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Structure and Energetics of the Samarium Diiodide−HMPA Complex in Tetrahydrofuran

J. Brad Shotwell, Jennifer M. Sealy, and Robert A. Flowers, II*

Department of Chemistry, The University of Toledo, Toledo, Ohio 43606

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The role of HMPA as a ligand for SmI_2 and the stoichiometry and energetics of formation for the SmI_2−HMPA complex in THF were investigated employing UV−vis spectroscopy, isothermal titration calorimetry (ITC), and vapor pressure osmometry (VPO). The aggregation number for SmI_2 in THF was found to be 0.98 ± 0.09 over the entire concentration range studied (6.71−84.0 mM), indicating that SmI_2 is monomeric. The UV−vis data suggest that four HMPA ligands coordinate to SmI_2, and this was supported by ITC experiments. The combined results are consistent with $[SmI_2(HMPA)_4]$ being the reductant responsible for the unique reactivity exhibited by SmI_2−HMPA cosolvent combinations.

Introduction

Ligands play an essential part in mediating many organometallic reactions. In the area of organolanthanide chemistry a central role is played by hexamethylphosphoramide (HMPA), which serves as a ligand for the entire lanthanide series. Coordination and crystallographic studies provide an enormous amount of insight into the solid-state structures of lanthanide−HMPA complexes. One striking feature of these complexes is the regularity of the stoichiometry through the series from lanthanum to lutetium. When lanthanide(III) perchlorates were dissolved in HMPA, the entire series from lanthanum to lutetium produced complexes containing six inner-sphere HMPA ligands and three outer-sphere perchlorate ions.[1] Other ligands, such as amides and sulfoxides, produce complexes with metal−ligand stoichiometries that depend on the size of the particular lanthanide, i.e., the early lanthanides exhibit higher coordination numbers than the later lanthanides.[2]

Aside from its unique behavior as a ligand, HMPA plays a crucial role in many lanthanide-mediated organic reactions.[3] The addition of HMPA to reduction reactions that employ SmI_2 as the reductant dramatically accelerates the electron-transfer process. Inanaga and coworkers reported an increase in the rate of reduction of organic halides when HMPA was added to SmI_2−THF solutions.[4] Curran and Hasegawa demonstrated that the time required for reductions by SmI_2 can be reduced from days to minutes in the presence of HMPA.[5] The SmI_2-mediated reductive coupling of alkyl iodides or bromides with carbonyls and the coupling of carbonyls with alkenes require HMPA (or other additives) in order for the reactions to be completed in a reasonable amount of time.[5] In addition to accelerating reductions by SmI_2, HMPA enhances the stereochemical outcome and diastereoselectivity of many reactions as well.[3,6]

Although most reductions of carbonyl-containing functional groups and unactivated olefins by SmI_2 usually utilize HMPA cosolvent, the exact role of HMPA in reactions of SmI_2 is not yet fully understood. The seminal work in this area was a study of the influence of HMPA concentration on the product distributions and diastereoselectivities of SmI_2-mediated reductive cyclizations of unactivated olefinic ketones.[6] In this report, Molander suggested that HMPA may act in two ways: (1) HMPA may disassociate SmI_2 aggregates in THF making the reductant more reactive, or (2) HMPA may perturb the electron-donating orbital of Sm(II) and raise its energy, thus increasing the Sm(II)/Sm(III) cell emf. It is also possible that a combination of these effects is responsible for the influence of HMPA on the reactivity of SmI_2.[6]

Although numerous crystal structures are available for various Sm−HMPA coordination compounds,[7] relatively little is known about the solution structures of these complexes. A detailed understanding of the structure and energetics of the interaction between HMPA and SmI_2 in THF would provide considerable insight into the reactivity of the complex. Herein we report a VPO, spectroscopic, and calorimetric study of SmI_2 and its interaction with HMPA in THF.

Experimental Section

Materials and General Procedures. THF was distilled from sodium benzophenone ketyl, under nitrogen. All solvents employed in this study were degassed by several cycles of evacuating the vessel and refilling with nitrogen or argon. HMPA was dried by vacuum distillation from CaO. The water contents of the distilled THF and HMPA were determined by Karl Fischer titration. Dried solvents were stored in an Innovative Technology, Inc. drybox containing a nitrogen atmosphere and a platinum catalyst for drying. The SmI_2 was

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Table 1. SmI_2 Concentrations and Aggregation Numbers (VPO) in Tetrahydrofuran

concn (mmolar)	concn (mmolal)	aggregation number[a]
6.71	7.63	1.06 ± 0.09
33.1	37.6	0.87 ± 0.03
41.4	47.1	1.02 ± 0.02
84.0	95.5	0.96 ± 0.02
		average value = 0.98 ± 0.09

[a] ± values are reported at the 95% confidence level.

prepared by the method of Curran and co-workers.[8] The concentration of SmI_2 in solution was determined by iodometric titration.[9]

Vapor-Pressure Osmometry. The aggregation number for SmI_2 was determined employing a Wescor 5500-XR vapor pressure osmometer operating at 37 °C in a drybox. Known molalities of SmI_2 were prepared in THF. Calibration curves of VPO reading vs molality were obtained employing biphenyl as the calibration standard. A least-squares analysis of 10 points provided a correlation coefficient of 0.990. A standardized solution of SmI_2 in THF was placed in the osmometer and the instrument reading was converted into concentration using the calibration curve. Each VPO datum was generated by making three independent solutions of SmI_2 at each of four concentrations and measuring each solution a minimum of four times.

UV−Vis Study. All UV−vis spectra were obtained on a Hewlett-Packard 89532A diode array spectrophotometer utilizing Hewlett-Packard UV−vis operating software. A Wilmad quartz spectrophotometer cell with a path length of 5 mm was used for all measurements. The SmI_2 solutions were prepared at a concentration of 0.01 M in the drybox. Each solution was placed in a cuvette and sealed with a Teflon stopper, and the spectrum was measured. Successive solutions containing 1−8 equivalents of HMPA/SmI_2 were prepared, and their spectra were measured.

Calorimetry. HMPA and SmI_2 solutions were prepared in distilled degassed THF at concentrations near 40 mM and 20 mM, respectively. A MicroCal Omega isothermal titration calorimeter was employed to determine the number of HMPA ligands bound to SmI_2 and the enthalpy and equilibrium binding constants of these interactions at 25 °C. The HMPA solution was placed in the 1.4 mL calorimetric cell, and the SmI_2 solution was loaded into a 250 mL calorimetry syringe. The instrument was modified with the appropriate inert seals and equipped with a small port capable of keeping a static inert gas atmosphere over the sample. These instrumental changes allow for calorimetric analysis of air-sensitive compounds in organic solvents. A 50−55 injection matrix was employed with each 5 mL injection lasting a duration of 10 s. A 3-min interval was allotted between each injection of SmI_2 into HMPA. The enthalpy (ΔH), binding constants (K), and number of binding sites (n) were determined from the calorimetric data employing OriginTM data analysis software.

Results

Vapor Pressure Osmometry. The aggregation numbers for SmI_2 in THF at four different concentrations are contained in Table 1. The anticipated precision for these measurements is approximately ±10%. The average value for the aggregation number of SmI_2 at the four different concentrations is 0.98 ± 0.09. These data clearly indicate that SmI_2 is monomeric in THF over the concentration range examined in this study.

UV−Vis Spectroscopy. Results of the influence of HMPA on the UV−vis spectroscopic properties of SmI_2 in THF are contained in Figure 1. The spectrum of SmI_2 displays two distinct bands at 558 and 616 nm. The effect of HMPA was studied by adding successive 1 equiv amounts of HMPA to SmI_2 and recording the UV−vis spectrum for each ratio. As successive equivalents of HMPA were added to the SmI_2 solution, the bands at 558 and 616 nm began to broaden. No further observable change in the spectrum occurred after the addition of 4 equiv of HMPA

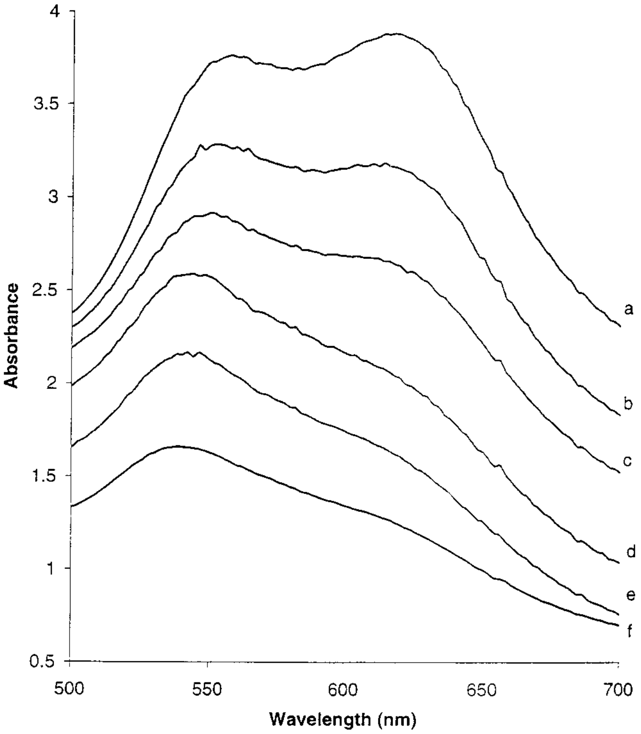

Figure 1. Variation of the UV-vis spectrum of SmI_2 as function of the concentration of HMPA. (a) SmI_2 only; (b) 1 equiv of HMPA; (c) 2 equiv of HMPA; (d) 3 equiv of HMPA; (e) 4 equiv of HMPA; (f) 8 equiv of HMPA.

Isothermal Titration Calorimetry. Addition of a solution of SmI_2 in THF to a solution of HMPA in THF in the calorimeter produced the thermogram and binding isotherm displayed in Figure 2. The concentration of SmI_2 and its HMPA complex was determined by iodometric titration.[9] No statistically significant differences were found between concentrations before and after the experiment. The thermodynamic parameters K, ΔH, ΔG, and ΔS were extracted by a nonlinear, least-squares analysis of the calorimetric data. An "identical interacting sites" model was utilized to fit the experimental calorimetric isotherm. In this model, there is no distinction as to which sites are saturated, only the number. All binding sites are treated as identical, but the equilibrium binding constants are defined relative to the progress of saturation.[10] The data are contained in Table 2.

Analysis of the calorimetric data shows that the interaction of the first HMPA ligand with $SmI_2(THF)_x$ is endothermic, with a favorable entropy of binding providing the driving force for the association. The binding of the next two HMPA molecules is exothermic, while the binding of the fourth HMPA ligand is the most exother-

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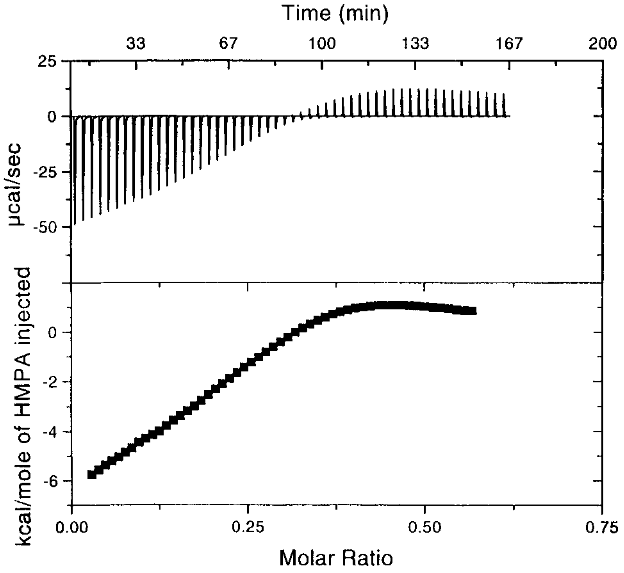

Figure 2. ITC thermogram of SmI_2 with HMPA. (Top) Heat change associated with addition of 5 μL aliquots of SmI_2 (40 mM) to HMPA (1.4 mL, 20 mM) at 25 °C. (Bottom) Binding isotherm.

Table 2. Thermodynamic Data for the Interaction between HMPA and SmI_2 in THF[a]

			calculated values	
ligand (HMPA)	K ($\times 10^4$)*	ΔH (kcal/mol)*	ΔG (kcal/mol)**	ΔS (cal/mol·K)**
first	3.8 ± 0.3	0.39 ± 0.01	-6.24 ± 0.03	22.3 ± 0.2
second	4.6 ± 0.3	-2.46 ± 0.03	-6.36 ± 0.02	13 ± 1
third	9.5 ± 0.3	-0.87 ± 0.01	-6.78 ± 0.02	19.8 ± 0.1
fourth	0.012 ± 0.002	-9.0 ± 2	-2.83 ± 0.10	-22 ± 6

[a] The data are averaged from the results of three independent runs. * Experimental values reported as $\pm\sigma$. ** Values calculated using $\Delta G = -RT \ln K$ and $\Delta G = \Delta H - T\Delta S$. Experimental uncertainties were propagated through these calculations.

mic. The equilibrium binding constants in Table 2 show that three HMPA ligands are tightly bound to the Sm. The coordination of the fourth HMPA ligand occurs with a binding constant that is approximately 2 orders of magnitude lower than those of the first three ligands.

Discussion

Most of the information concerning the structure of samarium compounds in both the II and III oxidation states has been provided through crystallographic analysis. Typically, crystals are grown by slow removal of the solvent, or by slow diffusion of a nonpolar solvent, such as hexane, into the samarium complex in THF. While crystallography provides enormous insight into solid-state structure, most of the chemistry involving samarium(II) is carried out in solution at relatively dilute (<0.1 M) concentrations. Solution chemistry is a dynamic process; therefore, it is important to obtain insight into the structures of samarium complexes in solution. Solution studies of structure and energetics provide important insight into the behavior of Sm(II) complexes in the medium in which essential organic transformations mediated by these elusive species are carried out.

Recently, Evans and co-workers obtained X-ray diffraction data on $[SmI_2(THF)_5]$, introducing the possibility that SmI_2 is a monomer in THF.[11] Our VPO experiment was designed to determine if SmI_2 is a solvated monomer in THF or if it is a higher order aggregate. It can be reasonably argued that the reliance on measurements based on colligative properties have potential drawbacks because structural detail is inferred and cannot always be verified by independent methods. For instance, if SmI_2 was actually a dimer or trimer in solution, an aggregation number of 2 or 3 would result, but these values could also be averages resulting from complex oligomers in solution. However, if SmI_2 is predominantly a monomer in solution, an aggregation number of 1 will result and this certainly cannot be the average of 0.5 and 1.5. The VPO data contained in Table 1 show unequivocally that SmI_2 is a monomer in THF at the concentrations examined in this study. The higher end of the concentration range studied in the VPO experiments is very close to the solubility limit of SmI_2 in THF; therefore, it is likely that SmI_2 is always monomeric under normal reaction conditions.

The next component of this work dealt with the stoichiometry of the complex formed between SmI_2 and HMPA. The importance of HMPA in reactions mediated by SmI_2 is undeniable, yet, there is virtually no structural information on this reducing species in solution. Information on the solution structure will provide insight into how a reducible ligand may interact with the complex. Recently, Hou and co-workers published the solid-state structures of two Sm(II) complexes produced by the ligation of HMPA with SmI_2.[7] In one experiment, 10 equiv of HMPA were placed in a solution of SmI_2 in THF. The crystals obtained from this solution had six HMPA ligands coordinated to Sm(II) and two iodide counterions in the outer sphere, i.e., $[Sm(HMPA)6]I_2$. In another experiment, 4 equiv of HMPA were placed in a solution of SmI_2 in THF. The complex which was isolated contained four HMPA ligands, and the two iodides remained bound to the inner sphere, i.e., $[SmI_2(HMPA)_4]$. To assess the reductant stoichiometry responsible for the unique reactivity of the SmI_2−HMPA complex under standard conditions utilized by synthetic chemists, we carried out titration experiments to determine the influence of HMPA concentration on the UV−vis spectrum of SmI_2. The results in Figure 1 show that after the addition of 4 equiv of HMPA, there is no significant change in the UV−vis spectrum of SmI_2, suggesting that the reductant in THF has four HMPA ligands coordinated to Sm(II). It is important to note that the broad bands observed in these spectra prevent definitive determination of the endpoint in this spectroscopic titration. However, this result is in agreement with our earlier electrochemical titration studies[12] and with the studies of Curran on the influence of HMPA concentration on the rate of reduction of primary alkyl radicals by SmI_2.[5]

To further delineate the stoichiometry of the SmI_2−HMPA complex and to determine the affinity of HMPA for SmI_2 in THF, we carried out an ITC study. ITC is a well-established technique for probing the thermodynamics of biomolecular interactions.[13] Although this technique is also suitable for determining the binding stoichiometry and thermodynamics of metal−ligand inter-

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Table 3. Tabulation of Sm−I and Sm−O Bond Distances (Å) and Bond Angles (deg) for Various Samarium Complexes

	bond distances, Å			bond angles, (deg)	
	Sm−I	Sm−O(THF)	Sm−O(P)	I−Sm−I	I−Sm−O(P)
$[SmI_2(DME)(THF)_3]^a$	3.235(1)	2.581(4)		178.8(1)	
	3.231(1)	2.553(4)			
		2.579(4)			
$[SmI_2(HMPA)_4]^b$	3.390(2)		2.515(6)	180.0	92.2(1)
			2.444(5)		89.1(1)
$[SmI_2(HMPA)_4]I^c$	3.118(3)		2.299(21)	178.5(1)	87.5(5)
	3.146(3)		2.301(20)		93.3(5)
			2.270(22)		85.9(6)
			2.257(20)		93.3(5)

[a] Reference 11. [b] References 7a,b. [c] Reference 7c.

actions, there has been little work performed in this area. We recently reported a calorimetric study of the interaction between HMPA and $YbCl_3$ in THF.[14] In this study we determined the stoichiometry of the $YbCl_3$−HMPA complex in THF and found that it agreed with the known crystal structure for this compound.[15]

The calorimetric data (Table 2) and resulting isotherm in Figure 2 show that four HMPA ligands bind to the Sm(II) metal center. The seminal work of Marks shows that THF coordinates exothermically to $SmCp'_2$ in toluene.[16] Surprisingly, the binding of the first HMPA ligand to SmI_2 is endothermic in THF with the entropic component providing the overall driving force for association. Since HMPA is undoubtedly a better ligand for Sm(II) than THF, the ITC data suggests that the first HMPA is displacing multiple THF ligands. The binding of the next two HMPA molecules is exothermic, but the entropic component of the binding is still favorable, again providing evidence that a ligand (THF or I^-), is being displaced from the Sm(II). The binding of the fourth HMPA ligand is the most exothermic, with an unfavorable entropic term. This can be rationalized in terms of crowding because the presence of three HMPA ligands may sterically hinder coordination of the fourth.

The two crystal structures reported by Hou raised the possibility that six HMPA molecules could ligate to Sm(II) and displace the iodide ligands. Numerous attempts were made to fit the experimental calorimetric data to the binding of six ligands, but none of these attempts provided a statistically stable fit. The calorimetric experiment was carried out by titrating SmI_2 into excess HMPA. If six ligands could bind to Sm(II) in solution, this would occur under our experimental conditions and as a result produce an ITC isotherm consistent with the coordination of six HMPA ligands. Although Hou's work clearly shows that Sm(II) can accommodate six HMPA ligands, this complex is apparently not thermodynamically favored under the standard reaction conditions utilized by synthetic chemists.

The calorimetric data show that while three HMPA ligands coordinate tightly to Sm(II), the fourth is bound less tightly. Nonetheless, it is unlikely that a poor Lewis base like an alkyl iodide or a carbonyl will displace even the most labile HMPA ligand. This supposition is supported by the work of Fry and colleagues.[17] In their study, they determined that the equilibrium constant for formation of the benzaldehyde−$LaBr_3$ complex in THF was approximately 65 M^{-1}. The equilibrium binding constant for interaction of a carbonyl group and SmI_2 may be even lower because of the decreased Coulombic attraction between a carbonyl and a lanthanide in the +II oxidation state compared with the same interaction for a lanthanide in the +III oxidation state.

With the solution stoichiometry of SmI_2−HMPA established, it is useful to carefully examine crystal structures of the corresponding species involved in the reduction process in order to make some reasonable inferences about the possible events that occur after the coordination of HMPA to SmI_2. Crystal structures are available for SmI_2 solvates and SmI_2−HMPA complexes in both the II and III oxidation states. Comparisons of the bond lengths between Sm and its ligands provide some insight into the relative strengths of these bonds. A list of selected bond lengths for $[SmI_2(DME)(THF)_3]$, $[SmI_2(HMPA)_4]$, and $[SmI_2(HMPA)_4]I$ is contained in Table 3. Evans recently reported the X-ray crystallographic analysis of divalent $SmI_2(THF)_5$, $SmI_2(DME)_2(THF)$, and $SmI_2(DME)(THF)_3$.[11] The Sm−I bond lengths could not be determined for $SmI_2(THF)_5$ due to the quality of the data. The Sm−I bond lengths for the other two complexes were determined to be 3.246(1) Å and 3.235(1) Å, respectively. The Sm−I bond distance in the $[SmI_2(HMPA)_4]$ structure reported by Hou is 3.390(2) Å.[7a,b]

Recently, Cabrera and co-workers isolated and characterized $[Sm(HMPA)_4I_2]I$.[7c] The complex contains the same spatial arrangement of ligands in the inner-sphere as the $[SmI_2(HMPA)_4]$ complex characterized by Hou except the Sm is in the +III oxidation state. The Sm−I bond length in $[Sm(HMPA)_4I_2]I$ is 3.118(3) Å. The shorter distance between samarium and iodide in $[Sm(HMPA)_4I_2]I$ is probably the result of increased electrostatic attraction between the Sm(III) and I^-. Comparison of the SmI_2 solvate and the SmI_2−HMPA complexes in both oxidation states (Table 3) shows that there are significant differences in the Sm−I bond lengths upon coordination of HMPA to Sm(II). Coordination of HMPA to SmI_2 decreases the Sm−I bond strength. Oxidation of the resulting complex to Sm(III) results in a decrease in the Sm−I bond distance. Although the Sm−HMPA and Sm−I bond distances decrease upon oxidation of the complex, there is very little change in the I−Sm−I and I−Sm−O bond angles.

Examination of available crystallographic data indicates that the Sm−I bond is weakened upon coordination of HMPA. Hou proposed that the unusually long Sm−I bond length in the crystal structure of $[SmI_2(HMPA)_4]$ made it likely that the solution structure would have the iodide ligands replaced by coordinated THF molecules.[7b]

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The combination of the three techniques utilized in the present study in combination with reported crystallographic evidence suggests that [$SmI_2(HMPA)_4$] is the reductant responsible for the behavior of SmI_2 in the presence of HMPA cosolvent.

During a reductive coupling or reduction reaction of SmI_2, a reducible functional group encounters the reductant. One potential mechanistic pathway would involve displacement of a labile iodide ligand. In this scenario, a reducible functional group (such as an alkyl iodide or a carbonyl) will have direct access to the metal center and be reduced by an inner-sphere electron transfer. Another potential mechanistic pathway would have the iodide ligand remaining bound to the Sm(II)−HMPA complex with the organic functional group being reduced via an outer-sphere electron transfer by the sterically crowded complex. Skrydstrup and co-workers have recently published results indicating that electron transfer from $SmI_2(THF)_x$ to acetophenone was clearly an inner-sphere process while electron transfer to benzyl bromide was closer to an outer-sphere process.[18] These results suggest that while the affinity of Sm(II) for THF is higher than that for an alkyl halide, carbonyls are capable of displacing THF ligands bound to SmI_2.

Determination of the affinity of an alkyl iodide or carbonyl for SmI_2 would provide some insight into the mechanistic quandary described above because a weakly bonded precursor complex (less than 4 kcal/mol) is one precondition for outer-sphere electron transfer.[19] If an alkyl iodide or carbonyl coordinates to SmI_2, it may produce a change in one of the charge-transfer bands in the UV−vis spectrum. It may also be possible to detect a heat change calorimetrically due to interaction of a functional group with the Sm metal center. We were unable to determine the affinity of alkyl halides or carbonyls via calorimetric methods because the reduction takes place too quickly and it is impossible to separate the heat of reaction from any heat due to coordination between SmI_2 and a halide or a carbonyl. We have carried out numerous titrations of various alkyl iodides and ketones into SmI_3 and attempted to measure the heat of interaction by ITC and any changes in the UV−vis spectrum of SmI_3. The only heat generated was due to the heat of dilution of the alkyl iodide or ketone. No changes were apparent in the UV−vis spectra. If there was any significant interaction between Sm and either alkyl iodides or ketones, we would have anticipated a small amount of heat due to coordination or small shifts of the bands in the UV−vis spectrum. The Sm(III) should have a higher affinity for alkyl halides and ketones than Sm(II) due to increased Coulombic attraction. The fact that no interaction was observed by calorimetry or spectroscopy suggests that the interaction between Sm(II)/(III) iodide and ketones or alkyl iodides is insignificant compared to that of HMPA.[20]

Conclusions

The results described in this paper show that SmI_2 is a monomer in THF. The addition of HMPA cosolvent to a solution of SmI_2 displaces the THF bound to the Sm metal. Calorimetry data show that four HMPA ligands are tightly bound to SmI_2 in THF. Examination of crystallographic data of [$SmI_2(THF)_3(DME)$][11] and [$SmI_2(HMPA)_4$][7a] shows that upon coordination of HMPA the Sm−I bond distance increases, suggesting that the Sm−I bond is weaker in the $SmI_2(HMPA)_4$ reductant. No interactions were detected between alkyl iodides or ketones and SmI_3 employing UV−Vis spectroscopy or calorimetry. While this analysis does not exclude the possibility that functional groups displace iodide ligands from [$SmI_2(HMPA)_4$] during a reduction, it supports the likelihood that reduction may take place via an outer-sphere process. We are currently carrying out rate studies and electrochemical experiments designed to elucidate the mode of electron transfer.

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