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Preparation and properties of hexamethylphosphoramide coordinated samarium(III) complexes

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Summary — Hexamethylphosphoramide (HMPA) coordinated Sm(III) complexes containing different counter anions are isolated and structurally characterized by X-ray crystallography. These complexes are classified into the following four types: tricationic complexes $[Sm(H_2O)_4(hmpa)_3]I_3$ **1** and $[Sm(H_2O)_5(hmpa)_2]I_3 \cdot (hmpa)_2$ **2**, dicationic complexes $[SmCl(H_2O)_4(hmpa)_2]Cl_2 \cdot THF$ **3** and $[SmCl(hmpa)_5][BPh_4]_2$ **4**, cationic complex $[Sm(OTf)_2(hmpa)_4]OTf \cdot CHCl_3$ **5**, neutral complex $[Sm(OTf)_3(H_2O)(hmpa)_3] \cdot CHCl_3$ **6**. Crystal data of these complexes are **1**: monoclinic, space group $P2_1/c$ with $a = 15.853(5)$ Å, $b = 14.495(3)$ Å, $c = 19.158(4)$ Å, $\beta = 95.57(2)°$, $V = 4381(1)$ Å^3, $Z = 4$, $R = 0.048$, $R_w = 0.076$; **2**: monoclinic, space group Cc with $a = 14.054(6)$ Å, $b = 19.163(2)$ Å, $c = 20.531(3)$ Å, $\beta = 100.90(2)°$, $V = 5129(1)$ Å^3, $Z = 4$, $R = 0.062$, $R_w = 0.067$; **3**: triclinic, space group $P\bar{1}$ with $a = 15.309(6)$ Å, $b = 15.339(3)$ Å, $c = 8.751(2)$ Å, $\alpha = 102.99(1)°$, $\beta = 103.05(3)°$, $\gamma = 107.36(3)°$, $V = 1813(1)$Å^3, $Z = 2$, $R = 0.054$, $R_w = 0.074$; **4**: monoclinic, space group $P2_1/a$ with $a = 20.128(5)$ Å, $b = 17.582(3)$ Å, $c = 25.512(7)$ Å, $\beta = 99.93(2)°$, $V = 8893(3)$ Å^3, $Z = 4$, $R = 0.048$, $R_w = 0.052$; **5**: triclinic, space group $P\bar{1}$ with $a = 15.174(3)$ Å, $b = 17.459(7)$ Å, $c = 11.977(4)$ Å, $\alpha = 104.28(2)°$, $\beta = 102.65(3)°$, $\gamma = 90.40(3)°$, $V = 2994(1)$ Å^3, $Z = 2$, $R = 0.060$, $R_w = 0.077$; **6**: triclinic, space group $P\bar{1}$ with $a = 13.440(3)$ Å, $b = 14.975(6)$ Å, $c = 12.655(3)$ Å, $\alpha = 90.95(3)°$, $\beta = 93.95(2)°$, $\gamma = 84.15(2)°$, $V = 2527(1)$ Å^3, $Z = 2$, $R = 0.071$, $R_w = 0.091$. The coordinative nature of these complexes is discussed on the basis of observed bond lengths and angles.

X-ray crystallography / samarium(III) complex / hexamethylphosphoramide

Résumé — **Préparation et propriétés des complexes du Sm(III) coordinés à l'hexaméthylphosphotriamide.** Des complexes du Sm(III) coordinés à l'hexaméthylphosphotriamide (HMPT) et contenant divers contre-ions ont été isolés et leur structure a été caractérisée par diffraction aux rayons X. Ces complexes ont été classés selon les quatre types suivants : complexes tricationiques $[Sm(H_2O)_4(hmpt)_3]I_3$ **1** et $[Sm(H_2O)_5(hmpt)_2]I_3 \cdot (hmpt)_2$ **2**, complexes dicationiques $[SmCl(H_2O)_4(hmpt)_2]Cl_2 \cdot THF$ **3** et $[SmCl(hmpt)_5][BPh_4]_2$ **4**, complexe cationique $[Sm(OTf)_2(hmpt)_4]OTf \cdot CHCl_3$ **5**, complexe neutre $[Sm(OTf)_3(H_2O)(hmpt)_3] \cdot CHCl_3$ **6**. La nature des coordinations de ces complexes est commentée d'après les longueurs de liaison et des angles observés.

cristallographie rayons X / complexe du samarium(III) / hexaméthylphosphotriamide

Introduction

Subsequent to the pioneering work of Kagan and coworkers [1, 2], samarium(II) iodide-mediated organic reactions have been extensively investigated [3]. A number of efficient reductions of organic functional groups have been established by the use of samarium(II) iodide. In many cases, reductions are dramatically accelerated by the addition of hexamethyl phosphoramide (HMPA) as a co-solvent. This HMPA effect is responsible for the coordination of HMPA to the samarium(II) atom. Hou and Wakatsuki revealed a direct evidence of the coordination of HMPA to SmI_2 by X-ray crystallographic analysis [4]. We observed that the strong reducing ability of samarium(II) species is ascribed also to the great stability of the resulting samarium(III) species by virtue of the coordination with HMPA. This consideration prompted us to study the coordinative nature and chemical properties of various HMPA-coordinated samarium(III) complexes.

Results and discussion

Our initial investigation was undertaken with the preparation, reactivities, and structural characterization of HMPA-coordinated samarium(III) iodide complexes. Samarium metal powder was allowed to react with 1.5 equiv of diiodomethane in a mixture

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of tetrahydrofuran (THF) and HMPA. The composition of the resulting crystalline solid is found to be $SmI_3(hmpa)_4$ by elemental analysis. The FAB mass spectrum of this complex is shown in figure 1. A molecular ion peak corresponding to $[SmI_3(hmpa)_4]^+$ was not observed, and relatively large peaks, which were assigned to $[SmI_2(hmpa)_4]^+$, $[SmI_2(hmpa)_3]^+$ and $[SmI_2(hmpa)_2]^+$, appeared in the spectrum. These results clearly indicate that this HMPA complex is represented as $[SmI_2(hmpa)_4]I$.

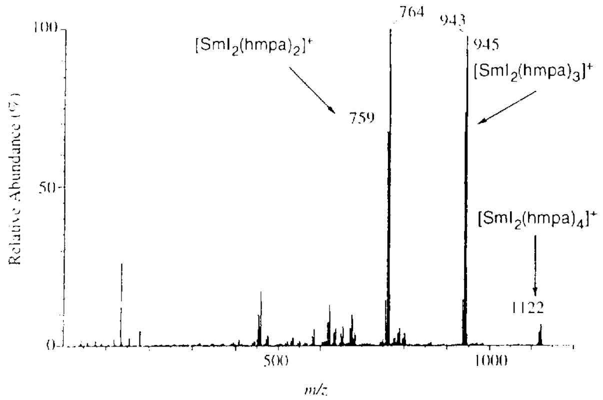

Fig 1. FAB mass spectrum of $SmI_3(hmpa)_4$.

The reactivities of this anhydrous SmI_3–HMPA complex were examined in comparison with that of SmI_3 itself. Previously, we found that SmI_3 was readily reduced to divalent samarium species on treatment with *n*-butyllithium or *sec*-butyllithium (eq (1)) [5]:

$$SmI_3 \xrightarrow[\text{THF, 0 °C–room temperature}]{n\text{-BuLi or } sec\text{-BuLi}} SmI_2 \qquad (1)$$

It was also reported from our laboratory that SmI_3 and samarium metal underwent a proportionation reaction to generate SmI_2 in almost quantitative yield (eq (2)) [6]:

$$2\ SmI_3 + Sm \xrightarrow[\text{room temperature–reflux}]{\text{THF}} 3\ SmI_2 \qquad (2)$$

In sharp contrast to these reactivities of SmI_3, $SmI_3(hmpa)_4$ was not reduced to divalent samarium species by *n*-butyllithium or *sec*-butyllithium in THF at room temperature. It was also found that no proportionation reaction between $SmI_3(hmpa)_4$ and samarium metal occurred even at reflux in THF. These results are reasonably interpreted by considering that this complex is well stabilized by the coordination of HMPA and can not accept one electron from the reductants.

In order to obtain suitable crystals for X-ray analysis, the complex was recrystallized from 3-pentanone to give cubic and irregular prismatic crystals. The molecular structures of both crystals were determined by X-ray diffraction analysis.

Figure 2 shows an ORTEP drawing of complex **1** of which the crystal form is irregular prismatic. The selected bond distances and angles are listed in table I. It is apparent that the complex consists of one samarium atom, three iodide anions, three HMPA and four H_2O molecules [7, 8]. The central samarium atom is hepta-coordinated by three HMPA oxygen atoms and four H_2O molecules to form a pentagonal bipyramidal structure. Three iodide anions are not coordinated to the samarium atom to form a tricationic complex. The

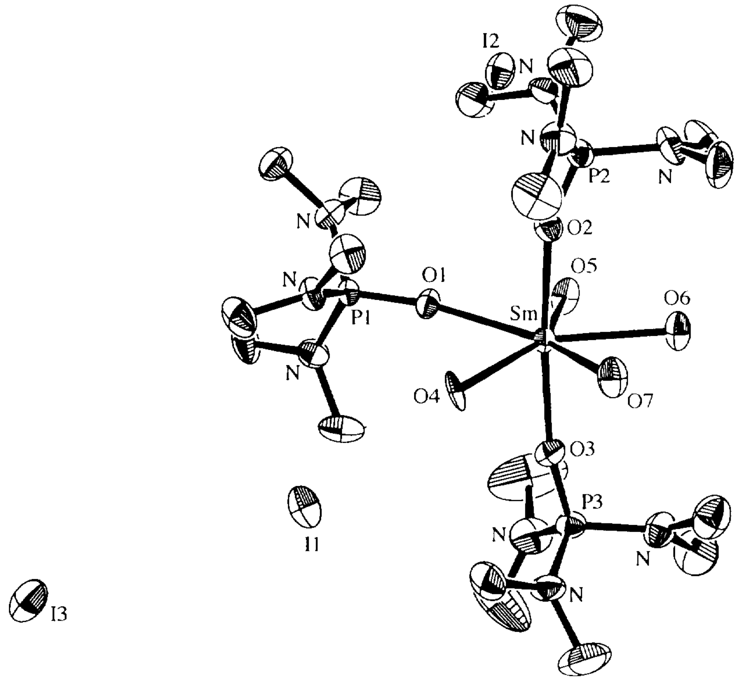

Fig 2. ORTEP drawing of $[Sm(H_2O)_4(hmpa)_3]I_3$ **1**.

Table I. Selected bond distances (Å) and angles (°) for complex **1**.

Sm–O(1)	2.333(8)	Sm–O(2)	2.296(9)
Sm–O(3)	2.262(8)	Sm–O(4)	2.474(8)
Sm–O(5)	2.441(7)	Sm–O(6)	2.441(8)
Sm–O(7)	2.468(10)	P(1)–O(1)	1.490(9)
P(2)–O(2)	1.494(10)	P(3)–O(3)	1.503(9)
I(1)–O(4)	3.529(8)		
O(1)–Sm–O(2)	83.6(3)	O(1)–Sm–O(3)	100.6(3)
O(1)–Sm–O(4)	74.9(3)	O(1)–Sm–O(5)	75.3(3)
O(2)–Sm–O(3)	175.2(3)	O(2)–Sm–O(4)	96.8(3)
O(2)–Sm–O(5)	92.5(4)	O(2)–Sm–O(6)	87.9(3)
O(2)–Sm–O(7)	85.8(3)	O(3)–Sm–O(4)	86.8(3)
O(3)–Sm–O(5)	86.2(3)	O(3)–Sm–O(6)	87.3(3)
O(3)–Sm–O(7)	92.2(3)	O(4)–Sm–O(7)	71.5(3)
O(5)–Sm–O(6)	71.2(3)	O(6)–Sm–O(7)	69.2(3)
Sm–O(1)–P(1)	162.7(6)	Sm–O(3)–P(2)	158.0(6)
Sm–O(3)–P(3)	168.2(6)		

average bond distance (2.297(8) Å) between the samarium atom and the three HMPA oxygen atoms is ca 0.16 Å shorter than the average bond distance (2.456(8) Å) between the samarium atom and the four H_2O oxygen atoms, indicating that the HMPA molecules coordinate to the samarium atom more strongly than the H_2O molecules. Judging from the atomic distance of I(1)–O(4) (3.529(8) Å), this H_2O oxygen atom is suggested to interact with the iodide anion through hydrogen bonds.

Figure 3 shows an ORTEP drawing of complex **2** whose crystal form is cubic. The selected bond distances and angles are listed in table II. The X-ray crystal structural analysis reveals that the complex contains a tricationic samarium(III) atom linked by the two HMPA oxygen atoms and five H_2O molecules to form a pentagonal bipyramidal structure [7, 8]. It is noted that the other two HMPA molecules are not directly coordinated to the samarium atom. Judging from the atomic distances of O5–O9 (2.66(3) Å), O6–O9 (2.54(3) Å), O6–O8 (2.67(3) Å) and O7–O8 (2.65(3) Å), these HMPA oxygen atoms interact with the coordinated H_2O molecules through hydrogen bonds.

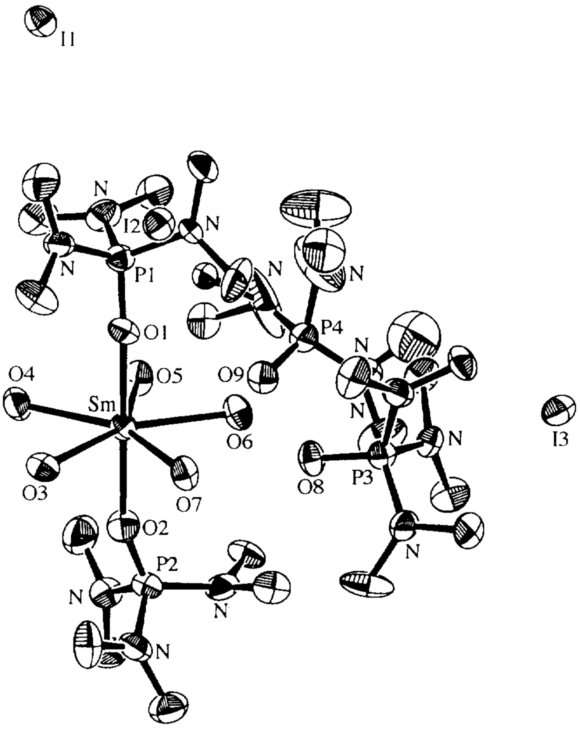

Fig 3. ORTEP drawing of $[Sm(H_2O)_5(hmpa)_2]I_3 \cdot (hmpa)_2$ **2**.

Table II. Selected bond distances (Å) and angles (°) for complex **2**.

Sm–O(1)	2.23(2)	Sm–O(2)	2.27(2)
Sm–O(3)	2.43(2)	Sm–O(4)	2.40(2)
Sm–O(5)	2.41(2)	Sm–O(6)	2.43(2)
Sm–O(7)	2.45(2)	P(1)–O(1)	1.50(2)
P(2)–O(2)	1.50(2)	P(3)–O(8)	1.48(2)
P(4)–O(9)	1.51(2)	O(5)–O(9)	2.66(3)
O(6)–O(8)	2.67(3)	O(6)–O(9)	2.54(3)
O(7)–O(8)	2.65(3)		
O(1)–Sm–O(2)	177.2(9)	O(1)–Sm–O(3)	89.0(7)
O(1)–Sm–O(4)	91.2(8)	O(1)–Sm–O(5)	94.6(8)
O(1)–Sm–O(6)	89.4(8)	O(1)–Sm–O(7)	88.8(8)
O(2)–Sm–O(3)	89.3(7)	O(2)–Sm–O(4)	90.5(8)
O(2)–Sm–O(5)	88.1(8)	O(2)–Sm–O(6)	90.7(8)
O(2)–Sm–O(7)	88.6(8)	O(3)–Sm–O(4)	74.3(8)
O(3)–Sm–O(7)	72.3(7)	O(4)–Sm–O(5)	71.1(8)
O(5)–Sm–O(6)	69.6(7)	O(6)–Sm–O(7)	72.8(7)
Sm–O(1)–P(1)	159(1)	Sm–O(2)–P(2)	161(1)

A samarium(III) chloride complex coordinated with HMPA was also prepared by treatment of samarium(III) chloride with HMPA in THF. X-ray crystallographic analysis of this complex revealed its molecular structure. The ORTEP drawing of the complex $[SmCl(H_2O)_4(hmpa)_2]Cl_2 \cdot THF$ **3** is shown in figure 4. The selected bond distances and angles are summarized in table III. The central samarium atom is hepta-coordinated by two HMPA oxygen atoms and four H_2O molecules and one chloride anion to form a pentagonal bipyramidal structure [8]. The Sm–Cl bond distance (2.743(3) Å) is longer than that (2.60–2.65 Å) (terminal) of the previously reported samarium(III) complex $(C_5Me_5)_{10}Sm_5Cl_5[Me(OCH_2CH_2)_4OMe]$ [9]. This bond

Table III. Selected bond distances (Å) and angles (°) for complex **3**.

Sm–Cl(1)	2.738(2)	Sm–O(1)	2.252(6)
Sm–O(2)	2.260(6)	Sm–O(3)	2.434(6)
Sm–O(4)	2.416(6)	Sm–O(5)	2.413(6)
Sm–O(6)	2.449(6)	P(1)–O(1)	1.479(7)
P(2)–O(2)	1.470(7)	Cl(2)–O(5)	3.074(7)
Cl(2)–O(6)	3.051(7)		
Cl(1)–Sm–O(1)	94.2(2)	Cl(1)–Sm–O(2)	93.9(2)
Cl(1)–Sm–O(3)	73.7(2)	Cl(1)–Sm–O(6)	73.5(2)
O(1)–Sm–O(2)	171.9(3)	O(1)–Sm–O(3)	94.9(2)
O(1)–Sm–O(4)	84.8(2)	O(1)–Sm–O(5)	88.4(2)
O(1)–Sm–O(6)	87.6(2)	O(2)–Sm–O(3)	87.6(2)
O(2)–Sm–O(4)	88.9(2)	O(2)–Sm–O(5)	84.9(2)
O(2)–Sm–O(6)	94.4(2)	O(3)–Sm–O(4)	69.7(2)
O(4)–Sm–O(5)	73.4(2)	O(5)–Sm–O(6)	70.1(2)
Sm–O(1)–P(1)	174.4(5)	Sm–O(2)–P(2)	173.6(4)

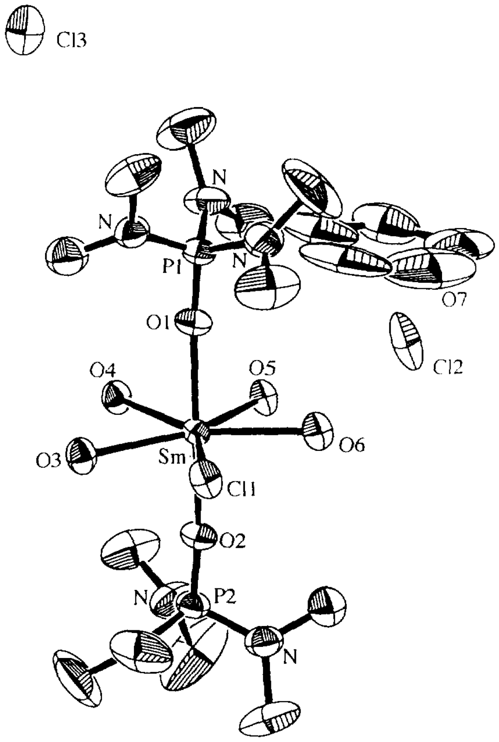

Fig 4. ORTEP drawing of $[SmCl(H_2O)_4(hmpa)_2]Cl_2 \cdot THF$ **3**.

elongation may be responsible for the strong coordination of HMPA and H_2O molecules to the samarium atom. The atomic distances of Cl(2)–O(5) (3.070(9) Å) and Cl(2)–O(6) (3.071(10) Å) imply that the Cl(2) atom interacts with O(5) and O(6) through hydrogen bonds.

It is interesting to compare this complex with complex **1**. The coordination geometries of both complexes are pentagonal bipyramidal. Two HMPA molecules are located at the axial positions and four H_2O molecules are placed at the equatorial plane in both complexes. A major difference is that a HMPA molecule coordinates to the samarium metal at an equatorial position in complex **1** and a chloride anion coordinates at the same position in complex **3**. This difference reflects the bond lengths between the samarium and the H_2O oxygen atoms. Thus, the average value (2.428(6) Å) of the four bond lengths between the samarium and the H_2O oxygens in complex **3** is smaller than the corresponding mean value (2.456(9) Å) of complex **1**. A similar tendency is also observed in the average bond length between the samarium metal and the HMPA oxygens at the axial positions (2.279(9) Å for complex **1** and 2.256(6) Å for complex **3**). These differences are ascribed to the fact that HMPA coordinates to the samarium metal more strongly than the chloride anion.

In order to obtain further knowledge on the coordinative nature of HMPA-coordinated dicationic samarium complexes, we have prepared an analogous complex $[SmCl(hmpa)_5][BPh_4]_2$ **4** by the reaction of anhydrous samarium(III) chloride with 2 equiv of sodium tetraphenylborate in a mixture solvent of HMPA and THF. The molecular structure of complex **4** is shown in figure 5. The selected bond distances and angles are listed in table IV. This complex has octahedral geometry coordinated by five HMPA ligands and one chloride anion. As is expected from the lack of coordination ability of tetraphenylborate, this complex is dicationic and its coordination geometry is similar to that of the neodymium(III) complex $[NdCl(hmpa)_5][PF_6]_2$ [10]. As shown in figure 5 and table IV, the bond angles around the samarium metal are distorted from regular octahedral geometry. The ligand–samarium–ligand angles at the equatorial plane considerably deviate from 90° ranging from 84.9(1)° to 101.0(1)°. The bond angle of Sm–O(3)–P(3) (151.1(2)°) is remarkably distorted in comparison with the Sm–O–P angles of the previously reported HMPA-coordinated samarium(III) complexes, eg, $Sm(OCHPh_2)_2(OAr)(hmpa)_2$ ($Ar{=}C_6H_3{-}^tBu_2{-}2,6$) (average 167.6(3)°), $Sm(OC(=CCH=CHCH_2CH=CH)Ph)_2(OAr)(hmpa)_2$ (average 172(1)°) [11], $Sm(SPh)_3(hmpa)_3$ (average 164.6(3)°) [12]. This deviation of the bond angles should probably be attributed to the steric congestion of HMPA at the axial position.

Table IV. Selected bond distances (Å) and angles (°) for complex **4**.

Sm–Cl	2.656(2)	Sm–O(1)	2.315(4)
Sm–O(2)	2.278(4)	Sm–O(3)	2.329(4)
Sm–O(4)	2.289(4)	Sm–O(5)	2.260(4)
P(1)–O(1)	1.498(4)	P(2)–O(2)	1.483(4)
P(3)–O(3)	1.509(4)	P(4)–O(4)	1.486(4)
P(5)–O(5)	1.510(4)		
Cl–Sm–O(1)	171.7(1)	Cl–Sm–O(2)	91.4(1)
Cl–Sm–O(3)	89.1(1)	Cl–Sm–O(4)	88.0(1)
Cl–Sm–O(5)	89.9(1)	O(1)–Sm–O(2)	95.0(1)
O(1)–Sm–O(3)	85.8(1)	O(1)–Sm–O(4)	86.5(1)
O(1)–Sm–O(5)	95.9(1)	O(2)–Sm–O(3)	88.2(1)
O(2)–Sm–O(4)	170.7(1)	O(2)–Sm–O(5)	84.9(1)
O(3)–Sm–O(4)	101.0(1)	O(3)–Sm–O(5)	173.1(1)
O(4)–Sm–O(5)	85.8(1)	Sm–O(1)–P(1)	173.5(2)
Sm–O(2)–P(2)	177.9(2)	Sm–O(3)–P(3)	151.1(2)
Sm–O(4)–P(4)	172.4(2)	Sm–O(5)–P(5)	173.1(3)

Lanthanide metal trifluoromethanesulfonates (triflates) are known to behave as characteristic Lewis acids, and they are often utilized as catalysts in carbon–carbon bond-forming reactions such as the aldol reaction, the hetero Diels–Alder reaction, the Friedel–Crafts reaction, and esterification of alcohols [13–24]. It has also been reported that $Sm(OTf)_2$ exhibits one electron reducing ability somewhat different from that of SmI_2 [25–27]. These facts lead us to analyzing the molecular structure of a HMPA-coordinated samarium(III) triflate. The desired crystals for X-ray analysis were obtained by treatment of $Sm(OTf)_3$ with HMPA in dry THF, followed by recrystallization from a mixed solvent of chloroform and ethyl acetate. The molecular structure of complex $[Sm(OTf)_2(hmpa)_4]OTf \cdot CHCl_3$ **5** is described in figure 6 [28]. The selected bond distances and angles found in **5** are listed in table V. This complex shows a hexa-coordinated octahedral structure. Two triflate anions are located at the *trans* position, while

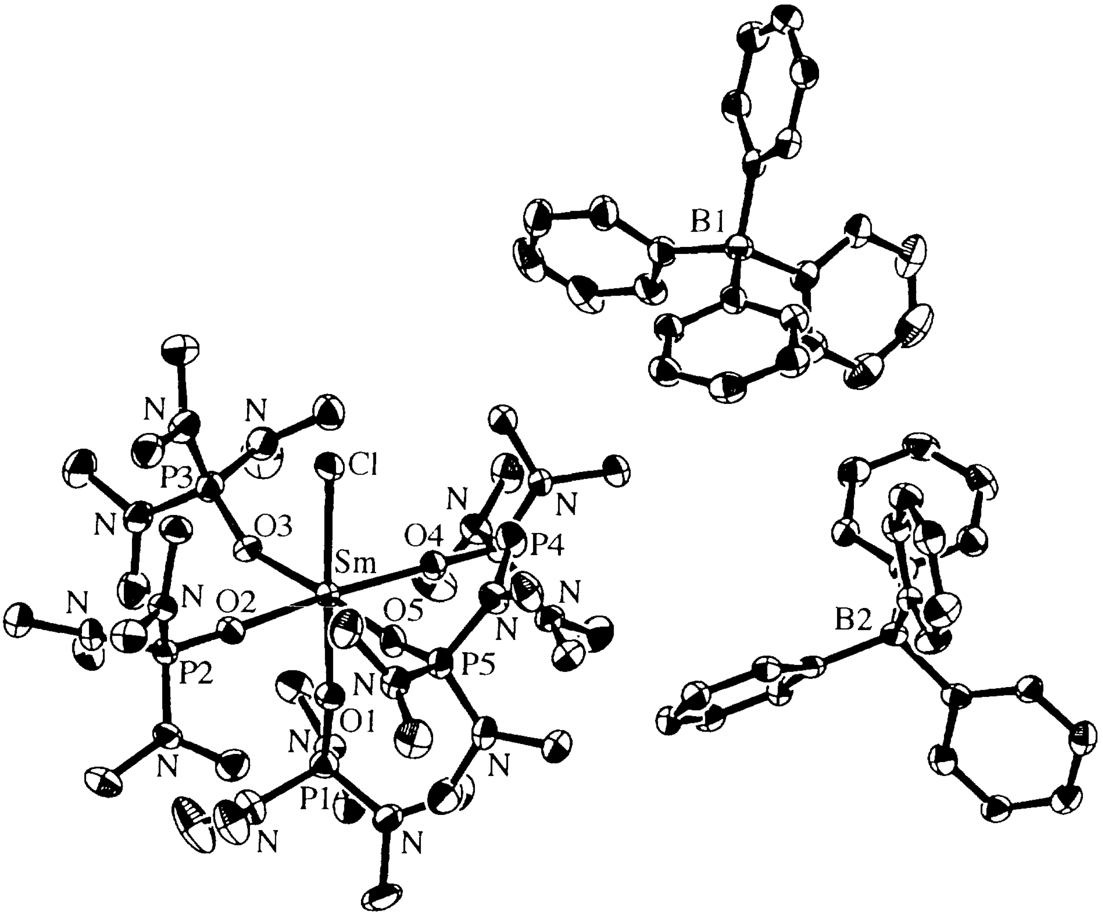

Fig 5. ORTEP drawing of $[SmCl(hmpa)_5](BPh_4)_2$ **4**.

Table V. Selected bond distances (Å) and angles (°) for complex **5**.

Sm–O(1)	2.356(5)	Sm–O(2)	2.345(5)
Sm–O(3)	2.254(4)	Sm–O(4)	2.260(4)
Sm–O(5)	2.276(4)	Sm–O(6)	2.247(4)
S(1)–O(1)	1.442(5)	S(1)–O(7)	1.415(6)
S(1)–O(8)	1.425(6)	S(2)–O(2)	1.414(5)
S(2)–O(9)	1.360(7)	S(2)–O(10)	1.424(7)
S(3)–O(11)	1.413(6)	S(3)–O(12)	1.380(7)
S(3)–O(13)	1.471(6)	P(1)–O(3)	1.491(5)
P(2)–O(4)	1.479(4)	P(3)–O(5)	1.477(5)
P(4)–O(6)	1.493(4)	O(11)–C(28)	3.43(1)
O(12)–C(28)	3.31(1)		
O(1)–Sm–O(2)	177.2(1)	O(1)–Sm–O(3)	93.5(2)
O(1)–Sm–O(4)	87.1(2)	O(1)–Sm–O(5)	90.6(2)
O(1)–Sm–O(6)	88.7(2)	O(2)–Sm–O(3)	88.1(2)
O(2)–Sm–O(4)	90.6(2)	O(2)–Sm–O(5)	87.8(2)
O(2)–Sm–O(6)	93.5(2)	O(3)–Sm–O(4)	90.2(2)
O(3)–Sm–O(5)	175.7(1)	O(3)–Sm–O(6)	90.2(2)
O(4)–Sm–O(5)	91.1(2)	O(4)–Sm–O(6)	175.9(1)
O(5)–Sm–O(6)	88.8(1)	Sm–O(1)–S(1)	158.2(3)
Sm–O(2)–S(2)	158.9(4)	Sm–O(3)–P(1)	175.9(3)
Sm–O(4)–P(2)	167.7(3)	Sm–O(5)–P(3)	171.5(3)
Sm–O(6)–P(4)	171.9(3)		

a third triflate anion is not coordinated to the samarium but interacts with chloroform through a hydrogen bond. The four HMPA ligands coordinate to the central samarium ion forming an equatorial plane. The average bond distance (2.259(4) Å) between the samarium atom and the four HMPA oxygen atoms is shorter than that (2.350(5) Å) between the samarium atom and the triflate oxygen atoms, indicating that HMPA molecules coordinate more strongly than triflate anions. Moreover, the bond distances of Sm–O (HMPA) are 0.05–0.1 Å shorter than those found in other trivalent samarium complexes such as $Sm(OCHPh_2)_2(OAr)(hmpa)_2$ ($Ar{=}C_6H_3{-}^tBu_2{-}2{,}6$) (average 2.364(5) Å) [11] and $Sm(SPh)_3(hmpa)_3$ (2.299(4) Å) [12]. These facts clearly indicate that the Lewis acidity of $Sm(OTf)_3$ is stronger than that of $Sm(OCHPh_2)_2(OAr)$ or $Sm(SPh)_3$.

A FAB mass spectrum of complex **5** is shown in figure 7. The fragmentation pattern resembles that of $[SmI_2(hmpa)_4]I$; three distinct ion peaks, that are assigned to $[Sm(OTf)_2(hmpa)_4]^+$, $[Sm(OTf)_2(hmpa)_3]^+$, and $[Sm(OTf)_2(hmpa)_2]^+$, are observed in the spectrum. These facts, in accordance with the structural evidence obtained by X-ray crystallography, clearly in-

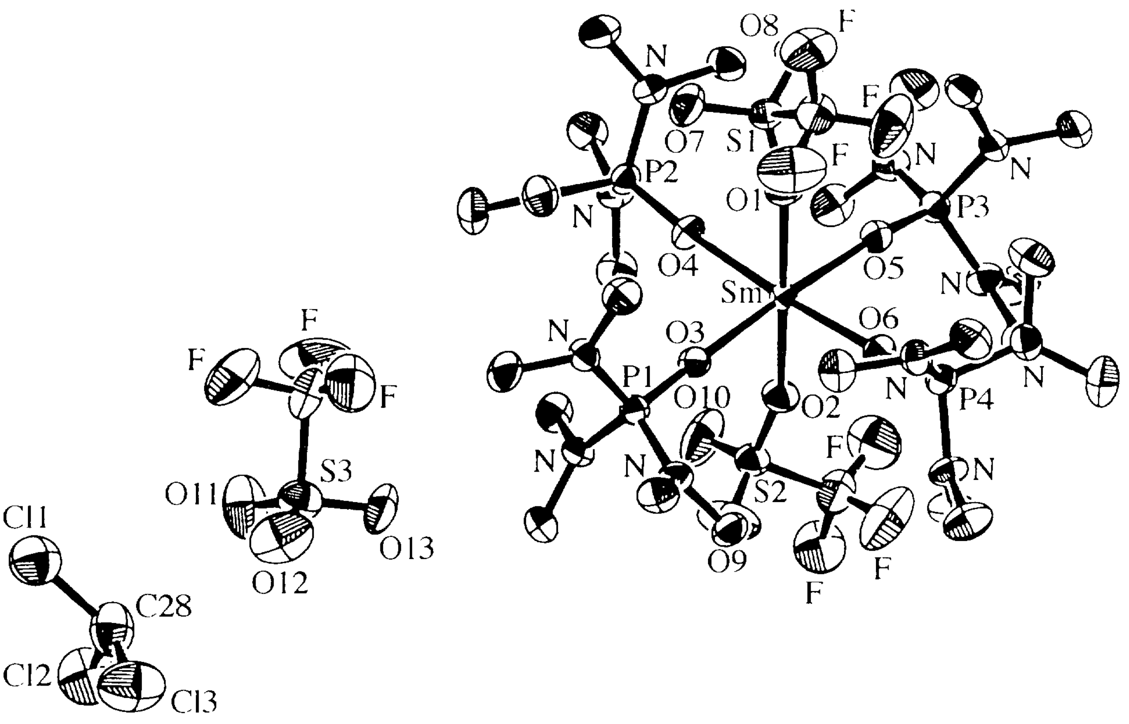

Fig 6. ORTEP drawing of $[Sm(OTf)_2(hmpa)_4]OTf{\cdot}CHCl_3$ **5**.

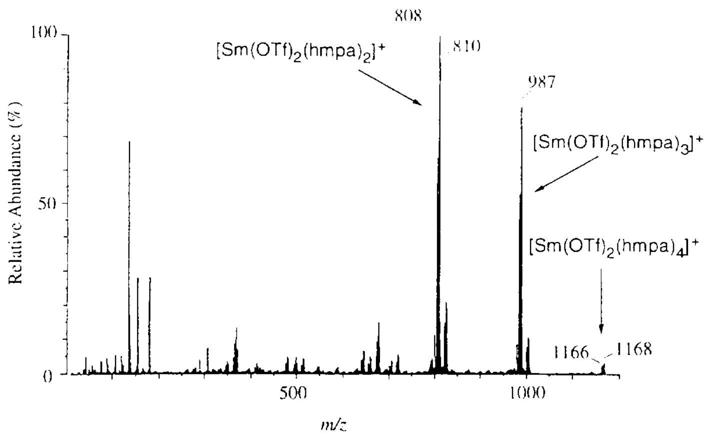

Fig 7. FAB mass spectrum of complex **5**.

dicate that the composition of this complex is represented as $[Sm(OTf)_2(hmpa)_4]OTf$.

It seems reasonable to consider that the formation of the monocationic complex **5** is mainly attributable to the coordination of four HMPA molecules to the samarium metal. This consideration suggests that one might obtain a neutral samarium(III) triflate complex containing three or two HMPA molecules as the ligands. Based on this idea we actually isolated such a complex by treatment of $Sm(OTf)_3$ with 2 equiv of HMPA, and subsequent X-ray crystallographic analysis revealed that this complex was $[Sm(OTf)_3(H_2O)(hmpa)_3]{\cdot}CHCl_3$ **6**. The molecular structure of complex **6** is depicted in figure 8. The selected bond distances and angles are listed in table VI. The formation of this complex, eve in the presence of only 2 equiv of HMPA molecules indicates that the samarium complex coordinated wit three HMPA molecules is more stable than the complexes containing one or two HMPA molecules. Th central samarium atom is hepta-coordinated by thre HMPA oxygen atoms and three triflate oxygen atom and one H_2O molecule to form a distorted pentagon bipyramidal structure [8]. The coordination geometr of three HMPA ligands is a T-shaped arrangement. Th average bond distances of Sm–O (HMPA) (2.270(7) Å Sm–O (OTf) (2.437(7) Å) and Sm–O (H_2O) (2.493(Å) decrease in this order. It is noted that the bondin interaction between the samarium atom and the triflat

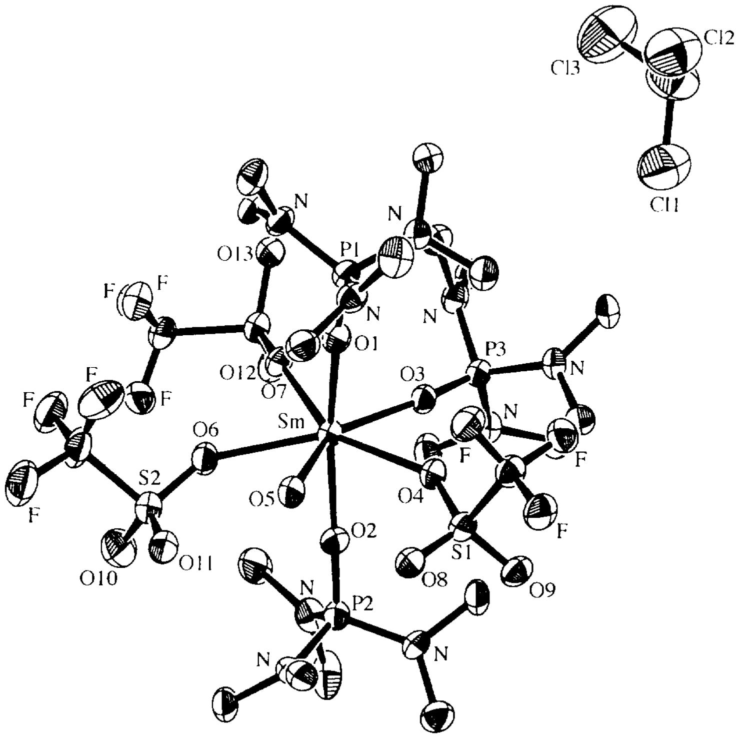

Fig 8. ORTEP drawing of $[Sm(OTf)_3(H_2O)(hmpa)_3]\cdot CHCl_3$ **6**.

Table VI. Selected bond distances (Å) and angles (°) for complex **6**.

Sm–O(1)	2.272(7)	Sm–O(2)	2.245(7)
Sm–O(3)	2.292(6)	Sm–O(4)	2.489(6)
Sm–O(5)	2.493(7)	Sm–O(6)	2.447(7)
Sm–O(7)	2.374(6)	S(1)–O(4)	1.435(7)
S(1)–O(8)	1.450(8)	S(1)–O(9)	1.427(7)
S(2)–O(6)	1.446(7)	S(2)–O(10)	1.395(9)
S(2)–O(11)	1.448(8)	S(3)–O(7)	1.450(7)
S(3)–O(12)	1.426(8)	S(3)–O(13)	1.441(8)
P(1)–O(1)	1.486(8)	P(2)–O(2)	1.509(7)
P(3)–O(3)	1.484(7)		
O(1)–Sm–O(2)	169.3(2)	O(1)–Sm–O(3)	92.7(2)
O(1)–Sm–O(4)	84.4(2)	O(1)–Sm–O(5)	83.1(2)
O(1)–Sm–O(6)	103.0(2)	O(1)–Sm–O(7)	87.3(2)
O(2)–Sm–O(3)	88.5(2)	O(2)–Sm–O(4)	85.6(2)
O(2)–Sm–O(5)	89.9(2)	O(2)–Sm–O(6)	81.9(2)
O(2)–Sm–O(7)	103.3(2)	O(3)–Sm–O(4)	76.1(2)
O(3)–Sm–O(7)	76.4(2)	O(4)–Sm–O(5)	69.6(2)
O(5)–Sm–O(6)	69.7(2)	O(6)–Sm–O(7)	71.8(2)
Sm–O(1)–P(1)	176.0(4)	Sm–O(2)–P(2)	173.6(4)
Sm–O(3)–P(3)	173.2(4)		

oxygen atoms is stronger than that between the samarium atom and the H_2O oxygen atom. Different from ionic complexes **1**–**5**, the coordination of all three triflate anions to the samarium atom makes this complex neutral.

Conclusion

In summary, we have studied the preparation and structural characterization of Sm–HMPA complexes. The six samarium complexes are classified into the following four types: tricationic complexes **1** and **2**, dicationic complexes **3** and **4**, cationic complex **5**, neutral complex **6**. These results indicate that counter anions as well as neutral ligands have great influence on the molecular structure of samarium complexes. The formation of these samarium(III) complexes supports the idea that the strong stabilization of trivalent samarium species by complexation with HMPA or H_2O is one of the driving forces for the facile one-electron transfer of divalent samarium species.

Experimental section

Material

Samarium oxide, samarium metal and samarium chloride ($SmCl_3\cdot 6H_2O$) were commercial products (Nippon Yttrium Co Ltd). Trifluoromethanesulfonic acid, hexamethylphosphoramide and diiodomethane were obtained from Wako Pure Chemical Industries Ltd and were used without further purification. Tetrahydrofuran, dichloromethane, hexane, toluene, ethyl acetate and chloroform were high-purity grade solvents.

Table VII. Crystal data and structure refinements for compounds **1**, **2**, **3**, **4**, **5** and **6**.

	$[Sm(H_2O)_4(hmpa)_3]I_3$ **1**	*$[Sm(H_2O)_5(hmpa)_2]I_3 \cdot (hmpa)_2$* **2**	*$[SmCl(H_2O)_4(hmpa)_2]Cl_2 \cdot THF$* **3**
Formula	$C_{18}H_{62}I_3N_9O_7P_3Sm$	$C_{24}H_{82}I_3N_{12}O_9P_4Sm$	$C_{16}H_{52}Cl_3N_6O_7P_2Sm$
Formula weight	1140.78	1337.96	759.33
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$ (# 14)	Cc (# 9)	$P\bar{1}$ (# 2)
a, Å	15.853(5)	14.054(6)	15.309(6)
b, Å	14.495(3)	19.163(2)	15.339(3)
c, Å	19.158(4)	20.531(3)	8.751(2)
α, deg	90	90	102.99(1)
β, deg	95.57(2)	100.90(2)	103.05(3)
γ, deg	90	90	107.36(3)
V, Å^3	4381(1)	5129(1)	1813(1)
Z	4	4	2
D_{calc}, g cm^{-3}	1.729	1.637	1.390
μ(Mo-Kα), cm^{-1}	36.07	29.56	19.68
Reflections collected	8306	3126	3971
Reflections used	4162 ($I > 3.00\delta(I)$)	2906 ($I > 3.00\sigma(I)$)	3939 ($I > 2.00\delta(I)$)
R	0.047	0.062	0.054
R_w	0.077	0.067	0.074
Min/max abs	1.22/1.49	2.16/1.74	0.98/0.41
Lattice parameters	371	476	317
Temperature	Room temperature	173 K	Room temperature
	$[SmCl(hmpa)_5](BPh_4)_2$ **4**	*$[Sm(OTf)_2(hmpa)_4]OTf \cdot CHCl_3$* **5**	*$[Sm(OTf)_3(H_2O)(hmpa)_3] \cdot CHCl_3$* **6**
Formula	$C_{78}H_{130}B_2ClN_{15}O_5P_5Sm$	$C_{28}H_{73}Cl_3F_9N_{12}O_{13}P_4S_3Sm$	$C_{22}H_{57}Cl_3F_9N_9O_{13}P_3S_3Sm$
Formula weight	1720.32	1433.78	1272.59
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/a$ (# 14)	$P\bar{1}$ (# 2)	$P\bar{1}$ (# 2)
a, Å	20.128(5)	15.174(3)	13.440(3)
b, Å	17.582(3)	17.459(7)	14.975(6)
c, Å	25.512(7)	11.977(4)	12.655(3)
α, deg	90	104.28(2)	90.95(3)
β, deg	99.93(2)	102.65(3)	93.95(2)
γ, deg	90	90.40(3)	84.15(2)
V, Å^3	8893(3)	2994(1)	2527(1)
Z	4	2	2
D_{calc}, g cm^{-3}	1.285	1.590	1.672
μ(Mo-Kα), cm^{-1}	8.37	14.15	16.33
Reflections collected	8578	6699	5654
Reflections used	7717 ($I > 2.00\delta(I)$)	6558 ($I > 2.00\delta(I)$)	5566 ($I > 2.00\delta(I)$)
R	0.048	0.060	0.071
R_w	0.052	0.077	0.091
Min/max abs	1.09/0.37	1.27/0.87	1.36/1.00
Lattice parameters	964	659	568
Temperature	173 K	173 K	123 K

X-ray diffraction analysis of complex **1**

A single crystal of complex **1** was mounted on a Rigaku AFC5R diffractometer with graphite-monochromated Mo-Kα radiation. Unit cell constants and orientation matrix for data collection were obtained from least-squares refinement of the setting angles of 25 well-centered reflections. The data were collected at room temperature using the ω–2θ scan technique. The structure was solved by a direct method using the ORIENT program [29]. Full-matrix least-squares refinements were carried out by minimizing the function $\sum_\omega(|F_o| - |F_c|)_2$ where F_o and F_c were observed and calculated structure factors. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Crystal data and other information are summarized in table VII.

X-ray diffraction analyses of complexes **2–6**

Suitable crystals sealed in a glass capillary were mounted on a R-AXISII diffractometer with graphite-monochromated Mo-Kα radiation. A laser-stimulated fluorescence image plate was used as a two-dimensional area detector. Because of the instability of the crystals, rapid analysis was required. The distance between the crystal and the detector was 100 mm. Thus, 27 frames were recorded at intervals of 6° and each exposure lasted for 5 min (ca 135 min for the total data collection). Structures were solved by direct methods using the programs SHELKS86 [30] and SIR92 [31], and patterson methods using SAPI91 [32]. Full-matrix least-squares refinements were carried out by minimizing the function $\sum_\omega(|F_o| - |F_c|)^2$ where F_o and F_c were observed and calculated structure factors. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Crystal data and other information are summarized in table VII.

- *Tetrakis(hexamethylphosphoramide)samarium triiodide, $SmI_3(hmpa)_4$*

Diiodomethane (1.3 mL, 16 mmol) was added under stirring to a mixture of samarium powder (ca 50 mesh, 1.5 g, 10 mmol), HMPA (8.7 mL, 50 mmol), and dry THF (30 mL) under argon atmosphere. After the initial exothermic reaction was subsided, the mixture was refluxed for 1 h. The solvent was removed under reduced pressure, and most of the residual solid material was dissolved in hot ethyl acetate/chloroform (1:1) (180 mL). The mixture was filtered to remove unsolved material and the filtrate stood at room temperature overnight. The crystallized pale yellow needles were collected, washed with ethyl acetate/chloroform (1:1) and dried in vacuo at 100 °C for 5 h to give a moisture-sensitive white powder (8.6 g, 69%). The composition of the dried complex was found to be $SmI_3(hmpa)_4$ by elemental analysis and FAB mass spectroscopy.

Mp > 250 °C.

IR (KBr) 2 890, 1 300, 1 190, 1 105, 990 cm^{-1}.

FAB MS m/z 1 122 (M^+–I).

Anal calc for $C_{24}H_{72}I_3O_4N_{12}P_4Sm$: C, 23.31; H, 5.87; N, 13.56. Found: C, 23.26; H, 5.84; N, 13.38.

- *Complexes **1** $[Sm(H_2O)_4(hmpa)_3]I_3$ and **2** $[Sm(H_2O)_5(hmpa)_2]I_3 \cdot (hmpa)_2$*

Tetrakis(hexamethylphosphoramide)samarium triiodide (5 mmol, 6.2 g) was dissolved in hot 3-pentanone, and the solution was left standing overnight at room temperature to give irregular prismatic crystals (complex **1**) and cubic crystals (complex **2**).

- *Complex **3** $[SmCl(H_2O)_4(hmpa)_2]Cl_2 \cdot THF$*

Anhydrous samarium chloride (2.6 g, 10 mmol) was stirred in a mixture of dry THF (30 mL) and HMPA (5.2 mL, 30 mmol) under argon atmosphere for 1 h, and the solvent was evaporated under reduced pressure. The resulting crystalline solid was washed with hexane to yield a white powder (6.3 g, 80%). The powder was dissolved in CH_2Cl_2/toluene/THF (1:2:2), and slow evaporation of the solvent at room temperature under air for a few days gave colorless prismatic crystals.

- *Complex **4** $[SmCl(hmpa)_5][BPh_4]_2$*

To a suspension of anhydrous samarium chloride (0.77 g, 3 mmol) and sodium tetraphenylborate (0.68 g, 2 mmol) in THF (20 mL) was added HMPA (2.6 mL, 15 mmol). After stirring for 1 h at room temperature, the solvent was removed under reduced pressure to leave a solid material, which was stirred with dichloromethane (30 mL). The mixture was filtered to remove sodium chloride, and the filtrate was evaporated. The residual solid was recrystallized from dichloromethane/ethyl acetate (1:1) to give crystals for X-ray diffraction analysis.

- *Complex **5** $[Sm(OTf)_2(hmpa)_4][OTf] \cdot CHCl_3$*

Anhydrous samarium triflate (3.0 g, 5 mmol) was stirred in dry THF (50 mL) containing HMPA (4.4 mL, 25 mmol) under argon atmosphere for 1 h. The solvent was evaporated and the residual solid was washed with ethyl acetate to give a white powder (5.7 g). In order to obtain suitable crystals for X-ray analysis, this powder was recrystallized from chloroform/ethyl acetate (1:2).

FAB MS m/z 1168 (M^+–OTf).

IR (KBr) 2 880, 1 480, 1 260, 990, 760 cm^{-1}.

- *Complex **6** $[Sm(OTf)_3(H_2O)(hmpa)_3] \cdot CHCl_3$*

Anhydrous samarium triflate (0.6 g, 1 mmol) was dissolved in a mixture of dry THF (5 mL), chloroform (20 mL), and HMPA (0.36 g, 2 mmol) under argon atmosphere. Hexane (10 mL) was slowly added to the solution, and the mixture was left standing overnight. The resulting crystals were used for X-ray diffraction analysis.

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Supplementary material available

Supplementary material data have been deposited with the British Library, Document Supply Centre at Boston Spa, Wetherby, West Yorkshire, LS23 6BQ, UK, as supplementary publication No SUP 90459 and are available on request from the Document Supply Centre.

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