Partially Fluorinated Rare Earth Metal Complexes

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The reaction of $LScBr_2$ (**1**), LYI_2 (**3**), $LHoI_2$ (**4**), or $LErI_2$ (**5**) [L = *N*,*N''*-(1,3-dimethyl-1,3-propanediylidene)bis(*N'*,*N'*-diethyl-1,2-ethanediamine)] with Me_3SnF was investigated. Treatment of **1** with Me_3SnF results in the formation of $(Me_3BrSn\text{-}\mu\text{-}F)_2LSc$ (**2**) while compounds **3**–**5** give $[LSnMe_2][Me_3SnI_2]$ (**6**) as the only product that could be isolated and characterized. Metathesis reactions of **1** with $AgSO_3CF_3$ led to $LSc(SO_3CF_3)_2$ (**7**). Compounds **1**, **2**, **6** and **7** were characterized by single-crystal X-ray structural analysis.

Introduction

The rapid development in the chemistry of the rare earth metals has resulted in the synthesis of a plethora of original compounds with various types of ligands, along with the widely exploited cyclopentadienyl substituents. Previous published work from our group concerning β-diketiminato derivatives of these elements includes new information about derivatives of scandium,[1] praseodymium,[2] samarium,[3] terbium,[4] holmium, erbium,[5] and ytterbium[3] with the ligand *N*,*N''*-(1,3-dimethyl-1,3-propanediylidene)-bis(*N'*,*N'*-diethyl-1,2-ethanediamine) $\{[N(CH_2CH_2NEt_2)C(Me)]_2CH\}^-$, abbreviated as L. These complexes are ideal candidates for use in a less-exploited research area of these metals, namely that of dihalo compounds as promising precursors for catalytically active species. However, we faced problems with metathesis reactions for the preparation of other derivatives when the chloro or bromo compounds were treated with alkyllithium or Grignard reagents, due to a number of side reactions. The pursuit of the complexes resulting from this kind of disubstitution reaction in which dihalo derivatives of rare-earth metals are involved[4] prompted us to study the fluorine-containing systems. More specifically, examples are known where trimethyltin fluoride is used as an effective fluorinating agent for the preparation of *d* and *f* transition metal complexes from chloride congeners.[6−8] However, reactions between other complexes and Me_3SnF are less well known. An interesting example is the oxidation of $[Sm(C_5H_4tBu)_2(THF)_2]$ with Me_3SnF for the preparation of $[(C_5H_4tBu)_2Sm(\mu\text{-}F)]_3$,[9] or the reaction of $CpTiF_3$ and $ZnMe_2$ in the presence of Me_3SnF.[10] In general, since lanthanide-fluorine bonds are very strong (124−135 kcal/mol for trivalent Eu, Yb, Er, Ho and Sm),[11] the metathesis reaction of lanthanide complexes containing Cl, Br, I, SCN or Me ligands with trimethyltin fluoride under mild conditions seemed feasible.

Besides the fluorine ion, another candidate for a successful metathesis is the quite well-known electron-withdrawing triflate group due to the oxophilic character of the rare earth metals.[12] Until now heteroleptic triflate compounds of lanthanides have been obtained using the $Ln(OTf)_3$ (Ln = lanthanide, OTf = triflate) as a starting material.[13] The synthesis of such complexes by substitution of other ligands at the coordination sphere of a metal that already contains an "ancillary" ligand (e.g. halogen) was not explored. In comparison to the homoleptic triflate derivatives, which are widely used as reusable catalysts,[14] it was expected that the heteroleptic compounds should suffer from a decrease of the Lewis acidity but still be advantageous in catalysis due to their high solubility in organic solvents.[15]

Herein, we analyze the results of the reactions of the dibromo derivative of scandium and the diiodo derivatives of yttrium, holmium, and erbium of composition $LLnX_2$ [L = *N*,*N''*-(1,3-dimethyl-1,3-propanediylidene)bis(*N'*,*N'*-diethyl-1,2-ethanediamine); Ln = Sc, Y, Ho, Er; X = Br, I] with trimethyltin fluoride. To the best of our knowledge reactions of trimethyltin fluoride with lanthanide diiodide complexes have not been explored before in non-aqueous solvents. We also report the metathesis reaction of $LScBr_2$ and $Ag(SO_3CF_3)$ with formation of monomeric $LSc(SO_3CF_3)_2$. The precursor $LScBr_2$ will be discussed in relationship to the fluorine-containing complexes.

Results and Discussion

The precursor $LScBr_2$ (**1**) was synthesized in a similar manner as the previously reported rare earth metal com-

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plexes with the same ligand from the lithium salt and scandium tribromide in toluene.[1,2] The X-ray structural analysis reveals the same type of coordination as the chloride congener (Figure 1, Table 1).[1]

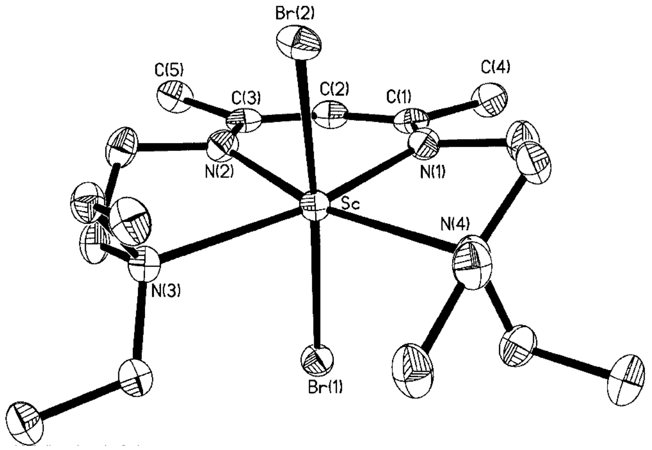

Figure 1. Molecular structure of **1**; thermal ellipsoids are drawn at the 50% probability level

Table 1. Selected bond lengths (Å) and angles (°) for **1**

C(1)−C(2)	1.394(3)	N(2)−Sc(1)−N(1)	85.21(6)
N(1)−C(1)	1.339(2)	N(1)−Sc(1)−N(4)	76.26(5)
Sc(1)−N(1)	2.155(1)	N(2)−Sc(1)−N(3)	79.44(5)
Sc(1)−N(2)	2.133(1)	N(4)−Sc(1)−N(3)	119.09(5)
Sc(1)−N(3)	2.541(1)	Br(1)−Sc(1)−Br(2)	172.274(1)
Sc(1)−N(4)	2.447(2)		
Sc(1)−Br(1)	2.610(1)		
Sc(1)−Br(2)	2.629(1)		

The reaction of $LScBr_2$ (**1**) with Me_3SnF in a 1:2 molar ratio [Equation (1)] led to compound **2** that comprises the anticipated difluorinated scandium derivative but bridged by fluorine to two Me_3SnBr molecules. The reaction of $LScCl_2$ with two equivalents of Me_3SnF gave the chloro analogue **2′** [Equation (2)].

$$\underset{\mathbf{1}}{LScBr_2} + 2\,Me_3SnF \xrightarrow[\text{room temp.}]{\text{toluene}} \underset{\mathbf{2}}{(Me_3BrSn\text{-}\mu\text{-}F)_2LSc} \tag{1}$$

$$LScCl_2 + 2\,Me_3SnF \xrightarrow[\text{room temp.}]{\text{toluene}} \underset{\mathbf{2'}}{(Me_3ClSn\text{-}\mu\text{-}F)_2LSc} \tag{2}$$

Crystals of **2** are extremely sensitive once the mother liquor is removed and they are rapidly decomposed within minutes. After that the substance cannot be dissolved again in toluene or any other solvent, indicating that decomposition and formation of insoluble fluorides has probably occurred. Therefore discussion of its structure will be based only on the X-ray analysis. Complex **2** crystallises in two phases (triclinic **2a** and monoclinic **2b**). The two phases differ only slightly in their bond lengths and angles. In the monoclinic phase **2a** the molecule lies on a twofold axis resulting in a completely planar arrangement of Sc within the β-diketiminato NCCCN plane, while deviation of the scandium atom from the same plane is 0.49 Å in **2a**. The major difference between **2a** and **2b** is found in the F−Sc−F angle [162.2 (**2a**) and 171.2° (**2b**)]. In the following discussion we will refer only to the triclinic phase due to the slightly better results of the refinement. At first glance the structure shows a trinuclear non-linear compound where the scandium atom has a pseudooctahedral geometry and the pentacoordinate tin is trigonal bipyramidal (F−Sn−Br av. 177.1°; Figure 2).

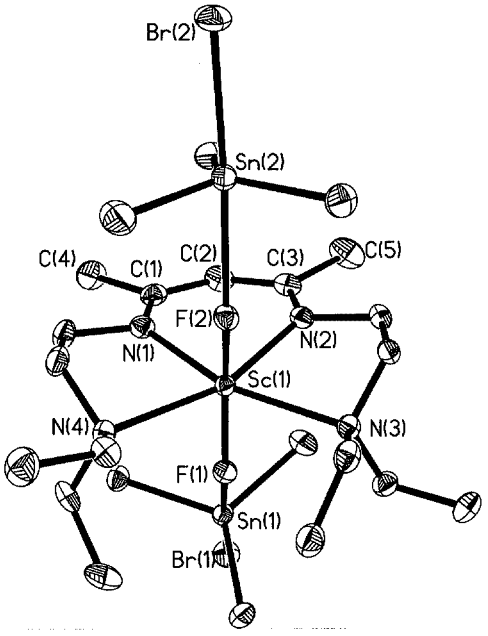

Figure 2. Molecular structure of **2a**; thermal ellipsoids are drawn at the 50% probability level

Scandium is σ-bonded to the β-diketiminato backbone similar to the dibromo derivative (distance from scandium to the backbone plane 0.49 Å). The analogous distances for **1** and **2** indicate that this kind of bonding is caused by the coordination of the metal to all four nitrogen atoms (eight-electron donor) of the ligand. Consequently the β-diketiminato backbone is acting as a four-electron donor.[16] The Sc−F bond lengths are similar to those reported in the literature (1.97 Å and 1.99 Å for **2a** and av. 2.03 Å for Cp_2ScF).[17] The Sn−F bond length (2.42 and 2.46 Å) is of the same order as the longest Sn−F distance in polymeric Me_3SnF,[18] which has the same pentacoordination. The Sc−F−Sn bond angle averages to 148.6°. A comparable intermediate was observed in the fluorination of a zirconium derivative[8a] with Me_3SnF. However, in the scandium case we cannot argue that **2** is an intermediate in the fluorination process although under electron impact conditions fragments corresponding to $LScF^+$ (359) and Me_3Sn^+ (165) are observed. Although compound **2** is quite unstable, we were not able to isolate the monomeric fluoride. Our results are in agreement with those found for the metathesis of $LScCl_2$ with Me_3SnF.

An X-ray structural analysis of **2′** established the connectivity of the structure but this cannot be discussed in any detail due to the poor quality of the crystals. A qualitative view reveals that **2′** has the same skeletal arrangement as **2b**, with the bromine bridges being replaced by chlorine. In **2** the Me_3Sn units are coordinated in a similar manner to those reported for a zirconium compound (Table 2).[8a]

Table 2. Selected bond lengths (Å) and angles (°) for **2a**

C(1)−C(2)	1.382(7)	N(2)−Sc(1)−N(1)	84.30(16)
N(1)−C(1)	1.323(6)	N(1)−Sc(1)−N(4)	77.77(15)
Sc(1)−N(2)	2.170(4)	N(2)−Sc(1)−N(3)	76.44(15)
Sc(1)−N(1)	2.148(4)	N(4)−Sc(1)−N(3)	121.46(14)
Sc(1)−N(4)	2.421(4)	F(1)−Sc(1)−F(2)	162.20(2)
Sc(1)−N(3)	2.381(4)	Sc(1)−F(1)−Sn(1)	149.28(14)
Sc(1)−F(1)	1.967(3)	Sc(1)−F(2)−Sn(2)	147.90(14)
Sc(1)−F(2)	1.991(3)	F(1)−Sn(1)−Br(1)	177.47(7)
F(1)−Sn(1)	2.419(3)	F(2)−Sn(2)−Br(2)	176.72(6)
F(2)−Sn(2)	2.455(5)		

The variation of the rare earth metal from scandium to yttrium, holmium and erbium, and of the halide from bromine to iodine led to an entirely different behaviour of the complexes $LLnX_2$ [Ln = Y (**3**), Ho (**4**), Er (**5**)] in the reaction with Me_3SnF (1:2). Independent of whether the reaction was carried out in toluene or THF, the isolated product is the same in all three cases, namely $[LSnMe_2][Me_3SnI_2]$ (**6**). Obviously a complete substitution of the rare earth metal with tin has occurred. A solid yellow residue remained which contains non-stoichiometric amounts of Ln, C, H, F, I and N.

$$\mathrm{LLnI_2} \;+\; 2\,\mathrm{Me_3SnF} \xrightarrow[\substack{\text{B. 1. THF, room temp.}\\ \text{2. pentane, -Me}_3\text{SnI}\\ \text{3. toluene}}]{\text{A. toluene, room temp.}} \underset{\mathbf{6}}{[\mathrm{LSnMe_2}][\mathrm{Me_3SnI_2}]}$$

Scheme 1. Reaction of $LLnI_2$ with Me_3SnF (Ln = Y, Ho, Er)

Crystalline **6** (Figure 3, Table 3) consists of well-separated cations and anions and crystallizes with one molecule of toluene. In the cation of **6** the β-diketiminato ligand coordinates to the tin(IV) center through three nitrogen atoms, less than in other lanthanide compounds with this ligand but similar to a reported aluminum complex.[1−5,19,20] The Sn(2) atom has a coordination number of five that can be regarded as being distorted trigonal bipyramidal with N(1) and N(4) axial and C(71), C(72), Sn(2) and N(2) coplanar [the angle N(1)−Sn(2)−N(4) is 163.5(3)°].

Table 3. Selected bond lengths (Å) and angles (°) for **6**

C(1)−C(2)	1.413(16)	N(2)−Sn(2)−N(1)	87.3(4)
N(1)−C(1)	1.337(15)	N(1)−Sn(2)−N(4)	163.5(3)
N(2)−C(3)	1.349(16)	C(71)−Sn(2)−N(4)	94.5(4)
C(2)−C(3)	1.344(15)	C(72)−Sn(2)−C(71)	126.4(5)
Sn(2)−N(2)	2.095(9)	N(2)−Sn(2)−C(71)	115.2(4)
Sn(2)−N(1)	2.161(10)	C(61)−Sn(1)−C(62)	116.4(7)
Sn(2)−N(4)	2.381(10)	C(61)−Sn(1)−I(1)	92.0(4)
Sn(2)−C(72)	2.126(11)	I(1)−Sn(1)−I(2)	177.32(4)
Sn(2)−C(71)	2.138(11)		
Sn(1)−C(61)	2.125(15)		
Sn(1)−I(1)	2.997(14)		
Sn(1)−I(2)	3.044(14)		

Cationic tin(IV) complexes are known with N-donor ligands and a number of those have been structurally characterized.[21] In the cationic part of **6**, the Sn(2)−N bond lengths of the pendant arm are longer than those of the backbone, similar to the corresponding distances in related compounds[1−5,19,20] and in **1** and **2** [Sn(2)−N(1) 2.161, Sn(2)−N(2) 2.095, Sn(2)−N(4) 2.381 Å]. The difference between the C−C and C−N bond lengths in the NCCCN unit is greater than in **1** or **2** and other complexes with the same ligand. This may indicate the alternation of single and double bonds in the bonding pattern of the metal to the nitrogen atoms. However, the difference between Sn(2)−N(1) and Sn(2)−N(2) is just greater than the three esd's limit consistent with N(2) as an amido nitrogen and N(1) as part of a C=N unit. The Sn(2)−N bond lengths are

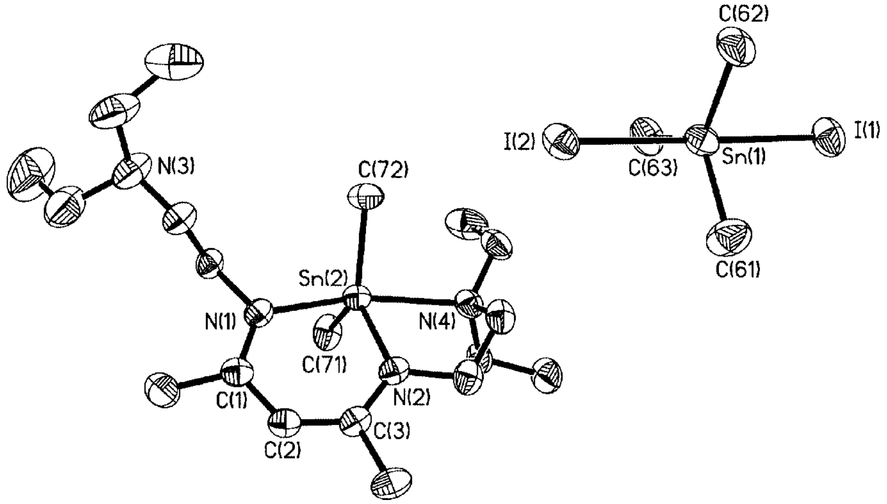

Figure 3. Molecular structure of **6**; thermal ellipsoids are drawn at the 50% probability level

similar to those found in the literature for β-diketiminato complexes of Sn^{4+}, such as $LSnMe_2Cl$ (Sn−N 2.110, 2.112 Å)[22a] and $LSnI_3$ (Sn−N 2.163, 2.176 Å; L = β-diketiminato ligand).[22b] The NCCCN backbone of the β-diketiminato ligand remains essentially planar (the deviation from planarity is 0.024 Å) with the tin atom 0.604 Å above the plane. The nitrogen atoms of the pendant arm lie out of the NCCCN plane with N(3) 1.43 Å below and N(4) 1.07 Å above the plane. The Sn(1)−I and Sn−Me bond lengths are similar to those found for Sn^{4+} complexes.[23]

In the anion the Sn(1) atom also has a five coordinate trigonal bipyramidal environment with I(1) and I(2) axial and C(61), C(62), Sn(1) and C(63) coplanar.

The unexpected composition of $[LSnMe_2][Me_3SnI_2]$ that resulted from the X-ray analysis is consistent with the data from mass spectrometry and elemental analysis. The EI mass spectrum of **6** exhibits the $[MeSnI_2^+]$ and $[Me_2SnI_2^+]$ ions and fragments of the β-diketiminato ligand, while in the FAB mass spectrum of **6** the $[LSnMe_2^-]$ ion and fragments of $[LSnMe_2][Me_3SnI_2]$ are observed. In the ^1H NMR spectrum of **6** a set of broad and overlapping resonances is observed.

Obviously, the slight variation of the properties of the metals in complexes $LLnX_2$ between scandium and yttrium as well as the presence of iodine instead of bromine resulted in a different complex. A possible explanation for this behaviour may be due to the formation of very strong Y−F (and Ho−F and Er−F) bonds that leads to complete elimination of the ligand from the coordination sphere of the starting material and migration to the tin atom in complex **6**. The analytical data of the insoluble residues indicate the formation of very impure polymeric fluorides.

As far as the iodine precursors are concerned, the preparation of the holmium and erbium complexes was already reported.[5] The yttrium compound was obtained from the potassium salt of the ligand and yttrium triiodide. LYI_2 was characterized by ^1H, and ^{13}C NMR spectroscopy, mass spectrometry and elemental analysis and is, to the best of our knowledge, the first β-diketiminatoyttrium complex.[24]

Extending our investigation to other fluorine-containing ligands, reaction of the dibromoderivate $LScBr_2$ with $AgSO_3CF_3$ occurs, as expected, with substitution of both bromine atoms due to the oxophilic character of scandium and the thermodynamically favored formation of AgBr [Equation (3)].

$$\underset{\mathbf{1}}{LScBr_2} + 2\,Ag(SO_3CF_3) \xrightarrow[\text{room temp.}]{\text{toluene}} \underset{\mathbf{7}}{LSc(SO_3CF_3)_2} + 2\,AgBr\downarrow \qquad (3)$$

Compound **7** is a yellow solid very soluble in aromatic solvents, diethyl ether and THF. The Lewis acidity of scandium is lower than in $Sc(SO_3CF_3)_3$ as a consequence of the substitution of one triflate ligand by the nitrogen-containing ligand L. Moreover, the two triflate ligands increase the electronic density on the scandium atom in **7** in comparison to **1**, documented by the substantial upfield shift of the scandium resonance in the ^{45}Sc NMR spectrum (δ = 335.8 ppm in **1** to 185.0 ppm in **7**).

The crystal structure analysis (Figure 4) reveals that the scandium atom in **7** is hexacoordinated with a pseudooctahedral geometry and the two triflate ligands are arranged in the apical positions [O(3)−Sc−O(1) 170.8° compared to Br(1)−Sc(1)−Br(2) 172.3° of **1**].

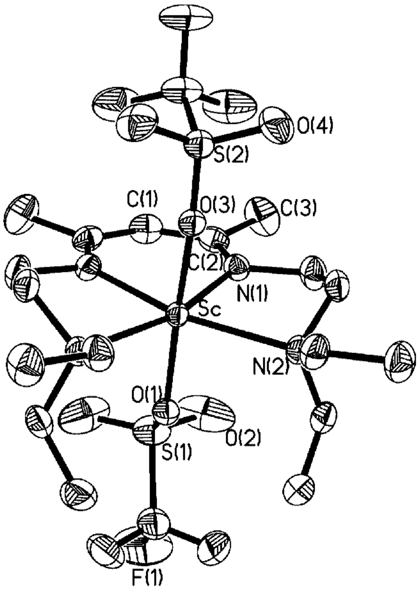

Figure 4. Molecular structure of **7**; thermal ellipsoids are drawn at the 50% probability level

For steric reasons, the triflate groups are not coordinated to scandium in a chelating fashion; they bind in a monodentate fashion through oxygen[13c,25] (Table 4). The NCCCN atoms of the β-diketiminato backbone as well as the nitrogen atoms of the ligand arms are almost coplanar. The distance from Sc to the NCCCN plane (0.28 Å) indicates a σ-bond interaction between scandium and the β-diketiminato ligand (in **1** the corresponding distance is 0.42 Å).[16]

Table 4. Selected bond lengths (Å) and angles (°) for **7** (symmetry transformations used to generate equivalent atoms #1 *x*, −*y* + 1/2, *z*)

C(1)−C(2)	1.393(2)	O(1)−Sc−O(3)	170.88(7)
N(1)−Sc	2.126(2)	N(1)−Sc−N(1)#1	85.38(8)
N(2)−Sc	2.378(1)	N(1)−Sc−N(2)	79.66(5)
O(1)−Sc	2.126(2)	N(2)#1−Sc−N(2)	115.12(7)
O(3)−Sc	2.108(2)		

A comparison of the bond lengths and angles of **1**, **2** and **7** showed that within the β-diketiminato frame these units are hardly influenced by the different substituents on scandium (see Tables 1, 2, and 4).

Conclusion

Herein we report some progress in the investigation of the reactivity of complexes of scandium, yttrium, holmium and erbium containing the β-diketiminato ligand L. On the basis of the hard-soft acid-base principle it is expected that rare earth metals should form very stable bonds with fluorine. Taking into account also the successful use of Me_3SnF as a fluorinating reagent, we considered that the chances of obtaining compounds of type $LLnF_2$ were realistic. However, reactions of Me_3SnF with $LScBr_2$ (**1**), LYI_2 (**3**), $LHoI_2$ (**4**), and $LErI_2$ (**5**), respectively, led to the isolation of compounds $(Me_3BrSn\text{-}\mu\text{-}F)_2LSc$ (**2**) and $[LSnMe_2][Me_3SnI_2]$ (**6**). The latter species was formed independently of the rare earth metal diiodide used as a starting material (LYI_2, $LHoI_2$, $LErI_2$) by substitution of the metal. Based on the yield of **6** we cannot argue that the fluorine derivatives of the rare earth metals were not formed but it is likely that, as in the case of compound **2**, it aggregates with formation of an insoluble product.

In view of the failure of the metathesis reaction of the scandium derivatives with the usual organometallic reagents we have reacted **1** with $AgSO_3CF_3$ to yield compound **7**.

Experimental Section

General Experimental Procedures: All operations involving air- and moisture-sensitive compounds were performed using standard Schlenk-line and dry-box techniques under purified dinitrogen atmosphere. Hexane and dichloromethane were dried from appropriate drying agents — Na/K alloy (hexane) and CaH_2 (dichloromethane) — and distilled under dinitrogen prior to use. $CDCl_3$, $[D_8]THF$ and C_6D_6 were dried from appropriate drying agents (CaH_2 and Na/K alloy respectively) and degassed. Literature methods for the preparation of the starting materials are cited within the text. $AgSO_3CF_3$ was purchased from Aldrich and used without purification. ^1H, ^{19}F, and ^{45}Sc NMR spectra were recorded on a Bruker AM 200 instrument. Mass spectra were recorded on a Finnigan MAT 8230 instrument, and elemental analyses were carried out at the Analytical Laboratories of the Institute of Inorganic Chemistry at the University of Göttingen. Melting points were determined in sealed capillary tubes under dinitrogen and are uncorrected. IR spectra were recorded using a Perkin−Elmer Bio-Rad Digilab FTS-7.

Preparation of $LScBr_2$ (1): Toluene (30 mL) was added to LLi (2.90 g, 9.6 mmol) obtained in situ following the procedure described previously.[2] This mixture was added dropwise to a suspension of $ScBr_3$ (2.76 g, 9.7 mmol) in toluene (25 mL) in a Schlenk flask. Then, the reaction mixture was refluxed overnight. The suspension was filtered hot, the solvent removed and the crude product washed with pentane (50 mL) to yield 4.35 g (86.6%) of $LScBr_2$. Large colorless crystals were obtained upon cooling the mother liquor to −26 °C. $C_{17}H_{35}Br_2N_4Sc$ (500.3): calcd. C 40.58, H 7.30, N 10.90; found C 40.81, H 7.05, N 11.20. ^1H NMR (200.13 MHz, TMS, 300 K, C_6D_6): δ = 4.82 (s, 1 H, C*H*), 3.08 [m, 16 H, $NCH_2CH_2N(CH_2)_2$], 1.55 (s, 6 H, $CHCCH_3$), 0.82 (t, 12 H, CH_2CH_3) ppm. ^{13}C NMR (125.75 MHz, TMS, 300 K, C_6D_6): δ = 165.3 (*C*CH*C*), 100.5 (*C*H), 54.7 ($CNCH_2$), 47.8 (NCH_2CH_2), 30.1 (CH_2NCH_2), 22.3 ($CHCCH_3$), 8.9 (NCH_2CH_3) ppm. ^{45}Sc NMR (121.49 MHz, referenced to $[Sc(H_2O)_6]^{3+}$ in D_2O, 300 K, C_6D_6): δ = 335.87 ppm. M.p. 131−136 °C. EI-MS: *m*/*z* (%) = 500 (10) $[M^+]$, 414 (100) $[M^+ - C_5H_{12}N]$.

Preparation of 2 and 2′: A mixture of **1** (0.50 g, 0.98 mmol) or $LScCl_2$ (0.51 g, 0.98 mmol)[1] and Me_3SnF[26] (0.35 g, 1.96 mmol) in a Schlenk flask in toluene (50 mL) was stirred for 1 day until all the Me_3SnF dissolved. The resulting solution was concentrated under reduced pressure and kept at −26 °C. After 3 days crystals of **2** and **2′** were obtained. Cold filtration afforded 0.43 g of **2** (yield 51%) or 0.45 g of **2′** (yield 66%). Attempts to redissolve the resulting products in $CDCl_3$ or C_6D_6 for characterizing **2** and **2′** by NMR spectroscopy failed as the compounds decomposed rapidly once they were taken out of the solution.
2: EI-MS: *m*/*z* (%) = 359 (15) $[LScF^+]$, 165 (5) $[Me_3Sn^+]$, 86 (100) $[C_5H_{12}N^+]$.
2′: EI-MS: *m*/*z* (%) = 359 (20) $[LScF^+]$, 165 (5) $[Me_3Sn^+]$, 86 (100) $[C_5H_{12}N^+]$.

Preparation of 3: LK (0.60 g, 1.8 mmol) was obtained in situ by refluxing LH (0.53 g, 1.8 mmol) with KH (0.10 g, 2.5 mmol) in toluene (30 mL) and filtering off the excess KH. The resulting solution was added dropwise to a suspension of YI_3 (0.8 g, 1.8 mmol) in toluene (25 mL) in a 100 mL Schlenk flask. Then, the reaction mixture was refluxed for 1 day. The suspension was filtered hot, the solvent removed and the crude product was washed with pentane (50 mL) then dried in vacuo. Yield: 8.08 g (70.4%). $C_{17}H_{35}I_2N_4Y$ (638.2): calcd. C 31.99, H 5.53, N 8.78; found C 32.20, H 5.40, N 8.56. ^1H NMR (200.13 MHz, 300 K, C_6D_6): δ = 4.80 (s, 1 H, C*H*), 3.10 [m, 16 H, $NCH_2CH_2N(CH_2)_2$], 1.55 (s, 6 H, $CHCCH_3$), 0.78 (t, 12 H, CH_2CH_3) ppm. ^{13}C NMR (125.75 MHz, 300 K, C_6D_6): δ = 166.3 (*C*CH*C*), 101.0 (*C*H), 55.1 ($CNCH_2$), 46.9 (NCH_2CH_2), 30.1 (CH_2NCH_2), 22.9 ($CHCCH_3$), 8.4 (NCH_2CH_3) ppm. M.p. 150−155 °C. EI-MS: *m*/*z* (%) = 511 (5) $[M^+ - I]$, 86 (100) $[C_5H_{12}N^+]$.

Preparation of 6. A: A mixture of **3** (1.15 g, 1.8 mmol) and Me_3SnF[26] (0.64 g, 3.5 mmol) in toluene (50 mL) in a Schlenk flask was stirred for 1 day then the turbid yellow solution was filtered. The resulting solution was concentrated under reduced pressure and kept at −26 °C. After one week crystals of **6** were obtained (0.94 g, 34%).
B: Me_3SnF (0.64 g, 3.5 mmol) and THF (40 mL) were added to LYI_2 (**3**; 1.15 g, 1.8 mmol), $LHoI_2$ (**4**; 1.28 g, 1.8 mmol) or $LErI_2$ (**5**; 1.29 g, 1.8 mmol). After stirring for 1 h all the Me_3SnF had dissolved. After the reaction was complete the THF was removed in vacuo, and the residue washed with two portions (20 mL) of pentane. The solid residue was extracted with toluene (60 mL) and the toluene solution concentrated to approximately 10 mL. After standing overnight colorless crystals suitable for X-ray analysis were formed, which were separated by filtration. Another crop of crystals of **6** was obtained by washing the residue with toluene. Yield 0.83 g, 30% (for **3**), 0.75 g, 22% (for **4** and **5**). The concentration of the toluene solution of **6** should proceed slowly, otherwise two liquid layers are formed and no crystallization is observed. $C_{22}H_{50}I_2N_4Sn_2$ (861.9): calcd. C 30.66, H 5.86, N 6.50; found C 30.01, H 5.55, N 6.10. ^1H NMR (200.13 MHz, TMS, 300 K, C_6D_6): δ = 0.29 [s, 6 H, $Sn(CH_3)_2$], 0.57 [s, 9 H, $Sn(CH_3)_3$], 1.00 (t, 12 H, CH_2CH_3), 1.91 (s, 6 H, CCH_3), 2.63 [m, 12 H, $CH_2N(CH_2CH_3)_2$], 3.31 (m, 4 H, $NCH_2CH_2NEt_2$), 4.61(s, 1 H, C*H*) ppm. M.p. 222−224 °C. EI-MS: *m*/*z* (%) = 403 (2) $[Me_2SnI_2^+]$, 388 (2) $[MeSnI_2^+]$, 273 (6) $[Me_2SnI^+]$, 247 (4) $[SnI^+]$, 210 (30) $[L^+ - NC_5H_{12}]$, 86 (100) $[C_5H_{12}N^+]$. EI-FAB: *m*/*z* (%) = 849 (1) $[(LSnMe_2)(Me_2SnI_2)^-]$, 721 (2) $[(LSnMe_2)(Me_2SnI)^-]$, 445 (8) $[LSnMe_2^-]$, 297 (100) $[L^-]$. IR (Nujol): $\tilde{\nu}$ = 1619 cm^{-1} (w), 1659 (w), 1572 (m), 1409 (w), 1289 (w), 1261 (vs), 1205 (w), 1168 (w), 1153 (w), 1095 (vs), 1029 (vs), 967 (w), 928 (w), 873 (w), 799 (vs), 728 (m), 699 (w), 668(w), 636 (w), 534 (m), 467 (m).

Table 5. Crystal data collection for **1**, **2**, **6**, and **7**

Complex	**1**	**2a**	**2b**	**6·0.5C$_7$H$_8$**	**7**
Formula	$C_{17}H_{35}Br_2N_4Sc$	$C_{23}H_{53}Br_2F_2N_4ScSn_2$	$C_{23}H_{53}Br_2F_2N_4ScSn_2$	$C_{25.5}H_{54}N_4Sn_2I_2$	$C_{19}H_{35}F_6N_4O_6S_2Sc$
Mol. wt.	500.27	865.85	865.85	907.91	638.59
Space group	*P*2$_1$/*n*	$P\bar{1}$	*C*2/*c*	*P*2$_1$/*n*	*Pnma*
Crystal system	monoclinic	triclinic	monoclinic	monoclinic	orthorhombic
a, Å	15.7672(7)	9.832(3)	10.801(2)	9.556(2)	21.6876(11)
b, Å	10.8019(3)	10.305(3)	17.220(5)	27.446(6)	14.4273(11)
c, Å	13.3651(6)	18.705(5)	18.512(5)	13.478(3)	8.9283(5)
α, deg		97.91(3)			
β, deg	107.609(4)	99.75(3)	103.87(3)	92.52(3)	
γ, deg		114.19(3)			
V, Å^3	2169.63(15)	1658.0(8)	3342.7(15)	3531.5(12)	2793.6(3)
Z	4	2	4	4	4
D_{calcd}, g/cm^3	1.532	1.734	1.721	1.708	1.518
Temp, K	133(2)	133(2)	133(2)	200(2)	133(2)
θ range, deg	2.32 to 24.71	2.23 to 27.49	2.27 to 27.53	3.66 to 24.99	1.88 to 24.71
Index ranges	$-18 \le h \le 18$ $-12 \le k \le 12$ $-15 \le l \le 15$	$-12 \le h \le 12$ $-13 \le k \le 7$ $-24 \le l \le 24$	$-14 \le h \le 11$ $-22 \le k \le 22$ $-24 \le l \le 23$	$-11 \le h \le 11$ $-16 \le k \le 32$ $-16 \le l \le 16$	$-25 \le h \le 25$ $-16 \le k \le 16$ $-10 \le l \le 9$
Reflections collected/unique	43718/3702 [*R*(int) = 0.0657]	25903/7516 [*R*(int) = 0.0760]	41276/3827 [*R*(int) = 0.0578]	10226/6149 [*R*(int) = 0.0461]	33172/2482 [*R*(int) = 0.0519]
Completeness to θ (%)	99.9	98.8	99.4	98.8	100.0
Data/restraint/parameter	3702/0/223	7516/0/320	3827/0/161	6149/257/319	2482/0/190
GOF	1.070	0.982	1.159	1.161	1.030
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0176$ $wR_2 = 0.0411$	$R_1 = 0.0455$ $wR_2 = 0.0931$	$R_1 = 0.0573$ $wR_2 = 0.1418$	$R_1 = 0.0555$ $wR_2 = 0.1884$	$R_1 = 0.0280$ $wR_2 = 0.0729$
R indices (all data)	$R_1 = 0.0196$ $wR_2 = 0.0417$	$R_1 = 0.0667$ $wR_2 = 0.0993$	$R_1 = 0.0678$ $wR_2 = 0.1616$	$R_1 = 0.0646$ $wR_2 = 0.1956$	$R_1 = 0.0355$ $wR_2 = 0.0749$
Largest diff. peak and hole (e/A^3)	0.294, −0.201	1.137 −1.048	2.723 −4.110	1.425 −1.088	0.403 −0.407

Preparation of 7: A mixture of **1** (0.50 g, 0.98 mmol) and $AgSO_3CF_3$ (0.11 g, 1.96 mmol) in toluene (35 mL) in a 50 mL Schlenk flask was stirred for 2 days. The suspension was filtered. The resulting clear solution was concentrated under reduced pressure to obtain yellow crystals of **7**, which were collected by filtration and washed with pentane (10 mL). Yield 0.31 g (68%) $C_{17}H_{35}F_6N_4O_6S_2Sc$ (614.6): calcd. C 35.74, H 5.52, N 8.77; found C 35.2, H 5.57, N 8.63. ^{1}H NMR (200.13 MHz, TMS, 300 K, C_6D_6): δ = 4.72 (s, 1 H, *CH*), 3.03 (t, *J* = 6.28 Hz, 4 H, N*CH$_2$*CH$_2$NEt$_2$), 2.82 (q, *J* = 6.47 Hz, 4 H, N*CH$_2$*CH$_3$), 2.64 (t, *J* = 6.24 Hz, 4 H, NCH$_2$*CH$_2$*NEt$_2$) 2.47 (m, *J* = 6.48 Hz, 4 H, N*CH$_2$*CH$_3$) 1.59 (s, 6 H, CHC*CH$_3$*), 0.66 (t, *J* = 7.16 Hz, 12 H, CH$_2$*CH$_3$*) ppm. ^{13}C NMR (125.75 MHz, TMS, 300 K, C_6D_6): δ = 165.3 (*C*CH*C*), 100.5 (*C*H), 54.7 (CN*C*H$_2$), 47.8 (NCH$_2$*C*H$_2$), 30.1 (CH$_2$N*C*H$_2$), 22.3 (CHC*C*H$_3$), 8.9 (NCH$_2$*C*H$_3$) ppm. ^{19}F NMR (188 MHz, C_6F_6 as external reference, 300 K, C_6D_6): δ = 85.01 ppm. ^{45}Sc NMR (121.49 MHz, referenced to $[Sc(H_2O)_6]^{3+}$ in D_2O, 300 K, C_6D_6): δ = 185.06 ppm. M.p. 95 °C. EI-MS: *m*/*z* (%) = 638 (74) [M$^+$], 552 (36) [M$^+$ − $C_5H_{12}N$], 489 (100) [M$^+$ − CF_3SO_3].

X-ray Crystallography: Crystal structure data were collected on a Stoe Image Plate IPDS II-system (**1**, **7**) or on a Stoe−Siemens−Huber four-circle diffractometer equipped with a Bruker AXS CCD detector (**2**, **6**). All structures were solved by direct methods (SHELXS-97)[27] and refined against F^2 using SHELXL-97.[27] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model with U_{iso} tied to U_{iso} of the parent atoms. Crystal data collection details, and the solution and refinement procedures are summarized in Table 5.

CCDC-175025 (**1**), -199568 (**2a**), -199569 (**2b**), -203966 (**6**), and -199567 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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