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

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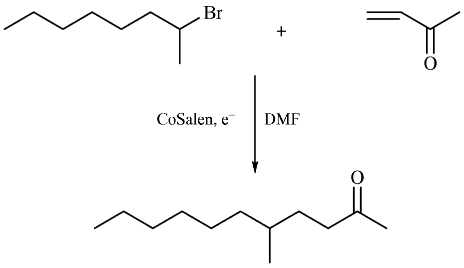
We report in this study the combined use of a CoSalen [H_2Salen = bis(salicylidene)ethane-1,2-diamine] complex and an undivided electrochemical cell process in the electroassisted reductive coupling of 2-bromooctane and methyl vinyl ketone with satisfactory results. Correlation between the electroanalytical analysis of the reactivity of CoSalen in the presence of 2-bromooctane and methyl vinyl ketone and the electrosynthesis performed in an undivided electrochemical cell with a sacrificial iron anode allows us to suggest that a heterobinuclear Co–Salen–Fe complex is the effective catalyst of the considered reaction. Stability of this intermediate during preparative electrolysis is also discussed.

Introduction

[Bis(salicylidene)ethane-1,2-diaminato]cobalt(II) (denoted Co^{II}Salen) is a transition metal complex used in various types of organic syntheses. It can react with molecular oxygen to form an oxygenated dimeric species [$(CoSalen)_2O_2$] which allows the oxygenation of olefins and alkanes.[1–3] The reduced form $Co^{I}Salen^-$ is a potent nucleophile which reacts with various electrophiles such as nitrogenous[4] or sulfurous[5] species, ketones[6] and alkyl halides.[7] Electrogenerated $Co^{I}Salen^-$ can also catalyse the polymerisation of unsaturated species such as butadiene, ethyl acrylate, acrylonitrile or crotononitrile.[8–10]

When electrogenerated $Co^{I}Salen^-$ is combined with alkyl halides (denoted as RX), it proceeds *via* a nucleophilic substitution mechanism to form alkylcobalt intermediates which lead to reductive homo- and hetero-coupling of RX.[11] But the most interesting and much sought-after reaction in which $Co^{I}Salen^-$ can be involved is the reductive coupling of alkyl halides with activated olefins. Indeed, this offers an easy and elegant alternative method to the development of conjugate addition-based organic syntheses with much milder experimental conditions than those usually required when using organometallic derivatives. Few examples of electroassisted reductive coupling reactions of alkyl halides with activated olefins catalyzed by CoSalen are reported in the literature.[12] These were carried out in HMPT (hexamethylphosphorous triamide) or HMPT–THF, in a double compartment electrochemical cell, on a mercury pool cathode and with poor and unsatisfactory yields.

The use of undivided electrochemical cells with a sacrificial anode has led during the last decade to important advancements in electrosynthesis.[13,14] This allowed us to anticipate that the combined use of CoSalen (as catalyst) with the undivided electrochemical cell process may offer substantial advantages in the reductive coupling of alkyl halides and activated olefins. This is exemplified in this study by the application of electrogenerated $Co^{I}Salen^-$ in dimethylformamide (DMF) in the conjugate addition of 2-bromooctane to methyl vinyl ketone [reaction (1)]:



(1)

We also report here the cyclic voltammetry study of the role played by the anodically generated metallic ions in the progress of this reaction.

Results and discussion

Cyclic voltammetry analysis of the activation of 2-bromooctane and methyl vinyl ketone by electrogenerated $Co^{I}Salen^-$

The electrochemical behaviour of CoSalen complex is now well known in various solvents.[15] A typical example of a cyclic voltammogram of this complex (10 mmol L^{-1}) in DMF solution (under our experimental conditions) is shown in Fig. 1 (curve a). It presents two well-defined couples of peaks that can be related to Co^{III}/Co^{II} and Co^{II}/Co^{I} centered one-electron redox processes at 0.082 V *vs.* SCE and −1.250 V *vs.* SCE, respectively. After addition of 2-bromooctane (10 mmol L^{-1}) to the solution, several changes in the cyclic voltammogram can be noticed (Fig. 1, curve b): (i) the reduction peak of the $Co^{II}/Co^{I}Salen^-$ process was slightly shifted (by 15 mV) toward

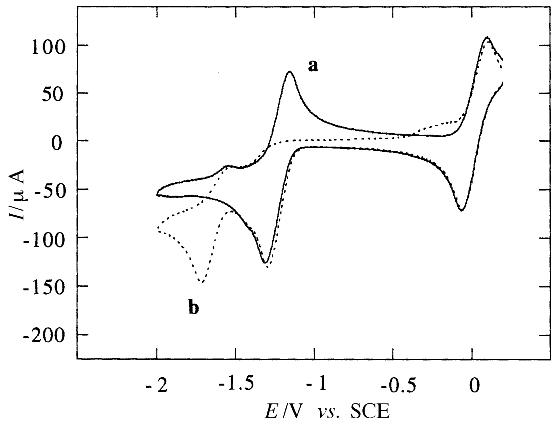
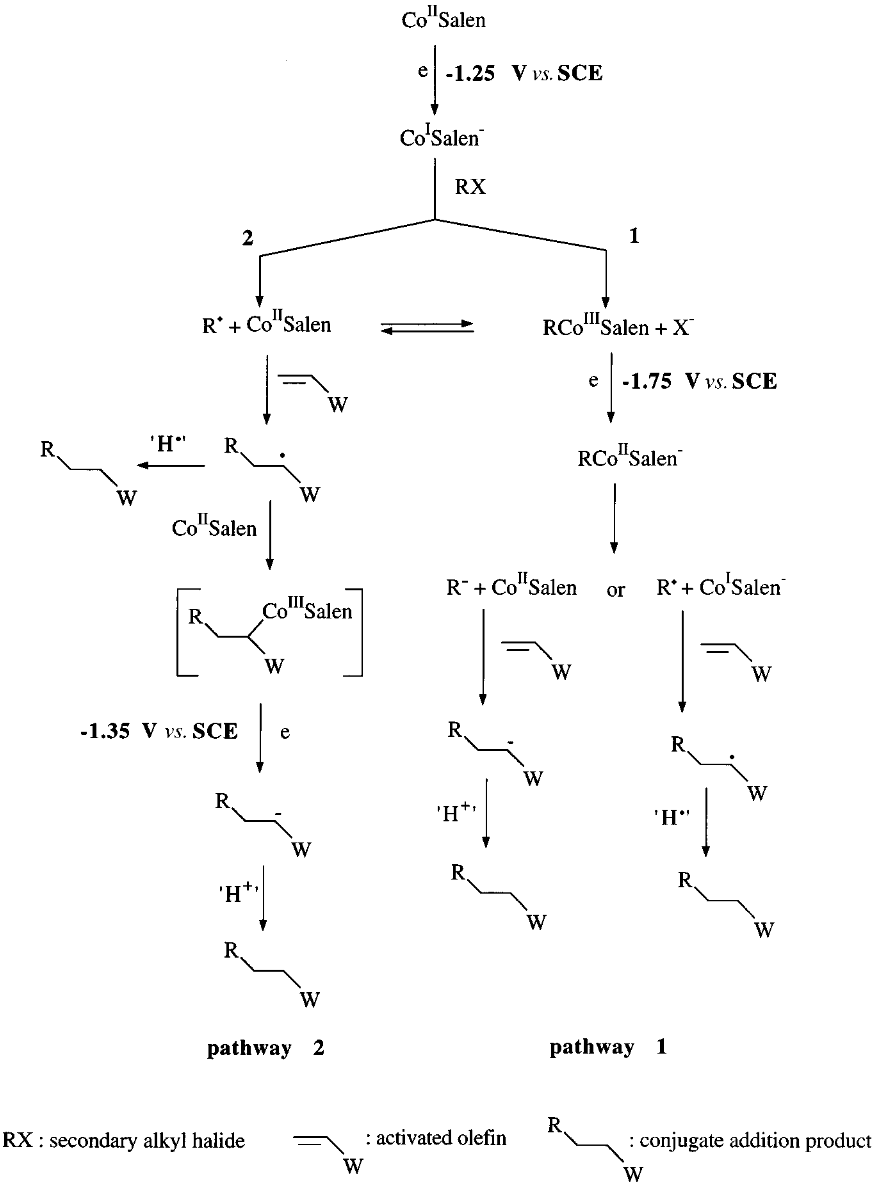


Fig. 1 Cyclic voltammograms of DMF + 0.1 mol L^{-1} Bu$_4^n$NBF$_4$ containing 10 mmol L^{-1} CoSalen without (curve a) and with (curve b) 10 mmol L^{-1} 2-bromooctane (vitreous carbon electrode; scan rate: 0.1 V s^{-1}).

more positive potential values, (ii) a new irreversible reduction peak appeared at approximately −1.750 V *vs.* SCE and (iii) the Co^{I}Salen$^-$/Co^{II}Salen reoxidation peak disappeared during the reverse anodic scan. This proves that the electrogenerated Co^{I}Salen$^-$ reacts rapidly with 2-bromooctane, leading to the formation of the corresponding electroreductive alkyl–CoSalen, as previously reported in the literature[11] for the general case of alkyl halides, RX.

The mechanism of the electroassisted activation of RX by electrogenerated Co^{I}Salen$^-$ can be described as follows: at −1.250 V *vs.* SCE, the electrogenerated Co^{I}Salen$^-$ reacts with the alkyl halide *via* a nucleophilic substitution to form the alkyl–Co^{III}Salen intermediate.[11] At −1.750 V *vs.* SCE, the reduction of this intermediate leads to the unstable alkyl–Co^{II}Salen$^-$ complex. Thus, R$^-$ anion or a R$^\bullet$ radical can be formed as Co^{II}Salen or Co^{I}Salen$^-$ is regenerated.[11,16] In the presence of an activated olefin R$^-$ anion or R$^\bullet$ radical could react to form the desired coupling product as reported in Scheme 1 (pathway 1). It is important to note that if the potential scan was carried out in the potential range 0.3 to −1.5 V *vs.* SCE, the oxidation peak relative to Co^{II}Salen was clearly observed during the reverse scan, at 100 mV s^{-1}. Thus, the decomposition of the alkyl–Co^{III}Salen complex to form Co^{II}Salen and R$^\bullet$ radical could be supposed to be very fast and R$^\bullet$ radical could then be formed through equilibrium (2):

$$\text{R–Co}^{\text{III}}\text{Salen} \rightleftharpoons \text{R}^\bullet + \text{Co}^{\text{II}}\text{Salen} \qquad (2)$$



Scheme 1 Suggested mechanisms for the electroassisted addition of a secondary alkyl halide to an activated olefin catalyzed by CoSalen complex.

The formation of $\mathrm{R^{\bullet}}$ radical and $\mathrm{Co^{II}Salen}$ can also be explained by the reaction of electrogenerated $\mathrm{Co^{I}Salen^{-}}$ with secondary alkyl halide (2-bromooctane, in this case) *via* an outer-sphere electron transfer mechanism, as previously suggested in the case of electroreduced vitamin $\mathrm{B_{12}}$ complex[17,18] (Scheme 1, pathway 2).

Fig. 2 shows the modification of the cyclic voltammogram of 5 mmol $\mathrm{L^{-1}}$ CoSalen in DMF + 0.08 mol $\mathrm{L^{-1}}$ $\mathrm{Bu^n_4NBr}$ + 0.02 mol $\mathrm{L^{-1}}$ $\mathrm{Bu^n_4NI}$ (curve a, restricted potential range [−0.9 to −1.5 V *vs.* SCE]) upon addition of 20 equivalents of 2-bromooctane (curve b) and both 20 equivalents of 2-bromooctane and 50 equivalents of methyl vinyl ketone (curve c). It clearly indicates that: (i) the $\mathrm{Co^{II}Salen/Co^{I}Salen^{-}}$ redox process becomes irreversible, (ii) its reduction peak is shifted to more positive value and (iii) a new reduction peak appears at −1.35 V *vs.* SCE (upon the addition of both 2-bromooctane and methyl vinyl ketone). Such electrochemical behaviour of reduced CoSalen is similar to that observed with vitamin $\mathrm{B_{12}}$ complex in the presence of a secondary alkyl halide and an activated olefin.[17,18] It can be summarized as follows: the electrogenerated $\mathrm{Co^{I}Salen^{-}}$ reacts with the secondary alkyl halide to form $\mathrm{R^{\bullet}}$ radical and $\mathrm{Co^{II}Salen}$. Then $\mathrm{R^{\bullet}}$ radical can be trapped by the activated olefin. If the solution contains radical hydrogen $\mathrm{H^{\bullet}}$ donors, the expected addition product can be formed. Otherwise, the obtained radical (by addition of $\mathrm{R^{\bullet}}$ to the activated olefin) combines with $\mathrm{Co^{II}Salen}$ and the 'olefin-inserted' alkyl–$\mathrm{Co^{III}salen}$ is formed. This complex could then be reduced at −1.35 V *vs.* SCE and lead to the conjugate addition product, after protonation (Scheme 1; pathway 2).

Preparative electrosyntheses

According to the above suggested mechanism, the electrosynthesis of the conjugate addition product from 2-bromooctane and methyl vinyl ketone could be run at two different potential values, either *ca.* −1.2 or *ca.* −1.6 V *vs.* SCE. Table 1 reports the results we obtained by carrying out reaction (1) in the presence of CoSalen, under various conditions, by using either double compartment or undivided electrochemical cells. It clearly appears from these results that: (i) if the electrolysis is carried out in a double compartment cell at either −1.2 or −1.6 V *vs.* SCE, the yield is very low (run 1). (ii) If the electrolysis is carried out in an undivided cell with an anode made of aluminium, magnesium or copper and at constant current, the yield is also very low (run 2). (iii) If the electrolysis is carried out in an undivided cell with an anode made of iron and at constant current, the yield increases significantly up to 43% (run 3). Note also than under these conditions, the cathode potential value was found to be −1.0 V *vs.* SCE. (iv) If the electrolysis is carried out in an undivided cell, with an anode made of iron, at −1.2 or −1.6 V *vs.* SCE, the yield is 43% (run 4) and 23% (run 5), respectively. The drop in the reaction yield, when the electrolysis is performed at −1.6 V *vs.* SCE, may be explained by the direct electrochemical reduction of methyl vinyl ketone at this potential. (v) If the electrolysis is carried out in an undivided cell with an anode made of aluminium and in the presence of added $\mathrm{FeCl_2}$ in the solution (with a molar ratio $\mathrm{Fe^{II}}$: CoSalen = 20 : 1) at constant current, the yield is close to 25% (run 6). It is obvious that the presence of $\mathrm{Fe^{II}}$ cations in the solution increases the reaction yield (even if the amount of added $\mathrm{Fe^{II}}$ was not optimised), as compared to the use of CoSalen alone (and an aluminum anode; run 2). Note than under these conditions, the cathode potential value was found to be −1.0 V *vs.* SCE. When higher amounts of $\mathrm{Fe^{II}}$ were used (up to a molar ratio $\mathrm{Fe^{II}}$: CoSalen of 40 : 1), the yield decreased significantly (data not shown). (vi) Finally, if the electrolysis is carried out in an undivided cell with an anode made of iron but without CoSalen (and at constant current), the yield is extremely low (run 7).

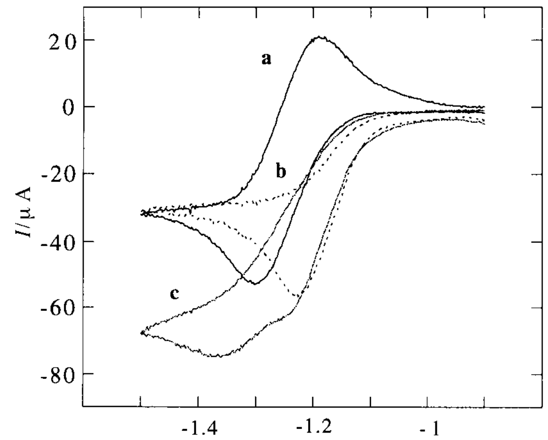


Fig. 2 Cyclic voltammograms of DMF + 80 mmol $\mathrm{L^{-1}}$ $\mathrm{Bu^n_4NBr}$ + 20 mmol $\mathrm{L^{-1}}$ $\mathrm{Bu^n_4NI}$ solution containing 5 mmol $\mathrm{L^{-1}}$ CoSalen (curve a) with (curve b) 0.1 mol $\mathrm{L^{-1}}$ 2-bromooctane and with (curve c) 0.1 mol $\mathrm{L^{-1}}$ 2-bromooctane + 0.25 mol $\mathrm{L^{-1}}$ methyl vinyl ketone (vitreous carbon electrode; scan rate: 0.02 V $\mathrm{s^{-1}}$).

Table 1 Results of the reductive coupling reaction of 2-bromooctane with methyl vinyl ketone, catalyzed by electrogenerated $\mathrm{Co^{I}Salen^{-}}$, in DMF solution and with various electrolysis conditions

Run	Catalyst	Electrolysis conditions	Yield (%)
1	CoSalen	Double separated compartment *E* = −1.2 or −1.6 V *vs.* SCE	<10
2	CoSalen	Undivided cell Anode = Al, Mg, Cu Current density = 0.3 mA $\mathrm{dm^{-2}}$	<10
3	CoSalen	Undivided cell Anode = Fe Current density = 0.3 mA $\mathrm{dm^{-2}}$	43
4	CoSalen	Undivided cell Anode = Fe *E* = −1.2 V *vs.* SCE	43
5	CoSalen	Undivided cell Anode = Fe *E* = −1.6 V *vs.* SCE	23
6	CoSalen + $\mathrm{Fe^{II}}$ (Fe : CoSalen = 20 : 1)	Undivided cell Anode = Al Current density = 0.3 mA $\mathrm{dm^{-2}}$	25
7		Undivided cell Anode = Fe Current density = 0.3 mA $\mathrm{dm^{-2}}$	2

One remarkable observation should be emphasized from the results shown in Table 1: both CoSalen complex and $\mathrm{Fe^{II}}$ cations are needed to allow the addition product formation with a maximum yield of 43%. Therefore, if one assumes that the above suggested mechanism of the intervention of $\mathrm{Co^{I}Salen^{-}}$ is still valid, further voltammetric analysis of the behaviour of the electrogenerated Fe cation, during the reductive coupling electrolysis, should be done to better understand its role.

Cyclic voltammetry analysis of the electrolytic solution of CoSalen containing 2-bromooctane and methyl vinyl ketone, during constant current electrolysis in an undivided electrochemical cell with an iron anode

Before the start of electrolysis the DMF solution contains 5 mmol $\mathrm{L^{-1}}$ of CoSalen, 20 equivalents of 2-bromooctane and 50 equivalents of methyl vinyl ketone and the cyclic voltammogram shows the two reductive peaks related to the $\mathrm{Co^{II}Salen/Co^{I}Salen^{-}}$ reduction process at −1.25 V *vs.* SCE and to the reduction of the supposed 'olefin-inserted' alkyl–$\mathrm{Co^{III}salen}$ at −1.35 V *vs.* SCE, as discussed above (Fig. 3, curve a). After 20 minutes of constant current electrolysis (at 3

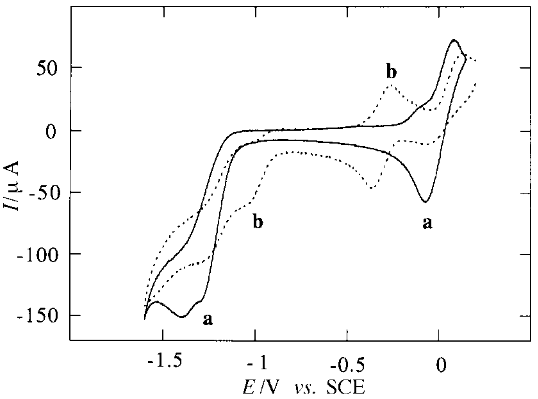


Fig. 3 Cyclic voltammograms of DMF + 0.1 mol L^{-1} Bu$_4^n$NBF$_4$ solution containing 5 mmol L^{-1} CoSalen and 0.1 mol L^{-1} 2-bromooctane + 0.25 mol L^{-1} methyl vinyl ketone before (curve a) and after 20 minutes of electrolysis at 0.3 A dm^{-2} in an undivided cell with an iron anode (curve b) (vitreous carbon electrode; scan rate: 0.1 V s^{-1}).

mA dm^{-2} which leads to 18 mmol L^{-1} of Fe^{II} cations arising from the oxidation of the iron anode), changes in the cyclic voltammogram can be noticed (Fig. 3, curve b): (i) the intensity of the reduction peak of Co^{III}Salen$^+$ at 0.08 V *vs.* SCE and Co^{II}Salen at −1.25 V *vs.* SCE decreased, (ii) a new reduction peak appeared at −1 V *vs.* SCE and (iii) a new reversible couple of peaks appeared at −0.3 V *vs.* SCE. The characterisation of these two new redox processes at −0.3 and −1 V *vs.* SCE could be easily resolved from the analysis of a DMF solution containing both Co^{II}Salen and Fe cations (without any added alkyl halide or activated olefin to avoid further complications due to their redox and chemical reactivities).

Fig. 4 shows the evolution of the cyclic voltammogram of a DMF solution containing Co^{II}Salen upon the addition of FeBr$_2$. The cyclic voltammogram obtained with 1.25 equivalents of Fe^{II} (curve b) shows the same characteristic features as that recorded at the beginning of the electrolysis (Fig. 3, curve b). It clearly indicates: (i) the presence of two new redox processes at −0.3 and −1 V *vs.* SCE, as revealed at the beginning of the electrolysis and (ii) the decrease of the CoSalen related redox processes. The modification of the cyclic voltammogram can be explained by the formation of a heterobinuclear Co^{II}–Salen–Fe^{II} complex, issued from Co^{II}Salen initially present in solution and Fe^{II}, as previously reported by Abe *et al.*[19] in DMSO solutions of Co^{II}Salen + Fe^{II}. The authors[19] suggested that this was a result of the formation of a hetero-metal binuclear Co^{II}–Salen–Fe^{II} complex. The reversible couple of peaks at −1 V *vs.* SCE is then related to the Co^{II}–Salen–Fe^{II}/[Co^{I}–Salen–Fe^{II}]$^-$ redox process. The reversible couple of peaks at −0.3 V *vs.* SCE may be related to the Fe^{III}Salen$^+$/Fe^{II}Salen process,[20] while the anodic peak at around 0.1 V *vs.* SCE may be associated with the oxidation of the Co^{II} centre in the binuclear complex. It is important to note that addition of a large excess of Fe cations (as FeBr$_2$ or arising by the oxidation of the iron anode) leads to the exclusive formation of FeSalen (as discussed below).

Cyclic voltammograms similar to those shown by a DMF solution containing Co^{II}Salen and Fe cations (either as FeBr$_2$ or arising from the iron anode oxidation) can also be obtained in a DMF solution containing both Fe^{III}Salen$^+$ and Co^{II}, as shown in Fig. 5. Prior to the addition of Co^{II} (curve a), the reversible couple of peaks at −0.3 V *vs.* SCE is related to the well-known Fe^{III}Salen$^+$/Fe^{II}Salen redox process[20] (and the second reversible couple of peaks at −1.85 V *vs.* SCE is related to Fe^{II}Salen/Fe^{I}Salen$^-$ redox process[20]). Upon the addition of a large excess of Co^{II} (curve b), the well-defined reversible couple of peaks appeared at −1 V *vs.* SCE and the Fe^{III}Salen$^+$/Fe^{II}Salen reduction peak shifted toward positive values and became irreversible (the oxidation peak of Fe^{II}-Salen disappeared. Note than the potential range was restricted to −1.2 V *vs.* SCE to avoid the cathodic reduction of excess Co^{II} in solution). This suggests the formation of the binuclear complex (which is reducible at −1 V *vs.* SCE to form [Co^{I}–Salen–Fe^{II}]$^-$) upon the reduction of Fe^{III}Salen$^+$ at −0.3 V *vs.* SCE and addition of Co^{II} in large excess.

According to these observations, one can consider that the binuclear complex can be formed either from a mixture of Co^{II}Salen + Fe^{II} with a low molar ratio Fe : CoSalen $\leqslant 4$: or from a mixture of Fe^{II}Salen + Co^{II} with a large molar ratio Co : Fe^{II}Salen $> 7:1$, according to equilibria (3):

$$\text{Co}^{II}\text{Salen} + \text{Fe}^{II} \rightleftharpoons \text{Co}^{II}\text{–Salen–Fe}^{II} \rightleftharpoons \text{Co}^{II} + \text{Fe}^{II}\text{Salen} \quad (3)$$

Addition of 2-bromooctane to DMF solutions containing FeSalen complex and Co^{II} (large excess) or Co^{II}Salen complex and Fe^{II} (small excess) led to a drastic change in the cyclic voltammogram, as can be seen in Fig. 6. Indeed, the [Co^{I}–Salen–Fe^{II}]$^-$/Co^{II}–Salen–Fe^{II} reoxidation peak disappeared during the reverse anodic scan. This proves that the electrogenerated [Co^{I}–Salen–Fe^{II}]$^-$ reacts rapidly with 2-bromooctane, leading probably to the formation of the corresponding electroreductive alkyl intermediate, as previously reported in the general case of CoSalen. This significant observation suggests that the binuclear Co–Salen–Fe complex may be the effective catalyst of the reductive coupling reaction of 2-bromooctane with methyl vinyl ketone (instead of the CoSalen complex). It corroborates the fact that during the electrosynthesis performed in the undivided cell with an iron anode, the cathode potential value was stabilized at −1.0 V *vs.* SCE.

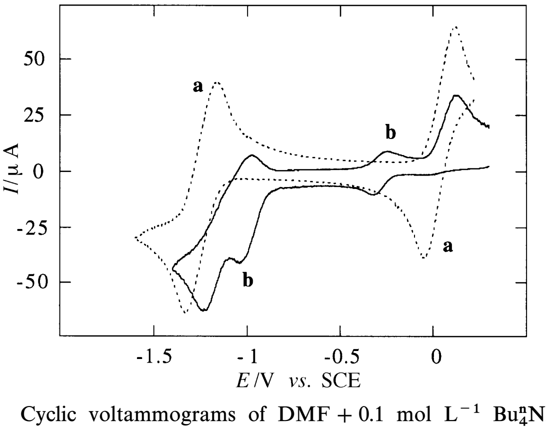


Fig. 4 Cyclic voltammograms of DMF + 0.1 mol L^{-1} Bu$_4^n$NBF$_4$ solution containing 5 mmol L^{-1} CoSalen before (curve a) and after (curve b) addition of 6.25 mmol L^{-1} FeBr$_2$ (vitreous carbon electrode; scan rate: 0.1 V s^{-1}).

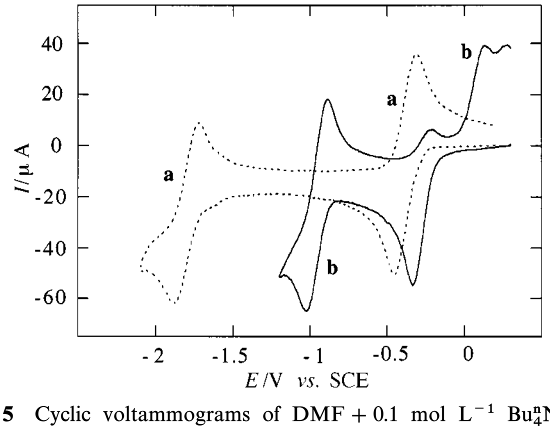


Fig. 5 Cyclic voltammograms of DMF + 0.1 mol L^{-1} Bu$_4^n$NBF$_4$ solution containing 5 mmol L^{-1} Fe^{III}Salen$^+$ without (curve a) and with (curve b) 50 mmol L^{-1} CoCl$_2$ (vitreous carbon electrode; scan rate: 0.1 V s^{-1}).

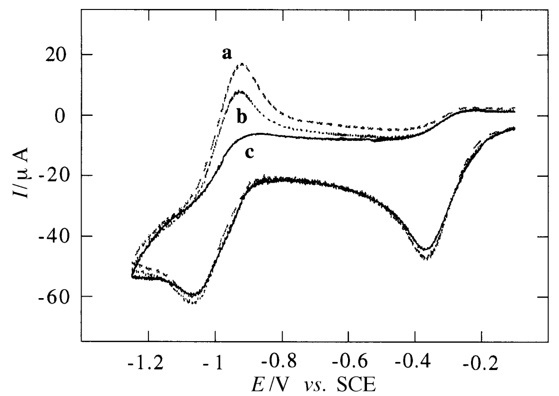


Fig. 6 Cyclic voltammograms of DMF + 0.1 mol L^{-1} $\mathrm{Bu^n_4NBF_4}$ solution containing 5 mmol L^{-1} $\mathrm{Fe^{III}Salen^+}$ + 35 mmol L^{-1} $\mathrm{CoCl_2}$ without (curve a) and with 2-bromooctane (curve b: 5 mmol L^{-1}; curve c: 0.1 mol L^{-1}) (vitreous carbon electrode; scan rate: 0.1 V s^{-1}).

Anyhow, the stability of the binuclear complex during electrolysis is questionable since the yield of the coupling reaction never exceeded 50%. Indeed, the evolution of the cyclic voltammograms of the electrolytic solution of CoSalen (containing 2-bromooctane and methyl vinyl ketone), during further constant current electrolysis (in the undivided electrochemical cell with an iron anode) showed two main features: (i) an increase in the intensity of the reduction peak at approximately -0.3 V *vs.* SCE up to a maximal value corresponding to the initial concentration of Salen introduced into the solution and (ii) a decrease of the intensity of the reduction peak of the $\mathrm{Co^{II}}$–Salen–$\mathrm{Fe^{II}}$ complex. This confirms that in the presence of a large excess of Fe cations arising from oxidation of the anode, no more binuclear complex is present in the solution. The total amounts of Salen ligand is then involved as the FeSalen complex. The exclusive formation of FeSalen as a consequence of the Salen exchange process between Co and Fe cations is effective (upon the addition of a large excess of Fe cations in DMF solution), as was confirmed by UV-visible spectrophotometry and hydrodynamic voltammetry measurements (data not shown). It is important to note that neither FeSalen nor $\mathrm{Fe^{II}}$ alone act as the effective catalyst of the considered reaction (either performed in a double compartment or an undivided electrochemical cell), since the obtained yields were lower than 2%. Thus, the fact that the formation of the binuclear Co–Salen–Fe complex occurs only when a small excess of Fe cations is present in the solution explains why the yields of the coupling reaction are still limited to 43%, at best (see Table 1).

The evolution of the initially introduced CoSalen complex during the constant current electrolysis in the undivided electrochemical cell with an iron anode may be viewed as follows: at the beginning of the electrolysis, the hetero-binuclear Co–Salen–Fe complex is formed as fast as Fe cations are electrogenerated by the anode oxidation. Provided that the ratio Fe : CoSalen is not too large ($<4:1$) this binuclear complex is relatively stable and it evolves into FeSalen for larger concentrations of Fe cations in solution.

Conclusion

Two main conclusions can be emphasized from this study. First, we report for the first time the electroassisted reductive coupling reaction of 2-bromooctane with methyl vinyl ketone, catalyzed by CoSalen complex, under mild experimental conditions and with yields up to 43%. This yield is less satisfactory than that obtained by Scheffold and coworkers,[21] using vitamin $\mathrm{B_{12}}$ (as catalyst) combined with a photoassisted electrosynthesis process in a double compartment electrochemical cell. But, it is important to note that our combined use of CoSalen with the undivided electrochemical cell process offers substantial advantages compared with Scheffold group's experimental conditions. Secondly, the cyclic voltammetry analysis of the composition of the electrolytic solution and its evolution during preparative electrolyses clearly shows the intervention of Fe cations arising from oxidation of the anode which results in the formation of a catalytically active Co–Salen–Fe binuclear complex. Anyhow, additional experiments should be investigated to better evaluate the performance of this binuclear complex in preparative electrosynthesis conditions where it is totally stable. In conclusion, our results corroborate the previously suggested existence of a binuclear Co–Salen–Fe complex and confirms the reported results on the effective role played by the anodically generated cations arising from the undivided electrochemical cell processes with sacrificial anodes, in the case of various electroassisted reductions of organohalides catalyzed by nickel complexes.[14]

Experimental

Chemicals

Dimethylformamide (DMF, from Merck) was dried over 4 Å molecular sieves and used without further purification. Tetrabutylammonium tetrafluoroborate ($\mathrm{Bu^n_4NF_4}$, from Aldrich), tetrabutylammonium bromide ($\mathrm{Bu^n_4NBr}$, from Aldrich), tetrabutylammonium iodide ($\mathrm{Bu^n_4NI}$, from Fluka), 2-bromooctane (Lancaster) and methyl vinyl ketone (Aldrich) were reagent grade and used without purification. CoSalen was either purchased (Aldrich) or prepared from 1 equivalent of $\mathrm{CoCl_2}$ (Aldrich) and 1 equivalent of $\mathrm{H_2Salen}$ (from Lancaster) in DMF solution containing 0.1 mol L^{-1} $\mathrm{Bu^n_4NBF_4}$ or ($\mathrm{Bu^n_4NBr}$ + $\mathrm{Bu^n_4NI}$). In the latter case, cyclic voltammetry and UV-visible spectroscopy proved the formation of the desired CoSalen (data not shown).

Instrumentation

Electroanalytical experimentations. All the electroanalytical experiments were carried out at room temperature with an EG&G-PAR Model 173/interface 270 potentiostat monitored with EG&G-PAR M270 electrochemical software. The working electrode was a vitreous carbon disc electrode of 3 mm diameter (CVJ, from Radiometer-Tacussel). The potentials were measured and referenced to a saturated calomel electrode (SCE) which was placed in a separate compartment containing the solvent (DMF) and the supporting electrolyte ($\mathrm{Bu^n_4NX_4}$ X = F, Br or I). The electrolytic solutions were routinely deoxygenated with argon.

Electrosyntheses. Electrosyntheses were carried out either in double compartment or undivided electrochemical cells. Electrosyntheses carried out in double compartment electrochemical cells with a fritted glass separation were performed with an anode and a cathode made of carbon fibers (total geometric area of 30 cm^2, from Prolabo). Both cathodic and anodic compartments were filled with 25 mL of DMF solution containing $\mathrm{Bu^n_4NBr}$ (0.236 mol L^{-1}) and $\mathrm{Bu^n_4NI}$ (0.054 mol L^{-1}) and kept under an argon atmosphere. CoSalen complex was introduced in the cathodic compartment (15 mmol L^{-1}) and the solution was stirred during 15 minutes. The reaction mixture was heated at 60–80 °C and 2-bromooctane (0.3 mol L^{-1}) and methyl vinyl ketone (0.75 mol L^{-1}) were added. The electrolysis was run at constant current density (0.3 A dm^{-2}) or constant potential (-1.2 V or -1.6 V). The potentials were measured and referenced to a saturated calomel electrode which was placed in a separate compartment containing the solvent and the supporting electrolyte. The reaction was monitored by GC analysis using a 25 m-DB1-capillary column and ethyl undecanoate as external standard. It was stopped after the 2-bromooctane was totally consumed.

Electrosyntheses carried out in an undivided electrochemical cell were performed with a cathode made from a nickel foam grid (geometric area of 30 cm^2) and a sacrificial anode made of a rod of aluminium, magnesium, copper, zinc or iron.

The electrochemical cell was filled with DMF solution (35 mL) containing Bu^n_4NBr (10 mmol L^{-1}) and Bu^n_4NI (8 mmol L^{-1}) and kept under an argon atmosphere. CoSalen complex (10 mmol L^{-1}) or a mixture $CoCl_2$–H_2Salen (10 mmol L^{-1}) was then added and heated at 60–80 °C. After 15 minutes stirring, 2-bromooctane (0.2 mol L^{-1}) and methyl vinyl ketone (0.535 mol L^{-1}) were introduced. The electrolysis was run at constant current density (0.3 A dm^{-2}) or constant potential (-1.2 or -1.6 V). The potentials were measured and referenced to a saturated calomel electrode which was placed in a separate compartment containing the solvent and the supporting electrolyte. The reaction was monitored by GC analysis using a 25 m-DB1-capillary column and ethylundecanoate as external standard. It was stopped after the 2-bromooctane was totally consumed.

In both cases, the reaction products were identified by ^1H and ^{13}C NMR (Bruker 200 MHz) and mass spectrometry (Finnigan ITD 800) and yields calculation were based on GC analysis. The reaction yield (%) was defined as being the ratio (amount of the addition product) : (initial amount of 2-bromooctane) × 100.

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