Molecular Structures of HMPA-Coordinated Samarium(II) and Ytterbium(II) Iodide Complexes. A Structural Basis for the HMPA Effects in SmI_2-Promoted Reactions

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The reaction of ytterbium(II) iodide (YbI_2) with 4.5 equiv of hexamethylphosphoric triamide (hmpa) in tetrahydrofuran (thf) gave $[Yb(hmpa)_4(thf)_2]I_2$ (**1**) as yellow crystals. A similar reaction of SmI_2 with hmpa afforded black-purple $[SmI_2(hmpa)_4]$ (**2**) after recrystallization from toluene. When 10 equiv of hmpa were used in the reaction with SmI_2, $[Sm(hmpa)_6]I_2$ (**3**) was obtained as purple blocks. Complexes **1**—**3** have been structurally characterized by crystallographic studies. The structural data of these complexes satisfactorily explain the hmpa effects observed in SmI_2-promoted reactions, and also provide a guideline for the use of HMPA in these reactions.

Since the first introduction of samarium(II) iodide (SmI_2) into organic chemistry by Kagan and co-workers in the early 1980s,[1)] extensive studies on this reactive species have been carried out, and SmI_2 has now been established as a standard one-electron reductant in synthetic organic laboratories.[2)] In 1987, Inanaga and coworkers found that addition of hexamethylphosphoric triamide (hmpa) to a blue THF solution of SmI_2 gave immediately a purple solution which showed a much stronger reducing power than the blue SmI_2/THF system.[3)] The subsequent studies by the groups of Curran,[4)] Molander,[5)] and Fang[6)] further showed that, in addition to the enhancement of the reducing power of SmI_2, hmpa could offer crucial influence on the regio- and stereo-selectivity of SmI_2-promoted reactions. These unique properties have thus made hmpa indispensable in many SmI_2-mediated important transformations.[2—7)]

Despite the extensive use of the SmI_2/hmpa system in organic synthesis, the role played by hmpa in these reactions was not well understood, and several questions remained to be answered. These include a) why does hmpa greatly increase the reducing power of SmI_2? b) why does addition of hmpa change the regio- and stereo-selectivity of SmI_2-mediated reactions? c) how much hmpa should be used to achieve the best hmpa effects? and d) why does the selectivity become worse when hmpa exceeds a certain amount? Although the coordination of hmpa to the Sm(II) ion was thought to be responsible for these effects, the lack of structural information on the complexation of SmI_2 with hmpa hampered further understanding. Although a variety of lanthanide complexes with hmpa ligands has been recently isolated and structurally characterized,[8)] structural data of these complexes could not offer satisfactory answers to these questions. To clarify this problem, isolation and structural characterization of hmpa-coordinated SmI_2 complexes are required. In this paper, we report the structural characterization of three types of hmpa-coordinated LnI_2 (Ln = Sm, Yb) complexes which are isolated directly from the reactions of LnI_2 with hmpa in THF. The structural data of these complexes constitute a fundamental basis for the understanding of the role which hmpa plays in SmI_2-promoted reactions. On the basis of these data, the above questions could be satisfactorily answered. A portion of this work has been previously communicated.[9)]

Experimental

General Methods. All manipulations were carried out under dry and oxygen-free argon atmosphere by using Schlenk techniques or under nitrogen atmosphere in an Mbraun glovebox. The argon was purified by passing through a DRYCLEAN column (4A molecular sieves, Nikka Seiko Co.) and a GASCLEAN GC-XR column (Nikka Seiko Co.). The nitrogen in the glovebox was constantly circulated through a copper/molecular sieves (4A) catalyst unit. The oxygen and moisture concentrations in the glovebox atmosphere were monitored by an O_2/H_2O COMBI-ANALYZER (Mbraun) to assure both were always below 1 ppm. Elemental analyses were performed by the chemical analysis laboratory of The Institute of Physical and Chemical Research (RIKEN). Tetrahydrofuran (THF), diethyl ether, and toluene were distilled from sodium/benzophenone ketyl, degassed by the freeze-thaw method (three times) and dried over fresh Na chips. C_6D_6 was degassed by the freeze-thaw method (three times) and dried over fresh Na chips in the glovebox. Hexamethylphosphoric triamide (hmpa) was distilled from sodium chips under reduced pressure, degassed by the freeze-thaw method (three times) and dried over molecular sieves (4A). Lanthanide metals (40 mesh) were obtained from Rare Metallic Co. and Aldrich. $[LnI_2(thf)_2]$ (Ln = Sm, Yb)[1b,10)] was prepared according to the literature.

$[Yb(hmpa)_4(thf)_2]I_2$ (1). To a yellow THF solution (25 ml) of YbI_2 (1 mmol) was added 0.8 ml of hmpa (ca. 4.5 mmol) at room temperature. The yellow color of the solution became a little deeper after addition of hmpa, but the color change was not very obvious. After being stirred for 30 min, the solvent was evaporated to give a light yellow crystalline product, which after recrystallization from THF afforded yellow blocks of [Yb(hmpa)$_4$(thf)$_2$]I$_2$ (**1**) (1.02g, 89% yield for **1**-2 thf). The two thf ligands in **1** were lost under vacuum, as confirmed by ^{1}H NMR and elemental analyses. ^{1}H NMR (C$_6$D$_6$, 22 °C, **1**-2 thf) $\delta = 2.55$ (d, $J = 9.57$ Hz, NMe). Anal. Calcd for C$_{24}$H$_{72}$I$_2$N$_{12}$O$_4$P$_4$Yb (**1**-2 thf): C, 25.21; H, 6.35; N, 14.70%. Found: C, 25.62; H, 6.31; N, 14.81%.

[SmI$_2$(hmpa)$_4$] (2). Addition of hmpa (0.8 ml, ca. 4.5 mmol) to a blue THF solution (10 ml) of SmI$_2$ (1 mmol) at room temperature gave immediately a purple mixture which was stirred for 30 min. After reduction of the solution volume under vacuum, toluene was added and the mixture was further concentrated. On leaving this solution to stand at room temperature for a few days, black-purple blocks of [SmI$_2$(hmpa)$_4$] (**2**, 1.01g, 90% yield) deposited. Anal. Calcd for C$_{24}$H$_{72}$I$_2$N$_{12}$O$_4$P$_4$Sm: C, 25.71; H, 6.47; N, 14.99%. Found: C, 25.96; H, 6.57; N, 15.07%.

Sm(HMPA)$_6$I$_2$ (3). Addition of hmpa (1.75 ml, ca. 10 mmol) to a blue THF solution (10 ml) of SmI$_2$ (1 mmol) at room temperature gave immediately a purple mixture which was stirred for 30 min. Evaporation of the THF solvent gave a purple residue which was washed with ether and redissolved into THF. After reduction of the solution volume under vacuum, toluene was added and the mixture was further concentrated. On leaving this solution to stand at room temperature for a few days, purple blocks of [Sm(HMPA)$_6$]I$_2$ (**3**, 1.33 g, 90% yield) deposited. Anal. Calcd for C$_{36}$H$_{108}$I$_2$N$_{18}$O$_6$P$_6$Sm: C, 29.23; H, 7.36; N, 17.04%. Found. C, 29.65; H, 7.39; N, 17.25%.

X-Ray Crystallographic Studies. Crystals for X-ray analyses were obtained as described in the preparations. The crystals were manipulated in the glovebox under a microscope (Wild M3Z, Leica) which was mounted on the glovebox window, and were sealed in thin-walled glass capillaries. Data collections were performed at 20 °C on an Enraf–Nonius CAD4 diffractometer (Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, graphite monochromator, ω-scan) and were corrected for X-ray absorption effects. Lattice constants and orientation matrices were obtained by least-squares refinement of 25 reflections with $30° \leq 2\theta \leq 35°$. Three reflections were monitored periodically as a check for crystal decomposition or movement; no significant decay was observed. The observed systematic absences were consistent with the space groups given in Table 1. The structures were solved by MULTAN[11] to locate the metal atoms, and the remaining non-hydrogen atoms were found from subsequent difference Fourier syntheses. Attempts to locate the hydrogen atoms were not made. Refinements were performed anisotropically for all non-hydrogen atoms by block-diagonal least squares method.[12] The function minimized in the least-squares refinements was $\sum(|F_o| - |F_c|)^2$. Neutral atomic scattering factors were taken from the "International Tables for X-Ray Crystallography."[13] Crystal data, data collection and processing parameters are given in Table 1.

Results and Discussion

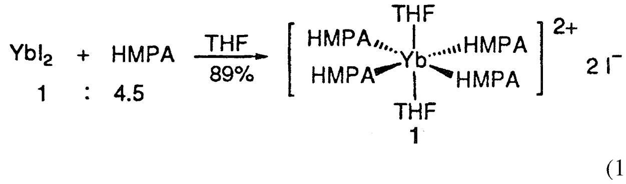
[Yb(hmpa)$_4$(thf)$_2$]I$_2$ (1). Reaction of hmpa (4.5 equiv) with YbI$_2$ was carried out in THF at room temperature for 30 min. No obvious color change was observed after addition of hmpa, though the yellow color of the mixture became a little deeper. Evaporation of the solvent yielded a yellow crystalline product, which after recrystallization from THF gave [Yb(hmpa)$_4$(thf)$_2$]I$_2$ (**1**) as yellow blocks in 89% yield (Eq. 1). An X-ray analysis has revealed that the central Yb atom in **1** is coordinated by four hmpa and two thf ligands in a distorted octahedral form, whereas the two iodide anions are located in the outer sphere (Fig. 1 and Table 2). The Yb atom lies on a twofold axis which also passes through the oxygen atoms (O(3) and O(4)) of both thf ligands. Since both hmpa and thf are bonded to the same central metal, complex **1** constitutes an ideal model for direct comparison of the coordination ability between hmpa and thf. The average

Table 1. Crystallographic Data for **1**—**3**

Compnd	**1**	**2**	**3**
Formula	C$_{32}$H$_{88}$I$_2$N$_{12}$O$_6$P$_4$Yb	C$_{24}$H$_{72}$I$_2$N$_{12}$O$_4$P$_4$Sm	C$_{36}$H$_{108}$I$_2$N$_{18}$O$_6$P$_6$Sm
F_w	1287.32	1121.02	1479.43
Cryst size/mm	0.35 × 0.35 × 0.30	0.51 × 0.45 × 0.44	0.45 × 0.44 × 0.40
Cryst system	Orthorhombic	Monoclinic	Orthorhombic
Space group	*Ibca*(No. 73)	$P2_1/n$(No. 14)	*Aba*2(No. 41)
a/Å	26.145(10)	12.644(3)	42.051(5)
b/Å	20.842(3)	14.763(8)	15.667(3)
c/Å	20.839(3)	13.312(3)	21.073(3)
β/deg		107.82(2)	
V/Å^3	11356(5)	2365(4)	13883(4)
Z	8	2	8
D_{calcd}/g cm^{-3}	1.51	1.57	1.42
Radiation, λ/Å	Mo $K\alpha$, 0.71073	Mo $K\alpha$, 0.71073	Mo $K\alpha$, 0.71073
Data collect	$+h, +k, +l$	$+h, +k, \pm l$	$+h, +k, +l$
Scan speed/deg min^{-1}	4	8	8
2θ range/deg	4—55	4—55	4—55
μ/cm^{-1}	28.728	27.088	19.115
No. of obsd reflns	3126($F > 5\sigma(F_o)$)	4550($F > 5\sigma(F_o)$)	4671($F > 5\sigma(F_o)$)
No. of variables	260	215	623
R/%$^{a)}$	4.91	4.30	5.34
R_w/%$^{b)}$	4.72	6.02	5.91

a) $R = \sum||F_o| - |F_c||/\sum|F_o|$. b) $R_w = [\sum(|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2}$.

bond distance of the Yb–O(hmpa) bonds in **1** is 2.357(6) Å, which is ca. 0.1 Å shorter than that of the Yb–O(thf) bonds (2.46(1) Å). This clearly shows that the electron donating ability of hmpa is much stronger than that of thf. It is also noteworthy that the four bulky hmpa ligands in **1** are placed in the same square plane, which is in contrast to what was observed in another four-hmpa-coordinated octahedral Yb(II) complex, *cis*-[Yb{(*μ*-OC)Mo(CO)$_2$Cp}$_2$(hmpa)$_4$], in which only three of the four hmpa ligands were located in a square plane.[8d)]



(1)

The two thf ligands in **1** could be easily removed under vacuum. After **1** was pumped at room temperature for about 30 min, its crystallinity was completely lost to give a yellow solid. The ^{1}H NMR spectrum of this solid in C_6D_6 did not show any signals for thf, and only a doublet for the hmpa ligands was observed at 2.55 ppm. Elemental analysis data were consistent with the formulation of this solid as thf-free [YbI$_2$(hmpa)$_4$]. Attempts to obtain a single crystal of [YbI$_2$(hmpa)$_4$] from toluene were, however, unsuccessful.

[SmI$_2$(hmpa)$_4$] (2). Reaction of SmI$_2$ with hmpa was carried out similarly as in the case of YbI$_2$ (Eq. 2). An immediate color change from blue to purple was observed after addition of hmpa. Although single crystals suitable for X-ray analysis were not obtained from THF, the use of toluene afforded good black-purple blocks of [SmI$_2$(hmpa)$_4$] (**2**) in 90% yield. The molecular structure of **2** is shown in Fig. 2, and the selected bond lengths and angles are given in Table 3. The Sm(II) ion in **2** sits on an inversion center and is bonded by two I$^-$ anions and four HMPA ligands in a distorted octahedral form. As required by this crystallographic symmetry, the central Sm(II) ion and the oxygen atoms (O(1), O(2), O(1′), and O(2′)) of the four hmpa ligands are exactly coplanar, and the two iodide anions are mutually *trans*. Reflecting the unusually strong electron donating ability of hmpa, the Sm–O(hmpa) bonds in **2** (av. 2500(6) Å) are much shorter than the bond distances between Sm(II) and other oxygen-donor ligands, e.g., Sm–O(diglyme): av. 2.699(4) Å in *trans*-[SmI$_2${O(CH$_2$CH$_2$OMe)$_2$}$_2$],[14)] Sm–O(thf): av. 2.571(4) and Sm–O(dme): av. 2.641(4) Å in [SmI$_2$(dme)(thf)$_3$].[15)] On the other hand, due to this strong coordination of the four polar hmpa ligands, the Sm–I bonds (3.390(2) Å) in **2** are much longer than those of the terminal Sm–I bonds found in other samarium(II) iodide complexes such as *trans*-[SmI$_2${O(CH$_2$CH$_2$OMe)$_2$}$_2$] (3.265(1) Å),[14)] *cis*-[SmI$_2${O(CH$_2$CH$_2$OMe)$_2$}$_2$] (av. 3.333(1) Å),[16)] and [SmI$_2$(dme)(thf)$_3$] (3.246(1) Å),[15)] indicating that the Sm–I bonds in **2** are very weak.

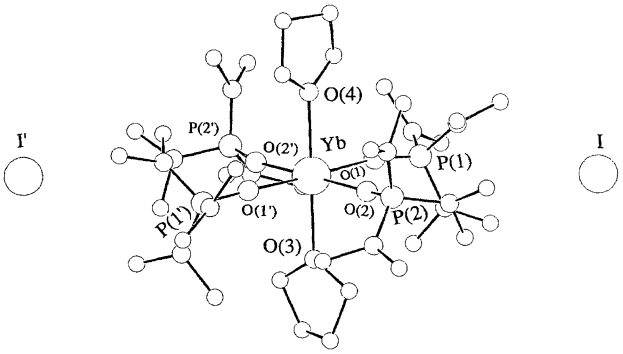
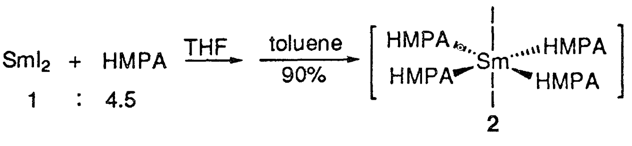


Fig. 1. X-Ray structure of **1**.

Table 2. Selected Bond Lengths (Å) and Angles (°) for [Yb(hmpa)$_4$(thf)$_2$]I$_2$ (**1**)

Yb–O	2.347(6)	Yb–O(2)	2.366(6)
Yb–O(3)	2.454(12)	Yb–O(4)	2.470(10)
P(1)–O(1)	1.489(7)	P(2)–O(2)	1.474(7)
O(1)–Yb–O(2)	90.1(2)	O(1)–Yb–O(3)	89.3(2)
O(1)–Yb–O(4)	90.7(2)	O(2)–Yb–O(3)	90.9(2)
O(2)–Yb–O(4)	89.1(2)	O(1)–Yb–O(1′)	178.6(2)
O(2)–Yb–O(2′)	178.3(2)	O(3)–Yb–O(4)	180.0



(2)

[Sm(hmpa)$_6$]I$_2$ (3). In order to probe the maximum capacity of Sm(II) ion to accept the coordination of hmpa ligands, reaction of SmI$_2$ with 10 equiv of hmpa was carried out. From this reaction, a six-hmpa-coordinated Sm(II) complex, [Sm(hmpa)$_6$]I$_2$ (**3**), was isolated as purple blocks (Eq. 3). Complex **3** also adopts an octahedral structure, and,

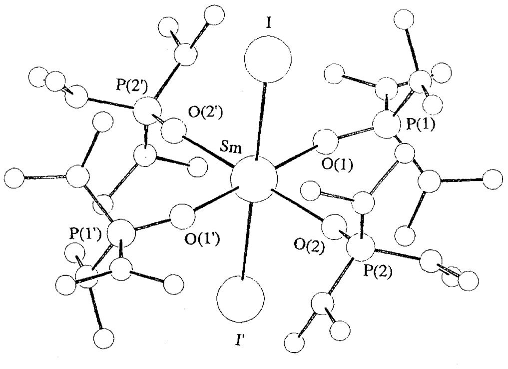
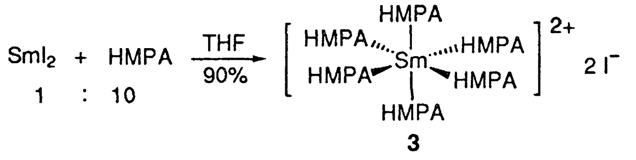


Fig. 2. X-Ray structure of **2**.

Table 3. Selected Bond Lengths (Å) and Angles (°) for [SmI$_2$(hmpa)$_4$] (**2**)

Sm–I	3.390(2)	Sm–O(1)	2.515(6)
Sm–O(2)	2.444(5)	P(1)–O(1)	1.496(7)
P(2)–O(2)	1.493(5)		
I–Sm–O(1)	92.2(1)	I–Sm–O(2)	89.1(1)
O(1)–Sm–O(2)	89.9(2)	I–Sm–I′	180.0
O(1)–Sm–O(1′)	180.0	O(2)–Sm–O(2′)	180.0

similar to complex **1**, the iodide anions are put in the outer sphere (Fig. 3 and Table 4). As far as we are aware, complex **3** is the first structurally characterized metal complex which bears six hmpa ligands. Probably due to the coordination of six bulky and electron-donating hmpa ligands, the bond distances of the Sm–O(hmpa) bonds in **3** (av. 2.53(1) Å) are slightly longer than those in **2**, but are still shorter than those between Sm(II) and other oxygen-donor ligands.[14,15]



(3)

On the hmpa Effects in SmI_2-Promoted Reactions. As seen in the structures of complexes **1**—**3**, it is now clear that the complexation of SmI_2 with hmpa can greatly change the environment around the Sm(II) ion both electronically and sterically. The isolation of **1** and **3** and the unusually long Sm–I bond distances in **2** suggest that the Sm–I bonds in hmpa-coordinated SmI_2 complexes are very weak and can be easily cleaved by a coordinative ligand, and therefore, complex **2** in THF should have a similar structure to that of **1**. The unusually short Ln–O(hmpa) bond distances in these complexes have clearly shown that the electron donating ability of hmpa is much stronger than that of thf. When a sufficient amount of hmpa is used, the Sm(II) ion will accept the coordination of as many as six such strong electron-donating hmpa ligands. This must explain why the reducing power of SmI_2 is greatly enhanced upon addition of hmpa.[3] The square planar coordination of four hmpa ligands to a central Ln(II) ion, which was observed in complexes **1** and **2**, is unprecedented.[8] This planar orientation of the hmpa ligands must be the key factor in determining the selectivity of reactions. It is reasonable to suppose that, during the reactions, substrates will approach the central metal from either below or above the square plane formed by the hmpa ligands. The steric repulsion between the substrates and these strongly coordinated bulky hmpa ligands will naturally change the regio- and stereo-selectivity of the reactions as compared to the non-hmpa system.[4—6] When more than 6 equiv of hmpa per SmI_2 are used, the Sm–I bonds will be cleaved and the central Sm(II) ion will be surrounded by six strongly coordinated hmpa ligands. In this case, the approach of substrates to the central metal would be blocked to some extent, which would force the reactions to take place in the outer sphere and thus decrease the selectivity as compared to the case when 4–5 equiv of hmpa are used.[4d,5b,6a] Therefore, it is not difficult to see that if one wants to pursue only the enhancement of the reducing power of SmI_2, the use of more than 6 equiv of hmpa per SmI_2 is most appropriate; however, to control the selectivity of a reaction, 4—5 equiv of hmpa should be used. The use of less than 4 equiv of hmpa per SmI_2 will not fully bring out the hmpa effects either electronically or sterically.

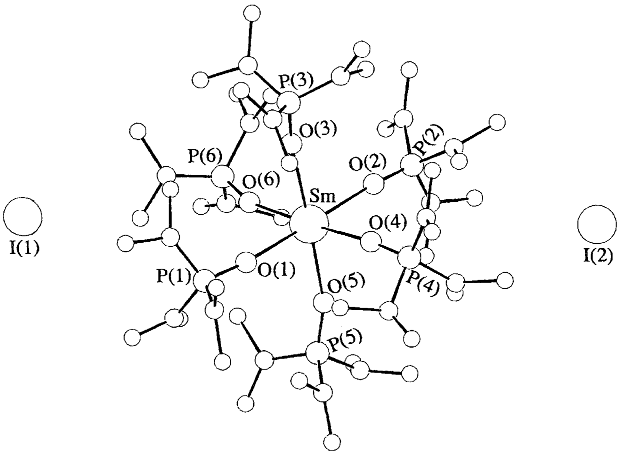


Fig. 3. X-Ray structure of **3**.

Table 4. Selected Bond Lengths (Å) and Angles (°) for $[Sm(hmpa)_6]I_2$ (**3**)

Sm–O(1)	2.566(13)	Sm–O(2)	2.562(13)
Sm–O(3)	2.566(12)	Sm–O(4)	2.551(14)
Sm–O(5)	2.509(14)	Sm–O(6)	2.447(13)
P(1)–O(1)	1.507(14)	P(2)–O(2)	1.450(14)
P(3)–O(3)	1.435(13)	P(4)–O(4)	1.438(15)
P(5)–O(5)	1.540(15)	P(6)–O(6)	1.527(14)
O(1)–Sm–O(2)	177.9(5)	O(1)–Sm–O(3)	89.5(4)
O(1)–Sm–O(4)	87.4(5)	O(1)–Sm–O(5)	90.0(5)
O(1)–Sm–O(6)	92.7(5)	O(2)–Sm–O(3)	89.1(5)
O(2)–Sm–O(4)	91.0(5)	O(2)–Sm–O(5)	91.5(5)
O(2)–Sm–O(6)	88.9(5)	O(3)–Sm–O(4)	89.6(4)
O(3)–Sm–O(5)	178.0(5)	O(3)–Sm–O(6)	87.0(4)
O(4)–Sm–O(5)	92.3(5)	O(4)–Sm–O(6)	177.6(4)
O(5)–Sm–O(6)	91.1(5)		

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