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The synthesis and structures of rare earth 2-fluorophenyland 2,3,4,5-tetrafluorophenyl-*N*,*N*′-bis(aryl)formamidinate complexes [☆]



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ABSTRACT

Redox transmetallation/protolysis (RTP) reactions between free rare-earth metals (La, Nd, or Yb), Hg (C_6F_5)₂, and FFormH (FFormH = *N*,*N*'-bis(2-fluorophenyl)formamidine) in thf afforded four rare-earth complexes: trivalent [La(FForm)₃(thf)₂]-thf, [Nd(FForm)₃(thf)_x], [Yb(FForm)₃(thf)] (when a slight excess of Yb was used), and divalent [Yb(FForm)₂(thf)₂] (when a large excess of Yb was used). With the exception of [Yb(FForm)₃(thf)], the complexes did not readily crystallise from thf. However, crystallisation from either dme (La, Yb) or diglyme (Nd), produced single crystals of [La(FForm)₃(dme)], [Yb(FForm)₂(dme)₂], and [Nd(FForm)₃(diglyme)], respectively. A Nd complex of *N*,*N*'-bis(2,3,4,5-tetrafluorophenyl)formamidine (TFFormH): [Nd(TFForm)₃(dme)], was also prepared by a similar RTP reaction, and was crystallised from dme. Heating the previously reported divalent TFForm complex: [Yb(TFForm)₂(thf)₂] from PhMe, or the mixed oxidation state, solvent separated ion pair (SSIP) [Yb(TFForm)(diglyme)₂][Yb (TFForm)₄] from diglyme. The SSIP complex is the first crystallographically characterised trivalent ytterbium complex coordinating four discrete amidinate ligands.

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1. Introduction

In efforts to explore *N*-donor based alternatives to cyclopentadienyl-type ligands [1–10], our attention has focused on the coordination of *N*,*N*'-bis(aryl)formamidinate ligands ({ArForm}⁻), to rareearth metals [11–17]. ArFormH ligands can be readily prepared from an acid catalysed reaction between a functionalised aniline and triethyl orthoformate (Scheme 1) [12,18].

Thus, with a wide variety of different ArForm ligands available, several different aspects of rare-earth ArForm chemistry has been investigated, providing $[Ln(ArForm)_3(solv)_n]$ (n = 0-2) [11] and $[Ln (ArForm)_2(solv)_n]$ (n = 2, 3) [12] complexes. Through the coordination of the sterically demanding DippForm (DippFormH = N,N'-bis (2,6-diisopropylphenyl)formamidine) ligand to rare-earth ions, it is possible to generate terminal fluorides, namely $[Ln(DippForm)_2F$ (thf)] (Ln = La, Ce, Nd, Sm, Tm) [11,17], from C–F activation reactions, or products from the reduction of benzophenone or CS₂

[20]. When ArForm ligands of low bulk are coordinated, namely *N*,*N'*-bis(4-methylphenyl)formamidinate (*p*-TolForm), the thf solvated complexes, [Ln(*p*-TolForm)₃(thf)₂] (Ln = La, Ce, Nd, Sm), rapidly dimerise into [{Ln(*p*-TolForm)₃}₂] (Ln = La, Ce, Nd, Sm), losing coordinated thf under mild conditions and adopting μ -1 κ (*N*,*N'*):2 κ (*N*,*N'*) coordination [14].

Recently fluorinated based ArForm ligands have attracted our attention [13,21]. We recently reported that homoleptic $[La(CF_3Form)_3]$ (CF_3FormH = N,N'-bis(2-trifluoromethylphenyl)formamidine), when heated in PhMe [13], rapidly decomposes via a C-F activation pathway forming LaF₃ and two organic species obtained from the combination of three CF₃Form ligands with one CF₃ group completely de-fluorinated [13]. In coordination chemistry, increasing the number of fluorine atoms on the phenyl substituent of the ArForm ligand has an impact on the coordination chemistry of divalent ArForm complexes. When TFForm (TFFormH = N,N'-bis(2,3,4,5-tetrafluorophenyl) formamidine) was coordinated to divalent ytterbium [12], it crystallised from a thf solution as seven coordinate [Yb(TFForm)₂(thf)₃]·2thf, whereas all non-fluorinated ArForm divalent ytterbium compounds crystallised with two coordinated thf ligands, [Yb(ArForm)₂(thf)₂], (e.g. ArForm = *N*,*N*'-bis(2,6-dimethylphenyl)formamidinate, or DippForm) [12]. Such an observation is rationalised by the increase



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Scheme 1. Synthesis of N,N'-bis(aryl)formamidines (ArFormH) [12,18], and common ArFormH abbreviations [12,13,15,19].

in Lewis acidity of Yb²⁺ induced by the electron withdrawing fluorine substituents of the TFForm ligand, thereby allowing a higher coordination number.

Herein, we report the coordination of *N*,*N*'-bis(2-fluorophenyl)formamidinate (FForm) to rare-earth metals: Yb, La, and Nd, isolating a divalent Yb complex, and three trivalent (La, Nd and Yb) complexes. In addition, a trivalent neodymium TFForm complex has been also prepared by RTP reactions. Heating known divalent [Yb(TFForm)₂(thf)₃] [12] in either PhMe or diglyme caused separation of the trivalent species [Yb(TFForm)₃(thf)₂] (from PhMe), or the mixed oxidation state, solvent separated ion pair (SSIP) [Yb (TFForm)(diglyme)₂][Yb(TFForm)₄] (from diglyme). Both were structurally characterised. These are the first reported eight coordinate trivalent ytterbium ArForm complexes, and the SSIP contains the first trivalent ytterbium complex coordinating four discrete amidinate ligands.

2. Results and discussion

2.1. Synthesis of rare-earth ArForm complexes

The rare-earth ArForm (FForm, or TFForm) complexes are synthesised by redox transmetallation/protolysis (RTP) reactions between Ln^0 metal (Ln = La, Nd, Yb), Hg(C_6F_5)₂, and ArFormH (FFormH, or TFFormH) in thf (Scheme 2).

The RTP reactions provide an effective route to both divalent (Yb) and trivalent (La, Nd, Yb) rare-earth complexes, giving good (50% [Yb(FForm)₃(thf)], (**Yb3**)) to high yields (82%,

[Yb(FForm)₂(thf)₂] (**Yb1**)). Varying the excess of Yb metal used in the RTP reaction enables either divalent or trivalent products. From thf solutions, the FForm compounds **Yb1**, $[La(FForm)_3(thf)_2]$ thf (**La1**), and the Nd analogue $[Nd(FForm)_3(thf)_x]$ (x = 1-2), required substantial amounts of vacuum drving to remove solvent. Although single crystals could not be obtained, the thf:ArForm ratio for **Yb1** and **La1** was determined by ¹H NMR spectroscopy. The IR spectrum of La1 suggested that there was both coordinating thf (893 cm^{-1}), and non-coordinating (926 cm^{-1}) thf. Thus, it is likely that one of the thf molecules is a lattice solvate. This is supported by comparison with the cerium *N*,*N*'-bis(2,6-diflorophenyl)formamidinate (DFForm) analogue, [Ce(DFForm)₃(thf)₂],[15] which has only two coordinated thf molecules, with a more fluorinated ligand, and the o-TolForm La analogue, which has two coordinating thf ligands and is a mono thf solvate, namely [La(o-TolForm)₃ $(thf)_2$ · thf [11].

The inability of the FForm complexes to crystallise readily from thf is surprising considering how easily other ArForm complexes crystallise from thf [11–13,15,21,22]. However, single crystals are obtained when the FForm complexes are crystallised from either dme (**La1**, **Yb1**), or diglyme/hexane ("[Nd(FForm)₃(thf)_x]") solutions, giving [La(FForm)₃(dme)] (**La2**), [Yb(FForm)₂(dme)₂] (**Yb2**), and [Nd(FForm)₃(diglyme)]·diglyme (**Nd1**·diglyme), respectively. Nevertheless, crystals of the trivalent ytterbium species [Yb (FForm)₃(thf)] (**Yb3**), are readily obtained from a thf/hexane solution. The neodymium *N*,*N*·-bis(2,3,4,5-tetrafluorophenyl)formamidinate complex, [Nd(TFForm)₃(dme)] (**Nd2**), is readily prepared from RTP reactions in thf, followed by crystallisation from a dme/PhMe solution. It is noteworthy that before dissolution in



Scheme 2. Synthesis of rare-earth ArForm (ArForm = FForm, or TFForm) complexes by RTP reactions. (i) Yb⁰ (excess), Hg(C₆F₅)₂, 2 FFormH, thf, sonication 1 d, $-Hg^0$, $-2C_6F_5H$; (ii) La⁰, 1.5 Hg(C₆F₅)₂, 3 FFormH, thf, 60 °C 2 d, -1.5 Hg⁰, $-3C_6F_5H$; (iii): Nd⁰, 1.5 Hg(C₆F₅)₂, 3 FFormH, thf, sonication 2 d, -1.5 Hg⁰, $-3C_6F_5H$; (iii) diglyme/hexane; (iv) Yb⁰ (slight excess), 1.5 Hg(C₆F₅)₂, 3 FFormH, thf, room temperature, 2 d, -1.5 Hg⁰, $-3C_6F_5H$; (va): Nd⁰, 1.5 Hg(C₆F₅)₂, 3 TFFormH, thf, sonication 2 d, -1.5 Hg⁰, $-3C_6F_5H$; (vb) evaporation then crystallisation from dme/PhMe.

dme, the thf adduct did not require substantial vacuum drying to give a fine flowing powder by contrast with **Yb1**, **La1** and [Nd (FForm)₃(thf)_x].

When the divalent TFForm complex, [Yb(TFForm)₂(thf)₃] (**Yb4**) [12], was heated in PhMe, the complex remained soluble. Upon several cycles where the solution was evaporated to dryness and redissolved in PhMe, a dark red insoluble precipitate formed, with a light yellow supernatant solution. Separation, concentration, and crystallisation of the yellow residue from a PhMe/hexane solution, gave a few yellow block crystals. X-ray crystallographic analysis revealed the formation of trivalent [Yb(TFForm)₃(thf)₂]·thf/1/2hexane (Yb5). Considering that it was crystallised from a PhMe/Hexane solution, it is surprising that the molecule contains two bound thf molecules and a lattice thf molecule. In contrast, Yb3 contains only one thf ligand when crystallised from a thf/hexane solution. It may be that **Yb5** is a trace trivalent impurity from the initial synthesis of **Yb4**, and through the heating and evaporation cycles, Yb5 eventually liberates thf, forming the dark red insoluble powder (probably [Yb(TFForm)₂]) leaving residual **Yb5** in solution. When Yb4 was heated in diglyme, a similar process occurred. A red precipitate formed with a light yellow solution. Crystallisation of the yellow product from a PhMe/hexane solution yielded two small crystals of a mixed oxidation state, solvent separated, ion pair: [Yb(TFForm)(diglyme)₂][Yb(TFForm)₄] (**Yb6**). Two previous SSIP rare-earth ArForm complexes have either Na or K counter ions [14,17], by contrast with the two Ln complexes of the present product.

Complex purity was established by either micro elemental analysis (**Yb2**, **Nd1**·diglyme, **Nd2**, **Yb3**) or metal analysis (**La2**). For complexes **Yb2**, **La2** and **Yb3**, the analyses corresponded to the crystal composition. However for **Nd1**·diglyme, the elemental analysis indicated loss of half the lattice diglyme molecule as **Nd1**·1/2diglyme. Upon further drying the lattice diglyme is completely removed, as indicated by the absence of free diglyme in the ¹H NMR spectrum of **Nd1**. The X-ray data for **Nd2** indicated the presence of two disordered, low occupancy PhMe molecules, but due to their disorder they were omitted from the refinement process (see X-ray experimental). Nevertheless, the elemental analysis indicated the retention of half a PhMe molecule upon drying the sample, giving the formula for the bulk product as [Nd(TFForm)₃(dme)]·1/2PhMe (**Nd2**·1/2PhMe).

2.2. Structural discussion

Crystal data for [Yb(FForm)₂(dme)₂] (Yb2) were solved and refined in the monoclinic space group C_2/c , with half the molecule (i.e. [Yb_{0.5}(FForm)(dme)]), occupying the asymmetric unit (full molecule shown in Fig. 1, left). The ytterbium atom is coordinated by two-*trans* κ -(*N*,*N'*)FForm ligands, and two dme ligands, giving the ytterbium centre a coordination number of eight. Not only does Yb2 have the highest coordination number for a divalent ytterbium ArForm complex (previous highest: seven coordinate, see above) [12], but it also has the largest ArForm-ArForm trans angle for rare-earth ArForm complexes (C7-Yb-C7': 179.68(16)°), and the dme ligands also coordinate *trans* to each other (centroid(C15/ C16)–Yb1–centroid(C15'/C16'): 179.48(15)°). There are several examples of divalent Ln complexes with two dme ligands crystallographically characterised [23], but the vast majority contain *cisoid* anionic ligands [23], such as [Yb(N(SiMe₃)Ph)₂(dme)₂] (N-Yb-N': 110.09(7)) [24], or $[Yb(Ph_2pz)_2(dme)_2]$ $(Ph_2pzH = 3,$ 5-diphenylpyrazole, N_(centroid)-Yb-N'_(centroid): 101.37(11)) [25], but eight coordinate $[Yb(Azin)_2(dme)_2]$ (AzinH = 7-azaindole) [26], has a similar ligand array to **Yb2**, but with a much smaller transoid angle (C9-Yb1-C18: 141.5(2)°).

X-ray data for $[La(FForm)_3(dme)]$ (**La2**) were solved and refined in the monoclinic space group $P2_1/n$, with the whole molecule within the asymmetric unit. The lanthanum atom is coordinated by three terminal $\kappa(N,N')$ FForm ligands, and one chelating dme ligand, giving the lanthanum atom a coordination number of eight. The only two other eight coordinated trivalent ArForm complexes similar to **La2** are [Ce(DFForm)_3(thf)_2] [15], and [La(*o*-TolForm)_3(thf)_2]·thf [11]. Of these two examples, the FForm array in **La2** resembles that of [La(*o*-TolForm)_3(thf)_2]·thf, as each FForm or *o*-TolForm ligand coordinates in an independent ligand plane (meaning there are three NCN ArForm planes and one solvent plane), whereas there are two coordination planes in



Fig. 1. Molecular structures of [Yb(FForm)₂(dme)₂] (**Yb2**, *left*), and [La(FForm)₃(dme)] (**La2**, *right*). Ellipsoids shown at 50% probability, and hydrogen atoms removed for clarity. Selected bond lengths (Å) and angle (°) for **Yb2**: Yb1–N1: 2.502(4), Yb1–N2: 2.515(4), Yb1–O1: 2.605(3), Yb1–O2: 2.608(3), C1–Yb1–C1': 179.70. Selected bond lengths (Å) and angle (°) for **La2**: La1–N1: 2.578(7), La1–N3: 2.551(7), La1–N4: 2.617(7), La1–N5: 2.577(6), La1–N6: 2.580(6), La1–O1: 2.599(6), La1–O2: 2.660(6), C7–La1–C20: 133.6(2), C20–La1–C33: 87.1(2), C33–La1–C7: 108.4(2).

[Ce(DFForm)₃(thf)₂] (one slightly twisted plane containing two DFForm ligands, and one plane containing one DFForm ligand and two thf ligands). This difference in arrangement might be attributed to the size of the rare-earth metal, as the ArForm coordination in the complex [Yb(*o*-TolForm)₃(thf)] of the smaller Yb³⁺, also exhibits two ligand planes: one ligand plane containing two *o*-TolForm ligands, and one plane containing the thf and the third *o*-TolForm ligand [11]. It is noteworthy that with the bulkier *N*,*N*'-bis(2,6-diethylphenyl)formamidinate (EtForm) complexes, [Ln(EtForm)₃] (Ln = La, Ce, Nd, Sm), the EtForm coordination array is the same across all the metals [11,15].

The structure of [Nd(FForm)₃(diglyme)]·diglyme (Nd1·diglyme) was solved and refined in the monoclinic space group C2/c with the whole molecule and one diglyme of crystallisation within the asymmetric unit (Fig. 2, left). The neodymium atom is coordinated by three terminal $\kappa(N,N')$ FForm ligands, and one diglyme ligand. giving the neodymium atom a coordination number of nine. Although a high coordination number for trivalent ArForm complexes, higher numbers of 10 and 12 are known in the unsolvated complexes [Ce(DFForm)₃], and [La(CF₃Form)₃], respectively [13,27], owing to intramolecular Ln-F interactions. However, dissolution of [Ce(DFForm)₃] in thf produces eight coordinate [Ce(DFForm)₃(thf)₂], a process which is irreversible [15], and nine coordinate [Ln(ArForm)₃(thf)₃] complexes are not known. The steric repulsion by diglyme is less than that of three thf ligands. Nd1 contains three ligand planes, one plane containing two FForm ligands (C7, C33), one plane has the diglyme ligand, and one plane the final FForm ligand (C20). It is noteworthy that C20 of the third FForm ligand is anent the diglyme coordination plane, with the nitrogen atoms (N3, N4) being perpendicular to this plane. Surprisingly, a search of the Cambridge structural database indicated there are currently no crystallographically characterised rare-earth amidinate complexes with diglyme ligated in a $\kappa(0,0',0'')$ manner [23], and only one other ArForm complex containing coordinating diglyme, namely $[{Eu_2(FForm)_3(O_2)(OH)(diglyme)}_2]$ where the diglyme ligand is bridging in a μ_2 -1 κ (0,0'):2 κ (0") manner [22].

X-ray data for Nd2 were solved and refined in the triclinic space group $P\bar{1}$ with two molecules within the asymmetric unit (Fig. 2. right, only one representative molecule shown). Two highly disordered, low occupancy PhMe molecules were present in the asymmetric unit, but due to difficulties in their refinement, their electron density was removed by the SQUEEZE program. The Nd atom is coordinated by three terminal $\kappa(N,N')$ TFForm ligands, and one dme molecule, giving the Nd centre a coordination number of eight. Nd2 is the first reported example of a trivalent rareearth TFForm complex. Unlike Nd1 and La2 which have the FForm ligands dispersed around the metal coordination sphere, the TFForm ligands in Nd2 favour one side of the coordination sphere, coordinating away from the dme ligand. This close TFForm-TFForm proximity gives rise to very low C-Nd-C angles (e.g. C7-Nd1-C20: 86.09(11)°). With the exception of Yb5, each trivalent complex has at least one small C-Ln-C angle. However in Nd2 the sum of all three C-Nd-C' angles (294.13°) is much smaller than the sum of the analogous angles of Nd1 (324.27°), La2 (329.1°), **Yb3** (337.4°) or **Yb5** (359.98°). There appear to be no obvious supramolecular interactions (e.g. o-H···F) which provide a significant influence to the TFForm coordination.

The X-ray data for [Yb(FForm)₃(thf)] (**Yb3**), were solved and refined in the monoclinic space group $P2_1/c$, with the whole molecule within the asymmetric unit (Fig. 3, *left*). The seven coordinate ytterbium complex has two coordination planes, one with two $\kappa(N, N')$ FForm ligands (N1, N2; N3, N4) and one plane coordinating one thf and one FForm ligand (N5, N6).

The trivalent TFForm complex **Yb5**, crystallises in the triclinic space group $P\bar{1}$ with the whole molecule, a thf molecule, and a half hexane molecule within the asymmetric unit (Fig. 3, *right*). There are two clear coordination planes within the molecule, one coordinating two TFForm ligands (N1, N2/N3, N4), and the other containing the two thf ligands and a TFForm ligand (N5/N6). Unlike the arrangement in **Nd2**, the TFForm ligands are distributed evenly around the ytterbium centre, giving rise to large C–Yb–C' angles (sum: 359.98°). The additional thf molecule in the crystal structure



Fig. 2. Molecular structures of [Nd(FForm)₃(diglyme)]diglyme (**Nd1**, *left*), and [Nd(TFForm)₃(dme)] (**Nd2**, *right*). Ellipsoids shown at 50% probability, hydrogen atoms and lattice solvent were removed for clarity. Selected bond lengths (Å) and angle (°) for **Nd1**: Nd1–N1: 2.495(3), Nd1–N2: 2.645(3), Nd1–N3: 2.555(3), Nd1–N4: 2.570(3), Nd1–N5: 2.486(3), Nd1–N6: 2.615(3), Nd1–O1: 2.598(2), Nd1–O2: 2.574(2), Nd1–O3: 2.634, C7–Nd1–C20: 102.38(10), C20–Nd1–C33: 87.66(10), C33–Nd1–C7: 134.23(11). Selected bond lengths (Å) and angle (°) for **Nd2**: Nd1–N1: 2.539(4), Nd1–N2: 2.539(3), Nd1–N3: 2.596(3), Nd1–N4: 2.515(3), Nd1–N5: 2.507(3), Nd1–N6: 2.545(3), Nd1–O1: 2.498(3), Nd1–O2: 2.515(3), C7–Nd1–C20: 86.09(11), C20–Nd1–C33: 91.91(11), C33–Nd1–C7: 116.13(11).



Fig. 3. Molecular structures of [Yb(FForm)₃(thf)] (**Yb3**, *left*), and [Yb(TFForm)₃(thf)₂]-thf/1/2Hexane (**Yb5**-thf/1/2Hexane, *right*). Ellipsoids shown at 50% probability, hydrogen atoms and lattice solvent were removed for clarity. Selected bond lengths (Å) and angle (°) for **Yb3**: Yb1–N1: 2.356(3), Yb1–N2: 2.380(3), Yb1–N3: 2.353(3), Yb1–N4: 2.368 (3), Yb1–N5: 2.349(3) Yb1–N6: 2.379(3), Yb1–O1: 2.314(2). C7–Yb1–C20: 141.3(1); C20–Yb1–C33: 91.87(10), C33–Yb1–C7: 104.23(10). Selected bond lengths (Å) and angle (°) for **Yb5**: Yb1–N1: 2.450(5), Yb1–N2: 2.376(4), Yb1–N3: 2.462(4), Yb1–N4: 2.387(4), Yb1–N5: 2.448(4), Yb1–N6: 2.446(4), Yb1–O1: 2.351(4), Yb1–O2: 2.355(4), C7–Yb1–C20: 136.00(14); C20–Yb1–C33: 112.43(15), C33–Yb1–C7: 111.55(14), O1–Yb1–O2: 153.36(12).

of **Yb5** compared with mono-solvated **Yb3**, highlights the increase in the Lewis acidity of Yb³⁺ from the greater number of electron withdrawing fluorine substituents in TFForm. TFForm ligands, and divalent Yb2, coordinated by one terminal κ (*N*,*N*') TFForm ligand, and two tridentate diglyme ligands.

The X-ray data for the mixed oxidation state, SSIP complex, [Yb (TFForm)(diglyme)₂][Yb(TFForm)₄] (**Yb6**), were solved and refined in the triclinic space group $P\bar{1}$, with the whole ion pair within the asymmetric unit (Fig. 4). The SSIP contains two eight coordinate ytterbium atoms, trivalent Yb1, which has four terminal $\kappa(N,N')$

Analysis of the Yb–N bond lengths between the two metals indicates that the average Yb–N distances are: 2.42 Å for Yb1 and 2.50 Å for Yb2, indicating that Yb1 is trivalent (*cf.* **Yb5**: <Yb–N>:2.43 Å), and Yb2 is divalent (*cf.* **Yb2**: <Yb–N>:2.51 Å). However, the difference is less than that (0.16 Å) between the ionic radii of eight coordinate Yb²⁺ and Yb³⁺ [28]. Compound **Yb6**



Fig. 4. Molecular structure of [Yb(TFForm)(diglyme)₂][Yb(TFForm)₄] (**Yb6**). Atoms shown are as spheres, and hydrogen atoms were removed for clarity. Selected bond lengths (Å) for **Yb6**: Yb1–N1: 2.398(10), Yb1–N2: 2.445(10), Yb1–N3: 2.447(10), Yb1–N4: 2.402(9), Yb1–N5: 2.430(11), Yb1–N6: 2.374(9), Yb1–N7: 2.482(9), Yb1–N8: 2.392(11), Yb2–N9: 2.518(10), Yb2–N10: 2.485(9), Yb2–O1: 2.487(9), Yb2–O2: 2.515(8), Yb2–O3: 2.553(9), Yb2–O4: 2.552(9), Yb2–O5: 2.521(9), Yb2–O6: 2.502(9).

contains the third example of a rare-earth complex coordinating four ArForm ligands to the metal centre, with the first example being tetravalent $[Ce(p-TolForm)_4]$ [15], and the other being charge separated [K(18-Crown-6)][Sm(p-TolForm)₄] [14]. However, what distinguishes Yb6 from these examples, is the coordination of four ArForm ligands to a much smaller ytterbium(III) ion. The additional electron withdrawing fluorine atoms make TFForm a weaker Lewis base than other ArForm ligands (hence weaker/longer bonds to Yb³⁺), but also increases the Lewis acidity of the metal. Thus, reduced steric repulsion due to the longer Yb-N bond lengths, allows the coordination of four TFForm ligands to Yb³⁺. Currently Yb6 this is the only crystallographically characterised example of a tetrakisamidinatoytterbium complex. However, there is one similar example with two dianionic di-benzamidinate ligands. namely N.N'-propane-1.3-divlbis(N''-(trimethylsilyl) benzamidinate) (benz), in [Li(dme)₂][Yb(benz)₂] [29]. In addition, there are no mixed oxidation state Yb SSIP complexes separated by diglyme, though there are a few examples separated by dme [30-34]. Of these examples, those with amide based ligands have two dianionic ligands around one ytterbium centre [30,31], such as with (Z)-ethene-1,2-diylbis((2,6-di-isopropyl-phenyl) amide) in $[Yb(tBuC(NC_6H_3-2,6-iPr_2)_2](dme)_2][{2,6-iPr_2C_6H_3NC}]$ $(H) = C(H)NC_6H_3 - 2, 6 - iPr_2 + 2 Yb [30].$

3. Conclusion

A series of rare-earth FForm complexes have been synthesised by means of redox transmetallation/protolysis reactions between free metals (Yb, La, Nd), $Hg(C_6F_5)_2$, and N,N'-bis(2-fluorophenyl)formamidine in thf. When an excess of Yb metal was used, a divalent complex was isolated, and crystallisation from dme gave the first eight coordinate Yb^{II} ArForm complex, [Yb(FForm)₂(dme)₂]. When only a small excess of Yb metal was used a trivalent species [Yb(FForm)₃(thf)] was isolated in moderate yield. Two other trivalent FForm complexes were isolated, namely [La(FForm)₃ (dme)] and [Nd(FForm)₃(diglyme)]. In addition, three N,N'-bis (2,3,4,5-tetrafluorophenyl)formamidinate (TFForm) complexes were obtained, one synthesised from an RTP reaction in thf, and crystallised from dme/PhMe, namely [Nd(TFForm)₃(dme)]. The other two TFForm complexes were isolated in trace amounts, from heating divalent [Yb(TFForm)₂(thf)₃] in PhMe or diglyme giving [Yb (TFForm)₃(thf)₂] (from PhMe), and a mixed oxidation state SSIP, [Yb(TFForm)(diglyme)₂][Yb(TFForm)₄] (from diglyme). The complexes are the first reported examples of eight coordinate ytterbium(III) ArForm complexes.

4. Experimental

4.1. General

All products, and Ln⁰ starting materials, are extremely air- and moisture-sensitive, requiring use of both vacuum line and glovebox techniques, with manipulations performed under a nitrogen atmosphere. Solvents (thf, PhMe, hexane, diglyme, dme) were dried/purified by distillation over sodium (hexane, PhMe) or sodium benzophenone ketyl (thf, dme, diglyme), and stored in J. Young Teflon valve ampoules. Metals were purchased from Santuko America and were freshly filed before use. NMR experiments were recorded on a Bruker Avance 300 MHz spectrometer. Samples were analysed in J. Young NMR tubes, protecting the samples from air. For compounds **Yb1**, **La1** and **La2**, the NCHN integration was lower than the expected, possibly owing to broadened resonances. All ¹⁹F NMR spectra reported were {¹H} decoupled. Microanalyses were performed on the bulk material by the elemental analysis service of the Campbell Microanalytical Service of The University of Otago New Zealand or the Elemental analysis service of London Metropolitan University (**Yb3**). IR spectra were recorded on a Perkin–Elmer 1600 Fourier transform infrared spectrometer ($\tilde{v} = 4000-500 \text{ cm}^{-1}$) as mulls in sodium-dried Nujol, or for **Yb3** dissolved in C₆D₆ and pressed in between NaCl plates. Melting points were measured in sealed glass ampoules under nitrogen and are uncalibrated. Hg(C₆F₅)₂ [35], and TFFormH [12] were synthesised by literature procedures.

4.2. FFormH

FFormH was synthesised by a modification of a literature procedure [18]: 2-fluoroaniline (5.5 g, 0.05 mol) and triethyl *ortho*formate (3.3 g, 0.03 mol) were stirred at 70 °C in an unstoppered round bottom flask with six drops of acetic acid added. The evolved ethanol, was replaced intermittently with hexane. After one hour the solution was slowly cooled to RT, and the resulting pure white solid was filtered off and recrystallised once from acetone, giving thin white needles of FFormH. Yield: 5.5 g, (96%); mp 159– 160 °C, (lit. mp 153 °C) [36]; IR (KBr, cm⁻¹): v = 3434 m, 3120 m, 3026 m, 2879 ms, 1671 vs 1618 m, 1606 m, 1589 m, 1518 m, 1494 s, 1468 s, 1454 s, 1321 s, 1272 wm, 1247 m, 1230 s, 1185 s, 1100 s, 1036 s, 997 s, 931 m, 846 m, 808 s, 744 s, 628 w, 609 wm, 559 wm, 508 w, 493 w, 469 w, 456 w; ¹H NMR (C₆D₆, ppm): $\delta = 7.45$, br s, 1H, NCHN; 6.99–6.87, m, 6H, Ar-H(3,5,6); 6.79–6.65, m, 2H, Ar-H(4); ¹⁹F NMR (C₆D₆, ppm): δ : –130.0, s.

4.3. [Yb(FForm)₂(thf)₂] (Yb1)

Yb⁰ (0.57 g, 3.2 mmol, excess), Hg(C₆F₅)₂ (0.31 g, 0.57 mmol), and FFormH (0.27 g, 1.2 mmol) were dissolved in thf (20 mL), and sonicated at 60 °C for one day. Once the mixture had settled, the solution was filtered and evaporated to dryness *in vacuo*. The resulting deep red powder was quickly washed with cold PhMe and evaporated to dryness giving red [Yb(FForm)₂(thf)₂]. Yield: 0.36 g, (80%); mp 218–222 °C; IR (Nujol, cm⁻¹): *v* = ~1570 w, 1529 s, 1305 s, 1261 s, 1172 m, 1150 m, 1099 m, 1032 m, 950 vw, 900 vw, 847 vw, 802 s, 722 s; ¹H NMR (C₆D₆, ppm): *δ* = 9.15, br s, 1H (expected 2H), NCHN; 7.00–6.38, m, 16H, Ar-H; 3.85, br s, 8H, α-thf; 2.47, br s, 8H, β-thf; ¹⁹F NMR (C₆D₆, ppm): *δ* = −128.9, s.

4.4. [Yb(FForm)₂(dme)₂] (Yb2)

[Yb(FForm)₂(thf)₂] (0.30 g, 0.38 mmol) was dissolved in dme (5 mL), concentrated *in vacuo*, filtered and stored at -30 °C, producing thick orange block crystals. X-ray crystallographic analysis revealed the formation of [Yb(FForm)₂(dme)₂]. Yield: 0.21 g, (69%); mp 222–226 °C; IR (Nujol, cm⁻¹): $v = \sim 1570$ m, 1534 s, 1305 m, 1261 s, 1229 m, 1099 s, 1019 m, 862 vw, 845 w, 800 m, 742 m, 722 m; ¹H NMR (C₆D₆, ppm): $\delta = 9.04$ s, 2H, NCHN; 6.94, br m, 12H, Ar-H(3,5,6); 6.64, s, 4H, Ar-H(4); 3.29, br s, 20H, dme; ¹⁹F NMR (C₆D₆, ppm): $\delta = -128.9$, br s; ¹⁷¹Yb NMR (C₆D₆ and C₇D₈, ppm) 490 s; *Anal.* Calc. for C₃₄H₃₈N₄O₄Yb (815.75): C, 50.06; H, 4.69; N, 6.87. Found: C, 49.89; H, 4.68; N, 7.00%.

4.5. [La(FForm)₃(thf)₂]·thf (La1)

 La^0 (0.32 g, 0.23 mmol, excess), $Hg(C_6F_5)_2$ (0.58 g, 1.1 mmol), and FFormH (0.50 g, 2.2 mmol) were stirred at 60 °C in thf for two days. Once the mixture had settled, the solution was filtered and evaporated to dryness *in vacuo*. The resulting yellow powder was washed with PhMe, and evaporated to dryness to yield colourless [La(FForm)₃(thf)₂]·thf (La1). Yield: 0.59 g, (78%); mp 122–124 °C; IR (Nujol, cm⁻¹): v = 1671 w, 1605 m, 1577 m, 1538 s, 1306 s, 1259 w, 1228 m, 1154 w, 1100 m, 1031 s, 985 w, 944 w, 926 w, 893 vw, 845 vw, 806 w, 722 w; ¹H NMR (C₆D₆, ppm): $\delta = 8.92$, br s, 2H, NCHN (expected 3H); 7.03–6.91, br m, 16H, Ar-*H*; 6.90–6.69, br m, 8 H, Ar-*H*; 3.97, s, 12H, α-thf; 1.43, s, 12H, β-thf; ¹⁹F NMR (C₆D₆, ppm): $\delta = -127.4$, s.

4.6. [La(FForm)₃(dme)] (La2)

La1 (0.40 g, 0.43 mmol) was dissolved in dme (20 mL). The solution was concentrated, filtered, and stored at -30 °C. After three weeks, thick colourless crystals formed and X-ray crystallography revealed the formation of [La(FForm)₃(dme)] (La1). Yield: 0.25 g, (71%); mp 164–166 °C; IR (Nujol, cm⁻¹): v = 1673 w, 1605 m, 1537 vs 1307 s, 1230 vs 1204 ms, 1155 m, 1102 s, 1061 s, 1035 s, 990 m, 946 m, 865 m, 847 m, 809 m, 747 vs 612 w; ¹H NMR (C₆D₆, ppm): $\delta = 9.08$, br s, 2.5H, NCHN (expected 3H); 6.94, br s, 6 H, Ar-H; 6.75, m, 12H, Ar-H; 6.61, m, 6H, Ar-H; 3.32, s, 4H, dme-CH₂, 3.0, s, 6H, dme-CH₃. ¹⁹F NMR (C₆D₆, ppm): $\delta = -127.5$ s; *Anal.* Calc. for C₄₃H₃₇F₆LaN₆O₂ (922.70): La, 15.05. Found: La, 14.77%.

4.7. [Nd(FForm)₃(diglyme)] (Nd1)

Nd⁰ (0.36 g, 2.5 mmol, excess), $Hg(C_6F_5)_2$ (0.56 g, 1.0 mmol), and FFormH (0.48 g, 2.1 mmol) were sonicated in thf (20 mL) for two days. Once the mixture had settled, the light blue solution was filtered and evaporated to dryness in vacuo. The resulting light blue powder was dissolved in diglyme (10 mL), and concentrated in vacuo. Layering with hexane and storage at -30 °C afforded light blue needles. X-ray crystallography revealed the formation of [Nd (FForm)₃(diglyme)]·diglyme (Nd1·diglyme), however exposure of the crystals to vacuum gave [Nd(FForm)₃(diglyme)] (Nd1) as a light blue powder. Yield: 0.47 g, (69%); mp 110–114 °C; IR (Nujol, cm^{-1}): v = 1601 m, 1572 vs 1537 vs 1353 s, 1312 vs 1261 m, 1239 s, 1217 s, 1195 ms, 1103 s, 1055 s, 992 m, 940 m, 875 m, 849 m, 806 m, 750 vs 612 vw; ¹H NMR (C_6D_6 , ppm): δ = 16.80, br s, 3H, NCHN; 7.27-7.16, br m, 18H, Ar-H(3,5,6); 6.57, br s, 6H, Ar-H(4); 3.08, br m, 6H, CH₃-diglyme; -1.84, br m, 8H, CH₂-diglyme; ¹⁹F NMR (C₆D₆, ppm): δ = -132.9, br s; Anal. Calc. for C₄₈H₄₈F₆N₆NdO_{4.5} (1039.16, loss of half lattice diglyme, performed on crystals which were partially dried): C, 55.47; H, 4.66; N, 8.08. Found: C, 55.41; H, 4.98; N, 8.12%.

4.8. [Nd(TFForm)₃(dme)] (Nd2)

Nd⁰ (0.38 g, 2.6 mmol, excess), Hg(C₆F₅)₂ (0.56 g, 1.0 mmol), and TFFormH (0.71 g, 2.1 mmol) were sonicated for two days in thf (20 mL). Once the mixture had settled, the light blue solution was filtered and evaporated to dryness *in vacuo*. The resulting light blue powder was dissolved in dme (10 mL), concentrated *in vacuo*, and slight amounts of PhMe were added. Large yellow block crystals were obtained at $-30 \,^{\circ}$ C suitable for X-ray crystallography, revealing the formula [Nd(TFForm)₃(dme)]-1/2PhMe (Nd2·1/2PhMe). Yield: 0.73 g, (81%); mp 158–161 °C; IR (Nujol, cm⁻¹): v = 1625 w, 1559 m, 1507 s, 1299 s, 1262 s, 1209 w, 1161 w, 1052 m, 975 wm, 941 wm, 862 w, 801 w, 722 ms; *Anal.* Calc. for C_{46.5}H₂₃F₂₄N₆NdO₂ (1297.92): C, 43.03; H, 1.78; N, 6.45. Found: C, 43.00; H, 1.53; N, 6.60%.

4.9. [Yb(FForm)₃(thf)] (Yb3)

 Yb^0 (0.13 g, 0.75 mmol, small excess), $Hg(C_6F_5)_2$ (0.52 g, 0.98 mmol), and FFormH (0.46 g, 2.0 mmol) were stirred in thf (15 mL) for two days at R.T. Once the mixture had settled, the

solution was filtered and evaporated to dryness *in vacuo*. The yellow powder was dissolved in thf (3 mL), layered with hexane (1 mL), heated to 60 °C, and slowly allowed to cool, resulting in thick yellow block crystals. X-ray crystallographic analysis performed on the crystals, giving the formula of [Yb(FForm)₃(thf)] (**Yb3**), Yield: ~0.31 g (~50%); mp 144–146 °C; IR (C₆D₆, cm⁻¹): $\tilde{\nu}$ = 1647 ms, 1653 ms, 1617 s, 1577 vs 1492 vs 1453 vs 1419 w, 1393 m, 1329 vs 1305 vs 1258 s, 1236 vs 1202 m, 1188 m, 1162 w, 1102 s, 1034 s, 998 s, 954 m, 925 m, 868 ms, 849 s, 812 vs 750 vs 731 m. ¹H NMR (C₆D₆, ppm): δ = 86.55, br s, 12H, Ar-H; 5.21, br s, 8H, thf; ¹⁹F NMR (C₆D₆, ppm): δ = -115.34, br s; *Anal.* Calc. for C₄₃H₃₅F₆N₂OYb (938.84): C, 55.01; H, 3.76; N, 8.95. Found: C, 55.73; H, 3.67; N, 9.00%.

4.10. [Yb(TFForm)₃(thf)₂] (**Yb5**) and [Yb(TFForm)(diglyme)₂][Yb (TFForm)₄] (**Yb6**)

[Yb(TFForm)₂(thf)₃] (Yb4, 0.22 g, 0.21 mmol) was synthesised by a literature procedure [12], and dissolved in PhMe (20 mL). The red solution was stirred at 90 °C for two days. The solution was evaporated (whilst hot) to dryness (*in vacuo*) and fresh PhMe was added. This process was repeated twice. Upon standing at RT a red powder and yellow solution formed. After separation from the insoluble red powder, the yellow solution was layered with hexane mixture and stored at -30 °C producing several small yellow block crystals after three days. X-ray crystallographic analysis of the crystals revealed the formation and crystallisation of of [Yb (TFForm)₃(thf)₂].thf.1/2hexane (**Yb5**.thf.1/2hexane); Yield: <2%; mp 160-162 °C. A similar experiment was performed where Yb4 was heated in diglyme at 60 °C for two days. After heating, the mixture separated into a yellow solution and red precipitate. After separation from the red powder, the yellow solution was evaporated to dryness in vacuo. The resulting light yellow powder was dissolved in a PhMe and hexane mixture, and stored at $-30 \circ C$, producing two yellow block crystals after 10 days. One of the crystals were suitable for X-ray crystallographic analysis, revealing the formation of [Yb(TFForm)(diglyme)₂][Yb(TFForm)₄] (Yb6).

4.11. X-ray crystallography

Complexes were measured on either a Bruker APEX II CCD diffractometer (**Yb2**, **La2**, **Nd1** diglyme, **Nd2**, **Yb5** thf/1/2hexane, **Yb6**) with integration and absorption corrections completed using APEX II program suite [37], or at the Australian Synchrotron on the MX1 (**Yb3**) macromolecular beam line, where the data and integration were completed by Blu-ice [38] and XDS [39] software programs. Structural solutions were obtained by either Direct methods [40], Patterson [40] or charge flipping [41] and solutions were refined using full matrix least squares methods against F^2 using SHELX2013, via the OLEX 2[42] interface.

4.12. [Yb(FForm)₂(dme)₂] (**Yb2**)

C₃₄H₃₈F₄N₄O₄Yb (*M* = 815.72 g/mol): monoclinic, space group C2/*c* (No. 15), *a* = 23.1448(11) Å, *b* = 10.0955(6) Å, *c* = 15.1972 (8) Å, β = 109.819(2)°, *V* = 3340.6(3) Å³, *Z* = 4, *T* = 123.15 K, μ(Mo Kα) = 2.865 mm⁻¹, *D*_{calc} = 1.622 g/cm³, 12408 reflections measured (4.448° ≤ 2Θ ≤ 54.996°), 3820 unique (*R*_{int} = 0.0366, *R*_{sigma} = 0.0367) which were used in all calculations. The final *R*₁ was 0.0416 (*I* > 2σ(*I*)) and *wR*₂ was 0.1117 (all data). Refinement details: Large residual peak remaining in structural solution due to slight crystal twinning.

4.13. [La(FForm)₃(dme)] (La2)

 $C_{43}H_{37}F_6LaN_6O_2$ (*M* = 922.70 g/mol): monoclinic, space group $P2_1/n$ (No. 14), *a* = 11.0054(7) Å, *b* = 21.2121(11) Å, *c* = 17.2015 (10) Å, β = 97.650(3)°, *V* = 3979.9(4) Å³, *Z* = 4, *T* = 123 K, μ (Mo K α) = 1.147 mm⁻¹, D_{calc} = 1.540 g/cm³, 25595 reflections measured (3.06° $\leq 2\Theta \leq 50°$), 6991 unique (R_{int} = 0.1107, R_{sigma} = 0.1163) which were used in all calculations. The final R_1 was 0.0597 (>2 σ (*I*)) and wR_2 was 0.2023 (all data). Refinement details: ISOR command used on NPD fluorine and carbon atoms that were disordered.

4.14. [Nd(FForm)₃(diglyme)]·diglyme (**Nd1**·diglyme)

C₅₁H₅₅F₆N₆NdO₆ (*M* = 1106.25 g/mol): monoclinic, space group C2/c (No. 15), *a* = 36.4999(15) Å, *b* = 13.7805(5) Å, *c* = 20.7940 (8) Å, *β* = 109.542(3)°, *V* = 9856.6(7) Å³, *Z* = 8, *T* = 123 K, μ(Mo Kα) = 1.132 mm⁻¹, *D*_{calc} = 1.491 g/cm³, 67796 reflections measured (2.36° ≤ 2*Θ* ≤ 50°), 8674 unique (*R*_{int} = 0.0558, *R*_{sigma} = 0.0331) which were used in all calculations. The final *R*₁ was 0.0276 (>2*σ* (*I*)) and *wR*₂ was 0.1084 (all data).

4.15. 2[Nd(TFForm)₃(dme)] (Nd2)

C₈₆H₃₈F₄₈N₁₂Nd₂O₄ (*M* = 2503.76 g/mol): triclinic, space group *P*1̄ (No. 2), *a* = 13.510(3) Å, *b* = 17.920(4) Å, *c* = 19.290(4) Å, *α* = 79.13(3)°, *β* = 88.79(3)°, *γ* = 89.54(3)°, *V* = 4585.2(16) Å³, *Z* = 2, *T* = 173.15 K, μ(Mo Kα) = 1.276 mm⁻¹, *D*_{calc} = 1.813 g/cm³, 71810 reflections measured (2.16° ≤ 2*Θ* ≤ 57.18°), 23206 unique (*R*_{int} = 0.0485, *R*_{sigma} = 0.0648) which were used in all calculations. The final *R*₁ was 0.0462 (>2*σ*(*I*)) and *wR*₂ was 0.1408 (all data). Refinement details: SQUEEZE used to remove two low occupancy PhMe molecules from the lattice, one aryl ring disordered over several positions attempted to refine over three positions but was unstable. Left over two positions refined as a 50:50, and it remains isotropic.

4.16. [Yb(FForm)₃(thf)] (Yb3)

C₄₃H₃₅F₆N₆OYb (*M* = 938.81 g/mol): monoclinic, space group *P*2₁/*c* (No. 14), *a* = 15.493(3) Å, *b* = 11.761(2) Å, *c* = 21.435(4) Å, β = 95.12(3)°, *V* = 3890.2(12) Å³, *Z* = 4, *T* = 123.15 K, μ(synchrotron) = 2.476 mm⁻¹, *D*_{calc} = 1.603 g/cm³, 55795 reflections measured (2.64° ≤ 2Θ ≤ 55°), 8530 unique (*R*_{int} = 0.0607, *R*_{sigma} = 0.0402) which were used in all calculations. The final *R*₁ was 0.0405 (>2σ(*I*)) and *wR*₂ was 0.1063 (all data). Refinement details: originally solved in *P*1, with two identical structures within the ASU, ran through PLATON and suggested monoclinic cell, considering the similarities between the two molecules proceeded to refine in monoclinic cell.

4.17. [Yb(TFForm)₃(thf)₂]·thf/1/2hexane (**Yb5**·thf/1/2hexane)

C_{52.5}H_{36.5}F₂₄N₆O₃Yb (*M* = 1428.42 g/mol): triclinic, space group *P*Ī (No. 2), *a* = 11.8417(5) Å, *b* = 12.0464(5) Å, *c* = 19.1090(8) Å, *α* = 81.598(2)°, *β* = 84.677(2)°, *γ* = 87.483(2)°, *V* = 2683.74(19) Å³, *Z* = 2, *T* = 100.15 K, μ(Mo Kα) = 1.876 mm⁻¹, *D*_{calc} = 1.768 g/cm³, 42670 reflections measured (2.16° ≤ 2*Θ* ≤ 55°), 12287 unique (*R*_{int} = 0.0793, *R*_{sigma} = 0.0906) which were used in all calculations. The final *R*₁ was 0.0434 (>2*σ*(*I*)) and *wR*₂ was 0.1448 (all data).

4.18. [Yb(TFForm)(diglme)₂][Yb(TFForm)₄] (**Yb6**)

 $C_{77}H_{43}F_{40}N_{10}O_6Yb_2$ (*M* = 2310.29 g/mol): triclinic, space group $P\bar{1}$ (No. 2), *a* = 13.674(3) Å, *b* = 17.597(4) Å, *c* = 19.530(4) Å,

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Appendix A. Supplementary data

CCDC 1423116–1423122 contains the supplementary crystallographic data for **Yb2**, **La2**, **Nd1**-diglyme, **Nd2**, **Yb5**-thf/1/2hexane, **Yb6**, **Yb3**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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