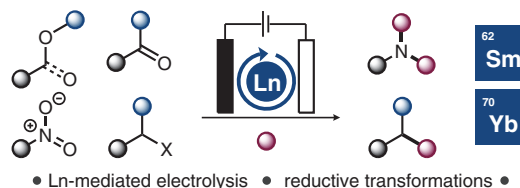   THIEME OPEN ACCESS

Samarium and Ytterbium in Organic Electrosynthesis

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● Ln-mediated electrolysis   ●   reductive transformations ●

Abstract   Low-valent lanthanide catalysts and reagents are well-established as versatile and tunable mediators for a variety of synthetic transformations. Despite the contemporary interest in electricity as a sustainable alternative to stoichiometric redox reagents, electrochemical (re)generation of such low-valent metal complexes in a synthetic setting is surprisingly limited. With focus on samarium and ytterbium, this review presents a comprehensive overview of electroreductive-mediated transformations with the hope of inspiring further work in this very useful field of research.

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1   Introduction

Lanthanide metals constitute highly important components in modern technology for a wide range of applications, including clean energy, electric vehicles, smartphones and magnetic resonance imaging (MRI) contrast agents.[1,2] In the context of organic synthesis, lanthanide complexes have well-established roles as catalysts and reagents in a variety of valence states. Elemental lanthanide metal reagents have successfully been used as single-electron reductants and as starting materials to generate divalent organometallic reagents for nucleophilic additions.[3] Further-

more, divalent lanthanide complexes are versatile reagents and catalysts in a wide range of radical transformations, including asymmetric reactions and total synthesis applications,[4–6] with samarium(II) iodide (Kagan's reagent) as the benchmark complex. Finally, trivalent lanthanide complexes are excellent Lewis acids, with trifluoromethanesulfonate (triflate) complexes being a particularly useful class of water-tolerant catalysts.[7] The versatility of lanthanide complexes is underscored by the tunable reducing power of the Ln(II)/Ln(III) redox couples as a function of ligands, addi-

tives and solvents,[4,8] with synthetically relevant electron transfers proceeding via either inner- or outer-sphere mechanisms.[9]

Various methods are at hand for the generation of divalent lanthanide complexes from their trivalent analogues using chemical reductants.[4] In contrast, the electrochemical formation of such divalent complexes is considerably less explored, with reported procedures generally being of low synthetic utility.[10,11] This lack of methods is surprising, especially considering the contemporary interest in electrochemistry as a sustainable alternative to stoichiometric redox reagents and as an enabling technology for new reactivity.[12,13] With the aim to inspire further developments in the field, this review presents an overview of synthetically relevant lanthanide-mediated reductive electrochemical protocols with a particular focus on samarium and ytterbium complexes.

2   Compounds Containing Carbon–Oxygen Bonds

The C–O bond is a ubiquitous and versatile motif in organic compounds, and is found in a vast number of synthetic as well as naturally occurring compounds. The oxophilicity of lanthanide complexes and their ability to act as Lewis acids and/or reductive electron transfer mediators make them particularly interesting in the context of catalytic C–O bond activation. The following section describes the use of lanthanide complexes under electroreductive conditions to facilitate activation of single and double bonds between carbon and oxygen in organic compounds.

2.1   Ethers

In 1992, Périchon and co-workers disclosed a Sm-catalyzed protocol for electroreductive cleavage of aryl and alkyl allyl ethers (Scheme 1), furnishing up to 90% of the deallylated product.[14] For substrates bearing both primary and secondary allyl ethers, the less substituted moiety was preferentially cleaved under the electroreductive conditions. Non-allylic ester groups were compatible with the reaction conditions, whereas aromatic halides were reductively removed prior to the allyl ether. Aldehydes were preferentially reduced to afford pinacol products in the presence of allyl ethers, however, ketones remained intact. While cleavage of aromatic allyl ethers proceeded in the absence of SmCl₃, their yields could be significantly increased by addition of the Sm(III) catalyst. In contrast, aliphatic substrates did not react in the absence of the Sm(III) catalyst and required KI as an additive to reach high yields (up to 85%). A control reaction using SmI₂ ($E_{1/2}$ = –0.89 V vs SCE)[8b] as the reductant under non-electrochemical conditions did not furnish the deallylated product. Based on these experimental findings, it was hypothesized that the SmCl₃ is ei-

ther reduced to a divalent species capable of acting as an electron transfer mediator (for example, $E_{1/2}$ = –1.78 V vs SCE for SmCl₂),[8b] or that it acts as a Lewis acid to assist the reductive deallylation by coordination to the ether function.

Scheme 1 Sm-mediated electrochemical deallylation of ethers
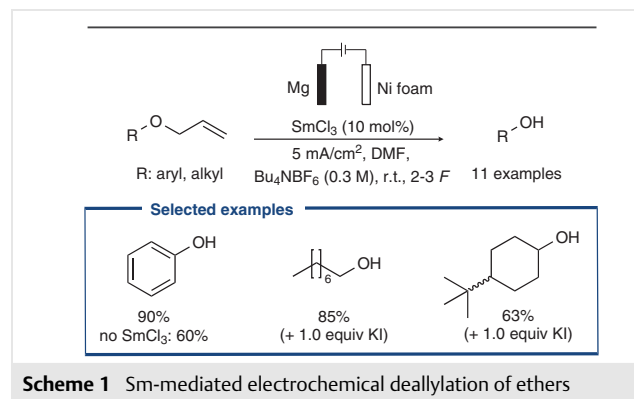
2.2   Aldehydes and Ketones

In 1989, Périchon and co-workers developed a Sm-mediated protocol for pinacol coupling of a small selection of aldehydes and ketones.[15] The electrolysis was carried out in an undivided cell in amide solvents, using sacrificial magnesium or aluminum anodes and a nickel or stainless-steel cathode in the presence of 5–10 mol% of SmCl₃ as the catalyst precursor (Scheme 2). Aromatic and aliphatic aldehydes were inter- and intramolecularly coupled to furnish the corresponding 1,2-diols in yields of up to 98%, with aryl chlorides being tolerated under the electroreductive conditions. Control reactions in the absence of a catalyst using heptan-2-one as the substrate demonstrated that no 1,2-diol was formed, whereas the reduction product heptan-2-ol and mixtures of aldol-type condensation products formed instead. Mechanistically, it was proposed that SmCl₃ is electrochemically reduced to a Sm(II) species that reacts with the carbonyl compound to form a Sm(III)-pinacolate


Scheme 2 Sm-mediated electroreductive pinacol coupling of aldehydes and ketones
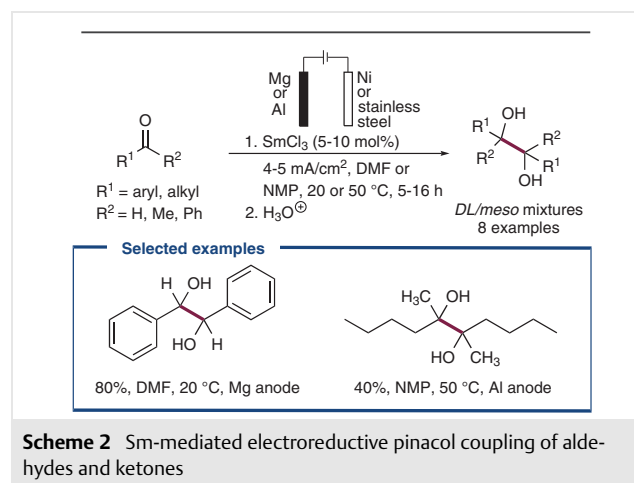
complex after coupling of two ketyl radical ions. A trans-metalation event with metal ions formed by dissolution of the anode was hypothesized to release the Sm(III) complex and enable turnover upon electrochemical reduction. The electrochemical formation of the divalent Sm complex was supported by an experiment in which a solution of $SmCl_3$ solution was electrolyzed for 1.1 F, after which an excess of acetophenone was added and the corresponding pinacol product was isolated in stoichiometric amounts after 3 hours in the absence of electricity.

In 2012, Mellah and co-workers disclosed an electrochemical protocol for the preparation of samarium diiodide by direct oxidation of a samarium anode for application in various Sm(II)-mediated transformations, including pinacol coupling.[16] Electrolysis using a samarium anode in THF resulted in a blue colored solution around the electrode surface that, supported by cyclic voltammetry and UV/vis analysis, was interpreted as the anodic formation of SmI_2 with the iodide originating from the supporting electrolyte nBu$_4$NI. In addition, the tetrabutylammonium cation in the supporting electrolyte was claimed to serve as a sacrificial oxidant at the cathode, resulting in the formation of a neutral radical that decomposes to a butyl radical and tributylamine after C–N bond cleavage (Scheme 3, left). The alkyl radical was hypothesized to undergo further reduction to the corresponding carbanion, followed by protonation via Hofmann elimination of another tetrabutylammonium cation. Using a one-pot procedure, electrochemically formed

SmI_2 was used to mediate homocouplings of a minor selection of aromatic aldehydes, ketones and imines with yields of up to 96%.

In 2013, the Mellah group developed a fully catalytic Sm(III)/Sm(II) system for pinacol coupling.[17] Using an undivided cell setup, a screening of a variety of cathode materials indicated that samarium was optimal for clean reduction of SmI_3 to SmI_2. To probe the role of SmI_2, a set of reactions in the absence and presence of catalyst (10 mol%) and different additives was carried out for symmetric pinacol formation from benzaldehyde and cyclohexanone, respectively. While addition of SmI_2 resulted in a decrease in yield (from 36% to 22%) for the pinacol product of benzaldehyde, a yield increase was observed in the presence of the catalyst for the less reducible cyclohexanone (from 4% to 22%). The combination of SmI_2 and trimethylsilyl chloride (TMSCl) proved successful and boosted the yield to 83% and 59% for the aldehyde and ketone pinacol products, respectively. Mechanistically, it was hypothesized that this yield increase was the result of silyl chloride facilitating catalyst turnover by promoting cleavage of the Sm(III)–O bond in the pinacol product, as well as activating the surface of the Sm cathode. In contrast, addition of hexamethylphosphoramide (HMPA), a well-established additive in Sm-mediated transformations, reduced the yields significantly. Finally, a method for *in situ* generation of the SmI_2 catalyst was devised. Pre-electrolysis using a samarium anode in the absence of substrate and additives was carried out to form 10 mol% of SmI_2 *in*
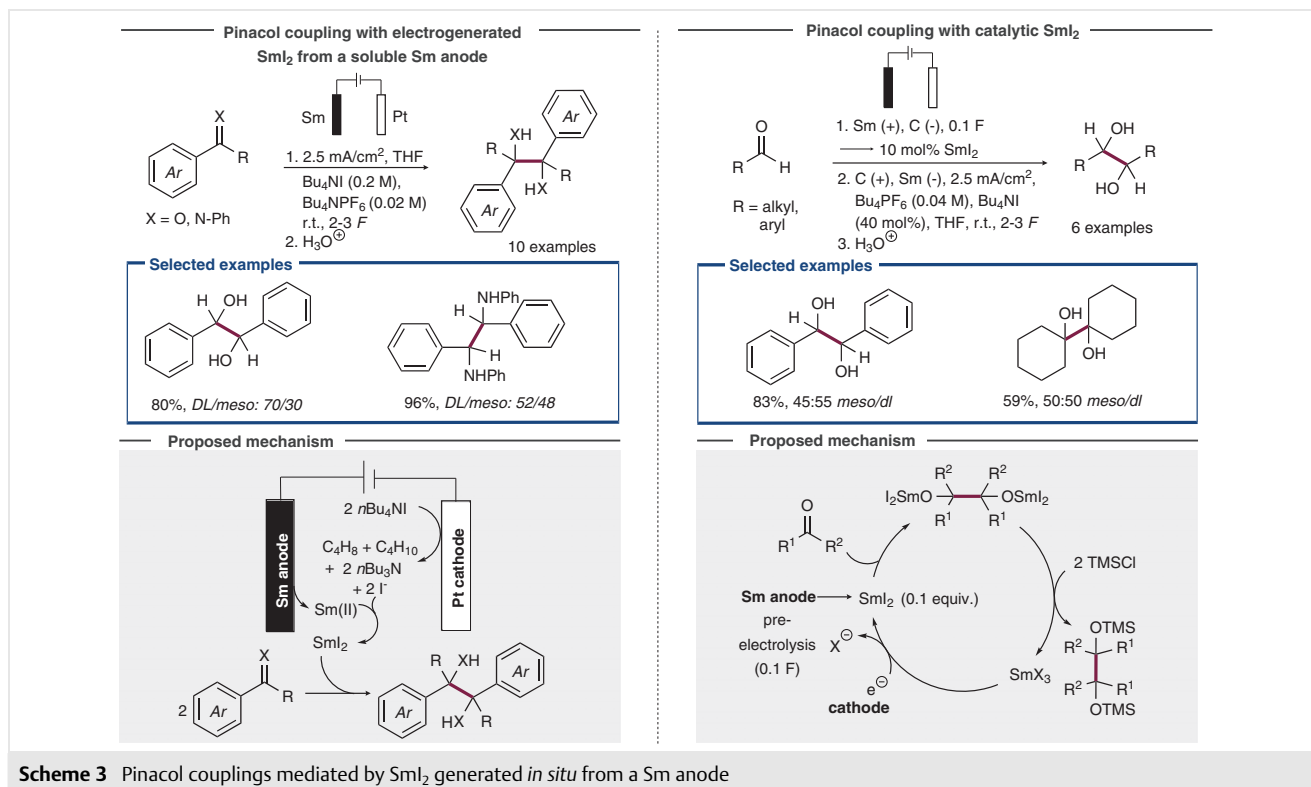
Scheme 3 Pinacol couplings mediated by SmI_2 generated *in situ* from a Sm anode

situ, after which a polarity switch was carried out and the carbonyl substrate and TMSCl were added. Using this protocol, a handful of symmetrical pinacol products was synthesized from benzaldehydes, acetophenone and cyclohexanone in yields of up to 83% (Scheme 3, right). Complementary to Mellah's approach, selective generation of SmI$_2$ from SmI$_3$ in a divided cell setup was reported by Nishibayashi and co-workers.[18]

Little and Parrish disclosed a protocol for the electrochemical generation of YbBr$_2$ from Yb(OTf)$_3$ and demonstrated its ability to mediate the reductive coupling of a dione via cyclic pinacol coupling in a divided cell under potentiostatic conditions (Scheme 4).[19] The method afforded the cyclic diol with complete diastereoselectivity for the *syn* isomer, in contrast to electrolysis in the absence of the Yb mediator that resulted in an isomeric mixture of the cyclic diol. Coordination of the metal ion between the two carbonyl units of the dione starting material was rationalized as the origin behind the observed selectivity enhancement. While the original protocol was carried out in acetonitrile, it was demonstrated that the addition of ethers had a positive effect on the electron-transfer kinetics of the Yb redox couple and enabled an exchange of cathode material from mercury to reticulated vitreous carbon.[20] Nevertheless, recycling of Yb(III) to Yb(II) in the pinacol reaction could not be achieved under these conditions, due to the stability of the alcoholate–Yb(III) complex, even in the presence of proton donors or trimethylsilyl bromide (TMSBr). Similarly, Andreu and Pletcher demonstrated that stoichiometric amounts of electrogenerated Yb(II) enabled stereoselective reductive cyclization of the same dione to give the *cis* isomer of the cyclic diol with the Yb(III) species being strongly bound to the product.[21] While release of the metal ion, and hence catalytic turnover, was enabled in this case by the use of an aluminum anode or by the addition of TMSBr, these modifications resulted in a decrease of the diastereomeric excess of the product diol.
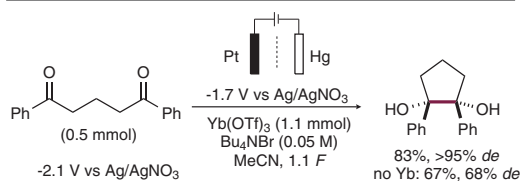
Scheme 4 Yb-mediated intramolecular pinacol formation

Furthermore, Little and Parrish studied the electrochemical generation of Sm(II) from trivalent precursor complexes and explored their effect on the electroreductive umpolung of Michael acceptors for subsequent intramolecular electrohydrocyclization.[19] In the case of Sm catalysis, SmI$_2$ was generated from Sm(OTf)$_3$ in a divided cell and was demonstrated to set off a cyclization event at a potential of −1.8 V vs SCE. Notably, this potential was nearly 1 V more

anodic compared to the potential required for the non-mediated transformation, thereby clearly demonstrating the benefit of the mediated route. On the same note, electroreductive Ln-mediated cyclizations were reported by the same group a few years later.[22] Under potentiostatic conditions in a divided H-type cell, the reductive transformation was carried out at −2.4 V vs SCE. It was demonstrated that the addition of Ln(III) salts improved the yields and enabled electrolysis at more anodic potentials in the case of Sm, or increased the diastereomeric selectivities in the case of Yb (Scheme 5). Similar to the mechanistic rationale for electroreductive dimerization of esters and intramolecular reductive pinacol formation of diones,[19,23] it was proposed that coordination of the Lewis acidic Yb ion to the two Lewis basic oxygen atoms results in a 6-membered transition state that favors the *trans* diastereomer of the cyclized product. Similarly, the presence of CeCl$_3$ or Mg(ClO$_4$)$_2$ resulted in increased diastereoselectivities and yields for the intramolecular electrohydrocyclization of a few substrates.
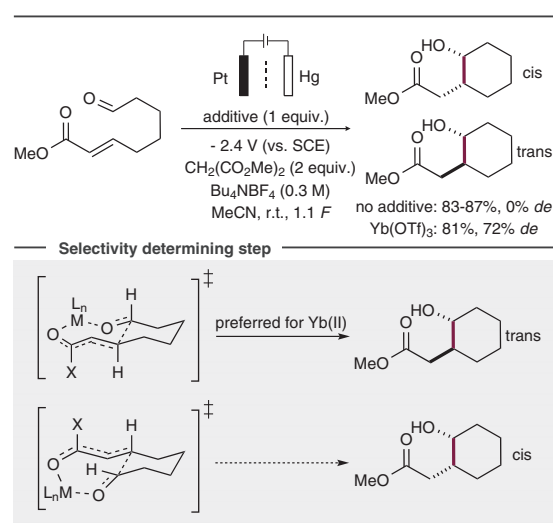

Scheme 5 Ln-mediated electroreductive umpolung with subsequent intramolecular cyclization

2.3 Esters and Phthalimides

In 1991, Périchon and co-workers disclosed a protocol for the selective electrochemical Sm-catalyzed dimerization of aromatic esters to give 1,2-diketone products.[23] As such, the work showcased an alternative electroreductive transformation of esters compared to the Bouveault–Blanc reaction (acyl C–O bond cleavage) and the Markó–Lam reaction (carboxyl C–O bond cleavage).[24] The electrochemical reactions were carried out in an undivided cell equipped with a sacrificial magnesium anode and a nickel foam cathode with SmCl$_3$ (10 mol%) at 20 °C under an argon atmosphere (Scheme 6). Using standard conditions, phenyl benzoate was converted into the corresponding 1,2-diketone in

85% yield, whereas arene substrates possessing fluoride or nitrile substituents resulted in yields of 55% and 50%, respectively. Aromatic chlorides and bromides were reductively removed prior to the formation of coupling products and aliphatic substrates were unreactive under the conditions applied. No product was observed in the absence of current or the Sm catalyst. Interestingly, stoichiometric SmI$_2$ did not afford the desired product. Likewise, and in contrast to the pinacol work by the same authors,[15] stoichiometric electroreduction of the SmCl$_3$ complex followed by addition of the benchmark ester methyl benzoate in the absence of current did not afford the product. Instead, it was hypothesized that the oxophilic Sm(III) catalyst facilitates reductive coupling by coordinating the oxyanions of two ketyl radical intermediates. Transmetalation with Mg(II) ions from the sacrificial anode was argued to liberate the Sm(III) catalyst to afford the 1,2-diketone products upon acidic hydrolysis.

**Scheme 6** Sm-catalyzed dimerization of benzoic esters
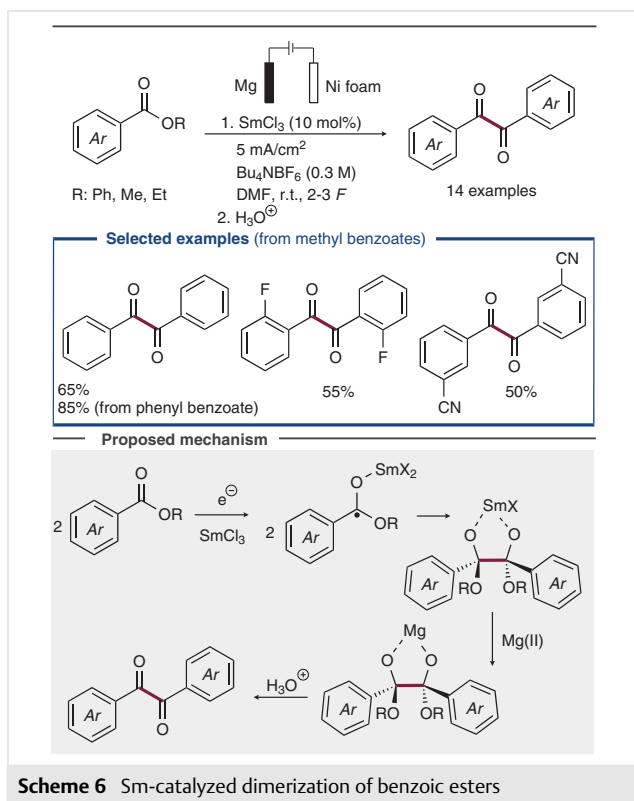
The following year, similar conditions were used by the same group for the Sm-catalyzed cyanomethylation of esters using acetonitrile as the solvent (Scheme 7).[25] Here, acetonitrile was electrochemically reduced to the stabilized anion and reacted with esters to form 1,3-ketonitriles in good yields. The addition of *t*BuOH was found to improve the yield of the benchmark product benzoylacetonitrile from 42% to 65%, and it was hypothesized that the alcohol acts as a precursor to an *in situ* formed magnesium alkoxide

that effectively deprotonates the nitrile substrate. Less than 10% of the product formed in the absence of the Sm catalyst, and it was proposed that the higher yield in its presence was due to its ability to activate the ester in either di- or trivalent form. The reaction could be performed with an excess of the nitrile substrate in DMF as the solvent to furnish the target products in isolated yields of up to 90%. While both aromatic and aliphatic esters could successfully undergo the transformation, the only non-alkyl substituents reported to survive the reaction conditions were aromatic fluorides and methoxy groups.


Scheme 7 Sm-catalyzed cyanomethylation of methyl esters and nitriles
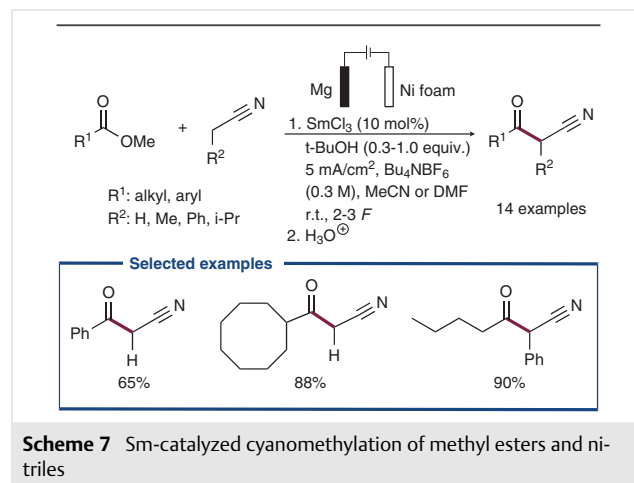
In addition to the limited number of Sm-catalyzed deallylations of allyl esters to the corresponding carboxylic acids reported by Périchon,[14] in 2002, Ishifune and co-workers showed that reduction of challenging aliphatic esters with low reduction potentials (ca. –3 V vs SCE) proceeded smoothly in the presence of catalytic amounts of metal catalysts, including SmCl$_3$, YbCl$_3$ and EuCl$_3$.[26] The transformation was carried out under galvanostatic conditions as a paired electrolysis with cathodic reduction of aliphatic esters to alkoxides and concomitant anodic oxidation of the THF solvent to furnish alkoxytetrahydrofuran derivatives as products (Scheme 8). To prevent cathode passivation, the reaction was carried out under ultrasound irradiation (47 kHz). For the benchmark substrate, methyl heptanoate, the acetal product was obtained in 60% yield by using 10 mol% of the Sm complex, whereas a decrease in catalyst loading to 1 mol% resulted in a significant drop in yield (37%). In contrast, the presence of 1 mol% of EuCl$_3$ or YbCl$_3$ resulted in yields of 50% and 72%, respectively. The use of Mg$_2$(ClO$_4$)$_2$ as a supporting electrolyte and potential mediator resulted in the formation of the desired product in a mere 11% yield, whereas Mg porphyrin complexes proved more successful with yields of up to 81%. While no mechanistic details were disclosed, it was hypothesized that electrogenerated low-valent metal species, such as Mg(0), Ln(II), or Ln(0), were acting as electron mediators in the transformation.

Scheme 8 Catalytic paired electrolysis of aliphatic esters to give acetals
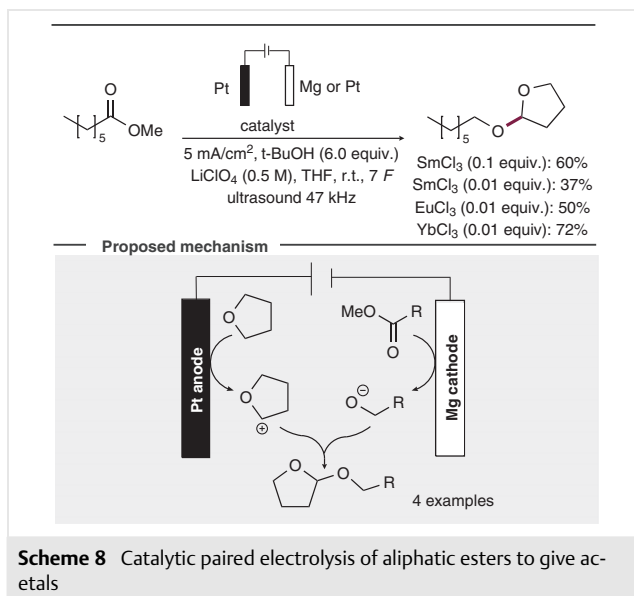
Recently, Zhang and Mellah explored the Sm(II)-catalyzed electroreductive alkoxylation of N-alkyl phthalimides with a variety of alcohols using catalytic amounts of SmCl$_3$ and non-sacrificial electrodes.[27] With an electrogenerated Sm(II) catalyst in the presence of TMSCl, more than 40 examples of N-substituted 3-alkoxyisoindolin-1-ones were isolated in yields of up to 98%, with functional groups such as alkenes, alkynes, alkyl and aryl bromides, nitriles, esters, amides, acetals and free and silyl-protected alcohols being tolerated under the reaction conditions (Scheme 9). Mechanistically, it was proposed that the Sm(II) catalyst mediates a single-electron reduction of one of the phthalimide carbonyls to give the corresponding ketyl anion radical that is trapped by TMSCl. A second mediated single-electron reduction results in a carbanion that is protonated by an alcohol. Displacement of a silyloxy anion, aided by the neighboring nitrogen lone pair, results in the formation of a stabilized carbocation that is intercepted by an alkoxide to furnish the product. Similar phthalimide reduction in the presence of TMSCl has previously been reported for intramolecular cyclization with carbonyls on the N-alkyl side chain under chemical SmI$_2$-mediated conditions as well as electrochemical conditions.[28]

3   Compounds Containing Nitrogen–Oxygen Bonds

Electrochemical reduction of N–O bonds in nitro groups is a powerful strategy to form a variety of organic nitrogen-containing building blocks and catalysis can enable more selective transformations.[29,30] In the context of Sm catalysis, the Mellah group disclosed a protocol for the electrosynthe-

Scheme 9 Sm-catalyzed electroreductive alkoxylation of phthalimides
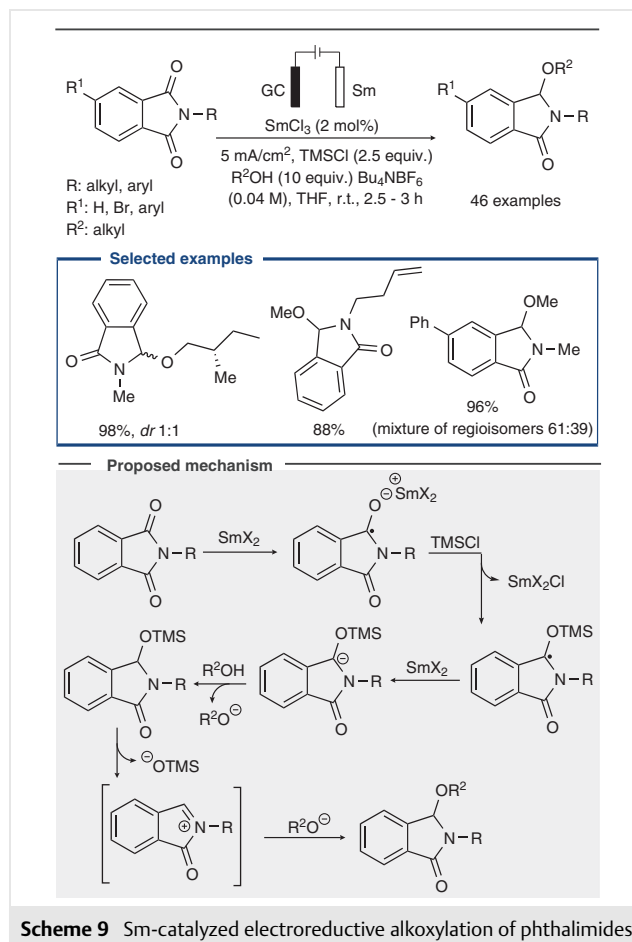
sis of azobenzenes from nitrobenzenes (Scheme 10).[31] Similar to the pinacol coupling protocol by the same group,[17] catalytic formation of SmI$_2$ was accomplished by galvanostatic electrolysis with a sacrificial samarium anode in the presence of 1.5 equivalents of Bu$_4$NI as the iodide source. A polarity switch along with the addition of the nitrobenzene substrate and 1.5 equivalents of TMSCl resulted in the formation of symmetric azobenzenes in yields of up to 95% with a functional group tolerance encompassing halides (Br, Cl, F), ethers, esters, cyano groups and anilines. Similar yields of unsymmetrical azo compounds could be obtained by electrolysis of a mixture of nitrobenzenes (ratio 1:3). Nitrobenzenes bearing electron-withdrawing groups underwent homocoupling more slowly than those bearing electron-donating groups, effectively resulting in the need for an excess of the less-electron-rich nitrobenzene for obtaining satisfactory yields of the desired unsymmetrical products. Mechanistically, the Sm-catalyzed process was proposed to proceed via initial reduction of the nitrobenzene to nitrosobenzene, followed by rapid dimerization to the azoxybenzene and final reduction to the azobenzene product.

Scheme 10 Sm-catalyzed electrochemical formation of azobenzenes from nitroarenes
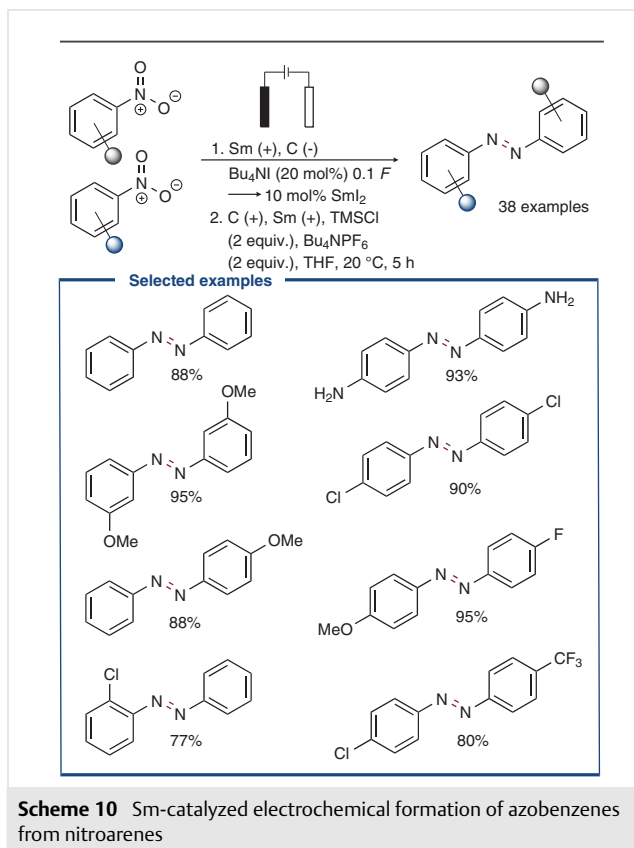
4 Compounds Containing Carbon–Halide Bonds

Reductive dissociative electron transfer of alkyl and aryl halides to afford carbon-centered radicals is a classic strategy that is utilized in, for example, dehalogenation of complex organic molecules and cross-electrophile coupling (XEC) reactions in chemical, photochemical and electrochemical settings.[32] In the context of lanthanides, it is well-established that divalent reagents based on, for example, samarium can furnish hydrodehalogenated products from a variety of alkyl and aryl halides.[3] Mellah and Sun studied the properties of electrochemically formed SmCl$_2$, SmBr$_2$ and Sm(OTf)$_2$.[33] While the redox potential of the Ln(II) complexes were found to become more negative in the order OTf < I < Br < Cl, with SmCl$_2$ having the most negative reduction potential, all electrochemically formed complexes were competent in mediating the reductive dechlorination of 1-chlorododecane to give the corresponding alkane in yields of around 80% in the absence of current.

Electroreductive hydrodehalogenation of aromatic and aliphatic organic halides to give the corresponding hydrocarbons was reported using Sm catalysis by Périchon and co-workers in 1991 (Scheme 11, top left).[34] The reaction was performed in an undivided cell using a magnesium sacrificial anode and a nickel foam cathode in the presence of 10 mol% of SmCl$_3$. The method worked well for aryl bromides and chlorides, furnishing the corresponding hydrodehalogenated arenes in up to quantitative yields, while the single example using aliphatic 1-bromodecane resulted in the dehalogenated product n-decane in 70% yield. Dehalogenation of the benzylic CF$_3$ group in (1,1,1)-trifluoromethylbenzene was accomplished in around 80% conversion to give a mixture of defluorinated toluene products, representing one of the few examples of C–F bond cleavage under electrochemical conditions.[35] As demonstrated in a control experiment, the Sm catalyst enabled a switch in product selectivity for the reduction of (2-halophenyl)allyl ethers. While reduction of (2-bromophenyl)allyl ether and (2-chlorophenyl)allyl ether in the absence of the Sm(III) complex resulted in the dehalogenated open-chain product with only a trace amount of the cyclized product, the addition of SmCl$_3$ resulted in 3-methyl-2,3-dihydrobenzofuran in 80% yield. This cyclization was attributed to a radical mechanism induced by the samarium complex that was hypothesized to undergo continuous electrochemical reduction to a catalytically active divalent species. However, as pointed out by the authors, the presence of the samarium complex did not favor radical intermediates in the electrolysis of 6-bromohex-1-ene, and no further support concerning the radical or anionic nature of intermediates was presented.

Electroreductive cross-coupling of 3-chloroesters with carbonyl compounds to furnish lactone products in the presence of a catalytic amount of SmCl$_3$ (10 mol%) was reported by Périchon and co-workers in 1993.[36] This procedure resulted in spirolactonization products in yields of up to 76% and thus outperformed the chemical Sm(II)-promoted protocol with yields of around 30% (Scheme 11, top right).[37] While both aliphatic and benzylic ketones were tolerated, the former resulted in slightly lower yields of the lactone product. In the absence of the Sm catalyst, electrode passivation, by-product formation and lower product yields were observed, whereas no reaction took place in the absence of current. The same electrochemical conditions were successfully extended to the reductive Barbier-type allylation of ketones with allyl chlorides to furnish homoallylic alcohols in up to 74% yield (Scheme 11, middle left).[38] While the addition of Sm(III) had no influence on the selectivity of the reaction, its presence resulted in increased yields of the desired products. Similar electrochemical Barbier-type allylations of aldehydes, ketones and aldimines with allyl iodide were demonstrated by Mellah and co-workers under stoichiometric and catalytic conditions. They used *in situ* generated SmI$_2$ from a soluble samarium anode to furnish homoallyl alcohol products in yields of up to 80% (Scheme 11, middle right).[16,17]

Mellah and co-workers extended their protocol for electrochemical *in situ* formation of Sm(II) reagents from soluble samarium anodes to the reductive carboxylation of aryl halides (Scheme 11, bottom left).[39] The reaction was
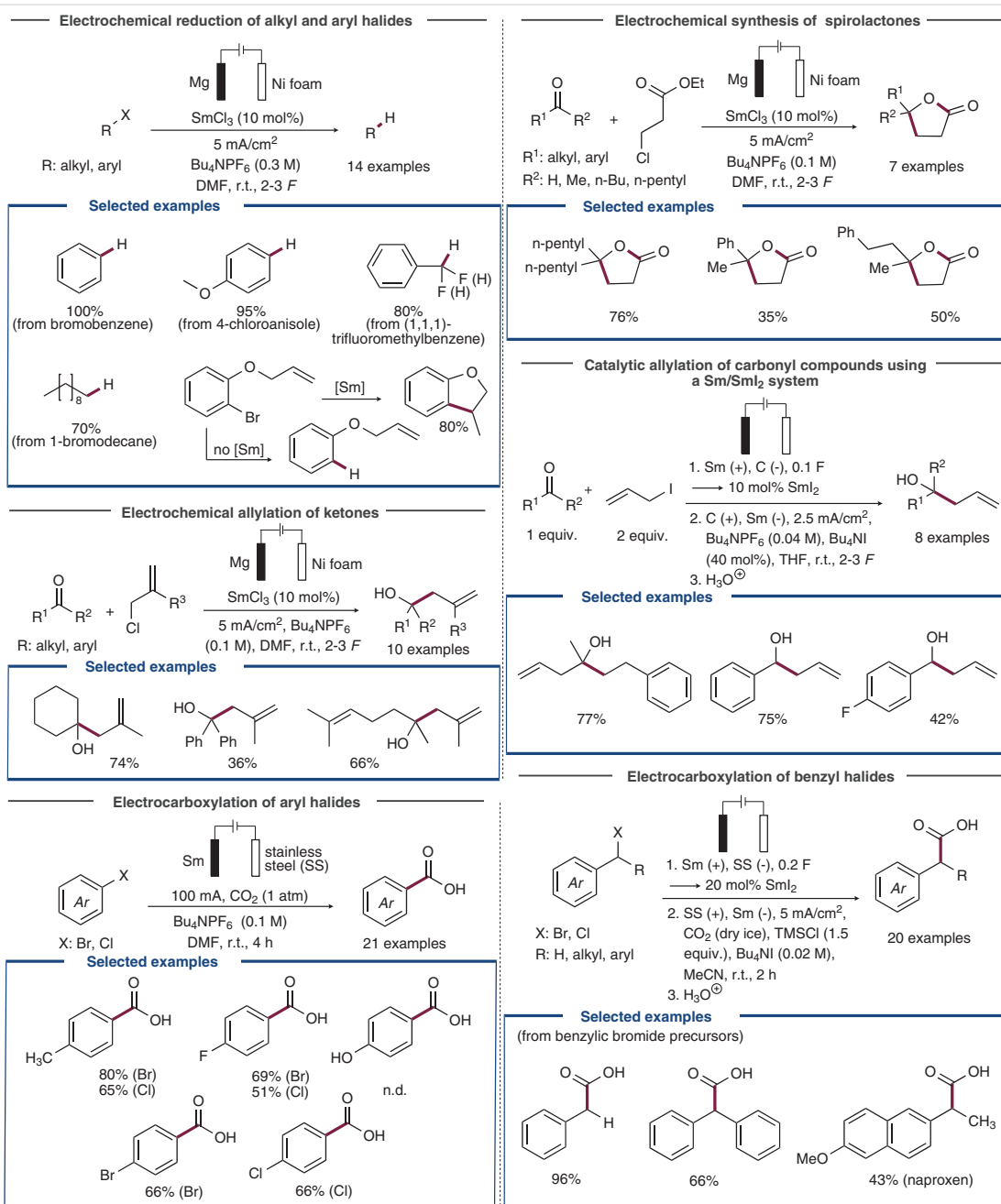
Scheme 11 Electroreductive dehalogenative Sm-catalyzed transformations

smoothly carried out using various aryl bromides and chlorides in yields of up to 80% by continuous bubbling of CO_2 through the reaction mixture in an undivided cell. It was found that free phenols inhibited the reaction, which was rationalized as the result of deactivating O-coordination to the catalyst. Dihalogenated arenes were selectively monocarboxylated in 66% yields from 1,4-dichlorobenzene and 1,4-dibromobenzene. Reducible functionalities such as es-

ters, benzylic trifluoromethyl groups and aryl fluorides were tolerated under the reaction conditions, as were S-heterocycles, whereas N-heterocycles failed to form the desired carboxylated products. On a similar note, a protocol for Sm-catalyzed electrocarboxylation of benzyl halides was disclosed by the same group (Scheme 11, bottom right).[40] This reaction used electrogenerated SmI_2 and dry ice as the CO_2 source to furnish aryl acetic acid derivatives

in yields of up to 96%, with similar functional group tolerance to that of aryl halide carboxylation.[39] Reductive Ln-mediated protocols for CO_2 capture have previously been reported under chemical and photochemical conditions.[41]

5   Conclusions

While low-valent lanthanide reagents have been used for decades for mediation of organic transformations, their use in an electrosynthetic settings remains limited. Considering their tunability and the chemo-, regio- and stereoselectivities that can be obtained by using lanthanide reagents, their potential for resource-efficient catalytic transformations by electrochemical (re)generation is substantial. While the chemical generation of redox-active lanthanide reagents is limited by the potential of the reductant and the stability of the formed species, electrochemical *in situ* generation at a set potential is likely to offer new opportunities for novel reagents with unusual redox potentials. In turn, the chemical affinity of such reagents may open new synthetic avenues via inner-sphere mechanisms. With the contemporary interest in electrochemically driven metal-mediated redox catalysis, further developments in the field from both synthetic and mechanistic perspectives are anticipated.[42]

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