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Electrochemical generation of low-valent lanthanides[†]

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Abstract—A new method is presented to produce divalent lanthanides (including the popular reductant samarium(II) iodide) from the corresponding trivalent triflate salts. This novel route to low-valent lanthanides suggests the development of a catalytic system employing the cathode as a co-reductant. © 2001 Published by Elsevier Science Ltd.

Samarium(II) iodide has become one of the most popular single-electron reductants in organic chemistry.[1] Recently, much work has been published concerning its electrochemical properties.[2] We reasoned that preparative-scale reductive electrolysis of samarium(III) salts would afford access to active samarium(II) species.[3] This approach contrasts with the popular method of oxidizing samarium metal to the divalent oxidation state. We decided to initiate our investigations employing the inexpensive and readily available $Sm(OTf)_3$ salt.[4] We report (a) a new means of electrochemically generating SmI_2 and $YbBr_2$ in situ, (b) a dramatic effect of the triflate counter-ion upon the redox potential of the metal, and (c) that using in situ electrochemically generated SmI_2 or $YbBr_2$ as a mediator, reductive coupling reactions can be conducted at significantly lower (less negative) potentials than is possible when the same substrates are reduced directly.

The chemistry described provides a general method for the development of electron-transfer reagents. Our approach uses the acquisition of electroanalytical data in the form of a voltammogram to provide a simple and systematic means of screening the properties of redox-active species. The data provide mechanistic insight and assist in determining which reagents are best suited for further investigation. Observations described in this paper suggest that one may be able to tune the properties of the metal to fit the redox needs of the problem at hand.[2a]

The effects of Lewis basic co-solvents and ligand variation on the reduction potential of samarium have been studied,[5] but, to our knowledge, the redox properties of the readily available triflate salts of samarium and ytterbium are unknown. Therefore, we performed cyclic voltammetry studies on $Sm(OTf)_3$ in acetonitrile. The salt showed a quasi-reversible reduction for the $3^+/2^+$ couple in the presence of a triflate-containing electrolyte. Under these conditions, the reduction potential of the samarium was −2.1 V.[6] When utilizing an iodide-containing electrolyte, the reduction potential shifted to −1.7 V (Fig. 1). The voltammetric data are similar to those already reported for SmI_2 in acetonitrile.[2c] Attempts to generate data with bromide and chloride electrolytes were unsuccessful.[7]

This change in reduction potential suggests that the triflate salt undergoes a ligand-exchange reaction with the supporting electrolyte to produce the corresponding samarium(III) halide (Scheme 1).

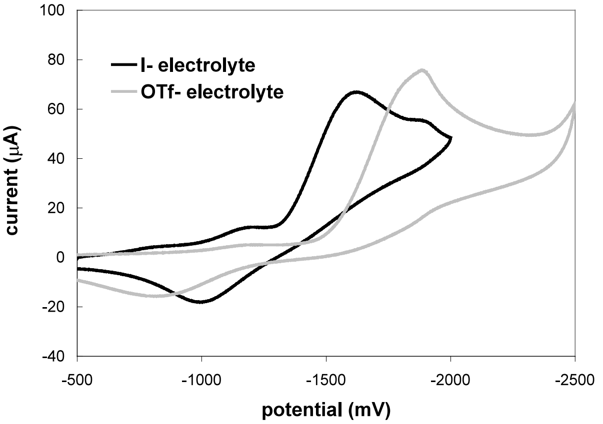

Figure 1. Cyclic voltammetry of samarium(III) triflate with varying electrolytes.

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[†] A preliminary account of this work was presented at the 220th National Meeting of the American Chemical Society, Washington, DC, August, 2000.

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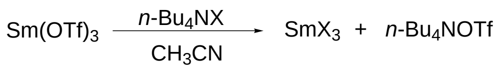
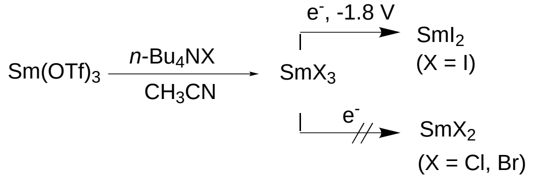


$$Sm(OTf)_3 \xrightarrow[CH_3CN]{n\text{-}Bu_4NX} SmX_3 + n\text{-}Bu_4NOTf$$

Scheme 1. Ligand metathesis to produce samarium halides.

The voltammetric data support the observation that SmI_3 can be reduced with rather mild reductants, such as zinc, aluminum, and magnesium,[8] whereas $Sm(OTf)_3$ requires more powerful reductants, such as Grignard reagents or organolithium species, to generate $Sm(OTf)_2$.[9]

In accord with our voltammetry data, we were unable to produce samarium(II) on a preparative scale in the presence of bromide- or chloride-containing electrolytes. However, reduction in the presence of iodide-containing electrolytes allowed reduction of the samarium salt to produce a deep-blue colored solution characteristic of SmI_2 (Scheme 2).



Scheme 2. Electrochemical generation of samarium(II) halides.

The identity of the samarium(II) species was confirmed by UV–vis spectroscopy. An aliquot of the electrochemically produced samarium(II) species had a spectrum almost identical to that of SmI_2 and markedly different than $Sm(OTf)_2$ (Fig. 2), both formed by known methods.[1,9]

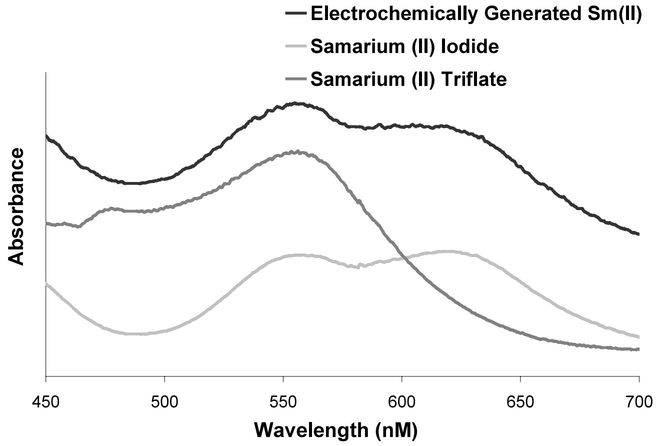
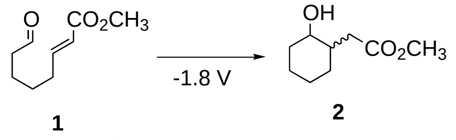


Figure 2. UV–vis spectrum of electrochemically produced SmI_2 in comparison to SmI_2 and $Sm(OTf)_2$ both prepared by known methods. The spectra are stacked for clarity.

To further verify the identity of the electrogenerated species, we explored the use of this species in a preparative transformation known to occur with SmI_2. Our model reaction was the intramolecular cyclization of aldehyde/unsaturated ester **1** (Scheme 3). This compound can be directly reduced to afford alcohol **2** at a controlled potential of −2.7 V.[6,10] Using samarium triflate as a mediator in an iodide-containing electrolyte, we were able to perform the same reduction at −1.8 V, *nearly one volt less negative* than the conditions required for the direct electrolysis. The controlled-potential conditions ensure that the low-valent lanthanide, not the cathode, is reducing the substrate. These milder reaction conditions could potentially allow for the appendage of electrochemically active groups (such as benzyl ethers) to similar substrates.



1
E_{pc} - 2.7 V[6,11]

2
(54 %, 1.4:1 *trans/cis)*

Scheme 3. Reductive cyclization mediated by samarium(II) iodide. *Conditions*: $Sm(OTf)_3$ (2.2 equiv.), *t*-BuOH (1.2 equiv.) in 0.05 M *n*-Bu_4NI/CH_3CN, 2 e^-. The *cis*-hydroxy ester was isolated as the corresponding lactone.

In addition, we investigated the use of low-valent ytterbium-based reagents. While $Yb(OTf)_3$ has received much attention for its use as a Lewis acid, there has been surprisingly little investigation into the use of ytterbium(II) reagents as mild reductants.[12] We found that, in analogy to our results with samarium, one can generate solutions of ytterbium(II) electrochemically, and that the reducing ability of the metal is strongly dependent on the counterion (Fig. 3).

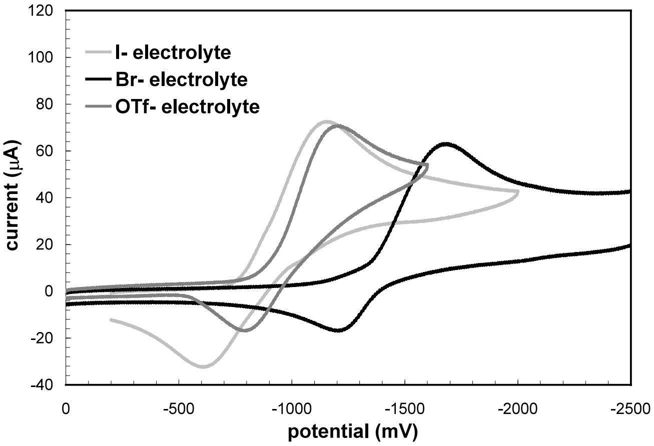
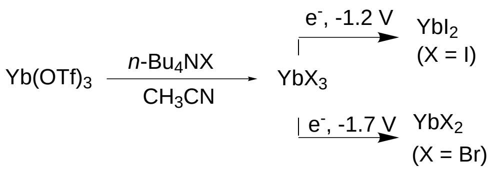


Figure 3. Cyclic voltammetry of ytterbium(III) triflate with varying electrolytes.

For ytterbium, the reduction potential of the triflate and iodide salts are similar (ca. −1.2 V). However, in contrast to samarium, it is possible to successfully reduce ytterbium using bromide-containing electrolytes. This occurs at a more negative potential of −1.7 V (Scheme 4).

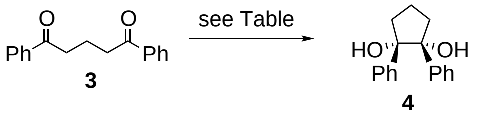
As a test reaction designed to verify the reducing properties of the electrogenerated ytterbium(II) reagent,



Scheme 4. Electrochemical generation of ytterbium(II) halides.

we investigated the pinacol cyclization of dione **3** (Table 1). This method cleanly affords the cyclic diol (**4**) with complete stereoselectivity. The stereoselectivity can be rationalized by coordination of the metal between the two carbonyl units of the dione starting material.[13] It should be noted that direct electrochemical reduction of dione **3** in acetonitrile affords a diastereomeric mixture of diols.[14]

Table 1. Pinacol cyclization of dione **3**



Conditions	Potential (V)[6]	Yield (%)	de (%)
Direct electrolysis[14]	−2.1	67	68
SmI_2 reduction[8b]	–	82	>95
$Yb(OTf)_3$-mediated electrolysis	−1.8	83	>95

In conclusion, we have found that the electrochemical reduction of easily obtained ytterbium and samarium(III) triflate salts provides a simple and convenient route to solutions of divalent lanthanides. We have successfully shown that these in situ-produced solutions can effectively induce preparative-scale cyclizations with results that are comparable to traditional LnI_2 reduction. This reductive entry into low-valent samarium and ytterbium opens the potential for development of a catalytic system using the cathode as a co-reductant.[15] Work on developing such a system is underway.

General procedure: A standard electrochemical H-cell was charged with 0.05 M *n*-Bu_4NI (*n*-Bu_4NBr for ytterbium) in acetonitrile and degassed with nitrogen. The lanthanide triflate salt (1.1 mmol) and substrate (0.5 mmol) were added to the catholyte. The cell was equipped with a mercury pool cathode, platinum anode and a reference electrode. A current, at a controlled potential of −1.8 V (versus Ag/$AgNO_3$, −1.7 V for ytterbium), was applied until 1.1 F of charge was consumed for the one-electron reduction of the lanthanide. At this point the catholyte takes on either a blue or yellow color due to excess divalent samarium or ytterbium, respectively. The catholyte was concentrated and the residue partitioned between 100 mL of ethyl ether and 100 mL of a saturated aqueous solution of Rochelle's salt (potassium sodium tartrate). The layers were separated and the aqueous layer was extracted with two additional portions of ether. The combined organics were washed with brine (1×100 mL), dried ($MgSO_4$), filtered and concentrated. Products were isolated using column chromatography and analyzed by ^1H and ^{13}C NMR to determine product ratios. All products gave satisfactory spectral data.

Acknowledgements

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