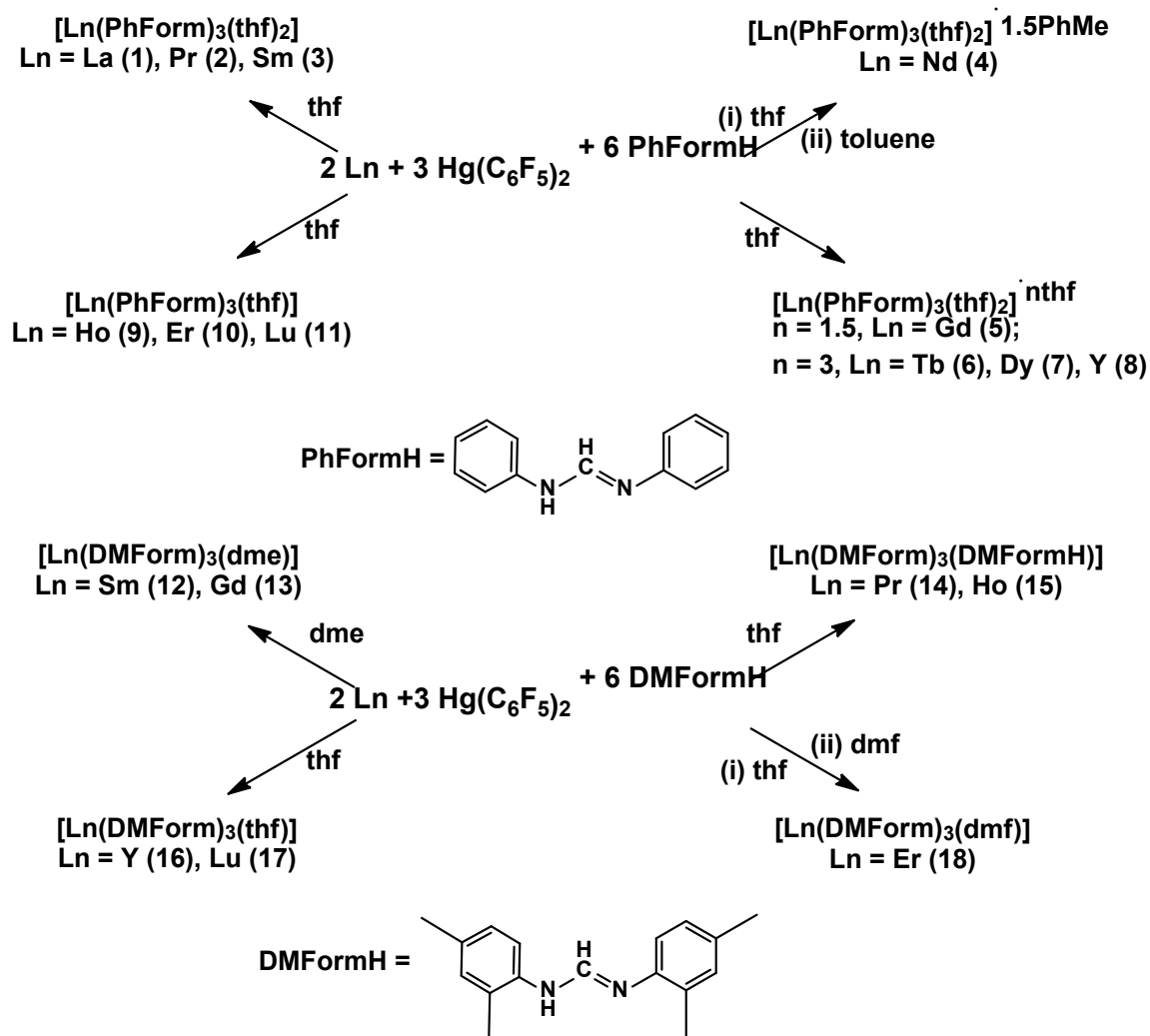
## Results and Discussion

### *Syntheses and characterization*

Redox transmetallation protolysis (RTP) reactions between free rare earth metals, bis(pentafluorophenyl)mercury and two different formamidines, PhFormH and DMFormH, in tetrahydrofuran (thf) or 1,2-dimethoxyethane (dme) were performed to synthesize rare earth formamidinate complexes. The metal surface was activated by one drop of mercury. The reactions and their outcomes are summarized in Scheme 2. From these reactions, the complexes  $[\text{Ln}(\text{PhForm})_3(\text{thf})_2] \cdot (\text{solv.})_m$  [  $m = 0$ , Ln = La (**1**), Pr (**2**);  $m = 0.5$ , solv. = thf, Ln = Sm (**3**);  $m = 1.5$ , solv. = PhMe, Ln = Nd (**4**);  $m = 1.5$ , solv. = thf, Ln = Gd (**5**);  $m = 3$ , solv. = thf, Ln = Tb (**6**), Dy (**7**), and Y (**8**);  $[\text{Ln}(\text{PhForm})_3(\text{thf})]$  Ln = Ho (**9**), Er (**10**) and Lu (**11**); and  $[\text{Ln}(\text{DMForm})_3(\text{solv.})]$  [Ln = Sm (**12**), Gd (**13**), solv. = dme; Ln = Pr (**14**), Ho (**15**), solv. = DMFormH; Ln = Y (**16**), Lu (**17**), solv. = thf; Ln = Er (**18**), solv. = dmf; dmf = *N,N*-dimethylformamide] were isolated. Single crystals of PhForm complexes were readily obtained by cooling the thf solutions from the filtered reaction mixtures, except for **4** where crystallization was effected from toluene. Reactions with DMFormH presented more problems with dme used as the reaction solvent for **12** and **13** and thf for **14-18**. Crystallization issues were also experienced with difficulty in removing unreacted starting materials. For **14** and **15**, the formamidine was the co-ligand, for **16** and **17** the co-ligand was thf, whilst **18** was crystallized from dmf.

Infrared spectra of bulk crystals showed no N-H stretching absorption, consistent with deprotonation of the formamidine, except in the case of **15** which has a DMFormH co-ligand. Difficulties were experienced in obtaining satisfactory microanalyses for the highly air and moisture sensitive bulk crystalline products, especially for DMForm complexes. Five PhForm complexes (**3**, **4**, **8**, **9**, **10**) gave expected values, though often for loss of lattice solvent (**3**, **4**, **8**),

as the samples were dried under vacuum before being sealed under nitrogen for dispatch. Of the DMForm complexes, **12** and **18** gave values consistent with the X-ray crystal composition. On the other hand, expected % metal values on freshly prepared samples were obtained for nearly all complexes with unsatisfactory microanalyses, and on representative examples with expected microanalysis values. Low %C analyses and inconsistent data for a series of compounds, are an endemic problem for lanthanoid and alkaline earth complexes [19], an issue that has been attributed to carbide formation on pyrolysis [20]. Potential issues of incomplete combustion of organometallics are outlined in an analysis manufacturer's instructions [21]. For **2**, **6**, **7** and **11**, satisfactory H,N values accompanied low %C values. Three complexes of diamagnetic metal ions (**8**, **16**, **17**) gave  $^1\text{H}$  NMR spectra as expected for the single crystal composition. Derivatives of paramagnetic ions mainly gave broad uninterpretable spectra, but the samarium complex **3** gave an explicable spectrum and some resonances of the erbium complex **10** could be assigned though not integrated.

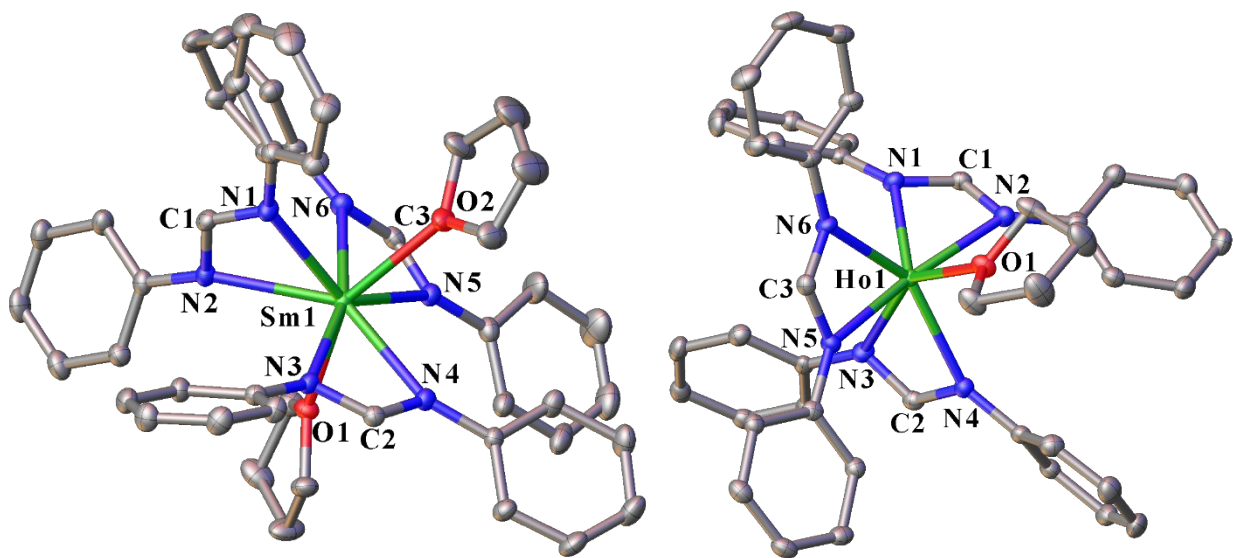


**Scheme 2.** Synthesis of rare earth PhForm (top) and DMForm (bottom) compounds (in all reactions  $\text{Hg}^0$  and  $\text{C}_6\text{F}_5\text{H}$  are produced)

#### Structures of $[\text{Ln}(\text{PhForm})_3(\text{thf})_n]$ ( $n = 1$ or $2$ ) complexes

For the series  $[\text{Ln}(\text{PhForm})_3(\text{thf})_2] \cdot m(\text{solvent})$  **1-3, 5-8**, the number of thf molecules of crystallization increases from 0 (**1, 2**) to 3 (**6-8**) as the ionic radius of the metal decreases. Complexes **3, 5-8** are isomorphous despite differing amounts of lattice thf, and **4** has a very similar unit cell despite having toluene of crystallization. In addition, **1** and **2** are isomorphous. For all of **1-8**, the metal atoms are eight coordinate with two *transoid* thf molecules (Fig. 1 and Table 1) in a distorted dodecahedral array. As judged by C-Ln-C angles subtended by the backbone carbon atoms at Ln (Table S1), the arrangement of PhForm ligands around Ln is quite irregular with values ranging

from *cis* though near tetrahedral to *transoid* (145.76(8)). By contrast **9-11** have seven coordinate metal atoms with only one thf coordinated and distorted pentagonal bipyramidal stereochemistry. The array of PhForm ligands is again quite irregular (Table S1). An interesting feature of the structures is **three** structural discontinuities, at Ho, Y, and Er, with the change from Ho (coordination number 7) to Y (eight coordinate) contrary to the effect of the lanthanoid contraction, which normally either leads to a decrease in coordination number or no change (see e.g. the contrasting behaviour in the structures of [LnCp<sub>3</sub>] and [LnCp<sub>3</sub>(thf)] compounds [22]). Thus, **1-7** (La-Dy) are eight coordinate and **9-11** (Ho, Er, Lu) are seven coordinate with the Y complex (Y<sup>3+</sup> between Ho<sup>3+</sup> and Er<sup>3+</sup> in size) [23] eight coordinate. We have recently shown that between the structures of [Dy(Ph<sub>2</sub>pz)<sub>2</sub>(μ-Ph<sub>2</sub>pz)]<sub>2</sub> and [Ho(Ph<sub>2</sub>pz)<sub>2</sub>(μ-Ph<sub>2</sub>pz)]<sub>2</sub> (Ph<sub>2</sub>pz = 3,5-diphenylpyrazolate), the coordination number increases from seven to eight [24] in contravention of ionic radius expectations, and the present structures provide another unexpected example.



**Figure 1.** Molecular structures of (left) [Sm(PhForm)<sub>3</sub>(thf)<sub>2</sub>] (**3**), as representative of **1-8**, and (right) [Ho(PhForm)<sub>3</sub>(thf)] (**9**), as representative of **9-11**. Hydrogen atoms removed for clarity.

**Table 1** Selected bond lengths (Å) and angles (°) of complexes **1-11**

Complex	Ln-N	Ln-N <sub>avg</sub>	Ln-O	Ln-O <sub>avg</sub>	O1-Ln-O2
---------	------	---------------------	------	---------------------	----------

[La(PhForm) <sub>3</sub> (thf) <sub>2</sub> ] <b>1</b>	2.512(15)-2.552(7)	2.541	2.527(6)/2.541(5)	2.534	153.16(17)
[Pr(PhForm) <sub>3</sub> (thf) <sub>2</sub> ] <b>2</b>	2.514(14)-2.580(18)	2.560	2.541(8)/2.550(8)	2.546	153.2(2)
[Sm(PhForm) <sub>3</sub> (thf) <sub>2</sub> ].0.5thf <b>3</b>	2.485(6)-2.543(6)	2.510	2.464(5)/2.501(5)	2.483	149.91(19)
[Nd(PhForm) <sub>3</sub> (thf) <sub>2</sub> ].1.5PhMe <b>4</b>	2.523(3)-2.572(2)	2.540	2.487(2)/2.504(2)	2.496	149.44(7)
[Gd(PhForm) <sub>3</sub> (thf) <sub>2</sub> ].1.5thf <b>5</b>	2.466(5)-2.531(5)	2.495	2.437(4)/2.476(4)	2.457	149.30(15)
[Tb(PhForm) <sub>3</sub> (thf) <sub>2</sub> ].3thf <b>6</b>	2.449(5)-2.487(5)	2.471	2.422(4)/2.476(5)	2.449	148.64(16)
[Dy(PhForm) <sub>3</sub> (thf) <sub>2</sub> ].3thf <b>7</b>	2.425(7)-2.478(7)	2.459	2.408(6)/2.469(6)	2.439	148.9(2)
[Y(PhForm) <sub>3</sub> (thf) <sub>2</sub> ].3thf <b>8</b>	2.420(2)-2.478(2)	2.452	2.3909(18)/2.4542(19)	2.423	148.96(6)
[Ho(PhForm) <sub>3</sub> (thf)] <b>9</b>	2.375(2)-2.445(2)	2.400	2.3748(18)		
[Er(PhForm) <sub>3</sub> (thf)] <b>10</b>	2.359(3)-2.439(3)	2.390	2.357(2)		
[Lu(PhForm) <sub>3</sub> (thf)] <b>11</b>	2.330(2)-2.409(2)	2.361	2.331(2)		

The bond lengths within each structural series generally show the expected decline with the lanthanoid contraction. The slight increase from **1** to **2** is not significant when 3 esds are considered.

Complexes of *p*-TolForm, the previous least bulky Form ligand used, are eight coordinate with two thf co-ligands for La-Sm, whilst the Lu complex is seven coordinate with one thf ligated [7], similar to the corresponding PhForm complexes, but the point of change was not established as less structures were obtained. However [Ln(*p*-TolForm)<sub>3</sub>(thf)<sub>2</sub>] species are less stable than the PhForm analogues and decompose into unsolvated dimers with loss of thf on addition of non polar solvents like toluene, whereas the present complex **4** was successfully crystallized from toluene. Thus the slight reduction in bulk by removal of the *p*-Me substituent contributes to stabilise the bis(thf) derivatives.

#### *Structures of [Ln(DMForm)<sub>3</sub>(solv)] (solv = dme, DMFormH, thf or dmf) complexes*

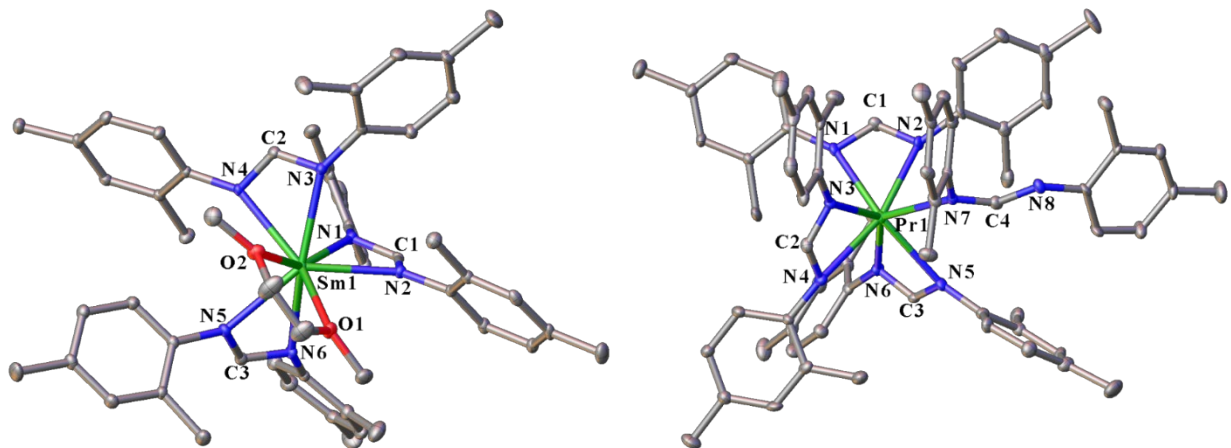
Whereas all PhForm complexes crystallized with thf co-ligands and generally with lattice solvent, compounds [Sm(DMForm)<sub>3</sub>(dme)] (**12**), [Gd(DMForm)<sub>3</sub>(dme)] (**13**), [Pr(DMForm)<sub>3</sub>(DMFormH)] (**14**), [Ho(DMForm)<sub>3</sub>(DMFormH)] (**15**), [Y(DMForm)<sub>3</sub>(thf)] (**16**), [Lu(DMForm)<sub>3</sub>(thf)] (**17**) and



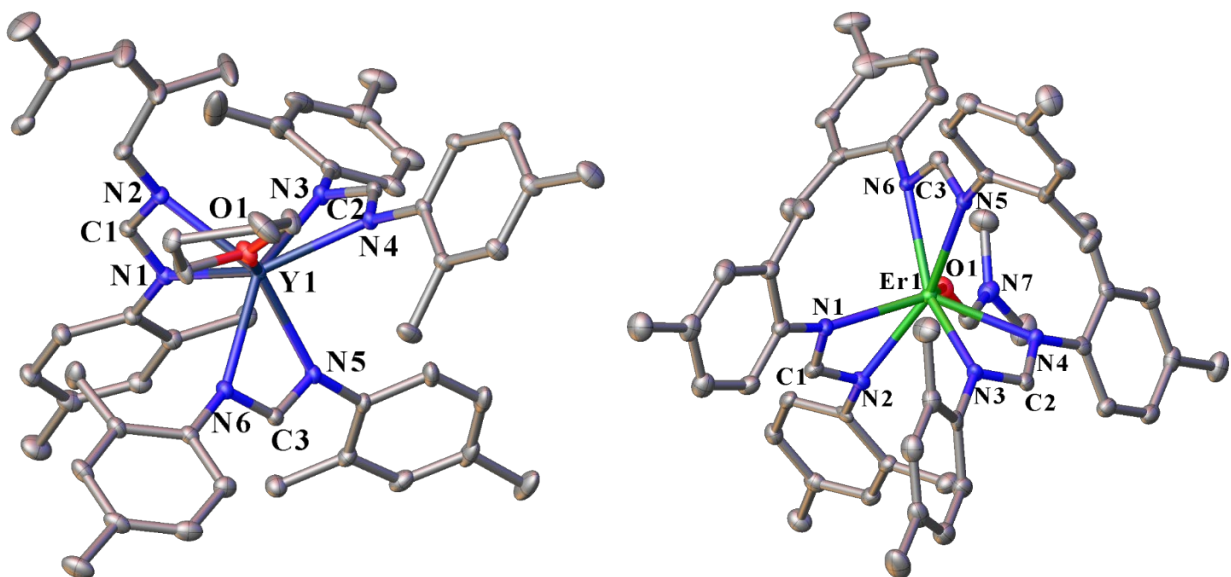
[Er(DMForm)<sub>3</sub>(dmf)] (**18**) have a variety of co-ligands owing to issues in obtaining single crystals, and none have lattice solvent. All of the compounds except [Er(DMForm)<sub>3</sub>(dmf)] (**18**) crystallized in the monoclinic space group  $P2_1/c$ , with the whole molecule occupying the asymmetric unit, but only **12** and **13** and **16** and **17** are isomorphous. Complexes **12** and **13** with chelating dme have eight coordinate Ln atoms whilst **14-18** have seven coordination. Representative structures are shown in **Figure 2** and **3**.

In the eight coordinate complexes **12** and **13**, the three DMForm ligands have an approximately *mer* arrangement as gauged from the backbone CLnC angles (Table S1) though the largest diverges considerably from *trans*. In the seven coordinate complexes **14-18**, these angles are nearer triangular with a more ordered array. Although there is a decrease in Ln-N(O) bond lengths from **12** to **13** corresponding to the decrease in ionic radii from Sm to Gd [23], several of the difference are within 3 esds (Table 2). The dme chelation is notably unsymmetrical (0.10-0.13 Å) (Table 2). Within the series **14-18**, there is a decrease in bond lengths with ionic radius decrease, but there is an unsurprising discontinuity from Ln-N (DMFormH) to Ln-O(thf) bond lengths of the coligands, and between Ln-O(thf) and Ln-O(dmf).

Only a limited comparison can be made with the structures of lanthanoid *o*-TolForm complexes, as only the structures of eight coordinate [La(*o*-TolForm)<sub>3</sub>(thf)<sub>2</sub>] and seven coordinate [Yb(*o*-TolForm)<sub>3</sub>(thf)] are known with [Er(*o*-TolForm)<sub>3</sub>·thf] unable to be suitably crystalized [5]. Moreover, the DMform complexes had to be crystallized with a range of coligands to obtain satisfactory single crystals. However based on this limited data, it appears DMForm complexes may be a reasonable structural proxy for *o*-TolForm complexes with a Ln size driven change of coordination number.



**Figure 2.** Molecular structures of (left) [Sm(DMForm)<sub>3</sub>(dme)] (**12**), as representative of **12** and **13**, and (right) [Pr(DMForm)<sub>3</sub>(DMFormH)] (**14**), as representative of **14** and **15**. Hydrogen atoms removed for clarity.



**Figure 3.** Molecular structures of (left) [Y(DMForm)<sub>3</sub>(thf)] (**16**), as representative of **16** and **17**, and (right) [Er(DMForm)<sub>3</sub>(dmf)] (**18**). Hydrogen atoms removed for clarity.

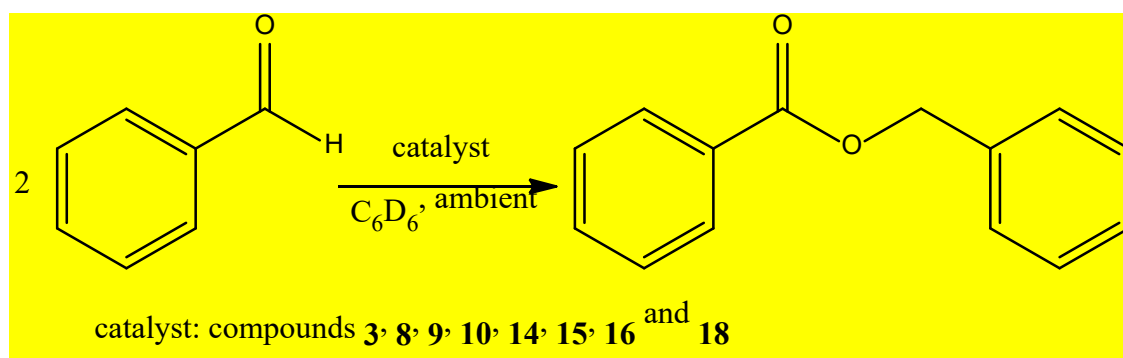
**Table 2 Selected bond lengths (Å) of complexes 12-18**

Complex	Ln-N	Ln-N <sub>avg</sub>	Ln-O or Ln-N7(DMFormH)
[Sm(DMForm) <sub>3</sub> (dme)] <b>12</b>	2.447(5)-2.559(5)	2.498	2.562(4)/2.661(4)

[Gd(DMForm) <sub>3</sub> (dme)] <b>13</b>	2.4341(19)-2.5423(19)	2.481	2.5119(17)/2.6418(17)
[Pr(DMForm) <sub>3</sub> (DMFormH)] <b>14</b>	2.515(8)-2.561(8)	2.530	2.599(6)
[Ho(DMForm) <sub>3</sub> (DMFormH)] <b>15</b>	2.397(6)-2.425(5)	2.410	2.527(6)
[Y(DMForm) <sub>3</sub> (thf)] <b>16</b>	2.357(2)-2.439(2)	2.401	2.409(2)
[Lu(DMForm) <sub>3</sub> (thf)] <b>17</b>	2.320(3)-2.415(3)	2.371	2.383(2)
[Er(DMForm) <sub>3</sub> (dmf)] <b>18</b>	2.360(4)-2.496(4)	2.411	2.298(3)

*Catalytic reactivity of the formamidinate complexes in the Tishchenko reaction*

The standard reaction of benzaldehyde to form benzyl benzoate was chosen to compare the activities of the compounds in this paper as catalysts in the Tishchenko reaction (Scheme 3).



**Scheme 3.** Tishchenko reaction of benzaldehyde giving benzyl benzoate.

Table 3 shows that the catalytic reactivity of the PhForm compounds examined is **8** (Y) > **9** (Ho) > **10** (Er) > **3** (Sm). This order is different from that observed previously where a La complex was found to be the most reactive [16]. The very low yield of the La complex **1** prevented its use. The lower yield for the largest Ln examined (Sm in complex **3**) may be attributable to the higher coordination number (8) and reduced accessibility to the metal in this complex compared with seven in complexes **8-10**, resulting in lower Lewis acidity. A better performance for the Y complex over its Ho and Er neighbours with similar ionic radii may relate to the Y<sup>3+</sup> electronic configuration, which is closed shell similar to La<sup>3+</sup>, whereas Ho<sup>3+</sup> and Er<sup>3+</sup> have 4f<sup>n</sup> configurations.

**Table 3 Reactivities towards Tishchenko Reaction of compounds 3, 8, 9, 10 and 14, 15, 16, 18**

Complex	Time (h)	Yield (%)	Time (h)	Yield (%)	Time (h)	Yield (%)	Time (h)	Yield (%)
[Sm(PhForm) <sub>3</sub> (thf) <sub>2</sub> ·0.5thf] <b>3</b>	24	48	96	85	120	88	172	90
[Y(PhForm) <sub>3</sub> (thf) <sub>2</sub> ·3thf] <b>8</b>	24	90	48	95	72	96	96	97
[Ho(PhForm) <sub>3</sub> (thf)] <b>9</b>	24	72	48	85	72	91	120	100
[Er(PhForm) <sub>3</sub> (thf)] <b>10</b>	24	67	48	77	72	83	96	87
[Pr(DMForm) <sub>3</sub> (DMFormH)] <b>14</b>	24	21	51	33	120	53	-	-
[Ho(DMForm) <sub>3</sub> (DMFormH)] <b>15</b>	24	70	51	78	120	87	-	-
[Y(DMForm) <sub>3</sub> (thf)] <b>16</b>	24	98*	-	-	-	-	-	-
[Er(DMForm) <sub>3</sub> (dmf)] <b>18</b>	24	18	96	30	144	37	-	-

\*Yields at 0.08, 1 and 2 h, 58, 79, and 86% respectively

The results of reactivity experiments suggest that [La(*o*-TolForm)<sub>3</sub>(thf)<sub>2</sub>] [18] is a far better catalyst in the Tishchenko reaction than the PhForm complexes examined despite the reduction in bulkiness of the Form ligand. Even the bulkier [La(XylForm)<sub>3</sub>(thf)] (XylForm = *N,N'*-bis(2,6-dimethylphenyl)formamidinate) or [La(EtForm)<sub>3</sub>] (EtForm = *N,N'*-(diethylphenyl)formamidinate) outperforms the PhForm complexes. Moreover in the present series, factors other than steric appear to play a part.

In the DMForm series, the reactivity of [Pr(DMForm)<sub>3</sub>(DMFormH)] (14), [Ho(DMForm)<sub>3</sub>(DMFormH)] (15), [Y(DMForm)<sub>3</sub>(thf)] (16) and [Er(DMForm)<sub>3</sub>(dmf)] (18) was studied (Table 3). Compounds 14, 15, 18 showed even lower reactivity than the PhForm complexes with the Ho and Er complexes providing a direct comparison though the co-ligands differ. However the surprise was that not only was the Y complex the best performer as in the PhForm case, but it was a much better catalyst than all others examined including the Y PhForm complex 8. This result suggests that the DMForm complex, [Y(DMForm)<sub>3</sub>(thf)], with an *o*-methyl group as in {La(*o*-TolForm)<sub>3</sub>(thf)<sub>2</sub>}<sup>3+</sup> and a closed shell configuration like La<sup>3+</sup>, may be a suitable proxy for the *o*-TolForm complex, and avoid the need for a carcinogenic ligand precursor.

## Conclusions

The formamidines PhFormH and DMFormH with a range of lanthanoid metals in RTP reactions yield an extensive series of lanthanoid formamidinate complexes. The least hindered *N,N'*-diarylformamidinate ligand, PhForm, gives eight coordinate  $[\text{Ln}(\text{PhForm})_3(\text{thf})_2]$  for La-Dy and Y, and seven coordinate  $[\text{Ln}(\text{PhForm})_2(\text{thf})]$  for Ho-Lu with structural discontinuities at Ho, Y, and Er, the second of which defies the lanthanoid contraction. Whilst the coordination number variation roughly parallels that of the less structurally defined *p*-TolForm analogues [7], the slight reduction in steric bulk is sufficient to enhance the stability of the eight coordinate complexes to loss of thf. The DMform complexes appear to have value as a structural proxy for the problematic *o*-TolForm with a Ln size driven reduction in coordination number from eight to seven.

As catalysts for the Tishchenko reaction, the PhForm complexes examined were much less effective than the benchmark  $[\text{La}(\textit{o}\text{-TolForm})_3(\text{thf})_2]$  [18], with the yttrium complex the most capable, contrary to previous results on rare earth size variation [16]. The DMForm complexes were less effective again, except for  $[\text{Y}(\text{DMForm})_3(\text{thf})]$ , which markedly outperformed all other complexes examined suggesting it has some promise as a replacement for the benchmark *o*-TolForm complex if the carcinogenic *o*-toluidine precursor is to be avoided.

## Experimental Section

### General considerations

All the samples were prepared using a glove box, Schlenk flask and vacuum line techniques in an inert atmosphere since lanthanoid metals and their products are air-sensitive and moisture-sensitive. Sodium or sodium/benzophenone were used for refluxing and distillation of solvents to dry and deoxygenate them prior to use in reactions. The lanthanoid metal reagents were purchased either in form of fine powders or metal ingots from Rhone Poulenc or Santoku. In the case of metal ingots, they were freshly filed under an inert atmosphere into metal filings. The PhFormH and DMFormH ligands were prepared by the literature method [3]. IR data were obtained from Nujol mulls for the region 4000-400  $\text{cm}^{-1}$  with a Nicolet-Nexus FT-IR spectrometer.  $^1\text{H}$  NMR spectra were recorded with a Bruker Avance 300 MHz spectrometer using dry degassed *deutero*-benzene ( $\text{C}_6\text{D}_6$ ) as solvent, and resonances were referenced to the residual  $^1\text{H}$  resonances of the deuterated solvent. Elemental analyses (C, H, N) were performed by the Micro analytical Laboratory, Science Centre, London Metropolitan University, England. Samples were sealed under  $\text{N}_2$  after drying under vacuum. Ln analyses were effected after decomposition of the complexes with dilute HCl and buffering with hexamine, by complexometric titration with  $\text{Na}_2\text{H}_2\text{edta}$  with Xylenol Orange indicator. CCDC **2151404-2151408** for compound **1-5**, **2151412** for compound **6**, **2151409-2151410** for compound **7-8**, **2151413-2151414** for compound **9** and **10**, **2151411** for compound **11**, **2151415-2151421** for compound **12-18**, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

### *PhForm Complexes*

#### $[\text{La}(\text{PhForm})_3(\text{thf})_2]$ (**1**)

Lanthanum filings (0.30 g, 2.15 mmol),  $\text{Hg}(\text{C}_6\text{F}_5)_2$  (0.62 g, 1.50 mmol), PhFormH (0.60 g, 3.00 mmol) and a drop of Hg metal were added to a Schlenk flask in thf (20 mL) and stirred at room temperature for one week. The resulting yellow solution was filtered through a filter cannula

from the metal residue and evaporated under vacuum to 5 mL and cooled to -5 °C for several days. A few small yellow crystals of **1** were produced. Yield  $\approx$  0.01 g;

#### [Pr(PhForm)<sub>3</sub>(thf)<sub>2</sub>] (**2**)

Praseodymium filings (0.30 g, 2.12 mmol), Hg(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> (0.62 g, 1.50 mmol), PhFormH (0.60 g, 3.00 mmol) and a drop of Hg metal were added to a Schlenk flask in thf (20 mL). The reaction mixture was stirred at room temperature for one week. The resulting yellow solution was filtered through a filter cannula from the metal residue and evaporated under vacuum to 5 mL and cooled to -5 °C for several days. Small yellowish green crystals of **2** were produced. Yield = 0.36 g (43%); M.P. 152-155 °C; IR (Nujol, cm<sup>-1</sup>):  $\nu$  = 1929 (w), 1864 (vw), 1756 (vw), 1719 (vw), 1673 (w), 1297 (s), 1170 (s), 1074 (s), 1022 (s), 986 (s), 934 (m), 889 (m), 806 (m), 755 (s), 693 (s), 619 (m), 597(m) cm<sup>-1</sup> (wv); <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 303.2 K): Broad uninterpretable resonances due to the paramagnetic nature of the compound. Elemental analysis calc. (%) for C<sub>47</sub>H<sub>49</sub>PrN<sub>6</sub>O<sub>2</sub> (M = 870.86 g.mol<sup>-1</sup>): C 64.82, H 5.67, N 9.65, Pr 16.18; Found: C 60.36, H 5.73, N 9.20, Pr 16.14.

#### [Sm(PhForm)<sub>3</sub>(thf)<sub>2</sub>].0.5thf (**3**)

Similarly, samarium filings (0.30 g, 2.00 mmol), Hg(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> (0.62 g, 1.50 mmol), PhFormH (0.60 g, 3.00 mmol) and a drop of Hg in thf (20 mL) at room temperature for one week gave small yellow crystals of **3**. Yield = 0.65 g (76%); M.P. 160-162 °C; IR (Nujol, cm<sup>-1</sup>):  $\nu$  = 1660 (w), 1327 (s), 1286 (vs), 1216 (vs), 1171 (s), 1151 (s), 1075 (s), 1025 (m), 987 (s), 942 (m), 895 (m), 869 (m), 808 (w), 757 (vs), 692 (s), 621 (vw), 602 (m), 518 (s) cm<sup>-1</sup> (wv); <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 303.2 K): Loss of 2 thf from crystal composition,  $\delta$  = 1.19(m, 2H,  $\beta$ -H(thf)), 3.42(m, 2H,  $\alpha$ -H(thf)), 6.89 – 7.42 (m, 30H, Ph-H), 7.81 (s, 3H, NC(H)N). Elemental analysis calc. (%) for C<sub>47</sub>H<sub>49</sub>SmN<sub>6</sub>O<sub>2</sub> (loss of 0.5 lattice thf, M = 880.31 g.mol<sup>-1</sup>): C 64.13, H 5.61, N 9.55, Sm 17.09; Found: C 63.66, H 5.90, N 9.42, Sm 16.99.

#### [Nd(PhForm)<sub>3</sub>(thf)<sub>2</sub>].1.5PhMe (**4**)

Neodymium filings (0.30 g, 2.08 mmol), Hg(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> (0.62 g, 1.50 mmol), PhFormH (0.60 g, 3.00 mmol) and a drop of Hg in thf (20 mL) were stirred at room temperature for one week. The resulting filtered yellow solution was dried under vacuum and small amount of toluene ( $\approx$  5 ml) was added. The solution was cooled to -5 °C for several day giving small white crystals of **4**. Yield

= 0.38 g (45%); M.P. 158-162 °C; IR (Nujol,  $\text{cm}^{-1}$ ):  $\nu$  = 1665 (vw), 1577 (m), 1535 (vs), 1508 (vs), 1326 (m), 1307 (vs), 1217 (s), 1176 (m), 1151 (m), 1075 (m), 1023 (w), 996 (w), 985 (m), 936 (m), 901 (w), 888 (w), 801 (vw), 757 (s), 722 (vw), 693 (s), 618 (vw), 593 (w)  $\text{cm}^{-1}$  (wv);  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 303.2 K): Uninterpretable broad resonances due to the paramagnetic nature of the compound. Elemental analysis calc. (%) for  $\text{C}_{47}\text{H}_{49}\text{NdN}_6\text{O}_2$  (loss of 1.5 lattice PhMe,  $M = 874.19 \text{ g}\cdot\text{mol}^{-1}$ ): C 64.58, H 5.65, N 9.61; Found: C 64.09, H 5.88, N 9.67.

#### [Gd(PhForm) $_3$ (thf) $_2$ ] $\cdot$ 1.5thf (**5**)

Similarly to **2**, gadolinium filings (0.30 g, 1.91 mmol),  $\text{Hg}(\text{C}_6\text{F}_5)_2$  (0.62 g, 1.50 mmol), PhFormH (0.60 g, 3.00 mmol) and a drop of Hg in thf (20 mL) stirred at room temperature for one week gave small yellow crystals of **5**. Yield = 0.62 g (72%); M.P. 161-163 °C; IR (Nujol,  $\text{cm}^{-1}$ ):  $\nu$  = 1651 (m), 1531 (vs), 1295 (vs), 1219 (s), 1170 (s), 1152 (m), 1074 (s), 1026 (s), 988 (m), 938 (m), 890 (m), 808 (m), 756 (s), 727 (vs), 694 (vs), 620 (m), 600 (m)  $\text{cm}^{-1}$  (wv);  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 303.2 K): Uninterpretable broad resonances due to the paramagnetic nature of the compound. Elemental analysis calc. (%) for  $\text{C}_{53}\text{H}_{61}\text{GdN}_6\text{O}_{3.5}$  ( $M = 995.32 \text{ g}\cdot\text{mol}^{-1}$ ): Gd 14.25. Found: Gd 14.28.

#### [Tb(PhForm) $_3$ (thf) $_2$ ] $\cdot$ 3thf (**6**)

As for **2**, terbium filings (0.30 g, 1.80 mmol),  $\text{Hg}(\text{C}_6\text{F}_5)_2$  (0.62 g, 1.50 mmol), PhFormH (0.60 g, 3.00 mmol) and Hg metal stirred in thf (20 mL) at room temperature for one week gave small yellow crystals of **6**. Yield = 0.51 g (46%); M.P. 160-163 °C; IR (Nujol,  $\text{cm}^{-1}$ ):  $\nu$  = 1657 (m), 1535 (s), 1291 (s), 1214 (s), 1169 (s), 1074 (m), 1023 (m), 985 (m), 938 (m), 893 (w), 807 (m), 756 (s), 723 (s), 693(s)  $\text{cm}^{-1}$  (wv);  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 303.2 K): Broad uninterpretable resonances owing to the paramagnetic nature of this compound. Elemental analysis calc. (%) for  $\text{C}_{43}\text{H}_{41}\text{N}_6\text{OTb}$  (lost 4 thf,  $M = 816.77 \text{ g}\cdot\text{mol}^{-1}$ ): Tb, 19.46. Found: Tb 19.41.

#### [Dy(PhForm) $_3$ (thf) $_2$ ] $\cdot$ 3thf (**7**)

Similarly, dysprosium filings (0.30 g, 1.85 mmol),  $\text{Hg}(\text{C}_6\text{F}_5)_2$  (0.62 g, 1.50 mmol), PhFormH (0.60 g, 3.00 mmol) and a drop of Hg in thf (20 mL) stirred at room temperature for one week gave small yellow crystals of **6**. Yield = 0.59 g (68%); M.P. 173-176 °C; IR (Nujol,  $\text{cm}^{-1}$ ):  $\nu$  = 1660 (w), 1327 (m), 1286 (vs), 1216 (s), 1171 (s), 1151 (m), 1075 (m), 1025 (m), 987 (m), 942 (m), 895 (m), 869 (m),



808 (w), 757 (s), 692 (s), 621 (vw), 602 (m), 518 (s)  $\text{cm}^{-1}$  (wv);  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 303.2 K): Uninterpretable broad resonances due to the paramagnetic nature of the compound. Elemental analysis calc. (%) for  $\text{C}_{43}\text{H}_{41}\text{DyN}_6\text{O}$  (loss of three lattice thf and one coordinated thf;  $M = 820.34 \text{ g.mol}^{-1}$ ): C 62.96, H 5.04, Dy 19.81, N 10.24; Found: C 57.00, H 5.29 Dy 15.06, N 10.21. calc.(%) for  $\text{C}_{59}\text{H}_{73}\text{DyN}_6\text{O}_5$  (no thf lost,  $M = 1108.73 \text{ g.mol}^{-1}$ ): Dy, 14.66.

#### $[\text{Y}(\text{PhForm})_3(\text{thf})_2] \cdot 3\text{thf}$ (**8**)

Likewise, yttrium filings (0.30 g, 3.37 mmol),  $\text{Hg}(\text{C}_6\text{F}_5)_2$  (0.62 g, 1.50 mmol), PhFormH (0.60 g, 3.00 mmol) and a drop of Hg stirred at room temperature for one week gave small crystals (almost colorless) of **7**. Yield = 0.417 g (51%); M.P. 171-175  $^\circ\text{C}$ ; IR (Nujol,  $\text{cm}^{-1}$ ):  $\nu = 1932$  (w), 1656 (vw), 1529 (s), 1291 (s), 1216 (s), 1171 (s), 1152 (s), 1076 (m), 1026 (m), 987 (m), 890 (w), 943 (m), 896 (m), 865 (m), 806 (m), 756(s), 688(s), 621(m), 602(m)  $\text{cm}^{-1}$  (wv);  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 303.2 K):  $\delta = 1.10$  (br m, 20 H,  $\beta\text{-H}(\text{thf})$ ), 3.40 (m, 20 H,  $\alpha\text{-H}(\text{thf})$ ) 6.66–6.95 (br m, 30H; Ar-H), 8.70 (s, 3 H, NC(H)N). Elemental analysis calc. (%) for  $\text{C}_{47}\text{H}_{49}\text{YN}_6\text{O}_2$  (loss of 3 lattice thf,  $M = 821.88 \text{ g.mol}^{-1}$ ): C 68.85, H 6.02, N 10.51; Found: C 68.73, H 5.85, N 10.17.

#### $[\text{Ho}(\text{PhForm})_3(\text{thf})]$ (**9**)

Similarly, holmium filings (0.30 g, 1.80 mmol),  $\text{Hg}(\text{C}_6\text{F}_5)_2$  (0.62 g, 1.50 mmol), PhFormH (0.60 g, 3.00 mmol) and a drop of Hg stirred in thf (20 mL) at room temperature for one week gave small yellow crystals of **10**. Yield = 0.46 g (57%); M.P. 167-170  $^\circ\text{C}$ ; IR (Nujol,  $\text{cm}^{-1}$ ):  $\nu = 1932$  (w), 1661 (vw), 1591 (s), 1578 (s), 1326 (s), 1283 (s), 1216 (s), 1171 (s), 1151 (s), 1076 (m), 1027 (m), 1012 (m), 996 (m), 987(s), 943 (s), 897 (w), 867(m), 757(s), 688(s), 622(vw), 603(m)  $\text{cm}^{-1}$  (wv);  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 303.2 K): Broad uninterpretable resonances due to the paramagnetic nature of this compound. Elemental analysis calc. (%) for  $\text{C}_{43}\text{H}_{41}\text{HoN}_6\text{O}$  ( $M = 822.77 \text{ g.mol}^{-1}$ ): C 62.77, H 5.02, N 10.21. Found: C 62.43, H 5.10, N 10.04.

#### $[\text{Er}(\text{PhForm})_3(\text{thf})]$ (**10**)

Likewise erbium filings (0.30 g, 1.79 mmol),  $\text{Hg}(\text{C}_6\text{F}_5)_2$  (0.62 g, 1.50 mmol), PhFormH (0.60 g, 3.00 mmol) and a drop of Hg stirred in thf (20 mL) at room temperature for one week gave small pink crystals of **11**. Yield = 0.49 g (61%); 168-173  $^\circ\text{C}$ ; IR (Nujol,  $\text{cm}^{-1}$ ):  $\nu = 1932$  (w), 1848 (vw), 1785

(vw), 1720 (vw), 1669 (w), 1590 (m), 1153 (s), 1077 (s), 942 (s), 893 (s), 808 (s), 721 (vs), 692 (s), 622(m), 603 (s)  $\text{cm}^{-1}$  (wv);  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 303.2 K): Limited interpretation and no integration of broad resonances owing to the paramagnetic nature of this compound.  $\delta$  = 0.66 (br s,  $\text{CH}_2$ ), 4.07 (br s,  $\text{CH}_2$ ), 8.64 (br s,  $\text{NC(H)N}$ ). Elemental analysis calc. (%) for  $\text{C}_{43}\text{H}_{41}\text{ErN}_6\text{O}$  ( $M = 825.10 \text{ g}\cdot\text{mol}^{-1}$ ): C 62.60, H 5.01, Er 20.27, N 10.19; Found: C 59.12, H 5.06, N 10.47, Er 20.31.

#### [Lu(PhForm) $_3$ (thf)] (**11**)

Similarly, lutetium filings (0.30 g, 1.71 mmol),  $\text{Hg}(\text{C}_6\text{F}_5)_2$  (0.62 g, 1.50 mmol), PhFormH (0.60 g, 3.00 mmol) and a drop of Hg in thf (20 mL) stirred at room temperature for one week gave small pale red crystals of **11**. Yield = 0.36 g (43%); M.P. 204-208  $^\circ\text{C}$ ; IR (Nujol,  $\text{cm}^{-1}$ ):  $\nu = 1932$  (vw), 1669 (vw), 1285 (vs), 1218 (s), 1204 (m), 1170 (s), 1076 (m), 1011 (m), 986 (m), 944 (m), 896 (w), 869 (w), 756 (s), 722 (s), 689 (s), 622 (vw)  $\text{cm}^{-1}$  (wv); Elemental analysis calc. (%) for  $\text{C}_{43}\text{H}_{41}\text{LuN}_6\text{O}$  ( $M = 832.79 \text{ g}\cdot\text{mol}^{-1}$ ): C 62.02 H, 4.96, N 10.09. Found: C 57.87, H 5.26, N 10.01.

#### *DMForm Complexes*

#### [Sm(DMForm) $_3$ (dme)] (**12**)

Samarium filings (0.30 g, 1.9 mmol),  $\text{Hg}(\text{C}_6\text{F}_5)_2$  (0.62 g, 1.50 mmol), DMFormH (0.75 g, 3.00 mmol) and a drop of Hg in DME (20 mL) were stirred at room temperature for one week. The resulting yellow solution was filtered through a filter cannula from the metal residue and evaporated under vacuum to 5 mL and cooled to  $-5 \text{ }^\circ\text{C}$  for several days giving small yellow crystals of **12**. Yield = 0.55 g (56%); M.P.: 181-183  $^\circ\text{C}$ ; IR (Nujol,  $\text{cm}^{-1}$ ):  $\nu = 1663$  (w), 1609 (w), 1540 (vs), 1489 (s), 1296 (vs), 1245 (m), 1210 (s), 1153 (w), 1119.49 (m), 1057 (s), 1010 (m), 998 (m), 948 (vw), 898 (vw), 864 (m), 814 (s), 721.33 (vw)  $\text{cm}^{-1}$  (wv);  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 303.2 K): Uninterpretable broad resonances due to the paramagnetic nature of the compound. Elemental analysis calc. (%) for  $\text{C}_{55}\text{H}_{67}\text{N}_6\text{O}_2\text{Sm}$  ( $M = 994.54 \text{ g}\cdot\text{mol}^{-1}$ ): C 66.42, H 6.79, N 8.45; Found: C 66.78, H 6.19, N 8.34.

#### [Gd(DMForm) $_3$ (dme)] (**13**)

Similarly, gadolinium filings (0.30 g, 1.90 mmol),  $\text{Hg}(\text{C}_6\text{F}_5)_2$  (0.62 g, 1.50 mmol) and DMFormH (0.75 g, 3.00 mmol) and a drop of Hg stirred in DME (20 mL) at room temperature for one week

gave small yellow crystals of **13**. Yield = 0.57 g (57%); M.P.: 184 °C; IR (Nujol,  $\text{cm}^{-1}$ ):  $\nu = 1867.94$  (vw), 1659.7 (s), 1607.65 (m), 1540.37 (s), 1296.65 (vs), 1243.14 (s), 1207.57 (vs), 1151.8 (m), 1119.97 (s), 1056.05 (m), 1034.56 (m), 1009.17 (m), 997.38 (m), 945.87 (vw), 935.2 (w), 880.9 (w), 866.19 (w), 814.8 (s), 776.79 (m), 720.06 (m), 604.81 (vw),  $\text{cm}^{-1}$  (wv);  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ , 303.2 K): Uninterpretable broad resonances due to the paramagnetic nature of the compound. Elemental analysis calc. (%) for  $\text{C}_{55}\text{H}_{67}\text{N}_6\text{O}_2\text{Gd}$  ( $M = 1001.43 \text{ g}\cdot\text{mol}^{-1}$ ): Gd 15.70; Found: Gd, 15.75.

#### [Pr(DMForm)<sub>3</sub>(DMFormH)] (**14**)

In a similar manner to **12**, prasodymium filings (0.30 g, 2.1 mmol),  $\text{Hg}(\text{C}_6\text{F}_5)_2$  (0.62 g, 1.50 mmol), DMFormH (0.75 g, 3.00 mmol) and a drop of Hg stirred in thf (20 mL) at room temperature for one week gave small green crystals of **14**. Yield = 0.72 g (63%); M.P.: 210-213 °C; IR (Nujol,  $\text{cm}^{-1}$ ):  $\nu = 1873$  (w), 1817 (vw), 1756 (vw), 1724 (vw), 1701 (vw), 1632 (vs), 1608 (s), 1297 (vs), 1211 (vs), 1154 (s), 1119 (s), 998 (s), 948 (s), 896 (m), 872 (m), 811 (vs), 771 (m), 722 (s), 656 (m), 632 (m), 610 (m)  $\text{cm}^{-1}$  (wv);  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ , 303.2 K): Gives broad peaks due to the paramagnetic nature of this compound. Elemental analysis calc. (%) for  $\text{C}_{68}\text{H}_{77}\text{N}_8\text{Pr}$  ( $M = 1147.33 \text{ g}\cdot\text{mol}^{-1}$ ): Pr 12.28; Found: Pr 12.29.

#### [Ho(DMForm)<sub>3</sub>(DMFormH)] (**15**)

Similarly, holmium filings (0.30 g, 1.80 mmol),  $\text{Hg}(\text{C}_6\text{F}_5)_2$  (0.62 g, 1.50 mmol), DMFormH (0.75 g, 3.00 mmol) and a drop of Hg stirred in thf (20 mL) at room temperature for one week gave small yellow crystals of **15**. Yield = 0.86 g (48%); M.P.: 215-217 °C; IR (Nujol,  $\text{cm}^{-1}$ ):  $\nu = 3457$  (w), 3375 (m), 1883 (w), 1828 (vw), 1733 (w), 1632 (vs), 1608 (vs), 1285 (vs), 1155 (vs), 1119 (vs), 1033 (vs), 957 (s), 899 (s), 872 (s), 811 (vs), 772 (s), 722 (vs), 659 (m), 637 (m), 612 (m),  $\text{cm}^{-1}$  (wv);  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ , 303.2 K): Uninterpretable broad resonances due to the paramagnetic nature of the compound. Elemental analysis calc. (%) for  $\text{C}_{68}\text{H}_{78}\text{HoN}_8$  ( $M = 1171.35 \text{ g}\cdot\text{mol}^{-1}$ ): Ho 14.08; Found: Ho 14.10.

#### [Y(DMForm)<sub>3</sub>(thf)] (**16**)

Similarly, yttrium filings (0.30 g, 3.3 mmol),  $\text{Hg}(\text{C}_6\text{F}_5)_2$  (0.62 g, 1.50 mmol), DMFormH (0.75 g, 3.00 mmol) and a drop of Hg stirred in thf (20 mL) at room temperature for one week gave small

colorless crystals of **16**. Yield = 0.62 g (68%); M.P.: 196-200 °C .IR (Nujol,  $\text{cm}^{-1}$ ):  $\nu$  = 1870 (vw), 1753 (vw), 1732 (vw), 1658 (m), 1610 (w), 1293 (vs), 1214 (vs), 1157 (s), 1119 (s), 998 (s), 951 (vs), 900 (m), 874 (s), 814 (s), 724 (m), 666 (w), 612 (m) and 560 (m)  $\text{cm}^{-1}$  (wv);  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 303.2 K):  $\delta$  = 0.92 (m, 4H;  $\beta$ -H(thf)), 2.16-2.26 (d, 36H;  $\text{CH}_3$ ), 3.51 (m, 4H;  $\alpha$ -H(thf)), 6.77–6.85 (m, 18H; Ar-H), 8.61 (s, 3 H, NC(H)N). Elemental analysis calc. (%) for  $\text{C}_{55}\text{H}_{65}\text{N}_6\text{OY}$  ( $M = 915.07 \text{ g}\cdot\text{mol}^{-1}$ ): Y 9.72. Found: Y 9.70.

#### [Lu(DMForm) $_3$ (thf)] (**17**)

Likewise, lutetium filings (0.30 g, 1.70 mmol),  $\text{Hg}(\text{C}_6\text{F}_5)_2$  (0.62 g, 1.50 mmol), DMFormH (0.75 g, 3.00 mmol) and Hg metal stirred in thf (20 mL) at room temperature for one week gave small colourless crystals of **17**. Yield = 0.63 g (63%); M.P.: 211-212 °C ;IR (Nujol,  $\text{cm}^{-1}$ ):  $\nu$  = 1754 (vw), 1660 (w), 1611 (vw), 1292 (vs), 1215 (vs), 1158 (s), 1119 (s), 1033 (s), 998 (s), 952 (s), 932 (m), 901 (m), 875 (s), 812 (s), 775 (w), 724 (m), 655 (vw), 613 (m), 560 (s),  $\text{cm}^{-1}$  (wv);  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 303.2 K):  $\delta$  = 1.19 (m, 4H;  $\beta$ -H(thf)), 2.15-2.24 (d, 36H;  $\text{CH}_3$ ), 3.56 (m, 4H;  $\alpha$ -H(thf)), 6.69–6.81 (m, 18H; Ar-H), 8.69 (s, 3 H, NC(H)N). Elemental analysis calc. (%) for  $\text{C}_{55}\text{H}_{65}\text{N}_6\text{OLu}$  ( $M = 1001.13 \text{ g}\cdot\text{mol}^{-1}$ ): Lu 17.48; Found: Lu 17.50.

#### [Er(DMForm) $_3$ (dmf)] (**18**)

Erbium filings (0.30 g, 1.80 mmol),  $\text{Hg}(\text{C}_6\text{F}_5)_2$  (0.62 g, 1.50 mmol), DMFormH (0.75 g, 3.00 mmol) and Hg metal stirred in thf (20 mL) at room temperature for one week gave a pale red solution. After filtration the residue was completely dried under vacuum. The resulting pink solid was dissolved in dried DMF (15 mL) and cooled to -5 °C for a day giving small pink crystals of **18**. Yield = 0.49 g (51%); M.P.: 200-202 °C; IR (Nujol,  $\text{cm}^{-1}$ ):  $\nu$  = 1878 (vw), 1762 (vw), 1734 (vw), 1647 (vs), 1608 (w), 1293 (vs), 1206 (s), 1154 (s), 1118 (s), 991 (m), 948 (m), 907 (m), 874 (m), 811 (s), 723 (vs), 684 (m), 614 (m), 559 (s),  $\text{cm}^{-1}$  (wv);  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 303.2 K): Gives broad peaks due to the paramagnetic nature of this compound. Elemental analysis calc. (%) for  $\text{C}_{54}\text{H}_{64}\text{N}_7\text{OEr}$  ( $M = 994.5 \text{ g}\cdot\text{mol}^{-1}$ ): C 65.25, H 6.48, Er 16.82, N 9.86; Found: C 64.62, H 7.00, Er 16.88, N 9.67.

#### Catalysis studies

The conversion of benzaldehyde into benzyl benzoate performed at room temperature using crystals of the formamidinate complexes as catalysts to ensure purity and  $^1\text{H}$  NMR spectroscopy

in C<sub>6</sub>D<sub>6</sub> was used to determine the yields and progress of the reaction. The yields were evaluated based on 1 mol% of the catalyst. The reactions were monitored in different time intervals of 24 hr, 48 hr, 72 hr, 96 hr and 120 hr after initiating the reaction. Decrease in the characteristic aldehyde proton signal (at 9.72 ppm) and increase in the intensity of the benzyl group proton signal (at 5.18 ppm) in the <sup>1</sup>H NMR spectra provide evidence for production of benzyl benzoate and the integration of these resonances were used to calculate the yields of the reactions at different time intervals.

### ***X-ray crystallography***

Single crystals coated with viscous hydrocarbon oil were mounted on glass fibres or loops. Crystals were measured at the Australian Synchrotron on the MX1 beamline, data integration was completed using Blue-ice [26] and XDS [27] software programs. Structural solutions were obtained by either direct methods [28] or charge flipping [29] methods and refined using full-matrix least-squares methods against F<sup>2</sup> using SHELX2018 [30], in conjunction with the Olex2 [29] graphical user interface. All hydrogen atoms were placed in calculated positions using the riding model. The graphical representations were generated using bitmap images GUI of Olex2 [29]. Crystal data and refinement details are given in Table 4.

**Table 4.** Crystal data and structural refinement for complexes **1-18**

	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>
Formula	C <sub>47</sub> H <sub>49</sub> LaN <sub>6</sub> O <sub>2</sub>	C <sub>47</sub> H <sub>49</sub> N <sub>6</sub> O <sub>2</sub> Pr	C <sub>49</sub> H <sub>53</sub> N <sub>6</sub> O <sub>2.5</sub> Sm	C <sub>57.5</sub> H <sub>61</sub> N <sub>6</sub> NdO <sub>2</sub>
<i>M<sub>r</sub></i>	868.83	870.83	916.32	1012.36
Space group	<i>Pca</i> 2 <sub>1</sub>	<i>Pca</i> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> (Å)	21.3685(10)	21.355(3)	17.140(7)	17.553(4)
<i>b</i> (Å)	10.2707(5)	10.2952(12)	14.769(9)	14.216(3)
<i>c</i> (Å)	19.5253(9)	19.527(2)	23.284(11)	20.855(4)
<i>α</i> (°)	90	90	90	90
<i>β</i> (°)	90	90	104.013(16)	107.18(3)

$\gamma$ (°)	90	90	90	90
$V$ (Å <sup>3</sup> )	4285.2(4)	4293.1(9)	5718(5)	4971.9(19)
$Z$	4	4	4	4
$\rho_{\text{calc}}$ , g cm <sup>-3</sup>	1.347	1.347	1.064	1.352
$\mu$ , mm <sup>-1</sup>	1.041	1.179	1.063	1.093
$N_{\tau}$	100904	53052	14472	62185
$N$ ( $R_{\text{int}}$ )	9785(0.0947)	9488(0.0981)	8453(0.0590)	8390(0.0605)
$R_1(I > 2\sigma(I))$	0.0354	0.0486	0.0549	0.0313
$wR_2$ (all data)	0.0942	0.1271	0.1700	0.0795
	<b>5</b>	<b>6</b>	<b>7</b>	<b>8</b>
Formula	C <sub>53</sub> H <sub>61</sub> GdN <sub>6</sub> O <sub>3.5</sub>	C <sub>59</sub> H <sub>73</sub> N <sub>6</sub> O <sub>5</sub> Tb	C <sub>59</sub> H <sub>73</sub> DyN <sub>6</sub> O <sub>5</sub>	C <sub>59</sub> H <sub>73</sub> N <sub>6</sub> O <sub>5</sub> Y
$M_r$	995.32	1105.15	1108.73	1035.14
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
$a$ (Å)	17.055(3)	17.122(3)	17.124(3)	17.128(3)
$b$ (Å)	14.644(2)	14.195(3)	14.155(3)	14.142(3)
$c$ (Å)	23.155(4)	22.883(5)	22.873(5)	22.886(5)
$\alpha$ (°)	90	90	90	90
$\beta$ (°)	104.122(3)	106.71(3)	106.70(3)	106.78(3)
$\gamma$ (°)	90	90	90	90
$V$ (Å <sup>3</sup> )	5608.2(15)	5327(2)	5310(2)	5307(2)
$Z$	4	4	4	4
$\rho_{\text{calc}}$ , g cm <sup>-3</sup>	1.179	1.378	1.387	1.295
$\mu$ , mm <sup>-1</sup>	1.225	1.382	1.462	1.153
$N_{\tau}$	33143	62293	48842	44220
$N$ ( $R_{\text{int}}$ )	12747(0.0698)	8880(0.0254)	8779(0.0311)	12543(0.0410)
$R_1(I > 2\sigma(I))$	0.0626	0.0536	0.0659	0.0474
$wR_2$ (all data)	0.1878	0.1342	0.1683	0.1280
	<b>9</b>	<b>10</b>	<b>11</b>	<b>12</b>
Formula	C <sub>43</sub> H <sub>41</sub> HoN <sub>6</sub> O	C <sub>43</sub> H <sub>41</sub> ErN <sub>6</sub> O	C <sub>43</sub> H <sub>41</sub> LuN <sub>6</sub> O	C <sub>55</sub> H <sub>67</sub> N <sub>6</sub> O <sub>2</sub> Sm
$M_r$	822.75	825.08	832.79	994.49

Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
$a$ (Å)	12.017(2)	12.010(2)	11.997(2)	11.2836(14)
$b$ (Å)	13.841(3)	13.802(3)	13.750(3)	25.826(3)
$c$ (Å)	22.169(4)	22.210(4)	22.224(4)	17.941(2)
$\alpha$ (°)	90	90	90	90
$\beta$ (°)	94.98(3)	95.11(3)	95.38(3)	97.734(7)
$\gamma$ (°)	90	90	90	90
$V$ (Å <sup>3</sup> )	3673.4(13)	3667.0(13)	3649.9(13)	5180.9(11)
$Z$	4	4	4	4
$\rho_{\text{calc}}$ , g cm <sup>-3</sup>	1.488	1.495	1.516	1.275
$\mu$ , mm <sup>-1</sup>	2.196	2.331	2.748	1.178
$N_r$	45585	44642	41747	58262
$N$ ( $R_{\text{int}}$ )	6452(0.0317)	6445(0.0817)	6285(0.0428)	9111(0.1598)
$R_1(I > 2\sigma(I))$	0.0230	0.0332	0.0244	0.0544
$wR_2$ (all data)	0.0619	0.0861	0.0616	0.1107
	<b>13</b>	<b>14</b>	<b>15</b>	<b>16</b>
Formula	C <sub>55</sub> H <sub>67</sub> GdN <sub>6</sub> O <sub>2</sub>	C <sub>68</sub> H <sub>77</sub> N <sub>8</sub> Pr	C <sub>68</sub> H <sub>77</sub> N <sub>8</sub> Ho	C <sub>55</sub> H <sub>65</sub> N <sub>6</sub> OY
$M_r$	1001.39	1147.28	1171.30	915.04
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P2_1/n$
$a$ (Å)	11.070(2)	10.717(2)	16.4175(5)	12.889(3)
$b$ (Å)	25.475(5)	21.627(4)	22.2459(7)	17.537(4)
$c$ (Å)	17.869(4)	27.219(5)	20.1078(6)	21.661(4)
$\alpha$ (°)	90	90	90	90
$\beta$ (°)	97.82(3)	94.820(11)	91.5140(10)	100.31(3)
$\gamma$ (°)	90	90	90	90
$V$ (Å <sup>3</sup> )	4992.3(18)	6286(2)	7341.2(4)	4817.1(17)
$Z$	4	4	4	4
$\rho_{\text{calc}}$ , g cm <sup>-3</sup>	1.332	1.212	1.060	1.262
$\mu$ , mm <sup>-1</sup>	1.375	0.820	1.116	1.256
$N_r$	91924	48867	103503	87953

$N (R_{int})$	14378(0.0492)	10204(0.1410)	12911(0.0978)	13889(0.0736)
$R_1(I > 2\sigma(I))$	0.0324	0.0655	0.0661	0.0609
$wR_2$ (all data)	0.0860	0.1435	0.2121	0.1765
	<b>17</b>	<b>18</b>		
Formula	C <sub>55</sub> H <sub>65</sub> LuN <sub>6</sub> O	C <sub>54</sub> H <sub>64</sub> ErN <sub>7</sub> O		
$M_r$	1001.10	994.38		
Space group	$P2_1/n$	$P2_1$		
$a$ (Å)	12.993(3)	10.350(2)		
$b$ (Å)	17.631(4)	18.139(4)		
$c$ (Å)	21.624(4)	12.726(3)		
$\alpha$ (°)	90	90		
$\beta$ (°)	99.32(3)	95.47(3)		
$\gamma$ (°)	90	90		
$V$ (Å <sup>3</sup> )	4888.3(17)	2378.3(8)		
$Z$	4	4		
$\rho_{calc}$ , g cm <sup>-3</sup>	1.360	1.389		
$\mu$ , mm <sup>-1</sup>	2.064	1.811		
$N_r$	58685	28789		
$N (R_{int})$	8585(0.0408)	7734(0.0453)		
$R_1(I > 2\sigma(I))$	0.0330	0.0235		
$wR_2$ (all data)	0.0897	0.0608		

## Acknowledgements

This research was supported by Australian Research Council (DP190100798), Part of the research were undertaken on the MX1 beamline at the Australian Synchrotron, part of ANSTO [31].



## References

- [1]. (a) F. T. Edelman, *Adv. Organomet. Chem.*, in: A.F. Hill, M.J. Fink (Eds.), 61, Elsevier Science, (2013) pp. 55–374; (b) F. T. Edelman, *Chem. Soc. Rev.* 38 (2009) 2253–2268; (c) F. T. Edelman, *Chem. Soc. Rev.* 41 (2012) 7657–7672; (d) F. T. Edelman, *Adv. Organomet. Chem.*, in: A.F. Hill, M.J. Fink (Eds.), 57, Elsevier Science, (2008) p. 183; (e) F. T. Edelman, D. M. Freckmann, H. Schumann, *Chem. Rev.* 102 (2002) 1851–1896.
- [2]. P. C. Junk, M. L. Cole, *Chem. Commun.* (2007) 1579-1590.
- [3]. R. M. Roberts, *J Org. Chem.* 14 (1949) 277-284.
- [4]. G. B. Deacon, Md. E. Hossain, P. C. Junk, M. Salehisaki, *Coord. Chem. Rev.* 340 (2017) 247-265.
- [5]. M. L. Cole, G. B. Deacon, C. M. Forsyth, P. C. Junk, K. Konstas, J. Wang, *Chem. Eur. J.* 13 (2007) 8092-8110.
- [6]. M. L. Cole, G. B. Deacon, C. M. Forsyth, P. C. Junk, K. Konstas, J. Wang, H. Bittig, D. Werner, *Chem. Eur. J.* 19 (2013) 1410-1420.
- [7]. G. B. Deacon, P. C. Junk, L. K. Macreadie, D. Werner, *Eur. J. Inorg. Chem.* (2014) 5240-5250.
- [8]. D. Werner, G. B. Deacon, P. C. Junk, R. Anwander, *Chem. Eur. J.* 20 (2014) 4426-4438.
- [9]. a) L. Claisen, *Ber. Dtsch. Chem. Ges.* 20 (1887) 646–650; b) W. Tishchenko, *Chem. Zentralbl.* 77 I (1906) 1309-1311.
- [10]. E. Hawkins, D. Long, F. Major, *J. Chem. Soc.* (1955) 1462-1468.
- [11]. a) F. J. Villani, F. Nord, *J. Am. Chem. Soc.* 69 (1947) 2605-2607; b) I. Lin, A. R. Day, *J. Am. Chem. Soc.*, 74 (1952) 5133-5135.
- [12]. K. Morita, Y. Nishiyama and Y. Ishii, *Organometallics.* 12 (1993) 3748-3752.
- [13]. P. R. Stapp, *J. Org. Chem.* 38 (1973) 1433-1434.
- [14]. B. M. Day, W. Knowelden, M. P. Coles, *Dalton Trans.* 41 (2012) 10930-10933.
- [15]. S. Onozawa, T. Sakakura, M. Tanaka, M. Shiro, *Tetrahedron* 52 (1996) 4291-4302.
- [16]. H. Berberich and P. W. Roesky, *Angew. Chem. Int. Ed.* 37 (1998) 1569-1571.
- [17]. G. B. Deacon, A. Gitlits, P. W. Roesky, M. K. Bürgstein, K. C. Lim, B. W. Skelton, A. H. White, *Chem. Eur. J.* 7 (2001) 127-138.

- [18]. A. Zuyls, P. W. Roesky, G. B. Deacon, K. Konstas and P. C. Junk, *Eur. J. Org. Chem.*, 2008, **4**, 693-697.
- [19]. a) G. J. Moxey, A. J. Blake, W. Lewis, D. L. Kays, *Eur. J. Inorg. Chem.* (2015) 5892–5902; b) R. P. Kelly, T. D. M. Bell, R. P. Cox, D. P. Daniels, G. B. Deacon, F. Jaroschik, P. C. Junk, X. F. Le Goff, G. Lemerrier, A. Martinez, J. Wang, D. Werner, *Organometallics*, 34 (2015) 5624-5636; c) H. Sitzmann, T. Dezember, O. Schmitt, F. Weber, G. Wolmershäuser, M. Ruck, *Z. Anorg. Allg. Chem.* 626 (2000) 2241–2244; d) L. Hirneise, C. Maichle-Mössmer, R. Anwander, *Inorg. Chem.* 60 (2021) 18211–18224; e) D. P. Daniels, G. B. Deacon, D. Harakat, F. Jaroschik, P. C. Junk, *Dalton Trans.* 41 (2012) 267-277.
- [20]. a) L. H. J. Lajunen, G. R. Choppin, *Rev. Anal. Chem.* 9 (1989) 91-129; b) G. Marshall, A. J. Wooles, D. P. Mills, W. Lewis, A. J. Blake, S. T. Liddle, *Inorganics* 2013, 1, 46–69.
- [21]. R. F. Culmo, *The Elemental Analysis of Various Classes of Chemical Compounds Using CHN*. PerkinElmer, Inc. Shelton, CT (2013).
- [22]. G. B. Deacon, P. MacKinnon, R. S. Dickson, G. N. Pain, B. O. West, *Appl. Organomet. Chem.* 4 (1990) 439-449.
- [23]. R. Shannon, *Acta Crystallogr. A*, 32 (1976) 751-767.
- [24]. N. E. Rad, P. C. Junk, G. B. Deacon, J. Wang, *Z. Anorg. Allg. Chem.* 645 (2019) 877-881.
- [25]. S. Hamidi, L. N. Jende, H. Martin Dietrich, C. c. Maichle-Mössmer, K. W. Törnroos, G. B. Deacon, P. C. Junk and R. Anwander, *Organometallics*, 2013, **32**, 1209-1223.
- [26]. T. M. McPhillips, S. E. McPhillips, H. J. Chiu, A. E. Cohen, A. M. Deacon, P. J. Ellis, E. Garman, A. Gonzalez, N. K. Sauter, R. P. Phizackerley, S. M. Soltis, J. P. Kuhn, *J. Synchrotron Radiat.* 9 (2002) 401-406.
- [27]. W. Kabsch, *J. Appl. Crystallogr.* 26 (1993) 795-800.
- [28]. G. M. Sheldrick, *Acta Crystallogr. Sect. A*. 64 (2008) 112-122.
- [29]. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* 42 (2009) 339-341.
- [30]. G. M. Sheldrick, *Acta Cryst. C*71 (2015) 3-8.

- [31]. N. P. Cowieson, D. Aragao, M. Clift, D. J. Ericsson, C. Gee, S. J. Harrop, N. Mudie, S. Panjkar, J. R. Price, A. Riboldi-Tunncliffe, R. Williamson, T. Caradoc-Davies, J. Synchrotron Rad. 22 (2015) 187-190.

## GRAPHICAL ABSTRACT

### Synthesis and reactivity of rare-earth-*N,N'*-(diphenyl)formamidinate and *N,N'*-bis(2,4-dimethylphenyl)formamidinate complexes

Mehdi Salehisaki Nazli E. Rad, Glen B. Deacon, Jun Wang, Zhifang Guo, and Peter C. Junk

Redox transmetallation/protolysis reactions were employed to synthesize a series of the rare earth bis(aryl)formamidinate complexes. Trivalent complexes were synthesized with three chelating formamidinate ligands about the metal centers. A study of the reactivity towards the Tishchenko reaction shows the compounds catalyse the Tishchenko reaction in the formation of esters from aldehydes.

