### Synthesis, Structures and Reactivity of Lanthanoid(II) Formamidinates of **Varying Steric Bulk**

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Dedicated to Professor Cameron Jones on the occasion of his 50th birthday

 $(\text{TFForm})_2(\text{thf})_3$ ] (7a), in which ytterbi-

um is seven coordinate and the thf li-

gands are "pseudo-meridional". Repre-

sentative complexes undergo C-X

(X = F, Cl, Br) activation reactions with

perfluorodecalin, hexachloroethane or

2,3,4,5-tetrafluorobenzene, giving [Yb-

 $(\text{EtForm})_2 F]_2$  (9),  $[Yb(o-PhPhForm)_2 F]_2$ 

(10),  $[Yb(o-PhPhForm)_2Cl(thf)_2]$  (11),

[Yb(DippForm)<sub>2</sub>Cl(thf)] (12) and [Yb-

(DippForm)<sub>2</sub>Br(thf)] (16). X-ray crys-

tallography has shown 9 to be a six-co-

Keywords: C-F/Cl/Br activation .

formamidinate · heteroleptic lan-

thanide compounds · lanthanides ·

and

1-bromo-

1.2-dichloroethane.

X-ray diffraction

Abstract: New reactive, divalent lanthanoid formamidinates [Yb(Form)<sub>2</sub>-(Form = [RNCHNR]; R = o- $(thf)_2$  $MeC_6H_4$  (o-TolForm; 1), 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>  $(XylForm; 2), 2,4,6-Me_3C_6H_2$  (Mes-Form; 3), 2,6-Et<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (EtForm; 4), o- $PhC_6H_4$  (o-PhPhForm; 5), 2,6-iPr<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (DippForm; **6**), *o*-HC<sub>6</sub>F<sub>4</sub> (TFForm; **7**)) and  $[Eu(DippForm)_2(thf)_2]$  (8) have been prepared by redox transmetallation/protolysis reactions between an excess of a lanthanoid metal,  $Hg(C_6F_5)_2$ and the corresponding formamidine (HForm). X-ray crystal structures of 2-6 and 8 show them to be monomeric with six-coordinate lanthanoid atoms, chelating N,N'-Form ligands and cis-thf donors. However, [Yb(TFForm)<sub>2</sub>(thf)<sub>2</sub>] (7) crystallizes from THF as [Yb-

#### Introduction

As part of our studies of N-donor alternatives to the cyclopentadienyl family of ligands,<sup>[1]</sup> we have previously reported the first syntheses of a wide range of tris(N,N'-di-(aryl)formamidinato)lanthanoid(III) complexes [Ln(Form)<sub>3</sub>-

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ordinate, fluoride-bridged dimer, 12 and 16 to be six-coordinate monomers with the halide and thf ligands cis to each other, and 11 to have a seven-coordinate Yb atom with "pseudo-meridional" unidentate ligands and thf donors cis to each other. The analogous terbium compound [Tb- $(DippForm)_2Cl(thf)_2$  (13), prepared by metathesis, has a similar structure to 11. C-Br activation also accompanies the redox transmetallation/protolysis reactions between La, Nd or Yb metals, Hg(2-BrC<sub>6</sub>F<sub>4</sub>)<sub>2</sub>, and HDipp-Form, yielding [Ln(DippForm)<sub>2</sub>Br(thf)] complexes (Ln=La (14), Nd (15), Yb (16)).

 $(thf)_n$ ].<sup>[2]</sup> Formamidinates (Form = [RNC(H)NR], R = aryl or alkyl)<sup>[3]</sup> are a subclass of amidinate ligands ([R<sup>1</sup>NCR<sup>2</sup>NR<sup>3</sup>]<sup>-</sup>). Formamidines (HForm) are readily synthesised from aromatic amines and triethyl orthoformate, permitting the tuning of their steric and electronic properties.<sup>[3]</sup> The availability of formamidines as neutral species (unlike many other groups of amidinates) makes them suitable for free-metal-based syntheses.<sup>[4]</sup> Accordingly, [Ln- $(Form)_3(thf)_n$  complexes were prepared by a redox transmetallation/protolysis reaction between lanthanoid metal, bis-(pentafluorophenyl)mercury or bis(2,3,4,5-tetrafluorophenyl)mercury and N,N'-di(aryl)formamidines [Eq. (1)] in tetrahydrofuran.<sup>[2,5]</sup> The steric bulk of the Form ligand affects not only the number of tetrahydrofuran co-ligands in the resulting complex, but, in the case of N,N-bis(2,6-diisopropylphenyl)formamidine (DippFormH), the bulkiest N,N'-di-(aryl)formamidine at our disposal, also causes the formation of [Ln(DippForm)<sub>2</sub>(F)(thf)] and a derivatised formamidine coproduct. This coproduct incorporates a ring-opened THF molecule and a trapped fluorobenzyne derivative as shown in Equation (2)].<sup>[2,5]</sup> The outcome was attributed to C-F activation of a  $[Ln(DippForm)_2(R')]$   $(R'=C_6F_5 \text{ or } 2-HC_6F_4)$ species formed by oxidation of a putative bis(formamidinato)lanthanoid(II) species by  $Hg(2-XC_6F_4)_2$  (X=H or F) [Eqs. (3) and (4)].

$$2 \operatorname{Ln} + 3 \operatorname{Hg}(C_6F_5)_2 + 6 \operatorname{Form} H \xrightarrow{\text{THF}} 2 [\operatorname{Ln}(\operatorname{Form})_3(\operatorname{thf})_n] + 6 \operatorname{C}_6F_5H + 3 \operatorname{Hg}; n = 0 - 2$$
(1)

$$2 \operatorname{Ln}+3 \operatorname{Hg}(2-\operatorname{XC}_6F_4)_2 + 6 \operatorname{DippForm}H^{\operatorname{IHF}}$$

$$2 [\operatorname{Ln}(\operatorname{DippForm})_2F(\operatorname{thf})] + 3 \operatorname{Hg} + 4 (2-\operatorname{XC}_6F_4H)$$

$$+2 (2-\operatorname{XHC}_6F_3O(\operatorname{CH}_2)_4(\operatorname{DippForm})); X = H \text{ or } F$$

$$(2)$$

 $\begin{array}{l} 2 \left[ Ln(DippForm)_2 \right] + Hg(2\text{-}XC_6F_4)_2 \rightarrow \\ \\ \text{``}2 \left[ Ln(DippForm)_2(2\text{-}XC_6F_4) \right] \text{''} + Hg \end{array} \tag{3}$ 

Support for this hypothesis was provided by the observed formation of [Sm(DippForm)<sub>2</sub>(F)(thf)] on reaction of [Sm- $(\text{DippForm})_2(\text{thf})_2$  with  $\text{Hg}(C_6F_5)_2$  and by the isolation of [Sm(DippForm)<sub>2</sub>(CCPh)(thf)] from the reaction of the same divalent precursor, [Sm(DippForm)<sub>2</sub>(thf)<sub>2</sub>], with Hg-(CCPh)2.<sup>[2]</sup> These observations serve to focus attention on the divalent lanthanoid formamidinates, of which only [Sm-(DippForm)<sub>2</sub>(thf)<sub>2</sub>] has been reported.<sup>[6]</sup> We have also reported a range of reactions of this complex with carbodiimides as a source of bulky [Sm(DippForm)<sub>3</sub>] and bulky [Sm(DippForm)<sub>2</sub>Form'] complexes.<sup>[7]</sup> Even in the broader area of benzamidinate chemistry, Ln<sup>II</sup> derivatives have been neglected.<sup>[1g-k]</sup> However, divalent ytterbium benzamidinates,  $[Yb{CAr(NSiMe_3)_2}_2(thf)_n]$  (Ar = Ph, 4-MeOC<sub>6</sub>H<sub>4</sub>, n=2; Ar = 4-PhC<sub>6</sub>H<sub>4</sub>, n = 0), formed from metathesis reactions, have been reported by Edelmann and co-workers.<sup>[8]</sup> More recently, Lee and co-workers have reported syntheses, structures and reactions of Ln<sup>II</sup> (Ln=Sm, Eu, Yb) complexes of a novel unsymmetrical benzamidinate ligand,<sup>[9a]</sup> and related guanidinates have been reported.<sup>[9b]</sup>

We now report the syntheses, structures and C-X activation reactions (X=F, Cl or Br) of a range of bis(formamidinato)ytterbium(II) complexes, the synthesis and structure of a europium(II) analogue and the trivalent [Ln- $(DippForm)_2(Br)(thf)$  complexes (Ln = La, Nd and Yb). Use of  $Hg(2-BrC_6F_4)_2$  with ytterbium metal provided access to the bromoytterbium(III) complex [Yb(DippForm)<sub>2</sub>(Br)-(thf)] by C-Br activation and the generality of this synthesis [Lnwas established by similar preparations of  $(DippForm)_2(Br)(thf)$  (Ln=La, Nd). Complexes of this type are potential sources of a wide range of functionalised bis(formamidinato)lanthanide(III) complexes, [Ln- $(Form)_2(L)$ ], where L = organoamide, organyl or organoxide. The C-X activation reactions suggest the possibility of a broad reaction chemistry for these divalent formamidinates.

#### **Results and Discussion**

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**Synthesis and spectroscopic characterisation**: Ytterbium(II) complexes were synthesised by the treatment of freshly filed Yb metal with two equivalents of the corresponding formamidine proligand and one equivalent of either bis(pentafluorophenyl)mercury or diphenylmercury in THF (Scheme 1). These one-pot reactions afforded seven new di-



Scheme 1. Synthesis of complexes **1–8**. Ln = Yb for **1–7** and Ln = Eu for **8**. Ar = 2-MeC<sub>6</sub>H<sub>4</sub> (*o*-TolForm) for **1**, 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (XylForm) for **2**, 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub> (MesForm) for **3**, 2,6-Et<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (EtForm) for **4**, 2-PhC<sub>6</sub>H<sub>4</sub> (*o*-PhPhForm) for **5**, 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (DippForm) for **6** and **8** and 2,3,4,5-F<sub>4</sub>C<sub>6</sub>H (TFForm) for **7**.

valent ytterbium-formamidinate complexes, that is, [Yb(o- $TolForm)_2(thf)_2$  (1),  $[Yb(XylForm)_2(thf)_2]$  (2), [Yb- $(MesForm)_2(thf)_2$ ] (3),  $[Yb(EtForm)_2(thf)_2]$  (4), [Yb(o-PhPhForm)<sub>2</sub>(thf)<sub>2</sub>]·2THF (5), [Yb(DippForm)<sub>2</sub>(thf)<sub>2</sub>]·2THF (6) and  $[Yb(TFForm)_2(thf)_2]$  (7), which yielded single crystals of [Yb(TFForm)<sub>2</sub>(thf)<sub>3</sub>]·2THF (7a) on crystallisation from THF (for abbreviations see Scheme 1). The europium analogue [Eu(DippForm)<sub>2</sub>(thf)<sub>2</sub>]·2THF (8) was prepared similarly by using Eu metal in place of Yb with HDippForm as the proligand. Compound 1 could be synthesised with either mercury reagent, compounds 2-4 and 6-8 were prepared from  $[Hg(C_6F_5)_2]$ , and compound 5 was synthesised with [HgPh<sub>2</sub>]. The corresponding  $[Yb(Form)_3(thf)_n]$ , (n=0,1) complexes have been previously prepared by a similar method.<sup>[2]</sup> However, for these syntheses of Yb<sup>II</sup> compounds, a larger Yb/Hg ratio was used. Compounds 1-5 and 7 are deep red in colour, compound 6 is orange, consistent with the divalent oxidation state of ytterbium,<sup>[10]</sup> and compound  ${\bf 8}$  is yellow. The colours of  ${\bf Ln}^{\rm II}$  species are usually more intense because of Laporte-allowed 4f→5d transitions.<sup>[10]</sup> Compounds 1-6, 7a and 8 were crystallised from THF and all complexes were isolated in good to high yields (58-81%). Evidently, both mercury reagents are suitable reagents to obtain the lanthanoid compounds in their divalent state, although the poorer oxidant of the two, [HgPh<sub>2</sub>], is often better suited for the synthesis of Ln<sup>II</sup> species.<sup>[11,12]</sup> Although the divalent complexes  $[Ln(DippForm)_2(thf)_2]$  (Ln = Eu, Yb) are freely accessible from lanthanoid metal, Hg- $(C_6F_5)_2$  and DippFormH, attempts to prepare the trivalent  $[Ln(DippForm)_3]$  (Ln=Eu, Yb) analogues by modification of the stoichiometry, as is possible for less bulky formamidines,<sup>[2]</sup> failed. [Ln(DippForm)<sub>2</sub>(F)(thf)] (Ln = Yb, Eu) derivatives were also unobtainable by such methods in contrast to reactions with other lanthanoid elements (Ln=La, Ce, Nd, Sm and Tm).<sup>[2]</sup>

Control reactions were carried out to investigate the reaction pathway. Firstly, the formamidine ligand was treated with Hg(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> in THF and ytterbium metal was treated with the formamidine ligand in THF. As was found for similar reactions of the alkaline earth metals,<sup>[13]</sup> IR spectra of the material isolated from the control-reaction mixtures indicated the presence of the  $\tilde{\nu}$ (N–H) absorption of the formamidine ligand (around 3350 cm<sup>-1</sup>) and the characteristic absorption bands of Hg(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>.<sup>[14]</sup> These results indicate that successful syntheses of Ln<sup>II</sup> complexes require all three reagents.

Compounds 2–7a and 8 were authenticated by single-crystal X-ray diffraction (see discussion below). In general, the compositions of 1–8 were supported by microanalyses, Ln analyses, and spectroscopic data. The <sup>1</sup>H NMR spectra and/ or microanalyses of some compounds (5, 6 and 8) indicated the loss of THF of solvation. Satisfactory carbon microanalysis values for 6 and 8 could not be obtained even on repeated preparation, whereas the Ln analyses performed promptly after preparation are more consistent with partial loss of lattice THF. Compounds 1–8 showed complete deprotonation of the formamidine reagents as indicated by the absence of an  $\tilde{\nu}(N-H)$  absorption in the infrared spectrum and the lack of an N–H resonance in the <sup>1</sup>H NMR spectrum of the dry, bulk crystalline material.

Because of the diamagnetic nature of divalent complexes 1–7 and their good solubility in  $C_6D_6$ , <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR data could be obtained but the paramagnetic compound 8 gave a broadened spectrum, which could not be satisfactorily integrated. Only a single, symmetrical formamidinate environment is evident in the <sup>1</sup>H NMR spectra of all compounds, an observation which is indicative of either a symmetrically bound ligand or a rapidly exchanging system.<sup>[15]</sup> The methine proton resonances (NCHN) in the <sup>1</sup>H NMR spectra of 1-8 are shifted to significantly higher frequencies relative to the value for the neutral ligand. For example, the methine proton resonance occurs at  $\delta = 7.72$ , 7.05 and 6.88 ppm for o-TolFormH, XylFormH and MesFormH, respectively, and at  $\delta = 8.88$ , 8.44 and 8.33 ppm in 1–3, respectively. In the case of 5 and 6 the methine resonances show <sup>171</sup>Yb satellites with <sup>3</sup>*J*(<sup>1</sup>H, <sup>171</sup>Yb) couplings of 44 and 45 Hz, respectively. <sup>171</sup>Yb NMR spectra were obtained for 2-6 showing broad signals in the range of  $\delta = 600-700$  ppm. In the case of 5 and 6, there were resolvable splittings giving a triplet from coupling to the methine protons with <sup>3</sup>J-(<sup>1</sup>H,<sup>171</sup>Yb)=48 and 44 Hz, respectively. The range of chemical shifts observed ( $\delta = 600-700$  ppm) corresponds closely to those known for a number of four-coordinate [Yb(NR<sub>2</sub>)<sub>2</sub>- $(solv)_2$  (solv = thf, Et<sub>2</sub>O, etc.) complexes,<sup>[16-19]</sup> but the shifts measured cannot be explained by loss of thf ligands in  $C_6D_6$ (or  $C_6D_6$ /toluene), a known phenomenon, because the addition of an excess of THF to representative solutions of complexes 2 and 4 had little effect on the spectra observed. However, the chemical shifts are similar to those of some six-coordinate Yb<sup>II</sup> complexes of bulky di(2-pyridyl)amides,<sup>[20]</sup> which, like the complexes studied herein, have a conjugated NCN backbone. Examination of seven-coordinate

**7a** in  $C_7D_8$  gave a lower chemical shift ( $\delta$ =501 ppm) that is consistent with the increased coordination number (seven instead of six) in related structures.<sup>[16,17,19]</sup>

The methine carbon (NCHN) resonances in the  ${}^{13}C{}^{1}H$  NMR spectra of **1** and **2** are observed at 163 ppm and 175 ppm, respectively. The observed chemical shifts are found at significantly higher frequencies than those for the neutral *o*-TolFormH and XylFormH ligands (147 ppm and 146 ppm, respectively). Similar changes in chemical shift for the methine carbon resonances were observed in the  ${}^{13}C{}^{1}H$  NMR spectra of **6**, **7** and **8**. The  ${}^{19}F$  NMR spectrum of **7** suggests that the substituent chemical shift of the NCN group is about 10 ppm for an *ortho* fluorine substituent.

**Reactivity studies**: Treatment of compounds **4** and **5** with perfluorodecalin in THF at room temperature resulted in the isolation of the trivalent ytterbium–fluoride complexes  $[{Vb(EtForm)_2(\mu_2-F)}_2]$  (**9**) and  $[{Vb(o-PhPhForm)_2(\mu_2-F)}_2]$  (**10**; Scheme 2). Perfluorodecalin acts as the oxidant and has



Scheme 2. Synthesis of complexes **9–12** and **16**. For **9**  $Ar=2,6-Et_2C_6H_3$ ,  $RX=C_{10}F_{18}$ , X=F, n=0, m=2; for **10**  $Ar=2-PhC_6H_4$ ,  $RX=C_{10}F_{18}$ , X=F, n=0, m=2; for **11**  $Ar=2-PhC_6H_4$ ,  $RX=C_2Cl_6$ ; X=Cl; n=2, m=1; for **12**  $Ar=2,6-iPr_2C_6H_3$ ,  $RX=1,2-Cl_2C_2H_4$ ; X=Cl; n=1, m=1; for **16**  $Ar=2,6-iPr_2C_6H_3$ ;  $RX=o-HBrC_6F_4$ ; X=Br; n=1, m=1.

been used in ytterbium(II) cyclopentadienyl and/or aryloxide chemistry to give [{YbCp<sub>2</sub>F(thf)}<sub>2</sub>] (Cp=cyclopentadienyl) and [{Yb(OAr')<sub>2</sub>F(thf)}<sub>2</sub>] (Ar'=C<sub>6</sub>H<sub>4</sub>tBu<sub>2</sub>-2,6-Y-4, Y=H, Me, tBu).<sup>[21,22]</sup> in the first examples of C-F activation of a saturated fluorocarbon by a lanthanoid complex. Intermolecular abstraction of fluorine from perfluorocycloalkanes by divalent lanthanoids is driven by the negative reduction potential of the Ln<sup>III</sup>/Ln<sup>II</sup> couple and the formation of very strong lanthanoid–fluoride bonds.<sup>[23]</sup>

Compound 9 was isolated as yellow crystals from hexane and compound 10 was isolated as a yellow powder from THF. Elemental analyses (C, H, N, Yb) and infrared spectra support the proposed formulae of both compounds (below). Additionally, the structure of 9 was established by X-ray crystallography. The infrared spectra ( $\tilde{\nu} = 4000-600 \text{ cm}^{-1}$ ) of 9 and 10 display similar features to those found for [Yb-(Form)<sub>3</sub>] complexes.<sup>[2]</sup> During formation of 9, an insoluble precipitate with no IR absorptions was also deposited, which may be YbF<sub>3</sub> possibly from the rearrangement of 9.

Reactions of **5** and **6** with hexachloroethane and 1,2-dichloroethane in THF or toluene at room temperature yielded  $[Yb(o-PhPhForm)_2Cl(thf)_2]\cdot 2THF$  (**11**) and [Yb- $(DippForm)_2Cl(thf)]\cdot THF$  (**12**), respectively (Scheme 2). Ox-

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idation was accompanied by a typical colour change from red or orange to yellow. In the <sup>1</sup>H NMR spectrum of **11**, the chemical shift of the backbone RN(*CH*)NR proton shifts from  $\delta = 8.93$  in **5** to 12.1 ppm as result of the oxidation. Otherwise, the broadness of the spectrum precluded satisfactory integration, and the compound was principally identified by its X-ray crystal structure (see discussion below). A crystal structure of **12** was also obtained in which the bulkier formamidine apparently leads to a lower coordination number than in **11**. However, to provide a further structural comparison, a synthesis by metathesis from TbCl<sub>3</sub> and Na-(DippForm) led to isolation of [Tb(DippForm)<sub>2</sub>Cl-(thf) l<sub>2</sub> 5THE (**13**) Com-

 $(thf)_2]$ -2.5THF (13). Compound 13 was shown to be seven coordinate by X-ray crystallography. Although Tb<sup>3+</sup> is somewhat (0.05 Å) larger than Yb<sup>3+</sup>,<sup>[24]</sup> it may be that the crystallisation solvent determines the observed structure, because crystals of 12 were obtained from toluene and those of 13 were obtained

sorptions in the spectra of both **10** and **11** at  $\tilde{\nu} = 390 \text{ cm}^{-1}$ may be assigned to  $\tilde{\nu}(\text{Yb-N})$ .

The syntheses of  $[Ln(DippForm)_2Br(thf)]$  complexes were achieved by two methods. In the first, C–Br activation reactions between excess Ln metal, Hg(2-BrC<sub>6</sub>F<sub>4</sub>)<sub>2</sub>, and HDipp-Form in THF at room temperature and subsequent crystallisation from toluene (Ln=La, Nd) or diethyl ether (Ln= Yb) yielded the complexes  $[Ln(DippForm)_2Br(thf)]$ ·solv (Ln=La (14), Nd (15); solv=none; Ln=Yb (16), solv= Et<sub>2</sub>O; Scheme 3). Although this method parallels the preparations of  $[Ln(DippForm)_2F(thf)]$  by C–F activation,<sup>[2,5,6]</sup> there is one notable difference in that neither further oxida-



Scheme 3. Formation of  $[Ln(DippForm)_2Br(thf)]$  complexes. For 14 Ln = La, for 15 Ln = Nd and for 16 Ln = Yb. Ar = 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub> for 14–16.

from THF. The microanalyses of 12 and 13 are indicative of the loss of lattice THF.

Bands in the far-IR spectrum of 10 at  $\tilde{\nu} = 336$  and 298 cm<sup>-1</sup> of medium to strong intensity were not observed in the spectrum of the analogous chloro complex, 11, and can be assigned to the two expected<sup>[25]</sup>  $\tilde{\nu}$ (Yb-F) modes of a  $[{Yb(o-PhPhForm)_2(\mu_2-F)}]_2$  structure analogous to that of the crystallographically established fluoride-bridged dimer 9. The frequencies are found in the expected range since ninecoordinate dimeric [{YbCp<sub>2</sub>F(thf)}<sub>2</sub>] has bridging fluoride ligands with  $\tilde{\nu}(Yb-F)$  at 298 cm<sup>-1</sup>,<sup>[21]</sup> trimeric [{YbCp<sub>2</sub>F}<sub>3</sub>] has a  $\tilde{\nu}$ (Yb-F) band at 336 cm<sup>-1</sup> (Raman active) and tetrameric  $[{YbCp'_2F}_4]$  (Cp' = MeC<sub>5</sub>H<sub>4</sub>) has a band at 328 cm<sup>-1</sup>.<sup>[22]</sup> Dimeric five-coordinate aryloxide complexes [{Yb(OAr')<sub>2</sub>F- $(thf)_{2}^{[22]}$  (Ar' as above) have intense  $\tilde{\nu}(Yb-F)$  absorptions in the range of 390–375 and at 300 cm<sup>-1</sup>. In three-coordinate YbF<sub>3</sub>, which was isolated in a matrix, the terminal  $\tilde{\nu}$ (Yb-F) absorptions are predictably at much higher frequencies ( $\tilde{\nu}$  = 569 and 546  $\rm cm^{-1}).^{[26]}$ 

In the far-IR spectrum of the chloro complex, **11**, there are medium to strong intensity bands at  $\tilde{\nu} = 261$  and 248 cm<sup>-1</sup>, which are not present with this intensity in the spectrum of the fluoro analogue **10**. One of these bands is presumably attributable to the  $\tilde{\nu}$ (Yb–Cl) of the monomeric complex. For terminal chloro ligands,  $\tilde{\nu}$ (Yb–Cl) is expected at 269–237 cm<sup>-1</sup> for monomeric six-coordinate [YbCl<sub>3</sub>-(thf)<sub>3</sub>],<sup>[27]</sup> at 274 cm<sup>-1</sup> in dimeric [{YbCl<sub>3</sub>(thf)<sub>2</sub>}],<sup>[27]</sup> and at 264 cm<sup>-1</sup> in eight-coordinate [YbCp<sub>2</sub>Cl(thf)].<sup>[28]</sup> In six-coordinate [YbCl<sub>6</sub>]<sup>3–</sup> the absorption is in the range of 263–253 cm<sup>-1</sup>.<sup>[29]</sup> The values for bridging chloro ligands are 223 and 211 cm<sup>-1</sup> in [{YbCp<sub>2</sub>Cl}<sub>2</sub>(thf)]<sup>[28]</sup> and 222 and 206 cm<sup>-1</sup> in [YbCp<sub>2</sub>Cl]<sub>2</sub>.<sup>[30]</sup> Thus, either band observed in the spectrum of **11**, at 261 or 248 cm<sup>-1</sup>, is consistent with a terminal chloro ligand in a seven-coordinate environment. Strong ab-

tion to  $[Yb(DippForm)_2(C_6F_5)(thf)_n]$  nor C-F activation giving  $[Yb(DippForm)_2F(thf)]$  occurs during the reaction between Yb metal,  $Hg(C_6F_5)_2$  and HDippForm. Instead, divalent compound **6** is obtained (Scheme 1). Ytterbium induced C-Br activation herein can be attributed to the reduced bond strength of C-Br than C-F. In the second synthesis, a C-Br activation occurs between **6** and 1-bromo-2,3,4,5-tetrafluorobenzene, giving **16** (Scheme 2).

THF seems to be readily lost from bulk **14** because it is not detected in either its <sup>1</sup>H or <sup>13</sup>C NMR spectra but the microanalysis suggests the presence of some THF, as observed in single crystals. In the case of the Nd complex, **15**, the presence of THF is evident from <sup>1</sup>H NMR spectroscopy and microanalysis. The structure of **16** as a diethyl ether solvate was established by X-ray crystallography and the microanalysis is consistent with the retention of both coordinated THF and diethyl ether of crystallisation in the bulk sample. The properties of these complexes closely resemble those of known Ln–F analogues.<sup>[2,5,6]</sup>

**X-ray crystallographic studies**: Compounds **1–6** and **8** contain isostructural metal complexes with six-coordinate Ln atoms surrounded by two chelating Form ligands and two *cis*-thf donors. Complex **2**, as shown in Figure 1, is a representative example of this geometry. Compounds **3** and **4** are isotypic, as are **6** and **8**. It is also likely that **1** has a similar structure. The average Yb–N and Yb–O bond lengths (Table 1) are near the average values (2.45 and 2.42 Å, respectively) for six-coordinate Yb<sup>II</sup> complexes found in the Cambridge Crystallographic Data Centre's structural database.<sup>[31]</sup> In **6**, which has the bulkiest formamidinate ligand (DippForm), the Yb–O(thf) bond lengths are not elongated and those in **5** are, marginally, the longest found in

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O(1) O(2) N(1) Yb(1) N(3) C(17) N(4) C(3)

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Figure 1. Molecular structure of cis-[Yb(XylForm)<sub>2</sub>(thf)<sub>2</sub>] (2; Hydrogen atoms are omitted for clarity and thermal ellipsoids are set to the 35% probability level). [Yb(MesForm)<sub>2</sub>(thf)<sub>2</sub>] (3), [Yb(EtForm)<sub>2</sub>(thf)<sub>2</sub>] (4), [Yb(o-PhPhForm)<sub>2</sub>(thf)<sub>2</sub>]·2THF (5), [Yb(DippForm)<sub>2</sub>(thf)<sub>2</sub>]·2THF (6) and [Eu(DippForm)<sub>2</sub>(thf)<sub>2</sub>]·2THF (8) are structurally similar.



Figure 2. Molecular structure of  $[Yb(TFForm)_2(thf)_3]$ -2 THF (7a). Hydrogen atoms are omitted for clarity and thermal ellipsoids are set to the 35% probability level.

Table 1. Selected bond lengths [Å] for  $[Yb(XylForm)_2(thf)_2]$  (2),  $[Yb(MesForm)_2(thf)_2]$  (3),  $[Yb(EtForm)_2(thf)_2]$  (4),  $[Yb(o-PhPhForm)_2(thf)_2]$ -2THF (5),  $[Yb(DippForm)_2(thf)_2]$ -2THF (6) and  $[Eu(DippForm)_2(thf)_2]$ -2THF (8)<sup>[a]</sup>.

| Complex      | 2        | 3        | 4        | 5        | 6              | 7        | 8              |
|--------------|----------|----------|----------|----------|----------------|----------|----------------|
| Yb(1)-N(1)   | 2.466(3) | 2.455(4) | 2.480(7) | 2.473(6) | 2.462(2)       | 2.577(5) | 2.593(7)       |
| Yb(1)-N(2)   | 2.476(3) | 2.481(4) | 2.478(6) | 2.519(7) | 2.462(2) (N1#) | 2.523(5) | 2.593(7) (N1#) |
| Yb(1)-N(3)   | 2.484(3) | 2.429(4) | 2.483(7) | 2.487(7) | 2.496(2) (N2)  | 2.593(4) | 2.597(6) (N2)  |
| Yb(1) - N(4) | 2.443(3) | 2.483(4) | 2.462(7) | 2.488(6) | 2.496(2) (N2#) | 2.486(5) | 2.597(6) (N2#) |
| Yb(1)-O(1)   | 2.429(3) | 2.441(4) | 2.409(6) | 2.425(6) | 2.461(2)       | 2.414(4) | 2.556(6)       |
| Yb(1)-O(2)   | 2.429(3) | 2.446(4) | 2.419(6) | 2.435(6) | 2.461(2) (O1#) | 2.431(4) | 2.556(3) (O1#) |
| Yb(1)-O(3)   | . ,      | . ,      | . ,      | . ,      | 2.420 (4)      |          | ,              |

[a] Symmetry operators used to generate equivalent atoms: #1 = -x, y, 3/2-z.

this study (Table 1). The o-PhPhForm ligands in 5 do not show any  $\pi$ -Ph···Yb interactions, because the shortest separation observed, 3.58 Å, is significantly larger than the accepted Ph(C)–Yb<sup>II</sup>  $\pi$ -bonding range of 2.76–3.18 Å as established in  $[Yb_2(Odpp)_4]$  (Odpp=2,6-diphenylphenolate).<sup>[32]</sup> The differences in corresponding bond lengths (Ln–N, O,  $\Delta$ 0.10–0.13 Å) between 6 and 8, are less than the difference in metal-centre ionic radii (0.15 Å),<sup>[24]</sup> indicating greater steric stress in 6. A surprising feature is the variation in the O-Yb-O angles (Table S1 in the Supporting Information), which cannot be wholly related to Form-ligand bulk. Whereas the smallest O-Yb-O angles are found in the structures of 6 and 8, consistent with the bulk of the DippForm ligand, the next smallest O-Yb-O angle is that found for the least bulky ligand, XylForm, in 2. Furthermore, the largest O-Yb-O angle is observed in 4, which has the second bulkiest Form ligand (EtForm).

In **7a** the coordination number is seven with two chelating TFForm ligands and three "pseudo-meridional" (that is, the ligands are located similarly to *mer*-ligands of octahedral complexes) thf donors (Figure 2). The higher coordination number can be attributed to a combination of reduced steric strain (*o*-F vs. *o*-Me), and the electron-withdrawing effect of the multiple fluorine substituents. Although the Yb–N bond lengths in **7a** (Table 1) are longer than those of **2–6** by more

comparable to the shorter Yb– O separations in **2–6**, reflecting the enhanced Lewis acidity of Yb resulting from the fluorinated ligands. Complex **7a** readily loses a thf ligand, as shown by the composition of the bulk material obtained from toluene, [Yb(TFForm)<sub>2</sub>-(thf)<sub>2</sub>], as was observed in **1–6**. All Yb…F interatomic distan-

than the amount expected for the change in ionic radius with

coordination number, the Yb-

O bond lengths (Table 1) are

ces ( $\geq$ 3.91 Å) are greater than the accepted distances for appreciable bonding contact.

The X-ray structure of 9 shows a fluoride-bridged dimer (Figure 3) in which the six-coordinate ytterbium atom is coordinated by two chelating formamidinate ligands and two bridging fluoride ligands. It is likely that 10, which could not be obtained as single crystals, has a similar structure on the basis of the  $\tilde{\nu}(Yb-F)$  absorptions observed (see discussion above). The Yb-N bond lengths (Table 2) found for 9 are shorter than those in 2-6 by approximately the expected difference (0.15 Å) for a change from six-coordinate  $Yb^{II}$  to Yb<sup>III</sup>. With bite angles approaching 60° and F–Yb–F angles of approximately 69° (see the Supporting Information), the coordination geometry of Yb in 9 is distorted trigonal prismatic. The Yb-F bond lengths are similar to those in a number of fluoride-bridged complexes. Examples of such complexes include [{YbCp<sub>2</sub>F(thf)}<sub>2</sub>],<sup>[21]</sup> [{Yb(MeCp)<sub>2</sub>F- $(thf)_{2}$ ,<sup>[22]</sup> [{Yb(OAr)<sub>2</sub>F(thf)}<sub>2</sub>]<sup>[22]</sup> (OAr = 2,6-di-*tert*-butyl-4Yphenolate; Y = tBu or H),  $[{YbCp_2F}_3]^{[22]}$  and  $[{Yb (MeCp)_{2}F_{4}]$ ,<sup>[22]</sup> in which, despite a variation of coordination numbers from 5 to 9, the Yb-F bond lengths fall within a narrow range (2.139(4)-2.143(9) Å). It seems that bulky alternatives to Cp ligands have much the same effect as Cp rings on bridging Ln-F distances, regardless of formal coordination numbers. As expected, the Yb-F bond lengths in 9

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Figure 3. Molecular structure of  $[\{Yb(EtForm)_2(\mu_2-F)\}_2]$  (9). Hydrogen atoms are omitted for clarity and thermal ellipsoids are set to the 35 % probability level.

Table 2. Selected bond lengths [Å] for  $[{Yb(EtForm)_2(\mu_2-F)}_2]$  (9).

| Atoms      | Length   | Atoms      | Length   | Atoms      | Length   |
|------------|----------|------------|----------|------------|----------|
| Yb(1)-N(1) | 2.309(3) | Yb(2)-N(5) | 2.338(3) | Yb(1)-F(1) | 2.177(2) |
| Yb(1)-N(2) | 2.315(3) | Yb(2)-N(6) | 2.305(3) | Yb(1)-F(2) | 2.168(2) |
| Yb(1)-N(3) | 2.341(3) | Yb(2)-N(7) | 2.334(3) | Yb(2)-F(1) | 2.179(2) |
| Yb(1)-N(4) | 2.306(3) | Yb(2)-N(8) | 2.302(3) | Yb(2)-F(2) | 2.160(2) |

are significantly longer than the terminal Yb–F bond lengths found in  $[Yb(C_5Me_5)_2F(OEt_2)]$  (2.015 Å)<sup>[23]</sup> and the six-coordinate  $[Tm(DippForm)_2F(thf)]$  (2.020(2) Å;<sup>[2]</sup> Tm<sup>3+</sup> and Yb<sup>3+</sup> have similar ionic radii<sup>[24]</sup>). Complex **9** appears to be the first crystallographically established example of a neutral ytterbium(III) fluoride-bridged amidinate complex.<sup>[1g–6]</sup> The related halogen-bridged Yb<sup>III</sup> amidinate compound  $[Yb_2(Me_3SiNC(Ph)N-(CH_2)_3NC(Ph)NSiMe_3)_2(\mu-Cl)_2(thf)]$  is the only

other known example of such a compound and has two inequivalent ytterbium centres (six and seven coordinate).<sup>[33]</sup>

The X-ray structures of **11** and **13** show sevencoordinate monomeric complexes with two chelating formamidinate ligands, a terminal chloride and two thf donors. The three unidentate ligands have a "pseudo-meridional" arrangement with the O atoms *cis* and O(1) *trans* to Cl(1) (Figure 4 for **11**). By contrast, **12** has a six-coordinate ytterbium atom with O(1) *cis* to Cl(1) (Figure 5). The change in coordination number is perhaps most clearly ex-

plained as arising from differences in crystallisation solvent (see discussion above). The Yb–N bond lengths in **12** (Table 3) are similar to those in the six-coordinate fluoridebridged dimer **9**. The Yb(1)–N and Yb(1)–Cl(1) bond lengths in **12** are shorter than the corresponding separations in seven-coordinate **11** by approximately 0.05 Å, which is similar to the difference in the appropriate ionic radii.<sup>[24]</sup> Surprisingly, the Yb–O distances in **11** are virtually the



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Figure 4. Molecular structure of  $[Yb(o-PhPhForm)_2Cl(thf)_2]$ -2 THF (11). Hydrogen atoms and lattice solvent have been omitted for clarity and thermal ellipsoids are set at 35%. Complex  $[Tb(DippForm)_2Cl-(thf)_2]$ -2.5THF (13) has a similar structure.



Figure 5. Molecular structure of [Yb(DippForm)<sub>2</sub>Cl(thf)]•THF (12). Hydrogen atoms and lattice solvent are omitted for clarity and thermal ellipsoids are set to the 35% probability level.

Table 3. Selected bond lengths [Å] for  $[Yb(o-PhPhForm)_2Cl(thf)_2]$ -2THF (11),  $[Yb-(DippForm)_2Cl(thf)]$ -THF (12) and  $[Yb(DippForm)_2Br(thf)]$ -Et<sub>2</sub>O (16).

| 11          |          | 12          | 2          | 16          |           |
|-------------|----------|-------------|------------|-------------|-----------|
| Atoms       | Length   | Atoms       | Length     | Atoms       | Length    |
| Yb(1)-O(1)  | 2.306(1) | Yb(1)-O(1)  | 2.3291(17) | Yb(1)-O(1)  | 2.343(2)  |
| Yb(1)–O(2)  | 2.323(1) | Yb(1)-N(1)  | 2.319(2)   | Yb(1)-N(1)  | 2.331(3)  |
| Yb(1)-N(1)  | 2.408(2) | Yb(1)-N(2)  | 2.357(2)   | Yb(1)-N(2)  | 2.361(3)  |
| Yb(1)-N(2)  | 2.338(2) | Yb(1)-N(3)  | 2.358(2)   | Yb(1)-N(3)  | 2.331(3)  |
| Yb(1)–N(3)  | 2.398(2) | Yb(1)-N(4)  | 2.310(2)   | Yb(1)-N(4)  | 2.366(3)  |
| Yb(1)-N(4)  | 2.389(2) | Yb(1)-Cl(1) | 2.5062(6)  | Yb(1)-Br(1) | 2.6659(7) |
| Yb(1)-Cl(1) | 2.562(1) |             |            |             |           |

same as in 12. The behaviour of 11 is associated with a *mer*array of unidentate ligands and mirrors the relationship between the Yb–O bond lengths in seven-coordinate 7a, which has *mer*-thf ligands, and those in the six-coordinate species 2–6.

Isotypic **14**, **15** and **16** (Figure 6) are isostructural with the corresponding chloride, **12**. There is some asymmetry in the DippForm chelation, as in **12**. As expected, the Yb–N and

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Figure 6. Molecular structure of  $[Yb(DippForm)_2Br(thf)] \cdot Et_2O$  (16). Hydrogen atoms and lattice solvent are omitted for clarity and thermal ellipsoids are set to the 35% probability level. Complexes [Ln-(DippForm)\_2Br(thf)] (Ln = La (14), Nd (15) have similar structures.

Yb–O bond lengths in **12** and **16** are comparable (Table 3). The Yb–Br bond length exceeds the corresponding Yb–Cl value by the amount expected from the  $Br^-$  and  $Cl^-$  ionic radii.<sup>[24]</sup> In **14** and **15** the expected difference<sup>[24]</sup> in Ln–N,O and Ln–Br bond lengths is observed.

#### Conclusion

A wide range of a rare class of divalent lanthanoid formamidinates,  $[Ln(Form)_2(thf)_2]$ , has been prepared by redox transmetallation/protolysis reactions. The complexes are generally monomeric with six-coordinate metal centres and *cis*-thf ligands. However,  $[Yb(TFForm)_2(thf)_3]$  (**7a**) with electron-withdrawing *o*-HC<sub>6</sub>F<sub>4</sub> substituents on the formamidinate ligands, is seven-coordinate with *mer*-thf ligands. The complexes are highly reactive in C–X (X=F, Cl, Br) activation reactions and provide access to a range of Ln<sup>III</sup> formamidinate complexes such as  $[{Yb(Form)_2F}_2]$  and [Yb- $(Form)_2X(thf)_n]$  (X = Cl or Br; *n* = 1 or 2). In addition, C–Br activation occurs durring the redox transmetallation/protolysis reactions between La, Nd or Yb, Hg(2-BrC<sub>6</sub>F<sub>4</sub>)<sub>2</sub> and HDippForm, yielding [Ln(DippForm)\_2Br(thf)] complexes.

#### **Experimental Section**

**General**: All manipulations were performed by conventional Schlenk and glovebox techniques under an atmosphere of purified nitrogen. Infrared spectra ( $\tilde{v}$ =4000–500 cm<sup>-1</sup>) of Nujol mulls, unless indicated otherwise, were recorded on a Perkin–Elmer 1600 Fourier transform infrared spectrometer. Far-IR spectra ( $\tilde{v}$ =500–100 cm<sup>-1</sup>) of Vaseline mulls were recorded on a Bruker 120HR spectrometer. <sup>1</sup>H NMR spectra of solutions in C<sub>6</sub>D<sub>6</sub> were recorded at 300.13 MHz and <sup>13</sup>C[<sup>1</sup>H] NMR spectra were recorded at 75.47 MHz on a Bruker AC 300 spectrometer at 303.2 K and at 400.13 MHz (<sup>1</sup>H) and 100.62 MHz (<sup>13</sup>C) on a Bruker AC 400 spectrometer at 303.2 K. Chemical shifts were referenced to the residual <sup>1</sup>H and <sup>13</sup>C resonances of deuterobenzene. <sup>19</sup>F NMR spectra were recorded on the Bruker AC300 spectrometer at 282.40 MHz and were referenced to external CFCl<sub>3</sub>. All microanalyses were carried out by the Campbell Microanalytical Laboratory, Chemistry Department, University of Otago, Dunedin, New Zealand. Metal analyses were carried out by EDTA titrations with Xylenol Orange indicator following acid digestion and buffering with hexamine. Melting points were determined in glass capillaries sealed under nitrogen and are uncalibrated. o-TolFormH, XylFormH, Mes-FormH, EtFormH, o-PhPhFormH and DippFormH were synthesised according to the published procedures<sup>[34]</sup> and [Na(DippForm)(thf)<sub>3</sub>] was prepared as reported.<sup>[3]</sup> Lanthanoid metals were purchased from Tianjiao (Baotou, China) or Santoku as metal ingots, stored under purified nitrogen and freshly filed prior to use. Polyfluoroaromatic compounds were obtained from Bristol Organics or Aldrich, perfluorodecalin from Avocado Chemicals and diphenylmercury, hexachloroethane and 1,2-dibromoethane from Aldrich. Bis(pentafluorophenyl)mercury  $^{\left[ 14\right] }$  and bis(2-bromo-3,4,5,6-tetrafluorophenyl)mercury<sup>[35]</sup> were prepared as reported. Caution! Diarylmercury compounds should be handled in a well-ventilated fume cupboard, protective gloves should be worn and residues should be included in heavy-metal waste or recycled as mercury metal. Tetrahydrofuran (THF) was pre-dried over sodium wire and freshly distilled from sodium benzophenone ketyl under nitrogen. Hexane and toluene were pre-dried over sodium and distilled from sodium under nitrogen.

#### Synthesis

TFFormH: 2,3,4,5-Tetrafluoroaniline (5.0 g, 0.030 mol) and a slight excess of triethyl orthoformate (2.78 g, 0.019 mol) were mixed in a flask charged with acetic acid (6 drops) catalyst. The unstoppered mixture was slowly stirred at 70 °C. The evaporated ethanol was replaced intermittently with hexane. After 1 h, hexane was no longer added and the solution was progressively cooled. After 15 min, stirring was stopped and a white precipitate settled. The pure white solid was collected and recrystallised from acetone to produce white blocks of TFFormH (4.74 g; 93%). M.p. 131-133 °C; <sup>1</sup>H NMR (300.13 MHz,  $C_6D_6$ , 303.2 K):  $\delta = 5.76$  (brs, 1H; C-NH), 6.74 ppm (s, 1H; N-CH=N); <sup>19</sup>F NMR (282.40 MHz, C<sub>6</sub>D<sub>6</sub>, 303.2 K): -139.7 (brs, 2F; F5), -155.2 (brs, 2F; F3), -156.6 (brs, 2F; F2),  $\delta =$ -163.38 ppm (brs, 2F; F4); IR (KBr):  $\tilde{\nu} = 3437$  (w), 3160 (m), 2726 (s), 2345 (w), 2200 (w), 1654 (vs),  $\approx 1520$  (vs), 1292 (s), 1261 (s), 1196 (s), 1124 (w), 1079 (s), 1055 (s), 1003 (m), 944 (s), 846 (s), 753 (s), 721 (s), 670 (vw), 591 (vw), 561 cm<sup>-1</sup> (vw); HRMS: (ESI): m/z calcd for  $C_{13}H_4N_2F_8 + H^+$ : 341.032 [*M*+H]; found: 341.032.

[Yb(o-TolForm)<sub>2</sub>(thf)<sub>2</sub>] (1): Method 1: Tetrahydrofuran (40 mL) was added to a Schlenk flask charged with an excess of freshly filed Yb metal (0.20 g, 1.15 mol), bis(pentafluorophenyl)mercury (0.54 g, 1.02 mmol) and o-TolFormH (0.45 g, 2.00 mmol) under purified nitrogen. The slurry was stirred at ambient temperature for 72 h before the red-coloured solution was filtered from the elemental mercury deposited and the excess of Yb metal. The solvent was removed in vacuo and the remaining material was extracted into THF (approximately 10 mL). The solution was concentrated (to 2-3 mL) and after standing at -6°C for several weeks no crystals formed and a red-coloured powder was obtained when all of the solvent was removed in vacuo to give 1 (0.58 g; 74%). M.p. 82-84°C, decomp 270°C; <sup>1</sup>H NMR (300.13 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = 1.53$  (br s, 8H; CH<sub>2</sub>, thf), 2.32 (s, 12H; CH<sub>3</sub>), 4.22 (brs, 8H; OCH<sub>2</sub>, thf), 6.92 (brm, 16H; ArH), 8.88 (br s, 2H; NC(H)N);  ${}^{13}C{H}$  NMR (75.47 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = 19.3$  (CH<sub>3</sub>), 26.6 (CH2, thf), 67.8 (OCH2, thf), 119.1 (Ar-CH), 121.7 (Ar-CH), 127.5 (Ar-CH), 130.5 (Ar-C), 131.0 (Ar-CH), 151.9 (Ar-CN), 163.5 (NC(H)N); IR (Nujol):  $\tilde{\nu} = 1665$  (s), 1595 (m–s), 1522 (s), 1302 (s), 1221 (s), 1183 (s), 1109 (s), 1031 (s), 980 (m), 934 (m), 877 (m), 837 (m), 775 (m), 751 (s), 719 (s), 613 cm<sup>-1</sup> (s); elemental analysis calcd (%) for  $C_{38}H_{46}N_4O_2Yb$ (763.85): C 59.75, H 6.07, N 7.33, Yb 22.65; found: C 58.95, H 5.98, N 7.54, Yb 23.02.

*Method* 2: Following the procedure used above, Yb metal (0.30 g, 1.74 mmol), HgPh<sub>2</sub> (0.35 g, 1.04 mmol) and *o*-TolFormH (0.45 g, 2.08 mmol) gave red complex **1** (0.51 g; 67%). M.p. 84–86°C, decomp 270°C; IR (Nujol): As for the product from method 1; elemental analysis calcd (%) for  $C_{38}H_{46}N_4O_2$ Yb (763.85): Yb 22.65; found: Yb 22.89.

**[Yb(XylForm)<sub>2</sub>(thf)<sub>2</sub>] (2):** Following the procedure used for **1**, Yb metal (0.20 g, 1.15 mol),  $Hg(C_6F_5)_2$  (0.49 g, 0.92 mmol) and XylFormH (0.46 g, 1.85 mmol) gave red rectangular crystals (0.42 g; 58%) of **2** from THF (2 mL) at room temperature. M.p. 182–186°C; <sup>1</sup>H NMR (300.13 MHz,  $C_6D_6$ ):  $\delta = 1.30$  (brs, 8H; CH<sub>2</sub>, thf) 2.16 (s, 24H; CH<sub>3</sub>), 3.58 (brs, 8H;

# **FULL PAPER**

OCH<sub>2</sub>, thf), 6.90 (t,  ${}^{3}J({}^{1}H, {}^{1}H) = 7.32$  Hz, 4H; H4); 7.06 (d,  ${}^{3}J({}^{1}H, {}^{1}H) =$ 7.34 Hz 8H: H3,5), 8.44 ppm (s, 2H: NC(H)N): <sup>13</sup>C{H} NMR(75.47 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = 20.2$  (CH<sub>3</sub>), 25.9 (CH<sub>2</sub>, thf), 68.8 (OCH<sub>2</sub>, thf), 126.2 (Ar-CH), 129.3 (Ar-CH), 132.2 (Ar-C), 141.9 (Ar-CN), 175.6 ppm (NC(H)N); <sup>171</sup>Yb NMR (52.55 MHz, C<sub>6</sub>D<sub>6</sub>/PhMe 1:4, 303 K):  $\delta = 668$  ppm (brs ( $\Delta w_{1/2} = 136$  Hz); after addition of THF (4 drops):  $\delta = 665 \text{ ppm} (\Delta w_{1/2} = 75 \text{ Hz})$ ; IR (Nujol):  $\tilde{\nu} = 1651 \text{ (m-s)}, 1594$ (m-s), 1536 (s), 1292 (s), 1232 (m), 1198 (s), 1092 (s), 1033 (s), 1004 (m), 934 (m), 918 (w-m), 879 (w-m), 760 (s), 699 cm<sup>-1</sup> (s); elemental analysis calcd (%) for C<sub>42</sub>H<sub>54</sub>N<sub>4</sub>O<sub>2</sub>Yb (819.96): C 61.47, H 6.64, N 6.83, Yb 21.10; found: C 61.10, H 6.34, N 6.41, Yb 20.70.

**[Yb(MesForm)<sub>2</sub>(thf)<sub>2</sub>] (3)**: Following the procedure used for **1**, Yb metal (0.20 g, 1.15 mol), Hg(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> (0.21 g, 0.40 mmol) and MesFormH (0.22 g, 0.81 mmol) gave red rectangular crystals (0.43 g; 65%) of **3** from THF (5 mL) at  $-6^{\circ}$ C. M.p. 176–178°C, decomp 280°C; <sup>1</sup>H NMR (300.13 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = 1.52$  (brs, 8H; CH<sub>2</sub>, thf), 1.90 (s, 12 H; *p*-CH<sub>3</sub>), 2.17 (s, 24 H; *o*-CH<sub>3</sub>), 3.32 (brs, 8H; OCH<sub>3</sub>, thf), 6.76 (brs, 8H; *m*-ArH), 8.33 ppm (s, 2H; NC(H)N); <sup>13</sup>C[H] NMR(75.47 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = 18.8$  (CH<sub>3</sub>), 21.2 (CH<sub>3</sub>), 26.1 (CH<sub>2</sub>, thf), 68.3 (OCH<sub>2</sub>, thf), 130.5 (Ar-CH), 134.5 (Ar-C), 135.5 (Ar-C), 141.7 (Ar-CN), 165.1 ppm (NC(H)N); <sup>171</sup>Yb NMR (52.55 MHz, C<sub>6</sub>D<sub>6</sub>/PhMe 1:4, 303 K):  $\delta = 678$  ppm (brs,  $\Delta w_{1/2} = 313$  Hz); IR (Nujol):  $\tilde{\nu} = 1663$  (m), 1531 (s), 1304 (m), 1287 (m), 1232 (m), 1213 (m), 1148 (w), 1073 (s), 1033 (s), 952 (w), 912 (w), 878 (w), 852 (m), 829 (w), 795 (w), 755 (m), 698 (s), 433 cm<sup>-1</sup> (w); elemental analysis calcd. (%) for C<sub>46</sub>H<sub>62</sub>N<sub>4</sub>O<sub>2</sub>Yb (876.06): C 63.07, H 7.13, N 6.40, Yb 19.75; found: C 62.41, H 7.07, N 6.61, Yb 19.66.

[Yb(EtForm)<sub>2</sub>(thf)<sub>2</sub>] (4): Following the procedure used for 1, Yb metal (0.20 g, 1.15 mol), Hg(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> (0.21 g, 0.40 mmol) and EtFormH (0.24 g, 0.80 mmol) gave red rectangular crystals (0.24 g; 65%) of 4 from THF (3 mL) at room temperature. M.p. 168-170°C; <sup>1</sup>H NMR (400.13 MHz,  $C_{h}D_{h}$ :  $\delta = 1.16$  (t,  ${}^{3}J({}^{1}H,{}^{1}H) = 7.4$  Hz, 24H; CH<sub>3</sub>), 1.23 (brs, 8H; CH<sub>2</sub>, thf), 2.75 (s,  ${}^{3}J({}^{1}H,{}^{1}H) = 7.4$  Hz, 16H; CH<sub>2</sub>), 3.53 (brs, 8H; OCH<sub>2</sub>, thf), 7.04 (t,  ${}^{3}J({}^{1}H,{}^{1}H) = 7.0$  Hz, 8H; Ar-H), 7.13 (d,  ${}^{3}J({}^{1}H,{}^{1}H) = 7.4$  Hz, 4H; Ar-H), 8.13 ppm (brs, 2H; NC(H)N); <sup>13</sup>C{H} NMR 100.62 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = 16.0$  (CH<sub>3</sub>), 25.0 (CH<sub>2</sub>, thf), 25.6 (CH<sub>2</sub>), 69.0 (OCH<sub>2</sub>, thf), 122.9 (Ar-CH), 126.4 (Ar-CH), 138.3 (Ar-C), 150.3 (Ar-CN), 167.5 ppm (NC(H)N); <sup>171</sup>Yb NMR (52.55 MHz, C<sub>6</sub>D<sub>6</sub>/PhMe 1:4, 303 K)  $\delta = 668$  ppm (brs,  $\Delta w_{1/2} = 95$  Hz); after addition of THF (4 drops):  $\delta = 657$  ppm (brs,  $\Delta w_{1/2} =$ 90 Hz); IR (Nujol):  $\tilde{\nu} = 1666$  (m), 1594 (m), 1525 (s), 1294 (s), 1256 (w), 1231 (s), 1192 (s), 1104 (m), 1073 (w), 1039 (m-s), 999 (w), 952 (w), 932 (w-m), 874 (w-m), 828 (w), 799 (w-m), 771 (m-s), 759 (s), 698 cm<sup>-1</sup> (s); elemental analysis calcd (%) for C<sub>50</sub>H<sub>70</sub>N<sub>4</sub>O<sub>2</sub>Yb (932.17): C 64.42, H 7.57, N 6.01, Yb 18.57; found: C 63.64, H 7.70, N 6.19, Yb 18.65.

[Yb(o-PhPhForm)2(thf)2]-2THF (5): Following the procedure used for 1, Yb metal (0.20 g, 1.15 mol), diphenylmercury (0.14 g, 0.32 mmol) and o-PhPhFormH (0.22 g, 0.63 mmol) gave red rectangular crystals (0.25 g, 81%) of 5 from THF (5 mL) at -6°C. M.p. 120-122°C, decomp > 300 °C; <sup>1</sup>H NMR (400.13 MHz, C<sub>6</sub>D<sub>6</sub>; loss of one THF of solvation):  $\delta = 1.34$  (brs, 12H; CH<sub>2</sub>, thf), 3.47 (brs, 12H; OCH<sub>2</sub>, thf), 6.81 (t, <sup>3</sup>J- $({}^{1}H,{}^{1}H) = 7.3$  Hz, 4H; p-ArH), 6.88 (d,  ${}^{3}J({}^{1}H,{}^{1}H) = 8.0$  Hz, 4H; m-ArH), 6.93 (td,  ${}^{3}J({}^{1}H,{}^{1}H) = 7.4$  Hz,  ${}^{4}J({}^{1}H,{}^{1}H) = 1.0$  Hz, 4H; *p*-ArH), 6.99 (t,  ${}^{3}J$ - $({}^{1}H,{}^{1}H) = 7.5 \text{ Hz}, 8 \text{ H}; m\text{-ArH}), 7.06 \text{ (d, } {}^{3}J({}^{1}H,{}^{1}H) = 7.0 \text{ Hz}, 8 \text{ H}; o\text{-ArH}),$ 7.14 (d,  ${}^{3}J({}^{1}H,{}^{1}H) = 7.1$  Hz, 4H; o-ArH), 7.21 (td,  ${}^{3}J({}^{1}H,{}^{1}H) = 7.7$  Hz,  ${}^{4}J$ - $({}^{1}H, {}^{1}H) = 1.6 \text{ Hz}, 4 \text{ H}; m-\text{ArH}), 8.93 \text{ ppm}$  (s,  ${}^{171}\text{Yb}$  satellites,  ${}^{3}J$ - $(^{171}Yb,^{1}H) = 44$  Hz, 2H; NC(H)N);  $^{13}C{H}$  NMR (100.62 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta =$ 26.0 (CH2, thf), 68.4 (OCH2 thf), 118.4 (Ar-CH), 121.5 (Ar-CH), 127.1 (Ar-CH), 128.9 (Ar-CH), 129.2 (Ar-CH), 130.0 (Ar-CH), 131.3 (Ar-CH), 134.5 (Ar-C), 144.3 (Ar-C), 149.3 (Ar-CN), 162.5 ppm (NC(H)N); <sup>171</sup>Yb NMR (52.55 MHz, C<sub>6</sub>D<sub>6</sub>, 303 K)  $\delta = 695$  ppm (brt,  $\Delta w_{1/2} = 55$  Hz, <sup>3</sup>J- $(^{171}\text{Yb}, ^{1}\text{H}) = 48 \text{ Hz}; \text{ NC(H)NYb}, \text{; IR (Nujol): } \tilde{\nu} = 1665 \text{ (m)}, 1597 \text{ (m)},$ 1520 (s), 1317 (s), 1265 (w), 1230 (s), 1159 (w), 1110 (w), 1073 (m), 1033 (m), 1008 (w), 947 (w), 921 (w-m), 874 (w), 829 (w-m), 776 (w), 760 (s), 746 (s), 699 (s), 612 (w), 434 cm<sup>-1</sup> (w); elemental analysis calcd (%) for C<sub>66</sub>H<sub>70</sub>N<sub>4</sub>O<sub>4</sub>Yb (1156.35): C 68.55, H 6.10, N 4.85, Yb 14.96; calcd (%) for C62H62N4O3Yb (loss of one THF of solvation; 1084.24): C 68.68, H 5.76, N 5.14, Yb 15.96; found: C 68.33, H 5.61, N 5.43, Yb 15.85.

**[Yb(DippForm)<sub>2</sub>(thf)<sub>2</sub>]-2 THF (6):** Ytterbium metal filings (0.12 g, 0.69 mmol), bis(pentafluorophenyl)mercury (0.37 g, 0.69 mmol) and

DippFormH (0.50 g, 1.37 mmol) in THF (50 mL) were stirred at ambient temperature for 24 h, yielding an orange solution after filtration. Evaporation to the point of crystallisation and cooling to -20°C for several days gave 6 (0.59 g; 72%) as large orange crystals. M.p. 232 °C (decomp), solvent loss at 108°C; <sup>1</sup>H NMR (300.1 MHz, C<sub>6</sub>D<sub>6</sub>, loss of THF of solvation):  $\delta = 1.16$  (d,  ${}^{3}J({}^{1}H, {}^{1}H) = 6.7$  Hz, 48H; CH(CH<sub>3</sub>)<sub>2</sub>), 1.34 (brm, 8H; thf), 3.37 (brm, 8H; thf), 3.55 (m, 8H; CH(CH<sub>3</sub>)), 7.07 (m, 8H; m-ArH), 7.12 (m, 4H; *p*-Ar*H*), 8.19 ppm (s, Yb<sup>171</sup> satellites,  ${}^{3}J({}^{1}H, {}^{171}Yb) = 45$  Hz, combined 15% by integration, 2H; NC(H)N); <sup>13</sup>C{<sup>1</sup>H} NMR (75.5 MHz,  $C_6D_6$ ):  $\delta = 25.3$  (CH(CH<sub>3</sub>)<sub>2</sub>), 28.4 (CH(CH<sub>3</sub>)<sub>2</sub>), 123.6 (Ar-CH), 123.8 (Ar-CH), 143.3 (Ar-C), 149.0 (Ar-C), 168.2 ppm (NCN); IR (Nujol): v=1922 (w), 1860 (w), 1793 (w), 1665 (m sh), 1592 (m), 1520 (s), 1439 (s), 1362 (msh), 1314 (m), 1293 (m), 1249 (m), 1233 (m), 1182 (msh), 1100 (m), 1090 (m), 1038 (m), 933 (m), 919 (m), 880 (m), 803 (msh), 758 cm<sup>-1</sup> (msh); elemental analysis calcd (%) for  $C_{66}H_{102}N_4O_4Yb$  (1188.58): C 66.69, H 8.65, N 4.71; calcd (%) for  $C_{58}H_{86}N_4O_2Yb$  (loss of THF of solvation; 1044.37): C 66.70, H 8.30, N 5.36; found: C 65.02, H 8.28, N 5.07. In a repeated synthesis of compound 6, orange crystals (0.47 g; 65%)identical to the above were obtained, the identity of which was confirmed by unit cell comparison. Crystal system: monoclinic: a = 23.85, b = 15.41. c = 19.99 Å;  $\beta = 115^{\circ}$ . M.p. 234–236 °C; <sup>1</sup>H and <sup>13</sup>C NMR spectra were in agreement with above; <sup>171</sup>Yb NMR (52.55 MHz, C<sub>6</sub>D<sub>6</sub>/PhMe, 303 K):  $\delta =$ 605 ppm (brt,  $\Delta w_{1/2} = 94$  Hz,  ${}^{3}J({}^{171}$ Yb,  ${}^{1}$ H) = 44 Hz; NC(H)NYb); elemental analysis calcd (%) for C<sub>58</sub>H<sub>86</sub>N<sub>4</sub>O<sub>2</sub>Yb (no THF of solvation; 1044.37): C 66.70, H 8.30, N 5.36, Yb 16.56; calcd for  $C_{62}H_{94}N_4O_3Yb$  (one THF of solvation; 1116.48): C 66.70, H 8.49, N 5.02, Yb 15.50; found: C 64.77, H 8.34. N 5.31. Yb 15.84.

[Yb(TFForm)<sub>2</sub>(thf)<sub>2</sub>] (7): Ytterbium metal (in large excess, 0.53 g, 3.06 mmol),  $Hg(C_6F_5)_2$  (0.31 g, 0.57 mmol) and TFFormH (0.39 g, 1.15 mmol) in THF (20 mL) were sonicated for one day. Once the mixture had settled, the solution was filtered to remove mercury and excess lanthanoid. Solvent and pentafluorobenzene were removed in vacuo. The resulting red powder was extracted into toluene and evaporated to dryness, giving red 7 (0.47 g; 82 %). M.p. 160-162 °C; <sup>1</sup>H NMR (300.13 MHz,  $C_6D_6$ , 303.2 K):  $\delta = 2.13$  (brs, 8H; thf), 3.51 (brs, 8H; thf), 6.56 (m, 4H; Ar-H), 7.96 ppm (s, 2H; N(CH)N); <sup>19</sup>F NMR (282.40 MHz, C<sub>6</sub>D<sub>6</sub>, 303.2 K):  $\delta = -136.0$  (s, 4F; Ar-F5), -152.0 (s, 4F; Ar-F3), -153.0 (s, 4F; Ar-F2), -162.9 ppm (s, 4F; Ar-F4); IR (Nujol): v=1622 (w-m), 1559 (m-s), 1298 (s), 1261 (s), 1199 (m), 1154 (m), 1073 (m), 1054 (m), 1023 (m), 974 (w), 938 (m), 861 (vw), 799 cm<sup>-1</sup> (w); UV/Vis (THF):  $\lambda_{max}$  ( $\epsilon$ ) =316 nm  $(13600 \text{ m}^{-1} \text{ cm}^{-1})$ ; elemental analysis calcd (%) for C34H22F16N4O2Yb (995.58): C 41.02, H 2.23, N 5.63, Yb 17.37; found: C 40.52, H 2.21, N 5.37, Yb 16.76.

Recrystallization of [Yb(TFForm)<sub>2</sub>(thf)<sub>2</sub>] from THF (5 mL) and cooling to  $-30^{\circ}$ C, yielded red crystals of [Yb(TFForm)<sub>2</sub>(thf)<sub>3</sub>]-2 THF (**7a**) suitable for X-ray crystallography after three months of storage at  $-30^{\circ}$ C. <sup>171</sup>Yb NMR: (52.55 MHz, C<sub>7</sub>D<sub>8</sub>, 303 K):  $\delta$ =501 ppm (brs).

**[Eu(DippForm)<sub>2</sub>(thf)<sub>2</sub>]-2 THF (8)**: Following the procedure used for **6**, europium metal filings (0.10 g, 0.66 mmol), bis(pentafluorophenyl)mercury (0.37 g, 0.69 mmol) and DippFormH (0.50 g, 1.37 mmol) in tetrahydrofuran (50 mL) were stirred at ambient temperature for 24 h and yielded a light-yellow solution after filtration. Concentration under reduced pressure until crystallisation and storage at  $-20^{\circ}$ C for several days gave large yellow crystals (0.26 g; 34%). M.p. 243 °C (decomp), solvent loss at 86 °C; IR (Nujol):  $\bar{\nu}$  = 1858 (w), 1793 (w), 1666 (msh), 1593 (m), 1530 (s), 1439 (s), 1360 (msh), 1317 (m), 1295 (m), 1255 (m), 1231 (m), 1182 (msh), 1098 (m), 1071 (m), 1054 (m), 1037 (m), 934 (m), 878 (m), 801 (msh), 766 (msh), 753 cm<sup>-1</sup> (msh); elemental analyses calcd (%) for C<sub>581</sub>H<sub>86</sub>EuN<sub>4</sub>O<sub>2</sub> (loss of THF of solvation; 1023.29): C 68.08, H 8.47, N 5.48; found: C 65.01, H 8.20, N 5.81.

In a repeated synthesis, compound **8** was similarly obtained (0.40 g, 60%) and confirmed by unit cell comparison. Crystal system: monoclinic; a = 23.90, b = 16.00, c = 18.79 Å;  $\beta = 114^\circ$ . M.p 218–220 °C; <sup>1</sup>H NMR (300.13 MHz, C<sub>6</sub>D<sub>6</sub>; satisfactory integration was not possible because of paramagnetic broadening):  $\delta = 1.00$  (brs, CH<sub>3</sub>), 1.30 (brm; thf), 3.10 (brm; thf), 3.40 (brm; CH(CH<sub>3</sub>)), 7.10 (brs; Ar-H), 10.01 ppm (brs; NC(H)N); <sup>13</sup>C NMR (75.47 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K):  $\delta = 23.8$  (CH(CH<sub>3</sub>)<sub>2</sub>),

28.1  $(CH(CH_3)_2)$ , 122.7, 123.9, 125.2, 138.8 (aromatic *C* resonances not assigned), 151.5 ppm (N*C*(H)N); elemental analysis calcd (%) for C<sub>58</sub>H<sub>86</sub>EuN<sub>4</sub>O<sub>2</sub>: (loss of THF of solvation; 1023.29): C 68.08, H 8.47, N 5.48, Eu 14.85; calcd (%) for C<sub>62</sub>H<sub>94</sub>EuN<sub>4</sub>O<sub>3</sub> (one THF of solvation; 1095.40): C 67.98, H 8.65, N 5.11, Eu 13.87; found: C 66.54, H 8.42, N 5.44, Eu 14.09.

$$\label{eq:product} \begin{split} & [\{ Yb(EtForm)_2(\mu_2\text{-}F)\}_2 ] \ (9): \mbox{ Perfluorodecalin } (0.08 \mbox{ g}, \ 0.19 \mbox{ mmol}) \mbox{ was} added to a red-coloured solution of 4 (0.18 \mbox{ g}, \ 0.19 \mbox{ mmol}) \mbox{ in THF} (10 \mbox{ mL}). The biphasic mixture was stirred for 24 h at room temperature. The resulting yellow solution was filtered to remove a green/grey precipitate and the solvent and other volatiles were removed under vacuum to give a yellow powder. The powder could be crystallised from hexane (3 \mbox{ mL}) at room temperature to give yellow block-shaped crystals (0.060 g; 40\%); IR (Nujol): <math display="inline">\tilde{\nu} = 1667$$
 (s), 1588 (m), 1519 (s), 1277 (s), 1202 (m), 1187 (m), 1102 (brm), 1015 (brm), 950 (w), 864 (w), 807 (m), 762 (m), 722 (w), 668 (w), 518 (w), 413 (m), 402 \mbox{ cm}^{-1} (m); It was not possible to obtain ^1H or ^{19}F NMR spectra because of the paramagnetic properties of the compound; elemental analysis calcd (%) for C\_{8t}F\_2H\_{108}N\_8Yb\_2 (1613.19): C 62.51, H 6.74, N 6.94; found: C 62.18, H 6.71, N 6.83. No infrared absorption peaks were observed for the grey precipitate between  $\tilde{\nu} = 4000 \mbox{ and }600 \mbox{ cm}^{-1}; m, p. > 360 \mbox{°C}. \end{split}$ 

**[{Yb(o-PhPhForm)<sub>2</sub>(\mu-F)}<sub>2</sub>] (10):** Perfluorodecalin (0.08 g, 0.18 mmol) was added to a red-coloured solution of **5** (0.20 g, 0.18 mmol) in THF (15 mL). The biphasic mixture was stirred for 24 h at room temperature. The resulting yellow precipitate (0.12 g; 38%) was filtered from a red solution and washed with THF (5 mL; the red solution was concentrated and left to crystallise at  $-6^{\circ}$ C. No crystals were obtained). M.p. 166-170°C, decomp 240–242°C; IR (Nujol):  $\tilde{\nu}$ =1663 (m), 1595 (m–s), 1533 (s), 1302 (s), 1214 (s), 1178 (w), 1158 (m), 1110 (w–m), 1066 (s), 1051 (w), 1030 (m), 1008 (w–m), 992 (s), 944 (s), 913 (s), 876 (s), 830 (m), 770 (s), 727 (s), 718 (s), 702 (s), 611 cm<sup>-1</sup> (m); far-IR (vaseline):  $\tilde{\nu}$ =565 (m), 547 (m), 512 (brm), 492 (w), 247 (m), 390 (s), 370 (sh w), 336 (sbr), 298 (m–s), 282 (sh w), 259 (w), 204 (s), 164 cm<sup>-1</sup> (w); elemental analysis calcd (%) for C<sub>100</sub>F<sub>2</sub>H<sub>76</sub>N<sub>8</sub>Yb<sub>2</sub> (1774.49): C 67.71, H 4.32, N 6.32, Yb 19.51; found: C 66.61, H 4.59, N 6.24, Yb 19.61.

**[Yb(o-PhPhForm)<sub>2</sub>Cl(thf)<sub>2</sub>]-2 THF (11)**: THF (10 mL) was added to a Schlenk flask charged with compound **5** (0.44 g, 0.44 mmol) and hexachloroethane (51 mg, 0.22 mmol). The mixture turned yellow and it was stirred at room temperature for 1 h. The solvent was removed under reduced pressure to give a yellow powder (0.45 g, 0.38 mmol, 86%). M.p. 132–134°C; IR (Nujol):  $\bar{\nu}$ =1661 (m), 1590 (shw), 1569 (shw), 1538 (s), 1298 (s), 1262 (sh w), 1205 (m), 1109 (m), 1070 (m), 1052 (shw), 1019 (m), 991 (w), 939 (m) 912 (m), 866 (m), 762 (m), 738 (s), 699 cm<sup>-1</sup> (s); far-IR (vaseline):  $\bar{\nu}$ =614 (m), 562 (s), 550 (s), 537 (s), 519 (s), 506 (s), 479 (w), 452 (w), 390 (sbr), 371 (shw), 340 (w), 327 (w), 289 (w), 261 (m-s), 248 (m-s), 217 (w), 200 (w), 187 (w), 160 (w), 148 (w), 125 cm<sup>-1</sup> (w); <sup>1</sup>H NMR (300.13 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$ =12.1 ppm (brs, NC(*H*)N), the rest of the spectrum could not be integrated owing to paramagnetic broadening, precluding unequivocal assignments.

A second reaction solution of **11** was concentrated, left to crystallise and small yellow needles formed at -4 °C after 5 days. After 10 weeks crystals suitable for X-ray crystal structure analysis were obtained.

**[Yb(DippForm)<sub>2</sub>Cl(thf)]·THF (12):** A solution of 1,2-dichloroethane (0.12 g, 1.2 mmol) in toluene (10 mL) was added, with stirring, at ambient temperature, to an orange solution of **6** (1.04 g, 1.0 mmol) in toluene (40 mL). The solution was heated to 70 °C and was kept, with stirring, at this temperature for 2 h. The volume of solution was reduced to 10 mL under vacuum and stored at -30 °C for 2 d, during which time bright-yellow crystalline complex **12** precipitated and was collected (0.74 g, 68 %). M.p. 280–284 °C; IR (Nujol):  $\tilde{\nu}$ =1592 (w), 1526 (s), 1461 (s), 1361 (w), 1319 (m), 1273 (s), 1236 (w), 1194 (m), 1179 (w), 1316 (w), 1008 (w), 1055 (w), 1043 (w), 1015 (m), 947 (w), 934 (w), 861 (w), 800 (m), 773 (m), 756 (m), 670 cm<sup>-1</sup> (w); elemental analysis calcd (%) for C<sub>54</sub>H<sub>78</sub>ClN<sub>4</sub>OYb (loss of lattice thf; 1007.72): C 64.36, H 7.80, N 5.56; found C 64.38, H 8.02, N 5.51.

 $[Tb(DippForm)_2Cl(thf)_2]$ -2.5THF (13): A colourless solution of [Na-(DippForm)(thf)\_3] (1.00 g, 1.66 mmol) in THF (50 mL) was added to a pale-yellow solution of anhydrous TbCl<sub>3</sub> (0.15 g, 0.57 mmol) in THF

(50 mL). The resulting colourless solution was stirred at room temperature overnight, filtered and concentrated until crystallization (approximately 10 mL). Storage at 0°C for 2 d yielded [Tb(DippForm)<sub>2</sub>Cl-(thf)<sub>2</sub>]-2.5THF as colourless rhombohedral prisms (0.27 g; 38%). M.p. 198°C; IR (Nujol):  $\tilde{\nu}$  = 1928 (w), 1867 (w), 1800 (w), 1667 (s), 1587 (m), 1520 (s), 1361 (m), 1279 (s), 1235 (s), 1189 (s), 1097 (m), 1039 (m), 1014 (m), 934 (m), 860 (w), 823 (w), 800 (m), 756 cm<sup>-1</sup> (m); elemental analysis calcd (%) for C<sub>68</sub>H<sub>106</sub>ClN<sub>4</sub>O<sub>4.5</sub>Tb (1245.94): C 65.55, H 8.58, N 4.50; calcd (%) for C<sub>58</sub>H<sub>86</sub>ClN<sub>4</sub>O<sub>2</sub>Tb (loss of lattice thf; 1065.71): C 65.37, H 8.13, N 5.26; found: C 65.29, H 8.21, N 5.37.

[La(DippForm)<sub>2</sub>Br(thf)] (14): Tetrahydrofuran (20 mL) was added to a Schlenk flask charged with freshly filed La metal (0.07 g, 0.50 mmol), Hg-(2-BrC<sub>6</sub>F<sub>4</sub>)<sub>2</sub> (0.45 g, 0.69 mmol) and DippFormH (0.50 g, 1.37 mmol). The colourless slurry was stirred at ambient temperature overnight to give a pale-yellow reaction mixture. Filtration, to remove elemental mercury and excess La metal, followed by removal of volatiles under vacuum gave an off-white solid that crystallised from toluene (4-5 mL) as pure 14 upon standing at ambient temperature for several days (0.17 g; 37%). M.p. 273 °C (decomp); IR (Nujol): v=1926 (w), 1860 (w), 1797 (w), 1667 (s), 1586 (s), 1381 (m), 1362 (m), 1334 (s), 1296 (s), 1235 (m), 1188 (s), 1107 (m), 1046 (w), 1013 (m), 934 (w), 824 (m), 800 (m), 756 (s), 728 (w), 674 (w),  $608\ \text{cm}^{-1}$  (m);  $^1\text{H}\ \text{NMR}$  (300.13 MHz,  $C_6D_6,$  vacuum dried sample, THF lost):  $\delta = 1.26$  (d,  ${}^{3}J({}^{1}H, {}^{1}H) = 6.8$  Hz, 48H; CH<sub>3</sub>, *i*Pr), 3.61 (septet,  ${}^{3}J_{HH} = 6.8$  Hz, 8H; CH, *i*Pr), 7.17 (m, 12H; Ar-H), 8.28 ppm (s, 2H; NC(H)N); <sup>13</sup>C<sup>1</sup>H} NMR (vacuum dried sample):  $\delta = 24.1$  (CH<sub>3</sub>, *i*Pr), 28.7(CH, iPr), 123.8 (Ar-CH), 125.4 (Ar-CH), 143.5 (Ar-C), 146.4 (Ar-C), 170.0 ppm (NC(H)N); elemental analysis calcd (%) for C54H78BrLaN4O (1018.02): C 63.71, H 7.72, N 5.50; calcd for C<sub>50</sub>H<sub>70</sub>BrLaN<sub>4</sub> (THF lost; 945.93): C 63.49, H 7.46, N 5.92; found: C 64.03, H 7.89, N 5.28. The <sup>1</sup>H NMR spectrum of the crude product showed evidence of the presence of o-HC<sub>6</sub>F<sub>4</sub>O(CH<sub>2</sub>)<sub>4</sub>(DippForm)<sup>[2,5]</sup> (Scheme 3), as confirmed by a unit cell determination of hand picked single crystals.

**[Nd(DippForm)<sub>2</sub>Br(thf)] (15):** Following a similar procedure to that for the synthesis of **14**, Nd metal (0.08 g, 0.55 mmol), Hg(2-BrC<sub>6</sub>F<sub>4</sub>)<sub>2</sub> (0.45 g, 0.69 mmol) and DippFormH (0.51 g, 1.40 mmol) gave blue-green blocks of **15** upon recrystallisation from toluene (approximately 4 mL) at 0 °C (0.22 g; 47 %). M.p. 279 °C (decomp); IR (Nujol):  $\bar{\nu}$  = 1936 (w), 1868 (w), 1797 (w), 1666 (s), 1592 (s), 1389 (s), 1366 (s), 1316 (m), 1278 (m), 1231 (s), 1192 (s), 1108 (m), 1044 (w), 1014 (m), 944 (m), 860 (w), 830 (w), 800 (m), 757 (s), 729 (w), 700 (s), 670 cm<sup>-1</sup> (w); <sup>1</sup>H NMR (300.13 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = −3.28 (brs, 48H; CH<sub>3</sub>, *i*Pr), 1.93 (m, 4H; CH<sub>2</sub>), 2.39 (brs, 8H; CH, *i*Pr), 3.89 (m, 4H; OCH<sub>2</sub>), 7.61 (m, 12H; Ar-H), 9.37 ppm (brs, 2H; NC(H)N); elemental analysis calcd (%) for C<sub>54</sub>H<sub>78</sub>BrN<sub>4</sub>NdO (1023.35): C 63.38, H 7.68, N 5.47; found: C 63.25, H 7.37, N 5.54. The co-product *o*-HC<sub>6</sub>F<sub>4</sub>O(CH<sub>2</sub>)<sub>4</sub>(DippForm) was characterised as for **14**.

**[Yb(DippForm)<sub>2</sub>Br(thf)]·Et<sub>2</sub>O (16)**: *Method 1*: Following a similar procedure to that for the synthesis of **14**, Yb metal (0.12 g, 0.69 mmol), Hg(2-BrC<sub>6</sub>F<sub>4</sub>)<sub>2</sub> (0.45 g, 0.69 mmol) and DippFormH (0.50 g, 1.37 mmol) gave a dark yellow solution in THF (50 mL) that was stirred overnight. Filtration, and removal of volatiles under vacuum gave a light-yellow microcrystalline powder that was recrystallised as dark-yellow prismatic crystals (0.43 g; 55%) from diethyl ether (50 mL) at  $-30^{\circ}$ C. M.p. 270°C (decomp). The co-product o-HC<sub>6</sub>F<sub>4</sub>O(CH<sub>2</sub>)<sub>4</sub>(DippForm) was detected as for **14**.

*Method* 2: 1-Bromo-2,3,4,5-tetrafluorobenzene (0.10 mL, 0.81 mmol) was added dropwise by syringe to a stirred deep-orange solution of **6** (0.15 g, 0.13 mmol) in diethyl ether (50 mL). The resulting yellow solution was stirred for 2 h, filtered and dried in vacuo for 2 h to yield **16** as a light-yellow powder (0.12 g, 84%). M.p. 268 °C (decomp); IR (Nujol):  $\bar{\nu}$ =1926 (w), 1860 (w), 1796 (w), 1666 (s), 1586 (s), 1381 (s), 1361 (s), 1334 (s), 1297 (s), 1254 (m), 1235 (s), 1188 (s), 1107 (m), 1096 (m), 1055 (m), 1013 (m), 957 (w), 934 (m), 884 (w), 825 (s), 800 (s), 757 (s), 674 (w), 608 cm<sup>-1</sup> (w); elemental analysis (vacuum dried sample) calcd (%) for C<sub>54</sub>H<sub>78</sub>BrN<sub>4</sub>OYb (loss of Et<sub>2</sub>O of crystallisation; 1052.15): C 61.64, H 7.47, N 5.32; calcd (%) for C<sub>58</sub>H<sub>88</sub>BrN<sub>4</sub>O<sub>2</sub>Yb (retention of THF and Et<sub>2</sub>O; 1126.27): C 61.85, H 7.88, N 4.97; found: C 62.25, H 7.55, N 5.04.

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#### **Control experiments:**

 $Hg(C_6F_5)_2$  and XylFormH: In a pre-weighed conical flask,  $Hg(C_6F_5)_2$ (0.10 g, 0.18 mmol) and XylFormH (0.09 g, 0.37 mmol) were dissolved in pre-dried THF (20 mL) and the conical flask was stoppered. The clear solution was left to stir at room temperature in air for 48 h. The solvent was removed by slow evaporation and the white material remaining (0.19 g) was weighed and characterised by IR spectroscopy. IR (Nujol):  $\tilde{v}=1649$  (s), <u>1637</u> (s), <u>1588</u> (s), <u>1578</u> (w), <u>1560</u> (w), <u>1556</u> (s), <u>1509</u> (s), <u>1473</u> (s), 1310 (s), <u>1277</u> (m), 1250 (s), 1201 (s), <u>1148</u> (s), 1091 (s), <u>1069</u> (vs), 1034 (m), <u>1018</u> (m), 1001 (w), 983 (w), <u>965</u> (vs), 924 (w), 820 (w), <u>807</u> (s), 758 (s), <u>719</u> (m), <u>668</u> (w), 661 (m), 620 cm<sup>-1</sup> (m; Underlined values correspond to the absorption bands for Hg(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> and others correspond to the absorption bands for XylFormH).

 $Hg(C_6F_5)_2$  and o-PhPhFormH: Following the procedure used in control experiment 1,  $Hg(C_6F_5)_2$  (0.10 g, 0.18 mmol) and o-PhPhFormH (0.12 g, 0.36 mmol) gave a white powder (0.22 g) which was identified by IR spectroscopy as above as the starting materials.

*Yb metal and XylFormH*: Tetrahydrofuran (15 mL) was added to a flask charged with excess Yb metal (0.05 g, 0.28 mmol) and XylFormH (0.05 g, 0.19 mmol) and left to stir at room temperature under purified N<sub>2</sub>. The clear solution was filtered and the solvent was removed under vacuum to give a white powder, which was identified as XylFormH by IR spectroscopy. IR (Nujol):  $\tilde{\nu}$ =1649 (s), 1588 (s), 1556 (s), 1464 (s), 1367 (s), 1311 (s), 1250 (s), 1203 (s), 1148 (s), 1091 (s), 1034 (m), 1001 (w), 985 (w), 924 (w), 820 (w), 758 (s), 661 (m), 620 cm<sup>-1</sup> (m).

**X-ray crystallography**: Crystalline samples of compounds **2–9** and **11–16** were mounted on glass fibres in highly viscous silicone oil at 123(2) K. A summary of the crystallographic data can be found in Table S5 in the Supporting Information. Data were collected on an Enraf–Nonius Kappa CCD or a Bruker X8 APEX CCD (compound **7a**) diffractometer with graphite monochromated  $Mo_{K\alpha}$  X-ray radiation ( $\lambda$ =0.71073 Å). Data were corrected for absorption by the DENZO-SMN package.<sup>[36]</sup> Lorentz polarisation and absorption corrections were applied. Structural solution and refinement were carried out with the SHELX suite of programs<sup>[37]</sup> with the graphical interface X-Seed.<sup>[38]</sup> Hydrogen atoms were refined as described in the .cif files.

CCDC-895082 (2), 895083 (3), 895084 (4), 895085 (5), 895086 (6), 895087 (7), 895088 (8), 895089 (9), 895090 (11), 895091 (12), 895092 (13), 895093 (14), 895094 (15) and 895095 (16) 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.

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