

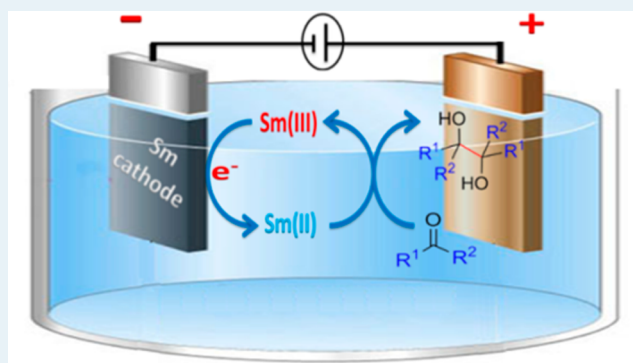
Use of Electrochemistry to Provide Efficient SmI₂ Catalytic System for Coupling Reactions.

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S Supporting Information

ABSTRACT: Samarium metal has been used for the first time as electrode material to perform as an efficient and versatile SmI₂ catalytic system assisted by electrochemistry. The established electrocatalytic procedure that excludes any metal additives was successfully applied in various transformations mediated by this useful reagent.

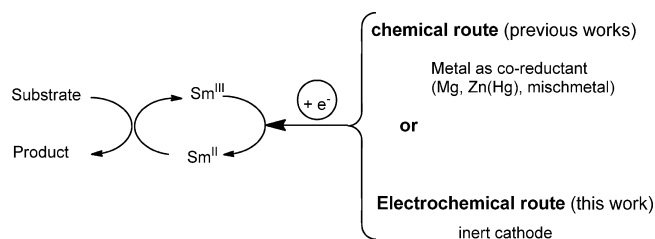


KEYWORDS: samarium diiodide, catalysis, electrochemistry, samarium cathode, coupling reactions

Samarium diiodide (SmI₂), first described by Kagan and Namy in 1977 is recognized to be one of the most useful and versatile reducing agent in organic synthesis.^{1a} Its importance and application has been highlighted by several important reviews, which demonstrate the prominent role of SmI₂ in synthesis.¹ However, the majority of organic reactions mediated by samarium diiodide (SmI₂) as reductive reagent require a stoichiometric amount or even a large excess of SmI₂. This drawback tends to decrease the synthetic potential of the reactions promoted by SmI₂ in large scale. Several research groups have investigated potential solutions that would allow the use of substoichiometric amounts of SmI₂ by employing magnesium metal^{2–4} or zinc amalgam (Zn(Hg))⁵ as coreductants associated with oxophilic additives TMSCl or TMSOTf, respectively.^{6,7} Namy and co-workers developed an alternative catalytic system using mischmetal as an original coreductant without the need for oxophilic additives because the lanthanides included in mischmetal (Ce, La, Nd, Pr, ...) are themselves oxophiles, and the resulting catalytic system was successfully applied in various reactions mediated by SmI₂.⁸ Alternatively, an electrochemical procedure based on the use of SmCl₃ as precatalyst associated with a Mg or Al sacrificial anode was proposed by Duñach and co-workers.⁹ Although this approach has been applied in several coupling reactions, it appears that the formation of samarium divalent species during the electrolysis is difficult to highlight.² In addition to the fact that the proposed metals coreductant for catalytic applications represent significant advances, they have not been extensively used, probably because of the incompatibility between the coreductants used in large excess and the substrates commonly encountered in SmI₂-induced reactions. In addition, the presence of additional metals in the reaction medium may

favor ligand redistribution, and the Sm(II) species regenerated during the catalytic process could be different from SmI₂. This is supported by the fact that lower chemoselectivities and stereoselectivities were generally observed in reactions involving catalytic SmI₂ by comparison with the stoichiometric system.^{1d} We recently reported a new method to generate SmI₂ by direct electrochemical dissolution of a samarium metal anode.¹⁰ Its efficient application in organic electrochemical procedures encouraged us to pursue our investigations toward the development of catalytic reactions with the aid of electrochemistry. The objective herein is to exclude the use of the metal additives required for the regeneration of the samarium divalent active reagent by replacing them with an inert electrode to achieve a more efficient and versatile SmI₂ catalytic system (Scheme 1).

Scheme 1. The Use of Coreductant To Achieve the Catalytic Cycle of SmI₂



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For this purpose, we have investigated the properties of several electrodes to reduce the trivalent into divalent samarium species.¹¹ All attempts to reduce a suspension of SmI₃ using cathodes based on platinum, carbon, nickel, lead, or stainless steel were not conclusive. Indeed, the initial SmI₃ suspension remained unchanged after the electrolysis (Table 1, entries 1–

Table 1. Screening of Cathode Materials for Reduction of SmI₃ Salts in THF/*n*Bu₄NPF₆^a

$$\text{SmI}_3 \xrightarrow[\text{THF, } n\text{Bu}_4\text{NPF}_6]{\text{M cathode}} \text{SmI}_2 + \text{I}^-$$

entry	cathode	current density (mA/cm ²)	UV–vis (λ _{max} , nm)
1	Pt	1.52	nd
2	C	2.10	nd
3	Pb	2.87	nd
4	Ni	1.80	nd
5	SS ^b	8.06	nd
6	Sm	1.25	612–557

^aConditions: electrolyte 0.04 M NBu₄PF₆ in THF, 0.1 mmol of SmI₃, *i* = 5 · 10⁻² A, standard vitreous carbon anode. ^bSS: stainless steel contains 72% Fe, 18% Cr, and 10% Ni.

5). Interestingly, we discovered that the use of a samarium metal as cathode effectively reduces SmI₃ to provide divalent samarium species (Table 1, entry 6). We found that when applying a current density of 1.25 mA/cm², the yellow suspension of SmI₃ in THF changes immediately from yellow to homogeneous dark blue, the characteristic color of low-valent samarium species.^{1a} Moreover the UV–vis analysis of the resulting solution showed absorptions bands at 612 and 557 nm (Figure 1) attributed to the formation of the SmI₂ complex in THF (Table 1, entry 6).¹²

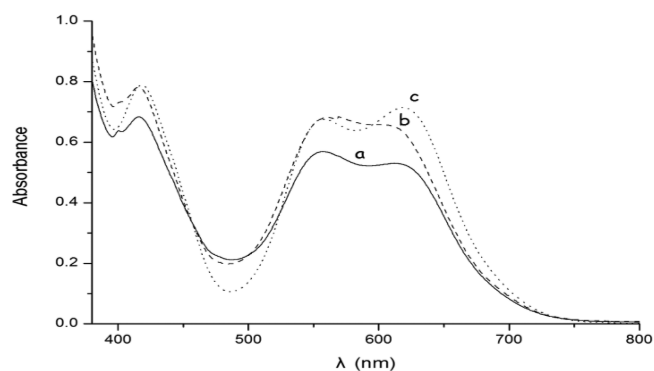


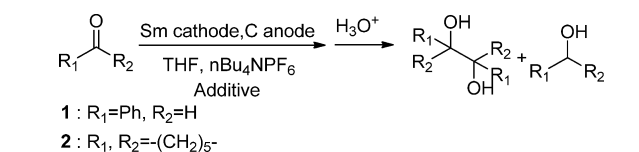
Figure 1. UV–vis analysis of samarium divalent species solutions. Spectra of the SmI₂ solution prepared (a) by electroreduction of SmI₃, (b) by electroreduction of SmCl₂, and (c) chemical SmI₂ solution. SmI₂ concentration ≈ 10 mM.

The complex formed was also well characterized by electrochemical analysis. The cyclic voltammogram of the resulting solution is in total accordance with those previously described¹⁰ (see Figure S4 in the Supporting Information). Samarium metal turned out to be the best cathode material with respect to the desired reduction. The screening of electrode material shows clearly that the nature of the cathode is crucial and suggests that there is likely some affinity between the Sm(III) complex free in solution and the samarium cathode itself. This efficiency is probably due to a better interaction between the complexes based on samarium and the surface of

the electrode, which is made from the same metal, that ensures a perfect electron transfer to reduce the trivalent complexes. Moreover, it was found that with an amount of current over that required to reduce totally the Sm(III) suspension into Sm(II), the solution color begins to fade. This indicates, on one hand, that the SmI₂ formed could be totally reduced to samarium metal (Sm(0)) onto the cathode, on the other hand, prove that the electrode does not produce SmI₂ under these electrochemical conditions.¹³ We have also verified that no reaction occurred for 48 h in the absence of imposed current intensity.

After demonstrating that Sm(II) can be efficiently generated by electrochemical reduction of Sm(III) at a samarium cathode, we turned our attention to checking the validity of our method in a benchwork reaction, such as the pinacol coupling of carbonyl derivatives, which has been widely studied with this reagent.¹⁵ For the implementation, benzaldehyde and cyclohexanone were chosen as substrates, and electrolysis experiments were successively performed with 10 mol % of SmI₂ in the presence of TMSCl (1.5 equiv). To our delight, both carbonyl substrates led to the expected pinacol products that were obtained in 83% and 59% yields, respectively (Table 2, entries 3 and 7).

Table 2. Additional Experiments To Identify the Mechanism of Pinacolization



entry	substrate	additives	conv ^a (%)	pinacol ^b (%)	alcohol ^b (%)
1	1		63	36	27
2	1	SmI ₂ ^c	73	22	51
3	1	SmI ₂ ^c , TMSCl	93	83	10
4	1	SmI ₂ ^c , TMSCl, HMPA	5	5	0
5	2		34	4	30
6	2	SmI ₂ ^c	33	22	11
7	2	SmI ₂ ^c , TMSCl	99	59	40
8	2	SmI ₂ ^c , TMSCl, HMPA	23	5	18

^aConversion determined by gas chromatography using undecane as internal standard relative to the substrate engaged. ^bIsolated yield. ^c10 mol % of SmI₂.

Additional experiments were carried out to identify the mechanism of the pinacolization reaction (see Table 2 and Table S1 in the Supporting Information). Thus, it was found that the pinacolization takes place without SmI₂ initially introduced in the case of benzaldehyde. Indeed, the pinacol adduct was isolated in only 36% yield and probably results from the direct reduction of benzaldehyde at the samarium cathode surface (Table 2, entry 1). This effect was amplified by the presence of TMSCl, since the pinacol was recovered in 83% yield. These results indicate that the samarium electrode surface is probably activated by the presence of TMSCl, as described by Honda and Katoh.¹⁶ In contrast, when the electrolysis is performed in the presence of cyclohexanone, an aliphatic ketone more difficult to reduce, pinacolization does not occur in the absence of SmI₂. Cyclohexanone was converted to

pinacol with 59% yield only in the presence of 10 mol % of SmI_2 and TMSCl in the electrochemical cell (entry 7, Table 2). Moreover, as observed in a previously reported procedure that uses magnesium as a coreductant,^{2–4} addition of TMSCl is required to cleave the $\text{Sm}^{\text{III}}\text{--O}$ bonds. These results are in good agreement with the proposed catalytic cycle. Moreover, addition of 4 equiv of hexamethylphosphoramide (HMPA) with respect to the catalytic amount of SmI_2 to reduce the formation of the alcohol was not effective. In the presence of HMPA, the alcohol resulting from the direct reduction of cyclohexanone is always observed as a byproduct, and the electrolysis efficiency is greatly diminished (only 23% of conversion instead of 99% (entry 7 and 8, Table 2). This effect was also observed when nichmetal was used as coreductant,^{8a} and as suggested by Namy and co-workers, the addition of HMPA probably impedes the reduction of $\text{Sm}(\text{III})$ species into $\text{Sm}(\text{II})$. This result is also in agreement with the work of Hoz and Farran, who have also observed that HMPA dramatically reduces the reactivity of ketyl radical intermediates in the reduction of carbonyl compounds.¹⁷

The procedure was then completed by in situ electro-generating the catalyst directly from the samarium electrode used as anode in a first step (pre-electrolysis).¹⁰ This modification avoids any manipulation of the sensitive catalyst out of the electrochemical cell. Reactions were carried out in an undivided cell simply flushed by argon, fitted with a Sm anode, carbon cathode, and charged with degassed anhydrous THF containing $n\text{Bu}_4\text{NPF}_6$ and $n\text{Bu}_4\text{NI}$ as the iodide source.

The pre-electrolysis was achieved at a constant current intensity of 5.0×10^{-2} A during the designated time to prepare 10 mol % SmI_2 with respect to the substrate, which is introduced in a second step. The characteristic deep blue solution of SmI_2 in THF is obtained after the first step. To perform the second electrolysis step, the carbonyl substrate and 1.5 equiv of TMSCl are added, and the polarity of the samarium electrode is inverted to act as the cathode during the whole course of the electrolysis. The catalysis was achieved at a constant current intensity of $-5 \cdot 10^{-2}$ A and followed by GC analysis. The results of the reductive coupling of various ketones and aldehydes are listed in Table 3.

Table 3. Catalytic Homocoupling of Carbonyl Compounds Using SmI_2/Sm Cathode Catalytic System^a

entry	substrate	conv (%) ^b	yield (%) ^c	meso/dl ^c
1	benzaldehyde	93	83	45:55
2	4-methylbenzaldehyde	90	51	55:45
3	4-methoxybenzaldehyde	63	46	30:70
4	3-methoxybenzaldehyde	83	42	50:50
5	acetophenone	95	62	30:70
6	cyclohexanone	99	59	50:50

^aElectrolytic conditions: THF, $n\text{Bu}_4\text{NPF}_6$ (0.04 M), 4 mmol of carbonyl substrate, charge of $2F/\text{mol}$. ^bConversion determined by gas chromatography using dodecane as internal standard relative to the substrate engaged. ^cIsolated yields, meso/dl ratio determined by ¹H NMR.

For other aromatic aldehydes, the reaction is effective only if the catalyst is generated. Without SmI_2 , their electroreduction led to the corresponding pinacols in low isolated yields (see Table S1 in the Supporting Information). In the presence of catalytic amounts of SmI_2 , all pinacol derivatives were obtained in moderate to good isolated yields (Table 3); however, compared with the stoichiometric version,¹⁰ yields for reactions of aldehydes are generally affected by the formation of the alcohols resulting from direct reduction of the aldehydes at the samarium cathode surface. Diastereoselectivities are generally the same as those measured for reactions performed under stoichiometric conditions (meso/dl ratio close to 1:1); these results are also in good agreement with a pinacolization mediated by SmI_2 .¹⁷

Compared with the cyclic voltammograms obtained for the SmI_2 solution, those of $\text{Sm}(\text{II})$ species prepared by electrochemical reduction of SmI_3 and SmI_2Cl are different (see the Supporting Information). This reflects the possibility that the electrogenerated $\text{Sm}(\text{II})$ reductant could be a mixture of species with probably an equilibrium between these various samarium divalent species during the electrocatalytic process. This hypothesis is highly probable because it is well-established and supported by the UV–vis spectra and electrochemical analysis (Figure 1 and Figure 2)¹⁸ that chloride has a higher affinity for Sm than iodide.

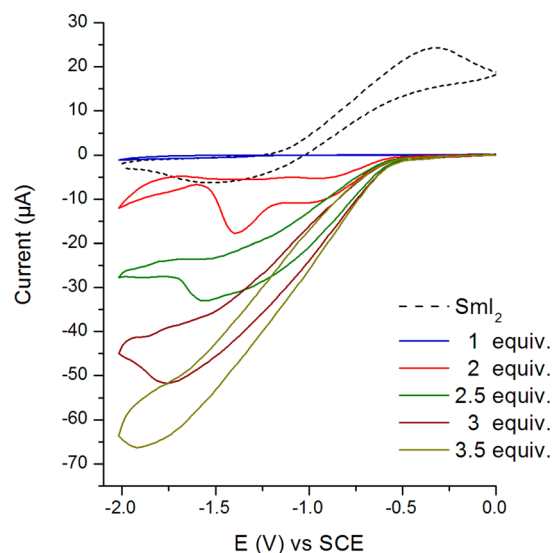


Figure 2. Cyclic voltammetry performed at a vitreous carbon disk electrode ($d = 2$ mm) at 25°C in THF containing $n\text{Bu}_4\text{NPF}_6$ (0.04 M) as the supporting electrolyte. Reduction of SmI_2 (0.1 mM, dashed line) at a scan rate of 50 mVs^{-1} . Reduction in the presence of increasing amounts of **1** (1, 2, 2.5, 3, and 3.5 equiv).

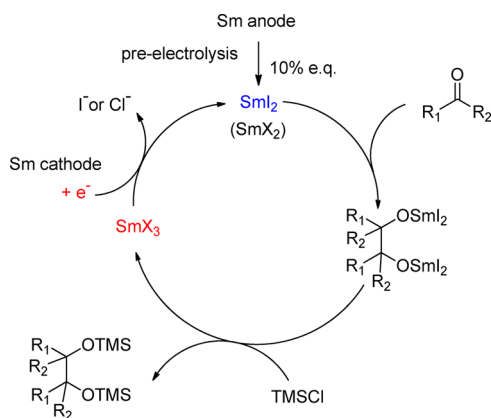
We have investigated this catalytic process by electrochemical analyses. The cyclic voltammogram of SmI_2 in THF (0.1 mM) at a scan rate of 0.05 V s^{-1} exhibited a quasireversible redox system (Figure 2, dashed line). Benzaldehyde and TMSCl analyzed as a solution in THF were not reduced until -2.0 V versus the standard calomel electrode (SCE). The SmI_2 redox signal disappeared upon addition of 1 equiv of benzaldehyde as carbonyl substrate in the presence of TMSCl (benzaldehyde/ TMSCl : 1/1.5) (blue line). This is consistent with the complete reaction of SmI_2 with the carbonyl substrate.

Two new reduction peaks were observed at $E^p = -0.95$ V and $E^p = -1.35$, and their current increased with increasing

amounts of the benzaldehyde/TMSCl mixture without reoxidation (from 1 to 4 equiv; Figure 2). From these experiments, one deduces that the one-electron reduction of SmX_3 species, generated during the chemical transformation, in the diffusion layer at the electrode, thus gives rise to a catalytic-reduction current, which is observed (Figure 2). In addition, one deduced therefrom by the observation of two reduction peaks that various Sm(III) species are generated during the catalytic process. These electrochemical experiments provide direct evidence for support of the proposed mechanism. Moreover, under these electrolytic conditions, we assume that the most likely half reaction that can occur at the anode is the oxidation of halide released during the catalytic cycle to produce Cl_2 or I_2 .¹³

The possible reaction pathway of the SmI_2 -catalytic pinacolization involves the reduction of carbonyl compounds by electrogenerated SmI_2 to give Sm(III) pinacolate, followed by metal exchange with TMSCl to provide the corresponding silyl ether and SmI_2Cl . Subsequent electron transfer from the Sm cathode regenerates Sm(II)X_2 from Sm(III)ClI_2 (Scheme 2). This last step was evidence by the direct electroreduction of

Scheme 2. Proposed Catalytic Cycle for Coupling Reactions Mediated by Electrogenerated SmI_2 and Using Electrochemistry As Co-reductant



a previously generated SmClI_2 . Indeed, when a THF suspension of SmClI_2 is reduced onto a samarium cathode, the color changes from orange-yellow to dark blue. UV-vis analysis of the resulting solution shows the characteristic absorptions bands at 603 and 562 nm attributed to the formation of the SmI_2 complex in THF (Figure 1, curve b).^{1a,12} A similar experiment could also be conducted from SmI_2Br to generate a THF solution of divalent samarium halides. These experiments indicate that SmI_2 could be regenerated from the trivalent species SmI_2X ($\text{X} = \text{Cl}$ or Br) intermediate under the electrochemical conditions described in Table 1, and the resulting colored solution may suggest that SmI_2 is the prevailing reducing species during the catalytic cycle (Scheme 2).

This catalytic approach was also applied in the allylation of carbonyl compounds. Reactions were performed according to a Barbier-type procedure in which the formation of an organo-samarium compound is generally admitted and confirmed by several mechanistic studies (Table 4).¹⁹ Pre-electrolysis and electrolysis were performed under the conditions established for the pinacolization reaction.

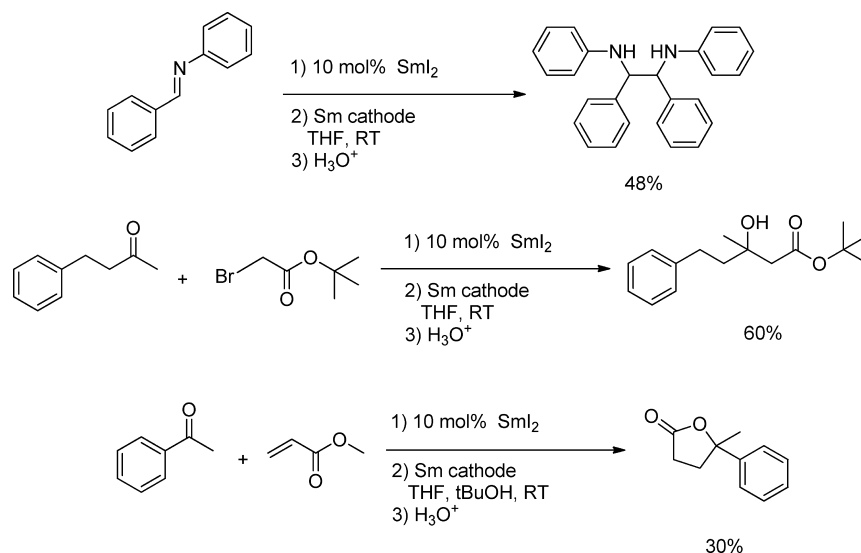
Table 4. Catalytic Allylation of Carbonyl Compounds^a

Entry	Substrat	Conv.(%) ^b	Isolated Yield(%) ^c
1		92	77
2		82	71
3		70	64
4		95	75
5		96	54 ^d
6		70	31 ^d
7		75	31 ^d
8		84	42 ^e

^aElectrolytic conditions: THF, $n\text{Bu}_4\text{NPF}_6$ (0.1 M), 2 mmol of carbonyl substrate, and 4 mmol of allyl iodide; charge of 2F/mol and TMSCl introduced by Syringe pump. ^bConversion determined by gas chromatography using dodecane as internal standard relative to the substrate engaged. ^cIsolated yields. ^dAlcohol detected as major byproduct around 20%. ^eCorresponding pinacol detected as major byproduct (40% yield).

Carbonyl substrates and allyl halide are introduced after the pre-electrolysis step, which delivers the catalytic samarium divalent species. A short survey of allyl halides highlights allyl iodide as the most effective, so it was subsequently used for all reactions. Under optimized conditions, the trimethylsilyl chloride and carbonyl compound diluted in dry THF were introduced dropwise by a syringe pump during the electrolysis. The corresponding homoallylic alcohols were obtained in good yields similar to those obtained under stoichiometric conditions (Table 4).¹⁰ It is to be noted that the dienes arising from a Wurtz coupling were generally observed as byproducts. We also verified that no reaction was observed in the absence of samarium diiodide, which strongly suggests the coupling reaction proceeds through the formation of an organometallic species in a catalytic manner. A possible reaction pathway involves a coupling reaction mediated by electrogenerated SmI_2 through the formation of an allylsamarium derivative that reacts with the carbonyl compound to afford Sm(III) alcoholate, followed by metal exchange with TMSCl to provide the corresponding silyl ether and SmI_2Cl . Samarium diiodide could be regenerated by direct electron transfer from the samarium cathode, as described earlier for the pinacolization reaction (Scheme 2).

To extend the scope of application of this new SmI_2/Sm cathode catalytic system, other reactions mediated by samarium diiodide were performed (Scheme 3). This electrocatalytic procedure could also be applied to the reductive coupling of

Scheme 3. Other Reactions Mediated by Catalytic SmI₂ in Electrochemistry-Assisted Procedure

imines, as exemplified by the coupling of *N*-benzylideneaniline, which leads to the isolations of the corresponding diamine (*meso/dl* = 52/48) in 48% yield (Scheme 3). The diastereoselectivity was similar to the one observed under stoichiometric conditions.^{10,20} Reformatsky type reactions between *tert*-butylbromoacetate and 4-phenyl-2-butanone gave the desired cross-coupling product in 60% yield (Scheme 3).

Finally, as a last illustration of the synthetic potential of this electrochemically assisted catalytic procedure, the cross-coupling between acetophenone and methyl acrylate was tried. Under the reaction conditions described in Scheme 3, the reaction between acetophenone and methyl acrylate leads to the corresponding lactone in 30% isolated yield. It should be noted that the efficiency in this case is strongly reduced because the pinacol product derived from acetophenone is also formed (up to 48% of isolated product). In all cases, we also verified that yields are close to those obtained under stoichiometric conditions, and no reaction occurred in the absence of samarium diiodide.

In summary, we have discovered a novel and reliable SmI₂ catalytic system based on the use of a samarium electrode as coreductant. SmI₂ can act as a catalyst through the use of a samarium cathode, which effectively reduces the trivalent samarium, formed during the chemical reaction, to regenerate the divalent samarium catalytic species. Various transformations mediated by this useful reagent were conducted under the established electrocatalytic conditions, and this method potentially provides an approach to catalytic Sm(II)-based reductants and reductive coupling reactions. We are currently exploring the potential of its application with a special focus on enantioselective transformations.

■ ASSOCIATED CONTENT

Supporting Information

Detailed experimental procedures, UV–vis analysis, electrochemical analysis, and additional experiment 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.

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(11) A typical procedure was as follows: In an undivided three electrode cell equipped with vitreous carbon anode (20 cm² area), a saturated calomel electrode (SCE) as reference and containing a magnetic stirring bar, was introduced 0.04 M of *n*Bu₄NPF₆ in anhydrous THF and the trivalent samarium salts as a suspension in 4 mL of electrolyte solution. The solution was flushed with argon before and during the electrolysis performed at 25 mA. After the electrolysis, the resulting solution was directly analyzed by UV–vis spectrophotometry.

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(13) An additional control experiment was performed by the reduction of 0.5 mmol SmI₃ using the samarium cathode. After complete color disappearance, if the electrolysis is prolonged, the solution becomes brown, indicating the probable formation of I₂. Upon quenching with a solution of thiosulfate, the resulting brown solution experiences an instantaneous bleaching, confirming the presence of I₂ at the end of this electrolysis experiment. Moreover, the weight of the electrode is increased to about 75 mg, which suggests that samarium metal was deposited onto the electrode.

(14) Electrolyses were carried out in an undivided electrochemical cell equipped with a vitreous carbon anode and samarium cathode and charged with 10 mol % of SmI₂ chemically prepared in presence of chlorotrimethylsilane (TMSCl). Electrolyses were performed at constant current intensities of 5·10⁻² A.

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