New Open Tetraaza Nickel(II) and Palladium(II) Complexes. Different Reactivity of the Electrogenerated M(0) Species toward Difunctional Substrates

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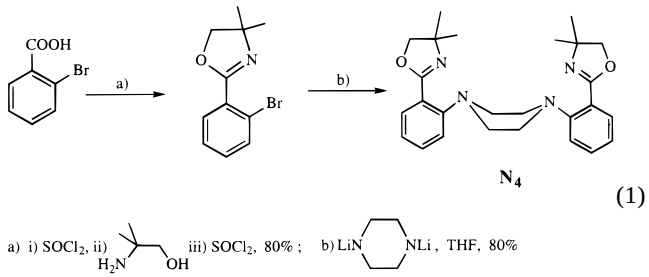
A series of neutral and cationic Ni(II) and Pd(II) complexes with the open tetraaza ligand bisoxazoline bisamine N_4, were prepared and characterized. Neutral complexes presented dimeric structures of stoichiometry $[M_2(\mu\text{-}N_4)X_4]$ (M = Ni (**1**), Pd (**2**)) and underwent slow decomplexation in coordinating solvents. Cationic monomeric $[M(N_4)]Y_2$ (M = Ni (**3**), Pd (**4**)) compounds were stable in solution and were efficient catalysts in electrochemical reactions involving difunctional substrates, unsaturated *o*-haloaryl and *o*-halobenzyl ethers. $[Ni(N_4)]^{2+}$-catalyzed reactions led to intramolecular cyclization products *via* initial oxidative addition on the C−X bond, whereas $[Pd(N_4)]^{2+}$-catalyzed processes involved the cleavage of the C−O bond. Furthermore, organometallic σ-Ni(II) (**7a**,**b**) and π-allylpalladium(II) (**8a**,**b**) complexes were prepared in order to study the intermediate species proposed in the catalytic cycles.

Introduction

In the past decade, the use of polydentate nitrogen compounds as donor ligands for coordination complexes has grown in the field of organometallic chemistry and catalysis.[1] Among these ligands, azacrown ethers and cryptands are strong selective complexing agents for metal cations and other charged and uncharged guest molecules.[2] These ligating compounds present several applications in organic synthesis and catalysis,[3] medicinal chemistry,[4] and analysis.[5] Much of the current interest in macrocyclic coordination chemistry stems from the hope that unusual geometric relationships imposed on the metal ions by the macrocyclic donor may be transformed into unusual bonding situations and novel reactivity. Thus, a Ni(II) center encircled by a tetraamine macrocycle such as cyclam (1,4,7,11-tetraazacyclotetradecane) allows access to the otherwise unstable Ni(III)[6] and Ni(I)[7] oxidation states. It has been shown that any modification of the ligand structure (ring size, ring substituents, unsaturations, etc.) may influence the catalytic activity of the resulting complexes.[8] On the other hand, little information has appeared on the formation and reactivity of palladium complexes with macrocyclic ligands.[9]

We have focused our attention on the particular case of open tetraaza ligands and on how the metal ion is held in the eventual macrocyclic cavity. The ligand N_4 (1,4-bis[2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)phenyl]-piperazine) (eq 1) has been chosen as an open-chain analog of certain cyclam derivatives, containing both oxazoline and amine donor groups. The use of oxazolines as ligands in organometallic catalysis has seen an



(1)

a) i) $SOCl_2$, ii) H_2N OH iii) $SOCl_2$, 80% ; b) LiN NLi , THF, 80%

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(1) (a) Togni, A.; Venanzi, L. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 497. (b) Van Veggel, F. C. J. M.; Verboom, W.; Reinhoult, D. N. *Chem. Rev.* **1994**, *94*, 794.

(2) (a) Lindoy, L. F. *The Chemistry of Macrocyclic Ligand Complexes*; Cambridge University Press: London, 1989. (b) Suh, M. P. *Adv. Inorg. Chem.* **1996**, *44*, 93. (c) Lee, D.; Suh, M. P.; Lee, J. W. *J. Chem. Soc., Dalton Trans.* **1997**, 577.

(3) Beley, M.; Collin, J. P.; Ruppert, R.; Sauvage, J. P. *J. Am. Chem. Soc.* **1986**, *108*, 7461.

(4) Lauffer, R. B. *Chem. Rev.* **1987**, *87*, 901.

(5) Hui-Zhi, C.; Kaden, T. A. *Helv. Chim. Acta* **1994**, *77*, 383 and references therein.

(6) Kinneary, J. F.; Albert, J. S.; Burrows, C. J. *J. Am. Chem. Soc.* **1988**, *110*, 6124. Ali, M.; Zilberman, I.; Cohen, H.; Shames, A. I.; Meyerstein, D. *Inorg. Chem.* **1996**, *35*, 5127.

(7) De Santis, G.; Fabrizzi, L.; Lichelli, M.; Sardone, N.; Velders, A. H. *Chem. Eur. J.* **1996**, *2*, 1243.

(8) (a) Fujita, E.; Haff, J.; Sanzenbacher, R.; Elias, H. *Inorg. Chem.* **1994**, *33*, 4627. (b) Abba, F.; De Santis, G.; Fabrizzi, L.; Lichelli, M.; Manotti Lanfredi, A. M.; Pallavicini, P.; Poggi, A.; Ugozoli, F. *Inorg. Chem.* **1994**, *33*, 1366. (c) Mochizuki, K.; Manaka, S.; Takeda, I.; Kondo, T. *Inorg. Chem.* **1996**, *35*, 5132.

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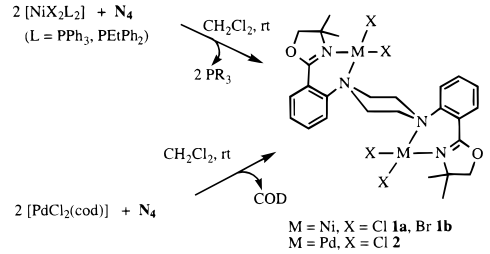
Scheme 1



exponential growth in the past few years, essentially due to the accessibility of chiral oxazolines for asymmetric catalysis.[10,11] However, the use of electron-rich amino oxazolines has been limited to pyridine oxazolines or to bisoxazolines,[12] and apart from our studies, no example of the use of such compounds as ligands in electrochemical reactions has been described. We present here our results on the characterization and reactivity of ionic and neutral Ni(II) and Pd(II) complexes associated with the bisoxazoline bisamine tetradentate ligand N_4. The chemical and electrochemical reactivity of these complexes has been examined, particularly in NiN_4-catalyzed intramolecular cyclizations. A preliminary communication on the electrochemical activity has been published.[13]

Results and Discussion

A. Synthesis of the N_4 Ligand. The two-step synthesis of N_4 (eq 1) started from commercial *o*-bromobenzoic acid, by treatment with thionyl chloride, followed by the addition of 2-amino-2-methylpropan-1-ol and further dehydration with thionyl chloride, according to the method of Meyers *et al.*[14]

Further treatment of the bromooxazoline with bislithiated piperazine[15] led directly to N_4 in 64% isolated yield (80% based on recovered bromooxazoline). The forward synthesis of N_4 presents sufficient flexibility for the further elaboration of other derivatives, differing in either their bisamino or their oxazoline moieties: such a modulation constitutes an interesting feature for the control of the physical and chemical properties of the derived transition metal complexes.

B. Synthesis of Neutral Compounds [$M_2(\mu$-N_4)X_4] (M = Ni, Pd). The neutral complexes [$Ni_2(\mu$-N_4)X_4] (**1a**, X = Cl, and **1b**, X = Br) were prepared by reaction of [NiX_2L_2] derivatives with low-basicity L ligands in CH_2Cl_2 at room temperature. Thus, with a phosphine ligand such as $PEtPh_2$, **1a** was obtained as a purple solid in 87% yield. Starting from [$NiBr_2(PPh_3)_2$], **1b** was obtained in 88% yield (Scheme 1). When the basicity of L was increased, the substitution reaction with N_4 did not take place, as was also the case with the complexes [$NiCl_2py_2$] and [$NiCl_2(PEt_2Ph)_2$]. Preparation of compounds **1** failed from mixtures of anhydrous NiX_2 with N_4. The [$Pd_2(\mu$-N_4)Cl_4] complex **2** was directly obtained from [$PdCl_2$(cod)] and N_4 as an orange solid in 76% isolated yield (Scheme 1).

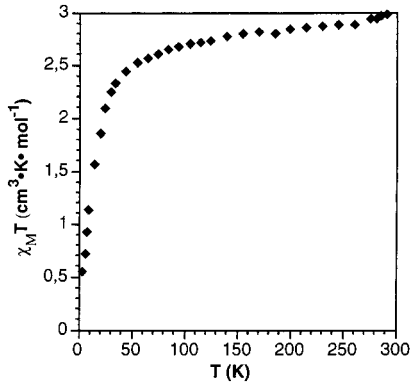


Figure 1. Temperature dependence of $\chi_M T$ for **1a**.

In the reactions of N_4 with [MX_2L_2]-type starting complexes, only dinuclear Ni(II) or Pd(II) aggregates were formed. No evidence for the presence of mononuclear neutral species of stoichiometry [$MX_2(N_4)$] could be obtained. These results are in contrast with those described in the case of cyclam as the ligand, for which the [$NiCl_2$(cyclam)] or [$NiBr_2$(cyclam)] complexes are easily obtained.[16] Most probably, the rigid square-planar arrangement of the four sp^3 nitrogen atoms in the cyclam stabilizes the octahedral complex.

The new compounds **1a**, **1b**, and **2** are air-stable solids and can be stored under nitrogen for several months. Complexes **1** and **2** are soluble only in coordinating solvents, although decoordination of N_4 is observed. Both Ni(II) complexes **1a** and **1b** are purple and paramagnetic. In contrast, the palladium dinuclear complex **2** is a diamagnetic orange solid. These complexes were characterized by elemental analysis, infrared spectroscopy, ^{1}H NMR (**2**), and magnetic susceptibility (**1a**, **1b**).

The measurements of the magnetic susceptibility for **1a** and **1b** were carried out at variable temperature. The measured $\mu_{eff} = 4.98\ \mu_B$ at 296 K was in the range of the expected values for a molecular system with four electrons (2 + 2), in two independent nickel atoms in a tetrahedral environement, μ_{eff} (spin-only) = $4.0\ \mu_B$, that large orbital contribution is usually shown.[17] No significant coupling was observed upon decreasing the temperature (Figure 1).

C. Synthesis of Ionic Compounds [$M(N_4)$]Y_2 (M = Ni, Pd). Although we were unable to obtain neutral mononuclear [$MX_2(N_4)$] complexes starting from Ni(II) or Pd(II) halides or *via* substitution reactions and only dinuclear complexes were isolated, the cationic mononuclear complexes could be obtained selectively in high yields starting from nickel and palladium BF_4^-, ClO_4^-, or PF_6^- salts.

Thus, the reaction of N_4 with either nickel(II) tetrafluoroborate or perchlorate led to the ionic compounds [$Ni(N_4)$]$(BF_4)_2$ (**3a**) and [$Ni(N_4)$]$(ClO_4)_2$ (**3b**), respectively (Scheme 2). From a mixture of palladium(II) acetate,

(9) (a) McAuley, A.; Whitcombe, T. W. *Inorg. Chem.* **1988**, *27*, 3090. (b) Lilie, J.; Waltz, W. L.; Chandrasekhar, S. *Inorg. Chim. Acta* **1996**, *246*, 59.

(10) (a) Gant, T. G.; Meyers, A. I. *Tetrahedron* **1994**, *50*, 2297. (b) Pfaltz, A. *Acc. Chem. Res.* **1993**, *26*, 339.

(11) Pfaltz, A. *Acta Chem. Scand.* **1996**, *50*, 189 and references therein.

(12) Bolm, C. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 542 and references therein.

(13) Clinet, J. C.; Duñach, E. *J. Organomet. Chem.* **1995**, *503*, C48.

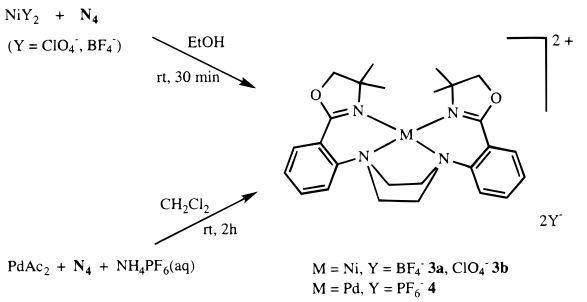
(14) Meyers, A. I.; Temple, D. L.; Haidukewych, D.; Mihelich, E. D. *J. Org. Chem.* **1974**, *39*, 2787.

(15) Meyers, A. I.; Gabel, R. A. *J. Org. Chem.* **1977**, *42*, 2653. Meyers, A. I.; Reuman, M.; Gabel, R. A. *J. Org. Chem.* **1981**, *46*, 783.

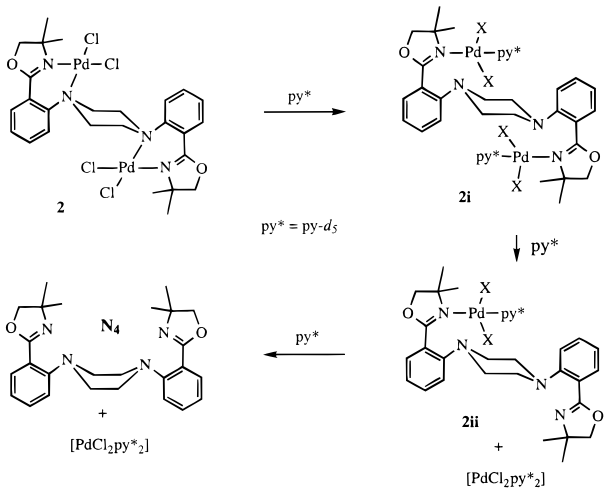
(16) Bosnich, B.; Poon, C. K.; Tobes, M. L. *Inorg. Chem.* **1965**, *4*, 1102.

(17) (a) Donoghue, J. T.; Drago, R. S. *Inorg. Chem.* **1996**, *1*, 866. (b) Goodgame, D. M. L.; Goodgame, M.; Cotton, F. A. *J. Am. Chem. Soc.* **1961**, *83*, 4161.

Scheme 2



Scheme 3



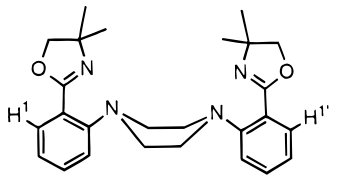
N_4, and ammonium hexafluorophosphate, mononuclear cationic complex **4** was isolated as a pale orange solid (Scheme 2). Compounds **3** and **4** are highly soluble in common organic solvents. These complexes are diamagnetic, and their analytical data are in agreement with the stoichiometry $[M(N_4)]Y_2$.

The solid state IR spectrum (KBr pellet) of the ligand N_4 shows four strong absorptions in the range 1638−1038 cm^{-1}. However, when the ligand is coordinated to the metal (**1**−**4**), the relative intensity of the bands changes, and only one very strong absorption in the range 1650−1625 cm^{-1} is observed.

D. NMR Analysis of 2−4. The proton NMR spectra for the ionic complexes **3** and **4** are well defined, and no decoordination of the N_4 ligand was observed. However, the neutral complex **2** gave broad NMR signals and showed a great tendency to dissociate N_4 in solution, the process being slower for the Pd(II) than for the Ni(II) complexes. N_4 decoordination took place in the usual coordinating solvents (acetonitrile, acetone, pyridine, dimethylformamide). The ligand dissociation reaction was monitored by ^1H NMR in the case of complex **2** when py-d_5 (py*) was added or used as solvent (Scheme 3 and Table 1). The time-dependent spectra are shown in Figure 2. The complex **2** was not soluble in $CDCl_3$, but, in the presence of 10% of py*, the spectrum showed a mixture of **2** and **2i** (spectrum A, Figure 2). When py* was used as solvent, evolution from **2** to free ligand was completed in 3.5 h (spectra B, C, and D). The proton signals corresponding to H^1 ($H^{1'}$) as well as the CH_2O, CH_2N, and CH_3 groups showed the consecutive formation of the species involved in the decoordination process.

E. Electrochemical Studies. Electrochemical Behavior of 3a. Cyclic voltammograms of **3a** in DMF solutions containing *n*-tetrabutylammonium tetrafluoroborate as supporting electrolyte presented two irreversible reducing peaks at −1.2 and −1.7 V *vs* Ag/

Table 1. Selected NMR Data (δ in ppm) for the Decoordination Reaction of 2 in py-d_5, with Coupling Constants (Hz) and Multiplicity[a] in Parentheses



	Me	CH_2-N	CH_2-O	H^1
N_4	1.70 (s, 12H)	3.70 (s, 8H)	4.42 (s, 4H)	8.30 (dd, 2H) (1.5, 7.6)
2[b]	1.66 (s, 12H)	3.20 (s, 8H)	4.14 (s, 4H)	8.89 (br d, 2H) (7.0)
2i	2.36 (s, 12H)	3.92 (br s, 8H)	4.83 (s, 4H)	9.91 dd (dd, 2H) (1.75, 7.75)
2ii	1.75 (s, 6H) 2.32 (s, 6H)	3.67 (br s, 8H)	4.44 (s, 2H) 4.78 (s, 2H)	8.28 (dd, 1H) (1.5, 7.5) 9.89 (dd, 1H) (1.75, 7.5)

[a] Multiplicity: br, broad; s, singlet; d, doublet; t, triplet. [b] Solvent was $CDCl_3$ + 10% py-d_5.

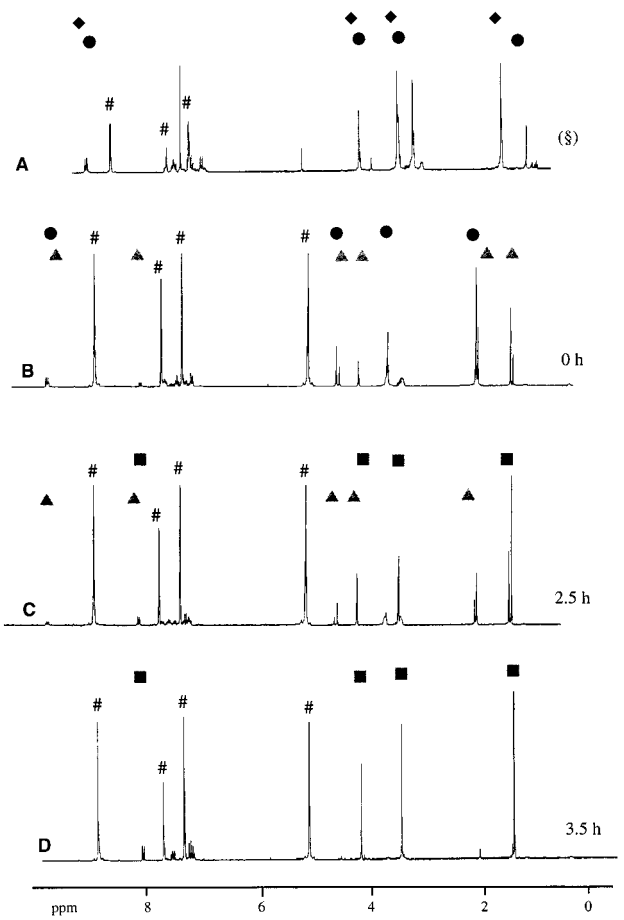


Figure 2. Time-dependent ^1H NMR spectra of $[Pd_2(\mu\text{-}N_4)Cl_4]$ (**2**). #, solvent impurities (py-d_5), §, 1 cm^3 of $CDCl_3$ + 0.1 cm^3 of py*; ◆, **2**; ●, **2i**; ▲, **2ii**; ■, N_4, following Scheme 3.

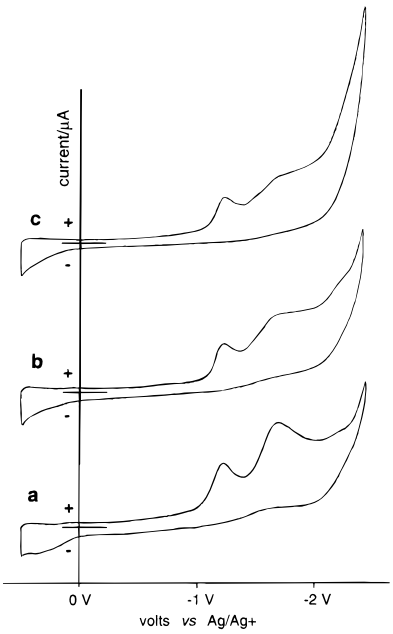
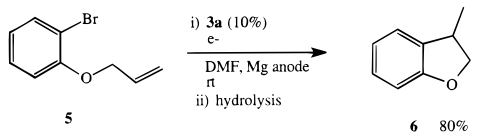


Figure 3. Cyclic voltammograms of **3a** (curve a) in DMF solutions containing *n*-tetrabutylammonium tetrafluoroborate as supporting electrolyte. Curve b, **5**/**3a** = 0.5; curve c, **5**/**3a** = 5.

AgCl, as shown in Figure 3, curve a. Reduction of the free ligand N_4 occurred at less than −2.3 V, at which potential we observed the reduction of the solvent. The electrochemical behavior of **3a** was different from that described for $[Ni(cyclam)]^{2+}$, for which a one-electron reduction process has been described as occurring at −1.5 V in MeCN solutions.[18] In the case of **3a**, "$Ni^{I}N_4$" and "$Ni^{0}N_4$" species are presumably generated under the electrochemical conditions, stabilized by the tetraaza ligand.

We examined the reactivity of electrogenerated "NiN_4" species with organic halides. As a model compound we chose the aromatic allyl 2-bromophenyl ether (**5**) (eq 2), which possesses an olefin function as unsaturated side chain. This substrate should faciliate the study of the



5 **6** 80% (2)

reactivity of the aryl−bromide bond, as well as the possibilities of intramolecular radical-type reactions involving the side chain.

The cyclic voltammetry behavior of **3a** in the presence of halide **5** is shown in Figure 3 (curves b and c). No modification of the reduction peak of **3a** at −1.2 V was observed upon addition of 0.5 molar equiv of substrate (curve b), the peak being irreversible. The peak at −1.7 V appeared wider. With a 1:1 or a 5:1 ratio of **5** to **3a** (curve c), no additional wave change was observed.

Preparative-Scale Electroreductive Cyclizations of 5 Catalyzed by 3a. When **3a** was electrolyzed in the presence of bromide **5** in a 1:5 molar ratio at a controlled potential of −1.2 V, in a DMF solution containing 10^{-1} M *n*-tetrabutylammonium tetrafluoroborate in a two-compartment cell, we observed a small charge transfer before passivation occurred. Analysis of the reaction mixture revealed the presence of unreacted **5**, together with traces of 2-bromophenol arising from the cleavage of the O−C bond of the allyl group. In contrast, when the electrolysis of a 1:3 mixture of **3a** and **5** was carried out at −1.8 V under the same conditions, the cyclized compound 3-methyldihydrobenzofuran (**6**) was obtained in 30% yield, together with unreacted **5** after the passage of 3 F/mol of **5** (eq 2).

These results indicate that the electrogenerated "NiN_4" complex at −1.2 V shows a very low reactivity toward **5**, but, at lower potentials, the Br−C(aryl) bond of **5** can be activated, and the reaction is followed by an intramolecular cyclization.

In order to obtain more efficient cyclization reactions from a preparative point of view, the reaction was carried out using a sacrificial anode in a single-compartment cell.[19] This electrochemical methodology enables electrolyses to run under intensiostatic conditions and allows the straightforward scale-up of the electrochemical reactions. The electrolysis of **5** under a one-compartment cell procedure was catalytic in Ni(II). The reactions were carried out using a magnesium anode and a carbon fiber cathode, with a catalytic amount of **3a** (10 molar % with respect to **5**), in DMF at room temperature, with a low concentration of supporting electrolyte (nBu$_4$N$^+$BF$_4^-$, 5×10^{-3} M). The reductive cyclization to **6** occurred selectively in 80% yield (eq 2).

Thus, in the presence of a magnesium anode in one-compartment cells, involving the continuous generation of Mg^{2+} ions in solution, the $[NiN_4]^{2+}$-catalyzed intramolecular cyclization of **5** becomes highly selective, compared to the electrolysis results in two-compartment cells (absence of Mg^{2+} ions). The presence of the magnesium ions plays an active role in enhancing the reactivity and the selectivity. Under the one-compartment cell procedure, no reaction was observed in the absence of electricity, and a nonselective reduction of **5** occurred in the absence of the nickel complex.

When the same one-compartment cell electrolysis was carried out with neutral **1b** as the catalyst, the reduction of **5** gave a mixture of products (cyclized **6**, phenol, 2-bromophenol, unreacted **5**, isomerized 1-propenyl ether, dimeric compounds) without any selectivity. This result, similar to that obtained in the noncatalyzed process, can be explained by the fast ligand decomplexation of **1b** in DMF solution, involving a cathodic deposition of metallic nickel upon electrochemical reduction.

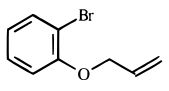
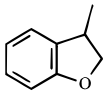
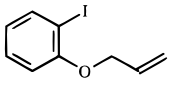
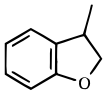
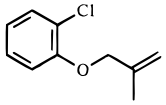
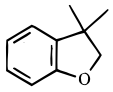
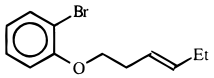
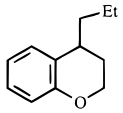
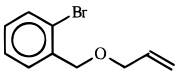
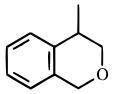
A series of substrates related to model compound **5** were prepared and further electrolyzed,[13] in reactions catalyzed by **3a**, under the single-compartment cell conditions. The results are summarized in Table 2.

The reductive cyclization procedure enabled the preparation of differently substituted bicyclic derivatives in good yields. Allyl aryl ethers afforded dihydrobenzofuran products in a selective reaction, without the presence of six-membered ring cyclization isomers. It is noteworthy that not only bromo but also iodo and, more interestingly, chloro aryl derivatives (entries 2, 3) underwent efficient cyclization. A dihydro-1-benzopyran compound (entry 4) could be prepared upon elec-

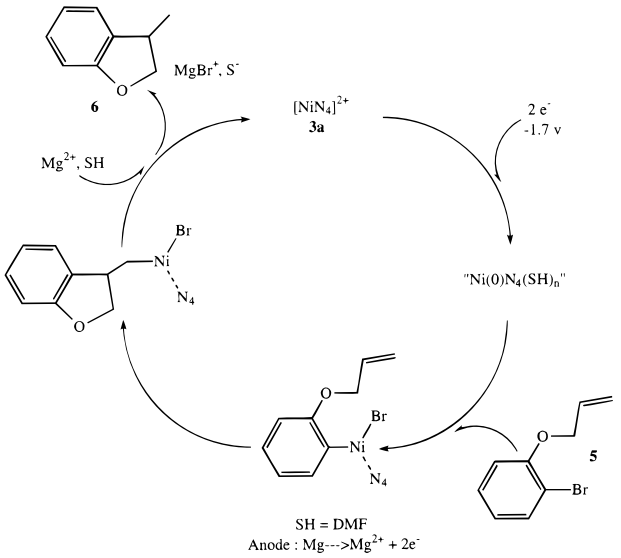
(18) Olson, D. C.; Vasilevski, J. *Inorg. Chem.* **1969**, *8*, 1611.

(19) Chaussard, J.; Folest, J. C.; Nédélec, J. Y.; Périchon, J.; Sibille, S.; Troupel, M. *Synthesis* **1990**, *5*, 369.

Table 2. Electrochemical Cyclization of *o*-Haloaryl and *o*-Halobenzyl Ethers Catalyzed by 3a

Entry	Starting ether	Cyclized Compound	Yield
1			80%
2			90%
3			77%
4			68%
5			52%

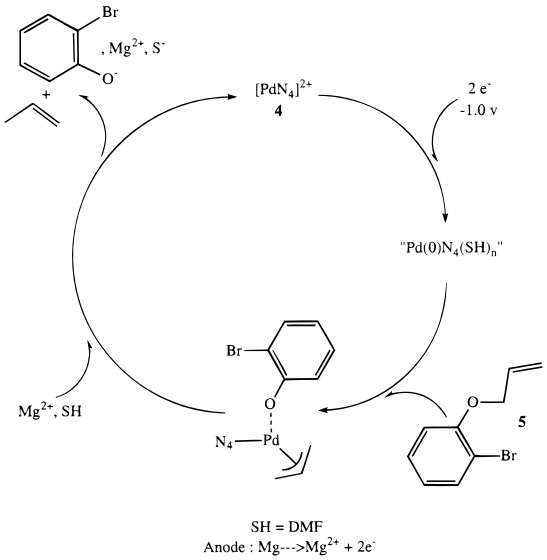
Scheme 4



trolysis of a homoallylic ether, and a dihydro-2-benzopyran analog (entry 5) was obtained from an allyl benzyl ether. The bulk electrolyses catalyzed by **3a** proceed with a consumption of 2−4 F/mol of halide.

According to cyclic voltammetry and controlled potential experiments, a two-electron reduction of **3a** to "NiN_4" at −1.7 V is necessary to obtain the intramolecular cyclization reaction. The process may be interpreted by a first oxidative addition of **5** over the electrogenerated Ni(0) species, followed by an olefin insertion in the σ(Ni−C) bond (Scheme 4). The last step involves the protonation of the Ni−C bond assisted by the Mg^{2+} ions. The proton sources were shown to be the supporting electrolyte and the DMF solvent.[20] Moreover, in a stoichiometric one-compartment cell cyclization of **5** in the presence of 1 molar equiv of *n*-tetrabutylammonium tetrafluoroborate, the quantitative formation of tributylamine, issued from the ammonium salt decomposition, was confirmed by GC analysis.

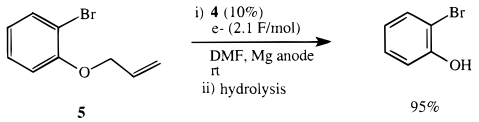
Scheme 5



The results of the aryl halide cyclizations are largely parallel to those described with $[Ni(cyclam)]^{2+}$ in electrochemical reactions, for which a radical-type reaction has been suggested.[21] However, in the case of nickel−cyclam complexes, a mechanism involving the electrochemical Ni(II) reduction to Ni(I) has been proposed.[22]

Electrochemical Behavior of 4. The cyclic voltammetry of **4** on a carbon fiber microelectrode showed an irreversible (two-electron) reduction process at −0.9 V *vs* Ag/AgCl. Upon the addition of the substrate **5** (in 1:1 and 5:1 ratios of **5:4**), a slight enhancement in the reduction peak at −0.9 V could be observed.

Preparative-Scale Electrochemical Cleavage of the Allyl Group of 5, Catalyzed by 4. The bulk electrolysis of substrate **5** in a Pd-catalyzed reaction by **4** under a single-compartment cell procedure in the presence of a magnesium anode led, after 1 F/mol, to a 50% conversion of **5**, with the formation of only 2-bromophenol. After 2.1 F/mol electrolysis, the complete consumption of **5** was attained, with 95% of bromophenol present (eq 3). If the electrolysis was continued,



(3)

dehalogenation took place, and phenol was formed progressively; thus, after 3 F/mol electrolysis, a mixture of 2-bromophenol (63%) and phenol (32%) was obtained.

In the presence of the palladium catalyst **4**, a highly selective cleavage of the O−C(allyl) bond of **5** occurred. The reaction presumably involves an initial electrogeneration of "Pd^0N_4" species, which reacts with the organic substrate to form a π-allyl Pd(II) intermediate (Scheme 5). Under the electrochemical conditions, and in the

(20) Dérien, S.; Duñach, E.; Périchon, J. *J. Am. Chem. Soc.* **1991**, *113*, 8447.

(21) (a) Olivero, S.; Duñach, E. *Tetrahedron Lett.* **1995**, *36*, 4429. (b) Ozaki, S.; Matsushita, H.; Ohmori, H. *J. Chem. Soc., Chem. Commun.* **1992**, 1120. (c) Ozaki, S.; Horiguchi, I.; Matsushita, H.; Ohmori, H. *Tetrahedron Lett.* **1994**, *35*, 725.

(22) (a) Gosden, C.; Pletcher, D. *J. Organomet. Chem.* **1980**, *186*, 401. (b) Healy, K. P.; Pletcher, D. *J. Organomet. Chem.* **1978**, *161*, 109.

presence of Mg^{2+} ions issued from anodic oxidation, 2-bromophenolate ion is formed by metal exchange, the allyl moiety being protonated by the reaction medium.[20] The $[Pd(N_4)]^{2+}$ complex can be liberated and recycled by continuous reduction.

The ability of Pd(0) complexes to form π-allyl Pd(II) species with allyl esters or carbonates is a well-known reaction,[23] with various applications in the field of asymmetric alkylations.[24] In the example with substrate **5**, the cleavage concerns an allyl ether and takes place without interference to the aryl−bromide bond.

The difference in reactivity observed for **3** and **4** toward difunctional **5** in one-compartment cells is noteworthy: nickel complex **3** chemoselectively orientates the reactivity toward activation of the aryl−bromide bond, whereas the electroreduction of the palladium complex **4** specifically activates the allyl ether moiety.

F. Intermediate "MN_4" Species. The results observed by cyclic voltammetry for Ni(II) (**3**) and Pd(II) (**4**) complexes showed the formation of Ni(I), Ni(0), and Pd(0) species. We were interested in the chemical preparations of such intermediates, in order to study their behavior and stability, and to get some comparative features concerning their chemical and electrochemical reactivity.

Thus, when N_4 was added to a toluene or THF solution of $[Ni(cod)_2]$ at room temperature, only decomposed black metallic nickel could be recovered. Alternatively, when N_4 was added to $[Ni(cod)_2]$ in toluene solution in the presence of PPh_3 in a 1:1:2 molar ratio, no mixed compounds $[Ni(PPh_3)_2(N_4)]$ were detected, and only $[Ni(PPh_3)_4]$ was obtained. The same process occurred upon adding dppe instead of PPh_3, with obtention of $[Ni(dppe)_2]$. However, when N_4 was added to $[Ni(cod)_2]$ in a DMF solution, no decomposition to black Ni(0) was observed. Therefore, the solvent plays a fundamental role in the stabilization of the "$Ni(0)N_4$" species.

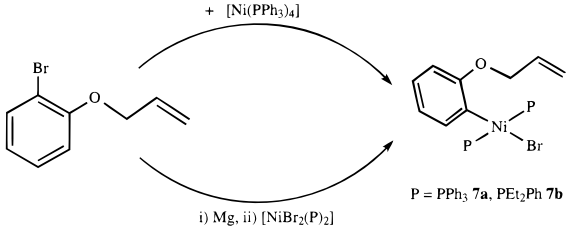
Since the cyclization reaction has been observed from Ni(I)−cyclam-type species[21] and we have observed the same Ni(I) species in the cyclic voltametry, we have tried to isolate the "Ni^IN_4" complexes. Attempts to prepare Ni^IN_4 species were performed from mixtures of $[NiCl(PPh_3)_3]$ and N_4. In toluene, no ligand exchange reaction occurred. However, stable orange solutions were obtained in DMF, although it was not possible to characterize pure solid compounds from these solutions. On standing for several days, the disproportionation reaction took place, and **1a** could be recovered.

A Ni(0)/Ni(II) comproportionation reaction was attempted by adding $[Ni(cod)_2]$, $[Ni(N_4)](ClO_4)_2$, and N_4 in an equimolar ratio in toluene, but no Ni^IN_4 species could be cleanly isolated. The direct chemical reduction of $[Ni(N_4)](ClO_4)_2$ with Na/Hg amalgam in DMF was monitored by EPR, but no Ni(II) reduction was observed, and **3b** was recovered.

The intramolecular cyclization observed with **5** induced by the electrochemical reduction in the presence of the cationic $[Ni(N_4)]^{2+}$ species could not be reproduced in stoichiometric reactions starting from $[Ni(cod)_2]$ or $[NiCl(PPh_3)_3]$ complexes in the presence of the N_4 ligand, either in toluene or in DMF.

The oxidative addition of **5** was not observed with $[Ni(cod)_2]$, with or without additional phosphine as stabilizing ligand, and no reaction products of the organic halide could be detected. The oxidative addition of **5** to $[Ni(PPh_3)_4]$ at room temperature gave small amounts of $[NiBr(2\text{-}(OCH_2CH{=}CH_2)C_6H_4)(PPh_3)_2]$ (**7a**), as could be monitored by ^{31}P NMR of the solution reaction. However, this complex was not isolated, and only PPh_3 and $OPPh_3$ could be recovered. The analysis of the reaction solution showed the presence of unreacted **5**, the coupling compound $[2\text{-}(OCH_2CH{=}CH_2)C_6H_4]_2$, and *o*-bromophenol. These results suggest that the oxidative addition of **5** is a competitive process between the Br−C and O−C bonds. Similar product mixtures were obtained by electrochemical reduction of neutral complex **1b** in the presence of **5**.

The syntheses of $[NiBr(2\text{-}(OCH_2CH{=}CH_2)C_6H_4)(P)_2]$ (where P = PPh_3 (**7a**) and PEt_2Ph (**7b**)) were achieved from reactions of $[NiBr_2P_2]$ and $BrMg(2\text{-}(OCH_2CH{=}CH_2)C_6H_4)$ in very low yields. The coupling product $(2\text{-}(OCH_2CH{=}CH_2)C_6H_4)_2$ from the decomposition of the organometallic compound,[25] allyl phenyl ether, and an unexpected compound *o*-$(OCH_2CH{=}CH_2)(CH_2CH{=}CH_2)$-$C_6H_4$, were observed, as well as the corresponding phosphine and its oxide (eq 4). Addition of N_4 to the

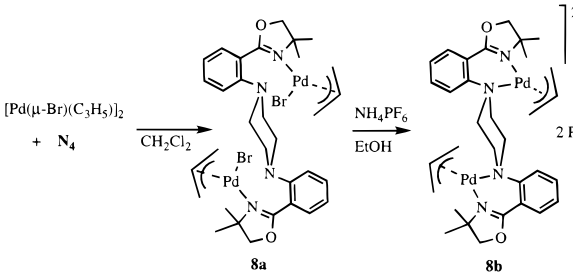


(4)

solutions of complexes **7** did not induce the substitution of coordinated phosphines.

The preparation of neutral mononuclear organometallic complexes containing the N_4 ligand was unsuccessfully attempted *via* substitution reactions starting from $[NiCl(2,4,6\text{-}Me_3C_6H_2)(PPh_3)_2]$ and $[PdBr(o\text{-}MeC_6H_4)(PPh_3)_2]$ with N_4. The action of Grignard reagents such as $BrMg(2,4,6\text{-}Me_3C_6H_2)$ on the neutral coordination complexes $[M_2(\mu\text{-}N_4)X_4]$ also failed to produce $[M_2X_2R_2(\mu\text{-}N_4)]$ or $[MXR(N_4)]$ compounds.

In the case of the catalytic reaction of **5** with $[Pd(N_4)]^{2+}$, a π-allylpalladium species has been proposed (Scheme 5) as intermediate. Therefore, neutral (**8a**) and ionic (**8b**) allyl dinuclear complexes were obtained in quantitative yields (eq 5). The proton NMR spectrum



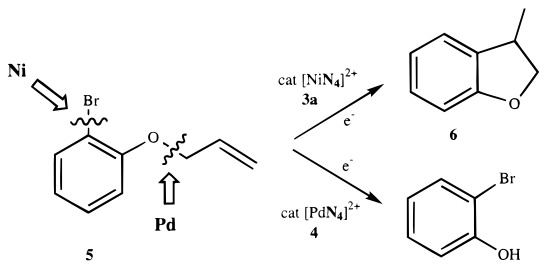
(5)

of **8b** was well defined, whereas for the neutral complex **8a** the signals were broad in the range 223−323 K, probably due to the fast substitution exchange of the

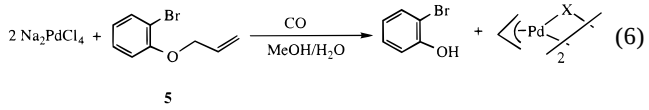
(23) Pregosin, P. S.; Salzmann, R. *Coord. Chem. Rev.* **1996**, *155*, 35.
(24) (a) Trost, B. M.; van Vranken, D. L. *Chem. Rev.* **1996**, *96*, 395. (b) Frost, C. G.; Howarth, J.; Williams, J. M. J. *Tetrahedron: Asymmetry* **1992**, *3*, 1089.

(25) Antón, M.; Muller, G.; Sales, J. *Transition Met. Chem.* **1983**, *8*, 79.

Scheme 6



ligands. In order to stabilize π-allylpalladium intermediates with **5**, we studied the stoichiometric reaction to prepare the dimeric allylic palladium complexes following the published conditions (eq 6).[26] The analysis of



(6)

the products showed the formation of 2-bromophenol and the dimeric allylic complex in low yields. This would seem to suggest that the π-allylpalladium intermediate (Scheme 5) is a dinuclear species stabilized by the tetraaza ligand.

Conclusion

For the neutral complexes $[M_2(\mu\text{-}N_4)X_4]$ (M = Ni (**1a**, **1b**), Pd (**2a**)), the potential tetradentate ligand acts only in a bidentate form, giving dinuclear compounds, where decomplexation of N_4 was observed in solution of coordinating solvents, as was established by NMR spectroscopy. However, the ligand N_4 acts as a tetradentate ligand in the monomeric ionic complexes $[M(N_4)]Y_2$ (M = Ni (**3**), Pd (**4**)). These complexes remain stable in coordinating solvents and present very different electrochemical reactivity toward difunctional organic substrates such as allyl 2-bromophenyl ether (**5**).

The difference in reactivity observed for complexes $[M(N_4)]Y_2$ (**3** and **4**) toward difunctional **5** in one-compartment cells is noteworthy: nickel complex **3** chemoselectively orientates the reaction toward activation of the aryl−bromide bond, whereas the electroreduction of the palladium complex **4** specifically activates the allyl ether moiety (Scheme 6).

The attemps to prepare the intermediate species with different oxidation states of the proposed cycles (Schemes 4 and 5) allowed us to confirm the activation of the C−Br bond by formation of σ(Ni−C) complexes (**7a**,**b**) and the activation of the C−O bond by formation of π-allylpalladium complexes (**8a**,**b**). Furthermore, the effect of the solvent is also important, both in the stabilization of the M(0) intermediate species and in providing the hydrogen neccesary to cleave the M−C bond.

The role of the ligand and oxidation state of the Ni complexes is also essential in determining the selectivity. Thus, with $[Ni(cyclam)]^{2+}$, the same intramolecular cyclization products were obtained from **5**, but in a process involving Ni(I) species. In contrast, Ni(0) associated with the 2,2′-bipy ligand induced the allyl−O cleavage reaction on **5**.[27]

Experimental Section

Reagents and Chemicals. All manipulations of the complexes in solution were carried out using Schlenk techniques under a nitrogen atmosphere. All solvents were dried and degassed by standard methods. $[PdCl_2(cod)]$ was prepared as reported.[28] Allyl 2-bromophenyl ether (**5**) (and other allyl ethers) was prepared from 2-bromophenol by treatment with allyl chloride and potassium carbonate on DMF.

Instrumentation and Cells. ^1H, ^{31}P, and ^{13}C NMR spectra were obtained using Varian Gemini-200, Unity 300, and Bruker DRX 250 spectrometers. Solvents used were $CDCl_3$, acetonitrile-d_3, acetone-d_6 benzene-d_6, or py-d_5. Infrared spectra were recorded as KBr disks on a Nicolet 520 FT-IR spectrometer. Microanalyses were performed by the Institut de Química Bio-Orgànica de Barcelona (CSIC) and by the Serveis Científico-Tècnics de la Universitat de Barcelona. Conductivity measurements were taken with a Radiometer CDM3 instrument in 10^{-3} M acetone or acetonitrile solutions at 20 °C. Magnetic measurements were carried out at variable temperature (300−4 K) on polycrystalline samples with a pendulum-type magnetometer (Manics DSM8) equipped with a Drusch EAF 16UE electromagnet. The magnetic field was approximately 1.5 T. Diamagnetic corrections were estimated from Pascal's tables.

Cyclic voltammetry experiments and controlled potential electrolyses were performed with the aid of PAR 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. Intensiostatic 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 ~40 cm^3 volume, already described,[19] 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 (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.[29]

N_4. In a 500 cm^3, three-necked flask, dried and flushed with argon, 2.15 g of dry piperazine was introduced, followed by 250 cm^3 of anhydrous THF. The resulting mixture was stirred for 20−30 min in order to obtain a homogeneous medium. This solution was then brought to −10 °C (ice/brine bath), and 33.5 cm^3 of a 1.5 N *n*-BuLi solution in hexane (0.05 mol) was added into the flask *via* a canula, keeping the temperature under 0 °C. There was an immediate precipitate of the dilithiated piperazine. The mixture was stirred for 30 min at −10 °C, and then a solution of 12.7 g of the 2-(2′-bromophenyl)-4,4-dimethyloxazoline[14] (0.05 mol) in 100 cm^3 of anhydrous THF was introduced dropwise *via* a canula. The reaction was exothermal, and the medium quickly turned to a dark red color. The resulting solution was then stirred for 12 h. The solvent was evaporated, and the residue was taken in a mixture of 100 cm^3 water and 200 cm^3 chloroform. The phases were separated. The aqueous phase was extracted twice with chloroform (100 cm^3). Then, the joined organic phases were washed three times with 100 cm^3 of clear water. The organic phase was dried over potassium carbonate and then concentrated under reduced pressure. The residue was stirred in diethyl ether to give a white precipitate, which was then recrystallized in a mixture of dichloromethane and ether. A total 13.8 g of a white solid was isolated in a 64% yield. The remaining oil of the recrystallization was essentially consti-

(26) Tatsuno, Y.; Yoshida, T.; Otsuka, S. *Inorg. Synth.* **1990**, *28*, 342.
(27) Olivero, S.; Duñach, E. *J. Chem. Soc., Chem. Commun.* **1995**, 2497.
(28) Drew, D.; Doyle, J. R. *Inorg. Synth.* **1990**, *28*, 346.
(29) Garnier, L.; Rollin, Y.; Périchon, J. *New J. Chem.* **1989**, *13*, 53.

tuted by 2-bromooxazoline, 2.5 g of which was recovered by vacuum distillation. The final yield based on the consumed bromooxazoline was 80%, mp = 178 °C.

^{1}H NMR ($CDCl_3$): δ 7.63 (d, 1H, J = 7.6 Hz), 7.38 (dd, 1H, J = 7.4 and 7.6 Hz), 7.04 (d, 1H, J = 8.0 Hz), 7.00 (dd, 1H, J = 7.4 and 8 Hz), 4.07 (s, 4H), 3.22 (s, 8H), 1.37 (s, 12H). ^{13}C NMR ($CDCl_3$): δ 163.3, 151.6, 131.7, 131.5, 122.0, 121.6, 118.2, 79.0, 67.4, 52.0, and 28.4. IR (Nujol): 1630, 1600, 1315, 1035 cm^{-1}. Anal. Calcd for $C_{26}H_{32}N_4O_2$: C, 72.19; H, 7.47; N, 12.95. Found: C, 71.98; H, 7.40; N, 12.54.

[Ni$_2$(μ-N$_4$)X$_4$] X = Cl (1a), Br (1b). To a solution of the N_4 ligand (0.11 g, 0.25 mmol) in THF (10 cm^3) at room temperature was added dropwise a solution of [NiX_2L_2] ([$NiBr_2$(PPh_3)$_2$], 0.38 g, 0.50 mmol; [$NiCl_2$($PEtPh_2$)$_2$], 0.28 g, 0.5 mmol) in 10 cm^3 of THF. The mixture was stirred for 1 h under these conditions, affording a purple solid. The precipitate was filtered off, washed with ether and hexane, and dried under vacuum. Data for **1a** follow. Yield: 0.15 g, 87%. Anal. Calcd for $C_{26}H_{32}Cl_4N_4O_2Ni_2$: C, 45.14; H, 4.66; N, 8.10. Found: C, 45.10; H, 4.25; N, 8.29. Data for **1b** follow. Yield: 0.19 g, 88%. Anal. Calcd for $C_{26}H_{32}Br_4N_4O_2Ni_2$: C, 35.91; H, 3.71; N, 6.44. Found: C, 35.80; H, 3.65; N, 6.45.

[Pd$_2$(μ-N$_4$)Cl$_4$] (2). A solution of the N_4 ligand (0.11 g, 0.25 mmol) in CH_2Cl_2 (10 cm^3) at room temperature was added dropwise to a solution of [$PdCl_2$(cod)] (0.14 g, 0.5 mmol) in CH_2Cl_2 (10 cm^3). The mixture was stirred for 2 h under these conditions, affording an orange solid. Then, the precipitate was filtered off and washed with ether and hexane. Finally, the solid was dried under vacuum. Yield: 0.15 g, 76%. Anal. Calcd for $C_{26}H_{32}Cl_4N_4O_2Pd_2$: C, 39.67; H, 4.10; N, 7.12. Found: C, 39.90; H, 4.25; N, 7.18.

[Ni(N$_4$)]Y$_2$ (Y = BF$_4$ (3a), ClO$_4$ (3b)). A suspension of NiY_2 (0.5 mmol; Y = ClO_4^-, 0.16 g, Y = BF_4^-, 0.14 g) in ethanol (20 cm^3) at room temperature was added dropwise to a solution of N_4 (0.22 g, 0.5 mmol) in ethanol (10 cm^3). The mixture was stirred for 1 h under these conditions. The solvent was partially removed under reduced pressure, and 20 cm^3 of ether was added, affording a white precipitate. The compounds **3** were separated by filtration, washed with ether and hexane, and dried under vacuum. Data for **3a** follow. Yield: 0.14 g, 84%. Molar conductivity (10^{-3} M, acetone): Λ_M = 190 cm^2 Ω^{-1} mol^{-1}. Anal. Calcd for $C_{26}H_{32}B_2F_8N_4O_2Ni$: C, 46.97; H, 4.10; N, 7.12. Found: C, 47.00; H, 4.95; N, 8.50. Data for **3b** follow. Yield: 0.16 g, 87%. Molar conductivity (10^{-3} M, acetone): Λ_M = 190 cm^2 Ω^{-1} mol^{-1}. ^{1}H NMR (CD_3CN, 298 K): δ 1.6 (s, 12H, Me), 3.40 (s, 8H, CH_2-N), 4.75 (s, 4H, CH_2-O), 7.45 (t, 2H, J = 7.5 Hz), 7.7 (d, 2H, J = 7.5 Hz), 7.9 (t, 2H, J = 7.5 Hz), 8.0 (d, 2H, J = 7.5 Hz). Anal. Calcd for $C_{26}H_{32}Cl_2N_4O_{10}Ni$: C, 45.25; H, 4.56; N, 8.12. Found: C, 45.80; H, 4.56; N, 8.24.

[Pd(N$_4$)](PF$_6$)$_2$ (4). A suspension of $Pd(OAc)_2$ (0.11 g, 0.5 mmol) and NH_4PF_6 (0.16 g, 0.1 mmol) in CH_2Cl_2 (20 cm^3) was added dropwise to a solution of N_4 (0.22 g, 0.5 mmol) in 10 cm^3 of the same solvent. The solution was stirred at room temperature for 2 h. Then, 20 cm^3 of the solvent was removed under reduced pressure, and 30 cm^3 of hexane was added. The solution was placed in the freezer overnight. The orange precipitate formed was filtered and washed with degassed water (3 × 10 cm^3) and dried under vacuum. Yield: 0.3 g, 74%. Molar conductivity (10^{-3} M, acetone): Λ_M = 195 cm^2 Ω^{-1} mol^{-1}. ^{1}H NMR ($CDCl_3$, 298 K): δ 2.05 (s, 12H, Me), 3.31 (s, 8H, CH_2-N), 4.17 (s, 4H, CH_2-O), 7.10 (t, 2H, J = 7.5 Hz), 7.4 (t, 2H, J = 7.5 Hz), 7.75 (d, 2H, J = 7.5 Hz), 8.0 (d, 2H, J = 7.5 Hz). Anal. Calcd for $C_{26}H_{32}F_{12}N_4O_2P_2Pd$: C, 37.67; H, 3.89; N, 6.76. Found: C, 37.02; H, 3.70; N, 6.50.

Solution of 2-(Allyloxy)benzene Magnesium Bromide. A mixture of allyl 2-bromophenyl ether (**5**, 0.86 g, 4 mmol) and magnesium turnings (0.24 g, 10 mmol) in THF (30 cm^3) was stirred at room temperature for 2 h. GC analysis of hydrolyzed drops of the solution showed the complete formation of (allyloxy)benzene.

[NiBr(2-(CH$_2$=CHCH$_2$O)C$_6$H$_4$)(PPh$_3$)$_2$] (7a). A solution of 2-(allyloxy)benzene magnesium bromide (22 cm^3, 3 mmol), obtained as reported above, was added slowly to a suspension of [$NiBr_2$(PPh_3)$_2$] (1.5 g, 2 mmol) in THF (10 cm^3) at −78 °C. The solution was allowed to warm to room temperature and was then stirred for 30 min. After 12 h at 0 °C, the resulting suspension was filtered, the solution was concentrated under reduced pressure, and 20 cm^3 of toluene was added. The solution was washed with 15% NH_4Cl aqueous solution. The organic layer was separated and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum. The oil obtained was washed with hexane, and, after addition of absolute ethanol, a yellow solid was precipitated. Yield: 0.2 g, 18%. ^{31}P{^{1}H} NMR ($CDCl_3$, 240 K): δ 22.2. ^{1}H NMR (C_6D_6, 308 K): δ 4.7 (CH$_2$=CH-, t, 1H, J = 7 Hz), 5.4 and 5.8 (CH_2=CH-, d, 1H, J = 5 Hz and d, 1H, J = 8 Hz), 6.38 and 6.49 (CH_2O, t, 1H, J = 7.5 Hz and t, 1H, J = 7.5 Hz), 7−8 (aromatic, m). Anal. Calcd for $C_{45}H_{39}BrNiOP_2$: C, 67.87; H, 4.94. Found: C, 66.7; H, 4.9.

[NiBr(2-(CH$_2$=CHCH$_2$O)C$_6$H$_4$)(PEt$_2$Ph)$_2$] (7b). A solution of 2-(allyloxy)benzene magnesium bromide (11 cm^3, 1.5 mmol), obtained as reported above, was added slowly to a suspension of [$NiBr_2$(PEt_2Ph)$_2$] (0.45 g, 1 mmol) in toluene (15 cm^3) at −78 °C. The solution was allowed to warm to room temperature and was further stirred for 30 min. The solvent was removed under reduced pressure. The solid obtained was washed with water, dissolved in toluene, and dried over anhydrous Na_2SO_4. The solvent was partially removed, and hexane was added. A yellow solid was precipitated and filtered off. Yield: 65 mg, 10%. ^{31}P{^{1}H} NMR (C_6D_6, 293 K): δ 11.0. ^{1}H NMR (C_6D_6, 308 K): δ 1.6 and 2.2 (PCH_2CH$_3$, br, 4H and 4H), 0.98 and 1.02 (PCH$_2$CH_3, both q, 6H and 6H, $J_H \approx J_{P,P'} \approx$ 8 Hz), 4.8 (CH$_2$=CH-, t, 1H, J = 7 Hz), 6.4 and 6.55 (CH_2=CH-, s, 1H and d, 1H, J = 7 Hz), 6.8−6.9 (CH_2O, m, 2H), 7−8 (aromatic, m). Anal. Calcd for $C_{29}H_{39}BrNiOP_2$: C, 57.65; H, 6.51. Found: C, 57.2; H, 6.7.

[Pd$_2$(μ-N$_4$)(C$_3$H$_5$)$_2$Br$_2$] (8a). A solution of N_4 (0.060 g, 0.14 mmol) in CH_2Cl_2 (10 cm^3) at room temperature was added to a solution of [$Pd_2(C_3H_5)_2(\mu$-Br)$_2$] (0.13 g, 0.28 mmol) in CH_2Cl_2 (10 cm^3). The mixture was stirred overnight. Then, 25 cm^3 of hexane was added, affording a yellow solid. The precipitate was filtered off and washed with ether and hexane. Finally, the solid was dried under vacuum. Yield: 0.10 g, 81%. Anal. Calcd for $C_{32}H_{42}Br_2N_4O_2Pd_2$: C, 43.32; H, 4.77; N, 6.31. Found: C, 42.70; H, 4.60; N, 5.95.

[Pd$_2$(μ-N$_4$)(C$_3$H$_5$)$_2$](PF$_6$)$_2$ (8b). A solution of **8a** (0.089 g, 0.20 mmol) in ethanol (10 cm^3) at room temperature was added to a solution of NH_4PF_6 (0.066 g, 0.40 mmol) in the same solvent (10 cm^3). The mixture was stirred overnight, affording a white solid. The precipitate was filtered off and washed with degassed water (3 × 10 cm^3). Finally, the solid was dried under vacuum. Yield: 0.090 g, 88%. Molar conductivity (10^{-3} M, acetonitrile): Λ_M = 200 cm^2 Ω^{-1} mol^{-1}. ^{1}H NMR (CD_3CN, 298 K): δ 1.44 (Me, s, 12H), 3.00 (H_{anti}HC=CH-, d, 4H, J = 12.5 Hz), 3.51 (CH_2-N, s, 8H), 4.03 (H_{syn}HC=CH-, d, 4H, J = 7.0 Hz), 4.45 (CH_2-O, s, 4H), 5.58 (CH$_2$=CH-, 2H, J = 12.5 and 7.0 Hz), 7.35 (t, 2H, J = 7.6 Hz), 7.50 (br d, 2H, J = 8.2 Hz), 7.70 (br t, 2H, J = 7.5), 7.80 (dd, 2H, J = 7.7 and 1.5 Hz). Anal. Calcd for $C_{32}H_{42}F_{12}N_4O_2P_2Pd_2$: C, 37.78; H, 4.16; N, 5.51. Found: C, 37.40; H, 4.20; N, 5.75.

General Procedure for One-Compartment Cell Electrolyses. A DMF solution containing **3a** (0.3 mmol), **5** (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 **5** 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, 3−4 F/mol of **5** 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 2. The products were compared to authentic samples.

General Procedure for Two-Compartment Cell Electrolyses. Both compartments were filled with a DMF solution (30 cm^3 each) of *n*-$Bu_4N^+BF_4^-$ (1 g, 3 mmol) under inert atmosphere. Complex **3a** (0.1 mmol) and **5** (0.3 or 0.5 mmol) were added to the cathodic compartment. The electrolyses were run at 20 °C at the desired potential 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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