Steric engineering of C–F activation with lanthanoid formamidinates

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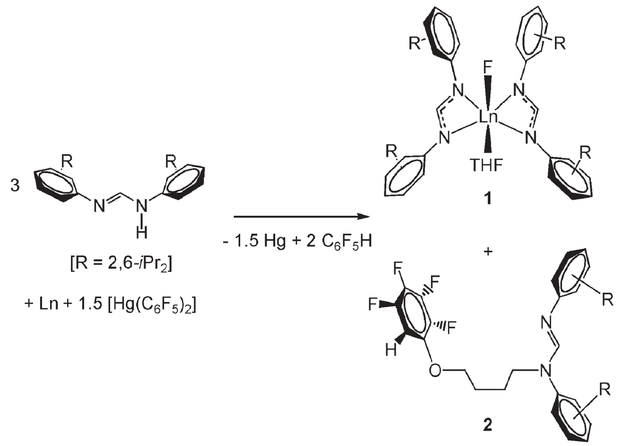
Reaction of lanthanum with $Hg(C_6F_5)_2$ and bulky *N*,*N*′-bis(2,6-diisopropylphenyl)formamidine (HDippForm) in tetrahydrofuran gives [LaF{DippForm}$_2$(THF)] with a rare terminal Ln–F bond, and a high yield of a novel functionalised formamidine, DippForm($(CH_2)_4OC_6F_4H$-*o*).

The activation of unsaturated and saturated fluorocarbon C–F bonds by divalent lanthanoid species is the main source of the few examples of heteroleptic lanthanoid fluorides [Ln(L)$_2$F] (L = anionic ligand).[1–3] As an alternative approach with general applicability, redox transmetalation/protolytic ligand exchange syntheses using bis(pentafluorophenyl)mercury[3] could be employed if the proposed [Ln(C_6F_5)L$_2$] intermediate were to undergo C–F activation to yield [Ln(F)L$_2$] and tetrafluorobenzyne[3] before protolysis (to give LnL$_3$) could occur. This demands steric inhibition of the final exchange step and obviates the need for an isolable divalent precursor. The ready accessibility[4] of *N*,*N*′-diarylformamidinates (potential cyclopentadienide mimics[5]) makes them attractive candidates for steric tuning, but no lanthanoid complexes have yet been published. We now report that with a suitable choice of ligand, sterically engineered C–F activation can be achieved leading to the first lanthanoid organoamide fluorides,[6] which have rare terminal Ln–F bonding. Unexpectedly, chemoselective trapping of the expelled tetrafluorobenzyne also occurs giving a novel functionalised formamidine.

Elemental lanthanum readily reacts with bis(pentafluorophenyl)mercury and *N*,*N*′-bis(2,6-diisopropylphenyl)formamidine (HDippForm) in THF in a 1 : 1.5 : 3 stoichiometry to form [LaF(DippForm)$_2$(THF)]·C_7H_8 (**1**·C_7H_8) after crystallisation from toluene (Scheme 1, Ln = La).‡ By contrast, reaction of La metal with $Hg(C_6F_5)_2$ and the smaller *N*,*N*′-bis(2,6-dimethylphenyl)formamidine yields a lanthanum tris(formamidinate) [La(XylForm)$_3$(THF)]·2THF.[7] **1**·C_7H_8 was characterised‡ by ^1H, $^{13}C\{^1H\}$ and IR spectroscopy, elemental analyses and location of a ^{19}F NMR resonance at +150.2 ppm (La–F).[8] Scheme 1 appears general across a range of lanthanoid sizes, having also been observed for Ln = Nd and Tm.

An X-ray crystal structure determination§ (Fig. 1) shows the lanthanum centre is six-coordinate with cisoid DippForm ligands. Its geometry may be described using the formamidinate ligands as point charges located at the NCN carbon atom. This generates a distorted tetrahedral geometry that boasts not only a rare terminal fluoride[2c,9] but also the first lanthanoid fluoride supported by organoamide ligands (F(1)–La(1)–C(25) 105.1(1)°, O(1)–La(1)–C(50) 104.0(1)°). The La–F bond length in **1** (2.136(2) Å) is short relative to known La–F interactions in metal organic compounds.[6a,10] These are all bridging in nature *e.g.* [{La(1,3-$(SiMe_3)_2C_5H_3)_2$F}$_2$]; 2.349(7) Å and 2.324(9) Å.[6a] However, this bond length is comparable with terminal Ln–F bond lengths found in [Yb(F)(C_5Me_5)$_2$(THF)] (2.026(2) Å), [Yb(F)(C_5Me_5)$_2$(Et_2O)] (2.015(4) Å)[2c] and [Sm(F)(Tp*)$_2$] (Tp* = hydrotris(3,5-dimethylpyrazolyl)borate, Sm–F 2.090(7) Å)[9] when allowance is made for differences in ionic radii (six-coordinate lanthanum; 1.032 Å, eight coordinate ytterbium; 0.985 Å and seven coordinate samarium;



Scheme 1

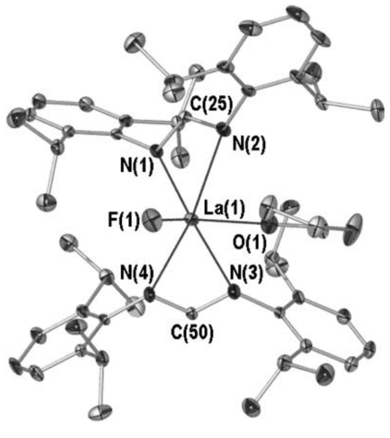


Fig. 1 Molecular structure of **1**, POV-RAY illustration, 40% thermal ellipsoids, all hydrogen atoms and lattice solvent omitted for clarity. Selected bond lengths (Å) and angles (°): La(1)–F(1) 2.136(2), La(1)–O(1) 2.539(3), La(1)–N(1) 2.538(3), La(1)–N(2) 2.578(3), La(1)–N(3) 2.543(3), La(1)–N(4) 2.560(3), O(1)–La(1)–F(1) 85.1(1), N(1)–La(1)–N(2) 53.0(1), N(3)–La(1)–N(4) 53.0(1), O(1)–La(1)–N(1) 132.1(1), O(1)–La(1)–N(2) 79.4(1), F(1)–La(1)–O(1) 85.1(1), F(1)–La(1)–N(1) 109.2(1), F(1)–La(1)–N(2) 104.0(1), F(1)–La(1)–N(3) 127.6(1), F(1)–La(1)–N(4) 97.7(1).

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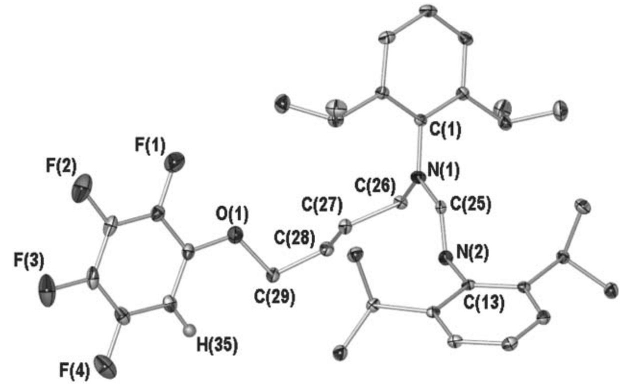

Fig. 2 Molecular structure of **2**, POV-RAY illustration, 40% thermal ellipsoids, all hydrogen atoms except H(35) omitted for clarity. Selected bond lengths (Å) and angles (°): N(1)–C(25) 1.358(2), N(2)–C(25) 1.277(2), N(1)–C(26) 1.472(2), C(29)–O(1) 1.444(2), N(1)–C(25)–N(2) 123.4(2).

1.020 Å).[11] The aryl groups of **1** are near-orthogonal to the NCN backbone as is typical of the DippForm ligand (range of aryl : NCN torsion angles; 74.1(3)° to 88.2(3)°).[4,12]

It is likely that compound **1** results from C–F activation in the pentafluorophenyllanthanum intermediate [La(C_6F_5)(DippForm)$_2$] (*cf.* isolable [Ln(C_6F_5)(L)$_2$] compounds, L = C_5H_5 or C_5Me_5),[2b,6c,13] wherein steric bulk prohibits protonation of the fluoroaryl group giving [La(DippForm)$_3$] by the remaining equivalent of HDippForm (*cf.* formation of [La(XylForm)$_3$(THF)], above[7]). Elimination of tetrafluorobenzyne from MC_6F_5 complexes (the archetypal path of Ln–F formation) normally gives complex fluoroaromatics, in particular 2-nonafluorobiphenyls, from insertion of the benzyne into M–C_6F_5 bonds.[1a,14] However, further work-up of the La–HDippForm–[Hg(C_6F_5)$_2$] reaction mixture enables high yield isolation (81%) of a *single* fluorocarbon co-product; *viz.* the functionalised formamidine **2**‡, identified by spectroscopic analysis and X-ray crystallography (Fig. 2).§

The structure exhibits a DippForm with discrete single (N(1)–C(25) 1.358(2) Å) and double (N(2)–C(25) 1.277(2) Å) C–N bonds tethered to a 2,3,4,5-tetrafluorophenyl group by a ring opened THF.[15] The formation of **2** can be attributed to protonation of tetrafluorobenzyne by HDippForm to give the formamidinate ion and $HC_6F_4^+$, the latter being trapped by THF. Nucleophilic attack of the amidinate on the resulting oxonium ion, $HC_6F_4^+OC_4H_8$, which is activated at the THF α-carbon, yields **2**.[15]

Thus, C–F activation for elements without a readily stable Ln^{II} state[16] can be achieved by steric engineering giving both the first organoamide supported lanthanoid fluorides and novel functionalised fluoroarenes/formamidines. Continuing studies suggest C–F activation of perfluoroaryls with a single *ortho*-fluorine substituent is also possible. Accordingly La metal, Hg(*o*-HC_6F_4)$_2$ and bis(2,6-diisopropylphenyl)formamidine yield **1** and DippForm{(CH$_2$)$_4$OC$_6$F$_3$H$_2$-2,6}.[7]

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Notes and references

‡ General procedure: Lanthanum metal filings (0.10 g, 0.72 mmol), bis(pentafluorophenyl)mercury (0.37 g, 0.69 mmol) and *N*,*N*′-bis(2,6-diisopropylphenyl)formamidine (0.50 g, 1.4 mmol) were stirred in tetrahydrofuran (20 cm^3) under purified nitrogen at room temperature for 48 h. Filtration followed by drying under vacuum yielded a colourless powdered material that was extracted into toluene (10 cm^3). Cooling at –30 °C yielded **1**·C_7H_8 as colourless elongated hexagonal plates in three batches over several days (total 0.37 g, 77% by [Hg(C_6F_5)$_2$]), mp 284 °C (dec.). Found: C 67.86; H 7.66; La 14.65; N 5.13 $C_{54}H_{78}FLaN_4O$; **1** (with loss of C_7H_8) requires C 67.76; H 8.21; La 14.51; N 5.85%. IR (Nujol): 1937 w, 1858 w, 1799 w, 1603 s, 1583 s, 1311 m, 1267 m, 1183 s, 1108 s, 1050 m, 1028 m, 1019 m, 800 m, 756 s, 730 s, 697 s, 673 w cm^{-1}. ^{1}H NMR (300.1 MHz, C_6D_6, 300 K): δ = 8.23 (s, 2H; NC(H)N), 7.27–7.06 (m, 17H; Ar–H), 3.58 (h, ^3J(H,H) = 6.8 Hz, 8 H; CH, *i*Pr), 3.47 (m, 4H; OCH$_2$, THF), 2.18 (s, 3H; CH$_3$, toluene), 1.31 (m, 4H; CH$_2$, THF), 1.27 (d, ^3J(H,H) = 6.8 Hz, 48 H; CH$_3$, *i*Pr). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6, 300 K): δ = 166.7 (NC(H)N), 145.2, 141.8, 137.9 (Ar–C), 129.2, 128.3, 125.5, 123.4, 122.2 (Ar–CH), 66.7 (OCH$_2$, THF), 27.5 (CH, *i*Pr), 24.9 (CH$_2$, THF), 22.5 (CH$_3$, *i*Pr), 20.1 (CH$_3$, toluene). ^{19}F NMR (282.4 MHz, C_6D_6, 300 K, CCl$_3$F): δ = 150.2 (s; La–F). **2**: Concentration of the mother liquor from **1**·C_7H_8 (<1 cm^3) and cooling at –30 °C overnight yielded compound **2** as colourless rods (0.10 g, 81% by [Hg(C_6F_5)$_2$]), mp 160 °C. High resolution ESMS: *m*/*z* 585.3462, $C_{35}H_{45}F_4N_2O$ [M + H]$^+$ requires 585.3390. IR (Nujol): 1665 s, 1636 s, 1528 m, 1523 s, 1386 m, 1364 m, 1289 m, 1233 m, 1150 w, 1097 m, 950 m, 923 m, 821 w, 756 s, 729 s, 687 s, 673 w cm^{-1}. ^{1}H NMR (300.1 MHz, C_6D_6, 300 K): δ = 7.31–7.14 (m, 7H; Ar–H and NC(H)N, DippForm), 5.96 (dddd, ^3J(*o*-H,F) = 11.3 Hz, ^4J(*m*-H,F) = 8.5 Hz, ^4J(*m*-H,F) = 5.7 Hz, ^5J(*p*-H,F) = 2.8 Hz, 1H; Ar–5-H), 3.85 (m, 2H; OCH$_2$), 3.48 (h, ^3J(H,H) = 6.8 Hz, 2H; CH, *i*Pr), 3.36 (m, 4H; NCH$_2$ and CH, *i*Pr), 1.96 (m, 2H; CH$_2$), 1.52 (m, 2H; CH$_2$), 1.31 (d, ^3J(H,H) = 6.9 Hz, 6H; CH$_3$, *i*Pr), 1.19 (d, ^3J(H,H) = 6.8 Hz, 12H; CH$_3$, *i*Pr), 1.15 (d, ^3J(H,H) = 6.9 Hz, 6H; CH$_3$, *i*Pr). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6, 300 K): δ = 147.0 (s; NC(H)N), 138.5, 138.1, 128.4, 128.0, 125.5, 124.4, 122.1, 121.9 (s; Ar–C), 96.6 (dd, ^3J(*o*-C,F) = 22.5 Hz, ^5J(*p*-C,F) = 2.9 Hz; Ar$_F$–CH), 68.5 (s; NCH$_2$), 48.9 (s; OCH$_2$), 27.5, 27.4, 27.1 (s; CH, *i*Pr), 25.8 (s; CH$_2$), 24.1 (s; CH$_3$, *i*Pr), 23.1 (s; CH$_2$), 22.9, 22.5 (s; CH$_3$, *i*Pr) (carbon resonances for the 2,3,4,5-tetrafluorophenyl group, excepting the CH resonance, not observed). ^{19}F NMR (282.4 MHz, C_6D_6, 300 K, CCl$_3$F): δ = −140.0 (ddd, ^3J(*o*-F,F) = 22.6 Hz, ^4J(*o*-F,H) = 11.3 Hz, ^5J(*p*-F,F) = 8.5 Hz, 1F; Ar–4-F), −155.8 (ddd, ^3J(*o*-F,F) = 21.3 Hz, ^3J(*o*-F,F) = 19.8 Hz, ^5J(*p*-F,H) = 2.8 Hz, 1F; Ar–2-F), −160.0 (dddd, ^3J(*o*-F,F) = 19.8 Hz, ^5J(*p*-F,F) = 8.5 Hz, ^4J(*m*-F,H) = 8.5 Hz, ^4J(*m*-F,F) = 2.8 Hz, 1F; Ar–1-F), −167.5 (dddd, ^3J(*o*-F,F) = 22.6 Hz, ^3J(*o*-F,F) = 21.3 Hz, ^4J(*m*-F,H) = 5.7 Hz, ^4J(*m*-F,F) = 2.8 Hz, 1F; Ar–3-F). Fluorines numbered as in Fig. 1. ^{19}F NMR monitoring of reaction mixtures revealed Hg(C_6F_5)$_2$, C_6F_5H and **2** as the sole fluorocarbon species.

§ Crystalline samples of compounds **1**·C_7H_8 and **2** were mounted upon glass fibres in silicone grease at 123(2) K (**2**) or 173(2) K (**1**·C_7H_8). Enraf-Nonius Kappa CCD diffractometer, graphite monochromated Mo Kα X-ray radiation (λ = 0.71073 Å). Data were corrected for absorption by the DENZO-SMN package. Lorentz polarisation and absorption corrections were applied. Structural solution and refinement was carried out using the SHELX suite of programs with the graphical interface X-Seed. Crystal data for **1**·C_7H_8: $C_{61}H_{86}F_1N_4O_1La_1$, M = 1049.25, triclinic, $P\bar{1}$ (no. 2), a = 12.6721(9), b = 13.6678(12), c = 17.264(3) Å, α = 92.904(4), β = 104.552(6), γ = 91.186(4)°, V = 2888.8(6) Å^3, Z = 2, D_c = 1.206 g cm^{-3}, F_{000} = 1108, μ = 0.784 mm^{-1}, $2\theta_{max}$ = 55.7°, 42471 reflections collected, 13485 unique (R_{int} = 0.1285). Final GooF = 1.012, $R1$ = 0.0576, $wR2$ = 0.1013, R indices based on 9041 reflections with $I > 2\sigma(I)$ (refinement on F^2), 694 parameters, 0 restraints. Crystal data for **2**: $C_{35}H_{44}F_4N_2O$, M = 584.72, monoclinic, $P2_1/n$ (no. 14), a = 10.6132(3), b = 20.4222(7), c = 14.8655(6) Å, β = 98.5310(10)°, V = 3186.37(19) Å^3, Z = 4, D_c = 1.219 g cm^{-3}, F_{000} = 1248, μ = 0.089 mm^{-1}, $2\theta_{max}$ = 56.3°, 25587 reflections collected, 7680 unique (R_{int} = 0.1111). Final GooF = 0.938, $R1$ = 0.0568, $wR2$ = 0.1118, R indices based on 3758 reflections with $I > 2\sigma(I)$ (refinement on F^2), 387 parameters, 0 restraints. CCDC 253456 for compound **1** and CCDC 253457 for compound **2**. See http://www.rsc.org/suppdata/cc/b4/b419047e/ for crystallographic data in .cif or other electronic format.

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