# Evidence for Ionic Samarium(II) Species in THF/HMPA Solution and Investigation of Their Electron-Donating Properties**

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**Abstract:** The fundamental nature of samarium(II) complexes in THF/HMPA (HMPA = hexamethylphosphoramide) solutions containing $SmI_2$ has been clarified by means of cyclic voltammetry, conductivity measurements, UV spectroscopy, and kinetic measurements. The principal species is not $[SmI_2(hmpa)_4]$ as previously suggested, but either the ionic cluster $[Sm(hmpa)_4(thf)_2]^{2+}2\,I^-$ if four equivalents of HMPA is present in the THF solution or $[Sm(hmpa)_6]^{2+}2\,I^-$ in the presence of at least 10 equivalents of HMPA. The formal potential of the $[Sm(hmpa)_4(thf)_2]^{3+}2\,I^-/[Sm(hmpa)_4(thf)_2]^{2+}2\,I^-$ redox couple determined by cyclic voltammetry was $-1.79 \pm 0.08$ V versus SCE. The order of reactivity of the samarium(II) complexes was found to be $[Sm(hmpa)_6]^{2+}2\,I^- > [Sm(hmpa)_4(thf)_2]^{2+}2\,I^- > SmI_2$ in their respective reactions with 1-iodobutane and with benzyl chloride. Very high rate enhancements, of the order of 1000–15000-fold, were observed upon addition of HMPA to the THF solution containing $SmI_2$. Comparison of these rate constants with the corresponding rate constants for electron transfer (ET) reactions involving aromatic radical anions revealed that none of the reactions studied can be classified as outer-sphere ET processes and that the inner-sphere electron-donating abilities of the $[Sm(hmpa)_4(thf)_2]^{2+}2\,I^-$ and $SmI_2$ complexes are comparable. The inner-sphere ET character of the transition state increases on going from 1-iodobutane and benzyl bromide to benzyl chloride and acetophenone.

**Keywords:** alkyl halides • electrochemistry • electron transfer • N ligands • samarium

## Introduction

Low-valent metal complexes have become important as single-electron transfer reagents for promoting organic synthetic transformations. One of the most widely used is the lanthanide(II) salt samarium diiodide ($SmI_2$), introduced to organic chemistry some 20 years ago by Kagan and coworkers.[1] It has been applied to a wealth of radical and anionic reactions, including pinacol coupling, Barbier- and Grignard-type reactions, aldol- and Reformatsky-type coupling, conjugate addition, nucleophilic acyl substitution, radical addition, ketyl–olefin coupling, deoxygenation, dehalogenation, and other reduction reactions.[2] Because of its moderate oxidation potential and high oxophilicity, the divalent samarium reagent displays functional group selectivity in the reduction step, and when relevant, generally leads to the formation of products with high diastereoselectivities. Yet the mechanism of its electron transfer (ET) processes is still not fully understood. Such knowledge would be of interest from a mechanistic point of view, but would also provide valuable information for the development of new applications of this single-electron donating agent to syntheses. Recently, we addressed the mechanistic aspects of $SmI_2$-induced ET reactions involving two organic substrates, benzyl bromide and acetophenone.[3] Inner-sphere/outer-sphere concepts were invoked in the description of the transition state structures: whereas the ET to acetophenone was clearly shown to involve an inner-sphere process, the ET to benzyl bromide was closer to an outer-sphere process. A prerequisite for the above description was the elucidation of the fundamental redox behavior of the $SmI_2^+/SmI_2$ couple by cyclic voltammetry, which provided the formal potential $E^\circ = -0.89$ V versus SCE ($-1.41$ V versus ferrocenium/ferrocene ($Fc^+/Fc$)) in tetrahydrofuran (THF).[3]

The addition of hexamethylphosphoramide (HMPA) to a THF solution of the divalent lanthanide reagent leads to a substantial increase in the electron-donating abilities of $SmI_2$.[2, 4] Other effects observed when this cosolvent is used include an increase in the stability of the organosamarium species formed, allowing reactions to be performed under Grignard conditions,[5] enhancement of stereoselectivities,[5c, 6]

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[**] HMPA = hexamethylphospharamide.

Supporting information (Rate data for the ET reaction between aromatic radical anions and 1-iodobutane and benzyl chloride) for this article is available on the WWW under http://www.wiley-vch.de/home/chemistry/ or from the authors.

and promotion of certain radical cyclizations.[6, 7] Recently, resolution of the crystal structures of [SmI$_2$(hmpa)$_4$] and [Sm(hmpa)$_6$]$^{2+}$2I$^-$ showed that both reside in an octahedral configuration.[8] The short Sm–O bonds (2.5 Å) suggest that the electron-donating ligands are strongly bonded to the lanthanide ion, and thus explain its enhanced reducing power. In the [SmI$_2$(hmpa)$_4$] complex the long Sm–I bonds (3.39 Å) imply that these bonds are rather weak, which is exemplified by the isolation of [Sm(hmpa)$_6$]$^{2+}$2I$^-$ in the solid state upon addition of excess HMPA (10 equiv).[8b] However, the solution structures of the complexes may differ; indeed, isothermal titration calorimetry experiments have indicated that a complex accommodating six HMPA ligands is not thermodynamically favored in THF, even in the presence of large amounts of HMPA.[9] Rather it was suggested that [SmI$_2$(hmpa)$_4$] was the reductant responsible for the unique reactivity exhibited by Sm$^{II}$ in all THF/HMPA mixtures.

Herein we describe the ability of HMPA-coordinated samarium(II) complexes to act as ET reagents, which we investigated by employing the procedure previously described for SmI$_2$.[3] For this purpose clarification of the fundamental structural and redox features of the samarium complexes in THF/HMPA solutions was desirable.[10] Four different experimental approaches were used: a) cyclic voltammetry; b) conductivity measurements; c) UV spectroscopy; d) kinetic studies of ET processes involving the electron acceptors 1-iodobutane and benzyl chloride. On this basis, we propose that the principal HMPA-coordinated samarium(II) complex in THF is not [SmI$_2$(hmpa)$_4$] but either the ionic cluster [Sm(hmpa)$_4$(thf)$_2$]$^{2+}$2I$^-$ or [Sm(hmpa)$_6$]$^{2+}$2I$^-$, depending on the amount of HMPA present in the THF. We have also ranked the ability of these complexes to act as inner-sphere electron donors.

## Results

**Cyclic voltammetry**: The fundamental redox properties of HMPA-coordinated samarium complexes in solution were assessed by cyclic voltammetry experiments in a supporting electrolyte solution of 0.2 M tetrabutylammonium hexafluorophosphate (Bu$_4$NPF$_6$) and 0.02 M tetrabutylammonium iodide (Bu$_4$NI) in various THF/HMPA cosolvent combinations (Figure 1). The voltammograms were recorded at a sweep rate of 0.1 V s$^{-1}$ for a solution of 2.5 mM SmI$_2$ in THF + $n$ equivalents of HMPA ($n = 0, 2, 4, 6, 10$). The tremendous effect on the electron-donating ability of Sm$^{II}$ as $n$ increased from 0 to 4 was shown by the large negative shifts observed in the positions of the oxidation wave (400 mV) and in particular of the reduction wave (1080 mV). The peak separation was enhanced to 830 mV for $n = 4$, compared with 150 mV observed for the SmI$_2^+$/SmI$_2$ redox system in THF ($n = 0$, sweep rate = 0.1 V s$^{-1}$), while the peak currents became smaller. At $n = 2$ an intermediate situation arose, in which the two redox systems pertaining to SmI$_2$ and the HMPA-coordinated samarium complex were evident in the voltammogram and the respective "corrected" peak currents were diminished by approximately one-half compared with the maximum values found at $n = 0$ and 4. Surprisingly, the reverse wave pertaining to SmI$_2^+$ had disappeared.[11] In the presence of additional HMPA ($n = 6$ and 10) the oxidation wave was shifted progressively in a negative direction by up to 150 mV although the reduction wave was unchanged. At $n = 20$ no further changes were observed in the cyclic voltammogram (not shown in Figure 1). The presence of 20 mM Bu$_4$NI in the THF/0.2 M Bu$_4$NPF$_6$ solution had no effect on the position of the peaks for the HMPA-coordinated complexes, contrary to the situation previously found for the SmI$_2^+$/SmI$_2$ redox system with a shift of more than 100 mV in a negative direction.[3]

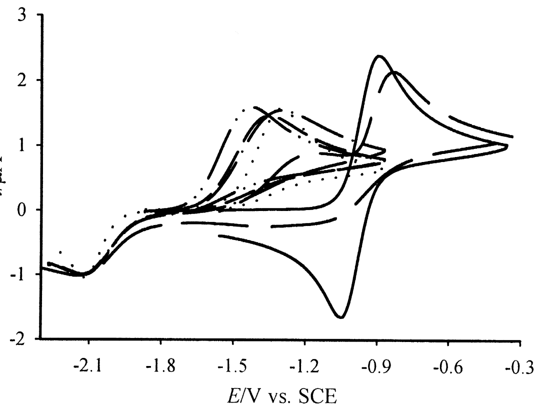

Figure 1. Cyclic voltammograms of 2.5 mM SmI$_2$ recorded in THF/0.2 M Bu$_4$NPF$_6$ + 0.02 M Bu$_4$NI at a glassy carbon electrode (diameter 1 mm) at a sweep rate of 0.1 V s$^{-1}$ for $n$ equivalents of HMPA added, where $n = 0$ (——), 2 (– – –), 4 (•–•–), 6 (- - - -), 10 (—••). The dotted curve represents a simulation for a simple quasi-reversible system at $n = 4$ based on the following parameters in Digisim 2.1: $E^\circ = -1.79$ V versus SCE, $k^\circ = 1.6 \times 10^{-6}$ cm s$^{-1}$, $D = 1.7 \times 10^{-6}$ cm$^2$ s$^{-1}$, transfer coefficient $\alpha = 0.6$, capacitance $C_d = 10^{-7}$ F.

**Conductivity measurements**: To identify more exactly the samarium complexes in the THF/HMPA solutions, the conductivity of SmI$_2$, SmI$_3$, and Bu$_4$NI was plotted against the number of equivalents of HMPA added (Figure 2). Whereas the conductivity of a solution of SmI$_2$ in pure THF was near zero as expected, it increased substantially upon addition of HMPA, surpassing even that of the corresponding Bu$_4$NI solution. For Bu$_4$NI there was a only weak, almost negligible increase in the conductivity, as the HMPA content and hence

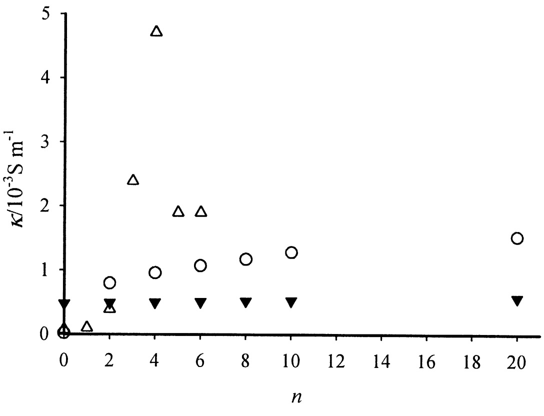

Figure 2. Variation of the conductivity $\kappa$ for 2.5 mM SmI$_2$ (○), SmI$_3$ (△) and Bu$_4$NI (▼) in THF with the number of equivalents of HMPA added ($n$).

the polarity of the solvent mixture were raised. Therefore any medium effect can be disregarded in further discussion. The initial increase observed in the conductivity for $SmI_2$ at $n = 2$ was much greater than the subsequent increases at $n > 2$, although the measurements were influenced somewhat by relatively slow reactions between the rather reactive HMPA-coordinated samarium(II) complex and any impurities present in the THF/HMPA solution, manifested as a slow drift in the read-off conductivity value which was enhanced substantially if water or oxygen was added deliberately to the solution. Taking that into account, we concluded that the structure of the samarium complex was relatively unchanged when $n \geq 10$.

The conductivity measurements of $SmI_3$ revealed some interesting features. A THF solution of $SmI_3$ had a low conductivity, which is attributed to the equilibrium process $SmI_3 \rightleftharpoons SmI_2^+ + I^-$.[3] The conductivity did not rise significantly upon addition of two equivalents of HMPA, whereas a large shift was observed as $n$ was increased to 3 and then 4. If more HMPA ($n > 4$) was added, precipitation caused an abrupt decrease in the conductivity.

**UV spectroscopy**: The UV spectrum of the blue solution of $SmI_2$ ($n = 0$) with the characteristic broad bands at 560 ($\varepsilon = 680\,\text{M}^{-1}\text{cm}^{-1}$) and 620 nm ($\varepsilon = 740\,\text{M}^{-1}\text{cm}^{-1}$) changed slightly as HMPA was added (Figure 3); the peak at 620 nm vanished while the 560 nm peak was shifted to 540 nm and enhanced ($\varepsilon = 870\,\text{M}^{-1}\text{cm}^{-1}$). There were no detectable differences in the spectra for $n \geq 6$. These overall features of the UV spectra have been described elsewhere[9], although in that case a substantial decrease in the absorption was noted over the whole wavelength range as HMPA was added.

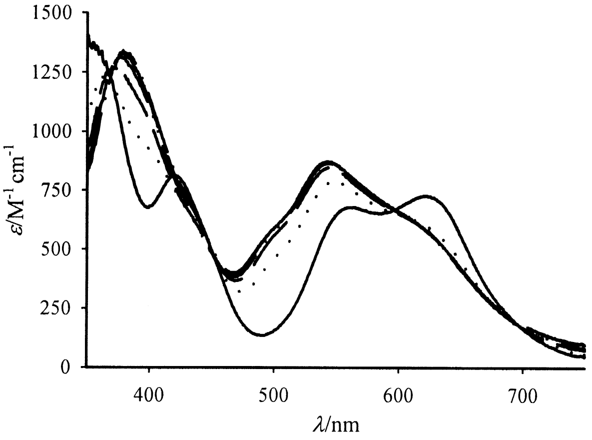

Figure 3. UV spectra of $SmI_2$ for $n$ equivalents of HMPA added to a THF solution, where $n = 0$ (——), 2 (••••), 4 (- - - -), 6 (—••), 8 (– – –), 10 (•–•–).

**Kinetics of electron transfer processes**: Rate constants $k_{obs}$ were measured for the reactions of $SmI_2$ with 1-iodobutane (Table 1) and with benzyl chloride (Table 2), for various concentrations of HMPA. Clearly, the rate was greatly enhanced: 15000-fold for 1-iodobutane and 1000-fold for benzyl chloride when the HMPA content was increased from $n = 0$ to $n = 20$. Most of the rate enhancement took place initially at $n = 0–4$, whereas almost no effect was evident for $n \geq 10$. The rate constants $k_{obs}$ were also measured in the presence of supporting electrolyte (0.2 M $Bu_4NPF_6$), that is, under the conditions employed in the electrochemical measurements. This increase in the ionic strength of the medium had essentially no influence on the rate constants obtained for benzyl chloride, but a notable rate enhancement was observed in the case of 1-iodobutane. We did not pursue this point further in the present work.

Table 1. Rate constants $k_{obs}$ for the reaction between $SmI_2$ and 1-iodobutane in THF containing $n$ equivalents of HMPA at 20 °C. The uncertainty on $k_{obs}$ is estimated to be 10 %.

| $n$ | $k_{obs}$ [$\text{M}^{-1}\text{s}^{-1}$] | $k_{obs}$ [$\text{M}^{-1}\text{s}^{-1}$][a] |
|---|---|---|
| 0 | $< 2.7 \times 10^{-4}$[b] | $< 2.3 \times 10^{-4}$[b] |
| 4 | 1.0 | 4.9 |
| 6 | 3.1 | 15 |
| 8 | 3.6 | 18 |
| 10 | 4.1 | 20 |
| 20 | 4.1 | 16 |

[a] Measured in the presence of 0.2 M $Bu_4NPF_6$. [b] The decay of $SmI_2$ in the presence of 1-iodobutane was only slightly faster than the "natural decay"

Table 2. Rate constants $k_{obs}$ for the reaction between $SmI_2$ and benzyl chloride in THF containing $n$ equivalents of HMPA at 20 °C. The uncertainty on $k_{obs}$ is estimated to be 10 %.

| $n$ | $k_{obs}$ [$\text{M}^{-1}\text{s}^{-1}$] | $k_{obs}$ [$\text{M}^{-1}\text{s}^{-1}$][a] |
|---|---|---|
| 0 | $2.4 \times 10^{-2}$ | $2.0 \times 10^{-2}$ |
| 4 | 9.4 | 12 |
| 6 | 20 | 24 |
| 8 | 19 | 29 |
| 10 | 20 | 29 |
| 20 | 21 | 20 |

[a] Measured in the presence of 0.2 M $Bu_4NPF_6$.

## Discussion

The substantial decrease observed in the peak potentials and currents in cyclic voltammetry as four equivalents of HMPA were added to a THF solution containing $SmI_2$ showed that a new and larger samarium(II) species was formed.[12] This was also reflected in the UV spectra, where the disappearance of the peak at 620 nm was accompanied by the appearance of a peak at 540 nm. At $n = 2$ distinct oxidation waves pertaining to both $SmI_2$ and the new samarium species were observed, the "corrected" peak currents being about one-half of their maximum values. The conversion of half the $SmI_2$ to an HMPA-coordinated samarium(II) complex containing four ligands is the most likely interpretation[10] although we cannot exclude completely the occurrence of equilibrium reactions involving different HMPA-coordinated samarium species. On the basis of existing literature,[8] the most likely identity of this solution species would be $[SmI_2(hmpa)_4]$. However, this is contradicted by the tremendous increase observed in the conductivity of the $SmI_2$ solution upon addition of HMPA. We suggest that the principal samarium species in THF at $n = 4$ is therefore $[Sm(hmpa)_4]^{2+}2\,I^-$, or more correctly $[Sm(hmpa)_4(thf)_2]^{2+}2\,I^-$ to emphasize the octahedral structure of the complex. This is also supported by the fact that the Sm–I bonds in the solid-state structure of $[SmI_2(hmpa)_4]$ are long and relatively weak and thus should be susceptible to cleavage in solution.[8] In Equation (1), the reaction between $SmI_2$ (or $Sm(thf)_5I_2$)[13] and HMPA is depicted as an equilibrium that is shifted to the right.

$$Sm(thf)_5I_2 + 4\,HMPA \rightleftharpoons [Sm(hmpa)_4(thf)_2]^{2+}2\,I^- + 3\,THF \quad (1)$$

It is the dissociated form(s) of the ionic cluster $[Sm(hmpa)_4(thf)_2]^{2+}2\,I^-$ which gives rise to the conductivity. Since the electrochemical measurements were carried out in the presence of a large excess of $Bu_4NPF_6$ we cannot rule out $[Sm(hmpa)_4(thf)_2]^{2+}2\,PF_6^-$ as the principal species in these particular experiments. Neither the cyclic voltammetric nor the conductivity measurements allow us to determine the relevant dissociation constants, although they must be small in a nonpolar solvent such as THF. It is noteworthy that the conductivities of $[Sm(hmpa)_4(thf)_2]^{2+}2\,I^-$ and $Bu_4NI$ are comparable and that the dissociation constant for $Bu_4NI$ can be estimated to be approximately $10^{-6}$ M in THF.[14]

The presence of 20 mM $Bu_4NI$ in the THF/0.2 M $Bu_4NPF_6$ solution containing $SmI_2$ and four equivalents of HMPA was found to have no effect on the cyclic voltammogram. This behavior stands in sharp contrast to the substantial influence exerted by 20 mM $Bu_4NI$ on the corresponding $SmI_2^+/SmI_2$ redox pair at $n = 0$, where the waves were shifted in a negative direction.[3] Digital simulations showed that the reason for these different behaviors could not be the slowing of the charge transfer step at the electrode surface upon addition of HMPA, as envisioned by the substantial increase in the peak separation from 150 to 830 mV. Thus, it seems that although $SmI_2^+$ and $I^-$ form $SmI_3$ in an equilibrium reaction,[3] neither ligand exchange reactions nor detectable shifts in the dissociation reactions involving $I^-$ could be observed electrochemically for either $[Sm(hmpa)_4(thf)_2]^{2+}2\,I^-$ or its oxidized form. We therefore attribute the electrochemical oxidation wave occurring on the forward scan at $n = 4$ to $[Sm(hmpa)_4(thf)_2]^{2+}2\,I^-$ and the reduction wave that was detectable on the reverse scan to $[Sm(hmpa)_4(thf)_2]^{3+}2\,I^-$. The latter species is also formed directly if $SmI_3$ is used as the starting compound in the THF/HMPA/0.2 M $Bu_4NPF_6$+0.02 M $Bu_4NI$ solution, giving rise to exactly the same reduction wave in the cyclic voltammogram. The high conductivity found in THF/HMPA for $SmI_3$ at $n = 4$, surpassing even those for $SmI_2$ and $Bu_4NI$, is consistent with this interpretation. Still, it should be emphasized that the electrochemical results could be interpreted equally well if $[Sm(hmpa)_4(thf)_2]^{2+}2\,PF_6^-$ were the principal species in the electrolyte solution. We did not pursue this particular point further since the electrochemical measurements in general were difficult to carry out because of adsorption phenomena (see Experimental Section), but in the further discussion the uncertainties involved in neglecting ion-pair equilibria should be kept in mind even if they have no effect on the overall interpretation concerning the existence of ionic samarium species.

With the reservations outlined above, the two species $[Sm(hmpa)_4(thf)_2]^{3+}2\,I^-/[Sm(hmpa)_4(thf)_2]^{2+}2\,I^-$ can be considered as a simple quasi-reversible redox system in which the peak separation increases as a function of the sweep rate. By comparing the experimental cyclic voltammograms recorded at three different sweep rates with simulated curves, the formal potential $E^\circ$ as well as the standard heterogeneous rate constant $k^\circ$ can be determined (see Figure 1). The main emphasis in the simulation procedure was on describing the reproducible development in the experimentally obtained peak potentials and currents, since presumably the shape of the experimental cyclic voltammograms is influenced somewhat by adsorption phenomena. This led to $E^\circ = -1.79 \pm 0.08$ V versus SCE ($-2.31 \pm 0.08$ V versus $Fc^+/Fc$) and to $\log k^\circ$ [$cm\,s^{-1}$] $= -5.8 \pm 0.7$. This $E^\circ$ value differs by only 40 mV from that determined in a recent study,[10b] although the simulation procedure used therein was based on the model proposed for the $SmI_2^+/SmI_2$ system[3] with an equilibrium process incorporated as a homogeneous follow-up reaction.[15]

A comparison of the above $E^\circ$ value with the corresponding value for the $SmI_2^+/SmI_2$ system previously determined ($E^\circ = -0.89$ V versus SCE)[3] reveals that the increase in reducing power $F\Delta E^\circ$ induced by the presence of HMPA is 0.90 eV. This explains the remarkable effect exerted by HMPA on the reactivity of $SmI_2$, as noted by Flowers et al.[10] However, the determination of a low $k^o$ value from the large peak separation shows that the ET processes involving $[Sm(hmpa)_4(thf)_2]^{2+}2\,I^-$ must be somewhat retarded by a high reorganization energy. For the $[Sm(hmpa)_4(thf)_2]^{3+}2\,I^-/[Sm(hmpa)_4(thf)_2]^{2+}2\,I^-$couple $k^\circ$ ($1.6 \times 10^{-6}$ $cm\,s^{-1}$) is approximately 1/4000 times that for the $SmI_2^+/SmI_2$ couple ($k^\circ = 6.5 \times 10^{-3}$ cm $s^{-1}$) and less than $10^{-6}$ times that for the anthracene/(anthracene radical anion) system ($k^\circ = 5$ $cm\,s^{-1}$ in *N,N*-dimethylformamide), for instance.[16] The self-exchange reorganization energies $\lambda(0)$ for the samarium complexes in THF can be estimated roughly from the heterogeneous $k^o$ values.[17] In this manner, $\lambda(0)$ is calculated to be approximately 70 kcal $mol^{-1}$ for $SmI_2^+/SmI_2$ and 110 kcal $mol^{-1}$ for $[Sm(hmpa)_4(thf)_2]^{3+}2\,I^-/[Sm(hmpa)_4(thf)_2]^{2+}2\,I^-$.[18] Should the electrochemical charge transfer process at the glassy carbon electrode not proceed by an outer-sphere ET as assumed herein, but rather by an inner-sphere ET, then the $\lambda(0)$ values might be even higher. The high reorganization energies are attributed mainly to the inner-sphere reorganization in terms of the profound molecular changes occurring in the structure of the ligands strongly bonded to the samarium nucleus.[19] The contribution from the solvent reorganization $\lambda_s$ is 12 kcal $mol^{-1}$ for $SmI_2^+/SmI_2$ and 9 kcal $mol^{-1}$ for $[Sm(hmpa)_4(thf)_2]^{3+}2\,I^-/[Sm(hmpa)_4(thf)_2]^{2+}2\,I^-$ when calculated from the simple continuum expression[20] $\lambda_s = e^2(D_o^{-1} - D_s^{-1})/2r$, where the static dielectric constant $D_s = 7.6$, the optical dielectric constant $D_o = 1.98$, and the radius $r$ is set at 5 Å for $SmI_2^+/SmI_2$ (assuming that the coordination sphere includes five THF molecules) and 7 Å for $[Sm(hmpa)_4(thf)_2]^{3+}2\,I^-/[Sm(hmpa)_4(thf)_2]^{2+}2\,I^-$, estimated from the crystal radii.[8, 13] No specific solvent interactions are taken into account in such a calculation. Furthermore, in this discussion we have completely neglected the effect of ion-pairing, which may raise the reorganization energy substantially for the $[Sm(hmpa)_4(thf)_2]^{3+}2\,I^-/[Sm(hmpa)_4(thf)_2]^{2+}2\,I^-$ couple.[20] Actually, this effect could be a major reason for the large difference of 40 kcal $mol^{-1}$ observed in the $\lambda(0)$ values for the two samarium systems.

When 6 or 10 equivalents of HMPA were added to the THF solution containing $SmI_2$ the oxidation wave in the cyclic voltammogram was shifted progressively in a negative direction by up to 150 mV, while the reduction wave was unaffected. At $n = 20$ no further changes were observed in the cyclic voltammogram, indicating that the coordination sphere of samarium(II) was unaffected. Nor did the presence of HMPA in such amounts introduce any appreciable medium effect due to changes in the polarity of the solvent. This behavior agrees well with the increase observed in the conductivity when $n$ was raised from 4 to 6 followed by the leveling off in the readings at $n \geq 10$. No appreciable changes were observed in the UV spectra for $n \geq 6$ , in which respect this technique is less sensitive. We propose that a $[Sm(hmpa)_6]^{2+}2I^-$ species is formed when $n \geq 6$, as shown in Equations (1) and (2), and that the presence of at least 10 equivalents of HMPA is required to shift the equilibrium completely to the right.

$$[Sm(hmpa)_4(thf)_2]^{2+}2I^- + 2HMPA \rightleftharpoons [Sm(hmpa)_6]^{2+}2I^- + 2THF \qquad (2)$$

The dissociation of $[Sm(hmpa)_6]^{2+}2I^-$ to form free ions is slightly more favored than the dissociation of $[Sm(hmpa)_4(thf)_2]^{2+}2I^-$ if it is to be consistent with the increase observed in conductivity on going from $n = 4$ to $n = 6$.

The $[Sm(hmpa)_6]^{2+}2I^-$ structure would be in line with the isolation and characterization of a samarium(II) complex containing six HMPA ligands in the solid phase.[8b] It is also noteworthy that the precipitation of such complexes usually requires the use of excess HMPA ($n \approx 10$). The relatively small difference in the oxidation waves for $n \geq 4$ indicates that the fifth and sixth HMPA ligands in $[Sm(hmpa)_6]^{2+}$ are rather loosely bonded to the samarium nucleus. Interestingly, there is no difference in the position of the reduction waves on the reverse scan. This suggests that the $[Sm(hmpa)_4(thf)_2]^{3+}2I^-$ complex is formed upon electrochemical oxidation of $[Sm(hmpa)_6]^{2+}2I^-$, unless the reduction wave of a $[Sm(hmpa)_6]^{3+}2I^-$ complex appears coincidentally at exactly the same potential as that of $[Sm(hmpa)_4(thf)_2]^{3+}2I^-$. Presumably $[Sm(hmpa)_6]^{3+}2I^-$ is generated initially but two HMPA ligands are then expelled, since the $Sm^{III}$ core, with shorter bond lengths than $Sm^{II}$, would become too encumbered if six large HMPA ligands surrounded it in an octahedral structure.[19] This chemical follow-up reaction would even induce a shift of the oxidation wave in a negative direction. The above interpretation has been further substantiated by the finding that a precipitate is formed when more than four equivalents of HMPA are added to a solution of $SmI_3$. A similar precipitate has been observed after reductive coupling reactions with $SmI_2$, where it was identified by high-resolution mass spectrometry and X-ray diffraction as a $[SmI_2(hmpa)_4]^+I^-$ complex.[19] Thus, the two THF ligands in the solution complex have been replaced by two iodides in the solid complex, leaving the four HMPA ligands untouched.

To assess how the different structural and redox features of the samarium species are reflected in the reactivity of the $SmI_2$, $[Sm(hmpa)_4(thf)_2]^{2+}$, and $[Sm(hmpa)_6]^{2+}$ complexes, rate constants $k_{obs}$ for the reaction of $SmI_2$ with 1-iodobutane and with benzyl chloride were measured for various concentrations of HMPA. The rate-controlling step in the mechanism is the reduction of the alkyl halide RX by the $Sm^{II}$ complex to form the alkyl radical $R^\bullet$ as shown in Equation (3).

$$Sm^{II}\text{ complex} + RX \xrightarrow{k_{obs}} Sm^{III}\text{ complex} + R^\bullet + X^- \qquad (3)$$

Whether the leaving group $X^-$ is coordinated to the $Sm^{III}$ complex depends on the nature of the species involved; $R^\bullet$ is further reduced by another molecule of $Sm^{II}$ in a fast reaction to the corresponding carbanion (coordinated to $Sm^{III}$).

The rate enhancement observed as a function of $n$ is enormous, at least 1000-fold (Tables 1 and 2). This is to be attributed to the formation of new HMPA–samarium complexes since any medium effect (that is, the slight increase in the polarity of the medium as HMPA is added) on $k_{obs}$ can be neglected as mentioned above in the discussion of the conductivity and cyclic voltammetry measurements. This complexation is also in line with the observation that the major part of the increase in the rate constant takes place between $n = 0$ and $n = 4$ whereas almost no effect is seen for $n \geq 10$. In other words, the order of reactivity of the samarium(II) species is: $[Sm(hmpa)_6]^{2+}2I^-$ $(n \geq 10) >$ $[Sm(hmpa)_4(thf)_2]^{2+}2I^-$ $(n = 4) > SmI_2$ $(n = 0)$.[21] For $4 < n < 10$ the first two of these samarium(II) species are both present. Overall, this reactivity pattern corresponds exactly to the development observed in the cyclic voltammograms and the conductivity measurements for the different values of $n$.

Since the redox behavior of the electron donors $SmI_2$ and $[Sm(hmpa)_4(thf)_2]^{2+}2I^-$ (but not $[Sm(hmpa)_6]^{2+}2I^-$) could be characterized by cyclic voltammetry, it would be interesting to compare the reactivity of these two specific complexes towards 1-iodobutane and benzyl chloride with the corresponding reactivity of well-known electron donors such as aromatic radical anions $A^{\bullet -}$. Aromatic radical anions are among the best candidates for being involved in outer-sphere ET processes[22] and the above approach can therefore be invoked in a description of the ability of various electron donors to act as outer-sphere or inner-sphere ET reagents.[23] The procedure involves the measurement of rate constants $k_{ET}$ for the reactions of various $A^{\bullet -}$ species with 1-iodobutane and with benzyl chloride. The rate-controlling step is shown in Equation (4).

$$A^{\bullet -} + RX \xrightarrow{k_{ET}} A + R^\bullet + X^- \qquad (4)$$

From free energy plots of $\log k_{ET}$ versus $E_A^\circ$ for the two alkyl halides (where $E_A^\circ$ denotes the standard potential of the aromatic compound), the expected rate constant for an ET process can be interpolated for any value of the potential from the straight line through the points determined by linear least-squares analysis (Figures 4 and 5). According to dissociative ET theory[23b] the plot should be parabolic, but we have employed a linear approach since no curvature could be detected in the small driving-force interval considered here. By comparing these expected rate constants with the actual rate constants $k_{obs}$ determined for the reaction between either of the two samarium complexes and the substrate in question, the degree of electronic interaction in the transition state

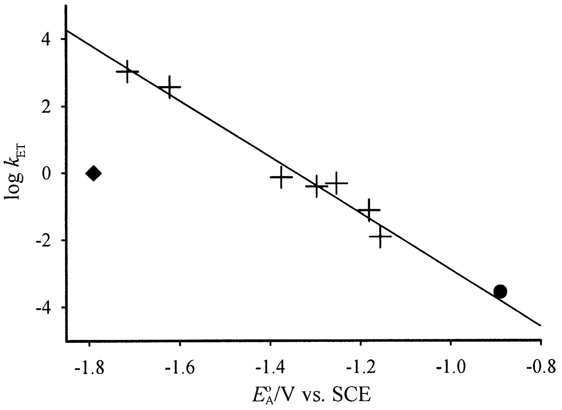

Figure 4. ET rate constants (+) for the reaction between radical anions of aromatic compounds (from left to right: benzophenone, perylene, (*E*)-2-aminoazobenzene, (*E*)-azobenzene, 9-fluorenone, (*E*)-3-chloroazobenzene, phenazine) and 1-iodobutane in THF/0.2 M $Bu_4NPF_6$. The rate constants of the reaction of $SmI_2$ with 1-iodobutane (●) and of $[Sm(hmpa)_4(thf)_2]^{2+}2I^-$ with 1-iodobutane (◆) in THF are also shown.

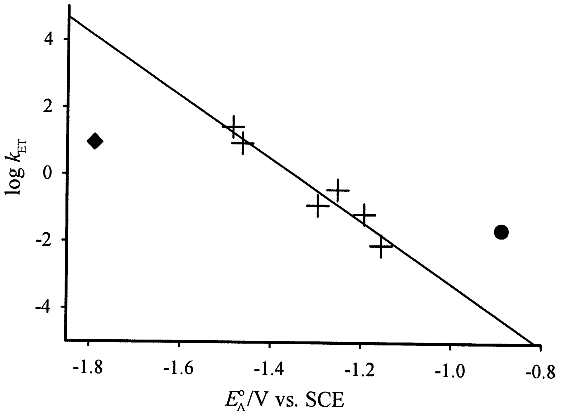

Figure 5. ET rate constants (+) for the reaction of radical anions of aromatic compounds (from left to right: 1-cyanoisoquinoline, 1,4-diacetylbenzene, (*E*)-azobenzene, 9-fluorenone, benzanthrone, phenazine) with benzyl chloride in THF/0.2 M $Bu_4NPF_6$. The rate constants of the reaction of $SmI_2$ with benzyl chloride (●) and of $[Sm(hmpa)_4(thf)_2]^{2+}2I^-$ with benzyl chloride (◆) in THF are also shown.

can be estimated. In principle, for an outer-sphere ET process $k_{obs}/k_{ET}$ should be unity; the higher the $k_{obs}/k_{ET}$ ratio, the more profound is the inner-sphere ET character of the process.

For both 1-iodobutane and benzyl chloride, the points pertaining to $SmI_2$ lie at or just above the straight line. The $k_{obs}/k_{ET}$ ratios are $<2$ and 450, respectively, which encompasses the value (6) obtained for benzyl bromide in our previous report.[3] The same tendency is seen for the rate constants for the $[Sm(hmpa)_4(thf)_2]^{2+}2I^-$ complex, although the points here lie below the line ($k_{obs}/k_{ET} = 1.7 \times 10^{-4}$ for 1-iodobutane and $6.9 \times 10^{-4}$ for benzyl chloride). These values show that the inner-sphere character of the ET processes increases in the halogen order $I < Br < Cl$, that is, the strongest coordination to the samarium nucleus is observed for the smallest and most electronegative halogen atom, chlorine.

The $k_{obs}/k_{ET}$ ratios obtained for the three alkyl halides are still much lower than the $10^9$ estimated for acetophenone and $SmI_2$, the ET process of which has a profound inner-sphere character.[3] At first sight the results also suggest that the stronger and more potent electron donor, $[Sm(hmpa)_4(thf)_2]^{2+}2I^-$, should react with less inner-sphere ET character than $SmI_2$ since the pertinent $k_{obs}/k_{ET}$ values are smaller. However, this interpretation is more doubtful since a comparison of $k_{obs}/k_{ET}$ for different samarium complexes should be carried out with caution. That experimental $k_{obs}/k_{ET}$ ratios below 1 are obtained for $[Sm(hmpa)_4(thf)_2]^{2+}2I^-$ underlines this point. Indeed, a thorough analysis should take into account the differences in the reorganization energies of the samarium complexes as well as including all relevant work terms.

The reorganization energies of the $SmI_2^+/SmI_2$ and the $[Sm(hmpa)_4(thf)_2]^{3+}2I^-/[Sm(hmpa)_4(thf)_2]^{2+}2I^-$ redox couples could be estimated approximately in this study from the heterogeneous $k^{o}$ values to be 70 and 110 kcal mol$^{-1}$, respectively. In comparison, the self-exchange reorganization energies for the aromatic radical anions used as ET donors are about 10 kcal mol$^{-1}$.[20] Consequently the $k_{obs}/k_{ET}$ ratios can attain values substantially below 1 with estimated minimum values of $3 \times 10^{-6}$ and $5 \times 10^{-10}$ for $SmI_2$ and $[Sm(hmpa)_4(thf)_2]^{2+}2I^-$, respectively.[24] In a recent calculation of the $k_{obs}/k_{ET}$ ratio for the reduction of the hexenyl radical by the HMPA-coordinated samarium complex, $k_{ET}$ was estimated from Marcus theory, taking 30 kcal mol$^{-1}$ as the self-exchange reorganization energy.[10b] Using the alternative value of 110 kcal mol$^{-1}$ (but keeping all other parameters unchanged) would increase the $k_{obs}/k_{ET}$ ratio from the calculated value (2) to $5 \times 10^7$ with the important result that the ET would then be assigned to an inner-sphere rather than an outer-sphere process.[10b]

The work terms are important for the reaction between the neutral alkyl halides RX and the samarium complexes, whereas they can be neglected for the reactions involving the aromatic radical anions. These terms arise because oppositely charged species ($SmI_2^+$ or $[Sm(hmpa)_4(thf)_2]^{3+}2I^-$ and $X^-$) are formed after a presumed outer-sphere ET process to RX. According to the simple continuum model (thereby neglecting any specific interactions), a correction of the reaction free energy of $e^2/r_{12}D_s$ should be included, where $r_{12}$ is the radius of the encounter complex (equal to the sum of the radii of the two reacting species).[20] Setting $r_{12}$ at an average value of 9 Å for all combinations of species discussed here would lead to a correction term of 4.8 kcal mol$^{-1}$ (0.21 eV).[25] Inclusion of the correction term would lead to a lowering of the experimentally obtained $k_{obs}/k_{ET}$ ratios by a factor of approximately 100, as can be deduced from the straight lines in Figures 4 and 5. For the experiments carried out in the presence of $Bu_4NPF_6$, however, the electrostatic contribution would be less important since it should be modified by the effect of ionic strength; accordingly, the work terms were neglected in our previous communication.[3]

Overall, the effects of the electrostatic contribution and the self-exchange reorganization energies on the $k_{obs}/k_{ET}$ ratio can be substantial, the reorganization energy being the most influential parameter. The above analysis shows that none of the reactions studied in this paper proceeds by an outer-sphere ET pathway, which should have a $k_{obs}/k_{ET}$ ratio close to the estimated minimum value. Perhaps the most surprising conclusion is that the inner-sphere ET abilities of the $[Sm(hmpa)_4(thf)_2]^{2+}2I^-$ and $SmI_2$ complexes as electron donors are comparable despite the rather encumbered nature of $[Sm(hmpa)_4(thf)_2]^{2+}2I^-$ and its better electron-donating ability as deduced from the relatively low $E^\circ$ value for the $[Sm(hmpa)_4(thf)_2]^{3+}2I^-/[Sm(hmpa)_4(thf)_2]^{2+}2I^-$ redox couple. The $[Sm(hmpa)_6]^{2+}2I^-$ species must also act as an inner-sphere ET reagent towards 1-iodobutane and benzyl chloride, if one considers its similarity to the $[Sm(hmpa)_4(thf)_2]^{2+}2I^-$ complex in terms of reactivity and electrochemical behavior. In the inner-sphere ET process one could imagine that the halogen X functions as a bridge between the two reactants in the transition state, which in the case of $SmI_2$ would lead to a ligand transfer affording $SmI_2X$. In any case, these considerations show that one should be very careful in classifying ET processes as the outer-sphere type before the various factors have been assigned precisely. At the present stage we prefer to develop a relative but still very useful $k_{obs}/k_{ET}$ scale in the description of ET processes involving samarium complexes.

## Conclusion

The fundamental nature of samarium(II) complexes in THF/HMPA solutions containing $SmI_2$ has been clarified by means of cyclic voltammetry, conductivity measurements, UV spectroscopy, and kinetic measurements. The principal species is not $[SmI_2(hmpa)_4]$ as previously believed, but either the ionic cluster $[Sm(hmpa)_4(thf)_2]^{2+}2I^-$ if four equivalents of HMPA are present in the THF solution or $[Sm(hmpa)_6]^{2+}2I^-$ in the presence of at least 10 equivalents of HMPA. The formal potential of the $[Sm(hmpa)_4(thf)_2]^{3+}2I^-/[Sm(hmpa)_4(thf)_2]^{2+}2I^-$ redox couple determined by cyclic voltammetry was $-1.79 \pm 0.08$ V versus SCE. The order of reactivity of the various samarium(II) complexes is $[Sm(hmpa)_6]^{2+}2I^- > [Sm(hmpa)_4(thf)_2]^{2+}2I^- > SmI_2$ in their reactions with 1-iodobutane and with benzyl chloride. Rate enhancements observed upon addition of HMPA to the THF solution containing $SmI_2$ were of the order of 1000–15000-fold. From a comparison of these rate constants with the corresponding rate constants for ET reactions involving aromatic radical anions, taking into account the effects of work terms and differences in the self-exchange reorganization energies, none of the reactions studied can be classified as outer-sphere ET processes. This is also true for the reduction of the hexenyl radical by $[Sm(hmpa)_4(thf)_2]^{2+}2I^-$ which was previously attributed to an outer-sphere ET process. Surprisingly, the inner-sphere ET abilities of the $[Sm(hmpa)_4(thf)_2]^{2+}2I^-$ and $SmI_2$ complexes as electron donors are comparable. The inner-sphere ET character of the transition state increases on going from 1-iodobutane and benzyl bromide to benzyl chloride and acetophenone.

## Experimental Section

**Materials**: 1-Iodobutane, benzyl chloride, the aromatic mediators, HMPA, and THF were obtained commercially. The supporting electrolyte was prepared by standard procedures and $SmI_2$ and $SmI_3$ were synthesized according to reference [1]. The solvents were distilled before use, THF from a solution containing sodium and benzophenone.

**Equipment and procedure**: Most of the electrochemical equipment was home-built; the experimental set-up has been described elsewhere.[26] The working electrode was a glassy carbon disk, diameter 1 mm. The electrode surface was polished with diamond paste (0.25 μm), then cleaned in an ethanol bath. The counter-electrode consisted of a platinum coil melted into glass and the reference electrode was a silver wire in sintered glass containing THF/0.2 M $Bu_4NPF_6$ + 0.02 M $Bu_4NI$. All potentials were reported relative to the $Fc^+/Fc$ redox couple, of which the measured potential was 0.52 V versus SCE in THF/0.2 M $Bu_4NPF_6$. Chemicals were always handled using a vacuum line and at no point during the different operations was the interference of dioxygen allowed. The cyclic voltammetric experiments were in general made difficult by blocking of the electrode surface by the samarium complexes after even a few scans. At the same time the samarium complexes decayed slowly because of reactions involving residual water or other impurities in the THF solution. Preparing a fresh solution of THF/$Bu_4NPF_6$/$SmI_2$ for each concentration of HMPA studied and polishing the electrode carefully before each experiment solved these problems. The small variations in peak currents observed at $n = 4$ and $n = 6$ in Figure 1 should therefore be attributed to no effects other than the experimental uncertainty associated with the procedure outlined. Digisim 2.1 software (Bioanalytical Systems, Inc.) was used for digital simulation. The diffusion coefficients of $SmI_2^+$ and $SmI_2$ were assumed to be equal, and likewise for the $[Sm(hmpa)_4(thf)_2]^{3+}2I^-$ and $[Sm(hmpa)_4(thf)_2]^{2+}2I^-$ complexes.

The conductivity measurements were carried out on a CDM210 MeterLab instrument from Radiometer. All UV spectra were recorded by means of a fiber-optic spectrometer S1000 (dip-probe) from Ocean Optics. The reaction kinetics was monitored by UV/Vis spectroscopy using the dip-probe technique described elsewhere.[27] The decay of $SmI_2$ and $[Sm(hmpa)_4(thf)_2]^{2+}$ upon addition of the alkyl halide was detected at 620 and 540 nm, respectively. No build-up of intermediates during the reaction could be detected in the wavelength range 450–800 nm. The kinetics for 1-iodobutane and benzyl chloride followed the same rate law [Eq. (5)].

$$\mathrm{d}[\text{samarium(II) complex}]/\mathrm{d}t = -2k_{obs}[\text{samarium(II) complex}][\text{alkyl halide}] \quad (5)$$

In each experiment $k_{obs}$ was determined under pseudo first-order conditions at 20 °C with an excess of alkyl halide. The ET rate constants $k_{ET}$ were determined by cyclic voltammetry[26] or the dip-probe technique from measurement of the decay of the absorption of the aromatic radical anion upon addition of the alkyl halide in THF/0.2 M $Bu_4NPF_6$.[27] The radical anion was generated at the required initial concentration by electrochemical reduction of the parent aromatic compound. Addition of HMPA in the amounts used in the $SmI_2$ experiments to the solutions of the aromatic radical anions had no effect on the reaction rates. The estimated uncertainty in the determination of rate constants was 10%.

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