Organometallics **1998,** *17,* 3747−3753

Electrochemical Studies of Ni(cyclam)$^{2+}$-Catalyzed Annulation Reactions

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Received March 31, 1998

Cyclic voltammetry and preparative-scale electrochemical studies on the intramolecular cyclization of allyl 2-halophenyl ethers catalyzed by Ni(II)−cyclam complexes leads us to propose a mechanism involving Ni(I) and Ni(III) intermediate species. The role of Mg^{2+} ions in the reactivity and selectivity of the process is discussed. The Ni(cyclam)Br_2-catalyzed electrosynthesis of dihydrobenzofurans and dihydrobenzopyrans from unsaturated side-chain aryl halide derivatives is effected in good yields in the presence of a magnesium anode.

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Introduction

Organometallic catalysis combined with the use of electrochemical methods is a growing field of interest, due to the numerous possibilities for selective coupling of organic molecules shown by electrosynthesis.[1] New catalytic systems as well as novel synthetic applications have recently been reported.[2]

Within this field, we have been interested in the catalytic activity of Ni(II) complexes associated with cyclam-type ligands (cyclam = 1,4,7,11-tetraazacyclotetradecane). We have described the electrochemical, nickel-catalyzed intramolecular cyclization of 2-haloaryl ethers containing unsaturated side chains[3] and the electrosynthesis of cyclic carbonates from epoxides and carbon dioxide catalyzed by Ni(cyclam)Br_2.[4]

Ni(II) complexes associated with tetraaza macrocyclic ligands related to cyclam have also been used as catalysts in electrochemical reduction of CO_2 to CO,[5] as well as in intramolecular cyclization reactions involving aryl or vinyl bromides,[6] bromoacetals,[7] or α-bromoamides[8] with double or triple bonds.

Mechanistic aspects have been described in the Ni(cyclam)$^{2+}$-catalyzed electroreduction of CO_2 in water medium, involving Ni(I) and Ni(III) intermediates.[5b] Ni(I) and Ni(III) intermediates with dppe ligands have also been proposed in the biphenyl electrosynthesis from bromobenzene[9] and in its carboxylation.[9b] However, within the topic of intramolecular cylizations, no mechanistic studies have yet, to our knowledge, been reported.

Ni(II) with cyclam or related ligands has been shown to undergo a reversible one-electron reduction to Ni(I) species,[10] the macrocyclic ligand stabilizing the Ni(cyclam)$^+$ complexes. Concerning the reactivity of such complexes, Gosden and Pletcher have reported their reaction in the presence of an alkyl bromide.[11] The authors propose an oxidative addition of Ni(I) to the alkyl halide, to form a Ni(III) intermediate in which the alkyl moiety presents a radical-type reactivity, shown by the formation of R−R-type dimers.

We present here some electrochemical and mechanistic aspects of the Ni−cyclam-catalyzed intramolecular cyclization of allyl 2-halophenyl ethers and related substrates. Some synthetic applications have been reported in a preliminary communication.[3]

Results and Discussion

The electroreduction reaction of allyl 2-bromophenyl ether (**1a**), carried out in DMF in a single-compartment cell fitted with a magnesium rod anode and a carbon fiber cathode, led to the synthesis of 3-methyl-2,3-dihydrobenzofuran (**2a**) in 86% yield. The electrolysis was catalyzed by Ni(cyclam)Br_2 (10% molar ratio with respect to the substrate) and run at room temperature and under constant controlled intensity (eq 1). The overall process consumes 2−3 F/mol of halide. The electrochemical methodology of using metal anodes in single-compartment cells has led to good yields in several electrosynthesis processes and allows the staightforward scale-up of the reactions.[12]

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[5] (a) Fischer, B. J.; Eisenberg, R. *J. Am. Chem. Soc.* **1980**, *102*, 7361. (b) Beley, M.; Collin, J. P.; Sauvage, J. P. *J. Am. Chem. Soc.* **1986**, *108*, 7461.

[6] (a) Ozaki, S.; Matsui, E.; Waku, J.; Ohmori, H. *Tetrahedron Lett.* **1997**, *38*, 2705. (b) Ozaki, S.; Horiguchi, I.; Matsushita, H.; Ohmori, H. *Tetrahedron Lett.* **1994**, *35*, 725. (d) Clinet, J. C.; Duñach, E. *J. Organomet. Chem.* **1995**, *503*, C48.

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[8] (a) Ozaki, S.; Matsushita, H.; Ohmori, H. *J. Chem. Soc., Perkin Trans. 1* **1993**, 2339. (b) Ihara, M.; Katsumata, A.; Setsu, F. Tokunaga, Y.; Fukumoto, K. *J. Org. Chem.* **1996**, *61*, 677.

[9] (a) Amatore, C.; Jutand, A. *Organometallics* **1998**, *7*, 2203. (b) Amatore, C.; Jutand, A. *J. Am. Chem. Soc.* **1991**, *113*, 2819.

[10] (a) Healy, K. P.; Pletcher, D. *J. Organomet. Chem.* **1978**, *161*, 109. (b) Gosden, C.; Kerr, J. B.; Pletcher, D.; Rosas, R. *J. Electroanal. Chem.* **1981**, *117*, 101. (c) Espenson, J. H.; Ram, M. S.; Bakac, A. *J. Am. Chem. Soc.* **1987**, *109*, 6892.

[11] Gosden, C.; Pletcher, D. *J. Organomet. Chem.* **1980**, *186*, 401.

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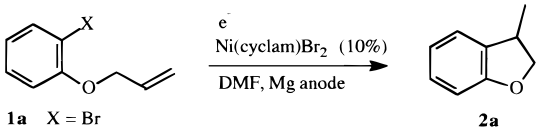


(1)

1a X = Br
1b X = I
1c X = Cl

2a

In the presence of the analogous cationic complex Ni(cyclam)$^{2+}$•2BF$_4$$^-$ as the catalyst, **1a** was converted into **2a** in 75% yield after 2.2 F/mol. The iodo derivative, **1b**, afforded the cyclic ether in 90% yield. Interestingly, allyl 2-chlorophenyl ether (**1c**) could also be cyclized to **2a** in 60% yield (Table 1). The presence of the catalyst was essential for a selective cyclization; in the absence of the nickel complex, a nonselective reaction took place in which the protodehalogenation and the double bond isomerization became the main processes.[13]

No 3-methylbenzofuran was found as a byproduct in the nickel-catalyzed electrochemical cyclization. Benzofurans are not intermediates in this reaction; when benzofuran as starting substrate was reacted under the same conditions as in eq 1, it was quantitatively recovered unreacted. Intramolecular reductive cyclizations of allyl ethers such as **1** can also be effected in the presence of tin hydrides[14] or Sm(II) species[15] but in stoichiometric reactions, which generally require the use of more activated iodo (or sometimes bromo) derivatives.

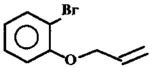
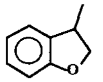
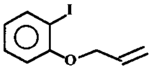
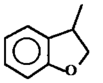
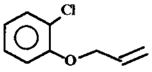
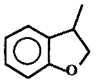
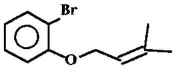
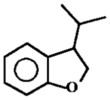
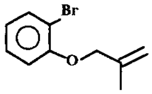
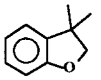
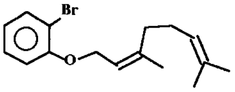
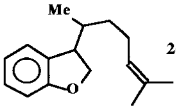
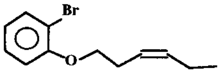
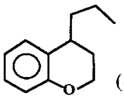
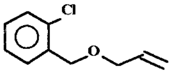
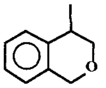
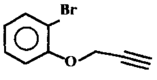
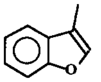
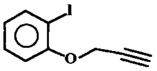
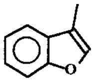
A. Cyclic Voltammetry Behavior. Cyclic voltammetry and related coulometric experiments show that a 1e$^-$ reversible reduction of Ni(cyclam)Br$_2$ occurs at −1.45 V vs Ag/AgCl (−2.0 V vs Fc/Fc$^+$) in tetrabutylammonium tetrafluoroborate-containing DMF solutions, as shown in Figure 1, curve a), in agreement with literature data.[10] The reduction peak corresponds to the transition of Ni(II) to Ni(I), according to eq 2. Upon

$$\mathrm{Ni(cyclam)}^{+2} + e^- \rightleftharpoons \mathrm{Ni(cyclam)}^+ \qquad (2)$$

addition of 1 molar equiv of **1a** (curve b), the peak becomes irreversible, and its intensity is doubled. Curves c and d show the behavior of the nickel complex in the presence of excess **1a**: the peak remains irreversible, and its intensity is not sensibly modified. The reduction of **1a** alone takes place above −2 V.

These results indicate that a two-electron reduction peak of the Ni(II) complex at −1.45 V occurs upon addition of **1a** (1 or more equiv), independent of the halide concentration, and that initial Ni(II) species are not recycled under the experimental conditions.

Table 1. Electrochemical Intramolecular Cyclization of Aryl Ethers 1 Catalyzed by Ni(cyclam)Br$_2$

Entry	Starting substrate	Cyclized Product (% Yield)
1	 1a	 2a (86%)
2	 1b	 2a (90%)
3	 1c	 2a (60%)
4	 1e	 2e (62%)
5	 1f	 2f (54%)
6	 1d	 2d + 2d' (71%)
7	 1g	 2g (40%)
8	 1h	 2h (56%)
9	 1i	 2i (32%)
10	 1j	 2i (31%)

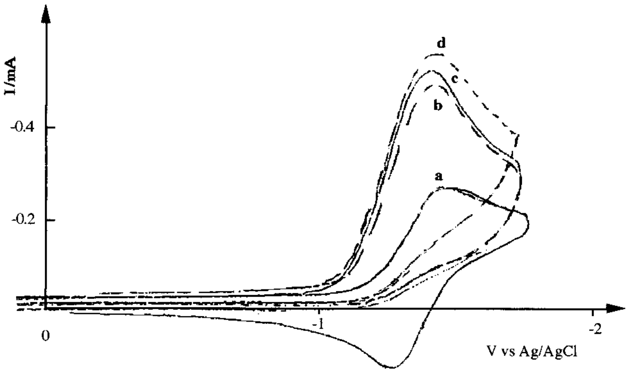


Figure 1. Cyclic voltammograms on a graphite carbon electrode at 0.1 V s^{-1} of Ni(cyclam)Br$_2$ (2.5 mM, curve a) in DMF solutions containing *n*-tetrabutylammonium tetrafluoroborate (0.1 M) and after addition of (b) 1, (c) 2, and (d) 10 equiv of **1a**.

According to the cyclic voltammetry behavior, we can propose a reaction between the electrogenerated Ni^{I}(cyclam) species and **1a**, with the formation of an intermediate that, in turn, undergoes a one-electron reduction at a potential equal to or more positive than that of Ni^{II}(cyclam), according to eqs 3−5. We propose a first oxidative additon of Ni(I) to the aryl bromide bond of **1a**, leading to a formally aryl−Ni(III) intermediate species, **3** (eq 3).

A similar mechanism involving oxidative addition of the electrogenerated Ni(I) species to alkyl halides, with formation of RNi(III) species, affording R−R-type dimers, has been reported.[10] The aryl−Ni(III) intermediate, **3**, induces a radical character to the aryl moiety and

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[13] Kimura, M.; Miyahara, H.; Moritani, N.; Sawaki, Y. *J. Org. Chem.* **1990**, *55*, 3897.

[14] (a) Shankaran, K.; Sloan, C. P.; Sniekus, V. *Tetrahedron Lett.* **1985**, *26*, 6001. (b) Beckwith, A. J. L.; Gara, W. B. *J. Chem. Soc., Perkin Trans. 2* **1975**, 795.

[15] (a) Curran, D. P.; Totleben, M. J. *J. Am. Chem. Soc.* **1992**, *114*, 6050. (b) Molander, G. A.; Harring, L. S. *J. Org. Chem.* **1990**, *55*, 6171. (c) Inanaga, J.; Ujikawa, O.; Yamaguchi, M. *Tetrahedron Lett.* **1991**, *32*, 1737.

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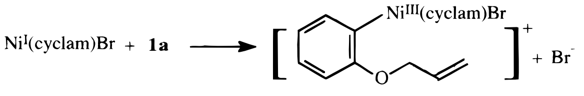
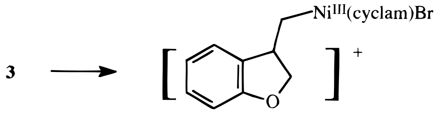


(3)

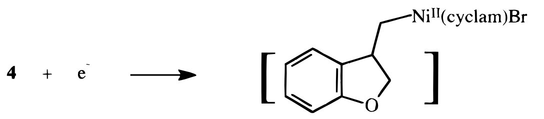
3

undergoes a rapid intramolecular cyclization on the side-chain double bond, to form an alkyl−Ni(III) species, **4** (eq 4). A further one-electron reduction of intermediate **4** at the initial potential of −1.45 V vs Ag/AgCl should afford an alkyl−Ni(II) species, **5** (eq 5).



(4)

4

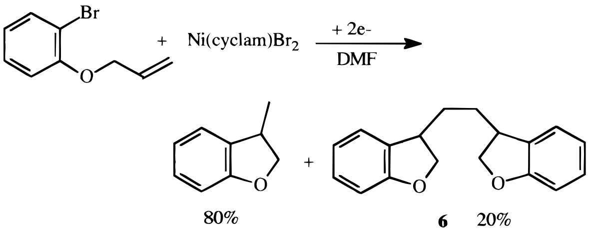


(5)

5

The cyclic voltammetry behavior of **1a** was also examined in the presence of the cationic complex Ni(cyclam)$^{2+}$•2BF$_4$$^-$. This complex exhibits a higher solubility in DMF as compared to Ni(cyclam)Br$_2$. Figure 2 shows the reduction peak of Ni(cyclam)$^{2+}$•2BF$_4$$^-$, which takes place at −1.3 V vs Ag/AgCl (−1.85 V vs Fc/Fc$^+$, curve a) and corresponds to the Ni(II) reduction to Ni(I) (eq 2). Here again, the excess of **1a** (curve b) doubles the intensity of the reduction peak, which becomes irreversible. A two-electron reduction process is observed, without recycling of the initial Ni(II) complex.

B. Controlled Potential Electrolyses. Several controlled potential electrolyses were carried out at −1.5 V vs Ag/AgCl in DMF solutions containing tetrabutylammonium tetrafluoroborate (0.1 M) in two-compartment cells. Thus, the electrolysis of **1a** and Ni(cyclam)Br$_2$ in a 1:1 molar ratio led, after the passage of 1 F/mol of nickel and further hydrolysis, to 40% of **2a**, together with 55% of starting material. After 2.1 F/mol electrolysis, a complete conversion of **1a** was achieved, with the formation of 80% of cyclized **2a** and 20% of the cyclized dimeric structure **6** (eq 6). Thus, the preparative-scale cyclization process consumes 2 F/mol, in agreement with cyclic voltammetry observations. The global 2e$^-$ cathodic reaction is shown in eq 7, by the formation of an anionic-type species, which is protonated by the electrolysis medium (DMF, ammonium salt).



(6)

The protonation by the electrolytic medium, and particularly by the tetrabutylammonium salt, was illustrated by the GC follow-up of the reaction. Increasing amounts of tributylamine were found in solution, in concentrations related to the number of electrons consumed. The proton-donor abilities of the ammonium salt, via its Hoffmann-type decomposition, and also of DMF have already been reported in electrochemical reactions.[16]

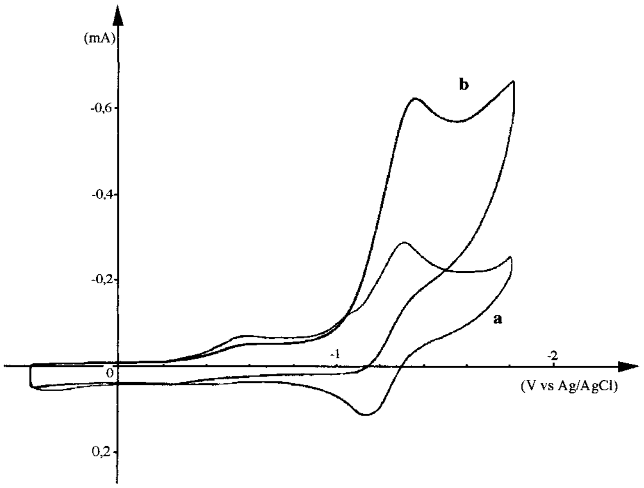
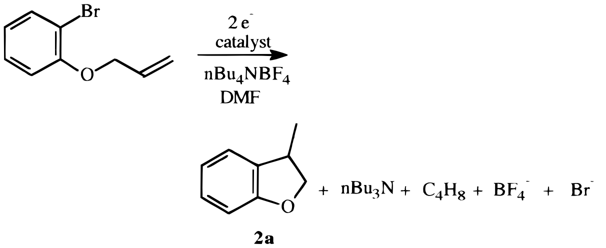


Figure 2. Cyclic voltammograms on a graphite carbon electrode at 0.1 V s^{-1} of Ni(cyclam)$^{2+}$•2BF$_4$$^-$ (2.5 mM, curve a) in DMF solutions containing *n*-tetrabutylammonium tetrafluoroborate (0.1 M) and (b) after addition of **1a**, 5 equiv.



(7)

2a

The preparative-scale catalytic electrolysis of **1a** and Ni(cyclam)$^{2+}$•2BF$_4$$^-$ in a 5:1 molar ratio at −1.5 V could be run up to the passage of 1 F/mol of **1a**, after which passivation occurred. A 20% consumption of **1a** was obtained, with formation of 10% of **2a** and 10% of dimer **6**. Under these conditions, the Ni(II) complex was not efficiently recycled.

A similar catalytic electrolysis with Ni(cyclam)Br$_2$ could be carried out up to 1.6 F/mol of **1a** before passivation (molar ratio **1a**/Ni of 5:1). The starting material was recovered in 40% yield, together with 50% of **2a**, 5% of **6**, and 5% of allyl phenyl ether, issued from the debromination of **1a**. In this case, the cyclization of **1a** to **2a** was catalytic in nickel, in the two-compartment cell procedure. The faradaic yield of formation of **2a** was of 62%, with 20% of Ni(II) present. However, these two-compartment cell electrolyses were very slow, and the nickel recycling was poorly efficient. Moreover, a lower selectivity was obtained when compared with that of the one-compartment cell procedure (eq 1).

C. Influence of the Magnesium Ions. Under the one-compartment cell electrolysis procedure using a magnesium rod as the anode, the electroreduction of **1a** was carried out catalytically and efficiently, with an apparent current density of 0.3 A dm^{-1} (applied constant current of 60 mA) (eq 1). The use of a Mg anode involves

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[16] Dérien, S.; Duñach, E.; Périchon, J. *J. Am. Chem. Soc.* **1991**, *113*, 8447.

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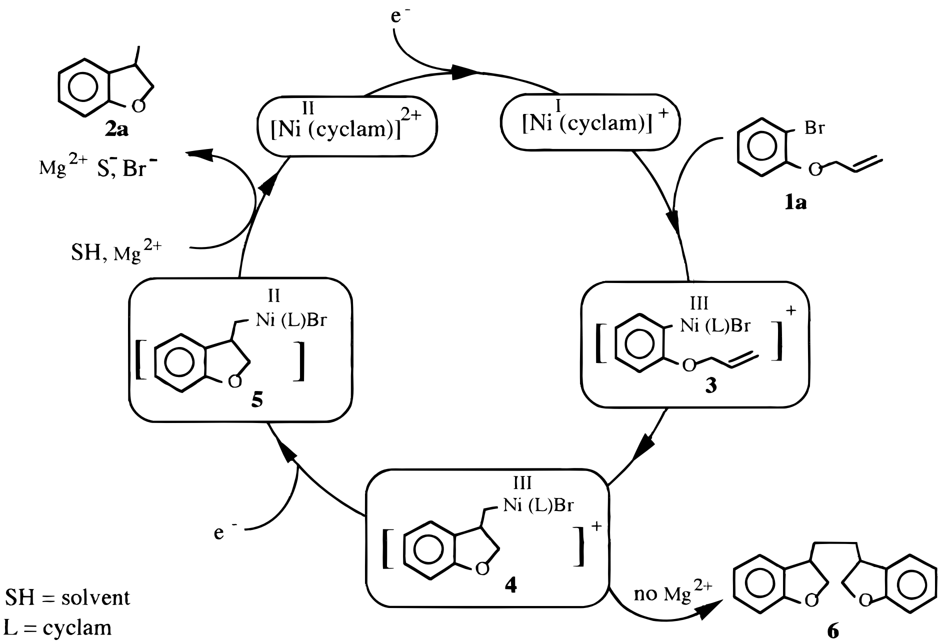
Scheme 1



its oxidation into Mg^{2+} ions, which accumulate progressively in solution.[12a]

We thus examined the influence of Mg^{2+} ions in the electroreduction of **1a** with Ni−cyclam systems by adding an anhydrous magnesium tetrafluoroborate solution to the electrolytic medium. The DMF solution of $Mg(BF_4)_2$ was prepared by prior electrolysis of tetrafluoroboric acid in a one-compartment cell, fitted with a Mg anode.

The cyclic voltammogram of $Ni(cyclam)^{2+}\cdot 2BF_4^-$ in the presence of $Mg(BF_4)_2$ (in a 1:1 molar ratio), indicated that the Ni(II) reduction was not modified with respect to the reduction of the nickel complex alone (see Figure 2, curve a).

The electrogenerated Ni(I) complex is thus stable in the presence of Mg^{2+} ions. The presence of added **1a** had the same influence as that already observed in Figures 1 and 2. The presence of Mg^{2+} ions in cyclic voltammetry experiments generally passivates the electrodes, preventing the measurements; however, in this case, passivation phenomena were not observed.

The preparative-scale controlled potential electrolysis of **1a**, $Ni(cyclam)^{2+}\cdot 2BF_4^-$, and $Mg(BF_4)_2$ in a 5:1:1 molar ratio in DMF at −1.5 V vs Ag/AgCl revealed, after the passage of 1 F/mol of **1a**, a 40% consumption, with the exclusive formation of **2a**. After 2 F/mol of **1a** electrolysis, the reaction was stopped; cyclized **2a** was formed in 80% yield, and 20% of unreacted **1a** was also recovered.

In the presence of Mg^{2+} ions, the reaction is catalytic in Ni(II), and the process needs 2 F/mol of substrate. The presence of Mg^{2+} ions enables the electrolysis to be followed up to the consumption of 2 F/mol of the substrate, with higher intensities and better efficiency and without passivation phenomena. Moreover, the selectivity of the process is enhanced. No formation of dimer **6** or other byproducts was observed.

D. Proposed Catalytic Cycle. Scheme 1 presents the catalytic cycle proposed for the reductive cyclization of **1a**, catalyzed by $Ni(cyclam)^{2+}$, according to the cyclic voltammetry and the controlled potential coulometry experiments. In the first step, $Ni(cyclam)^{2+}$ is reduced to $Ni(cyclam)^+$. This Ni(II)-to-Ni(I) reduction step takes place at −1.45 V for $Ni(cyclam)Br_2$ and at −1.3 V for $Ni(cyclam)^{2+}\cdot 2BF_4^-$.

$Ni(cyclam)^+$ rapidly reacts with **1a** by oxidative addition to the aryl−bromide bond, to form an aryl−Ni(III) intermediate, **3**, which undergoes a rapid intramolecular cyclization involving the double bond. Only cyclization to the five-membered-ring ether was observed, no six-membered-ring products being formed. The cyclized alkyl−Ni(III) intermediate **4** can undergo a further one-electron reduction at the initial Ni(II)-to-Ni(I) potential, to afford an alkyl−Ni(II) species, **5**.

This reduction process is in competition with the dimerization to give **6**, as a result of the radical character of **4**. In the electrolysis at −1.5 V catalyzed by $Ni(cyclam)^{2+}\cdot 2BF_4^-$ in the absence of Mg^{2+} ions, dimer **6** was obtained in low yield but high selectivity (50%), in agreement with the results reported by Gosden and Pletcher.[11] However, in the presence of Mg^{2+}, dimer **6** was not formed. These results indicate that the Mg^{2+} ions might coordinate to intermediate **4** and modify its reactivity, inhibiting the dimerization to **6**. The Ar−Ar coupling product issued from the dimerization of the Ni(III) intermediate **3** was not observed, with or without magnesium ions. Under the electrolysis conditions, the intramolecular cyclization of **3** to **4** is very selectively favored with respect to dimerization or protonation.

The reduction of alkyl−Ni(III) intermediate **4** takes place at −1.3 V with the $Ni(cyclam)^{2+}\cdot 2BF_4^-$ system. The reduction of intermediate **4** affords the alkyl−Ni^{II}(cyclam) species **5**, which presents some nucleophilic-type reactivity. Species **5** can abstract a proton from the electrolytic medium, affording **2a** and recycling the starting $Ni(cyclam)^{2+}$. The presence of Mg^{2+} ions accelerates this last step and renders the recycling of the $Ni(cyclam)^{2+}$ species more efficient.

It is also noteworthy that intermediate **5** does not undergo any β-hydride elimination to 3-methylenedi-

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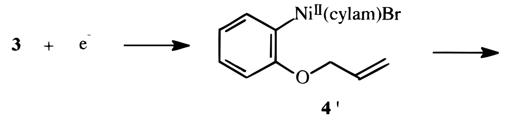
hydrobenzofuran or its rearranged isomer 3-methylbenzofuran under any of the reductive electrolysis conditions.

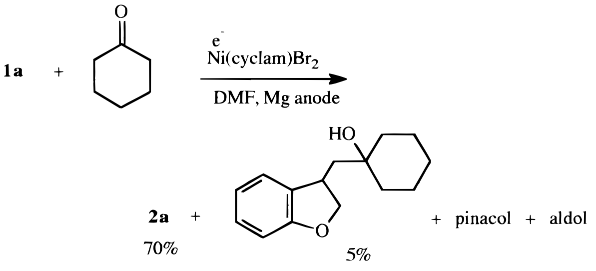
According to cyclic voltammetry, there is an alternative mechanism to the ECCE proposed in eqs 3−5, namely through an ECEC process as illustrated in eq 8. In this case, complex **3** would be first reduced to **4′**, followed by the ArNi^{II} addition to the double bond to afford **5**. The cyclization step would then be similar to a Heck-type reaction, which is known to be slow compared to oxidative additions.[17] This slow step would be responsible for the nonrecycling of the initial Ni(II) complex in cyclic voltammetry. The role of the Mg^{2+} ions would then be to react with the bromide intermediate **4′**, affording a cationic complex, which would be more reactive with the double bond than the neutral complex **4′**. Thus, with Mg^{2+}, the formation of **5** would be accelerated, as would be the recycling of the Ni(II) species. Although this ECEC mechanism cannot be excluded, we propose the ECCE mechanism of eqs 3−5 to be more plausible, in agreement with the radical nature of the Ni(III) intermediate **4**, which can afford dimer **6** (eq 6), and according to related results reported by Pletcher et al.[10,11]



(8)

E. Electrolysis in the Presence of an Electrophile. The protonation of the Ni(II) intermediate **5** by the electrolytic medium led us to examine its reactivity with other electrophiles. The cyclic voltammetry behavior of the Ni−cyclam system with **1a** and added cyclohexanone was examined, and the curves were not modified appreciably with respect to those of Figures 1 or 2. Cyclohexanone alone is reduced at potentials lower than −2 V. The preparative-scale electrolysis of **1a** in the presence of cyclohexanone and Ni(cyclam)$^{2+}\cdot 2BF_4^-$ in a 3:3:1 molar ratio was carried out in a two-compartment cell at −1.5 V. After the passage of 2 F/mol of nickel, **2a** was formed in 33% yield. No coupling products were obtained, and cyclohexanone remained unreacted.

The one-compartment cell electrolysis of a 1:3:1 mixture of **1a**, cyclohexanone, and Ni(cyclam)Br$_2$ in the presence of a magnesium anode led to **2a** in 70% yield, together with homocoupling products arising from the ketone (pinacol and aldol compounds). The expected heterocoupling alcohol adduct was formed in only 5% yield (eq 9).



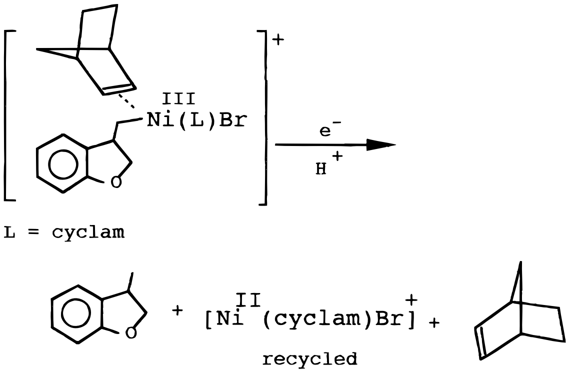
(9)

These experiments in the presence of a carbonyl compound as electrophile indicate a low nucleophilic character of the proposed intermediate **5**, slightly increased by the presence of Mg^{2+} ions. The competition clearly favors the protonation of **5** by the electrolytic medium.

F. Electrolysis in the Presence of an Olefin. To examine the possibilities of further reaction of radical-type intermediates such as **3** or **4** with a double bond, some experiments were carried out in the presence of an added olefin. Norbornene was chosen as a reactive olefin; its direct reduction does not interfere with the system. Norbornene alone is reduced beyond −2 V, and its addition to a Ni(cyclam)$^{2+}\cdot 2BF_4^-$ solution in DMF does not modify the Ni(II)/Ni(I) reduction.

The cyclic voltammetry behavior of a DMF solution of Ni(cyclam)$^{2+}\cdot 2BF_4^-$ and **1a** in the presence of norbornene (in a 1:3:3 ratio) showed a substantial increase of the irreversible reduction peak of the Ni(II) at −1.3 V. The peak intensity was approximately doubled with respect to the intensity in the absence of norbornene (Figure 2). The presence of the olefin induces a catalytic wave at the Ni(II)/Ni(I) reduction potential, thus involving a partial recycling of the Ni(II) species, which further react with the excess of **1a**.

The Ni(II) recycling can be explained by a coordination of the olefin to the cationic intermediate **4**, and/or to intermediate **5**, by partial decoordination of the cyclam ligand (eq 10). The olefin coordination might accelerate the last steps of the catalytic cycle.



(10)

The two-compartment cell electrolysis of a 1:3:3 mixture of Ni(cyclam)$^{2+}\cdot 2BF_4^-$, **1a**, and norbornene, at the controlled potential of −1.5 V, led to **2a** in 15% yield after the passage of 2 F/mol of nickel, together with 85% of unreacted **1a**. The formation of **2a** corresponds to a 45% yield with respect to the electricity passed. After the passage of 6 F/mol of nickel, e.g. 2 F/mol of **1a**, the cyclization yield was 35%, and **2a** was formed in 68% yield after 4 F/mol of **1a**. No coupling compounds involving **1a** and the norbornene double bond were observed. The norbornene concentration remained unchanged during the electrolysis, which could be run efficiently and without passivation phenomena.

The reaction was very selective in the presence of the olefin; even if the conversion of **1a** was not complete, the cyclized compound **2a** was the only product formed in the electrolysis. The catalytic effect observed by cyclic voltammetry in the presence of norbornene led us to examine the reactivity in the case of an intramolecular double bond. Thus, we examined the reactivity of 1-((2-

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[17] Heck, R. F. *Acc. Chem. Res.* **1979**, *12*, 146.

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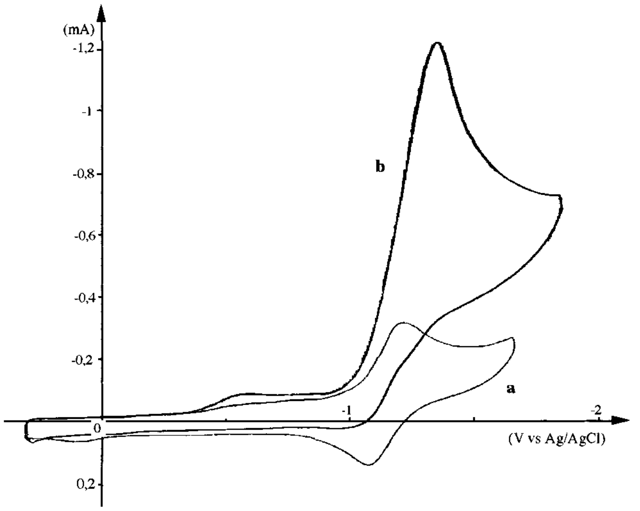
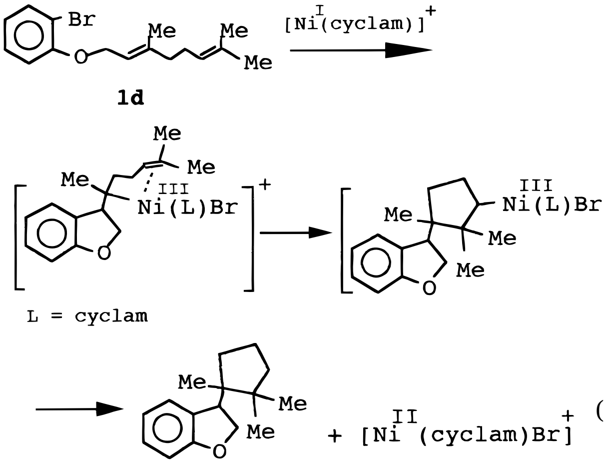


Figure 3. Cyclic voltammograms on a graphite carbon electrode at 0.1 V s^{-1} of Ni(cyclam)$^{2+}$•2BF$_4^-$ (2.5 mM, curve a) in DMF solutions containing *n*-tetrabutylammonium tetrafluoroborate (0.1 M) and (b) after addition of **1d**, 3 equiv.

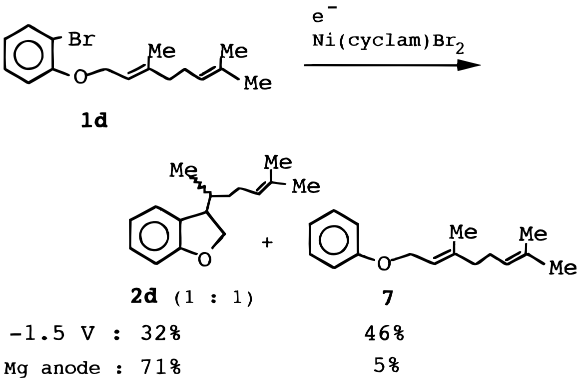
bromophenyl)oxy)-3,7-dimethyl-2,6-octadiene (**1d**). The position of the double bond in **1d** should enable its coordination to the nickel complexes analogous to **4** or **5** and could also favor a second intramolecular cyclization process of intermediate radical species (eq 11).



(11)

The cyclic voltammetry curves obtained for a DMF solution of Ni(cyclam)$^{2+}$•2BF$_4^-$ in the presence of **1d** (3 equiv) are presented in Figure 3. Similarly, as observed with norbornene, the Ni(II)-to-Ni(I) reduction peak at −1.3 V became irreversible, slightly shifted toward −1.4 V in this case, and its intensity was remarkably increased. Here again, the presence of the double bond favors the recycling of the nickel species.

The preparative-scale, two-compartment cell electrolysis of **1d** and Ni(cyclam)$^{2+}$•2BF$_4^-$ in DMF in a 3:1 molar ratio at −1.5 V led to a 95% conversion of **1d** after the passage of 4 F/mol of substrate. The main product was compound **7**, formed in 46% yield, and issued from the reductive debromination of **1d**. The cyclized compound **2d** was obtained in 32% yield as a mixture of two diastereoisomers (approximate 1:1 ratio, eq 12). No double cyclization involving the additional side-chain double bond (see eq 11) occurred.



(12)

Under the controlled potential conditions, the protonation of the aryl−Br bond of **1d** constitutes the preferred pathway.

In a similar experiment but in a one-compartment cell with a Mg anode at a constant current of 60 mA, the electrolysis of **1d** and Ni(cyclam)$^{2+}$•2BF$_4^-$ in DMF in a 10:1 molar ratio led to 71% of **2d** (1:1 ratio of diastereoisomers) after the passage of 3.7 F/mol of **1d**. However, here again, no double cyclization process could be observed.

The contribution of the Mg^{2+} ions and the constant intensity mode of electrolysis strongly modified the selectivity of the reaction. The coordination of the additional double bond of **1d** to the metal center of intermediate **3** or the competitive coordination of Mg^{2+} to **3** might explain this dfference in reactivity.

G. Electroreductive Cyclization of Substrates 1.[3] The results of the preparative-scale cyclization of several unsaturated aromatic ethers, **1**, in a Ni(cyclam)-Br$_2$-catalyzed electrolysis under constant intensity in a single-compartment cell fitted with a Mg anode, are summarized in Table 1.

As already noted in eq 1, chloro, bromo, and iodo derivatives undergo efficient cyclization (entries 1−3). Dihydrobenzofuran derivatives are also obtained with substituted allyl ethers (entries 4−6). 1- or 2-dihydrobenzopyran products could be prepared from the reaction of homoallyl ethers (entry 7) or allyl benzyl ethers (entry 8), respectively. The reductive cyclization of aryl propargyl ethers (entries 9, 10) led to the formation of 3-methylbenzofuran.

Conclusions

In conclusion, the electrochemical method allows the reductive cyclization of unsaturated aromatic halides, **1**, in a Ni(II)-catalyezed reaction. Ni(cyclam)Br$_2$ and Ni(cyclam)$^{2+}$•2BF$_4^-$ have been used as the catalyst precursors. The cyclic voltammetry behavior of these systems, together with the results of preparative-scale controlled potential electrolyses, indicates first a monoelectronic reduction of the Ni(II) to Ni(I) species, followed by oxidative addition to the carbon−halogen bond of the substrate, with further intramolecular cyclization and a second reduction.

The presence of Mg^{2+} ions during the electrolyses has an important effect in controlling the reactivity and the selectivity of the system.

The nature of the organometallic catalytic system and, particularly, of the ligand on nickel can strongly determine the reactivity, the selectivity, and the mechanism of the electrochemical reaction. Thus, although the use of Ni(cyclam)Br_2 and Ni(cyclam)$^{2+}\cdot 2BF_4^-$ led to similar results concerning cyclization, when Ni(II) complexes associated with 2,2′-bipyridine instead of cyclam were used, the electrolyses of substrates **1** led to selective deallylation products without any cyclization.[18] With Ni(II) complexes associated with open tetraaza ligands of bisamine bisoxazoline type,[19] the proposed cyclization mechanism involved the electrogeneration of Ni(0) instead of Ni(I) species.

Experimental Section

Reagents and Chemicals. All solvents were dried and degassed by standard methods. DMF was freshly distilled over 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. ^1H and ^{13}C NMR spectra were recorded on a Bruker Ac-200 spectrometer. Infrared spectra were recorded as KBr disks on a Nicolet 520 FT-IR spectrometer. Mass spectra were obtained with a Finnigan MAT INCOS 500E spectrometer (GC/MS).

Cyclic voltammetry experiments and controlled potential electrolyses were performed with the use of PAR scanning potentiostat model 362 equipment and were carried out at 25 °C by utilizing Pt or carbon fiber microelectrodes (Tacussel). All potentials are 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/n-$Bu_4N^+BF_4^-$. Controlled constant intensity electrolyses were carried out by using a stabilized constant current supply (Sodilec, EDL 36.07). The electrochemical one-compartment cell is a cylindrical glass vessel of approximately 40-mL volume, already described,[12a] 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 plate (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 n-$Bu_4N^+BF_4^-$ (0.2 mmol) was placed in the cell and stirred at room temperature under nitrogen atmosphere. 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 4−5 h. Generally, 2−4 F/mol of **1** was necessary to achieve a complete conversion. The solution was hydrolyzed with 50 cm^3 of 0.1 N HCl solution and extracted with Et_2O, and the organic layer was washed with H_2O, dried over $MgSO_4$, and evaporated. The products were purified by column chromatography on silica gel with pentane/Et_2O mixtures as eluent. The yields are quoted in Table 1. The products are known compounds, and their spectral data were compared to those of authentic samples.

General Procedure for Two-Compartment Cell Electrolyses. Both compartments were filled with a DMF solution (30 mL each) of n-$Bu_4N^+BF_4^-$ (1 g, 3 mmol) under inert atmosphere. The desired Ni(II)−cyclam complex (0.1 mmol) and **1a** (0.1−0.5 mmol) were added to the cathodic compartment. 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 that described above, the reaction being followed by GC.

Acknowledgment. We thank CNRS for financial support. We would also like to thank the reviewers for their positive comments.

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