Selectivity in the Tandem Cyclization – Carboxylation Reaction of Unsaturated Haloaryl Ethers Catalyzed by Electrogenerated Nickel Complexes

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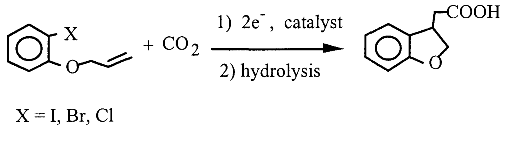
The electrochemical reduction of a series of 2-haloaryl ethers containing allyl and propargyl groups under CO_2 allows the synthesis of benzofuranacetic acid derivatives. This novel intramolecular cyclization–carboxylation reaction is carried out in single-compartment cells and is catalyzed by [Ni(cyclam)Br_2].

Introduction

We have recently explored the possibilities of direct synthesis of substituted dihydrobenzofuran and dihydrobenzopyran derivatives, and we have described a nickel-catalyzed electrochemical method involving the intramolecular reductive cyclization of *o*-haloaryl ethers containing unsaturated side chains.[1] The possibility of intramolecular cascade cyclization reactions involving trapping with CO_2 should allow the construction of carboxylic acids (or their derivatives) in polycyclic structures. Carboxylic acids in benzofuran-, benzopyran-, and indole-type derivatives constitute products of interest in the field of pharmacology[2] and agrochemicals.[3] Moreover, the direct and selective incorporation of CO_2 into cyclic compounds may widen the field of its utilization as a carbon source for organic compounds.[4]

We present here our results on the tandem cyclization−carboxylation reaction of substrates such as **1** in the presence of CO_2, for the electrosynthesis of a series of dihydrobenzofuran- and dihydrobenzopyran-containing carboxylic acids (Equation 1).

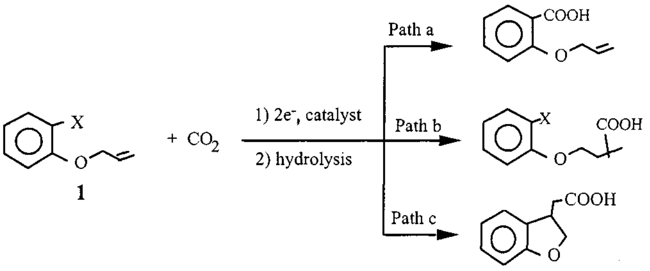


Intramolecular reductive cyclizations of ether derivatives such as **1** can be effected in the presence of tin hydrides[5] or Sm^{II} species[6] as stoichiometric reagents, and require generally the more activated iodo (or sometimes bromo) derivatives. Electrochemical methods with Co[7] or Ni[8] complexes have also been reported for related reactions. We have shown that [Ni(cyclam)Br_2] (cyclam = 1,4,7,11-tetraazacyclotetradecane) is an efficient catalyst for the electrochemical cyclization of substrates **1**.[1] However, no tandem cyclization−CO_2 incorporation processes have, to the best of our knowledge, yet been described.[9]

The electrochemical CO_2 fixation into organic substrates deals with the problem of the direct CO_2 reduction. It is worth noting that Ni^{II} complexes, and particularly [Ni(cyclam)$^{2+}$ · 2 ClO_4^-] have been reported to be efficient catalysts for the CO_2 electroreduction to carbon monoxide with high selectivities, in water-containing solvents.[10]

According to literature data on electrochemical carbon dioxide incorporation into aromatic halides or into unsaturated hydrocarbons, different reaction products can be expected from the electroreductive heterocoupling reaction between substrates **1** and CO_2 (Scheme 1). On one hand, as illustrated by path a, the direct electrocarboxylation of aromatic halides to afford benzoic acid derivatives may constitute a possible coupling reaction of substrates such as **1** with carbon dioxide.[11] This Ar → ArCOOH electrochemical reaction has been reported to afford good yields with the use of consumable anodes[12] or in the presence of (phosphane)nickel complexes as the catalysts[13] in the case of phenyl bromide.

On the other hand, the direct CO_2 fixation on the double (or triple) bond of the unsaturated side chain of **1** (path b) should also be considered as a possible reaction pathway, in the light of the examples of electrochemical carboxylation of unsaturated hydrocarbons (alkynes,[14] olefins[15]) in the presence of Ni^{II} associated to catalytic 2,2′-bipyridine systems.



Scheme 1. Possibilities of electrocarboxylation of substrates **1**

Our own results on the [Ni(cyclam)Br_2]-catalyzed electrochemical cyclization of substrates **1** leading to 3-methyldihydrobenzofuran led us to explore a third and not yet re-

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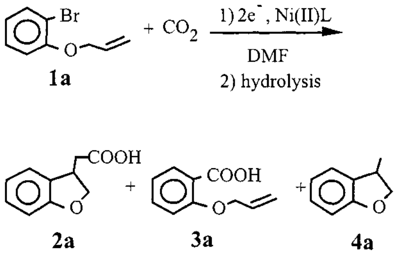
ported possibility, involving a tandem cyclization−CO_2 uptake process, as illustrated by path c.

Results and Discussion

1. Influence of the Catalytic System on the Electrochemical Cyclization−Carboxylation of 1a

In order to study the possibilities of an electrochemical tandem cyclization−carboxylation reaction, we first examined the influence of the nickel catalyst in the electroreduction of **1a** (Equation 2), by varying the nature of the ligand associated to the nickel complex.



The results are presented in Table 1. Carboxylic acids **2a** and **3a**, in cyclized and noncyclized structures, respectively, were obtained, together with cyclized, noncarboxylated 3-methyldihydrobenzofuran (**4a**).

The electrochemical methodology was based on the use of single-compartment cells fitted with a consumable magnesium anode. This methodology has already shown a wide applicability in several electrosynthetic processes.[16][17] The reactions were carried out in freshly distilled DMF, under constant current intensity, at room temperature and atmospheric CO_2 pressure, with a 10% molar ratio of nickel complex to substrate and a magnesium/carbon fiber couple of electrodes.

Table 1. Influence of the catalyst system on the electrocarboxylation of **1a** (CO_2, 1 atm, 20 °C)

Entry	Nickel complex[a]	F/mol[b]	Products (% yield) 2a	3a	4a	Ratio 2a/3a
1	$Ni(cyclam)Br_2$	2.3	33	4	49	8.3:1
2	$Ni(cyclam)^{2+} \cdot 2\,BF_4^-$	4.1	50	10	40	5:1
3	$Ni(tmc)Br_2$	3.6	8	5	19	1.5:1
4	$Ni(dme)Br_2 + 4\,PPh_3$[c]	4.4	45	−	38	−
5	$Ni(dme)Br_2 + 2$ dppe	4.6	16	−	48	−
6	$Ni(bipy)_3{}^{2+} \cdot 2\,BF_4^-$[d]	2	−	−	6	−
7	$Ni(dme)Br_2 + 2$ PMDTA[e]	5	−	−	8	−

[a] A 10:1 molar ratio of **1a**/Ni^{II} was used with Mg/C as couple of electrodes. − [b] F/mol needed for complete conversion. − [c] dme = dimethoxyethane. − [d] With 2,2′-bipyridine as the ligand, phenol and 2-bromophenol were obtained in 45% and 40% yield, respectively. − [e] With PMDTA as the ligand, phenol and 2-bromophenol were obtained in 35% and 35% yield, respectively.

The results in Table 1 show the important influence of the nickel complex and particularly of the nature of the ligand, which can determine the nature of the reaction products as well as the selectivity of the process.

In the absence of the catalyst, a nonselective reaction occurred and a mixture of compounds was formed in low yield. No reaction occurred in the absence of electricity.

The use of $[Ni(cyclam)Br_2]$[18] as the catalyst in the electrochemical reduction of **1a** occurred with 85% faradic yield and afforded dihydrobenzofuran-3-ylacetic acid (**2a**), furnished by the cascade cyclization−carboxylation reaction, in 33% chemical yield (Table 1, entry 1). 3-Methyldihydrobenzofuran (**4a**) was also formed in 49% yield. Carboxylated, noncyclized **3a**, issued from the direct carboxylation of the aryl moiety, was obtained in only 4% yield. The selectivity of carboxylated compounds **2a/3a** was 8.3:1.

When cationic $[Ni(cyclam)^{2+} \cdot 2\,BF_4^-]$ was used as the catalyst (entry 2), **2a** was formed in 50% yield with a **2a/3a** selectivity of 5:1.

We can conclude that in the presence of the catalytic (cyclam)nickel system, the cyclization−carboxylation process is preferred to the direct carboxylation of the aryl−halogen bond.

Interestingly, the good faradic yield obtained in the electrolysis of **1a** with $[Ni(cyclam)Br_2]$ (R_f of 85%) indicates that in anhydrous DMF, $[Ni(cyclam)Br_2]$-catalyzed intramolecular cyclization−carboxylation under CO_2 can be performed, and that the direct CO_2 electroreduction to give CO[10] can be inhibited in the presence of the substrate. The catalyst thus effects a very selective substrate selectivity able to orient the reactivity towards the organic halide and not towards the carbon dioxide reduction.

With $[Ni(cyclam)^{2+} \cdot 2\,BF_4^-]$, the faradic yield was of 48% (consumption of 4.1 F/mol for complete conversion), the process involving some parallel CO_2 electroreduction.

In sharp contrast to these results, when the electrolysis of **1a** was run with the analogous tetramethylcyclam (tmc) as the ligand of nickel, the (tmc)Ni system resulted in a less efficient and less selective carboxylation reaction (entry 3).

The $(Ph_3P)Ni$ system seemed more efficient towards the cyclization, and afforded **2a** in 45% yield (entry 4). The use of (diphenylphosphanyl)ethane (dppe) as the ligand lowered the yield of **2a** to 16% (entry 5). The presence of phosphanes involved a difficult and low-yield purification of the reaction products. The low faradic yield in these cases indicates that the CO_2 reduction process takes place simultaneously to the Ar−Br reduction.

By changing the ligand to 2,2′-bipyridine (entry 6) or to PMDTA (entry 7, PMDTA = pentamethyldiethylenetriamine), the entire chemoselectivity of the process was modified: No cyclization nor carboxylation products **2a** and **3a** were obtained, and no CO_2 incorporation into the unsaturated double bond of that side chain could be observed (Scheme 1, path b).

With $[Ni(bipy)_3{}^{2+} \cdot 2\,BF_4^-]$[14] or catalytic (PMDTA)Ni systems and **1a**, deallylation and dehalogenation occurred; the cleavage of the carbon−oxygen bond of the allyl group was carried out selectively to afford a mixture of phenol and 2-bromophenol in 85 and 70% yield, respectively. The deallylation reaction could be run more selectively in the absence of CO_2.[19]

Our results in Table 1 clearly indicate that the nature of the ligand associated to the nickel center (phosphane, bipyridine, or cyclam-type ligand) plays an important role in determining the chemoselectivity of the carboxylation process.

2. Influence of the Nature of the Electrodes

The reaction yields and selectivities were shown to be dependent on the reaction conditions, particularly on the nature of the electrodes. Table 2 presents the results obtained with the use of Mg and Zn as the anodes, and of carbon fiber, nickel foam or stainless steel as the cathode materials for the electrocarboxylation of **1a** with [Ni(cyclam)Br_2] as the catalyst.

Table 2. Influence of the nature of the electrodes and of the CO_2 pressure in the electrocarboxylation of **1a** with Ni(cyclam)Br_2 as the catalyst

Entry	Anode	Cathode	CO_2 [atm]	Products (% yield) **2a**	**3a**	**4a**	Ratio **2a/3a**
1	Mg	C	1	33	4	49	8.3:1
2	Zn	C	1	3	3	67	1:1
3	Mg	Ni	1	50	36	14	1.4:1
4	Mg	Stainless steel	1	30	10	10	3:1
5	Mg	Stainless steel	3	48	28	20	1.7:1

At 1 atm of CO_2 with a magnesium/carbon fiber couple of electrodes, 33% of **2a** and 49% of **4a** were obtained, with a **2a/3a** ratio of 8.3:1 (entry 1). The nature of the anodic material strongly determined the yields or reactivity in carbon dioxide fixation. Thus, the replacement of the magnesium by a zinc anode (with a carbon fiber cathode, entry 2) made the global carboxylation yield of **1a** drop from 37 to 6%. With a zinc anode the faradic yield dropped to 30%; the reduction of the electrogenerated zinc ions affording metallic zinc, at potentials similar to those of the reduction of the nickel(II) complex, took place preferentially.

The nature of the cathodic material could also strongly influences the carboxylation selectivity, as shown by comparing entries 1 and 3. With an Mg/Ni couple of electrodes, **1a** afforded 50% yield of the expected carboxylic acid **2a** and 36% of carboxylated, noncyclized **3a**. However, the ratio of carboxylation/cyclization to **2a** versus direct aryl carboxylation to **3a** went down to 1.4:1 (entry 3).

The use of a magnesium/stainless steel couple of electrodes (entry 4) led to 30% of **2a** with a **2a/3a** ratio of 3:1.

A carbon fiber cathode seems to favor the cyclization and/or cyclization−carboxylation processes (entry 1), whereas a nickel foam cathode offers a high carboxylation yield but tends to orient the reaction towards the direct carboxylation of the Ar−Br bond (entry 3). The observed differences in yield and selectivities could partially be due to a different current density.

3. Influence of the Carbon Dioxide Pressure

The electrocarboxylation of **1a** catalyzed by [Ni(cyclam)Br_2] was carried out in DMF at a CO_2 pressure of 3 atm, with a magnesium/stainless steel couple of electrodes. Among the products, **2a** was obtained in 48% yield, together with **3a** (28%) and **4a** (20%). The CO_2 pressure also influenced the results, and an increase of the pressure from 1 to 3 atm improved the carboxylation yield of **1a** by 18% (Table 2, entries 4, 5). However, the ratio **2a/3a** was lowered to 1.7:1. Under 3 atm of CO_2 the rate of the direct CO_2 electroreduction was enhanced, thus decreasing the faradic yield to 20%.

4. Tandem Cyclization−Carboxylation Reaction

The catalytic (cyclam)Ni system, which afforded the best carboxylation selectivity, was chosen for the cyclization−carboxylation of other substrates in electrolyses with Mg/C or Mg/Ni electrodes at 1 atm of CO_2. The results concerning the carboxylic acid electrosyntheses are presented in Table 3.

Entries 1−3 involve the cyclization of allyl 2-halophenyl ethers with either iodo, bromo, or chloro substituents. In the electrochemical reductive carboxylation of the 2-(allyloxy)-1-iodobenzene (**1b**) the expected dihydrobenzofuran-3-ylacetic acid (**2a**) was obtained in 41% yield, together with **3a** (13%). The cyclized dimerization product **5a** was the major compound (46% yield, see Scheme 3). The formation of dimer **5a** was specific of the iodo derivative, thus indicating a possible radical reactivity of the intermediate cyclized species in this case (entry 2).

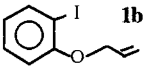
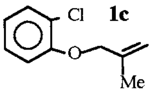
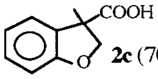
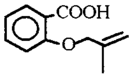
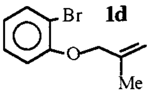
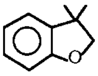
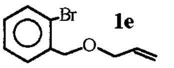
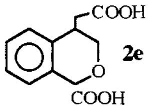
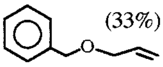
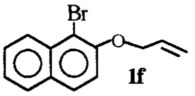
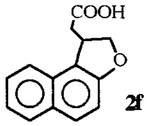
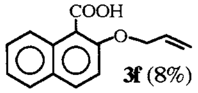
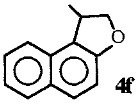
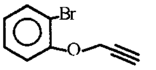
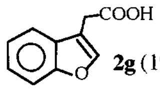
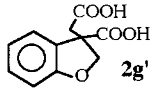
The possibility of activation of the C−Cl bond (entry 3) in **1c** is interesting, considering that the less available iodo (or bromo) derivatives are required in the R_3Sn-H[5] or SmI_2[6]-mediated cyclizations. In the case of the electrocarboxylation of **1c**, a mixture of two carboxylic acids was formed in 85% yield (with a 64% conversion): the bicyclic carboxylic acid **2c** (70%) and the benzoic acid derivative **3c** (15%).

The cyclization of the analogous bromo methallyl derivative **1d** (entry 4) led to the formation of the dihydrobenzofuranylacetic acid derivative **2c** with a quaternary carbon center, in 40% yield together with 50% of cyclized compound **4c**.

The synthesis of the dihydropyran-2-ylacetic acid **2e** (24%) could be carried out by the cyclization−carboxylation of an allyl benzyl ether derivative (**1e**, entry 5). Direct debromination to the corresponding allyl benzyl ether also took place in 33% yield.

Naphthyl derivative **1f**, electrolyzed with a carbon fiber as the cathode (entry 6), mainly afforded cyclization to **4f** (47%), together with cyclization−carboxylation to **2f** (8%) and direct carboxylation of the aromatic position (**3f**, 8%). The same reaction with a nickel foam cathode (entry 7) led to a preferential CO_2 fixation in the aromatic position, forming 2-allyloxy-1-naphthoic acid (**3f**) in 60% yield. Here again, the nature of the cathodic material strongly influ-

Table 3. Tandem intramolecular cyclization−carboxylation of substrates **1** with the catalytic [Ni(cyclam)$^{2+}$] system (CO_2 pressure, 1 atm, 20 °C)

		Products	
Entry	**Substrate**	**Carboxylated**	**Non-Carboxylated**
1[a]	**1a**	**2a** (50%) **3a** (36%)	**4a** (14%)
2[a]	 **1b**	**2a** (41%) **3a** (13%)	**5a** (46%)
3[b,c]	 **1c**	 **2c** (70%)  **3c** (15%)	**4c** (4%)
4[d]	 **1d**	**2c** (40%)	 **4c** (50%)
5[d]	 **1e**	 **2e** (24%)	 (33%)
6[e]	 **1f**	 **2f** (8%)  **3f** (8%)	 **4f** (47%)
7[b]	**1f**	**3f** (60%) **2f** (13%)	**4f** (10%)
8[b]	 **1g**	 **2g** (19%)  **2g'** (20%) **2a** (27%)	

[a] [Ni(cyclam)Br_2] as the catalyst and Mg/Ni as the electrodes. − [b] [Ni(cyclam)$^{2+}$ · 2 BF_4^-] as the catalyst and Mg/Ni as the electrodes. − [c] Conversion of 64% after 8 F/mol. − [d] [Ni(cyclam)Br_2] as the catalyst and Mg/C as the electrodes. − [e] [Ni(cyclam)$^{2+}$ · 2 BF_4^-] as the catalyst and Mg/C as the electrodes.

enced the carboxylation selectivity; the nickel foam cathode selectively orients the process towards the direct carboxylation of the Ar−Br bond.

The carboxylative cyclization could also be carried out with propargyl derivatives such as *o*-bromophenyl propargyl ether (**1g**, entry 8). The [Ni(cyclam)$^{2+}$]-catalyzed carboxylation led to three different cyclized carboxylic acids in a global 67% yield: the expected benzofuran-3-ylacetic acid (**2g**) its reduced analog **2a** and a dicarboxylic acid **2g′**.

5. Electrochemical Studies

Some mechanistic aspects of this tandem reaction were investigated. Cyclic voltammetry experiments showed that a 1e$^-$ reversible reduction of Ni(cyclam)$^{2+}$ to Ni(cyclam)$^+$ occurs at −1.45 V vs Ag/AgCl in DMF solutions containing tetrabutylammonium tetrafluoroborate, as shown in Figure 1, curve a), in agreement with literature data.[20][21]

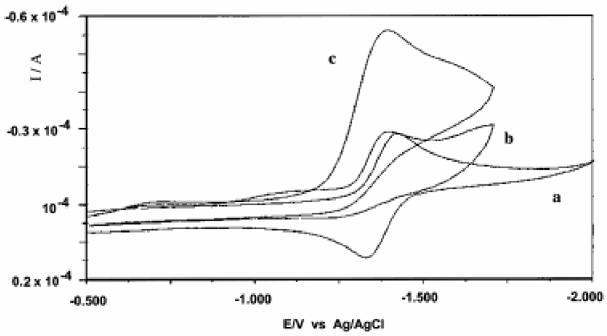
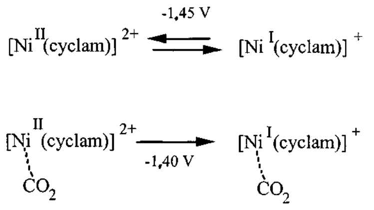


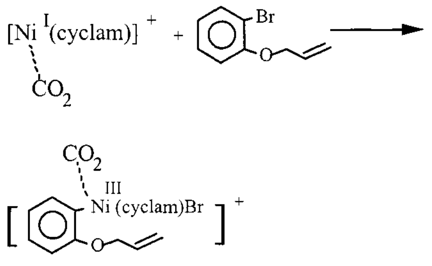
Figure 1. Cyclic voltammetry on a carbon graphite electrode (v = 100 mVs^{-1}) of a DMF/nBu$_4$N$^+$BF$_4$$^-$ solution containig: curve **a**: [Ni(cyclam)Br$_2$] (2.5 M); curve **b**: [Ni(cyclam)Br$_2$] (2.5 M) and CO$_2$ (saturated solution at 1 atm); curve **c**: [Ni(cyclam)Br$_2$] (2.5 M) and CO$_2$ (saturated solution at 1 atm) + **1a** (3 equiv.)

Upon addition of CO$_2$ (saturated solution at 1 atm), the Ni^{II}/Ni^{I} reduction potential was slightly shifted to −1.40 V (curve b) with the same initial intensity, the process being irreversible. This is compatible with a CO$_2$ coordination to the Ni^{II} and to the Ni^{I} species, as illustrated in Scheme 2.



Scheme 2. Reduction of Ni(cyclam)$^{2+}$ complexes

The cyclic voltammetric behavior of Ni(cyclam)$^{2+}$ in the presence of CO$_2$ in anhydrous DMF (Figure 1) is in contrast to the catalytic wave of CO$_2$ reduction to CO reported in water.[10] In DMF, no catalytic current was observed. When one or more equivalents of **1a** with respect to Ni^{II} were added to the electrolytic solution (3 equiv., curve c), the Ni^{II}/Ni^{I} reduction peak at −1.40 V doubled its initial intensity and remained irreversible. A similar behavior was observed in the absence of CO$_2$.[21] We can propose a chemical reaction between the electrogenerated Ni^{I} species and **1a**, with formation of a new intermediate, according to Equation 3, which in turn undergoes a one-electron reduction at the same potential.



Curve c indicates that the process consumes 2 F/mol of nickel, and that it is not catalytic. We carried out some preparative-scale electrolyses at the controlled potential of −1.5 V in two-compartment cells in DMF containing nBu$_4$N$^+$BF$_4$$^-$ (0.1 M). Ni(cyclam)Br$_2$ and **1a** (in a 1:3 molar ratio) were introduced into the cathodic compartment under CO$_2$ bubbling and could be electrolyzed up to the passage of 1.6 F/mol of nickel, after which passivation occurred. Starting compound **1a** could be recovered in 75% yield and the reaction led to 10% of **2a** (40% according to conversion), 6% of **4a** and 5% of dimer **5a**. Under these experimental conditions, the tandem cyclization−carboxylation reaction takes place, but the Ni^{II} species are not efficiently recycled. However, when the electrolysis was carried out in a single-compartment cell with a Mg anode, no passivation occurred and the reaction could be run catalytically with a Ni^{II}/**1a** molar ratio of 1:10. These results give evidence of the important role of the magnesium ions (issued from the anodic oxidation process) in the recycling of the nickel species and therefore in allowing the reaction to be catalytic.

6. Proposed Catalytic Cycle

A catalytic cycle is proposed in Scheme 3, illustrating plausible pathways to the different reaction products that have been isolated from the carboxylation reaction of **1a**.

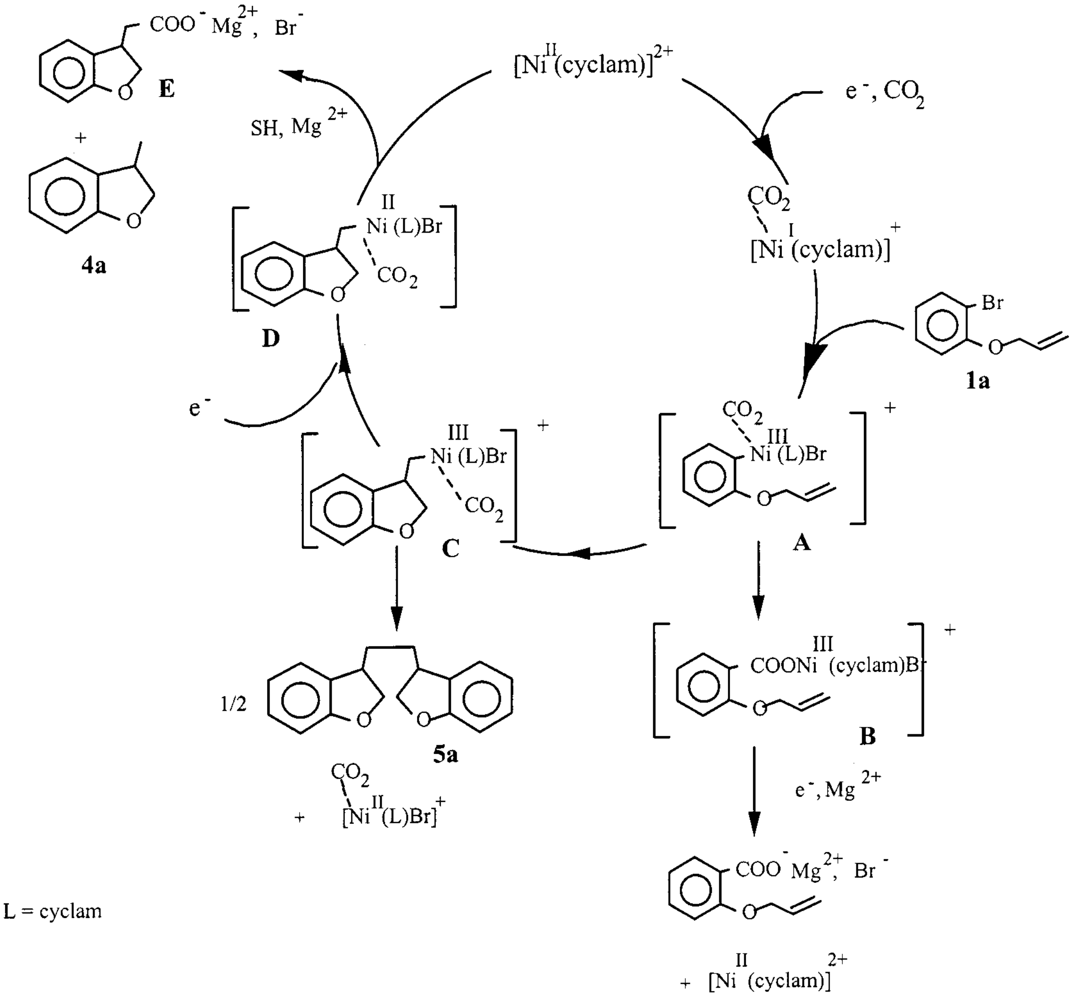
The electrochemical reduction of Ni(cyclam)$^{2+}$ affords Ni^{I} species. In the tandem cyclization−carboxylation process, we have a competition of the electrogenerated Ni^{I} species, either for the reaction with the aryl halide[21] or for the direct CO$_2$ reduction.[10] According to the results of the electrosynthesis and to the electrochemical behavior shown by cyclic voltammetry, we propose a preferred oxidative addition of the Ni^{I} species (coordinated to CO$_2$) to the C(aryl)−halogen bond of **1a**. After oxidative addition, the formation of Ni^{III} intermediate species **A** is proposed. This Ni^{III} intermediate induces a radical character to the aryl moiety, resulting in a rapid intramolecular cyclization on the double bond in the side chain, leading to **C**. The oxidative addition of the electrogenerated Ni^{I} species to alkyl halides followed by a radical-type reaction has already been reported.[20][21]

Further one-electron reduction of Ni^{III} intermediate species **C** should form an alkylnickel(II) species **D**, able to undergo CO$_2$ uptake, forming a nickel(II) carboxylate. The overall reaction is a two-electron process. Competitive protonation of **D** by the electrolytic medium (solvent) affords cyclized, noncarboxylated **4a**.

In the one-compartment cell procedure with a magnesium anode, the presence of the magnesium ions issued from the anodic oxidation process, enables the formation of a magnesium carboxylate **E** liberating the nickel species for further recycling. Magnesium carboxylate **E** is stable under the reaction conditions, it accumulates during electrolysis and it is simply hydrolyzed (or esterified to the corresponding methyl esters) at the end of the reaction.

In a competitive reaction, intermediate **A** can also be directly reduced and carboxylated to afford the corresponding benzoic acid derivatives via intermediate **B**.

Intermediate **C**, an alkylnickel(III) species possessing some radical character, can also undergo a radical-type di-



Scheme 3. Proposed catalytic cycle

merization leading to product **5**. This dimer was only obtained in reactions in the absence of Mg^{2+} ions, or when starting with the iodo substrate **1b**.

As shown by our experimental results, slight modifications of the reaction conditions or of the nature of the substrates may direct the main catalytic cycle towards the different reaction products.

Conclusions

In conclusion, we studied a new example of a tandem cyclization−carboxylation reaction under electrochemical conditions. [Ni(cyclam)Br$_2$] and [Ni(cyclam)$^{2+}$ · 2 BF$_4$$^-$] were shown to be efficient and selective catalysts for the incorporation of carbon dioxide in a sequential electrochemical cyclization−carboxylation reaction of a series of allyl *o*-haloaryl ethers and related compounds. The direct, one-step synthesis of carboxylic acid in bicyclic structures of benzofuran and benzopyran-type was achieved under very mild conditions (room temperature, atmospheric CO_2 pressure).

By careful control of the reaction conditions, competitive reactions such as the direct carboxylation of the aromatic ring or the direct reduction of CO_2 may become less favored processes. The ligand was shown to be dominant in controlling the reactivity and the chemoselectivity of the processes. The nature of the electrodes may also strongly influence the selectivity of the CO_2 fixation.

Experimental Section

General: All solvents were dried and degassed by standard methods. DMF was freshly distilled from calcium hydride before electrolyses. Allyl 2-bromophenyl ether (**1a**) (and other allyl ethers) was prepared from 2-bromophenol by treatment with allyl chloride and potassium carbonate in DMF.

Instrumentation and Cells: NMR: Bruker AC-200 spectrometer (200 MHz and 50.3 MHz for ^1H and ^{13}C, respectively), with $CDCl_3$ as solvent, TMS as internal standard. − IR: KBr disks; Nicolet 520 FT-IR spectrometer. − MS: Finnigan MAT INCOS 500E spectrometer (GC/MS, 70 eV). − Cyclic voltammetry experiments and controlled potential electrolyses were performed with the aid of P.A.R. Scanning Potentiostat model 362 equipment, and were carried out at 25°C by utilizing Pt or carbon fiber microelectrodes (Tacussel). All potentials were quoted with respect to Ag/AgCl electrode at room temperature, which correspond to a potential difference from that of Fc/Fc$^+$ of -0.55 V in DMF/nBu$_4$N$^+$BF$_4$$^-$. Controlled constant intensity electrolyses were carried out with a stabilized constant current supply (Sodilec, EDL 36.07). The electrochemical one-compartment cell is a cylindrical glass vessel of approx. 40 mL volume, equipped with a carbon fiber cathode (20 cm^2) and a magnesium rod anode immersed to 3 cm. In the two-compartment cell, the two compartments are separated by a sintered glass frit (no. 4); the anodic compartment has a Pt wire as the anode, and the cathodic compartment is equipped with a carbon fiber cathode and a Ag/AgCl electrode.

General Procedure for One-Compartment Cell Electrolyses: A DMF solution (40 mL) containing [Ni(cyclam)Br$_2$] (0.3 mmol, **1a**) (or the other ether derivatives, 3 mmol) and nBu$_4$N$^+$BF$_4$$^-$ (0.2 mmol) was placed in the cell and stirred at room temperature under nitrogen. A current of 60 mA was applied between the electrodes connected to a DC power supply (apparent current density of 0.3 A·dm^{-2}, applied voltage ca. 3−15 V). The consumption of **1** was monitored by GC analysis of aliquots withdrawn from the reaction mixture, and the electrolysis was continued until the starting material was almost depleted, e.g. about 4−6 h. Generally, 2−5 F/mol of **1** was necessary to achieve a complete conversion. The electrolytic solutions were directly esterified by adding K$_2$CO$_3$ and methyl iodide, stirring at 50°C for 10 h, and then hydrolyzing with aqueous HCl (0.1 M up to pH = 1−2) and extracting with Et$_2$O. Methyl esters of the corresponding carboxylic acids were prepared for ease of purification. The organic layers, dried with MgSO$_4$, were filtered and concentrated. The products were purified by column chromatography on silica gel with pentane/Et$_2$O mixtures as eluent. Most of the products are known compounds[22−24] and their spectral data were compared to authentic samples. Spectral data for other compounds:

1,2-Bis(dihydrobenzofuran-3-yl)ethane (5a): ^{1}H NMR (CDCl$_3$, TMS): δ = 7.15−7.00 (4 H, m), 6.85−6.65 (4 H, m), 4.56 (2 H, t; J = 0.7), 4.14 (2 H, dd, J = 0.7, 0.4), 3.29−3.45 (2 H, m), 1.40−1.75 (4 H, m). − ^{13}C NMR (CDCl$_3$, TMS): δ = 160.1, 130.5, 128.3, 124.3, 124.2, 120.5, 76.6, 41.9, 32.3. − MS (70 eV); m/z (%): 266 [M$^+$], 133, 132, 119, 91(100), 65.

Methyl 3-Methyldihydrobenzofuran-3-carboxylate (2c): ^{1}H NMR (CDCl$_3$, TMS): δ = 7.23−6.83 (4 H, m), 4.63 (1 H, d, J = 9.5), 4.32 (1 H, d, J = 9.5), 3.49 (3 H, s); 2.70 (2 H, d, J = 3.8), 1.45 (3 H, s). − ^{13}C NMR (CDCl$_3$, TMS): δ = 172.8, 159.7, 129.1, 128.5, 124.6, 121.6, 109.7, 76.7, 51.8, 45.3, 43.6, 38.3). − MS (70 eV); m/z (%): 206 [M$^+$], 175, 146, 131, 120, 92, 86, 77, 63, 55(100).

General Procedure for Two-Compartment Cell Electrolyses: Both compartments were filled with a DMF solution (30 mL each) of nBu$_4$N$^+$BF$_4$$^-$ (1 g, 3 mmol) under inert atmosphere. The desired (cyclam)Ni$^{\mathrm{II}}$ complex (0.1 mmol) and **1a** (0.3 mmol) were added to the cathodic compartment, saturated with CO$_2$. The electrolyses were run at 20°C at the controlled potential of -1.5 V and were stopped when the current was negligible. The workup was the same as described above, the reaction being followed by GC.

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