

Supporting Information

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

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1. Materials and General Procedures

THF was distilled from sodium metal/benzophenone before use. All commercially available chemicals were used without purification. ^1H NMR and ^{13}C NMR spectra were recorded on either a Bruker AM 360 (360 MHz), AM 300 (300 MHz), or AM 250 (250 MHz) instrument with samples dissolved in CDCl_3 . Mass spectra were recorded on a microTOF-q Bruker Daltonics spectrometer. UV/Vis spectroscopy experiments were performed on a VARIAN CARY 300 Bio UV-visible spectrophotometer controlled by Cary WinUV (version 4.10) software. The gas chromatography (GC) were performed on a spectrometer Varian GC-430 (injection: split/splitless, FID detector, column VF1-MS: 15m x 0.25 mm x 0.25 microns, program: 1 min 50°C, 10°C/min to 250°C, 250°C 2min, 23min total). Electrolysis were performed with a AUTOLAB potentiostat/galvanostat (model: PGSTAT302N), in an undivided three-electrodes cell containing samarium rod working electrode, a standard glassy carbon counter electrode and a saturated calomel electrode (SCE) as reference.

The chemical SmI_2 is prepared using Kagan's method. The dark blue solution obtained is used at the concentration of 0.1mol/L in SmI_2 .

2. Samarium electrode

The samarium electrode used is based on a samarium rod of 12.7mm (0.5in) diameter, directly connected to a copper wire to ensure current conductivity. This self-made electrode is stored under inert atmosphere when it is not used. All the samarium rods are purchased from Alfa Aesar (99.9% metals basis excluding Ta).

3. Screening of cathode for trivalent samarium salts reduction

3.1 Synthesis of trivalent samarium salts

SmI_3 was prepared by the reaction of SmI_2 with 0.5 equiv. of iodine in THF.

SmCl_2 was synthesized by the reaction of SmI_2 with 1 equiv. of benzyl chloride in THF.

The yellow suspensions obtained were used immediately after their synthesis. The

concentration of trivalent samarium in the suspension was not determined in this experiment.

3.2 Size of electrodes for the screening of cathode

Platinum gauze: 3.5cm height, 1.5cm diameter, surface area \approx 16.5cm²

Glassy carbon: 3cm height, 1.6cm width, 0.3cm thickness, surface area= 11.9cm²

Lead piece: 3.5cm height, 0.8cm width, 0.4cm thickness, surface area= 8.7cm²

Nickel foil: 4.1cm height, 1.7cm width, surface area \approx 13.9cm²

Stainless steel: 4.3cm height, 1.65cm width, mesh 37% opened surface, surface area \approx 3.1 cm²

Samarium rod: 1.27 cm diameter, 5cm height, surface area=20.0cm²

3.3 Procedure for trivalent samarium electrochemical reduction

In an undivided three electrodes cell equipped with vitreous carbon anode (20 cm² area), a cathode of material M (M=Pt, glassy carbon, Pb, Ni, SS, Sm), a saturated calomel electrode (SCE) as reference and containing a magnetic stirring bar, was introduced 0.04M of *n*Bu₄NPF₆ in anhydrous THF and the trivalent samarium salts as suspension in 4mL electrolyte solution. The solution was flushed with argon before and during the electrolysis performed at 25mA. After the electrolysis, the resulting solution was directly analyzed by UV-visible spectrophotometry and cyclic voltammetry.

4. UV-vis analysis of SmI₂ solutions

Classical chemical SmI₂ solution and the electrochemical ones prepared by the reduction of SmI₃ and SmCl₂ were analyzed by UV-Vis spectroscopy using a VARIAN CARY 300 Bio UV-visible spectrophotometer controlled by Cary WinUV (version 4.10) software. All the spectrums are recorded between 800nm and 380nm under double beam mode with a tube containing 0.04M *n*Bu₄NPF₆/THF solution as blank. The scan rate was 600nm/min. Data interval was 1nm.

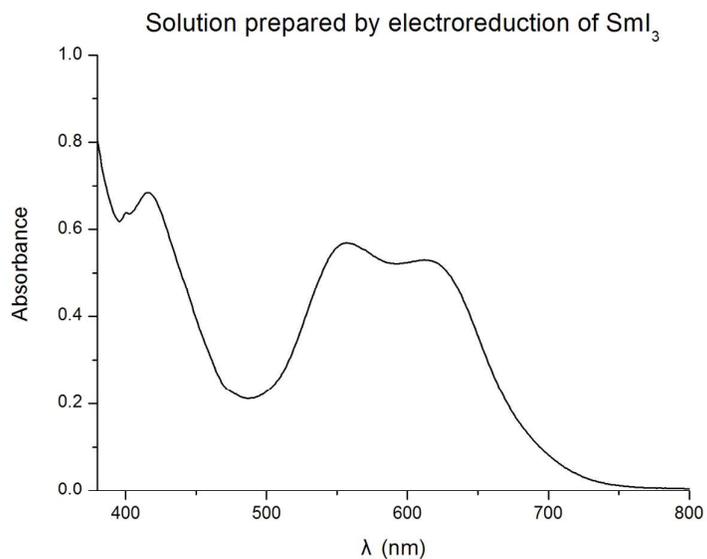


Figure S1: UV-vis spectrum of SmI_2 solution prepared by electroreduction of SmI_3 at samarium cathode

The concentration of SmI_2 in the solution was estimated about 10mmol/L in the presence of the suspension of SmI_3 and $n\text{Bu}_4\text{NPF}_6$ as supporting electrolyte. λ_{max} is found at 612nm and 557nm.

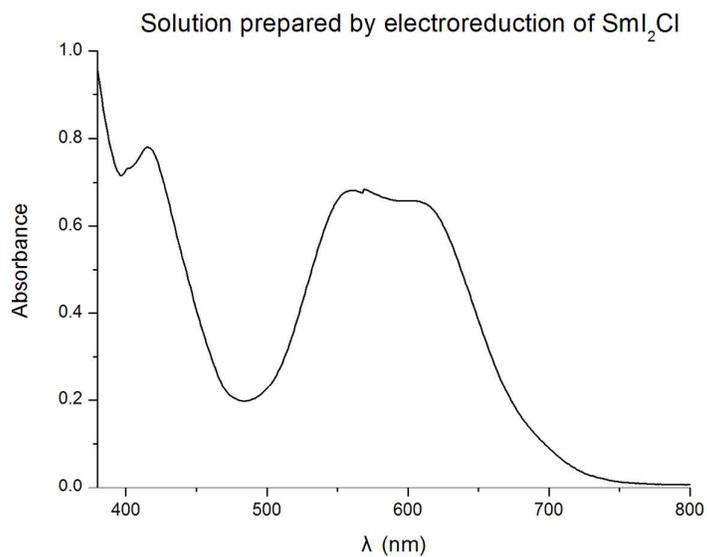


Figure S2: UV-vis spectrum of SmI_2 solution prepared by electroreduction of SmI_2Cl at samarium cathode

The concentration of SmI_2 in the solution was estimated about 10mmol/L in the presence of the suspension of SmI_2Cl and $n\text{Bu}_4\text{NPF}_6$ as supporting electrolyte. λ_{max} is found at 603nm and 562nm.

Chemical SmI_2 solution is prepared using Kagan's method and then diluted in the solution of 0.04M $n\text{Bu}_4\text{NPF}_6/\text{THF}$ in a UV tube.

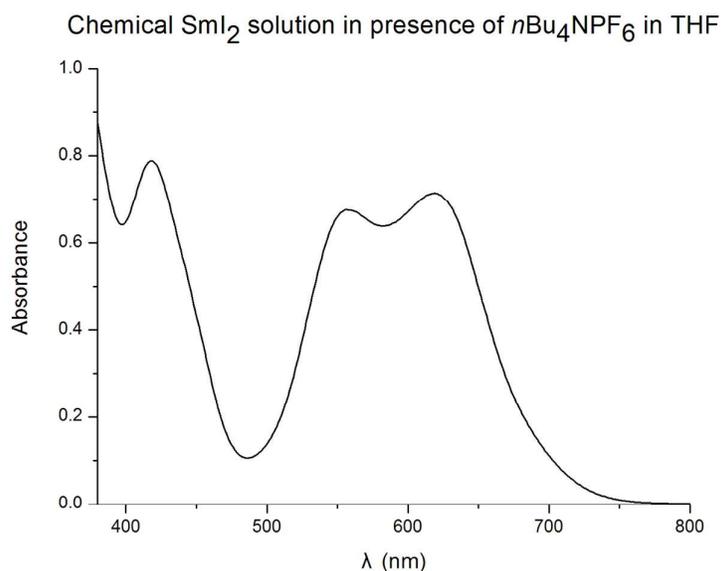


Figure S3: UV-vis spectrum of SmI_2 solution chemically prepared

The concentration of SmI_2 in the solution was estimated about 10mmol/L with $n\text{Bu}_4\text{NPF}_6$ as supporting electrolyte. λ_{max} is found at 619nm and 559nm.

5. Cyclic voltammogram of electrogenerated SmI_2

The redox potential of SmI_2 was measured by using cyclic voltammetry, employing an AUTOLAB potentiostat/galvanostat (model: PGSTAT302N). The working electrode was a glassy carbon electrode ($\Phi = 2\text{mm}$). The electrode was polished before use. The auxiliary electrode was a platinum grid, and the reference electrode was a saturated calomel electrode. The scan rate for the experiment was $100\text{mV}\cdot\text{s}^{-1}$, the scan potential is between -2.1V and 0V versus SCE. The supporting electrolyte used was $n\text{Bu}_4\text{NPF}_6$ at the concentration of 0.04mmol/L.

The solution was prepared *in situ*, as described in 3.3 using a cathode of samarium ($\Phi = 12.7\text{mm}$, height=5cm), before electrochemical analysis.

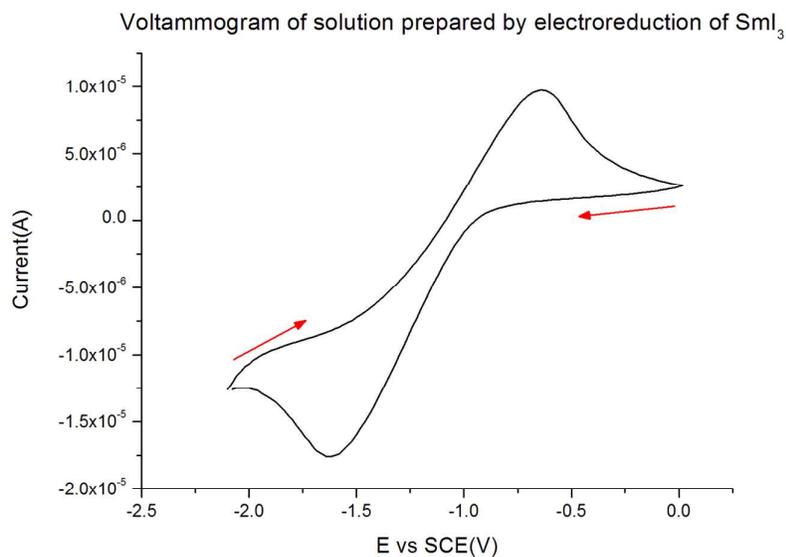


Figure S4: Cyclic voltammogram of SmI_2 solution prepared by electroreduction of SmI_3 at samarium cathode

The concentration of SmI_2 in the solution was estimated about 10mmol/L in the presence of the suspension of SmI_3 . This curve shows a reversible redox couple $\text{Sm}^{3+}/\text{Sm}^{2+}$, $E_{pc} = -1.63\text{V}$ vs SCE, $E_{pa} = -0.64\text{V}$ vs SCE, $E(\text{Sm}^{3+}/\text{Sm}^{2+}) = 1/2(E_{pc} + E_{pa}) = -1.14\text{V}$ vs SCE.

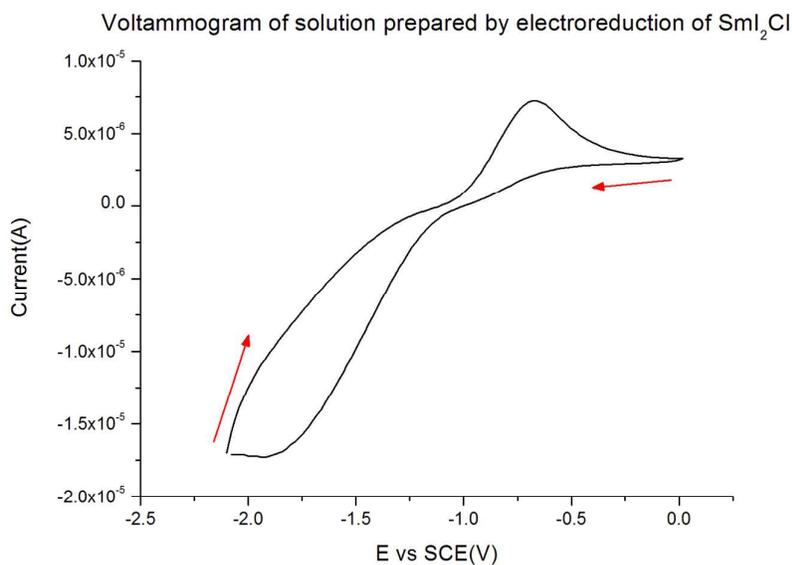


Figure S5: Cyclic voltammogram of SmI_2 solution prepared by electroreduction of SmI_2Cl at samarium cathode

The concentration of SmI_2 in the solution was estimated about 10mmol/L in the

presence of the suspension of SmI_2Cl , Cl^- may cause the shift of the redox potential. This curve shows a reversible redox couple $\text{Sm}^{3+}/\text{Sm}^{2+}$, $E_{\text{pc}}=-1.93\text{V}$ vs SCE, $E_{\text{pa}}=-0.66\text{V}$ vs SCE, $E(\text{Sm}^{3+}/\text{Sm}^{2+}) = 1/2(E_{\text{pc}}+E_{\text{pa}}) = -1.30\text{V}$ vs SCE.

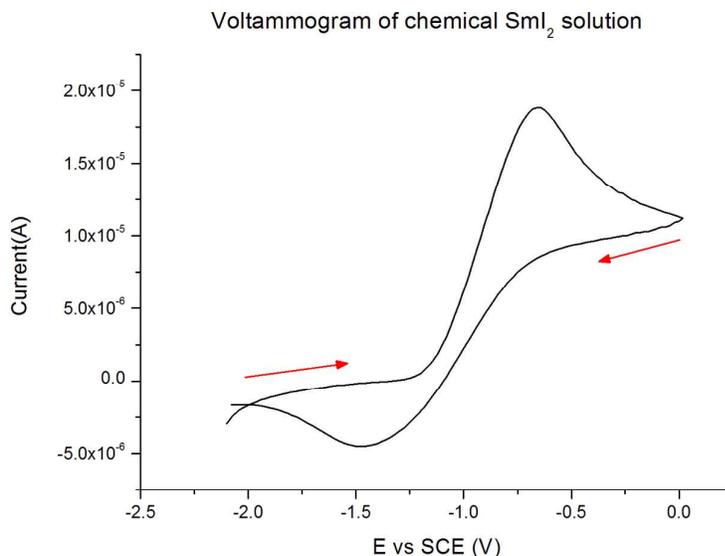


Figure S6: Cyclic voltammogram of SmI_2 solution chemically prepared

The concentration of SmI_2 in the solution was estimated about 20mmol/L without any additive. This curve shows a reversible redox couple $\text{Sm}^{3+}/\text{Sm}^{2+}$, $E_{\text{pc}}=-1.48\text{V}$ vs SCE, $E_{\text{pa}}=-0.65\text{V}$ vs SCE, $E(\text{Sm}^{3+}/\text{Sm}^{2+}) = 1/2(E_{\text{pc}}+E_{\text{pa}}) = -1.07\text{V}$ vs SCE.

6. Additional experiments for the origin of pinacolisation

An undivided three electrodes cell contain a vitreous carbon anode (20 cm^2 area) a cathode of samarium and a saturated calomel electrode (SCE) as reference. The cell, containing a magnetic stirring bar, was stored in a dry atmosphere and flushed with argon before the electrochemical experiments.

Tetrabutylammonium hexafluorophosphate was employed as supporting electrolyte at concentration of 0.04M in 30mL anhydrous THF. 2mmol of benzaldehyde (substrate A) or cyclohexanone (substrate B) was introduced to the cell.

The chosen additives are:

- Chemical SmI_2 solution 10mol% (0.2mmol, 2mL)

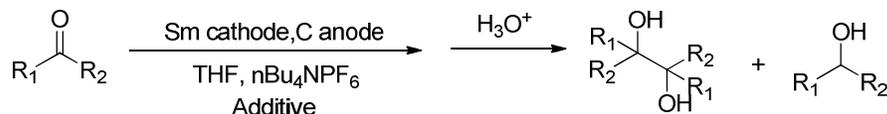
- Trimethylsilyl chloride (3mmol) was diluted in 4mL electrolyte solution (0.04M $n\text{Bu}_4\text{NPF}_6$ in THF) and this mixture was added drop wise to the cell during 3 hours

electrolysis.

-HMPA 0.4mmol (that is 4equiv. to SmI₂)

The electrolysis was performed at 25mA for 3 hours. After the electrolysis, the mixture was quenched with HCl(0.1M) and extracted with ether (3×20mL). The combined extracts were washed with sodium thiosulfate and brine. The organic layer was dried over MgSO₄ and the crude solution is analyzed by gas chromatography.

Table S1: Additional experiments to identify the mechanism of pinacolisation



1 : R₁=Ph, R₂=H

2 : R₁,R₂=(CH₂)₅-

3 : R₁=*p*-Me-Ph, R₂=H

4 : R₁=*p*-MeO-Ph, R₂=H

5 : R₁=*p*-F-Ph, R₂=H

Entry	Substrate	Additive	Current density, mA.cm ⁻²	GC conversion ^[a] %	Pinacol yield ^[b] %	Other by product ^[b] %
1	1	none	1.25	63	36	27
2	1	SmI ₂	1.25	73	22	51
3	1	TMSCl	1.25	93	70	23
4	1	TMSCl	0	62	45	17
5	1	SmI ₂ , TMSCl	1.25	93	83	10
6	1	SmI ₂ , TMSCl	0	83	25	58
7	1	SmI ₂ , TMSCl, HMPA	1.25	5	5	0
8	2	none	1.25	34	4	30
9	2	SmI ₂	1.25	33	22	11
10	2	TMSCl	1.25	2	0	2
11	2	SmI ₂ , TMSCl	1.25	99	59	40
12	2	SmI ₂ , TMSCl	0	2	2	0
13	2	SmI ₂ , TMSCl, HMPA	1.25	23	5	18
14	3	none	1.25	17	13	4
15	3	TMSCl	1.25	95	16	79
16	4	none	1.25	15	9	6
17	4	TMSCl	1.25	90	15	75
18	5	TMSCl	1.25	97	11	86

[a] Conversion determined by gas chromatography using undecane as internal standard relative to the substrate engaged. [b] Yield

7. General catalytic procedure

7.1 General procedure for aldehydes and ketones homocoupling

Under argon, reactions were carried out in a one compartment cell containing a magnetic stirring bar, samarium anode (20 cm² area), glassy carbon cathode (20 cm²

area) and SCE as reference electrode. The cell is then charged with 30mL of electrolyte solution containing 0.04M $n\text{Bu}_4\text{NPF}_6$ in degassed anhydrous THF and $n\text{Bu}_4\text{NI}$ (1.6 mmol) as the source of iodide. The pre-electrolysis was performed at $i = 50\text{mA}$ during 2200 seconds (time estimated for generating 0.4mmol SmI_2). After the pre-electrolysis a dark blue solution was observed and corresponding carbonyl substrates (4mmol) was then added in the mixture. The polarity of electrodes is then reversed, that means, samarium rod act as cathode and glassy carbon as anode. Trimethylsilyl chloride (6mmol) was diluted in 4mL electrolyte solution and this mixture was added drop wise by a syringe pump into the cell during the electrolysis which was performed at $i = 50\text{mA}$ during 3 hours. The mixture was then quenched with HCl (0.1M) and extracted with ether ($3 \times 20\text{mL}$). The combined extracts were washed with sodium thiosulfate and brine. The organic layer was dried over MgSO_4 and the solvent was removed under reduced pressure. The conversion of the departure substrate is analyzed by gas chromatography. The crude product was purified by flash chromatography on silica gel. The resulting compounds were identified by comparison of their physical and spectral data with those given in the literature.

7.2 General procedure for Barbier type “allylation” reaction

Under argon, reactions were carried out in a one compartment cell containing a magnetic stirring bar, samarium anode (20 cm^2 area), glassy carbon cathode (20 cm^2 area) and SCE as reference electrode. The cell is then charged with 30mL of electrolyte solution containing 0.04M $n\text{Bu}_4\text{NPF}_6$ in degassed anhydrous THF and $n\text{Bu}_4\text{NI}$ (1.6 mmol) as the source of iodide. The pre-electrolysis was performed at $i = 50\text{mA}$ during 2200 seconds (time estimated for generating 0.4mmol SmI_2). After the pre-electrolysis a dark blue solution was observed and corresponding carbonyl substrates (2mmol) and allyl iodide (4mmol) were then added in the mixture. The polarity of electrodes is then reversed, that means, samarium rod act as cathode and glassy carbon as anode. Trimethylsilyl chloride (3mmol) was diluted in 4mL electrolyte solution and this mixture was added drop wise by a syringe pump into the cell during the electrolysis which was performed at $i = 50\text{mA}$ during 3 hours. The mixture was then quenched with HCl (0.1M) and extracted with ether ($3 \times 20\text{mL}$). The combined extracts were washed with sodium thiosulfate and brine. The organic layer was dried over MgSO_4 and the solvent was removed under reduced pressure. The conversion of the departure substrate is analyzed by gas chromatography. The crude product was purified by flash chromatography on silica gel. The resulting compounds were identified by comparison of their physical and spectral data with those given in the literature.