Highly electrophilic lanthanide complexes containing fluorinated amido ligands: multiple Ln···F interactions, agostic interactions and η^6-arene coordination

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Highly fluorinated amido ligands have been employed as supporting ligands for homoleptic lanthanide complexes; X-ray diffraction studies reveal multiple Ln···F interactions and a rare example of an η^6-bound toluene solvent molecule.

The chemistry of the transition metals coordinated by mono-, di- and tri-amido ligands has recently generated a considerable amount of interest, due to many interesting observations of catalytic activity,[1] small molecule activation[2] and unusual coordination modes of neutral ligands.[3] A number of these studies have involved amido ligands which have electron-withdrawing fluorinated phenyl groups directly attached to nitrogen.[4] Lanthanide amido complexes[5] are also experiencing renewed attention, due in part to the emergence of this class of compounds as effective catalysts[6] and their use as source molecules for rare-earth doping of semiconducting materials.[7] We are currently interested in the chemistry of highly electrophilic metal amido complexes as potential catalysts for olefin polymerization. We report here the results of a structural study of lanthanide metals (Ln = Nd, Sm) coordinated by a series of highly electron-withdrawing amido ligands: $-NH(C_6F_5)$,$-N(SiMe_3)(C_6F_5)$ and $-N(C_6F_5)_2$.

Reaction of $Sm[N(SiMe_3)_2]_3$ **1**[8] with 3 equiv. of pentafluoroaniline in toluene leads to the formation of a pale yellow solution. Removal of solvent, followed by dissolution of the solid in THF and low-temperature crystallization, allows isolation of the thf adduct $[Sm(NHC_6F_5)_3(thf)_3]$ **2** in 58% yield.† An X-ray diffraction study‡ revealed a highly distorted nine-coordinate geometry about the metal center (Fig. 1), which may best be described as a distorted capped square antiprism in which F(18) caps the face defined by N(1), N(3), O(2) and O(3). Sm–N distances to the amido ligands are 2.352(5), 2.360(5) and 2.371(5) Å while Sm–O distances to the thf ligands lie in the range 2.444(4)–2.502(4) Å. The Sm–N distances are found to be very similar to those observed for the terminal arylamido ligands in the anionic samarium complex $[Sm(\mu\text{-}NHC_6H_3Me_2\text{-}2,6)(NHC_6H_3Me_2\text{-}2,6)_3]_2^{2-}$, which average 2.354(9) Å.[5b] Three relatively weak Sm···F interactions[9] of 2.847(4), 2.870(3) and 2.876(3) Å are made by an *ortho*-fluorine substituent of each $-NH(C_6F_5)$ ligand. A hydrogen-bonding network with F···H distances of 2.688 Å and N–H–F angles of 163.8° is observed within the extended three-dimensional structure of **2**, which may explain the low solubility of the complex in non-polar solvents. In addition, intermolecular π-stacking of the arene rings[10] with interplanar contacts of 3.227 Å is observed.

Reaction of **1** with 3 equiv. of *N*-trimethylsilylpentafluoroaniline in toluene allowed the isolation of the base-free homoleptic complex $Sm[N(SiMe_3)(C_6F_5)]_3$ **3**. Single crystal X-ray diffraction‡ revealed an unusual trigonal planar SmN_3 skeleton (planar to within 0.01 Å), with *six* additional secondary contacts with ligand substituents (Fig. 2). Three short Sm···F interactions of 2.561(6), 2.566(5) and 2.587(6) Å with *ortho*-fluorine substituents from each $-N(SiMe_3)(C_6F_5)$ ligand, and three agostic interactions [Sm–C 3.058(11), 3.148(10) and 3.142(10) Å] with trimethylsilyl groups complete the overall nine-coordinate, tricapped trigonal prismatic geometry about the metal center. Sm–N–C_{ipso} and Sm–N–Si angles are almost equal for each amido ligand [*e.g.* Sm(1)–N(3)–C(19) 119.9(6), Sm(1)–N(3)–Si(3) 113.3(4)°], unlike the situation encountered in the related neodymium complex $Nd[N(C_6H_5)(SiMe_3)]_3(THF)$,[11] in which significant Nd–C_{ipso} and Nd–C_{ortho} interactions cause the Nd–N–C_{ipso} angles (110.2° av.) to be much more acute than Nd–N–Si angles (134.1° av.). In common with many similar interactions between $-SiMe_3$ groups and an f-element metal center, no solid-state IR or solution NMR evidence (*e.g.* lowered C–H stretching frequency) was found for

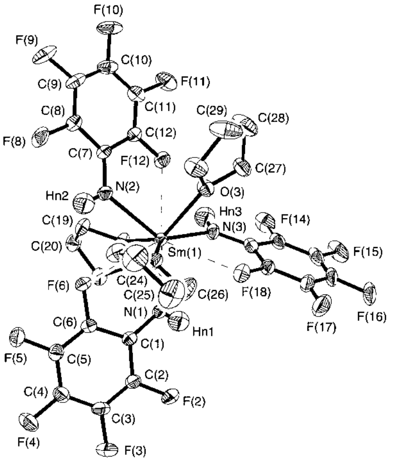

Fig. 1 ORTEP view (30% probability ellipsoids) of the molecular structure of $[Sm(NHC_6F_5)_3(thf)_3]$.thf **2**. Selected bond distances (Å): Sm(1)–N(1) 2.360(5), Sm(1)–N(2) 2.371(5), Sm(1)–N(3) 2.352(5), Sm(1)–O(1) 2.444(4), Sm(1)–O(2) 2.500(4), Sm(1)–O(3) 2.502(4), Sm(1)–F(6) 2.876(3), Sm(1)–F(12) 2.870(3), Sm(1)–F(18) 2.847(4).

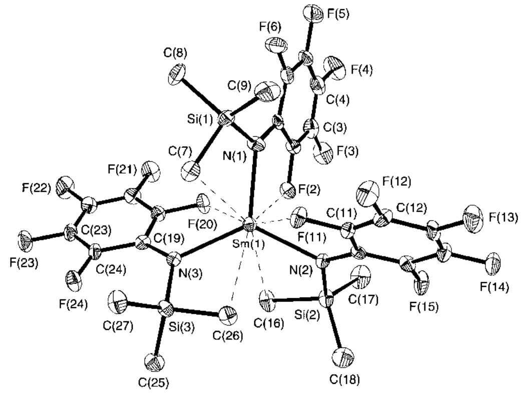

Fig. 2 ORTEP view (30% probability ellipsoids) of the molecular structure of $Sm[N(SiMe_3)(C_6F_5)]_3$ **3**. Selected bond distances (Å): Sm(1)–N(1) 2.329(8), Sm(1)–N(2) 2.330(7), Sm(1)–N(3) 2.362(8),Sm(1)–F(2) 2.566(5),Sm(1)-F(11) 2.587(6), Sm(1)–F(20) 2.561(6), Sm(1)–C(7) 3.058(11), Sm(1)–C(16) 3.148(10), Sm(1)–C(26) 3.142(10).

these 'agostic' interactions. ^{19}F NMR spectra of **3** (room temperature, toluene-d$_8$) reveal a 2 : 2 : 1 pattern for the *ortho-*, *meta-* and *para*-fluorine substituents. The resonances for the *para-* and *meta*-fluorines are sharp, whereas the *ortho* resonance is broadened almost into the baseline due to interaction with the paramagnetic samarium metal center. The observation of equivalent *ortho-* and *meta*-F resonances indicates rapid rotation about the N–C$_{ipso}$ bond on the NMR timescale (indicative of a weak C–F···Sm interaction). No significant changes in the ^{19}F spectrum were observed upon cooling the sample. Reaction of **3** with stoichiometric quantities of Lewis bases such as thf results in the formation of adducts with reduced numbers of Sm···F–C and Sm···Me–Si interactions (*e.g.* structurally characterized Sm[N(C$_6$F$_5$)(SiMe$_3$)]$_3$(thf)[12] displays two Sm···F–C and one Sm···Me–Si interaction).

Reaction of Nd[N(SiMe$_3$)$_2$]$_3$ **4**[8] with 3 equiv. of decafluorodiphenylamine, [(C$_6$F$_5$)$_2$NH],[13] in toluene followed by crystallization from the same solvent leads to isolation of (η-C$_6$H$_5$Me)Nd[N(C$_6$F$_5$)$_2$]$_3$ **5** in good yield. An X-ray diffraction study‡ revealed a distorted three-legged piano-stool geometry about the metal center (Fig. 3). Nd–N distances to the amido ligands are 2.362(6), 2.392(7) and 2.397(7) Å, which is somewhat longer than those previously observed in neodymium amido complexes (*e.g.* 2.309 Å (av.) in Nd[N(C$_6$H$_5$)(SiMe$_3$)]$_3$(thf),[11] 2.309(8) Å in Nd(NHC$_6$H$_3$Pr$^i{}_2$-2,6)$_3$(thf)$_3$,[5b] and 2.270(2) Å in NdCl[N(SiMe$_3$)(C$_6$H$_3$Pr$^i{}_2$-2,6)]$_2$(thf)[11]]. Three significant Nd···F interactions of 2.572(5), 2.616(5) and 2.696(5) and one weak Nd···F interaction of 2.940(5) Å are also observed within the structure. The toluene ligand is bound in a rather asymmetric manner, with Nd–C distances lying in the range 2.98(2)– 3.324(13) Å. Although a number of lanthanide complexes exhibiting η^6-arene interactions have been described in the literature,[14] the majority of these interactions occur *via* intra- or inter-molecular ligand chelation. The only lanthanide complexes which have previously been shown to bind aromatic solvent molecules are of the class (η-arene)Ln(η^2-AlX$_4$)$_3$ (Ln = La, Nd, Sm, Er; X = Cl, Br).[15] We do note, however, that the Nd–C bond distances in **5** are somewhat longer than those found in the neodymium complex (η-C$_6$H$_6$)Ln(η^2-AlCl$_4$)$_3$ (2.93 Å (av.)],[15c] presumably indicative of a somewhat weaker Ln–arene interaction in the present case. Complexes such as **5** may also be considered as models for cationic Group 4 metallocene and related bis-amido olefin polymerization systems which have been found to bind toluene and other aromatic solvent, often to the detriment of catalytic activity.[16]

In conclusion, we have shown that fluorinated amido ligands may be used to support highly electrophilic lanthanide metal centers, which enter into multiple secondary interactions with C–F, C–H and C–C bonds of both ligands and solvent.

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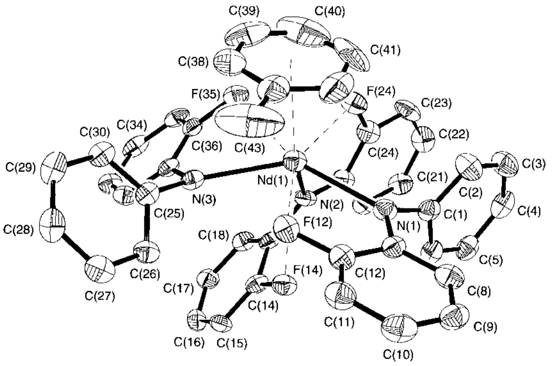

Fig. 3 ORTEP view (30% probability ellipsoids) of the molecular structure of (ηC$_6$H$_5$Me)Nd[N(C$_6$F$_5$)$_2$]$_3$ **5**. For clarity, only the fluorine atoms making Nd···F contacts are shown. Selected bond distances (Å): Nd(1)–N(1) 2.397(7), Nd(1)–N(2) 2.392(7), Nd(1)–N(3) 2.362(6), Nd(1)–F(12) 2.572(5), Nd(1)–F(24) 2.616(5), Nd(1)–F(35) 2.696(5), Nd(1)–F(14) 2.940(5), Nd(1)–C(41) 2.982(13), Nd(1)–C(40) 2.98(2), Nd(1)–C(42) 3.103(10), Nd(1)–C(39) 3.167(13), Nd(1)–C(37) 3.313(10), Nd(1)–C(38) 3.324(13).

Notes and references

† Experimental details for the preparation and characterization of **2**, **3**, and **5** are provided as electronic supplementary information (http//www.rsc.org/suppdata/cc/1999/633).

‡ *Crystallography*: in all X-ray diffraction studies, data were collected on a Siemens P4/PC diffractometer with Mo-Kα radiation (λ = 0.71069 Å). Patterson techniques were used to locate the lanthanide metal and the majority of all other atoms in the molecule. Subsequent Fourier synthesis gave the remaining light atom positions. Hydrogen atoms were refined using the riding model in the HFIX facility in SHELXL 93. CCDC 182/1182. See http://www.rsc.org/suppdata//cc/1999/633/ for crystallographic files in .cif format.

Crystal data: **2**·0.5thf: C$_{32}$H$_{35}$F$_{15}$N$_3$O$_{3.5}$Sm, M = 952.98, triclinic, space group $P\bar{1}$, a = 10.745(1), b = 10.773(1), c = 18.216(2) Å, α = 98.42(1), β = 95.81(1), γ = 114.02(1), V = 1874.8 Å^3, Z = 2, T = 203 K, μ = 16.79 cm^{-1}. The N–H hydrogens were located from the difference map and refined with free coordinates and fixed isotropic temperature factors (0.08 Å^2). The atoms of the solvent thf were refined isotropically at 1/2 occupancy. The final refinement (7673 reflections collected, 6535 independent) included anisotropic thermal parameters on all non-hydrogen atoms (except for atoms of the solvent thf) and converged to $R1$ = 0.0404 and $wR2$ = 0.1165.

3: C$_{27}$H$_{27}$F$_{15}$N$_3$Si$_3$Sm, M = 913.14, triclinic, space group $P\bar{1}$, a = 10.196(4), b = 10.868(4), c = 16.461(7) Å, α = 94.96(1), β = 107.33(1), γ = 95.26(1), V = 1721.4(12) Å^3, Z = 2, T = 198 K, μ = 19.16 cm^{-1}. The final refinement (5381 reflections collected, 4479 independent) included anisotropic temperature factors on all non-hydrogen atoms and converged to $R1$ = 0.0556 and $WR2$ = 0.1341.

5·C$_6$H$_5$Me: C$_{50}$H$_{16}$F$_{30}$N$_3$Nd, M = 1372.90, monoclinic, space group $P2_1/c$, a = 22.964(4), b = 8.712(2), c = 24.927(4) Å, β = 107.47(1), V = 4757 Å^3, Z = 4, T = 198 K, μ = 12.52 cm^{-1}. The final refinement (7834 reflections collected, 6217 independent) included anisotropic thermal parameters on all non-hydrogen atoms and converged to $R1$ = 0.0577 and wR_2 = 0.1015.

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