

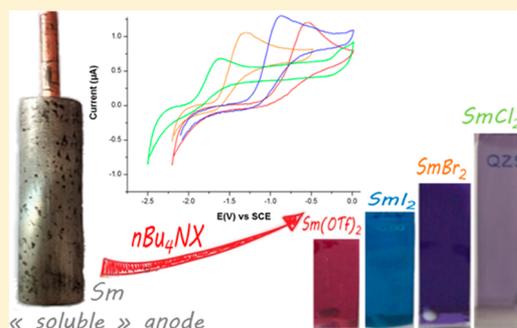
Efficient Electrosynthesis of SmCl_2 , SmBr_2 , and $\text{Sm}(\text{OTf})_2$ from a "Sacrificial" Samarium Anode: Effect of $n\text{Bu}_4\text{NPF}_6$ on the Reactivity

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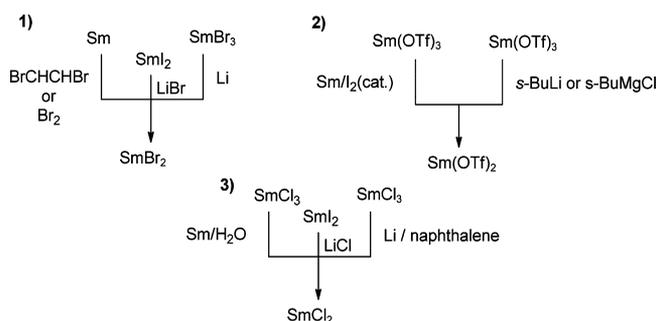
Supporting Information

ABSTRACT: Divalent samarium complexes SmX_2 ($X = \text{Cl}, \text{Br}, \text{OTf}$) have been efficiently synthesized in one electrochemical step using a sacrificial samarium anode in the presence of tetrabutylammonium salts $n\text{Bu}_4\text{NX}$ ($X = \text{Br}, \text{Cl}, \text{OTf}$) as samarium ligand sources free of any metal additives. All complexes were analyzed by electrochemical measurements and UV–vis spectroscopy in tetrahydrofuran under an inert atmosphere. The oxidation potentials of SmCl_2 and SmBr_2 in THF vs SCE are more negative than that of SmI_2 , while the oxidation potential of $\text{Sm}(\text{OTf})_2$ was found to be less negative, confirming that the ligand nature is important in samarium redox chemistry. The electrogenerated SmX_2 species were evaluated in the reduction of 1-chlorododecane in order to correlate their redox potentials with their reactivities. We discovered that ammonium salts used for the electro-synthesis of these complexes significantly increase their reactivity regardless of their redox potentials.



Since Kagan et al. introduced samarium diiodide (SmI_2 , "Kagan's reagent") to chemists at the end of the 1970s, this reagent has attracted a great deal of interest and has become a usual reductant in most organic laboratories.¹ The importance of SmI_2 for synthetic chemists is the result of its versatility in promoting numerous important organic reactions, including reductions, reductive couplings, and tandem reactions.² Among the lanthanide(II) reagents, one of the features that makes SmI_2 useful is its ease of synthesis and commercial availability. The preparation of SmI_2 typically involves the treatment of excess Sm metal with organic oxidants such as 1,2-diiodoethane.³ In addition to SmI_2 , some other samarium complexes exist in a divalent oxidation state, and these also act as strong reductants in various synthetic chemistry applications; they include samarium(II) dibromide (SmBr_2), samarium(II) dichloride (SmCl_2), samarium(II) ditriflate ($\text{Sm}(\text{OTf})_2$; Tf = trifluoromethanesulfonyl), and samarium(II) dicyclopentadienyl (Cp_2Sm) complexes.⁴ These single-electron reductants are generally characterized by higher reduction potentials in comparison to that of SmI_2 (see Table 2) and they act as better reagents for recalcitrant substrates and also provide a high degree of chemo-, regio-, and diastereoselectivity with good functional-group tolerance. In recent years there has been many exciting advances in the reductive chemistry of new samarium divalent reagents. However, their preparation in some cases involves a number of nonroutine steps, and until now their syntheses have still needed improvement (Scheme 1). Among these reagents, SmBr_2 can be conveniently prepared by the reduction of SmBr_3 with metallic lithium,⁵ by the oxidation of samarium metal with tetrabromoethane,⁶ or by generation in situ from SmI_2 and LiBr ^{7,8} (reaction 1 in Scheme 1). The preparation of SmCl_2 can also be realized not only by the in situ reaction between SmI_2 and LiCl ⁸ but also from reduction of SmCl_3 with Sm ⁹ or Li metals¹⁰ (reaction 2 in

Scheme 1. Synthesis of Samarium(II)-Based Reductants



Scheme 1). $\text{Sm}(\text{OTf})_2$ reagent can be synthesized in situ by reduction of $\text{Sm}(\text{OTf})_3$ with alkylmagnesium bromide¹¹ and *sec*-butyllithium reagents.¹² Flowers and co-workers have also reported a practical method for the synthesis of $\text{Sm}(\text{OTf})_2$ by mixing $\text{Sm}(\text{OTf})_3$ and Sm metal (reaction 3 in Scheme 1).¹³

The properties of $\text{Sm}(\text{II})$ complexes formed by these methods can undoubtedly be influenced by metallic salts present in the solution. This hypothesis could be supported by a recent report in which lithium cation also seems to affect the level of diastereoselectivity in some cross-coupling reactions mediated by SmBr_2 .^{14–16} Furthermore, the concentrations of these new reagents are very low in organic solvents (e.g., SmBr_2 0.06 M in THF, $\text{Sm}(\text{OTf})_2$ 0.09 M in THF, and SmCl_2 still unknown),

Special Issue: Organometallic Electrochemistry

Received: March 4, 2014

Published: June 27, 2014



which have also limited the use of these reagents in organic synthesis.^{13a}

Recently, we have reported that the use of a “sacrificial” samarium anode can be applied as an original electrochemical method for the rapid and easy in situ preparation of SmI₂ species for synthetic and catalytic applications.¹⁷ This alternative route for the synthesis of SmI₂ is particularly efficient and can be carried out with routine methods in a galvanostatic mode, with the advantage of being able to carry out syntheses without reaching saturation conditions. On the basis of this electrochemical procedure, we have examined its potential for the synthesis of other Sm divalent compounds. In this paper, we report the electroynthesis and characterization of various divalent samarium complexes in THF, as well as some studies on their reactivity.

In our previous study, we have successfully generated samarium diiodide directly from samarium anode in the presence of *n*Bu₄NI salt as iodide source.¹⁷ Inspired by this initial work, we planned to generate other Sm(II)-based reagents by varying only the anion source during the electrolysis. The proposed electrolysis principle is shown in Figure 1.

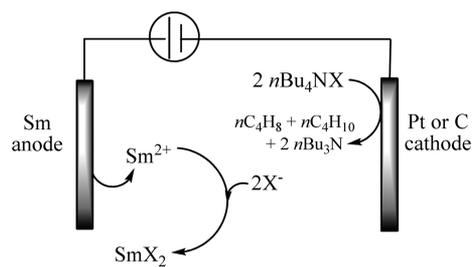


Figure 1. Schematic diagram for the electrolytic preparation of Sm(II)-based reagents from a samarium anode in THF.¹⁷

We have already proved the feasibility of generating SmI₂ species by oxidation of a samarium rod.¹⁷ THF was used as the privileged solvent for Sm(II) chemistry. Among all tetrabutylammonium salts, *n*Bu₄NPF₆ was used as electrolyte support due to its total solubility in THF and the noncoordinative nature of the PF₆⁻ anion to the samarium. The electrolytic preparation of different Sm(II)-based reagents was performed under galvanostatic conditions, applying a fixed current of 15×10^{-3} A. The introduction of *n*Bu₄NBr, *n*Bu₄NCl, or *n*Bu₄NOTf instead of *n*Bu₄NI using conditions identical with those employed for the preparation of SmI₂ (4×10^{-2} M in THF) resulted in a color change. With *n*Bu₄NBr the solution was purple, with *n*Bu₄NCl the solution was gray-green, and with *n*Bu₄NOTf the solution was red (see the Supporting Information). The identity of each electrogenerated Sm(II) species with different counteranions was confirmed by UV–vis spectroscopy.

Characteristic λ_{\max} values were compared with those reported in the literature (Table 1). The UV–vis spectra of the electrogenerated Sm(II) complexes (SmBr₂, Sm(OTf)₂, and SmI₂) in THF were identical with those previously reported.^{6b,13a} In comparison to the SmI₂ complex in THF, the charge-transfer bands at 557 and 618 nm were shifted to lower wavelengths with the addition of *n*Bu₄NBr or *n*Bu₄NCl. These results suggest that the reducing properties of Sm^{II} complexes should increase.^{13a} To the best of our knowledge, this is the first report of the UV–vis spectrum of SmCl₂ in THF with Cl⁻ as the unique possible ligand. The electrochemical in situ generation associated with in situ UV–vis spectroscopy in our case provides

Table 1. Characteristic λ_{\max} of Electrogenerated Sm(II) Complexes in THF

| anion source | Sm(II) complex | λ_{\max} (nm) | |
|-------------------------------|----------------------|-----------------------|----------------------------|
| | | detected | reported |
| <i>n</i> Bu ₄ NCl | SmCl ₂ | 545, 586 | no report |
| <i>n</i> Bu ₄ NBr | SmBr ₂ | 541, 592 | 547, 594 ^{6b} |
| <i>n</i> Bu ₄ NI | SmI ₂ | 557, 618 | 557, 618 ^{6b,13a} |
| <i>n</i> Bu ₄ NOTf | Sm(OTf) ₂ | 558 | 563 ^{13a} |

a new and flexible way to obtain and characterize all these complexes.

Recent research studies have showed that the redox potential of Sm(II) complexes could be changed either by addition of a coordinating cosolvent such as hexamethylphosphoramide (HMPA)^{7a,18} or by a change of the halide coordinating to Sm(II).¹⁹ Therefore, we were interested in examining the redox potentials for Sm(II) electrogenerated complexes, which should provide more insight into their reducing properties (Figure 2).

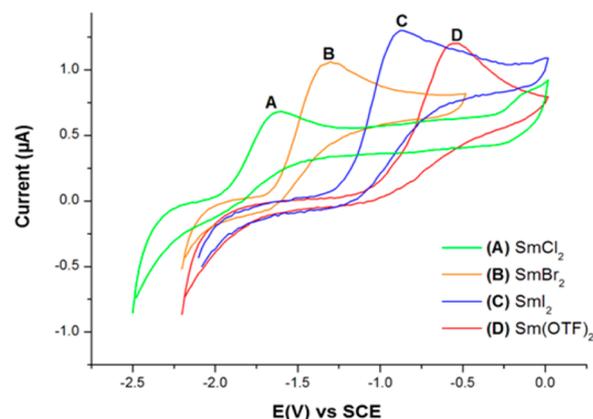


Figure 2. Cyclic voltammograms of electrogenerated SmCl₂ (A), SmBr₂ (B), SmI₂ (C) and Sm(OTf)₂ (D) in THF containing *n*-Bu₄NPF₆ (0.02 M) at a stationary vitreous carbon-disk electrode (1.5 mm diameter) and 20 °C. Scan rate: 0.1 V s⁻¹. The concentrations of the Sm(II) complexes are estimated to be about 5 mM.

Table 2. Electrochemical Data for Various Sm(II) Complexes in THF

| Sm(II) | E_p^{Ox} | E_p^{Ox} reported ^{a,7} |
|----------------------|------------------|------------------------------------|
| SmCl ₂ | -1.63 ± 0.03 | -1.78 ± 0.10 |
| SmBr ₂ | -1.35 ± 0.03 | -1.55 ± 0.07 |
| SmI ₂ | -0.89 ± 0.03 | -0.98 ± 0.04 |
| Sm(OTf) ₂ | -0.55 ± 0.03 | no report |

^aPotential measured vs SCE (V).

Table 2 contains electrochemical data for the oxidation potentials of SmCl₂, SmBr₂, SmI₂, and Sm(OTf)₂ in THF. These data were similar to those reported in the literature,⁷ which confirms again the formation of expected Sm^{II} complexes. SmCl₂ and SmBr₂ both display oxidation potentials more negative than that of SmI₂; they are all within a few hundred millivolts of each other (SmCl₂ -1.63 V, SmBr₂ -1.35 V, and SmI₂ -0.89 V vs SCE).

These results are in agreement with previous work showing that SmCl₂ and SmBr₂ are more powerful reductants than SmI₂ in THF. In the case of Sm(OTf)₂, although its redox potential has

not been determined until now, the reagent is known to be able to ensure transformations analogous to those promoted by SmI_2 , with higher yields in some cases.^{4e} However, under the same electroanalytical conditions we found that $\text{Sm}(\text{OTf})_2$ displays a less negative oxidation potential in comparison to SmI_2 (-0.55 V vs SCE, see Table 2); this suggests that $\text{Sm}(\text{OTf})_2$ is less reducing than SmI_2 .

It is noteworthy that, during the electrolysis, the formation of colored precipitates can be observed for SmCl_2 and SmBr_2 , indicating the low solubility of both complexes in THF. Therefore, to explore the reducing properties of the electrogenerated $\text{Sm}(\text{II})$ complexes in organic applications by bypassing the saturation problem, the substrate was introduced before starting electrolysis. The beneficial effect in this case is that the electrogenerated SmX_2 species are consumed as soon as they are produced, thereby avoiding the saturation of the solution with the reagent; the time of electrolysis should be determined so as to generate enough $\text{Sm}(\text{II})$ reductant for the desired transformation.¹⁷ The reduction of carbon–halogen bonds has been chosen to evaluate the reducing efficiency of the electrogenerated complexes according to the nature of the ligand. To our knowledge 1-chlorododecane is very difficult to reduce to dodecane (**a**) under mild conditions. In Kagan's early work, this reaction has totally failed with SmI_2 even at 60°C for 2 days (Table 3, entry 1).³ After that Inanaga found a remarkable effect

Table 3. Reduction of 1-Chlorododecane Mediated by $\text{Sm}(\text{II})$ Complexes

| entry | reductant | Reductant, additive | | |
|----------------|-----------------------------|--------------------------|----------|--|
| | | T ($^\circ\text{C}$) | time (h) | yield a / b (%) ^d |
| 1 ^e | SmI_2^a | 60 | 48 | no reaction |
| 2 ^e | $\text{SmI}_2^{a,b}$ | 60 | 8 | >95/0 |
| 3 | SmI_2^c | room temp | 2 | 77/2 |
| 4 | SmBr_2^c | room temp | 2 | 80/2 |
| 5 | SmCl_2^c | room temp | 2 | 82/4 |
| 6 | $\text{Sm}(\text{OTf})_2^c$ | room temp | 2 | 86/2 |

^aChemically produced. ^bIn the presence of 2 equiv of HMPA. ^c $\text{Sm}(\text{II})$ produced by applying $i = 15$ mA to samarium anode over 2 h with 4×10^{-2} M of $n\text{Bu}_4\text{N}(\text{X})$ in THF ($\text{X} = \text{I}, \text{Br}, \text{Cl}, \text{OTf}$). ^dGC yields. ^eData from ref 3 and 19.

of HMPA to increase the reducing power of SmI_2 ; the reduction of 1-chlorododecane has been effective but heating and a long reaction time were needed to get a good conversion (Table 3, entry 2).²⁰ To our delight, electrolyses based on the use of a soluble samarium anode allowed us to achieve very good results in this reaction. Without any additive, only 2 h of electrolysis under galvanostatic mode ($i = 15$ mA) is needed to achieve almost complete reduction of 1-chlorododecane, whatever the electrogenerated $\text{Sm}(\text{II})$ reductant (SmI_2 , SmCl_2 , SmBr_2 , or $\text{Sm}(\text{OTf})_2$). Dodecane **a** was detected in good conversions (77–86% GC yields, entries 3–6 in Table 3), and the dimerization product tetracosane **b** was obtained only in a trace amount.

According to the GC analysis, it appears to be difficult to correlate the reduction properties of electrogenerated SmX_2 with their redox potentials; variations in term of reactivity are not very convincing. Unexpectedly, all supposed SmX_2 species prove to be very reactive for the reduction of 1-chlorododecane under these electrosynthetic conditions, as if there were no ligand effect on reactivity. Additional control experiments were performed to rationalize this unexpected reactivity. First of all, when the same

electrolysis conditions were applied without electrogenerated $\text{Sm}(\text{II})$ reagents, using carbon anode instead of samarium anode, it was found that the halogenated compound can be directly reduced but only 38% of dodecane was detected in this case (See Table S1, entry 1 in Supporting Information). This suggests that the participation of the electrogenerated $\text{Sm}(\text{II})$ reductant undoubtedly affects the yield of the reduction reaction.

Also, to estimate the importance of the direct electrochemical reduction of 1-chlorododecane onto the carbon cathode, SmI_2 , SmCl_2 , SmBr_2 , and $\text{Sm}(\text{OTf})_2$ were synthesized by dissolution of samarium anode before introducing the chlorinated substrate in the electrolytic medium. Under these second conditions all SmX_2 derivative proves once again to be highly reactive, producing dodecane around 80% of conversion after only 10 min (See entries 2–5, Table S1 in Supporting Information). These results confirm that the conversions observed when the substrate is initially present in the electrolytic medium could mainly be attributed to the reactivity of samarium divalent species (see entries 3–6 in Table 3). Moreover, since the electrochemical experiments were all realized at low concentration ($c = 5 \times 10^{-3}$ M), it was verified that the concentration of SmX_2 had no effect on the reactivity.

Finally, chemical SmI_2 solution was prepared by mixing diiodoethane and Sm metal powder in the presence of $n\text{Bu}_4\text{NPF}_6$. The resulting solution turns out to be very reactive under both concentrated and diluted conditions. Dodecane was recovered with up to 77% of conversion after 10 min (See entries 7 and 8, Table S1 in Supporting Information). The presence of $n\text{Bu}_4\text{PF}_6$ during the preparation of chemical or electrochemical SmI_2 solution appears to be crucial and seems to be at the origin of this increased reactivity. In our electrochemical procedure, $n\text{Bu}_4\text{NPF}_6$ is always needed to ensure the medium conductivity. These additional experiments lead us to suppose that the presence of $n\text{Bu}_4\text{NPF}_6$ increased the medium polarity that probably prevents a possible aggregation of SmI_2 complex to make it more reactive. The supposed aggregation state seems difficult to break, since the addition of $n\text{Bu}_4\text{NPF}_6$ to the initial chemical solution of SmI_2 is not sufficient to recover the reactivity (See entry 6, Table S1 in Supporting Information). However, Flowers showed that the aggregation number for SmI_2 in THF was 0.98 ± 0.09 over a range of concentrations, indicating that SmI_2 is in monomeric form as well as the fact that the addition of 6 equiv or more of HMPA forces the iodide ions to switch from an inner-sphere to an outer-sphere position.²¹ This effect can also be considered and in this case seems particularly enhanced by the presence of ammonium salts. In our initial work we have shown that the electrochemical procedure leads also to a high reactivity toward pinacolization of aliphatic ketones that are deemed to be more difficult to reduce.¹⁷ Considering the influence of ammonium salt on the reduction of 1-chlorododecane, we assume that the increased reactivity probably has the same origin. However, since carbonyl substrates are thought to react through inner-sphere electron transfer, it appears difficult to attribute this enhancement in reactivity only to an inner-sphere–outer-sphere displacement. We also have to consider also the very recent report about the effective redox potentials of SmX_2 salts combined with water, in which electrostatic interactions are alleged to have an important role in processes mediated by $\text{Sm}(\text{II})$ reductants. This effect, in our case, could be also considered associated with ligand reorganization around the metal. Consequently, the ammonium salt could have different effects depending on the process involved.²²

Finally, it appears to be difficult to correlate the redox potential with the reactivity of electrogenerated SmX_2 . However, we have highlighted that when SmX_2 reagent are prepared in the presence of $n\text{Bu}_4\text{NPF}_6$, their reactivity significantly increases and remains equivalent for all divalent samarium derivatives. The supporting electrolyte, thought to be innocent, is in fact a key additive for increasing the reactivity of SmX_2 derivatives studied.

In summary, SmBr_2 , SmCl_2 , and $\text{Sm}(\text{OTf})_2$ complexes were synthesized in one step thanks to the use of a sacrificial samarium anode. This electrochemical procedure avoids the presence of additional metals such as Li and Mg. The combination of a soluble samarium anode and $n\text{Bu}_4\text{NX}$ salts ($\text{X} = \text{Cl}, \text{Br}, \text{OTf}$) as ligand sources proves to be very reliable for the preparation of complexes well characterized by electrochemistry and UV-vis spectroscopy. Attempts to correlate their redox potentials with their reactivities in the reduction of a recalcitrant substrate such as 1-chlorododecane showed unexpected results. Additional experiments demonstrated that the presence of $n\text{Bu}_4\text{NPF}_6$ during the synthesis of $\text{Sm}(\text{II})$ complexes is responsible for the observed increase in reactivity. What is particularly interesting is that it is only when the $n\text{Bu}_4\text{NPF}_6$ was present during the formation of the SmI_2 complex that reactivity was observed, which leads us to assume that the initial structure of the complex was probably changed, favoring electrostatic interactions needed for the substrate activation. This ammonium salt effect opens up very interesting prospects in the field of samarium divalent reductants, and work is ongoing to understand the mechanism and to evaluate this effect on more challenging substrates.

■ ASSOCIATED CONTENT

■ Supporting Information

Text, figures, and tables giving detailed experimental procedures, UV-vis analysis, electrochemical analysis, and additional experimental data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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■ Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the University Paris-Sud and the CNRS for their financial support.

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