



Cobalt-Salen Catalyzed Electroreductive Alkylation of Activated Olefins

Sylvie Condon, Céline Cannes, Fethi Bedioui

► To cite this version:

Sylvie Condon, Céline Cannes, Fethi Bedioui. Cobalt-Salen Catalyzed Electroreductive Alkylation of Activated Olefins. *Journal of Chemistry* , 2019, 2019, pp.9832639. 10.1155/2019/9832639 . hal-03021617

HAL Id: hal-03021617

<https://hal.science/hal-03021617>

Submitted on 24 Nov 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Research Article

Cobalt-Salen Catalyzed Electroreductive Alkylation of Activated Olefins

Sylvie Condon ¹, Céline Cannes ² and Fethi Bedioui³

¹Institut de Chimie et des Matériaux Paris-Est (UMR 7182), CNRS, UPEC, Université Paris-Est, Equipe Electrochimie et Synthèse Organique, 2 Rue Henri Dunant, 94320 Thiais, France

²Institut de Physique Nucléaire, CNRS, Université Paris Saclay, 91406 Orsay Cedex, France

³Chimie ParisTech - PSL Research University, CNRS 2027, Institute of Chemistry for Life and Health Sciences (i-CLeHS), 75005 Paris, France

Correspondence should be addressed to Sylvie Condon; condon@icmpe.cnrs.fr and Céline Cannes; cannes@ipno.in2p3.fr

Received 8 December 2018; Revised 7 January 2019; Accepted 16 January 2019; Published 17 February 2019

Academic Editor: Hideto Miyabe

Copyright © 2019 Sylvie Condon et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Cobalt-Salen mediated electroreductive and regioselective alkylation of electron deficient olefins is reported in one step in an undivided electrochemical cell, in the presence of an iron rod as sacrificial anode. Although the reactivity depends on the class of alkyl halides, the reported study offers a green and expeditious electrosynthetic route for Csp3-Csp3 bond formation in mild conditions. This study also confirms the possible formation of the heterobinuclear cobalt-Salen-iron complex previously reported as the effective catalyst.

1. Introduction

In the context of sustainable organic chemistry, electro-synthesis has gained a renewable interest because of its relevant green aspects [1–3]. This versatile process involves electrons as clean surrogates of dangerous, toxic, hazardous reductive or oxidative reagents. Furthermore, the possibility to generate *in situ* the active catalytic species, or the disposal of high valuable products in one step reaction pathway is on contemporary concerns. Various papers of our laboratory report the activation of aryl halides under cobalt or nickel catalysis for Csp2-Csp2 bond formation (biaryl access) [4–6] or Csp2-Csp3 bond formation (conjugate addition reaction) [7, 8] by using the sacrificial anode process [9]. However, less attention has been devoted to the Csp3-Csp3 bond formation. Some years ago, we have described the coupling of halogenated and pseudohalogenated glycerol carbonate with electron deficient olefins under nickel catalysis in greener solvent [10].

The most common method of alkylation of activated olefin is a multistep procedure requiring the preparation of

the alkylcopper reagent and then its reaction with the activated olefin [11]. This can be circumvented advantageously by activation of the alkyl halide by a transition metal complex and its further reaction with the electrophile. Such reactions can be carried out in one step procedure, in mild conditions. In most cases, the transition metal complex is reduced *in situ* either chemically, by Zn [12–14] or Mn [15], or electrochemically [16].

The conjugate addition reactions catalyzed by transition metal complexes involve mainly nickel [8, 17–19] or cobalt [7, 20–23] complexes or chromium compounds [24–26]. In the case of cobalt [20–23], the catalyst is generally coordinated to Schiff base ligands, such as the vitamin B₁₂ and cobaloximes, and the addition product is obtained with good yield in one step procedure. However, the reaction was generally conducted in a divided cell, by controlled potential electrolysis, and vitamin B₁₂ is an expensive catalyst [20–23]. Few models of vitamin B₁₂, such as N,N'-ethylenebis(salicylideneiminato)-cobalt (noted CoSalen), more simple and cheaper, have been then used as catalyst for the heterocoupling of organic halides and alkylation of alkyl

halides with activated olefins [23]. In most cases, the reactions were carried out in hexamethylphosphoramide or hexamethylphosphoramide/tetrahydrofuran, in a double compartment electrochemical cell, on a mercury pool cathode and with poor and unsatisfactory yields.

Thus, in the course of our work on the electrochemical activation of organic halides using the sacrificial anode process [9], we have found that alkylation of activated olefins can be carried out with a simple and cheap cobalt complex formed *in situ*. This allowed us to show that the combined use of cobalt-Salen (as catalyst) with the undivided electrochemical cell process offers substantial advantages in the reductive coupling of 2-bromooctane and methyl vinyl ketone (MVK) [27]. We report here a systematic study of some examples of reductive coupling of alkyl halides and activated olefins using cobalt complexes to assess the influence of the experimental parameters (ligand, solvent, temperature, and electrolysis conditions) in order to optimize the yield and to get a better insight into the electroassisted catalytic mechanism.

2. Experimental

All solvents and reagents were purchased from commercial sources and used as received. Dimethylformamide (DMF) was stored under an argon atmosphere. Electrosyntheses were carried out either in a double compartment cell or in an undivided electrochemical cell.

Electrosyntheses carried out in a double compartment electrochemical cell equipped with a fritted glass separation were performed with an anode and a cathode made of carbon fibers (total geometric area of 30 cm², from Prolabo). Both cathodic and anodic compartments were filled with 25 mL of DMF solution containing tetrabutylammonium bromide, noted TBABr (0.236 mol·L⁻¹) and tetrabutylammonium iodide, noted TBAI (0.054 mol·L⁻¹) and kept under argon atmosphere. The catalyst precursor was introduced in the cathodic compartment (15 mmol·L⁻¹), and the solution was stirred during 15 minutes.

Electrosyntheses carried out in an undivided electrochemical cell were performed with a cathode made of a nickel foam grid (geometric area of 30 cm²) and a sacrificial anode made of a rod of aluminum, magnesium, copper, zinc, or iron. The electrochemical cell was filled with DMF solution (35 mL) containing TBABr (10 mmol·L⁻¹) and TBAI (8 mmol·L⁻¹) and kept under argon atmosphere. CoSalen complex (10 mmol·L⁻¹) or a mixture CoCl₂/ligand (10 mmol·L⁻¹ and 20 mmol·L⁻¹, respectively) was then added and heated at 60–80°C. After stirring for 15 minutes, 2-bromooctane (0.2 mol·L⁻¹) and MVK (0.535 mol·L⁻¹) were introduced.

In both cases, the electrolysis was run at constant current density (0.3 A·dm⁻²) or constant potential (–1.2 V or –1.6 V). The cathode potential was measured and referenced to a saturated calomel electrode (SCE) which was placed in a separate compartment containing the solvent and the supporting electrolyte. The reaction was monitored by gas

chromatography analysis (GC) using ethyl undecanoate as internal standard and was stopped after 2-bromooctane was totally consumed. The reaction mixture was then hydrolyzed with hydrochloric acid (1 N, 30 mL). The aqueous layer was extracted with diethyl ether (2 × 30 mL). The combined organic layers were washed with water, dried over MgSO₄, and concentrated. Finally, the product was purified by preparative column chromatography (silica gel 70–230 mesh; eluent: pentane/ether 95/5). The reaction products were identified by ¹H and ¹³C-NMR (Bruker 200 MHz) in CDCl₃ and mass spectrometry (Finnigan ITD 800). GC analyses were carried out using a 25 m DB1-capillary column. Elemental analyses were made by the Service Central de Microanalyses (CNRS, Lyon). Physical and spectral data are given as follows.

2.1. Ethyl 4-Methyl Decanoate 3. Colorless liquid, 0.65 g (43%). ¹H-NMR (200 MHz, CDCl₃): δ ppm 4.04 (q, 2H, J = 7.1 Hz), 2.20 (m, 2H), 1.55 (m, 2H), 1.15–1.37 (m, 14H), 0.8 (m, 6H). ¹³C-NMR (50.32 MHz, CDCl₃): δ ppm 173.8, 59.8, 36.5, 32.1, 31.8, 31.6 (2C), 29.3, 26.6, 22.4, 19.0, 13.8. MS: 215, 157, 101 (100%), 88, 73, 55.

2.2. Ethyl 3-Cyclohexylpropanoate 4. CAS Registry Number 10094-36-7, colorless liquid, 0.47 g (37%) [28]. ¹H-NMR (200 MHz, CDCl₃): δ ppm 4.06 (q, J: 6.8 Hz, 2H), 2.24 (t, J: 7.6 Hz, 2H), 1.64–1.70 (m, 5H), 1.48 (m, 2H), 1.06–1.24 (m, 7H), 0.88 (m, 2H). ¹³C-NMR (50.32 MHz, CDCl₃): δ ppm 173.1, 59.5, 37.0, 32.7 (2C), 32.0, 31.4, 26.2, 26.0 (2C), 13.8. MS: 185, 155, 121, 101, 81, 73, 67, 60, 55 (100%).

2.3. Ethyl 4,4-Dimethylpentanoate 5. CAS Registry Number 10228-99-6, colorless liquid, 0.37 g (33%). ¹H-NMR (200 MHz, CDCl₃): δ ppm 4.00 (q, J: 7.1 Hz, 2H), 2.15 (m, 2H), 1.45 (m, 2H), 1.15 (t, J: 7.1 Hz, 3H), 0.80 (s, 9H). ¹³C-NMR (50.32 MHz, CDCl₃): δ ppm 174.1, 60.0, 38.5, 30.00 (4C), 28.8, 14.0. MS: 159, 143, 113, 102, 97, 74, 69, 57 (100%).

2.4. Ethyl 4-Phenylbutanoate 6. CAS Registry Number 10031-93-3, 0.20 g (14%), colorless liquid [29]. ¹H-NMR (200 MHz, CDCl₃): δ ppm 7.15 (m, 5H), 4.02 (q, J: 7.15 Hz, 2H), 2.55 (t, J: 7.35 Hz, 2H), 2.20 (m, 2H), 1.86 (m, 2H), 1.15 (t, J: 7.15 Hz, 3H). ¹³C-NMR (50.32 MHz, CDCl₃): δ ppm 173.3, 141.3, 126.38 (2C), 126.26 (2C), 125.85, 60.1, 35.0, 33.5, 26.5, 14.1. MS: 192, 146, 104, 91 (100%), 70, 65.

2.5. 5-Methylheptadecan-2-one 7. Colorless liquid, 0.98 g (52%) [30]. ¹H-NMR (200 MHz, CDCl₃): δ ppm 2.35 (m, 2H), 2.04 (s, 3H), 1.50 (m, 2H), 1.10–1.38 (m, 23H), 0.8 (m, 6H). MS: 269, 97, 85, 71 (100%), 55. Elemental analysis for C₁₈H₃₆O, calculated: C, 80.5; H, 13.5, found: C, 80.8; H, 13.2.

2.6. 4-Methyldecanenitrile 8. CAS Registry Number 97763-97-8, colorless liquid, 0.58 g (50%) [30]. ¹H-NMR (200 MHz, CDCl₃): δ ppm 2.26 (m, 2H), 1.68–1.40 (m, 3H), 1.01–1.38

(m, 10H), 0.81 (m, 6H). ^{13}C -NMR (50.32 MHz, CDCl_3): δ ppm 196.2, 35.9, 32.0, 31.7, 31.5, 29.1, 26.4, 22.3, 18.4, 14.5, 13.7. MS: 168, 124, 110, 96, 82, 69, 55 (100%).

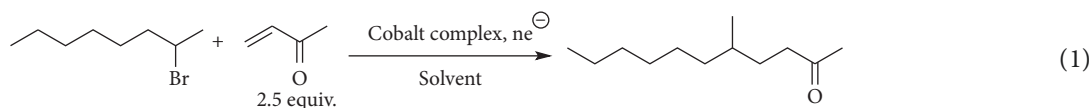
2.7. Dimethyl 2-(1-Methylheptyl)butan-1,4-dioate 9. CAS Registry Number 1622297-77-1, 0.90 g (50%), colorless liquid. ^1H -NMR (200 MHz, CDCl_3): δ ppm 3.60 (m, 6H), 2.70 (m, 2H), 2.25 (m, 1H), 1.04–1.36 (m, 11H), 0.8 (m, 6H). MS: 259, 227, 185, 146, 55. Elemental analysis for $\text{C}_{14}\text{H}_{26}\text{O}_4$, calculated: C, 65.1; H, 10.1, found: C, 64.9; H, 10.2.

2.8. Ethyl 3,4-Dimethyldecanoate 10. Colorless liquid, 128 mg (8%), ^1H -NMR (200 MHz, CDCl_3): δ ppm 4.04 (q, J : 7.1 Hz, 2H), 2.1 (m, 2H), 1.1–1.36 (m, 15H), 0.76 (m, 9H). MS: 229, 115(100%), 101, 88, 69, 55.

Physical and spectral data of ethyl undecanoate **1** and dodecan-2-one **2** are similar to commercial samples.

3. Results and Discussion

Addition of 2-bromooctane to methylvinylketone (MVK) was studied as the model reaction in DMF as solvent (equation (1)):



We have first analyzed the influence of the cobalt ligands on the conjugate addition reaction yield (Table 1).

In the absence of cobalt salt (run 1) or ligand (run 2), poor yields of alkylated product are obtained. Among the examined ligands, H_2Salen (run 3 and 4) and ephedrine (run 7) are the most appropriate ones to provide highest chemical yields for the conjugate addition reaction. Therefore, the supposed active catalyst is a simple and cheap cobalt complex which can be prepared *in situ*.

Solvent influence was also examined (Table 2). We found that the best solvent is dimethylformamide either pure (run 1) or in the presence of proton donor. For example, in the case of NH_4Cl ($5.10^{-2} \text{ mol}\cdot\text{L}^{-1}$) as supporting electrolyte added to DMF (run 2) or DMF/ethanol (EtOH) (1/1) mixture (run 4), the yields, calculated by GC analysis with internal standard, are, respectively, 55% and 59%. Despite the fact the coupling product was obtained with moderate yields in solvent mixtures such as DMF/EtOH (1/1) or DMF/Acetonitrile (AN) (1/1), pure EtOH and AN are not suitable solvents (see Table 2).

Anyhow, for reaction carried out in pure DMF (Table 1, run 3), we have found that the yield was very dependent on the temperature: 27% at 20°C , 61% at 80°C . Also, we have noticed that if the electrolysis potential was more negative than -1.2 V/SCE , both the chemical yield (26%) and the Faradaic yield decrease. This could be due to the direct reduction of the MVK which occurs at ca -1.7 V/SCE . In this case, other reactions, such as MVK polymerization, take place.

The stoichiometry of the reaction between MVK and 2-bromooctane was examined. The results reported in Table 3 reveal the importance of using excess amount of MVK to improve the yield of the coupling product. However, a large excess of olefin does not improve significantly the yields (run 3 and 4).

Finally, we have observed that the nature of the anode is crucial to form selectively the addition product. Indeed, results in Table 4 show that an iron rod is the most efficient anode, indicating a possible role of the cations

anodically generated by its oxidation during the electrolysis.

Such a crucial role of anodically generated cations has also been reported in other processes related to electro-assisted reductions of organohalides catalyzed by nickel complexes [31]. Their occurrence in this reaction was analyzed by cyclic voltammetry and showed the possible formation of a catalytically active Co-Salen-Fe binuclear complex [27]. Indeed, Table 5 recapitulates the comparative analysis of the significant results obtained for reactions carried out with CoSalen, in various conditions, by using either a double compartment or an undivided electrochemical cell. It clearly appears from these results that both CoSalen complex and Fe^{II} cations issued from the anode dissolution are needed to allow the product formation with satisfactory yields (Table 4, run 3).

Table 6 reports the results obtained in the reaction of the three classes of alkyl halides with electron deficient olefins under the optimized experimental conditions issued from the above described results. These results show that the addition product yield is low for a primary alkyl bromide (run 1–3) and medium for a secondary (run 4 and 5) or a tertiary alkyl bromide (run 6). The best yields are obtained for the reaction of 2-octyl bromide as secondary alkyl halide either with acrylonitrile (run 9), MVK (run 8), and dimethyl maleate (run 10). The reaction yield is lower if the olefin is disubstituted (run 11–13). Note that same trend has previously been observed in the arylation of activated olefins [32]. In view of these results, it appears that the coupling reaction is regioselective, without formation of 1, 2- addition product. Alkane and alkene which are produced, respectively, by a direct electrochemical reduction and by dehydrohalogenation reaction are the only byproducts observed. Finally, this study shows that the reaction procedure is more efficient when performed with secondary or tertiary alkyl halides than with primary alkyl halides.

This observation suggests that radical R^\bullet resulted from alkyl halide reduction may be involved in the reaction

TABLE 1: Results of the reductive coupling reaction of 2-bromooctane with methylvinylketone with various cobalt complex catalysts.

Run	Catalyst	Yield ^a (%)
1	—	2
2	CoCl ₂ (5%)	8
3	CoCl ₂ (5%) + H ₂ Salen (5%)	51 ^b
4	CoSalen ^c (5%)	43
5	CoCl ₂ (5%) + 2, 2'-bipyridine (5%)	24
6	CoCl ₂ (5%) + phenantroline (10%)	20
7	CoCl ₂ (5%) + ephedrine (10%)	56

Experimental conditions: anode = Fe; cathode = Ni grid (surface area = 30 cm²); current intensity I = 0.1 A; solvent = DMF + TBABr (10⁻² mol·L⁻¹) + TBAI (8.10⁻³ mol·L⁻¹); T = 60°C; 2-bromooctane = 0.1875 mol·L⁻¹; methylvinylketone = 0.47 mol·L⁻¹; ^aGC yield, with ethyl undecanoate as internal standard; ^bat 20°C, yield = 27%; at 80°C, yield = 61%; ^cfrom Sigma-Aldrich.

TABLE 2: Results of the reductive coupling reaction of 2-bromooctane with methylvinylketone in various solvents under CoCl₂+ H₂Salen catalysis.

Run	Solvent	Yield ^a
1	DMF	51%
2	DMF + NH ₄ Cl ^b	55%
3	DMF/EtOH (8/2)	46%
4	DMF/EtOH (1/1)	59%
5	DMF/EtOH (3/7)	22%
6	EtOH	4%
7	DMF/MeOH (1/1)	15%
8	DMF/AN (1/1)	46%
9	AN	Traces

Experimental conditions: anode = Fe; cathode = Ni grid (surface area = 30 cm²); current intensity I = 0.1 A; supporting electrolytes: TBABr (10⁻² mol·L⁻¹) + TBAI (8.10⁻³ mol·L⁻¹); catalyst: CoCl₂ (9.4.10⁻² mol·L⁻¹) + H₂Salen (9.4.10⁻² mol·L⁻¹); T = 60°C; 2-bromooctane = 0.1875 mol·L⁻¹; methylvinylketone = 0.47 mol·L⁻¹; ^aGC yield, with ethyl undecanoate as internal standard; ^bNH₄Cl was used as supporting electrolyte (5.10–2 mol·L⁻¹) and as proton source.

TABLE 3: Stoichiometric study of the reaction between MVK and 2-bromooctane.

Run	Equiv. MVK	Yield ^a (%)
1	1	36
2	2.5	51
3	5	57
4	25	46

Experimental conditions: anode = Fe; cathode = Ni grid (surface area = 30 cm²); current intensity I = 0.1 A; solvent = DMF + TBABr (10⁻² mol·L⁻¹) + TBAI (8.10⁻³ mol·L⁻¹); catalyst: CoCl₂ (9.4.10⁻² mol·L⁻¹) + H₂Salen (9.4.10⁻² mol·L⁻¹); methylvinylketone 1 to 25 equiv.; 2-bromooctane = 0.1875 mol·L⁻¹; T = 60°C; ^aGC yield, with ethyl undecanoate as internal standard.

mechanism [27]. This radical is trapped by the electron deficient olefin added in excess (2.5 equiv.). The heteronuclear Co^{II}-Salen-Fe^{II} complex prepared *in situ* from CoSalen and from the release of Fe^{II} cations arising from the oxidation of the anode (equation (2)) is likely the key active species [27].

TABLE 4: Results of the reductive coupling reaction of 2-bromooctane with methylvinylketone with various anodes in an undivided cell.

Run	Anode	Yield* (%)
1	Fe	51
2	Zn	33
3	Al	8
4	Mg	6
5	Cu	3

Experimental conditions: anode = metal rod; cathode = Ni grid (surface area = 30 cm²); current intensity I = 0.1 A; T = 60°C; solvent = DMF + TBABr (10⁻² mol·L⁻¹) + TBAI (8.10⁻³ mol·L⁻¹); catalyst = CoCl₂ (9.4.10⁻² mol·L⁻¹) + H₂Salen (9.4.10⁻² mol·L⁻¹); 2-bromooctane = 0.1875 mol·L⁻¹; methylvinylketone = 0.47 mol·L⁻¹; *GC yield, with ethyl undecanoate as internal standard.

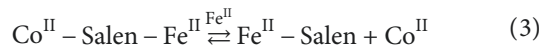
TABLE 5: Results of the conjugate addition of 2-bromooctane to methylvinylketone, catalyzed by Co^ISalen⁻, in DMF solution and with various electrolysis conditions.

Run	Catalyst	Electrolysis conditions	Yield* (%)
1	CoSalen	Double separated Compartment cell E = -1.2 V/SCE or -1.6 V/SCE	<10
2	CoSalen	Undivided cell Anode = Al, Mg, Cu Current density = 0.3 mA·dm ⁻²	<10
3	CoSalen	Undivided cell Anode = Fe Current density = 0.3 mA·dm ⁻²	43
4	CoSalen + Fe ^{II}	Undivided cell Anode = Al Current density = 0.3 mA·dm ⁻²	25
5	—	Undivided cell Anode = Fe Current density = 0.3 mA·dm ⁻²	<10

*Yield is calculated by GC analysis with ethyl undecanoate as an internal standard.



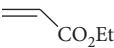
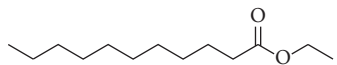
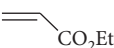
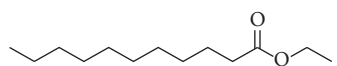
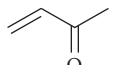
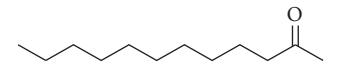
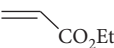
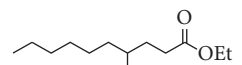
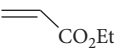
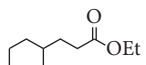
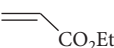
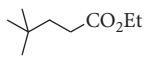
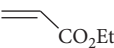
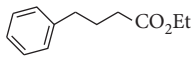
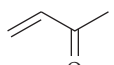
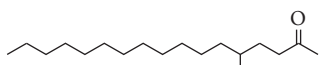
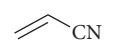
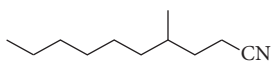
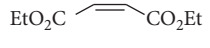
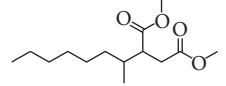
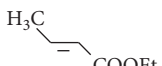
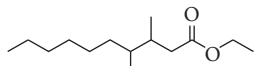
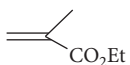
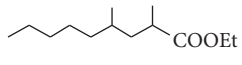
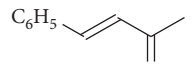
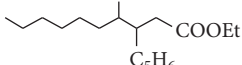
This complex is stable enough to promote the electro-reductive coupling to some extent. Indeed, the continuous release of iron cations during the process is responsible for the Salen ligand displacement to produce Co^{II} and Fe^{II}Salen (equation (3)). These two species do not catalyze the coupling reaction. This unwanted reaction accounts for the relatively moderate yields, around 50% under the optimized conditions.



4. Conclusion

If β -elimination of HX from alkyl halides is a classic reaction in organic chemistry to get olefins, the described electro-synthesis procedure allows activation of alkyl halides and to some extent the further reaction with electron deficient olefins. From a methodological point of view, the conjugate

TABLE 6: Electroreductive alkylation of activated olefins electrocatalyzed by cobalt-Salen in an undivided cell with an iron anode.

Run	Alkyl bromide	Olefin	N°	Product	Isolated yield (%)
1	1-Bromooctane		1		16
2	1-Bromooctane		1		19
3	1-Bromooctane		2		20
4	2-Bromooctane		3		43
5	Bromocyclohexane		4		37
6	2-Bromo-2-methylpropane		5		33
7	(Bromomethyl)benzene		6		14
8	2-Bromotetradecane		7		52
9	2-Bromooctane		8		50
10	2-Bromooctane		9		50
11	2-Bromooctane		10		8
12	2-Bromooctane		11		<5
13	2-Bromooctane		12		<5

Experimental conditions: anode = Fe; cathode = Ni grid (surface area = 30 cm²); current intensity I = 0.1 A; T = 60°C; solvent = DMF + TBABr (10⁻² mol·L⁻¹) + TBAI (8.10⁻³ mol·L⁻¹); catalyst: CoCl₂ (9.4.10⁻² mol·L⁻¹) + H₂Salen (9.4.10⁻² mol·L⁻¹); alkyl bromide = 0.187 mol·L⁻¹; olefin = 0.47 mol·L⁻¹.

addition products are obtained from available substrates, and the catalyst is generated *in situ* from cheap cobalt salt and Salen in an undivided cell fitted with an iron rod. This method based on the use of electricity as green reagent is accompanied by inherent release of iron salt which is not considered as toxic. This investigation also shows the crucial role of the anodically generated metallic cations with a particular emphasis on iron. This study completes advantageously the described voltammetric analysis and confirms the hypothesis of the formation of a catalytically active binuclear Co-Salen-Fe complex during the electrosynthesis.

Data Availability

The NMR source data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

The authors thank Prof. Jean-Yves Nédélec (CNRS, 94320 Thiais, France) and Dr. Jacques Devynck (CNRS, 75005 Paris, France) for their support.

References

- [1] M. Yan, Y. Kawamata, and P. S. Baran, "Synthetic organic electrochemical methods since 2000: on the verge of a renaissance," *Chemical Reviews*, vol. 117, no. 21, pp. 13230–13319, 2017.
- [2] A. Wiebe, T. Gieshoff, S. Möhle, E. Rodrigo, M. Zirbes, and S. R. Waldvogel, "Electrifying organic synthesis," *Angewandte*

- Chemie International Edition*, vol. 57, no. 20, pp. 5594–5619, 2018.
- [3] H. Lund, “A century of organic electrochemistry [journal of the electrochemical society, 149, S21 (2002)],” *Journal of Electrochemical Society*, vol. 149, no. 4, pp. S21–S33, 2002.
- [4] R. Rahil, S. Sengmany, E. Le Gall, and E. Léonel, “Nickel-catalyzed electrochemical reductive homocouplings of aryl and heteroaryl halides: a useful route to symmetrical biaryls,” *Synthesis*, vol. 50, no. 1, pp. 146–154, 2018.
- [5] S. Sengmany, A. Vitu-Thiebaud, E. Le Gall et al., “An electrochemical nickel-catalyzed arylation of 3-amino-6-chloropyridazines,” *Journal of Organic Chemistry*, vol. 78, no. 2, pp. 370–379, 2013.
- [6] C. Cannes, S. Condon, M. Durandetti, J. Périchon, and J.-Y. Nédélec, “Nickel-catalyzed electrochemical couplings of vinyl halides: synthetic and stereochemical aspects,” *Journal of Organic Chemistry*, vol. 65, no. 15, pp. 4575–4583, 2000.
- [7] P. Gomes, C. Gosmini, J.-Y. Nédélec, and J. Périchon, “Cobalt bromide as catalyst in electrochemical addition of aryl halides onto activated olefins,” *Tetrahedron Letters*, vol. 41, no. 18, pp. 3385–3388, 2000.
- [8] S. Condon and J.-Y. Nédélec, “Overview on nickel-catalyzed electrochemical conjugate addition of organic halides on electron-deficient olefins,” *Synthesis*, vol. 18, pp. 3070–3078, 2004.
- [9] J. Chaussard, J. C. Folest, J.-Y. Nédélec, J. Périchon, S. Sibille, and M. Troupel, “Use of sacrificial anodes in electrochemical functionalization of organic halides,” *Synthesis*, vol. 1990, no. 5, pp. 369–381, 1990.
- [10] J. Bensemhoun and S. Condon, “Valorization of glycerol 1,2-carbonate as a precursor for the development of new synthons in organic chemistry,” *Green Chemistry*, vol. 14, no. 9, pp. 2595–2599, 2012.
- [11] P. Perlmutter, *Tetrahedron Organic Chemistry Series, Conjugate Addition Reactions in Organic Synthesis*, Vol. 9, Pergamon Press, Oxford, UK, 1992.
- [12] G. P. Boldrini, D. Savoia, E. Tagliavini, C. Trombini, and A. U. Ronchi, “Nickel-catalyzed coupling of activated alkenes with organic halides,” *Journal of Organometallic Chemistry*, vol. 301, no. 3, pp. 62–64, 1986.
- [13] S. A. Lebedev, V. S. Lopatina, E. S. Petrov, and I. P. Beletskaya, “Condensation of organic bromides with vinyl compounds catalysed by nickel complexes in the presence of zinc,” *Journal of Organometallic Chemistry*, vol. 344, no. 2, pp. 253–259, 1988.
- [14] R. Sustmann, P. Hopp, and P. Holl, “Reactions of organic halides with olefins under NiO-catalysis. Formal addition of hydrocarbons to CC-double bonds,” *Tetrahedron Letters*, vol. 30, no. 6, pp. 689–692, 1989.
- [15] J. Augé, R. Gil, and S. Kalsey, “Conjugate additions of alkyl-chromium reagents mediated by chromium(III) chloride/manganese,” *Tetrahedron Letters*, vol. 40, no. 1, pp. 67–70, 1999.
- [16] G. Bontempelli, F. Magno, S. Daniele, and G. Schiavon, “An electroanalytical investigation on the nickel-triphenylphosphine system in the presence of acrylonitrile,” *Journal of Electroanalytical Chemistry*, vol. 159, no. 1, pp. 117–126, 1983.
- [17] S. Ozaki, H. Matsushita, and H. Ohmori, “Indirect electroreductive addition of alkyl radicals to activated olefins using a nickel(II) complex as an electron-transfer catalyst,” *Journal of Chemical Society, Perkin Transactions 1*, vol. 1, no. 6, pp. 649–651, 1993.
- [18] K. P. Healy and D. Pletcher, “The chemistry of electro-generated transition metals species - the insertion of olefins into a nickel-carbon bond,” *Journal of Organometallic Chemistry*, vol. 161, no. 1, pp. 109–120, 1978.
- [19] C. Gosden and D. Pletcher, “The catalysis of the electrochemical reduction of alkyl bromides by nickel complexes: the formation of carbon-carbon bonds,” *Journal of Organometallic Chemistry*, vol. 186, no. 3, pp. 401–409, 1980.
- [20] R. Scheffold, M. Dike, S. Dike, T. Herold, and L. Walder, “Carbon-carbon bond formation catalyzed by vitamin B12 and a vitamin B12 model compound. Electrosynthesis of bicyclic ketones by 1,4 addition,” *Journal of American Chemical Society*, vol. 102, no. 10, pp. 3642–3644, 1980.
- [21] R. Orlinski and T. Stankiewicz, “Vitamin B12 photoelectrocatalyzed (B12/pec) synthesis of 2-aminoesters,” *Tetrahedron Letters*, vol. 29, no. 13, pp. 1601–1602, 1988.
- [22] R. Scheffold, S. Abrecht, R. Orlinski et al., “Vitamin B12-mediated electrochemical reactions in the synthesis of natural products,” *Pure and Applied Chemistry*, vol. 59, no. 3, pp. 363–372, 1987.
- [23] J. M. Duprilot, F. Bédoui, J. Devynck, J. C. Folest, and C. Bied-Charreton, “Etude Electrochimique de Complexes Dérivés de l'éthylène Bis (Salicylidene iminato) Cobalt; Application à la Réduction Electroassistée d'halogénures Organiques,” *Journal of Organometallic Chemistry*, vol. 286, no. 1, pp. 77–90, 1985.
- [24] H. I. Tashtoush and R. Sustmann, “Chromium(II)-Mediated intermolecular free-radical carbon-carbon bond formation,” *Chemische Berichte*, vol. 125, no. 1, pp. 287–289, 1992.
- [25] H. I. Tashtoush and R. Sustmann, “Free-radical coupling of alkyl and aryl halides with electron-deficient alkenes mediated by chromium(II) complexes,” *Chemische Berichte*, vol. 126, no. 7, pp. 1759–1761, 1993.
- [26] K. Takai, N. Matsukawa, A. Takahashi, and T. Fujii, “Three-component coupling reactions of alkyl iodides, 1,3-dienes, and carbonyl compounds by sequential generation of radical and anionic species with CrCl₂,” *Angewandte Chemie International Edition*, vol. 37, no. 1, pp. 152–155, 1998.
- [27] C. Cannes, F. Bédoui, S. Condon-Gueugnot, J.-Y. Nédélec, and J. Devynck, “Electroassisted catalysis of the reductive coupling of 2-bromooctane and methyl vinyl ketone by a binuclear cobalt-salen-iron complex in DMF solution: electrosynthesis and cyclic voltammetry analysis,” *New Journal of Chemistry*, vol. 23, no. 5, pp. 489–494, 1999.
- [28] T. Kawamoto, S. Uehara, H. Hirao, T. Fukuyama, H. Matsubara, and I. Ryu, “Borohydride-mediated radical addition reactions of organic iodides to electron-deficient alkenes,” *Journal of Organic Chemistry*, vol. 79, no. 9, pp. 3999–4007, 2014.
- [29] Q. Cao, J. L. Howard, E. Wheatley, and D. L. Browne, “Mechanochemical activation of zinc and application to negishi cross-coupling,” *Angewandte Chemie International Edition*, vol. 57, no. 35, pp. 11339–11343, 2018.
- [30] N. Ono, A. Kamimura, H. Miyake, I. Hamamoto, and A. Kaji, “New synthetic methods. Conjugate addition of alkyl groups to electron deficient olefins with nitroalkanes as alkyl anion equivalents,” *Journal of Organic Chemistry*, vol. 50, no. 20, pp. 3692–3698, 1985.
- [31] J.-Y. Nédélec, J. Périchon, and M. Troupel, “Organic electroreductive coupling reactions using transition metal complexes as catalysts,” *Topics in Current Chemistry*, vol. 185, pp. 141–173, 2005.
- [32] S. Condon-Gueugnot, E. Leonel, J.-Y. Nédélec, and J. Périchon, “Electrochemical arylation of activated olefins using a nickel salt as catalyst,” *Journal of Organic Chemistry*, vol. 60, no. 23, pp. 7684–7686, 1995.

