Electrochemical Studies on the Nickel-Catalyzed O−C(allyl) Bond Cleavage of Allyl Ethers

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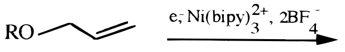
The chemoselective electrochemical cleavage of allyl aryl ethers catalyzed by $Ni(bipy)_3^{2+}2BF_4^-$ was shown to proceed through electrogenerated Ni(0) complexes with the formation of π-allyl Ni(II) species, which are in turn reduced at the same potential as the initial Ni(II)/Ni(0) reduction. The important role of magnesium ions in the recycling of the nickel species was established.

Introduction

The insertion of Ni(0) complexes into carbon−halogen bonds and particularly into those of allylic substrates is a well-known reaction and has proven its wide application in organic synthesis.[1] However, these reactions are generally not catalytic and need stoichiometric amounts of Ni(0) complexes.

Electrosynthesis, involving generated Ni(0) complexes from Ni(II) compounds, constitutes an alternative method for carbon−halogen activation whose efficiency in various catalytic coupling reactions has already been demonstrated.[2]

We have been interested in the nickel-catalyzed electrochemical reductive deprotection of allyl ethers. The cationic complex $Ni(bipy)_3^{2+}2BF_4^-$ (bipy = 2,2′-bipyridine) has been shown to be a good catalyst for the cleavage of the oxygen−carbon bond of allyl ethers, affording the parent alcohols or phenols in good yields under mild conditions, according to eq 1.[3]



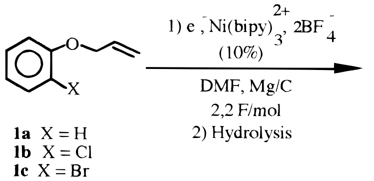
(1)

The interesting chemoselectivity obtained with the Ni−bipy complex prompted us to examine the electrochemical reaction of allyl ether cleavage in more detail. We present here our results concerning the selective reactivity of electrogenerated Ni(0)−bipy complexes with allyl aryl ether substrates in one- or two-compartment cells, the electrochemical behavior of such systems, and the influence of Mg^{2+} ions on the catalytic reactions.

Ni−bipy complexes (e.g., $Ni(bipy)Br_2$) have been used as catalysts in the electrochemical allylation of carbonyl compounds with allyl chlorides or acetates.[4] However, to our knowledge and apart from our work, no studies on electrochemical reactivity involving nickel complexes and allyl ethers have been reported.

Results and Discussion

A. Ni-Catalyzed Electrochemical Allyl Aryl Ether Cleavage. The electrolysis of allyloxybenzene, **1a**, in the presence of a catalytic amount of $Ni(bipy)_3^{2+}2BF_4^-$ afforded phenol in a quantitative yield (eq 2). The reaction, followed by GC, consumed 2.2 F/mol of substrate for a complete conversion. In the standard electrolysis conditions, the reactions were carried out at constant current intensity at room temperature in DMF containing $n\text{-}Bu_4N^+BF_4^-$ as supporting electrolyte (5×10^{-3}M) in a single-compartment cell fitted with a magnesium anode and a carbon fiber or stainless steel cathode. The Ni(II) catalyst was introduced in a 10% molar ratio with respect to the substrate. No reaction occurred in the absence of current.



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

(2)

Under the same conditions but in the absence of the nickel complex, the electrolysis of **1a** led, after the passage of 3 F/mol, to an incomplete conversion with 60% of phenol and 30% of (*Z*)-1-propenoxybenzene, issued from the double-bond isomerization of the allyl moiety. Thus, the presence of the Ni(II) complex induces

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[1] Yamamoto, T.; Ishizu, J.; Yamamoto, A. *J. Am. Chem. Soc.* **1981**, *103*, 6863.

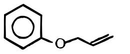
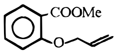
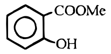
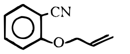
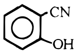
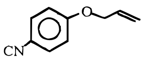
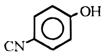
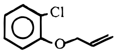
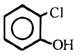
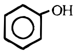
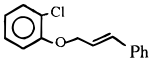
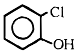
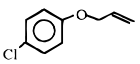
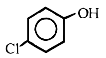
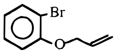
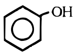
[2] (a) Nédélec, J. Y.; Périchon, J.; Troupel, M. In *Organic Electroreductive Coupling Reactions Using Transition Metal Complexes as Catalyst, Topics in Current Chemistry*; Steckhan, E., Ed.; Springer-Verlag: Berlin, 1997; pp 141−173. (b) Chaussard, J.; Folest, J. C.; Nédelec, J. Y.; Périchon, J.; Sibille, S.; Troupel, M. *Synthesis* **1990**, *369*.

[3] Olivero, S.; Duñach, E. *J. Chem. Soc., Chem. Commun.* **1995**, 2497.

[4] Durandetti, S.; Sibille, S.; Périchon, J. *J. Org. Chem.* **1989**, *54*, 2198.

10.1021/om9909385 CCC: $19.00

Table 1. Electrochemical Deprotection of Functionalized Allyl Aryl Ethers, Catalyzed by $Ni(bipy)_3^{2+}2BF_4^-$

Entry	Starting Ether	F/mol	Reaction Product	Yield
1		2.2	PhOH	99%
2		2.2		86%
3		5.2		99%
4		5.2		99%
5		3.5	 	75% 25%
6		2.2		96%
7		2.2		86%
8		4.5		99%

a high selectivity with quantitative yields of phenol and better faradic yields.

The $Ni(bipy)_3^{2+}2BF_4^-$-catalyzed electrolysis of 2-allyloxychlorobenzene, **1b**, led to 2-chlorophenol in 75% yield. The cleavage of the C−O bond takes place preferentially to the reduction of the C−Cl bond. This process appears to be specific to the Ni−bipy catalyst; the use of $Ni(cyclam)Br_2$ has been reported to catalyze the intramolecular cyclization of **1b** to 3-methyl dihydrobenzofuran under similar conditions, through the initial activation of the C−Cl bond.[5]

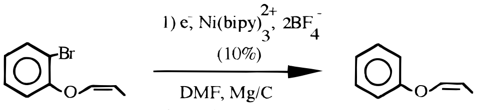
The $Ni(bipy)_3^{2+}2BF_4^-$-catalyzed electrolysis of 2-allyloxybromobenzene, **1c**, afforded phenol in quantitative yield, with the simultaneous cleavage of the C−O and the C−Br bonds.

The nickel-catalyzed O−C bond cleavage is a general process in allyl ether substrates, and it is compatible with the presence of other functional groups, as reported below (see Table 1).

B. Selectivity in the Allyl Ether Cleavage. Electrolysis of Related Substrates. Concerning the mechanism of this electrochemical reaction, we first considered the possibility of a Ni(0)-promoted double-bond isomerization from the allyl ether to an enol ether. Ni(0) complexes can be formed in situ by a two-electron reduction of the starting Ni(II)−bipy complex.[6] Intermediate enol ethers are the species proposed in classical allyl ether deprotection methods, such as in the Rh(I)[7] or in the KO-t-Bu[8] allyl ether isomerization treatments. Alcohols (or phenols) are then generally obtained after acidic hydrolysis of the intermediate enol ethers.

During the nickel-catalyzed electrolysis of allyl aryl ethers, **1**, the presence of enol ethers was not detected, even when the final hydrolysis step was carried out under neutral (nonacidic) conditions.

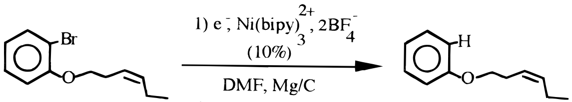
To ensure that the isomerization of the allyl ether to an enol ether was not operating in the electrochemical reaction, we prepared 1′-propenoxy-2-bromobenzene, **2**.[8] When **2** (9:1 mixture of cis and trans isomers) was electrolyzed under the standard conditions in the presence of $Ni(bipy)_3^{2+}2BF_4^-$, the enol ether **3** was isolated in 75% yield after a hydrolysis under neutral conditions (eq 3). The C−Br cleavage reaction occurred without the carbon−carbon double bond of the enol ether being affected, even after the passage of 4 F/mol.



2 **3** 75% (3)

We take this to indicate that the cleavage of the allyl ether bond in the nickel-catalyzed electrolysis does not proceed via the isomerization of the allylic moiety to an enol ether.

On the other hand, the electrolysis of an homoallyl ether such as (*Z*)-2-(3′-hexenoxy)bromobenzene, **4**, in the presence of $Ni(bipy)_3^{2+}2BF_4^-$ led mainly to a protodehalogenation reaction of the aromatic halide (eq 4), without modification of the unsaturated ether unit.



4 50% (4)

The electrochemical method of C−O cleavage is selective for allyl ethers, and the catalyst plays a determinant role in the selectivity of the process.

C. Electrosynthesis of π-Allyl Intermediates. As an alternative mechanism for the cleavage of the C−O bond of allyl ethers we can consider the formation of a π-allyl−Ni(II) intermediate, from the insertion of electrogenerated Ni(0) to the allylic carbon−oxygen bond of **1**. Ni(0) as well as Pd(0) complexes are well known to efficiently react with allyl halides, acetates, and carbonates to form π-allyl Ni(II)[9,10] or Pd(II) species,[11] but no extensive studies have been reported with allyl aryl ethers, for which the leaving group is a phenate anion.

The reaction of $Ni(COD)_2$ (COD = 1,5-cyclooctadiene) with allyloxybenzene in the presence of triphenylphosphine has been described to afford a π-allyl Ni(II) complex in a stoichiometric process.[12]

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(5) Olivero, S.; Rolland, J. P.; Duñach, E. *Organometallics* **1998**, *17*, 3747.

(6) Bartlett, P. N.; Eastwick-Field, V. *Electrochim. Acta* **1993**, *38*, 2515.

(7) Corey, E. J.; Suggs, J. W. *J. Org. Chem.* **1973**, *38*, 3224.

(8) Gigg, J.; Gigg, R. *J. Chem. Soc. C* **1966**, 82.

(9) Hegedus, L. S.; Wagner, S. D.; Waterman, E. L.; Siirala-Hansen, K. *J. Org. Chem.* **1975**, *40*, 593.

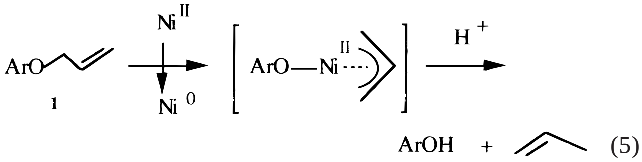
(10) Ishizu, J.; Yamamoto, T.; Yamamoto, A. *Chem. Lett.* **1976**, 1091.

(11) Yamamoto, T.; Akimoto, M.; Saito, O.; Yamamoto, A. *Organometallics* **1986**, *5*, 1559.

(12) Eisch, J. J.; Im, K. R. *J. Organomet. Chem.* **1977**, *139*, C45.

On the other hand, π-allyl Ni(II) complexes prepared from allyl bromide and Ni(0) have been reported to be in equilibrium between their monomeric and dimeric forms and to have a tendency (in polar solvents such as DMF and at high temperatures) to form bis(π-allyl)Ni complexes.[13] These complexes are poorly nucleophilic and mainly evolve toward the dimerization of the allyl units.[14]

In the electrochemical process, Ni(0) formed from Ni(II) could oxidatively add to the C−O bond of **1** to form a π-allyl−Ni(II) complex, whose further hydrolysis would afford phenol and propene (or its C-6 dimer) (eq 5).



(5)

During the electrolysis of **1a**−**c** no unsaturated C_6 compounds issued from the dimerization of the allyl moiety could be observed. To better examine the possibility of dimerization of the allyl unit with less volatile products, we studied the reactivity of 2-cinnamyloxy-1-chlorobenzene. The $Ni(bipy)_3^{2+}2BF_4^-$-catalyzed electrolysis of this cinnamyl derivative under the standard conditions led to 2-chlorophenol (96%) and to *trans*-methylstyrene (60%) after 2.2 F/mol, and no diphenylhexadienes or other dimers of methylstyrene were formed.

This experiment indicates that the cinnamyl moiety is mainly protonated and not dimerized in the course of the electrochemical reaction.

D. Electrochemical Studies. Cyclic Voltammetry of $Ni(bipy)_3^{2+}2BF_4^-$ in the Presence of Allyl Aryl Ethers. Allyl ethers **1** were used as model compounds for the electrochemical studies. Figure 1 presents the cyclic voltammetry curves of $Ni(bipy)_3^{2+}2BF_4^-$ in DMF containing tetrabutylammonium tetrafluoroborate (0.1 M) (curve a) with the progressive addition of **1c** (curves b−d). Potential data are referred to Ag/AgCl as the reference electrode. Curve a shows a quasi-reversible Ni(II) reduction to Ni(0) at −1.2 V. This peak is followed by a reversible one-electron reduction of the Ni(0) species at −1.9 V, according to Scheme 1. The reversible reduction of free bipyridine occurs at −2.2 V. These results are in agreement with the literature data reported for the $Ni(bipy)_3^{2+}2ClO_4^-$ complex,[6] its BF_4^- analogue in DMF,[15] or $Ni(bipy)Br_2$ in acetonitrile[16] or in NMP.[17]

The addition of 0.5 equiv of **1c** to the Ni(II) solution resulted in an increase of the reduction peak at −1.2 V as well as a decrease in the reverse reoxidation peak (curve b). In the presence of 1 equiv of **1c** with respect to Ni(II) (curve c) the intensity of the Ni(II)/Ni(0) reduction peak is increased by one-half and the process becomes almost irreversible. The reduction at −1.2 V thus corresponds to three electrons per nickel. With the addition of 2 or 5 equiv of **1c** (curve d) the reduction peak at −1.2 V does not increase further.

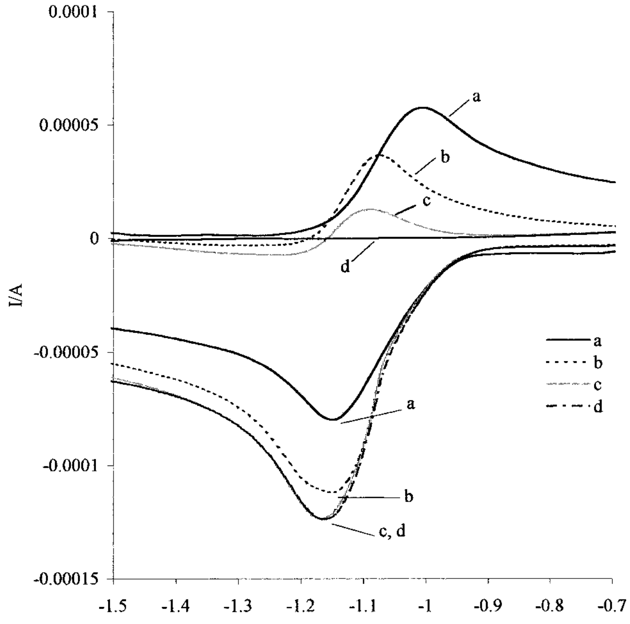


Figure 1. Cyclic voltammograms on a carbon graphite electrode ($v = 100$ mV s^{-1}) of DMF + $n\text{-}Bu_4N^+BF_4^-$ (10^{-1} M) solutions containing (a) $Ni(bipy)_3^{2+}2BF_4^-$ (5×10^{-3}M); (b) after addition of **1c** (0.5 equiv); (c) after addition of **1c** (1 equiv); (d) after addition of **1c** (5 equiv).

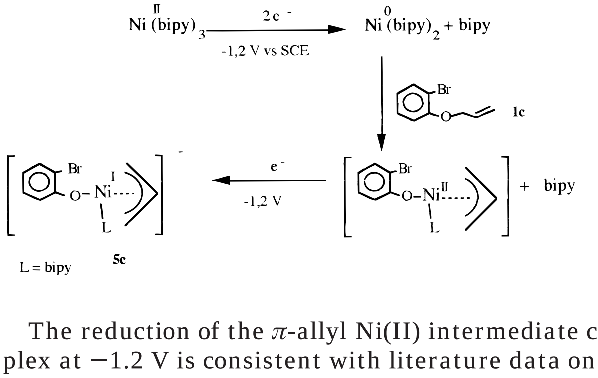
Scheme 1

$$Ni^{II}(bipy)_3^{2+} + 2e^- \xrightleftharpoons{-1,2\ V} Ni^{0}(bipy)_2 + bipy$$

$$Ni^{0}(bipy)_2 + e^- \xrightleftharpoons{-1,9\ V} [Ni(bipy)\ ]^{\bullet -} + bipy$$

$$bipy + e^- \xrightleftharpoons{-2,2\ V} bipy^{\bullet -}$$

This three-electron process is consistent with a first two-electron reduction of Ni(II) to Ni(0) followed by a chemical reaction between the electrogenerated Ni(0) complex and **1** and a further one-electron reduction of the intermediate at the same potential. Considering the formation of a π-allyl Ni(II) complex as in eq 5, under the electrochemical conditions and according to the cyclic voltammetry, this complex should be further reduced to a formal Ni(I) intermediate, **5**, at the potential of −1.2 V (eq 6).



(6)

The reduction of the π-allyl Ni(II) intermediate complex at −1.2 V is consistent with literature data on the

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[13] Hegedus, L. S.; Thompson, D. H. P. *J. Am. Chem. Soc.* **1985**, *107*, 5663.

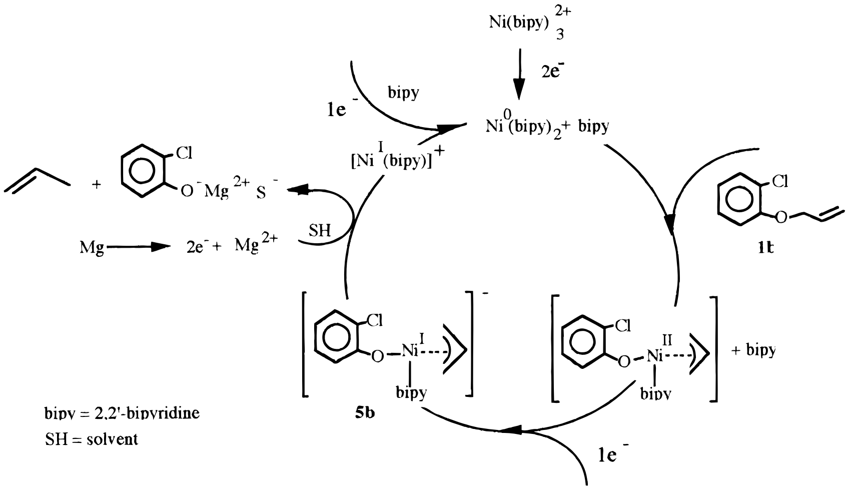
[14] Semmelhack, M. F. *Org. React.* **1972**, *19*, 115.

[15] Derien, S.; Duñach, E.; Périchon, J. *J. Am. Chem. Soc.* **1991**, *133*, 22, 8447.

[16] Daniele, S.; Ugo, P.; Bontempelli, G.; Fiorani, M. *J. Electroanal. Chem. Interfacial Electrochem.* **1987**, *219*, 259.

[17] Garnier, L.; Rollin, Y.; Périchon, J. *New J. Chem.* **1989**, *13*, 53.

Scheme 2



reduction of ArNi(II) intermediates[18] and on that of allyl species.[19]

E. Preparative-Scale Controlled Potential Electrolyses at −1.2 V. The electrolysis of **1b** and Ni(bipy)$_3^{2+}$2BF$_4^-$ (3:1 molar ratio) in a DMF solution was carried out in the cathodic compartment of a two-compartment cell at −1.2 V. After the passage of 1.6 F/mol of substrate (4.8 F/mol of nickel) the reaction was stopped because the current became negligible. The hydrolysis of the reaction medium afforded 65% of 2-chlorophenol and 35% of unreacted starting material. This experiment indicates on one hand that the C−O cleavage reaction occurs at the potential of −1.2 V, which corresponds to that of the initial Ni(II)/Ni(0) reduction. On the other hand, the cleavage reaction of the allyl group is chemoselective and catalytic in Ni(II), although the nickel complex was slow and difficult to recycle.

To better mimic the electrolysis carried out in a one-compartment cell, under constant intensity with a magnesium anode (which could be run efficiently, with no passivation and up to the complete consumption of the substrate), a similar experiment was carried out in the presence of added Mg^{2+} ions in a two-compartment cell at controlled potential. The important role of Mg^{2+} ions and their influence on the reactivity and selectivity of several electrochemical processes have already been reported.[5,15] The electrolysis of Ni(bipy)$_3^{2+}$2BF$_4^-$ and **1c** was carried out in the presence of a stoichiometric amount of Mg(BF$_4$)$_2$[20] (relative ratio of 0.25:1:1) at −1.2 V, and it could be run up to the passage of 2 F/mol of **1c**. Complete conversion of **1c** was attained, and 2-bromophenol was formed quantitatively.

We can conclude that in the presence of Mg^{2+} the reaction is catalytic in nickel and the nickel species are more efficiently recycled.

F. Proposed Catalytic Cycle. The controlled-potential electrolyses of allyl aryl ethers at −1.2 V gave evidence of a Ni(II)-catalyzed chemoselective O−C cleavage reaction, although no catalytic wave appeared in the cyclic voltammograms run at 0.1 V s^{-1}. The presence of Mg^{2+} ions accelerates the recycling of the nickel species. The proposed catalytic cycle for the reduction of **1b** is presented in Scheme 2 and is consistent with the observed electrochemical behavior.

In the first step Ni(II) is reduced to Ni(0) at −1.2 V according to cyclic voltammetry and to Scheme 1. The electrogenerated Ni^0(bipy)$_2$ can oxidatively add to the allyl ether **1b** to form a π-allyl−Ni(II) intermediate. This intermediate is then reduced by one electron at the potential of −1.2 V to form a formally π-allyl−Ni(I) complex, **5b**. A Mg^{2+}/nickel exchange reaction liberates the Ni(I) species, which is rapidly reduced to Ni(0) and recycled. Magnesium phenates are formed, and the allyl moiety is protonated by the electrochemical medium (solvent, SH, and/or supporting electrolyte). Several examples of protonation of electrochemically reduced intermediates in DMF have already been reported,[5,15] as was shown in the electroreduction of 2-cinnamyloxy-1-chlorobenzene. The overall reaction consumes 2 F/mol of substrate.

G. Reactivity of the Ni^0(bipy)$_2$−Allyl Ether System. To further examine the reactivity of electrogenerated Ni^0 species with substrates **1**, we carried out a series of experiments in which we first prepared Ni^0(bipy)$_2$ from the electrolysis of Ni(bipy)$_3^{2+}$2BF$_4^-$ at −1.2 V in DMF. Figure 2 presents the results obtained by rotating disk voltammetry (RDV) after the stepwise addition of **1a** to the Ni(0) solution. Curve a corresponds to the Ni^0(bipy)$_2$ generated after the passage of 2 F/mol of Ni(II), and its intensity is representative of the amount of initial Ni(0) in solution.

The progressive addition of 0.25, 0.5, and 1 equiv of **1a** (curves b−d) results in an immediate decrease of the relative intensity of the Ni(0) oxidation wave, indicative of a fast chemical reaction between the nickel complex and **1a**. Within experimental error these results are consistent with the 1:1 reaction of Ni^0(bipy)$_2$ with **1** to form a π-allyl complex (eq 6), including a partial reduction of the π-allyl complex by the Ni(0) species. Similar results were obtained with substrates **1b** and **1c**.

Figure 3 exhibits the RDV curves for Ni(bipy)$_3^{2+}$2BF$_4^-$ and **1b** in a two-compartment cell. Curve a corresponds

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[18] Amatore, C.; Jutand, A. *J. Am. Chem. Soc.* **1991**, *113*, 2819.

[19] Lund, H.; Daasbjerg, K.; Lund, T.; Occhialini, D.; Pedersen, S. U. *Acta Chem. Scand.* **1997**, *51*, 135.

[20] The Mg^{2+} salts were prepared by electrolysis of tetrafluoroboric acid in DMF in the presence of a Mg anode in a one-compartment cell.

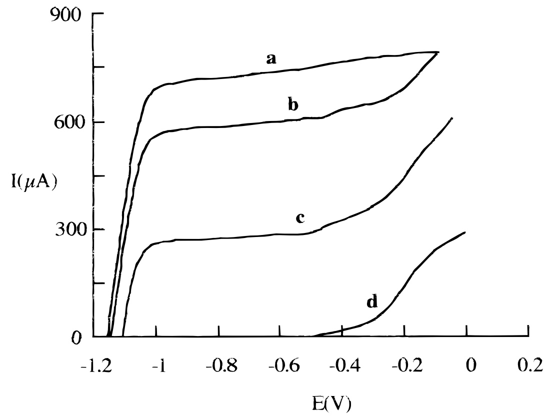


Figure 2. Rotating disc voltammograms on a gold disk electode (2 mm diameter, rotation 2000 rpm), at a scan rate of 0.02 V s^{-1}, of DMF + n-$Bu_4N^+BF_4^-$ (10^{-1} M) solutions containing (a) $Ni(bipy)_3{}^{2+}2BF_4^-$ (10^{-1} M) and bipy (10^{-1} M) after 2 F/mol electrolysis at −1.2 V; (b) curve a after addition of 0.25 equiv of **1a**; (c) curve a after addition of 0.5 equiv of **1a**; (d) curve a after addition of 1 equiv of **1a**.

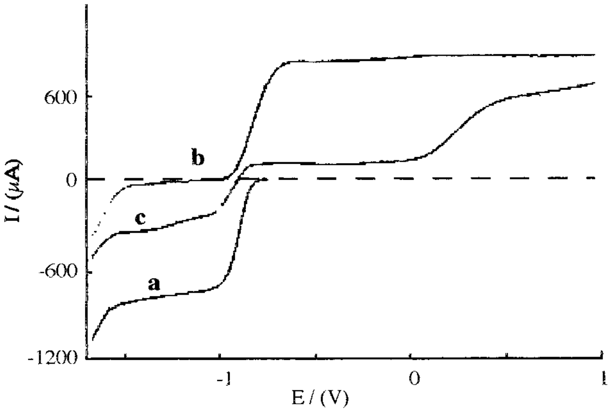


Figure 3. Rotating disc voltammograms on a carbon microelectode (1 mm^2, rotation 2000 rpm), at a scan rate of 0.02 V s^{-1}, of a DMF + n-$Bu_4N^+BF_4^-$ (10^{-1} M) solution containing (a) $Ni(bipy)_3{}^{2+}2BF_4^-$ (25 mM) before electrolysis; (b) $Ni(bipy)_3{}^{2+}2BF_4^-$ (25 mM) after 2 F/mol electrolysis at −1.2 V; (c) curve b after addition of 1 equiv of **1b**.

to the initial Ni(II) complex in a DMF solution, and curve b was obtained after the 2 F/mol reduction of this complex. The relative equal heights of curves a and b indicate that the formation of Ni(0) from Ni(II) occurs quantitatively and efficiently under the experimental conditions.

The addition of 0.9 equiv of **1b** to the solution of electrogenerated Ni(0) afforded curve c, which presents an oxidation current around 0.4 V as well as a reduction current at −1.2 V, each one corresponding to approximately one-half of the initial intensity of curve a. No apparent change in curve c was observed after 30 min. These results suggest that the reaction of $Ni^0(bipy)_2$ with **1b** forms the expected π-allyl Ni(II) complex, but in the absence of further electrolysis, this complex is not reduced (as in eq 6). In this case, the π-allyl Ni(II) intermediate can undergo a disproportionation reaction to form a Ni(II) phenate complex and a bis(π-allyl)Ni(II) complex, in agreement with previous results on Ni−allyl complexes[13,14] and according to Scheme 3.

In agreement with curve c (Figure 3) Ni(II)−phenoxide species could be reduced into Ni(0) species at −1.2 V, with a global consumption of 1 F/mol for half of the Ni(II). To our knowledge, no literature data are available on the redox properties of bis(π-allyl)Ni species, but we propose that they could be oxidized at 0.4 V.

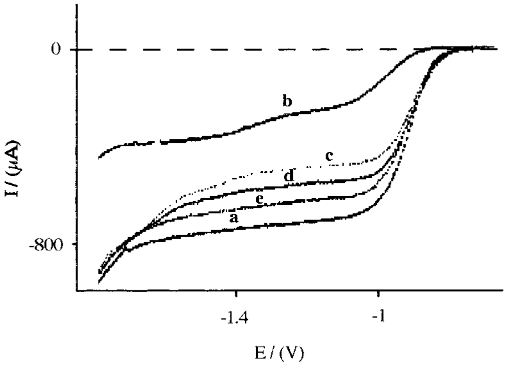
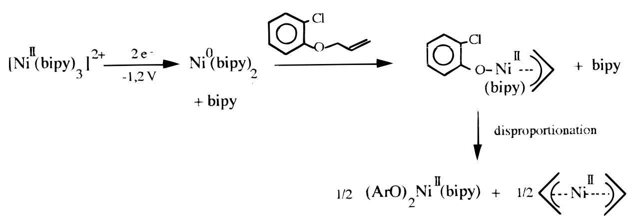


Figure 4. Rotating disc voltammograms on a carbon microelectode (1 mm^2, rotation 2000 rpm), at a scan rate of 0.02 V s^{-1}, of a DMF + n-$Bu_4N^+BF_4^-$ (10^{-1} M) solution containing (a) $Ni(bipy)_3{}^{2+}$, $2BF_4^-$ (25 mM) before electrolysis; (b) $Ni(bipy)_3{}^{2+}2BF_4^-$ (25 mM) after 2 F/mol electrolysis and after addition of 0.9 equiv of **1b**; (c) curve b after addition of 1 equiv of $Mg(BF4)_2$; (d) curve c after 20 min; (e) curve d after 1.5 h; (a′) $Ni(bipy)_3{}^{2+}2BF_4^-$ (25 mM) after 2 F/mol electrolysis; (b′) curve a′ after addition of 0.9 equiv of **1b**; (c′) curve b′ after addition of 1 equiv of $Mg(BF4)_2$; (d′) curve c′ after 20 min; (e′) curve d′ after 1.5 h.

Scheme 3



These results suggest that different reaction pathways can occur to the π-allyl−Ni(II) species according to the experimental conditions; under continuous electrolysis a reduction to species **5** is proposed (eq 6), whereas in the chemical reaction with Ni(0) and in the absence of a further reduction source, a ligand disproportionation can be considered (Scheme 3).

The disproportionation mechanism shown in Scheme 3 is not operating under electrolysis conditions and is not consistent with the cyclic voltammetry results. A reduction peak equivalent to 4 electrons per nickel (instead of the observed 3 electrons per nickel, Figure 1) should be present in cyclic voltammetry at −1.2 V.

Role of the Magnesium Ions. In a different experiment we examined the reactivity of $Ni^0(bipy)_2$ and allyl ethers in the presence of Mg^{2+} ions. Figure 4 presents the RDV curves of the reduction of the nickel(II) species. $Ni(bipy)_3{}^{2+}2BF_4^-$ (curve a) was first reduced to $Ni^0(bipy)_2$, and without any further electrolysis, substrate **1b** was added (curve b). $Mg(BF_4)_2$ (1 equiv) was then introduced, and curves c−e were recorded at different time intervals.

The addition of Mg^{2+} resulted in a progressive increase of the reduction wave at −1.2 V, as shown by curves c−e, which slowly tend toward the initial value of curve a. The initial amount of Ni(II) is thus recovered in the presence of Mg^{2+}. On the other hand, Mg^{2+} slowly decomposes the nickel species oxidizing at 0.4 V in favor

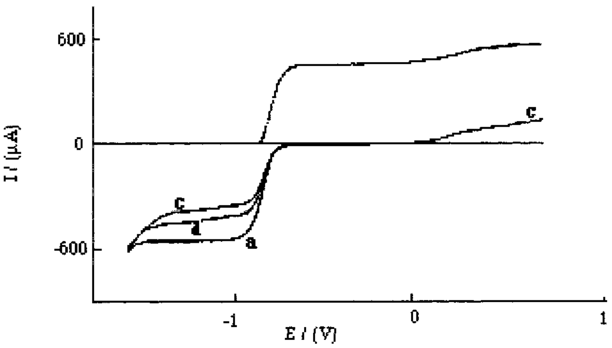
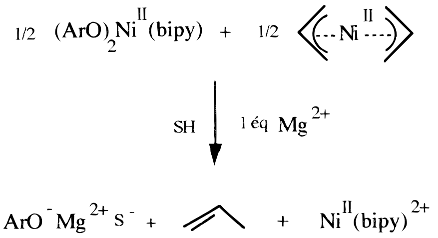


Figure 5. Rotating disc voltammograms on a gold disk electrode (2 mm diameter, rotation 2000 rpm) at a scan rate of 0.02 V s^{-1}, in a single compartment cell with a magnesium anode, of DMF + *n*-$Bu_4N^+BF_4^-$ (10^{-1} M) solutions containing (a) $Ni(bipy)_3{}^{2+}2BF_4^-$ (20 mM) and bipy (20 mM); (b) curve a after 2 F/mol electrolysis at −1.2 V; (c) curve b, 5 min after addition of 1 equiv of **1a**; (d) curve c after 20 min.

Scheme 4



of the Ni(II) species reducing at −1.2 V. Scheme 4 illustrates these results. In the presence of Mg^{2+} ions, the bis(π-allyl)Ni species are decomposed; a Ni(II)/Mg^{2+} exchange reaction occurs and the initial amount of Ni(II)−bipy is liberated.

The RDV curves indicate that under the nonelectrolysis conditions (Figure 4) Mg^{2+} ions also constitute an important factor for the quantitative regeneration of the initial Ni(II) species.

To ensure that electrogenerated $Ni^0(bipy)_2$ was stable in the presence of Mg^{2+} ions, we carried out the electrolysis of $Ni(bipy)_3{}^{2+}2BF_4^-$ in a single-compartment cell fitted with a Mg anode. By this procedure, Mg^{2+} ions were progressively formed in solution from the beginning of the Ni(II) electrolysis. Figure 5 presents the voltammetric curves obtained for $Ni(bipy)_3{}^{2+}2BF_4^-$ (curve a) and for the electrogenerated Ni^0 after the passage of 2 F/mol in the presence of Mg^{2+} (curve b). Curve b in Figure 5 is similar to that obtained in the absence of Mg^{2+} (see curve b, Figure 3), indicating that the $Ni^0(bipy)_2$ is stable in the presence of magnesium ions in DMF.

The introduction of 1 equiv of **1b** to the Ni(0)−Mg^{2+} solution afforded curve c, which shows a reduction process occurring at −1.2 V and an oxidation around 0.4 V, with different intensities. After 15 min, an increase of the reduction wave can be observed in curve d, with an intensity approaching the value of the initial Ni(II) reduction. The recycling of the nickel species proceeds at a similar rate when the Mg^{2+} ions are slowly introduced from the beginning of the electrolysis and when their addition takes place after the formation of the π-allyl complex (as in the above experiment, Figure 4).

H. Applications to Organic Synthesis. Electrolysis of Functionalyzed Allyl Aryl Ethers. The selective cleavage of the O−C bond of allyl ethers by $Ni(bipy)_3{}^{2+}2BF_4^-$ has some direct applications in the field of deprotection of allyl ether functions in polyfunctional molecules. Selective protection and deprotection of functional groups are important processes in organic synthesis.[21] Allylic ethers can be used as selective protecting groups for alcohols and phenols,[22] and their removal is usually accomplished by a two-step procedure, involving strong base isomerization of the allyl double bond by KO-t-Bu in DMSO, followed by acidic hydrolysis of the enol ether intermediate.[8] Other methods include double-bond rearrangement using transition-metal complexes such as Rh(I).[7] Recently, allyl ether deprotection procedures based on the combined use of hydrides with Pd catalysis have also been reported.[23]

The $Ni(bipy)_3{}^{2+}2BF_4^-$-catalyzed electrochemical method constitutes an alternative deprotection method.[3] The electrochemical, preparative-scale deprotection of allyl ether functions in polyfunctional aryl derivatives was carried out in DMF, at constant current and at room temperature in a single-compartment cell. A 10% mol ratio of nickel catalyst with respect to the starting ether was used.

As mentioned in eq 1, the electrolysis of **1a** led cleanly to phenol in a quantitative yield. To evaluate the functional group selectivity of the electrochemical method, other aryl ethers with reductible functional groups were electrolyzed, and the results are summarized in Table 1.

Reducible ester and nitrile groups were not affected by the electrolysis of methyl 2-allyloxybenzoate or that of 2- or 4-allyloxycyanobenzene. The corresponding phenol−ester and phenol−nitrile derivatives were obtained in excellent yields (entries 2−4).

Aryl chloride substituents were not extensively reduced, and the electrosynthesis of *o*- or *p*-chlorophenols was carried out from the corresponding allyl or cinnamyl chlorophenyl ethers in yields of 75−96% (entries 5−7). Interestingly, the O−C(allyl) bond was selectively cleaved before the C−Cl bond under the Ni-catalyzed electrochemical conditions.

The reduction of 2-allyloxybromobenzene (entry 8) afforded, directly, phenol in quantitative yield.

Conclusions

The electrochemical method constitutes an interesting alternative for the deprotection of allyl aryl ethers to the parent alcohols under mild conditions. Simple experimental conditions for the selective cleavage of the C−O bond of allyl ethers are the use of $Ni(bipy)_3{}^{2+}2BF_4^-$ as the catalyst in a single-compartment cell with a magnesium anode, operating at constant intensity. The cleavage of the C−O bond is performed in good yields,

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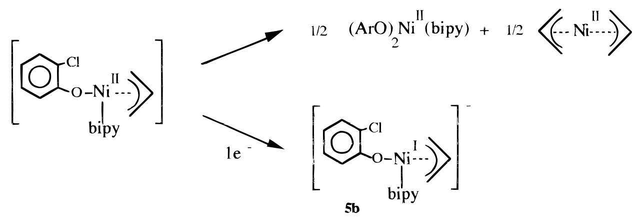
(21) (a) Greene, T. W.; Wutts, P. G. M. *Protective Groups in Organic Synthesis*, 2nd ed.; John Wiley: New York, 1991; pp 42−43. (b) Kocienski, P. J. *Protecting Groups*; Thieme, Stuttgart, 1994; pp 61−68.

(22) Cunninghan, J.; Gigg, R.; Warren, C. D. *Tetrahedron Lett.* **1964**, 1191.

(23) (a) Beugelmans, R.; Bourdet, S.; Bigot, A.; Zhu, J. *Tetrahedron Lett.* **1994**, *35*, 4349. (b) Zhang, H. X.; Guibé, F.; Balavoine, G. *Tetrahedron Lett.* **1988**, *29*, 619.

Scheme 5



the process being compatible with the presence of several functional groups.

Different reaction pathways can be proposed according to the operating experimental conditions, and Scheme 5 summarizes the mechanistic pathways under the different conditions: Ni^0(bipy)$_2$ is efficiently electrogenerated from the cationic Ni(II)−bipy complex and forms a π-allyl−Ni(II) complex upon addition of an allyl aryl ether in DMF. This same intermediate can be formed by a continuous electrolysis of Ni(II) in the presence of the substrate. Under continuous electrolysis conditions the π-allyl complex is reduced to form a formal Ni$^{\rm I}$ intermediate of type **5**, which recycles the Ni(0) complex, with or without Mg^{2+} ions (Scheme 2).

In the absence of any further current supply, a disproportionation of the π-allyl complex can be considered, with the formation of both a bis(phenoxide)Ni(II) and a bis(π-allyl)Ni(II) complex. The addition of Mg^{2+} allows the rapid regeneration of Ni(II)−bipy species able to be reduced at the initial potential of −1.2 V (Scheme 4).

The presence of Mg^{2+} ions accelerates the recycling of the nickel species in both cases and constitutes an important factor to enhance the catalytic activity in preparative-scale reactions.

Experimental Section

Reagents and Chemicals. All solvents were dried and degassed by standard methods. DMF was freshly distilled over calcium hydride before electrolyses. Allyl aryl ethers, **1**, were prepared from the corresponding phenols by treatment with allyl chloride and potassium carbonate in DMF. Ni(bipy)$_3^{2+}$-2BF$_4^-$ was prepared according to ref 24.

Instrumentation and Cells. ^{1}H 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 aid of an EG&G M273 potentiostat, Autolab PGSTAT 10, or EG&G scanning potentiostat model 362 equipment and were carried out at 20 °C by utilizing Au wire or carbon rods inserted in polymer resin electrodes or rotating electrodes (Au or carbon disk). Speed control was monitored by EDI 1011 and CTV 1001 Radiometer Equipement. All potentials were quoted with respect to Ag/AgCl at room temperature. 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, equipped with a carbon fiber cathode (apparent surface 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 (no. 4); the anodic compartment has a Mg rod as the anode, and the cathodic compartment is equipped with Ni foam or steel grid cathode and a Ag/AgCl reference electrode. The reduction potential of the nickel(II) complex (at −1.2 V vs Ag/AgCl) appeared at −1.7 V versus Cp$_2$Fe$^+$/Cp$_2$Fe°.

General Procedure for One-Compartment Cell Electrolyses. A DMF solution (40 mL) containing Ni(bipy)$_3^{2+}$2BF$_4^-$ (0.3 mmol), **1a** (or the other ether derivatives, 3 mmol), and n-Bu$_4$N$^+$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. 3−10 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 3−4 h. Generally, 2−2.2 F/mol of **1** were necessary to achieve a complete conversion. The solution was hydrolyzed with 50 cm^3 of aqueous 0.1 N HCl solution and extracted with Et$_2$O, dried over MgSO$_4$, and evaporated. The products were purified by column chromatography on silica gel with pentane/Et$_2$O mixtures as eluent. The yields are quoted in Table 1. The products are known compounds, and their spectral data were compared to authentic samples.

General Procedure for Two-Compartment Cell Electrolyses. Both compartments were filled with a DMF solution (50 mL each) of n-Bu$_4$N$^+$BF$_4^-$ (1 g, 3 mmol) under inert atmosphere. The Ni(II) complex (0.1 mmol) and **1a** (0.1 to 0.5 mmol) were added to the cathodic compartment. The electrolyses were run at 20 °C at the controlled potential of −1.2 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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(24) Duñach, E.; Périchon, J. *J. Organomet. Chem.* **1988**, *352*, 239.