Dalton Transactions

Cite this: *Dalton Trans.*, 2012, **41**, 8624

www.rsc.org/dalton

PAPER

The effects of light lanthanoid elements (La, Ce, Nd) on (Ar)CF–Ln coordination and C–F activation in *N*,*N*-dialkyl-*N*′-2,3,5,6-tetrafluorophenylethane-1,2-diaminate complexes†

Glen B. Deacon,* Craig M. Forsyth, Peter C. Junk,* Rory P. Kelly, Aron Urbatsch and Jun Wang

Received 16th March 2012, Accepted 4th May 2012
DOI: 10.1039/c2dt30604b

A new class of homoleptic organoamido rare earth complexes [Ln(L^{Me} or L^{Et})$_3$] (Ln = La, Ce, Nd; L$^{Me/Et}$ = *p*-HC$_6$F$_4$N(CH$_2$)$_2$NMe$_2$/Et$_2$) exhibiting (Ar)CF–Ln interactions has been isolated from redox–transmetallation/protolysis (RTP) reactions between the free metals, Hg(C$_6$F$_5$)$_2$ and L$^{Me/Et}$H in tetrahydrofuran, together with low yields of [Ln(L^{Me})$_2$F]$_3$ (Ln = La, Ce) or [Nd(L^{Et})$_2$F]$_2$ species, resulting from C–F activation reactions. The structures of the homoleptic complexes have eight-coordinate Ln metals with two tridentate (*N*,*N*′,*F*) amide ligands including (Ar)CF–Ln bonds and either a bidentate (*N*,*F*) ligand (Ln = La, Ce, Nd; L^{Et}) or a bidentate (*N*,*N*′) ligand (Ln = Nd; L^{Me}), in an unusual case of linkage variation. All (Ar)CF–Ln bond lengths are shorter than or similar to the corresponding Ln–NMe$_2$/Et$_2$ bond lengths. In [Ln(L^{Me})$_2$F]$_3$ (Ln = La, Ce) complexes, there is a six-membered ring framework with alternating F and Ln atoms and the metal atoms are eight-coordinate with two tridentate (*N*,*N*′,*F*) L^{Me} ligands, whilst [Nd(L^{Et})$_2$F]$_2$ is a fluoride-bridged dimer.

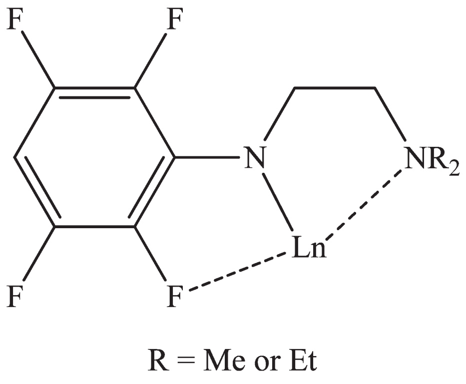
Introduction

Fluorine-mediated interactions between fluorocarbon groups and metals, –CF–M,[1] are attracting considerable and increasing attention both for intrinsic interest and also as possible precursors for C–F activation reactions,[2] since –F–M coordination weakens the C–F bond.[3] This is particularly relevant in lanthanoid chemistry since the strength of the Ln–F bond[4] makes it competitive with the strong C–F bond.[5] Reported examples of –CF–Ln coordination generally have an additional supporting donor atom, *e.g.* C, N, O, S[6–18] or a second –CF–Ln bond[19] but discrete fluorocarbon-rare earth coordination has been observed in [Sc(C$_5$Me$_5$)$_2$(L)]BPh$_4$ (L = PhF or *o*-C$_6$H$_4$F$_2$).[20] Complexes with –CF–Ln bonds may undergo C–F activation reactions[9,10,16,18] giving either LnF$_3$ (potentially of atomic layer deposition interest)[16] or heteroleptic fluorides, *e.g.* [Ln(L)$_2$F][9,10] or cages.[18] In other cases, where heteroleptic fluorides are formed by Ln-induced C–F activation, intermediates with proven –CF–Ln bonding have not been isolated but are likely.[4,21–24] In further examples of such activation reactions, the interest has been on the organic products[25,26] or on the mechanism of activation.[27] As for alternative routes to lanthanoid heteroleptic fluorides,[28–30] cleavage reactions of [LnL$_3$] complexes with masked HF have been the most widely applicable[28,30] and have recently yielded the spectacular cages [Ln$_{28}$F$_{68}$(SePh)$_{16}$(py)$_4$].[30] These give intense near IR emissions, have a much higher F : Ln ratio (2.42) than previously observed (1.67) in [Er$_3$(C$_6$H$_2$Bu$^t_2$-2,6-OMe-4)$_4$F$_5$][23] and defy rearrangement into insoluble and highly stable LnF$_3$. Heteroleptic lanthanoid fluorides should be useful olefin polymerization catalysts in view of success with Group 4 metal amide fluorides.[31] We have recently introduced the bulky ethane-1,2-diaminate ligands [*p*-HC$_6$F$_4$N(CH$_2$)$_2$NR$_2$]$^-$ (R = Me or Et) (L = L^{Me} or L^{Et}) into lanthanoid metal–organic chemistry with the syntheses of [Yb(L$^{Me/Et}$)$_2$(solv)$_2$] (solv = thf or $\frac{1}{2}$ dme) complexes, which exhibit tridentate (*N*,*N*′,*F*) coordination and undergo C–F activation reactions in solution on standing or heating to give the attractive novel [Yb$_4$(L$^{Me/Et}$)$_6$F$_6$] cages.[18] In these, the ligands remain tridentate (*N*,*N*′,*F*) and hence are poised for further activation reactions. The initial choice of the ligands was based on their potential to form an *o*-F–Ln interaction anchored in a five-membered chelate ring by a charged amide nitrogen atom together with an amine nitrogen atom in a further five-membered ring (Scheme 1). Two *ortho* fluorine atoms increase the possibility of at least transitory Ln–F interactions in solution, even with some rotation about the *p*-HC$_6$F$_4$–N bond. With the probability that *ortho* fluorine resonances might be broadened or shifted by Ln–F coordination (as observed, see below), the *meta* fluorine atoms being further away from the Ln atoms and characteristically shifted by the 4-H substituent,[32] provide a structural integration marker in the ^{19}F NMR spectra. Although the ligands were initially prepared in a template synthesis on platinum to give potential ‘rule-breaker’ anticancer drugs,[33,34] the amine ligand precursors *p*-C$_6$F$_4$N(H)(CH$_2$)$_2$NR$_2$ (R = Me, Et) are readily prepared by

---

School of Chemistry, Monash University, Clayton, VIC 3800, Australia. E-mail: glen.deacon@monash.edu, peter.junk@monash.edu

† Electronic supplementary information (ESI) available. CCDC 859374 and 859380–859386. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt30604b



Scheme 1 Potential ligand binding mode.

nucleophilic substitution between the amines $R_2N(CH_2)_2NH_2$ (R = Me, Et) and pentafluorobenzene.[18,35] So far, homoleptic rare earth complexes of $L^{Me/Et}$ ligands have not been isolated but formation of $[Ln(L^{Me/Et})_3]$ is favoured by charge balance for the Ln^{III} state. Because such complexes would have crowded coordination spheres, there is uncertainty over the coordination number and whether *N*,*N*′,*F*-ligation and –CF–Ln bonding would be possible for some or all ligands. The previous Ln-induced C–F activation of $L^{Me/Et}$ involved an isolable Yb^{II} intermediate with –CF–Ln bonding but is C–F activation possible for rare earths with a much less stable Ln^{II} state?[36] We have addressed these issues by the synthesis and structure determination of homoleptic $[Ln(L^{Me/Et})_3]$ (Ln = La, Ce, Nd) complexes, which exhibit a fascinating linkage variation, by utilizing the largest Ln elements to maximize the possibility of –CF–Ln coordination. In addition, C–F activation products $[Ln(L^{Me})_2F]_3$ (Ln = La, Ce) and $\mathbf{[Nd(L^{Et})_2F]_2}$ have been isolated and structurally characterized, albeit in low yields, with the elements having much less stable Ln^{II} states than ytterbium.[36]

Results and discussion

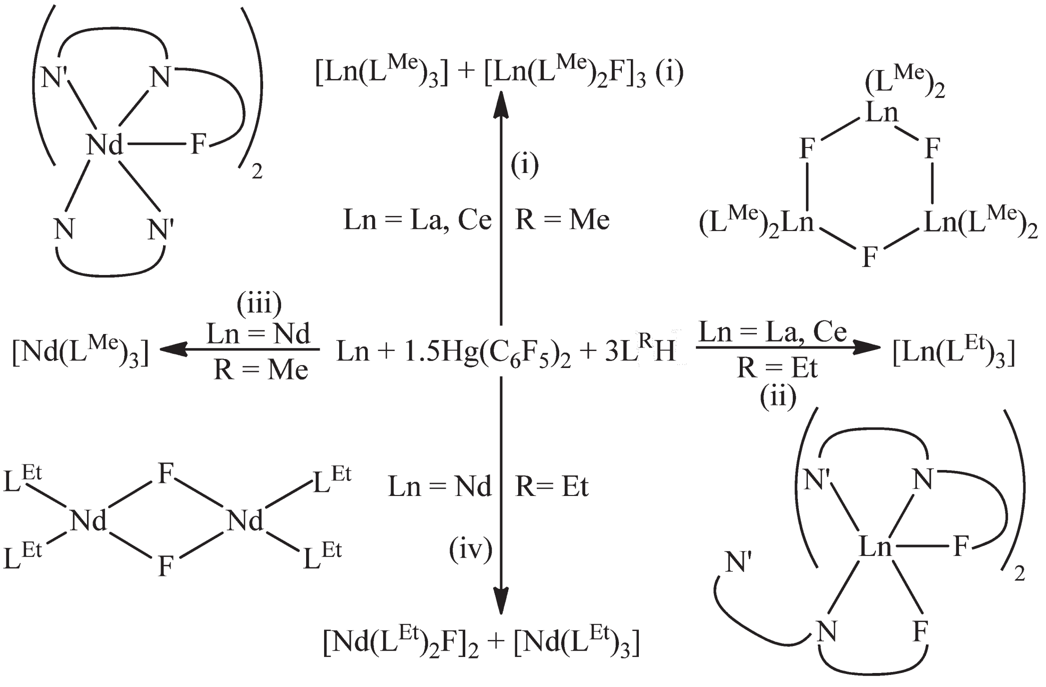
Syntheses

Redox-transmetallation/protolysis (RTP) reactions between lanthanum or cerium metals, bis(pentafluorophenyl)mercury and *N*,*N*-dimethyl-*N*′-2,3,5,6-tetrafluorophenylethane-1,2-diamine ($L^{Me}H$) in thf at room temperature, yield the homoleptic complexes $[Ln(p\text{-}HC_6F_4N(CH_2)_2NMe_2)_3]$, $[Ln(L^{Me})_3]$ (Ln = La or Ce) in good yield (Scheme 2, (i)), together with the corresponding trimeric heteroleptic fluorides $[Ln(L^{Me})_2F]_3$ (Ln = La or Ce) in low yield. The cerium complex $\mathbf{[Ce(L^{Me})_2F]_3}$ was also obtained from an analogous RTP reaction with $Hg(CCPh)_2$ instead of $Hg(C_6F_5)_2$. From a similar synthesis with La metal, only $\mathbf{[La(L^{Me})_3]}$ was isolated. By contrast, the corresponding reactions with *N*,*N*-diethyl-*N*′-2,3,5,6-tetrafluorophenylethane-1,2-diamine ($L^{Et}H$) gave solely the homoleptic complexes $[Ln(L^{Et})_3]$ (Ln = La or Ce) (Scheme 2, (ii)). Analogous reactions with neodymium and either ligand gave the homoleptic complexes $\mathbf{[Nd(L^{Me})_3]}$ and $\mathbf{[Nd(L^{Et})_3]}$ (Scheme 2, (iii), (iv)). However, from some reactions involving $L^{Et}H$, it was also possible to isolate the dimeric heteroleptic fluoride $\mathbf{[Nd(L^{Et})_2F]_2}$ in addition to $\mathbf{[Nd(L^{Et})_3]}$. Overall, the synthetic method readily provides homoleptic $[Ln(L^{Me/Et})_3]$ complexes in good yield but the concurrent formation of heteroleptic fluorides $[Ln(L^{Me/Et})_2F]_n$ is limited in extent and yield. Heating reaction mixtures appeared to increase the complexity of the reactions (see below for two examples of heat-induced transformations).

Analytical and spectroscopic characterization

Homoleptic $[Ln(p\text{-}HC_6F_4N(CH_2)_2NR_2)_3]$ complexes (R = Me or Et)

Bulk samples of all six homoleptic complexes $[Ln(L^{Me/Et})_3]$ (Ln = La, Ce, Nd) were characterized by microanalysis or metal



Scheme 2 Summary of syntheses.

analyses. The larger sample used for the latter can provide a good assessment of bulk purity. Analyses were consistent with the single crystal compositions, except for **[La(L^{Et})$_3$]**·C_7H_8 and **[Ce(L^{Et})$_3$]**·1/2C_7H_8 where the data indicated loss of toluene of crystallization and this was confirmed by ^{1}H NMR spectra of the bulk samples. The ^{19}F{^{1}H} NMR spectra of diamagnetic **[La(L$^{Me/Et}$)$_3$]** at room temperature show two equal intensity broad singlets indicative of either free rotation of the polyfluorophenyl groups and no (Ar)CF–Ln bonding in contrast to solid **[La(L^{Et})$_3$]** (below), or rapid exchange between coordination of F2 and F6. At low temperatures, the ^{19}F{^{1}H} NMR spectrum of **[La(L^{Et})$_3$]** gives twelve separate resonances consistent with the two different tridentate (*N*,*N*′,*F*) and one bidentate (*N*,*F*) L^{Et} ligands of the solid-state structure (below). Cooling **[La(L^{Me})$_3$]** also leads to multiple resonances also indicative of (Ar)CF–La interactions. With less distinct resonances than **[La(L^{Et})$_3$]**, it is possible that there are two tridentate (*N*,*N*′,*F*) ligands and one bidentate (*N*,*N*′) ligand (the latter only giving two resonances since free rotation of the fluorocarbon group is possible), as observed in solid **[Nd(L^{Me})$_3$]**, but single crystals have not yet been obtained. The ^{1}H NMR spectra of paramagnetic **[Ce(L$^{Me/Et}$)$_3$]** and **[Nd(L$^{Me/Et}$)$_3$]** at room temperature show resonances consistent with the compositions but with substantial shifts and broadening and a chemical shift range of 23 ppm (**[Ce(L^{Et})$_3$]**). In the ^{19}F{^{1}H} NMR spectrum of **[Ce(L$^{Me/Et}$)$_3$]** and **[Nd(L$^{Me/Et}$)$_3$]** at room temperature, a single broad feature is observed. This is close (*ca.* 5 ppm) to the expected value for F *ortho* to H in diamagnetic systems. Cooling of representative samples only caused broadening of this resonance. However, spectra of **[Ce(L$^{Me/Et}$)$_3$]** and **[Nd(L$^{Me/Et}$)$_3$]** at 70 °C reveal two resonances: one near the position in the room temperature spectrum, reasonably attributable to F3,5; and a very broad and substantially paramagnetically shifted signal at −180 to −200 ppm for **[Ce(L$^{Me/Et}$)$_3$]** and **[Nd(L$^{Me/Et}$)$_3$]**, attributable to F2,6 which are nearer the paramagnetic centres. A detailed study of **[Nd(L^{Me})$_3$]** (as representative) from 30–70 °C shows that the low frequency resonance is not clearly evident until 40 °C and is broadened into the baseline at 30 °C. The substantial broadening and paramagnetic shifting of F2,6 may suggest exchange between different ligand coordination modes (see structures **[Ce(L^{Et})$_3$]** and **[Nd(L$^{Me/Et}$)$_3$]** below), possibly indicating (Ar)CF–Ln interactions.

The IR spectra of all complexes are consistent with loss of the NH proton of the reactant *p*-$HC_6F_4NH(CH_2)_2NR_2$ and characteristic *v*(CF) absorptions are observed at 954–957 cm^{-1} and 926–927 cm^{-1} for R = Me and 943–947 cm^{-1} for R = Et. The close similarity between the infrared spectra of [Ln(L^{Me})$_3$] (Ln = La, Ce) and **[Nd(L^{Me})$_3$]**, the structure of which has been established by X-ray crystallography (below), is consistent with the complexes being isostructural.

Organoamidolanthanoid fluorides [Ln(*p*-HC$_6$F$_4$N(CH$_2$)$_2$NR$_2$)$_2$F]$_n$ (Ln = La, Ce; *n* = 3; Ln = Nd; *n* = 2)

Satisfactory microanalyses were obtained for the three heteroleptic fluorides **[La(L^{Me})$_2$F]$_3$**, **[Ce(L^{Me})$_2$F]$_3$** and **[Nd(L^{Et})$_2$F]$_2$**. In the case of **[La(L^{Me})$_2$F]$_3$**, the bulk sample had lost the toluene of crystallization of the single crystals, as confirmed by the ^{1}H NMR spectrum, whereas isostructural **[Ce(L^{Me})$_2$F]$_3$** analysed with the single crystal composition of **[Ce(L^{Me})$_2$F]$_3$**·3/2C_7H_8 and resonances of C_7H_8 could be qualitatively distinguished from residual proton resonances of C_7D_8 in the ^{1}H NMR spectrum. Very low solubility required use of elevated temperatures to obtain NMR spectra of **[La(L^{Me})$_2$F]$_3$** and **[Ce(L^{Me})$_2$F]$_3$**, whilst paramagnetism allied with low solubility precluded satisfactory spectra for **[Nd(L^{Et})$_2$F]$_2$**. For diamagnetic **[La(L^{Me})$_2$F]$_3$**, the spectra were consistent with the proposed composition without toluene of crystallization and with free rotation of the fluoroaryl groups but a little **[La(L^{Me})$_3$]** was also observed, presumably formed by rearrangement induced by heating to achieve dissolution.

$$3[\mathrm{La}(\mathrm{L}^{\mathrm{Me}})_2\mathrm{F}] \rightarrow 2[\mathrm{La}(\mathrm{L}^{\mathrm{Me}})_3] + \mathrm{LaF}_3$$

The spectrum of paramagnetic **[Ce(L^{Me})$_2$F]$_3$** is more complicated, showing two sets of ^{1}H resonances for the ligand at 100 °C. In the ^{19}F{^{1}H} NMR spectrum, two very close (unequal) F3,5 resonances are evident at 50 °C, 70 °C and 100 °C but the corresponding F2,6 resonances are superimposed in a very broad, paramagnetically shifted signal at −200 ppm. As solid **[Ce(L^{Me})$_2$F]$_3$** is trimeric, it is plausible that the features are due to two species of different nuclearity *e.g.* the trimeric species and a lower coordinate monomer. As the ratio of the major to the minor resonance in the ^{19}F{^{1}H} NMR spectrum (sample totally dissolved by prior heating) increases from 1.8 : 1 (50 °C) to 2.2 : 1 (70 °C) and 4.0 : 1 (100 °C), the major resonance is reasonably attributable to a monomer and the minor resonance to the trimer. Resonances of the skeletal fluoride ligands could not be resolved, a not unexpected result of low solubility and expected broad signals, especially in view of the very broad resonances for the aromatic fluorine atoms even for diamagnetic **[La(L^{Me})$_2$F]$_3$**. With [Ln(DippForm)$_2$F(thf)] (DippForm = *N*,*N*′-bis(2,6-diisopropylphenyl)formamidinate) complexes, which have terminal Ln–F bonds, fluoride resonances could only be resolved for two of the compounds.[24]

Significant *v*(NH) or *v*(OH) absorptions are not detectable in the infrared spectra and *v*(CF) bands are observed close to the values for the corresponding homoleptic complexes. Comparison of the far infrared spectra of **[La(L^{Me})$_2$F]$_3$** with **[La(L^{Me})$_3$]** and of **[Ce(L^{Me})$_2$F]$_3$** with **[Ce(L^{Me})$_3$]** led to the assignment of bands at 355 and 378 cm^{-1} respectively to *v*(Ln–F). A relatively strong analogous band of **[Nd(L^{Et})$_2$F]$_2$** (341 cm^{-1}) is attributed to *v*(Nd–F).

Molecular structures

Homoleptic [Ln(*p*-HC$_6$F$_4$N(CH$_2$)$_2$NR$_2$)$_3$] complexes

Only one of the three [Ln(*p*-$HC_6F_4N(CH_2)_2NMe_2$)$_3$] complexes (*viz.* **[Nd(L^{Me})$_3$]**) could be obtained as single crystals suitable for X-ray crystallography, whereas all three [Ln(*p*-HC_6F_4N-$(CH_2)_2NEt_2$)]$_3$ complexes, **[La(L^{Et})$_3$]**, **[Ce(L^{Et})$_3$]** and **[Nd(L^{Et})$_3$]**, were structurally characterized. Unit cell and refinement data are given in the Experimental section.

All structures are eight-coordinate with two tridentate (*N*,*N*′,*F*) ligands and one bidentate ligand but **[Nd(L^{Me})$_3$]** differs from the

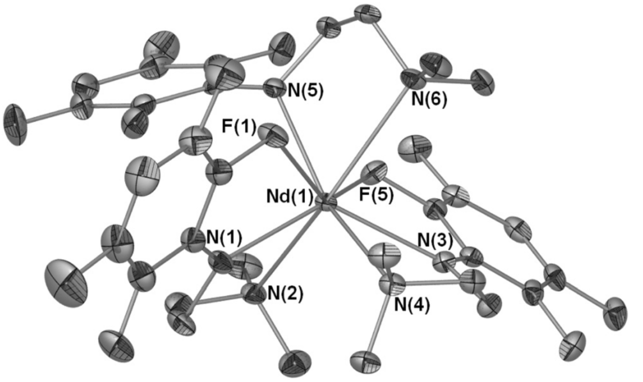


Fig. 1 Molecular diagram of $[Nd(p\text{-}HC_6F_4N(CH_2)_2Me_2)_3]$ **$[Nd(L^{Me})_3]$** shown with 50% probability thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

Table 1 Selected bond lengths (Å) in $[Nd(p\text{-}HC_6F_4N(CH_2)_2NMe_2)_3]$ (**$[Nd(L^{Me})_3]$**), $[La(p\text{-}HC_6F_4N(CH_2)_2NEt_2)_3]\cdot C_7H_8$ (**$[La(L^{Et})_3]$**$\cdot C_7H_8$), $[Ce(p\text{-}HC_6F_4N(CH_2)_2NEt_2)_3]\cdot 1/2C_7H_8$ (**$[Ce(L^{Et})_3]$**$\cdot 1/2C_7H_8$) and $[Nd(p\text{-}HC_6F_4N(CH_2)_2NEt_2)_3]$ (**$[Nd(L^{Et})_3]$**)

	$[Nd(L^{Me})_3]$	**$[La(L^{Et})_3]$**$\cdot C_7H_8$	**$[Ce(L^{Et})_3]$**$\cdot 1/2C_7H_8$	**$[Nd(L^{Et})_3]$**
Ln(1)–N(1)	2.4163(16)	2.479(6)	2.452(8)	2.395(6)
Ln(1)–N(3)	2.4827(15)	2.473(6)	2.453(9)	2.412(6)
Ln(1)–N(5)	2.4092(16)	2.388(6)	2.363(9)	2.378(6)
Ln(1)–N(2)	2.6870(16)	2.731(6)	2.728(8)	2.709(6)
Ln(1)–N(4)	2.7273(16)	2.717(6)	2.687(8)	2.658(6)
Ln(1)–F(1)	2.5793(11)	2.773(4)	2.686(5)	2.647(4)
Ln(1)–F(5)	2.6138(11)	2.699(4)	2.779(6)	2.615(4)
Ln(1)–N(6)	2.7782(16)	—	—	—
Ln(1)–F(9)	—	2.765(4)	2.764(5)	2.705(4)

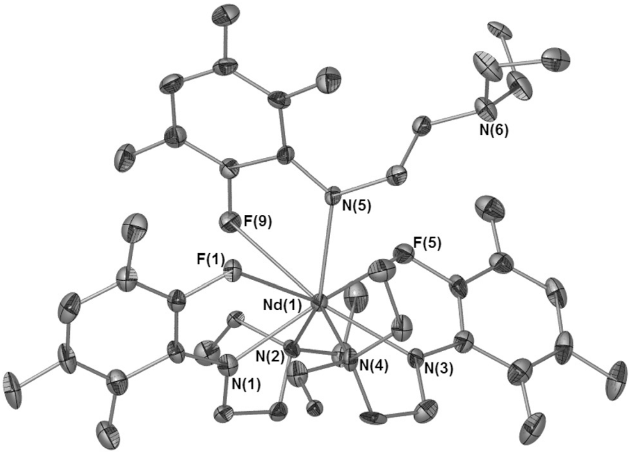


Fig. 2 Molecular diagram of $[Nd(p\text{-}HC_6F_4N(CH_2)_2NEt_2)_3]$ **$[Nd(L^{Et})_3]$** shown with 50% thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

$[Ln(L^{Et})_3]$ complexes in the mode of attachment of the third ligand, in an unusual case of linkage variation.

$[Nd(L^{Me})_3]$. The structure of the eight-coordinate Nd complex is shown in Fig. 1 together with the numbering scheme. Selected bond distances are given in Table 1. Two of the amido ligands are tridentate (*N*,*N*′,*F*), as observed in $[Yb(L^{Et})_2(dme)]$ or $[Yb_4(L^{Me/Et})_6F_6]$ complexes,[18] whereas the third ligand is only bidentate (*N*,*N*′) with the Ln–*o*-F contacts non-bonding ≥ 3.699(1) Å. In the absence of *o*-F bonding, the dihedral angle for the bidentate (*N*,*N*′) ligand between the N(5)N(6)Nd plane and the N(5) phenyl ring plane is 65.18(7)°, whereas for the tridentate ligands, the corresponding angle is 22.07(8)° for the N(1)(N2)Nd plane and the N(1) ring plane and 4.99(12)° of the N(3)N(4)Nd plane and the N(3) aryl ring plane. Bonding of the amide nitrogen is 0.20–0.34 Å shorter than the bonds to the amine nitrogen and the Nd–$NMe_2(CH_2–)$ bonds are some 0.1 Å longer than the corresponding Nd–*o*-F interactions for the N(1) and N(3) ligands, as noted for Yb^{II} and Yb^{III} complexes of the tridentate (*N*,*N*′,*F*) ligands.[18] Whether this shortening can be attributed to stronger Nd–F than Nd–$NMe_2(CH_2–)$ bonding is arguable given that the third ligand prefers *N*,*N*′ over *N*,*F* chelation, where both would give five-membered rings.

$[La(L^{Et})_3]$, $[Ce(L^{Et})_3]$ and $[Nd(L^{Et})_3]$. The three complexes are isostructural and the representative structure of **$[Nd(L^{Et})_3]$** is shown in Fig. 2 with selected bond distances in Table 1. All three complexes are eight-coordinate with two tridentate (*N*,*N*′,*F*) *N*,*N*-diethyl-*N*′-2,3,5,6-tetrafluorophenylethane-1,2-diaminate(1−) ligands but the third ligand has *N*,*F* coordination with an uncoordinated $–(CH_2)_2NEt_2$ group (Nd–NEt_2 contacts ≥5.502(6) Å for **$[Nd(L^{Et})_3]$**). This contrasts the preferred *N*,*N*′ binding of the third ligand in **$[Nd(L^{Me})_3]$**. This significant change vividly highlights the lower steric demands of the L^{Me} ligand compared with L^{Et}. Coordination of the first two ligands results in less available coordination space for the third ligand in $[Ln(L^{Et})_3]$ than in $[Ln(L^{Me})_3]$ complexes, leading to the adoption of a less bulky coordination mode by using chelating *N*,*F* donors. With reduction in size from NEt_2 to NMe_2, the metal atom in **$[Nd(L^{Me})_3]$** is less crowded and can adopt the bulkier and evidently more stable coordination mode of chelating *N*,*N*′ for the third ligand. The structures feature bicapped distorted trigonal prismatic geometries with two capping atoms. Atoms N(1)N(2)F(9) form one triangular face, while atoms N(3)N(4)N(5) form the other face in the $[Ln(L^{Et})_3]$ complexes, whereas N(1)N(2)N(5) and N(3)N(4)N(6) form the two triangular faces in the case of **$[Nd(L^{Me})_3]$**; atoms F(1) and F(5) are capping in both cases.

In the $[Ln(L^{Et})_3]$ complexes, the Ln–N(amide) bonds are shorter than the Ln–N(amine) bonds by 0.24–0.30 Å, similar to **$[Nd(L^{Me})_3]$** (above). For the La and Ce complexes, the shortest Ln–N(amide) bond is for the bidentate ligand but this is not observed in **$[Nd(L^{Et})_3]$**. The Ln–F and Ln–N(amine) bonds are of similar length, in contrast to **$[Nd(L^{Me})_3]$** where the Ln–F bond lengths are approximately 0.1 Å shorter than Ln–N(amine) values. Comparison of the Nd complexes **$[Nd(L^{Me})_3]$** and **$[Nd(L^{Et})_3]$** indicates longer Nd–N(amine) bonds in the former and longer Nd–F bonds in the latter.

The Ln size range for the $[Ln(L^{Et})_3]$ complexes reveals some interesting structural effects. Comparison of the La and Nd complexes **$[La(L^{Et})_3]$** and **$[Nd(L^{Et})_3]$** shows that whilst three Ln–N bonds decrease by at least the expected (from ionic radii differences) 0.05 Å, two, Ln–N(5) (amide) and Ln–N(2) (amine), show no differences, *i.e.* they are effectively lengthened. By contrast, all three Ln–F bonds are shortened by more than 0.05 Å from **[La(L$^{\mathrm{Et}}$)$_3$]** to **[Nd(L$^{\mathrm{Et}}$)$_3$]**. Thus, in response to the smaller size of Nd^{3+}, all ligands bring the sterically undemanding C–F unit relatively closer and two of the more crowded N donor atoms are effectively further away.

Although the <Nd–N(amide)> bond distances in **[Nd(L$^{\mathrm{Et}}$)$_3$]** and **[Nd(L$^{\mathrm{Me}}$)$_3$]** are longer than in the six-coordinate Nd complex, [Nd{N(SiMe$_3$)C$_6$H$_4$(2-OCH$_3$)}$_3$] (2.37 Å),[37] and the <La–N(amide)> bond distance in **[La(L$^{\mathrm{Et}}$)$_3$]** (2.45 Å) is longer than in the six-coordinate La complex [La(NH-2,6-Pr$^i_2$C$_6$H$_3$)$_3$-(thf)$_3$] (2.39 Å),[38] the increase is less than expected from ionic radii for a change of two in the coordination number,[39] indicative of lower steric demands of the present amide ligands.

Structures of the heteroleptic fluoride [Ln(*p*-HC$_6$F$_4$N(CH$_2$)$_2$NR$_2$)$_2$F]$_n$ complexes

Two isomorphous complexes **[La(L$^{\mathrm{Me}}$)$_2$F]$_3$**·3/2C$_7$H$_8$ and **[Ce(L$^{\mathrm{Me}}$)$_2$F]$_3$**·3/2C$_7$H$_8$ crystallized from toluene in the $R\bar{3}$ space group (Experimental section). Each compound has two similar but crystallographically independent molecules, hence only one is chosen to describe their structures (Fig. 3 and Table 2). Both heteroleptic fluoride complexes are trinuclear species and the metal centres are eight-coordinate. Each metal atom is ligated by two tridentate (*N*,*N′*,*F*) *N*,*N*-dimethyl-*N′*-2,3,5,6-tetrafluorophenylethane-1,2-diaminate(1−) ligands and two bridging fluoride ions with a flat, distorted, hexagonal [Ln$_3$F$_3$] (Ln = La, Ce) core. There is distorted bicapped trigonal prismatic coordination, *e.g.* N(1)N(2)F(9) forms one triangular face while N(3)N(4)F(9#) forms the other with bridging F(1) and F(5) as the capping atoms for La(1). A similar [Ln$_3$F$_3$] core has been seen previously in [YbCp$_2$F]$_3$[21c] and [ScCp$_2$F]$_3$.[40] The average La–N(amide) bond distance (2.50 Å) is slightly longer than in **[La(L$^{\mathrm{Et}}$)$_3$]** (2.45 Å) and the average Ce–N(amide) bond distance (2.48 Å) is somewhat longer than that in **[Ce(L$^{\mathrm{Et}}$)$_3$]** (2.42 Å). Compensating for this trend, the mean Ln–*o*-F bond lengths (La 2.64Å; Ce 2.64 Å) are shorter than in **[La(L$^{\mathrm{Et}}$)$_3$]** (2.74 Å) and **[Ce(L$^{\mathrm{Et}}$)$_3$]** (2.73 Å) respectively. As expected the framework Ln–F bonds are considerably shorter (approximately 0.3 Å) than the (Ar)CF–Ln bonds but they are *ca.* 0.2 Å longer than *terminal* Ln–F bonds in six-coordinate [Ln(DippForm)$_2$F(thf)] (Ln = La, Ce; DippForm = *N*,*N′*-(2,6-diisopropylphenyl)formamidinate) complexes.[24] On the other hand, the framework La(1)–F(9)/F(9)$^{\#}$ bond lengths are very similar to the La–F bond length (2.349(7) Å) of dimeric, eight-coordinate [La(C$_5$H$_3$(SiMe$_3$)$_2$-1,3)$_2$F]$_2$.[28a] These bond length similarities and structural analogy with [YbCp$_2$F]$_3$ [21c] suggest that tridentate *N*,*N*-dialkyl-*N′*-2,3,5,6-tetrafluorophenylethane-1,2-diaminate(1−) ions may be considered as Cp replacement ligands and the similarity is supported by similar Ln–F bond lengths when ionic radii differences are considered.

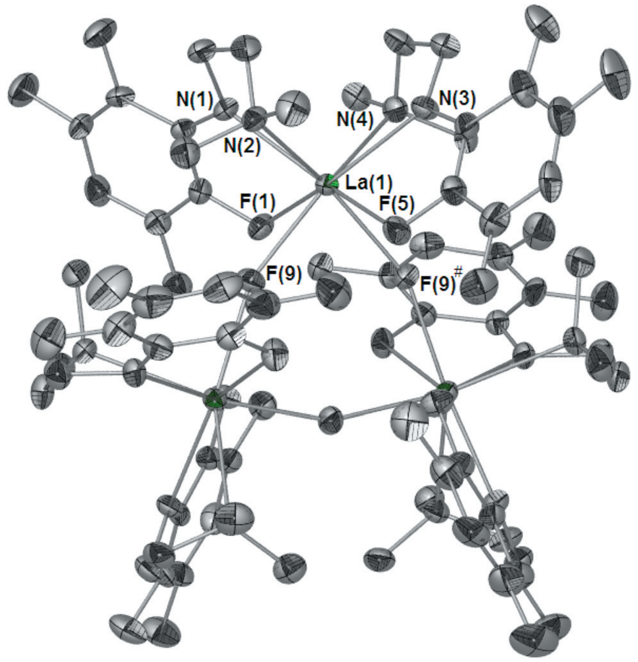


Fig. 3 Molecular diagram of [La(*p*-HC$_6$F$_4$N(CH$_2$)$_2$NMe$_2$)$_2$F]$_3$·3/2C$_7$H$_8$ **[La(L$^{\mathrm{Me}}$)$_2$F]$_3$**·3/2C$_7$H$_8$ shown with 50% probability thermal ellipsoids. Hydrogen atoms and lattice C$_7$H$_8$ have been omitted for clarity (symmetry code for F(9)$^{\#}$: $-x + y, 1 - x, z$).

Table 2 Selected bond lengths (Å) in [La(*p*-HC$_6$F$_4$N(CH$_2$)$_2$NEt$_2$)$_2$F]$_3$·3/2C$_7$H$_8$ **[La(L$^{\mathrm{Me}}$)$_2$F]$_3$**·3/2C$_7$H$_8$, [Ce(*p*-HC$_6$F$_4$N(CH$_2$)$_2$NEt$_2$)$_2$F]$_3$·3/2C$_7$H$_8$ **[Ce(L$^{\mathrm{Me}}$)$_2$F]$_3$**·3/2C$_7$H$_8$ and [Nd(*p*-HC$_6$F$_4$N(CH$_2$)$_2$NEt$_2$)$_2$F]$_2$·C$_6$H$_{14}$ **[Nd(L$^{\mathrm{Et}}$)$_2$F]$_2$**·C$_6$H$_{14}$

	[La(L$^{\mathrm{Me}}$)$_2$F]$_3$·3/2C$_7$H$_8$	**[Ce(L$^{\mathrm{Me}}$)$_2$F]$_3$**·3/2C$_7$H$_8$	**[Nd(L$^{\mathrm{Et}}$)$_2$F]$_2$**·C$_6$H$_{14}$
Ln(1)–N(1)	2.510(6)	2.484(8)	2.428(2)
Ln(1)–N(3)	2.492(7)	2.467(8)	2.416(2)
Ln(1)–N(2)	2.701(7)	2.673(8)	2.723(2)
Ln(1)–N(4)	2.710(6)	2.706(8)	2.666(2)
Ln(1)–F(1)	2.628(4)	2.642(5)	2.6565(14)
Ln(1)–F(5)	2.642(5)	2.642(5)	2.6384(15)
Ln(1)–F(9)	2.339(4)	2.325(5)	2.2838(15)
Ln(1)–F(9)$^{\#}$	2.345(4)	2.332(5)	—
Ln(1)–F(10)	—	—	2.3260(14)

The eight-coordinate heteroleptic neodymium fluoride complex [Nd(p-HC$_6$F$_4$N(CH$_2$)$_2$NEt$_2$)$_2$F]$_2$ was isolated as **[Nd(L$^{\mathrm{Et}}$)$_2$F]$_2$** from toluene and **[Nd(L$^{\mathrm{Et}}$)$_2$F]$_2$**·C$_6$H$_{14}$ from hexane. Except for the absence/presence of hexane in the lattice, both structures are very similar. Thus, data of the more precise structure of **[Nd(L$^{\mathrm{Et}}$)$_2$F]$_2$**·C$_6$H$_{14}$ (Fig. 4 and Table 2) are discussed. The complex is dinuclear and the binding modes between metal and L$^{\mathrm{Et}}$ closely resemble those seen in the trinuclear fluoride complexes **[La(L$^{\mathrm{Me}}$)$_2$F]$_3$** and **[Ce(L$^{\mathrm{Me}}$)$_2$F]$_3$**. Both metal atoms are bridged by two fluoride atoms, forming a [Nd$_2$F$_2$] core. A similar core has been seen previously in five-coordinate [Yb(OC$_6$H$_2$-2,6-^{t}Bu$_2$-4-X)$_2$F(thf)]$_2$ (X = H or ^{t}Bu),[21c] nine-coordinate [Yb(Cp or MeCp)$_2$F(thf)]$_2$ [21b,c] and eight-coordinate [Ln(C$_5$H$_3$(SiMe$_3$)$_2$-1,3)$_2$F]$_2$ (Ln = La, Nd, Sm, Gd).[28a] In bicapped distorted trigonal prismatic coordination geometry for Nd(1), N(1)N(2)F(9) forms one triangular face and N(3)N(4)F(10) forms the other, with F(1) and F(5) as the capping atoms, whilst for Nd(2), N(5)N(6)F(9) forms one triangular face while N(7)N(8)F(10) forms the other, with F(11) and F(15) as the capping atoms. The average Nd–N(amide) bond distance (2.42 Å) is midway between those of **[Nd(L$^{\mathrm{Et}}$)$_3$]** (2.40 Å) and **[Nd(L$^{\mathrm{Me}}$)$_3$]** (2.44 Å). The Nd–*o*-F contacts (ave. 2.65 Å) are near those of **[Nd(L$^{\mathrm{Me}}$)$_3$]** (ave. 2.60 Å) and **[Nd(L$^{\mathrm{Et}}$)$_3$]** (ave. 2.66 Å) but longer than the framework bonds

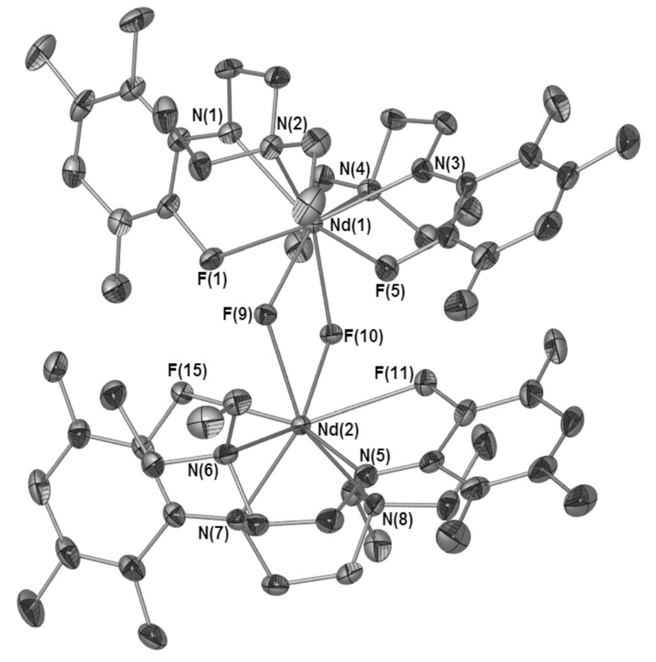


Fig. 4 Molecular diagram of $[Nd(p\text{-}HC_6F_4N(CH_2)_2NEt_2)_2F]_2{\cdot}C_6H_{14}$ **$[Nd(L^{Et})_2F]_2$**$\cdot C_6H_{14}$ shown with 50% probability thermal ellipsoids. Hydrogen atoms and hexane of crystallization have been omitted for clarity.

(ave. 2.30 Å) which are similar to those of $[Nd(C_5H_3(SiMe_3)_2\text{-}1,3)_2F]_2$ [28a] (2.337(1) Å). The similarity to this complex reinforces the concept that $L^{Me/Et}$ are Cp replacement ligands.

Adoption of a dimeric structure for the smaller Nd in **$[Nd(L^{Et})_2F]_2$** rather than a trimer as in $[Ln(L^{Me})_2F]_3$ (Ln = La, Ce) appears to reduce steric strain in response to the smaller size of Nd^{3+}. Repulsion between the two bulky amide ligands is the biggest source of steric strain and in the dimeric Nd complex, *N*(amide)–Nd–N(amide) is 118.79(16)°, far more open than in the Ce or La complexes (110.4(3)° and 110.6(2)° respectively). Although the F–Ln–F angles show the opposite trend (67.78(11), 82.6(3) and 82.3(2) respectively, fluoride has very low steric demand.

Comments on C–F activation

From hydrolysis of the reaction mixture giving **$[La(L^{Me})_3]$** and **$[La(L^{Me})_2F]_3$**, species with *m*/*z* 298 $[C_{12}H_2F_8]^+$, 236 $[L^{Me}H]^+$, 233 $[L^{Me}H - 3H]^+$ and 384 $[L^{Me}H - F + C_6F_5]^+$ were identified, the last being attributable to a defluorinated species and involvement of a $Ln(C_6F_5)$ species as well. By contrast, hydrolysis of the reaction mixture giving **$[Ce(L^{Me})_3]$** and **$[Ce(L^{Me})_2F]_3$** yielded species with *m*/*z* 218 $[L^{Me}H - F + H]^+$ and 432 $[L^{Me} - F]_2{}^+$, in addition to *m*/*z* 384, 236 and 233 (above), providing clear evidence of defluorination of L^{Me}. An NMR scale experiment showed significant conversion of **$[Ce(L^{Me})_3]$** into the heteroleptic fluoride **$[Ce(L^{Me})_2F]_3$** in 48 h in C_7D_8 at 110 °C but **$[La(L^{Me})_3]$** was much less reactive and **$[La(L^{Me})_2F]_3$** was not detected under similar conditions. On the contrary, heating **$[La(L^{Me})_2F]_3$** caused some rearrangement into **$[La(L^{Me})_3]$**. The formation of **$[Ce(L^{Me})_2F]_3$** in C_7D_8 was accompanied by observation of additional low intensity ^{19}F NMR resonances that cannot be identified at this stage but a resonance in the −120 to −130 ppm region suggests a fluorine with two *ortho*-H neighbours, indicative of a defluorinated species.

The conversion of **$[Ce(L^{Me})_3]$** into **$[Ce(L^{Me})_2F]_3$** by C–F activation without apparent redox, in contrast to $Yb^{II}(L^{Me/Et})_2$ species,[18] has parallels in C–F activation of CF_3 containing Ca complexes.[41] The contrast between the behaviour of **$[La(L^{Me})_3]$** and **$[Ce(L^{Me})_3]$** raises the question of possible intervention of $Ce^{III} \rightleftharpoons Ce^{IV}$ and *m*/*z* 432 $[L^{Me} - F]_2{}^+$ can be rationalized as dimerization of a $(p\text{-}HC_6F_3)N(CH_2)_2NMe_2)^{2\cdot}$diradical, a possible product of such a process.

Apart from the observation of defluorinated ligand species, the synthesis of **$[Ce(L^{Me})_2F]_3$** using $Hg(CCPh)_2$ establishes L^{Me} as a fluoride source. Implicitly, defluorination involves one (or both) of the *ortho*-fluorine atoms, since these are involved in –C–F–Ln coordination (Fig. 1 and 2). However, the low yields of the multiple C–F activation organic products, compounded by the difficulty in separating very small amounts of them, limit probing the reaction paths but the species detected suggest more than one path. Nevertheless, the reactions have provided well-characterized organoamidolanthanoid fluorides, a rare compound class, albeit in low yields.

Observation of C–F activation in the Nd/L^{Et} system but not for Ln/L^{Et} (Ln = La, Ce), may in part relate to the considerable shortening of <Ln–F> from La, Ce to Nd, far greater than expected for the lanthanoid contraction (Table 2) and partly due to isolation of a less crowded dimer for Nd than the trimers observed for $[Ln(L^{Me})_2F]_3$ (Ln = La, Ce) (above).

Conclusions

Coordination of the organoamide ligands $p\text{-}HC_6F_4N\text{-}(CH_2)_2NMe_2/Et_2(1-)$ to three light rare earth metals features (Ar)CF–Ln coordination in the homoleptic complexes $[Ln(L^{Me/Et})_3]$ (Ln = La, Ce, Nd) and the heteroleptic fluorides $[Ln(L^{Me})_3F]_3$ (Ln = La, Ce) and **$[Nd(L^{Et})_2F]_2$**. Tridentate (*N*,*N*′,*F*) coordination is mainly observed. However, in the eight-coordinate $[Ln(L^{Me/Et})_3]$ complexes, one ligand is bidentate with either *N*,*N*′-binding (L^{Me}) or *N*,*F*-ligation (L^{Et}) with a free $-(CH_2)_2NEt_2$ group. This novel linkage variation appears to be driven by steric factors. Although C–F activation giving heteroleptic fluorides occurred, the extent of it was much lower than previously observed for $[Yb(L^{Me/Et})_2(thf)_2]$ complexes.[18] Thus, less stable Ln^{II} states (Ln = La, Ce, Nd)[36] inhibit but do not prevent C–F activation with these ligands.

Experimental

General: the compounds described herein were prepared and handled using conventional inert atmosphere techniques. IR spectra were recorded as Nujol mulls between NaCl plates using either a Perkin Elmer 1600 Series FTIR instrument or a Perkin Elmer Spectrum RX I FTIR Spectrometer within the range 4000–600 cm^{-1}. Far IR spectra were obtained as Vaseline mulls between polyethylene disks on a Bruker IFS120HR instrument (with Mylar far IR optics). Multinuclear NMR spectra were recorded on a Bruker DPX 300 spectrometer. Chemical shifts (*δ*/ppm) were referenced to the residual ^1H resonances of the deuterated solvents (^{1}H) or external CCl_3F (^{19}F). Melting points were determined in sealed glass capillaries under nitrogen and are not calibrated. Microanalyses were determined by the Campbell Microanalytical Service, University of Otago (New Zealand), whereas metal analyses were determined by Na_2H_2edta titration following decomposition of the sample with HNO_3/H_2SO_4.[42,43] GC/MS data were obtained with an Agilent 6890 series GC fitted with a 5% phenylmethylsiloxane capillary column (Agilent 19091S-433HP-5mS) interfaced to an Agilent 5987 network mass selective detector. Dme, hexane and thf were pre-dried over sodium metal and distilled over sodium benzophenone ketyl before being stored under an atmosphere of nitrogen. Toluene, C_7D_8 and C_6D_6 were pre-dried over sodium and then distilled under nitrogen from sodium metal before being stored under an atmosphere of nitrogen. Absolute ethanol was used as received. Pentafluorobenzene was stored over molecular sieves (4 Å) but was otherwise used as purchased from Aldrich. Lanthanoid metals were purchased from Santoku (America Int.) or Tianjiao (Baotou, China) as ingots, powders or rods and stored under nitrogen in a glove box. $Hg(C_6F_5)_2$,[44] $Hg(CCPh)_2$,[45] p-$HC_6F_4NHC_2H_4NMe_2$ ($L^{Me}H$)[18,35] and p-$HC_6F_4NHC_2H_4NEt_2$ ($L^{Et}H$)[18] were prepared by literature methods.

Synthesis of [La(p-$HC_6F_4N(CH_2)_2NMe_2)_3$] [La($L^{Me})_3$] and [La(p-$HC_6F_4N(CH_2)_2NMe_2)_2F]_3$ [La($L^{Me})_2F]_3$

Method 1: Freshly filed lanthanum metal (0.80 g, 6.0 mmol), $Hg(C_6F_5)_2$ (1.60 g, 3.0 mmol), $L^{Me}H$ (1.42 g, 6.0 mmol) and one drop of Hg were stirred in thf (30 mL) for three days at room temperature. The reaction mixture was filtered and then the solvent was removed *in vacuo* leaving a small amount of dark brown oil. Toluene (10 mL) was then added and overnight storage of the solution at −30 °C yielded colourless crystals of **[La($L^{Me})_2F]_3$**$\cdot 3/2C_7H_8$ (0.14 g, 10%). M.p. 235 °C (dec.); (Found C 38.62, H 3.65, N 8.40; $C_{60}H_{66}F_{27}La_3N_{12}$ requires (loss of C_7H_8 of solvation, 1884.92) C 38.23, H 3.53, N 8.92%); IR (Nujol): v = 1640 (s), 1572 (m), 1525 (w), 1495 (s), 1406 (w), 1354 (m), 1296 (w), 1275 (w), 1154 (w), 1139 (s), 1072 (m), 1056 (m), 1037 (m), 952 (m), 926 (m), 869 (w), 784 (w), 756 (w), 726 (w) cm^{-1}; far IR (Vaseline): v = 547 (s), 497 (w), 473 (s), 447 (m), 398 (s), 379 (w), 355 (m), 319 (w), 279 (m), 250 (m), 184(s) cm^{-1}; ^{1}H NMR (C_6D_6, 300 MHz, 343 K): loss of C_7H_8 of solvation: 1.93 (s, 36H; Me_2N), 1.96 (s, br, 12H; CH_2NMe_2, 3.59 (s, br, 12H; CH_2NAr), 5.80 (m, 6H; HC_6F_4); $^{19}F\{^1H\}$ NMR (C_6D_6, 282.4 MHz, 343 K): −142.4 (br, s, 12F; F3,5), −154.6 (br, s, 12F; F2,6); the spectra also show the presence of a small amount of the homoleptic complex **[La($L^{Me})_3$]**. Further concentration of the filtrate to 2 mL gave colourless crystalline **[La($L^{Me})_3$]** (1.04 g, 62%). M.p. 180 °C (dec.); (Found C 42.70, H 3.99, N 9.69; $C_{30}H_{33}F_{12}LaN_6$ (844.51) requires: C 42.67, H 3.94, N 9.95%); IR (Nujol): v = 1640 (s), 1573 (s), 1353 (m), 1284 (m), 1264 (w), 1238 (w), 1160 (w), 1134 (m), 1059 (m), 1039 (m), 954 (s), 926 (s), 872 (m), 791 (m), 760 (m) cm^{-1}; far IR (Vaseline): v = 576 (s), 545 (s), 498 (m), 474 (s), 453 (br, s), 401 (m), 376 (m), 330 (w), 276 (m), 227 (w), 195 (w), 168 (s) cm^{-1}; ^{1}H NMR (C_6D_6, 300 MHz, 303 K): 1.85 (s, 18H; Me_2N), 2.11 (t, $^3J_{H,H}$ = 6.0 Hz, 6H; CH_2NMe_2, 3.55 (br, s, 6H; CH_2NAr, 5.86 (m, 3H; HC_6F_4); $^{19}F\{^1H\}$ NMR (C_6D_6, 282.4 MHz, 303 K): −143.5 (br, s, 6F; F3,5), −156.6 (br, s, 6F; F2,6); $^{19}F\{^1H\}$ NMR (C_7D_8, 282.4 MHz, 193 K): −144.3 (s, 4F), −146.8 (s, 1F), −150.8 (s, 1F), −156.3 (s, 1F), −157.2 (s, 2F), −162.7 (s, 1F), −163.7 (s, 2F).

Method 2: Freshly filed lanthanum metal (0.28 g, 2.0 mmol), $Hg(CCPh)_2$ (0.40 g, 1.0 mmol), $L^{Me}H$ (0.47 g, 2.0 mmol) and one drop of Hg were stirred in thf (10 mL) for three days at room temperature. The mixture was then filtered and the solvent removed *in vacuo* leaving a pale solid crude product. Crystallization from toluene (1 mL) gave a pale crystalline product **[La($L^{Me})_3$]** (0.34 g, 61%); identification by IR, ^{1}H and $^{19}F\{^1H\}$ NMR spectroscopy.

GC/MS analyses of the reaction mixture from Method 1 forming [La($L^{Me})_3$] and [La($L^{Me})_2F]_3$

After the reaction from *Method 1* was complete, some of the solution (0.5 mL) was transferred to a sample vial and EtOH (two drops) was added. The insoluble materials were filtered off and the solution was then diluted with EtOH (0.5 mL) and submitted for analysis. GC/MS: $R_t(m/z)$ = 10.483 (m/z 298) $[C_{12}H_2F_8]^+$, 11.677 (m/z 236) $[L^{Me}H]^+$, 13.306 (m/z 233) $[L^{Me}H - 3H]^+$, 16.152 (m/z 384) $[L^{Me}H - F + C_6F_5]^+$.

Attempted transformation of [La($L^{Me})_3$] into [La($L^{Me})_2F]_3$

A solution of **[La($L^{Me})_3$]** (0.04 g) in C_7H_8 (0.7 mL) was heated at 110 °C for 72 h. No appreciable transformation of **[La($L^{Me})_3$]** into **[La($L^{Me})_2F]_3$** was detected by $^{19}F\{^1H\}$ NMR spectroscopy.

Synthesis of [La(p-$HC_6F_4N(CH_2)_2NEt_2)_3$] [La($L^{Et})_3$]

Freshly filed lanthanum metal (0.84 g, 6.0 mmol), $Hg(C_6F_5)_2$ (1.60 g, 3.0 mmol), $L^{Et}H$ (1.59 g, 6.0 mmol) and one drop of Hg were stirred in thf (30 mL) for three days at room temperature. The solvent was then removed *in vacuo* and replaced with toluene (20 mL). The mixture was filtered and the volume of the solution was reduced *in vacuo* to 3 mL. The solution was stored at ambient temperature for two days yielding colourless crystals **[La($L^{Et})_3$]**$\cdot C_7H_8$ (0.84 g, 45%). M.p. 138 °C (dec.); (Found C 46.61, H 5.02, N 8.86; $C_{36}H_{45}F_{12}N_6La$ requires (loss of C_7H_8 of solvation, 928.67) C 46.56, H 4.88, N 9.05%); IR (Nujol): v = 1646 (s), 1578 (m), 1498 (m), 1295 (m), 1263 (w), 1246 (w), 1200 (w), 1182 (w), 1140 (s), 1064 (m), 1046 (w), 1006 (w), 977 (m), 944 (m), 918 (w), 873 (w), 826 (w), 796 (w), 761 (m), 752 (m), 691 (w), 656 (w), 614 (w) cm^{-1}; ^{1}H NMR (C_6D_6, 300 MHz, 303 K): loss of C_7H_8 of solvation, 0.71 (t, 18H; Me), 2.45 (m, 18H; CH_2Me + CH_2NEt_2), 3.67 (m, 6H; CH_2NAr), 5.78 (m, 3H; HC_6F_4); $^{19}F\{^1H\}$ NMR (C_6D_6, 282.4 MHz, 303 K): −142.8 (s, 6F; F3,5), −155.7 (s, br, 6F; F2,6); $^{19}F\{^1H\}$ NMR (C_7D_8, 282.4 MHz, 203 K): −139.0 (s, 1F), −139.5 (s, 1F), −139.9 (s, 1F), − 143.9 (s, 1F), −144.5 (s, 1F), −145.3 (s, 1F), −145.5 (s, 1F), −146.7 (s, 1F), −154.7 (s, br, 1F), −163.0 (s, 1F), −163.7 (s, 1F), −164.0 (s, 1F).

Synthesis of [Ce(p-$HC_6F_4N(CH_2)_2NMe_2)_3$] [Ce($L^{Me})_3$] and [Ce(p-$HC_6F_4N(CH_2)_2NMe_2)_2F]_3$ [Ce($L^{Me})_2F]_3$

Method 1: Freshly filed cerium metal (0.84 g, 6.0 mmol), $Hg(C_6F_5)_2$ (1.60 g, 3.0 mmol), $L^{Me}H$ (1.42 g, 6.0 mmol) and one drop of Hg were stirred in thf (30 mL) for three days at room temperature. The reaction mixture was filtered and then the solvent was removed *in vacuo* leaving a pale brown solid. Toluene (10 mL) was then added and concentration of the solution *in vacuo* to 5 mL overnight deposited colourless crystals of **$[Ce(L^{Me})_2F]_3$**$\cdot 3/2C_7H_8$ (0.20 g, 15%). M.p. 248 °C (dec.); (Found C 41.32, H 4.03, N 8.36; $C_{70.5}H_{78}F_{27}N_{12}Ce_3$ (2026.76) requires C 41.78, H 3.88, N 8.29%); IR (Nujol): ν = 1644 (vs), 1574 (vs), 1407 (vs), 1354 (vs), 1295 (s), 1275 (s), 1294 (w), 1200 (m), 1139 (vs), 1088 (w), 1073 (s), 1056 (s), 1035 (w), 951 (vs), 926 (vs), 870 (s), 786 (s), 762 (sh), 752 (s), 727 (vs), 707 (w), 658 (s), 653 (w), 577 (m) cm^{-1}; far IR (Vaseline): 576 (m), 546 (m), 378 (s), 322 (m), 254 (s), 201 (s) cm^{-1}; ^{1}H NMR (C_7D_8, 300 MHz, 373 K): proposed monomer (see Results and discussion): −0.86 (br, s, 12H; Me_2N), 2.13 (s; MePh), 3.07 (br, s, 2H; HC_6F_4), 7.08 (m; C_7H_8), 8.16 (br, s, 4H; CH_2NMe_2), 15.91 (br, s, 4H; CH_2NAr); proposed trimer: −2.55 (br, s, 36H; Me_2N), 2.80 (br, s, 12H; CH_2NMe_2), 10.95 (br, s, 6H; HC_6F_4), 19.85 (br, s, 12H; CH_2NAr). Both species are evident at 323 K (trimer : monomer 0.55 : 1 by integration), 343 K (trimer : monomer 0.45 : 1) and at 373 K (trimer : monomer 0.25 : 1); $^{19}F\{^1H\}$ NMR: (C_7D_8, 282.4 MHz, 373 K): monomer and trimer indistinguishable: −147.7 (s, F3,5), −199.8 (vvbr, s, F2,6) (1 : 1 integration ratio).

The filtrate following isolation of **$[Ce(L^{Me})_2F]_3$** was further concentrated *in vacuo* to 1 mL and stored overnight. The solution was decanted to collect **$[Ce(L^{Me})_3]$** as a pale brown solid (0.91 g, 54%). M.p. 157–161 °C; (Found C 42.64, H 4.12, N 9.65; $C_{30}H_{33}F_{12}N_6Ce$ (845.72) requires C 42.61, H 3.93, N 9.94%); IR (Nujol): ν = 1642 (s), 1573 (m), 1494 (vs), 1355 (vs), 1284 (m), 1201 (vw), 1137 (s), 1057 (s), 1040 (s), 955 (m), 926 (s), 871 (w), 790 (w), 763 (w), 722 (m), 690 (vw), 652 (vw), 578 (w) cm^{-1}; far IR (Vaseline): ν = 630 (m), 578 (s), 545 (m), 474 (m), 454 (s), 402 (s), 374 (w), 324 (m), 276 (w), 228 (m), 197 (w), 168 (m) cm^{-1}; ^{1}H NMR (C_7D_8, 300 MHz, 303 K): −10.32 (br, s, ≈18H; Me_2N), −2.38 (vbr, s, ≈6H; CH_2NMe_2), 8.64 (s, 3H; HC_6F_4), 17.79 (br, s, ≈6H; CH_2NAr); considerable broadening of some resonances prevented accurate integration but better resolution was obtained by heating; T = 343 K: −7.81 (br, s, 18H; Me_2N), 0.14 (br, s, 6H; CH_2NMe_2), 7.68 (br, m, 3H; HC_6F_4), 15.75 (br, s, 6H; CH_2NAr); $^{19}F\{^1H\}$ NMR (C_7D_8, 282.4 MHz, 303 K): −142.0 (m; F3,5); T = 343 K: −141.8 (s, 6F; F3,5), −180.1 (s, br, 6F; F2,6).

Method 2: Freshly filed cerium metal (0.28 g, 2.0 mmol), $Hg(CCPh)_2$ (0.40 g, 1.0 mmol), $L^{Me}H$ (0.47 g, 2.0 mmol) were stirred in thf (10 mL) for five days at room temperature. The mixture was then filtered and the solvent removed *in vacuo* leaving a brown solid. Toluene (10 mL) was added and a small amount of dark residue settled out overnight. The solution was filtered and from it, **$[Ce(L^{Me})_2F]_3$** was identified by $^{19}F\{^1H\}$ NMR spectroscopy; **$[Ce(L^{Me})_3]$** was also present.

GC/MS analyses of the reaction mixture forming $[Ce(L^{Me})_3]$ and $[Ce(L^{Me})_2F]_3$

After the reaction detailed in *Method 1* was complete, some of the solution (0.5 mL) was transferred to a sample vial and EtOH (two drops) was added. The insoluble materials were filtered off and then the solution was diluted with EtOH (0.5 mL) and submitted for analysis. R_t: 11.872 (m/z 236) $[L^{Me}H]^+$, 12.552 (m/z 218) $[L^{Me}H - F + H]^+$, 12.923 (m/z 233) $[L^{Me}H - 3H]^+$, 15.570 (m/z 384) $[L^{Me}H - F + C_6F_5]^+$, 19.690 (m/z 408), 20.348 (m/z 432) $[L^{Me}H - F - H]_2{}^+$.

Transformation of $[Ce(L^{Me})_3]$ into $[Ce(L^{Me})_2F]_3$

A solution of **$[Ce(L^{Me})_3]$** (0.030 g) in C_7D_8 (0.7 mL) was heated at 110 °C for 48 h. The ^{1}H and $^{19}F\{^1H\}$ NMR spectra indicate 40% transformation of **$[Ce(L^{Me})_3]$** into **$[Ce(L^{Me})_2F]_3$** based on integration values.

Synthesis of $[Ce(p\text{-}HC_6F_4N(CH_2)_2NEt_2)_3]$ $[Ce(L^{Et})_3]$

Freshly filed cerium metal (0.84 g, 6.0 mmol), $Hg(C_6F_5)_2$ (1.60 g, 3.0 mmol), $L^{Et}H$ (1.59 g, 6.0 mmol) and one drop of Hg were stirred in thf (30 mL) for three days at room temperature. The reaction mixture was filtered and then the solvent was removed *in vacuo* leaving a small amount of dark orange/brown oil. Toluene (10 mL) was then added and concentration of the solution *in vacuo* to 3 mL and storage for three weeks deposited large colourless plates **$[Ce(L^{Et})_3]$**$\cdot 1/2C_7H_8$ (0.69 g, 37%). M.p. 190–194 °C; (Found Ce 14.67; $C_{36}H_{45}F_{12}N_6Ce$ (loss of C_7H_8 of solvation, 929.88) requires Ce 15.07%); IR (Nujol): ν = 1644 (s), 1576 (m), 1497 (m), 1398 (w), 1378 (w), 1368 (w), 1350 (w), 1296 (w), 1138 (s), 1076 (w), 1048 (m), 1003 (w), 946 (s), 904 (w), 874 (w), 788 (w), 760 (w), 748 (w), 728 (w), 657 (w) cm^{-1}; ^{1}H NMR (C_6D_6, 300 MHz, 343 K): loss of most C_7H_8 of solvation, −3.00–3.60 (br, m, 36H; Me + CH_2Me + CH_2NEt_2), 2.50 (t, 3H; HC_6F_4), 19.24 (br, s, 6H; CH_2NAr); $^{19}F\{^1H\}$ NMR (C_6D_6, 282.4 MHz, 303 K): −150.3 (br, s, $\Delta\nu_{1/2}$ = 1099 Hz, 6F; F3,5); T = 343 K: −148.1 (s, 6F; F3,5), −201.5 (vvbr, s, $\Delta\nu_{1/2}$ = 2015 Hz, 6F; F2,6).

Synthesis of $[Nd(p\text{-}HC_6F_4N(CH_2)_2NMe_2)_3]$ $[Nd(L^{Me})_3]$

Neodymium powder (1.73 g, 12.0 mmol), $Hg(C_6F_5)_2$ (1.60 g, 3.0 mmol), $L^{Me}H$ (1.42 g, 6.0 mmol) and one drop of Hg were stirred in thf (30 mL) for three days at room temperature. The reaction mixture was filtered and then the solvent was removed *in vacuo* leaving a small amount of dark brown oil. Hexane (5 mL) was then added and the solution was stored overnight at room temperature yielding **$[Nd(L^{Me})_3]$** as pale blue crystals (0.70 g, 41%). M.p. 174–178 °C; (Found C 42.44, H 3.88, N 9.65; $C_{30}H_{33}F_{12}N_6Nd$ (849.84) requires C 42.40, H 3.91, N 9.89%); IR (Nujol): ν = 1645 (s), 1573 (m), 1494 (vs), 1411 (w), 1399 (w), 1379 (w), 1300 (w), 1286 (m), 1264 (w), 1200 (vw), 1159 (w), 1136 (s), 1098 (vw), 1057 (sh), 1043 (vs), 1017 (sh), 957 (m), 927 (vs), 874 (m), 786 (m), 770 (m), 736 (sh), 716 (m), 690 (w), 641 (w), 578 (w), 543 (w) cm^{-1}; ^{1}H NMR (C_7D_8, 300 MHz, 303 K): −11.44 (br, s, 18H; Me_2N), 3.95 (br, s, 6H; CH_2NMe_2), 7.44 (s, 3H; HC_6F_4), 29.23 (br, s, 6H; CH_2NAr); $^{19}F\{^1H\}$ NMR (C_6D_6, 282.4 MHz, 303 K): −142.9 (br, s; F3,5); $^{19}F\{^1H\}$ NMR (C_6D_6, 282.4 MHz, 343 K): −143.5 (s, 6F; F3,5), −190.1 (s, br, 6F; F2,6).

Synthesis of [Nd(*p*-HC$_6$F$_4$N(CH$_2$)$_2$NEt$_2$)$_3$] [Nd(L^{Et})$_3$]

Neodymium powder (0.86 g, 6.0 mmol), Hg(C$_6$F$_5$)$_2$ (1.07 g, 2.0 mmol), L^{Et}H (1.59 g, 6.0 mmol) and one drop of Hg were stirred in thf (30 mL) for three days at room temperature. The reaction mixture was filtered and then the solvent was removed *in vacuo* and replaced with toluene (10 mL). The solution was concentrated *in vacuo* (2 mL) and stored overnight at room temperature yielding pale blue plates **[Nd(L^{Et})$_3$]** (0.67 g, 36%). Crystals suitable for X-ray crystallography were obtained by crystallization from hexane. M.p. 132–140 °C; (Found Nd 14.91; $C_{36}H_{45}F_{12}N_6Nd$ (934.01) requires Nd 15.44%); IR (Nujol): *ν* = 1647 (vs), 1579 (s), 1524 (sh), 1499 (vs), 1352 (w), 1297 (s), 1263 (m), 1247 (w), 1201 (m), 1182 (w), 1140 (vs), 1071 (s), 1048 (w), 1034 (w), 1008 (vw), 979 (s), 947 (vs), 919 (w), 876 (w), 825 (vw), 797 (w), 764 (s), 727 (s), 708 (vw), 692 (vw), 658 (w), 617 (m), 576 (w) cm^{-1}; ^{1}H NMR (C$_6$D$_6$, 300 MHz, 343 K): −3.37 (br, s, 30H; Et), 0.82 (s, 3H; HC$_6$F$_4$), 1.40 (br, s, 6H; CH$_2$NEt$_2$), 22.89 (br, s, 6H; CH$_2$NAr); ^{19}F{^{1}H} NMR (C$_6$D$_6$, 282.4 MHz, 303 K): −144.0 (br, s, F3,5); ^{19}F{^{1}H} NMR (C$_6$D$_6$, 282.4 MHz, 343 K): −146.8 (s, 6F; F3,5), −192.5 (br, s, 6F; F2,6).

Synthesis of [Nd(*p*-HC$_6$F$_4$N(CH$_2$)$_2$NEt$_2$)$_2$F]$_2$ [Nd(L^{Et})$_2$F]$_2$

A similar reaction procedure for the synthesis of **[Nd(L^{Et})$_3$]** was used but the solution was concentrated *in vacuo* to 5 mL. The solution was stored at ambient temperature for four weeks giving dichroic blue/orange crystals (yield: 0.34 g, 25%). Crystals suitable for X-ray crystallography were obtained from crystallization from either toluene or hexane. (Found C 42.24, H 4.70, N 8.21; $C_{48}H_{60}F_{18}N_8Nd_2$ (1379.49) requires C 41.79, H 4.38, N 8.12%); IR (Nujol): *ν* = 1645 (s), 1576 (m), 1522 (w), 1498 (s), 1400 (w), 1369 (w), 1350 (w), 1296 (m), 1261 (w), 1246 (w), 1199 (w), 1139 (s), 1076 (w), 1048 (w), 946 (s), 904 (w), 875 (w), 791 (w), 760 (w), 748 (w), 728 (w), 668 (w), 657 (w) cm^{-1}; far IR (Vaseline): *ν* = 574 (s), 553 (w), 533 (m), 510 (w), 482 (s), 462 (w), 441 (m), 427 (w), 397 (w), 381 (m), 341 (s), 272 (w), 239 (w), 196 (m), 176 (vs) cm^{-1}.

Concurrent synthesis of [Nd(L^{Et})$_3$] and [Nd(L^{Et})$_2$F]$_2$

Neodymium powder (0.86 g, 6.0 mmol), Hg(C$_6$F$_5$)$_2$ (1.60 g, 3.0 mmol), L^{Et}H (1.59 g, 6.0 mmol) and one drop of Hg were

Table 3 Crystal data and structure refinement for complexes **[La(L^{Et})$_3$]**·C$_7$H$_8$ –**[Nd(L^{Me})$_2$F]$_2$**·C$_6$H$_{14}$

	[La(L^{Et})$_3$]·C$_7$H$_8$	**[Ce(L^{Et})$_3$]**·1/2C$_7$H$_8$	**[Nd(L^{Me})$_3$]**	**[Nd(L^{Et})$_3$]**
Formula	$C_{43}H_{53}F_{12}N_6La$	$C_{39.5}H_{49}F_{12}N_6Ce$	$C_{30}H_{33}F_{12}N_6Nd$	$C_{36}H_{45}F_{12}N_6Nd$
M_r	1020.82	975.97	849.86	934.02
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a (Å)	10.168(2)	10.233(2)	9.7596(3)	21.120(4)
b (Å)	11.251(2)	11.421(2)	9.7779(3)	10.559(2)
c (Å)	20.709(4)	18.757(4)	17.8383(6)	17.562(4)
α (°)	102.76(3)	81.03(3)	89.367(2)	90
β (°)	99.50(3)	78.85(3)	75.192(2)	103.42(3)
γ (°)	92.84(3)	85.71(3)	81.488(2)	90
V (Å^3)	2269.9(8)	2122.2(7)	1626.98(9)	3809.4(13)
Z	2	2	2	4
μ (mm^{-1})	1.028	1.161	1.697	1.457
ρ_{calc} (g cm^{-3})	1.494	1.527	1.735	1.629
N_{τ}	28 485	23 644	28 652	42 892
$N(R_{int})$	7800(0.0515)	7417(0.2295)	7464(0.0194)	6723(0.1969)
R_1/wR_2 ($I > 2\sigma(I)$)	0.0667/0.1517	0.0726/0.1097	0.0202/0.0511	0.0622/0.1305
R_1/wR_2 (all data)	0.0750/0.1561	0.2101/0.1474	0.0217/0.0522	0.1184/0.1557
GOF	1.221	0.970	1.069	1.030
max/min Δ*e* (e Å^{-3})	3.669/−3.018	0.919/−0.928	1.251/−0.364	1.499/−1.034

	[La(L^{Me})$_2$F]$_3$·3/2C$_7$H$_8$	**[Ce(L^{Me})$_2$F]$_3$**·3/2C$_7$H$_8$	**[Nd(L^{Et})$_2$F]$_2$**	**[Nd(L^{Et})$_2$F]$_2$**·C$_6$H$_{14}$
Formula	$C_{70.5}H_{78}F_{27}N_{12}La_3$	$C_{70.5}H_{78}F_{27}N_{12}Ce_3$	$C_{48}H_{60}F_{18}N_8Nd_2$	$C_{54}H_{70}F_{18}N_8Nd_2$
M_r	2023.18	2026.81	1379.52	1461.66
Space group	$R\bar{3}$	$R\bar{3}$	$P\bar{1}$	*Pbca*
a (Å)	22.6999(3)	22.712(3)	12.115(2)	18.5793(5)
b (Å)	22.6999(3)	22.712(3)	12.644(3)	22.1566(6)
c (Å)	53.1241(12)	53.514(11)	20.204(4)	28.3427(7)
α (°)	90	90	72.95(3)	90
β (°)	90	90	76.68(3)	90
γ (°)	120	120	68.60(3)	90
V (Å^3)	23 706.6(7)	23 907 (7)	2728.4(9)	11 667.4(5)
Z	12	12	2	8
μ (mm^{-1})	1.705	1.796	1.985	1.861
ρ_{calc} (g cm^{-3})	1.701	1.689	1.679	1.664
N_{τ}	178 448	42 852	23 861	86 381
N (R_{int})	9264(0.0625)	9362(0.1634)	9087(0.0618)	13 399 (0.0439)
R_1/wR_2 ($I > 2\sigma(I)$)	0.0559/0.1352	0.0641/0.1428	0.0503/0.1370	0.0308/0.0713
R_1/wR_2 (all data)	0.0978/0.1780	0.1573/0.1894	0.0550/0.1415	0.0463/0.0803
GOF	1.156	1.074	1.047	1.039
max/min Δ*e* (e Å^{-3})	2.361/−2.137	3.109/−0.961	1.312/−1.322	1.336/−0.571

stirred in thf (30 mL) for two days at room temperature. Filtration and evaporation of the solvent *in vacuo* gave a small amount of dark brown oil. Hexane (30 mL) was added to the oil and a small amount of dark solid precipitated. After filtration and concentration *in vacuo* to 10 mL and storage at −30 °C for two days, a brownish solid precipitated, to which hexane (10 mL) was added. After heating and cooling twice, the solution was filtered to remove a small amount of orange-brown solid. The filtrate was concentrated *in vacuo* to 5 mL and left at ambient temperature, giving a large amount of non-crystalline solid. Hexane (20 mL) was added and the mixture was again heated and filtered to remove some blue solid (**a**) which was dissolved in toluene (10 mL) and the solution concentrated to 5 mL and layered with hexane. Some small blue crystals formed and the mixture was gently heated and left at ambient temperature. After three days, light blue solid precipitated and isolation by decantation and washing with cold hexane and drying *in vacuo* gave **$[Nd(L^{Et})_3]$** (0.17 g, 9%); identification by ^1H, $^{19}F\{^1H\}$ NMR and IR spectroscopy. The filtrate obtained from the isolation of (**a**) deposited orange needles and blue-green blocks. Sufficient needles were separated manually and identified by X-ray crystallography as **$[Nd(L^{Et})_2F]_2$**$\cdot C_6H_{14}$. The IR spectrum of the bulk dried product corresponded to that of unsolvated **$[Nd(L^{Et})_2F]_2$**, consistent with ready loss of C_6H_{14}.

X-ray diffraction structure determinations

Single crystals coated with viscous hydrocarbon oil were mounted on glass fibres. Data were obtained at −150 °C (123 K) on a Bruker X8 APEX II CCD diffractometer (**$[La(L^{Et})_3]$**$\cdot C_7H_8$, **$[La(L^{Me})_2F]_3$**$\cdot 3/2C_7H_8$, **$[Nd(L^{Me})_3]$**, **$[Nd(L^{Et})_2F]_2$**$\cdot C_6H_{14}$) or an Enraf-Nonius Kappa CCD diffractometer (**$[Ce(L^{Et})_3]$**$\cdot 1/2C_7H_8$, **$[Ce(L^{Me})_2F]_3$**$\cdot 3/2C_7H_8$, **$[Nd(L^{Et})_3]$**, **$[Nd(L^{Et})_2F]_2$**); all are equipped with graphite-monochromated Mo-K$_\alpha$ radiation (λ = 0.71073 Å). Each data set was empirically corrected for absorption (SORTAV[46a] and SADABS[46b]) then merged. The structures were solved by conventional methods and refined by full-matrix least-squares on all F^2 data using SHELX97,[46c] in conjunction with the X-Seed graphical user interface.[46d] All hydrogen atoms were placed in calculated positions using the riding model. Crystal data and refinement details are given in Table 3. CCDC-859374 and CCDC-859380–859386 contain the supplementary crystallographic data for this paper.†

Variata for $[Ce(L^{Me})_2F]_3\cdot 3/2C_7H_8$. Voids exist in the crystal structure of $[CeF(L^{Me})_2]_3\cdot 1.5PhMe$, as shown from the crystallography data. SQUEEZE was used and shows a void volume of 869.4 Å^3 and an electron count of 49 per unit cell. This is negligible compared with the large size (23907(7) Å^3) and content (moiety formula $C_{70.50}H_{78}Ce_3F_{27}N_{12}$, Z = 12) of the unit cell. Overall, apart from the 1.5 PhMe molecules of crystallization shown in the formula, no more solvent molecules are considered to be present in the voids.

Acknowledgements

We gratefully acknowledge the Australian Research Council for funding assistance (Grant Number: DP0984775), the Faculty of Science for a Faculty of Science Dean's Scholarship to RPK, and Dr Samar Beaini for X-ray crystallography assistance.

References

1 H. Plenio, *ChemBioChem*, 2004, **5**, 650–655; H. Plenio, *Chem. Rev.*, 1997, **97**, 3363.

2 (*a*) J. L. Kiplinger, T. G. Richmond and C. L. Osterberg, *Chem. Rev.*, 1994, **94**, 373; (*b*) H. Dorn, E. F. Murphy, S. A. A. Shah and H. W. Roesky, *J. Fluorine Chem.*, 1997, **86**, 121; (*c*) J. Burdeniuc, B. Jedicka and R. H. Crabtree, *Chem. Ber.*, 1997, **130**, 145; (*d*) F. Alonso, I. P. Beletskaya and M. Yus, *Chem. Rev.*, 2002, **102**, 4009; (*e*) H. Amii and K. Uneyama, *Chem. Rev.*, 2009, **109**, 2119; (*f*) G. Meier and T. Braun, *Angew. Chem., Int. Ed.*, 2009, **48**, 1546; (*g*) A. D. Sun and J. A. Love, *Dalton Trans.*, 2010, **39**, 10362; (*h*) L. Keyes, A. D. Sun and J. A. Love, *Eur. J. Org. Chem.*, 2011, 3985.

3 H. Takemura, S. Nakashima, N. Kon, M. Yasutake, T. Shinmyozu and T. Inazu, *J. Am. Chem. Soc.*, 2001, **123**, 9293.

4 P. L. Watson, T. H. Tulip and I. Williams, *Inorg. Chem.*, 1990, **29**, 1999.

5 D. O'Hagan, *Chem. Soc. Rev.*, 2008, **37**, 308.

6 F. Castillo and T. D. Tilley, *J. Am. Chem. Soc.*, 2001, **123**, 10526.

7 P. G. Hayes, G. C. Welch, D. J. H. Emslie, C. L. Noack, W. E. Piers and M. Parvez, *Organometallics*, 2003, **22**, 1577.

8 G. B. Deacon and C. M. Forsyth, *Organometallics*, 2003, **22**, 1349.

9 L. Maron, E. L. Werkema, L. Perrin, O. Eisenstein and R. A. Andersen, *J. Am. Chem. Soc.*, 2005, **127**, 279.

10 E. L. Werkema and R. A. Andersen, *J. Am. Chem. Soc.*, 2008, **130**, 7153.

11 D. R. Click, B. L. Scott and J. G. Watkin, *Chem. Commun.*, 1999, 633.

12 H. Memmler, K. Walsh, L. H. Gade and J. W. Lauher, *Inorg. Chem.*, 1995, **34**, 4062.

13 A. Lara-Sanchez, A. Rodriguez, D. L. Hughes, M. Schormann and M. Bochmann, *J. Organomet. Chem.*, 2002, **663**, 63.

14 K. Norton, T. J. Emge and J. G. Brennan, *Inorg. Chem.*, 2007, **46**, 4060.

15 J. H. Melman, C. Rohde, T. J. Emge and J. G. Brennan, *Inorg. Chem.*, 2002, **41**, 28.

16 J. H. Melman, T. J. Emge and J. G. Brennan, *Inorg. Chem.*, 2001, **40**, 1078.

17 S. Bannerjee, T. J. Emge and J. G. Brennan, *Inorg. Chem.*, 2004, **43**, 6307.

18 G. B. Deacon, C. M. Forsyth, P. C. Junk and J. Wang, *Chem.–Eur. J.*, 2009, **15**, 3082.

19 (*a*) X. Li, J. Baldamus, M. N. Nishura, O. Tardif and Z. Hou, *Angew. Chem., Int. Ed.*, 2006, **45**, 8184; (*b*) W. J. Evans, K. J. Forrestal, M. A. Ansari and J. W. Ziller, *J. Am. Chem.Soc.*, 1998, **120**, 2180.

20 M. W. Bouwkamp, P. H. M. Budzelaar, J. Gorcama, I. D. H. Morales, J. de Wolf, A. Meetsma, S. I. Troyanov, J. H. Teuben and B. Hessen, *J. Am. Chem. Soc.*, 2005, **127**, 14310.

21 (*a*) C. J. Burns, D. J. Berg and R. A. Andersen, *J. Chem. Soc., Chem. Commun.*, 1987, 272; (*b*) G. B. Deacon, S. C. Harris, G. Meyer, D. Stellfeldt, D. L. Wilkinson and G. Zelesny, *J. Organomet. Chem.*, 1998, **552**, 165; (*c*) G. B. Deacon, G. Meyer and D. Stellfeldt, *Eur. J. Inorg. Chem.*, 2000, 1061.

22 C. J. Burns and R. A. Andersen, *J. Chem. Soc., Chem. Commun.*, 1989, 136.

23 G. B. Deacon, G. D. Fallon, C. M. Forsyth, S. C. Harris, P. C. Junk, B. W. Skelton and A. H. White, *Dalton Trans.*, 2006, 802.

24 (*a*) M. L. Cole, G. B. Deacon, P. C. Junk and K. Konstas, *Chem. Commun.*, 2005, 1581; (*b*) M. L. Cole, G. B. Deacon, C. M. Forsyth, P. C. Junk, K. Konstas and J. Wang, *Chem.–Eur. J.*, 2007, **13**, 8092; (*c*) M. L. Cole and P. C. Junk, *Chem. Commun.*, 2005, 2695.

25 G. B. Deacon, A. J. Koplick, W. D. Raverty and D. G. Vince, *J. Organomet. Chem.*, 1979, **182**, 121.

26 (*a*) G. B. Deacon, P. I. MacKinnon and T. D. Tuong, *Aust. J. Chem.*, 1983, **36**, 43; (*b*) G. B. Deacon, C. M. Forsyth and J. Sun, *Tetrahedron Lett.*, 1994, **35**, 1095.

27 (*a*) E. L. Werkema, R. A. Andersen, L. Maron and O. Eisenstein, *Dalton Trans.*, 2010, **39**, 6648; (*b*) E. L. Werkema, E. Messines, L. Perrin, L. Maron, O. Eisenstein and R. A. Andersen, *J. Am. Chem. Soc.*, 2005, **127**, 7781.

28 (*a*) Z. Xie, K. Chui, Q. Yang, T. C. W. Mak and J. Sun, *Organometallics*, 1998, **17**, 3937; (*b*) Z. Xie, Z. Lui, F. Xue and T. C. W. Mak, *J. Organomet. Chem.*, 1997, **539**, 127.

29 (*a*) H. Schumann, M. R. Keitsch, J. Winterfeld and J. Demschuk, *J. Organomet. Chem.*, 1996, **525**, 279; (*b*) A. C. Hillier, X. W. Zhang, G. H. Maunder, S. Y. Liu, T. A. Eberspacher, M. V. Metz, R. McDonald, A. Domingos, N. Marques, V. W. Day, A. Sella and J. Takats, *Inorg. Chem.*, 2001, **40**, 5106.

30 M. Roanelli, A. Kumar, T. J. Emge, R. E. Riman and J. G. Brennan, *Angew. Chem.*, 2008, **120**, 6136–6140; M. Roanelli, A. Kumar, T. J. Emge, R. E. Riman and J. G. Brennan, *Angew. Chem., Int. Ed.*, 2008, **47**, 6049.

31 S. A. A. Shah, H. Dorn, A. Voigt and H. W. Roesky, *Organometallics*, 1996, **15**, 3176.

32 M. I. Bruce, *J. Chem. Soc. A*, 1968, 1459.

33 (*a*) D. P. Buxton, G. B. Deacon, B. M. Gatehouse, I. L. Grayson and D. St. C. Black, *Aust. J. Chem.*, 1988, **41**, 943; (*b*) G. B. Deacon, B. M. Gatehouse and J. Ireland, *Aust. J. Chem.*, 1991, **41**, 943; (*c*) A. Battle, A. M. Bond, A. Chow, D. P. Daniels, G. B. Deacon, T. W. Hambley, P. C. Junk, D. M. Mason and J. Wang, *J. Fluorine Chem.*, 2010, **131**, 1229.

34 For the biological activity of these platinum complexes, see T. Talanico, D. R. Phillips, G. B. Deacon, S. Rainone and L. K. Webster, *Invest. New Drugs*, 1999, **17**, 1.

35 D. P. Buxton, G. B. Deacon, A. M. James, S. J. Knowles and T. L. Williams, *Polyhedron*, 1989, **8**, 2943.

36 (*a*) M. N. Bochkarev, *Coord. Chem. Rev.*, 2004, **248**, 835; (*b*) W. J. Evans, *Inorg. Chem.*, 2007, **46**, 3435; (*c*) P. B. Hitchcock, M. F. Lappert, L. Maron and A. V. Protchenko, *Angew. Chem.*, 2008, **120**, 1510, (*Angew. Chem., Int. Ed.*, **47**, 1488); (*d*) G. Meyer, *Angew. Chem.*, 2008, **120**, 5040, (*Angew. Chem., Int. Ed.*, **47**, 4962); (*e*) F. Jaroschik, A. Momin, F. Nief, X.-F. Le Goff, G. B. Deacon and P. C. Junk, *Angew. Chem., Int. Ed*, 2009, **48**, 1117; (*f*) M. Fang, D. S. Lee, J. W. Ziller, R. J. Doedens, J. E. Bates, F. Furche and W. J. Evans, *J. Am. Chem. Soc.*, 2011, **133**, 3784; (*g*) M. R. MacDonald, J. W. Ziller and W. J. Evans, *J. Am. Chem. Soc.*, 2011, **133**, 15914.

37 G. B. Deacon, C. M. Forsyth and N. M. Scott, *Eur. J. Inorg. Chem.*, 2002, 1425.

38 G. R. Giesbrecht, J. C. Gordon, D. L. Clark, P. J. Hay, B. L. Scott and C. D. Tait, *J. Am. Chem. Soc.*, 2004, **126**, 6387.

39 R. D. Shannon, *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.*, 1976, **32**, 751.

40 F. Bottomley, D. E. Paez and P. S. White, *J. Organomet. Chem.*, 1985, **291**, 35.

41 A. G. M. Barrett, M. R. Crimmin, M. S. Hill, P. B. Hitchcock and P. A. Procopiou, *Angew. Chem., Int. Ed.*, 2007, **46**, 6339.

42 J. L. Atwood, W. E. Hunter, A. L. Wayda and W. J. Evans, *Inorg. Chem.*, 1981, **20**, 4115.

43 G. B. Deacon, G. D. Fallon, C. M. Forsyth, H. Schumann and R. Weimann, *Chem. Ber.*, 1997, **130**, 409.

44 G. B. Deacon, C. M. Forsyth, D. L. Wilkinson and E. T. Lawrenz, in *Synthetic Methods of Organometallic and Inorganic Chemistry*, ed. W. A. Herrman, Thieme, New York, 1997, vol. 6, pp. 48–51.

45 (*a*) R. Johnson and W. L. McEwan, *J. Am. Chem. Soc.*, 1926, **48**, 469; (*b*) G. Eglinton and W. McCrae, *J. Chem. Soc.*, 1963, 2295.

46 (*a*) R. H. Blessing, *J. Appl. Crystallogr.*, 1997, **30**, 421; (*b*) G. M. Sheldrick, *SADABS: Program for Scaling and Absorption Correction of Area Detector Data*, Universität Göttingen, 1997; (*c*) G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2007, **64**, 112; (*d*) L. J. Barbour, *J. Supramol. Chem.*, 2001, **1**, 189.