Intramolecular Allyl Transfer Reaction from Allyl Ether to Aldehyde Groups: Experimental and Theoretical Studies

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Abstract: The intramolecular transfer of the allyl group of functionalized allyl aryl ethers to an aldehyde group in the presence of Ni⁰ complexes was studied from chemical, electrochemical and theoretical points of view. The chemical reaction involves the addition of Ni⁰ to the allyl ether followed by stoichiometric allylation. The electrochemical process is catalytic in nickel and involves the reduction of intermediate η^3 -allylnickel(II) complexes.

Introduction

Alcohols and phenols can be easily protected as their corresponding allyl ethers.^[1] The selective deprotection of such relatively stable functional groups is classically carried out by two-step procedures involving double-bond isomerization and further treatment under strongly acidic or basic conditions.^[2] More recently, one-step procedures for allyl ether deprotection have been reported, such as NaI/Me₃SiCl,^[3] [Pd(PPh₃)₄] with NaBH₄^[4] or Bu₃SnH^[5] as reducing agent, PdCl₂/CuCl/O₂,^[6] and [NiCl₂(dppp)]/DIBAL (dppp = 1,3-bis(diphenylphosphanyl)propane; DIBAL = diisobutyl-aluminum hydride).^[7] Electrochemical reduction in association with catalysis by Sm^{III},^[8] Ni^{II[9]} or Pd^{II[10]} complexes is also used.

We have been particularly interested in Ni-catalyzed electrochemical allyl ether deprotection,^[9a] and in the further reactivity of the reductively cleaved allyl moiety.^[11] Whereas the allyl group formed in Pd-catalyzed chemical allyl cleavage was reported to react with nucleophiles (alkylation reactions),^[12, 13] we found that the allyl species formed under

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electrochemical conditions were able to react with electrophiles (carbonyl compounds) in both Ni^{II_[11]} and Pd^{II}-catalyzed^[10] allylation reactions.

Here we present some further chemical, electrochemical and theoretical studies on the nickel-catalyzed cleavage of allyl ethers in substrates such as 1, which involves an intramolecular allyl transfer process (Scheme 1). Related electrochemical allylation of carbonyl compounds with allyl halides or acetates has been reported to afford the corresponding homoallyl alcohols in intermolecular reactions.^[14]

Results and Discussion

The nickel-catalyzed electrochemical reduction of 2-allyloxybenzaldehyde (1) causes O–C bond cleavage of the allyl ether moiety and allyl transfer to the carbonyl group (Scheme 1). After hydrolysis, the homoallyl alcohol **2** was obtained in 87 % yield.^[11]



Scheme 1. a) 1) e^- , **3** (10 mol%), 2 Fmol⁻¹, Mg anode/stainless steel cathode, $nBu_4N^+BF_4^-$, DMF, 20°C; 2) hydrolysis.

The reaction was carried out in DMF in a single-compartment cell, fitted with a consumable magnesium anode and a stainless steel cathode, and was catalyzed by $[Ni(bpy)_3]^{2+}$ - $(BF_4)_2$ (**3**; bpy = 2,2'-bipyridine; 10 mol % with respect to **1**). The electrolysis was conducted at room temperature and I(under constant current intensity and consumed 2 F per mole of **1** for complete conversion.

Electrochemical studies: *Cyclic voltammetry*: The cyclic voltammetric behavior of the Ni^{II}/1 system (with excess bpy) was examined in DMF containing tetrabutylammonium tetrafluoroborate (Figure 1). The cyclic voltammetric behavior of complex **3** (Figure 1 a) has already been reported.^[15] It



Figure 1. Cyclic voltammetry with a vitreous carbon working electrode and an SCE reference electrode ($v = 100 \text{ mVs}^{-1}$) in a DMF solution of $n\text{Bu}_4\text{N}^+\text{BF}_4^-$ (80 mM). a) [Ni(bpy)₃]²⁺(BF₄⁻)₂ (8 mM) + bpy (1:2). b) [Ni(bpy)₃]²⁺(BF₄⁻)₂ (8 mM) + bpy + **1** (1:2:1).

exhibits a first quasireversible Ni^{II} to Ni⁰ reduction peak at -1.2 V versus the saturated calomel electrode (SCE), followed by reversible one-electron reduction of the Ni⁰ complex at -2.0 V [Eqs. (1) and (2)].

$$[\text{Ni}^{\text{II}}(\text{bpy})_3]^{2+} + 2e^{-} \xrightarrow{-1.2V} [\text{Ni}^0(\text{bpy})_2] + \text{bpy}$$
(1)

$$[\operatorname{Ni}^{0}(\operatorname{bpy})_{2}] + e^{-} \xrightarrow{-2.0 \, \text{v}} [\operatorname{Ni}(\operatorname{bpy})_{2}]^{-}$$
(2)

When one equivalent of **1** was added to the Ni^{II} solution, several changes in the cyclic voltammograms could be observed (Figure 1b). The first Ni^{II} to Ni⁰ reduction peak became irreversible; new reduction peaks appeared at -1.4and -1.6 V; and the reduction peak of Ni⁰, initially at -2.0 V, shifted to -1.9 V and was less well defined. The direct reduction of **1** in the absence of **3** took place beyond -2.2 V.

The interaction of the electrogenerated Ni⁰ species with **1** can involve both the allyl ether and the carbonyl group. We therefore analyzed separately the nature of these two interactions with the allyl aryl ether **4** (see Scheme 2) and benzaldehyde as model compounds. In the absence of **3**, both model substrates were reduced beyond -2.2 V. The cyclic voltammogram of **4** in the presence of nickel complex **3** is shown in Figure 2.

The addition of one equivalent of **4** to the Ni^{II} solution invoked irreversibility of the Ni^{II}/Ni⁰ transition with an increase in the reduction peak of one-half. The new peak corresponds to a $3e^-$ process, which is not affected by an excess of **4**. In addition, the reduction peak of the Ni⁰ species appeared at -1.8 V. Synthetic and mechanistic aspects of an electrochemical system involving the cleavage of simple allyl aryl ethers were recently reported.^[16] The $3e^-$ reductive



Figure 2. Cyclic voltammetry with a graphite carbon working electrode and an Ag/AgCl reference electrode ($\nu = 100 \text{ mV s}^{-1}$) in a DMF solution of $nBu_4N^+BF_4^-$ (0.1 mM). a) $[Ni(bpy)_3]^{2+}(BF_4^-)_2$ (5 × 10⁻³ mM). b) $[Ni(bpy)_3]^{2+}(BF_4^-)_2$ (5 × 10⁻³ mM) + 4 (1:1)

process at -1.2 V versus SCE was assigned to a $2e^{-1}$ Ni^{II} to Ni⁰ reduction, followed by oxidative addition of **4** to electrogenerated Ni⁰ to form η^{3} -allylnickel(II) species **5**, which undergoes a $1e^{-1}$ reduction at the same potential of -1.2 V versus SCE to form a reduced Ni^I species **6**, as shown in Scheme 2.



Scheme 2.

The electrochemical behavior of benzaldehyde in the presence of complex 3 has, to the best of our knowledge, not been described. Figure 3b shows the cyclic voltammetric behavior of a 1:1 mixture of PhCHO and 3 in DMF. The addition of PhCHO to the Ni^{II} solution slightly shifted the Ni^{II} to Ni⁰ reduction peak at -1.2 V to more negative potentials, and the peak became less reversible. A large reoxidation peak appeared around -0.7 V and was tentatively assigned to the oxidation of a PhCHO – Ni^0 complex. The new peak at – 1.7 V should involve the 1e⁻ reduction of the carbonyl group coordinated to the Ni⁰ complex, with the formation of the radical anion of PhCHO (Scheme 3), which could then undergo coupling to form pinacol. To test this hypothesis, preparative-scale electrolysis of a 1:1 mixture of 3 and PhCHO in DMF was carried out at -1.7 V. After hydrolysis, a mixture of meso- and dl-pinacol adducts was obtained in 40% yield (Scheme 4).



Figure 3. Cyclic voltammetry with a vitreous carbon working electrode and an SCE reference electrode ($\nu = 100 \text{ mV s}^{-1}$) in a DMF solution of $n\text{Bu}_4\text{N}^+\text{BF}_4^-$ (80 mM). a) [Ni(bpy)_3]²⁺(BF_4^-)_2 (8 mM). b) [Ni(bpy)_3]²⁺-(BF_4^-)_2 (8 mM) + benzaldehyde (1:1).



Scheme 3.

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A study of the electrochemical behavior of model compounds **4** and PhCHO with complex **3** enabled a better understanding of Figure 1. By analogy with Figure 2, the peak at -1.4 V was assigned to the reduction of the η^3 -allylnickel(II) complex **7**, formed by oxidative addition of the electrogenerated Ni⁰ with the allyloxy group of **1**, as illustrated in

Scheme 5. The peak at -1.6 V was assigned to the reduction of the ArCHO-Ni⁰ complex, by analogy with the peak at -1.7 V in Figure 3.

Varying the scan rate in the cyclic voltammetry of **1** in the presence of **3** from 10 to 500 mV s⁻¹ led to a change in the relative intensities of the different peaks, depending upon the interaction of Ni⁰ with the allyl and/or the carbonyl groups.

Preparative-scale electrolyses: Electrolyses of a 1:1 mixture of substrate **1** and Ni^{II} complex **3** were carried out at controlled potentials of -1.46 V and -1.75 V. The reaction at -1.46 V could be run up to a consumption of 2 F per mole of **1**, after which passivation occurred. The electrolysis led to homoallylic alcohol **2** in 36% yield and to deallylated **9** in 11% yield,





together with 41% of unconverted **1** (Scheme 6). At this potential, the reaction was incomplete and poorly selective. However, the consumption of 2 F for about 60% of **1** suggests a 3 Fmol^{-1} process, in accordance with cyclic voltammetry (Figure 1) and Scheme 5.

The controlled-potential electrolysis of a 1:1 mixture of **1** and **3** at -1.75 V consumed 2 F per mole of **1** and afforded 96% conversion with a 92% yield of **2** and 2% of **9**. After 3F electrolysis at this potential, the reaction was



completed with 98% yield of **2** (Scheme 6). No pinacol adducts were formed.

At -1.75 V, an excellent yield and selectivity for **2** could be obtained. Although the reaction was complete and could be run up to 3 F per mole of **1**, a good yield of **2** was already obtained after 2 F. This result was taken to indicate that the η^3 -allylnickel(II) complex **7** (which needs 2 F to be formed from Ni^{II}) was able to transfer its allyl moiety to the aldehyde group in a chemical reaction, without being reduced to complex **8** (Scheme 5). η^3 -Allylnickel(II) complexes are known to be poorly reactive towards electrophiles.^[17] However, a slow reaction of η^3 -allylnickel(II) complexes with aldehydes in stoichiometric reactions at 60 °C to give homoallylic alcohols has been reported.



Scheme 4. a) 3e⁻, -1.7 V versus SCE; b) homocoupling; c) H⁺.

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Electrolyses at constant intensity with an equimolar ratio of **1** and **3** were carried out in order to compare the results with those of controlled-potential electrolyses. In a first experiment, complex **3** was first reduced in DMF with 2 Fmol^{-1} to form [Ni⁰(bpy)₂] in situ. Substrate **1** was then added without any further electrolysis. The reaction resulted in the formation of **2** (20%) and **9** (30%), with 80% consumption of **1**. Here again, reduction of Ni^{II} with 2 Fmol^{-1} resulted in an incomplete and nonselective process. In a second experiment, Ni^{II} was reduced to Ni⁰ (2 Fmol^{-1}) and, after addition of **1**, the solution was electrolyzed for a further 1 Fmol⁻¹. In this case, consumption of **1** was complete, and the reaction afforded **2** and **9** in 57 and 43% yield, respectively.

An electrolysis at -1.75 V was carried out in a twocompartment cell under catalytic conditions with a 10:1 molar ratio of **1** and **3**. A consumption of 80% of **1** was reached after 3 F mol⁻¹. Compounds **2** and **9** were obtained in 32 and 30% yield, respectively. Although the reaction was not very selective, the results indicated that the nickel species could be recycled under these electrochemical conditions, and the process was catalytic with respect to the nickel complex. When a similar electrolysis was run in the presence of Mg²⁺ ions in a single-compartment cell fitted with a consumable magnesium anode, the consumption of **1** was complete after 2 F per mole of **1**, and **2** was isolated in 87% yield. Thus, the presence of Mg²⁺ ions facilitated the recycling of the nickel species and also played an important role in controlling the chemoselectivity of the reaction.

The electrochemical studies indicated that Ni^0 complexes of 2,2'-bipyridine can be generated from complex **3**. Oxidative addition of **1** forms a complex of type **7** (Scheme 5), which can form the homoallyl alcohol **2** in a chemical intramolecular allyl transfer reaction. Complex **7** could also be further reduced to **8**, which also undergoes intramolecular allyl tranfer. The presence of Mg²⁺ ions enhanced the selectivity of the catalytic electrochemical reaction.

Chemical versus electrochemical reactions: To the best of our knowledge, no example of intramolecular chemical allylation reaction of carbonyl compounds has been reported for nickel complexes. However, the formation of η^3 -allylnickel(II) complexes from Ni⁰ and allyl halides is well documented.^[18] The preparation of η^3 -allyl nickel complexes was also reported for allyl phenyl ether and Ni^{0.[19]} Allylation of carbonyl compounds by these η^3 -allyl complexes has been described,^[17] although the reaction is slow (at 60 °C) and works only with

aldehydes. Allyl aryloxide nickel compounds with a O-bonded ArO groups are also known.^[20] In particular, binuclear nickel allyl complexes with bridging aryloxide ligands have been used to catalyze the polymerization of diynes.^[21] Mononuclear nickel allyl complexes have been recently reported for bulky aryloxide groups.^[22]

To obtain further mechanistic insight into the intramolecular allylation process, some chemical reactions with Ni⁰ or η^3 allyl Ni^{II} complexes and substrate **1** or analogues were carried out.

Thus, when $[Ni(cod)_2]$ (cod = 1,5-cyclooctadiene) reacted with 1 in a 1:1 ratio in toluene at -78 °C to room temperature in the presence or absence of 2,2'-bipyridine, none of the expected complex 7 could be isolated. After hydrolysis of the solution, 2 was obtained in 90% yield (Scheme 7). Repeating the above reaction and keeping the temperature at -78 °C gave a red precipitate that could be filtered off. The compound was not very stable. The NMR spectrum in CD_3COCD_3 at $-33^{\circ}C$ showed broad signals (paramagnetic compound) that indicated the presence of a terminal allyl group and bpy in a 1:2 ratio and absence of an aldehydic proton. The magnetic susceptibility was $+(1.88 \text{ to } 2.66) \times$ 10⁻⁴ cm³mol⁻¹. The effective magnetic moment suggests an octahedral arrangement around the nickel center with $\mu_{\rm eff} =$ $3.22 \ \mu_B$. A structure such as 10 was tentatively assigned to this complex.

Complex 10 was too unstable for elemental analysis. The IR spectrum showed the presence of C=N, C=C, and C-O bonds, consistent with the presence of bpy and dialcoholate ligands. The FAB mass spectrum of 10 showed a peak at m/z 376 corresponding to a complex with a single bpy ligand. The instability of the compound could account for the loss of one bpy ligand in the mass spectrometer. The negative FAB mass spectrum revealed the presence of an anionic bidentate alcoholate/phenolate ligand. The above results suggest that 10 has two bipyridine ligands and an anionic bidentate alcoholate/phenolate ligand in an octahedral arrangement around the nickel center. This intermediate, which contains the final structure of the homoallylic alcohol 2, indicates a fast chemical allylation reaction. Complex 10 is a plausible intermediate in the formation of 2; it could form rapidly at low temperature from the proposed intermediate 7.

In an alternative strategy, cationic η^3 -allylnickel(II) complex **11**, prepared from [Ni(cod)₂] and allyl chloride in the presence of bpy and ammonium hexafluorophosphate,^[23] was treated with the potassium salt of salicylaldehyde in a 1:1 ratio at



Scheme 7. a) bpy (2 equiv), toluene, -78 °C; b) hydrolysis.

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room temperature (Scheme 8). When the reaction was carried out in toluene/acetone (40/60), 2 was obtained in 75% yield. The same reaction in DMF led to 2 in 82 % vield. To better mimick the electrochemical reaction, which presumably involves reduction of the η^3 -allyl intermediate, the reaction of 11 with salicylaldehyde anion was also carried out in the presence of one equivalent of zinc powder as reducing agent in DMF. In this case, 2 was formed in 90% yield in a more selective reaction.



Proposed chemical and electrochemical mechanisms: The electrochemical and chemical studies indicate different mechanisms for chemical and electrochemical allylation with catalysis by nickel complexes. Indeed, the cyclic voltammetry curves showed several reduction potentials at which the allylation reaction can occur. Preparative-scale electrolysis carried at a controlled potential of -1.75 V versus SCE in a two-compartment cell with stoichiometric amounts of nickel complex was more selective for homoallylic alcohol formation than the electrolysis carried out at -1.46 V versus SCE. In the first case, the homoallylic alcohol 2 was obtained in 98% yield, without passivation of the electrode. Moreover, the stoichiometric electrochemical allylation reaction needs between 2 and 3 Fmol⁻¹ for completion. Chemical allylation occurs with Ni⁰ or with preformed η^3 -allylnickel(II) complexes. In the electrochemical reaction, the η^3 -allylnickel(II) complex

is additionally reduced at -1.2 V. We therefore propose two different pathways for the reaction mechanism. The chemical pathway involving formation of Ni⁰ and its further chemical reaction with 1 is presented in Scheme 7. The intramolecular allylation is stoichiometric with respect to the Ni complex, which is transformed from Ni⁰ to Ni^{II}.

The electrochemical pathway should involve the formation and further one-electron reduction of the mixture Ni⁰/1. The electrochemical process is catalytic in nickel complex, because the nickel species can be recycled by electroreduction. We could show that the best catalytic conditions were obtained with an Mg anode in a single-compartment cell, that is, in the presence of Mg²⁺ ions in solution. The proposed catalytic cycle for the electrochemical allylation is presented in Scheme 9. The Mg²⁺ ions play an important role in the magnesium - nickel exchange process that liberates the nickel



Scheme 9. Proposed catalytic cycle for the electrochemical reaction.

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species for further recycling. The overall catalytic cycle needs 2 F per mole of allylic substrate and involves initial generation of Ni⁰ from Ni^{II} followed by formation of an η^3 -allylnickel(II) complex. This complex is further reduced to a formal Ni^I complex that undergoes allyl transfer to the carbonyl group to give a species of type **12**. Metal exchange with anodically generated Mg²⁺ ions forms the magnesium phenolate/alcoholate **13** and liberates Ni^I, which is rapidly reduced to Ni⁰ under electroreductive conditions.

Chemical studies with Ni⁰ or η^3 -allylnickel(II) complexes and substrate **1** or analogues seem to confirm the two reaction pathways. Indeed, the allylation of salicyladehyde occurred in the presence of the η^3 -allylnickel(II) complex **11** (with 82% yield), but the allylation was enhanced in the presence of a reductant such as zinc (90% yield). This chemical reaction with Zn can be compared with the stoichiometric electrochemical reaction that needs 3 F mol⁻¹ at controlled potential.

Theoretical studies: To evaluate the possibility of η^3 -allylnickel(II) reduction, as in 7, and to validate the chemical and electrochemical mechanisms, calculations were performed on the Ni-mediated allylation reaction. From a theoretical point of view, the reaction pathway from 1 to 2 (Scheme 1) can be split into three steps. Starting from the separate reagents LNi⁰ and 1, a first step should lead to an intermediate in which the 2-allyloxybenzaldehyde is already split into two moieties, as in 7. A second step involves an intermediate in which the homoallylic alcoholate is already formed (as in 10). Finally, the separate products 2 and LNi are obtained. Since our goal is to determine the feasibility of the two proposed mechanisms, the present work deals with optimized stable intermediates.

Two possible reaction pathways, elucidated from the results of chemical and electrochemical experiments, were investigated theoretically. The main difference between these two mechanisms is that an electron is added to the intermediate η^3 -allyl complex of type **7** in the course of the electrochemical reaction. Therefore, for the chemical process, the intermediates were optimized with a formal charge of zero, while for the electrochemical process an electron was formally added to the structures, and the complexes were re-optimized. Since experimental evidence indicates that differences between these two pathways exist as early as the first step, an electron was added to the separate reagents to evaluate their electron affinities.

Model compounds: Although density functional theory (DFT) methods can handle a relatively large number of atoms, the use of complete structures for the bipyridine and aldehyde ligands would require excessive computing time. Therefore, relatively simple models were chosen for these molecules. Two models (**M1** and **M2**) were investigated for 2,2'-bipyridine. Their structures were compared with that of 2,2'-bipyridine, optimized at the B3LYP/LanL2DZ level, and with experimental data.^[24] Some representative distances and angles are summarized in Table 1. The optimized geometrical parameters of the three structures are in good agreement with the experimental data. Since the results for **M1** model have the smallest deviations from the experimental data and those



Table 1. Geometrical parameters for 2,2'-bipyridine and the model compounds.

	bpy	M1	M 2	Expt ^[a]
d_1 [Å]	1.50	1.49	1.36	1.50
d_2 [Å]	1.36	1.30	1.41	1.35
α [°]	119.0	113.1	119.0	116.7
β [°]	117.3	123.2	123.7	116.1

[a] See ref. [21].

calculated for 2,2'-bipyridine, this model was used in subsequent calculations. Ligand **M1** was coordinated to the metal center, that is, the Ni–**M1** complex was considered. Addition of an electron to this structure leads, after optimization, to a calculated electron affinity (EA) of 0.65 eV.

For 2-allyloxybenzaldehyde, model structures **M3** and **M4** were investigated. They gave similar results, and comparison with optimized geometrical parameters for 2-allyloxybenzaldehyde did not lead to a clear preference. Therefore, model



M3, which has fewer atoms, was used in subsequent calculations. The calculated electron affinity of **M3** is only slightly negative (0.10 eV). Thus, it appears that the addition of the ancillary electron is more favourable for the Ni-**M1** compound. Therefore, it can be assumed that in the electrochemical reaction, the formal charges on the separate reagents are -1 for the Ni-**M1** complex and 0 for **M3**.

Characterization of the intermediates: For the chemical reaction, two stable forms of the first intermediate were characterized (Figure 4). In intermediate I1, the allyl moiety is linked to the metal atom in an η^3 fashion, while the aldehyde moiety is attached by an Ni–O σ bond. In this structure, a hydrogen bond is formed between the oxygen atom of the carbonyl group and a hydrogen atom of M1. Note that formation of this hydrogen bond is not possible if the complete structure of 2,2'-bipyridine is used instead of its model. In I1', the allyl moiety is linked to the metal by an Ni–C bond, and the aldehyde moiety is bound in a bidentate fashion. In this complex, the two Ni–O distances are similar (Ni–O1 1.94, Ni–O2 2.10 Å), and O2 is almost perpendicular to the plane defined by the N1, N2, C1, O1 and Ni (see Figure 4 for numbering of the atoms). Complex I1' is more



I1⁻

Figure 4. Structures of the optimized intermediates for the chemical mechanism (see text for details).

stable than the **I1** by $6.30 \text{ kcal mol}^{-1}$, and **I1** and **I1'** are respectively 56.37 and 62.67 kcal mol}^{-1} more stable than the separate reagents Ni-**M1** and **M3**. The second intermediate **I2** (see Figure 4) is 12.83 and 6.53 kcal mol}^{-1} lower in energy than the **I1** and the **I1'**, respectively.

The evolution of charge distribution in these complexes is given in Table 2 for the metal atom and the adducts. In the neutral forms Ni-M1, I1' and

12, the 2,2'-bipyridine ligand plays a considerable role as an electron reservoir. In the first intermediate, this electron transfer leads to a nickel atom with a partial charge of +0.55 e and enhances the Lewis acidic character of the metal atom. In the second part of the reaction, the excess charge held by the 2,2'-bipyridine ligand is transferred to the aldehyde and the allyl groups or to the homoallyl alcohol product.

In the exploration of the potential energy surface for the electrochemical reaction, no intermediate corresponding to the **I1** structure was found. However, two structures close to the **I1'** and **I2** were found (Figure 5). Only slight geometrical deviations were observed between these structures and those found on the potential energy surface. The major difference concerns the **I1**⁻ structure, in which O2 is only weakly bonded to the metal atom (2.84 Å vs 2.10 Å in **I1**⁻ and **I1'**, respectively). Intermediate **I1**⁻ is 101.56 kcalmol⁻¹ more

Table 2. Total NPA charges for the metal center and the different fragments of the calculated complexes (in electrons) for the chemical (charge = 0) and electrochemical (charge = -1) mechanisms.

	Charge = 0		Charge = -1			
	Ni-M1	Ĩ1′	I2	(Ni-M1)-	I1-	I 2-
Ni	0.55	1.02	1.01	- 0.09	0.96	0.98
M1	-0.55	-0.15	0.05	-0.91	-0.62	-0.58
aldehyde ^[a]	-	-0.66	_	-	-0.83	_
allyl ^[b]	-	-0.21	_	-	-0.51	_
product[c]	-	-	-1.06	-	-	-1.40

Figure 5. Structures of the optimized intermediates for the electrochemical mechanism (see text for details). a considerable role as an stable than the separate reagents $Ni-M1^{-1}$ and M3. Intermediate, this electron mediate $I2^{-}$ is 10.52 kcal mol⁻¹ more stable than $I1^{-}$.

> Although the structures of the complexes are very similar to those found previously, some important remarks concerning the charge distribution can be made. In the first intermediate, the excess of charge is delocalized mostly on the 2,2'bipyridine ligand (see Table 2). This fragment acts as an electron reservoir all along the reaction path. These results show that the formation of the first intermediates is truly favourable, particularly when an electron is added. On the other hand, the energy gain from the first intermediate to the second is small in both cases. Therefore, it is not possible to explain, solely on the basis of thermodynamical considerations, the fact that the first intermediates were not experimentally characterized. It can be assumed that the kinetic constant between I1' and I2, or I1⁻ and I2⁻, plays an important role. Moreover, the results obtained here can also be analyzed in terms of electron affinity (EA) for each of the above mentioned intermediates. The EA of I1' is 1.78 eV, and that of I2 1.96 eV (i.e., 41.09 and 45.09 kcal mol⁻¹, respectively). Keeping in mind that the electron affinity of Ni-M1 is 0.65 eV, one can conclude that the feasibility of the reaction is enhanced by the addition of an electron in the course of the reaction.

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Conclusion

In conclusion, the experimental and theoretical data obtained on nickel-mediated intramolecular allyl transfer from 1 to 2

[a]	Aldehyde fragme	nt of M3 . [b] Allyl fragmen	t of M3 mode	l. [c] Homo
all	ylic alcohol.				

indicate that the allylation reaction can occur by two different mechanisms. In both mechanisms $[Ni^0(bpy)_2]$, formed chemically or electrochemically, is needed to effect the oxidative addition to the allyl ether group of **1** and form an η^3 -allylnickel(II) complex. In a first mechanism, via a classical Nimediated allylation reaction, the η^3 -allylnickel(II) complex **7** can attack the aldehyde group to form the homoallylic alcohol phenol product **2** via the proposed Ni^{II} intermediate **10**.

In a more original pathway, the electrochemical reaction involves the one-electron reduction of the η^3 -allylnickel(II) intermediate **7**, followed by intramolecular allyl transfer from reduced **8**. The reduction of the η^3 -allylnickel(II) complexes at relatively low reduction potential (-1.2 V versus SCE) is reported here for the first time for allylation reactions. The electrochemical formation of reduced η^3 -allylnickel(II) species has only been recently reported in the cleavage of allyl ethers.^[16]

Theoretical studies on model compounds confirmed the possibility of stabilized intermediates in both the chemical and electrochemical mechanisms. However, calculations indicate that under reductive electrochemical conditions, allyl transfer to the carbonyl group should be facile.

The electrochemical allylation is catalytic in nickel, in contrast to the stoichiometric chemical reaction. Moreover, in the electrochemical process, Ni^{II} complexes can be used as the starting materials, and the use of low-stability Ni⁰ species is avoided.

Experimental Section

General: All solvents were dried and degassed by standard methods. DMF was freshly distilled over calcium hydride before use in electrolyses.

Instrumentation and cells: 1H and 13C 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 EG&G Model 362 equipment and were carried out at 20 °C with an SCE or Ag/AgCl reference electrode, a graphite rod as working electrode for cyclic voltammetry and a platinum counterelectrode. Controlled constantintensity electrolyses were carried out by using a stabilized constantcurrent supply (Sodilec, EDL 36.07). The single-compartment electrochemical cell was a cylindrical glass vessel (capacity 20 mL), equipped with a magnesium rod anode (99.9% purity, immersed to 3 cm) and a stainless steel grid cathode (apparent area: 20 cm²). In the two-compartment cell, the two compartments were separated by sintered glass (no. 4); the anodic compartment contained an Mg rod as anode, and the cathodic compartment was equipped with a carbon fiber cathode and an SCE reference electrode.

Tris(2,2'-bipyridine)nickel(II) bis(tetrafluoroborate) was prepared according to ref. [25].

(η^3 -Allyl)(2,2'-bipyridine)nickel(η) hexafluorophosphate: [Ni(cod)₂] (430 mg, 1.5 mmol), prepared according to ref. [23], was introduced with distilled toluene (5 mL) into a purged Schlenk flask, and 2,2'-bipyridine (246 mg, 1.6 mmol) in toluene (1 mL) was added with a syringe. The mixture was cooled -78 °C, allyl chloride (129 mL, 1.6 mmol) was added and the mixture allowed to warm to ambient temperature with stirring. The solution turned orange-red. NH₄+PF₆⁻ (257 mg, 1.6 mmol) was added with distilled THF (20 mL). After 1 h of stirring, the THF was evaporated and the mixture was stirred overnight and then filtered under nitrogen. The solid was dried under reduced pressure. Yield: 85%. ¹H NMR (250 MHz, [D₆]acetone, 25 °C, TMS): $\delta = 8.77$ (dd, ⁴J(H,H) = 6.5, ³J(H,H) = 1.0 Hz,

2 H), 8.46 (dd, ${}^{4}J$ (H,H) = 7.2, ${}^{3}J$ (H,H) = 1.0 Hz, 2 H), 8.26 (td, ${}^{4}J$ (H,H) = 6.5, ${}^{3}J$ (H,H) = 1.0 Hz, 2 H), 7.68 (td, ${}^{4}J$ (H,H) = 6.5, ${}^{3}J$ (H,H) = 1.0 Hz, 2 H), 6.27 (m, 1 H); 3.78 (d, ${}^{3}J$ (H,H) = 7.2 Hz, 2 H_{syn}); 3.0 (d, ${}^{3}J$ (H,H) = 12.6 Hz, 2 H_{anti}); IR (KBr): $\tilde{\nu} = 1602$ (s, C=N), 1446, 557 (aromatics), 847 cm⁻¹ (s, PF); elemental analysis calcd (%) for C₁₃H₁₃F₆N₂NiP (400.89): C 38.94, H 3.27, N 6.98; found: C 38.6, H 3.60, N 6.90.

Reaction of [Ni(cod)₂] with 2-allyloxybenzaldehyde (1) in the presence of 2,2'-bipyridine: A solution of 2,2'-bipyridine (139 mg, 0.89 mmol) and 2-allyloxybenzaldehyde (144 mg, 0.89 mmol) in distilled toluene (5 mL) was added to [Ni(cod)₂] (245 mg, 0.89 mmol) in a purged Schlenk flask. The mixture was cooled to -78° C for 5 min. After addition of toluene (5 mL) the mixture was stirred for 3 h at room temperature. The initial yellow solution became brown. A dark red solid precipitated after addition of hexane (5 mL) and storing the solution for 24 h at 4°C. The unstable solid was filtered off under nitrogen and dried under reduced pressure. $\mu_{eff} = 3.22 \,\mu_{B}$; MS (FAB positive): m/z: 376 [Ni(bipy)(1)]. Neither satisfactory elemental analysis nor ¹H NMR data could be obtained because of the instability and paramagnetic nature of the solid.

General procedure for one-compartment cell electrolyses: Preparation of 2-(1'-hydroxybut-3'-enyl)phenol (2): Freshly distilled DMF (20 mL), $nBu_4N^+BF_4^-$ (10⁻²M), [Ni(bipy)₃]²⁺(BF₄⁻)₂ (0.1 mmol) and the substrate 1 (1 mmol), prepared from the corresponding ortho-hydroxybenzaldehyde by stirring at 50 °C with allyl bromide and potassium carbonate in DMF, were introduced into the cell. The solution was stirred at room temperature and electrolyzed at a constant current of 60 mA (current density of 0.2 A/ dm², 5-15 V between the electrodes), up to total consumption of the starting material (monitored by GLC analysis of aliquots), unless electrode passivation occurred. After evaporation of the DMF under vacuum, the crude mixture was hydrolyzed with 0.1M HCl saturated with NaCl up to pH 1-2 and extracted with Et₂O. The organic layers, dried over MgSO₄, were filtered and evaporated. The major product 2 was purified by column chromatography on SiO2 with pentane/diethyl ether (90/10) as eluent and analyzed by NMR and IR spectroscopy and mass spectrometry. Yield: 87%. To facilitate analysis, 2 was also converted into its methyl ether by treatment with methyl iodide. ¹H NMR (200 MHz, CDCl₃, 25 °C, TMS): $\delta = 7.90$ (s, 1H; OH), 7.10 (m, 1H), 6.90 (m, 1H), 6.85 - 6.70 (m, 2H), 5.84 $(dddd, {}^{3}J(H,H)_{trans} = 17.1, {}^{3}J(H,H)_{cis} = 10.5, {}^{3}J(H,H) = 7.1, {}^{3}J(H,H) = 7.1 Hz,$ 1 H), 5.3 (dd, ${}^{3}J(H,H)_{cis} = 10.5$, ${}^{2}J(H,H) = 1.1$ Hz, 1 H), 5.25 (dd, ${}^{3}J(H,H)_{trans} = 17.1, {}^{2}J(H,H) = 1.1 Hz, 1 H), 4.87 (dd, {}^{3}J(H,H) = 7.6,$ ${}^{3}J(H,H) = 7.7$ Hz, 1 H), 2.90 (s, 1H; OH), 2.70–2.60 (ddd, ${}^{3}J(H,H) = 7.6$, ${}^{3}J(H,H) = 7.1, {}^{2}J(H,H) = 1.0 \text{ Hz}, 1 \text{ H}), 2.65 - 2.55 \text{ (ddd, } {}^{3}J(H,H) = 7.7,$ ${}^{3}J(H,H) = 7.1, {}^{2}J(H,H) = 1.0 \text{ Hz}, 1 \text{ H}); {}^{13}C \text{ NMR} (200 \text{ MHz}, \text{ CDCl}_{3}, 25 \,^{\circ}\text{C},$ TMS): 155.5, 134.0, 129.0, 127.2, 126.6, 119.9, 119.3, 117.3, 74.7, 42.2; MS: m/z: 164 [M⁺], 146, 131, 121, 107, 91, 77, 65, 43 (100%); IR (KBr): 3366, 3071, 1235, 755 cm⁻¹; HRMS calcd for $C_{10}H_{12}O_2$: 164.083730; found: 164.083091.

General procedure for two-compartment cell electrolyses: Both compartments were filled with a solution of $nBu_4N^+BF_4^-$ (1 g, 3 mmol) in DMF (50 mL each) under inert atmosphere. The Ni^{II} complex (0.1 mmol) and **1** or benzaldehyde (0.1 mmol) were added to the cathodic compartment. The electrolyses were run at 20 °C at the desired controlled potential and were stopped when the current was negligible. The workup was as described above; the reaction was monitored by GC.

Methods of calculation: It is now generally accepted that DFT methods are well suited to the study of transition metals complexes. Preliminary calculations confirmed that the classical HF and post-HF ab initio methods still remain too expensive in term of computational time. DFT methods seem to be a good option for the study of systems in which a metal and a large number of heavy atoms are involved. We chose the B3LYP method, which uses the gradient-corrected functional of Becke^[26] and the correlation functional proposed by^[27] Lee, Yang and Paar. Geometry optimizations were performed at the B3LYP/LanL2DZ^[28] level. Thermodynamic corrections^[29] were applied to the optimized structures and led to the differences in Gibbs free energy ΔG between the stationary points. To refine the charge distributions for the atoms of the molecules, the charges were calculated by using the natural population analysis (NPA) theory of the natural bond orbital (NBO)[30] program. Solvent effects were not taken into account in the calculations, since the aim was only to compare the stability of the different conformations that can be adopted by the studied complexes. A polar solvent would have certainly have slightly modified the

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geometries and therefore the energetics. The most important modification probably would have been that the weak oxygen-metal bonds would be broken in competition with a polar solvent. Nevertheless, the conclusions reached here would not have been modified in an important manner, since these changes would not affect the relative electron delocalization or the relative energies. All the calculations with performed with the Gaussian 98/ DFT^[31] program suite on the SGI Octane of the "Centre de Modélisation et d'Imagerie Moléculaire" of Université de Nice Sophia Antipolis and at IDRIS, France.

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- T. W. Greene, P. G. M. Wuts in *Protective Groups in Organic Synthesis*, 2nd ed., Wiley, New-York, **1991**.
- [2] J. Gigg, R. Gigg, J. Chem. Soc. C. 1966, 82-86.
- [3] A. Kamal, E. Laxman, N. V. Rao, Tetrahedron Lett. 1999, 40, 371-374.
- [4] R. Beugelmans, S. Bourdet, A. Bigot, J. Zhu, *Tetrahedron Lett.* 1994, 35, 4349-4350.
- [5] H. X. Zhang, F. Guibé, G. Balavoine, *Tetrahedron Lett.* 1988, 29, 619– 622.
- [6] H. B. Mereyala, S. Guntha, Tetrahedron Lett. 1993, 34, 6929-6930.
- [7] T. Taniguchi, K. Ogasawara, Angew. Chem. 1998, 110, 1137–1139; Angew. Chem. Int. Ed. 1998, 37, 1136–1137.
- [8] B. Espanet, E. Duñach, J. Périchon, *Tetrahedron Lett.* 1992, 33, 2485 2488.
- [9] a) S. Olivero, E. Duñach, J. Chem. Soc. Chem. Commun. 1995, 2497 2498; b) A. Yasuhara, A. Kasano, T. Sakamoto, J. Org. Chem. 1999, 64, 4211–4213.
- [10] D. Franco, D. Panyella, M. Rocamora, M. Gómez, J. C. Clinet, G. Muller, E. Duñach, *Tetrahedron Lett.* 1999, 40, 5685-5688.
- [11] D. Franco, S. Olivero, E. Duñach, *Electrochim. Acta* 1997, 42, 2159– 2164.
- [12] F. Guibé, Tetrahedron 1997, 53, 13509-13556.
- [13] B. M. Trost, D. L. van Vranken, *Chem. Rev.* **1996**, *96*, 395–422, and references therein.
- [14] a) M. Tokuda, M. Uchida, Y. Katoh, H. Suginome, *Chem. Lett.* 1990, 461–462; b) A. Jutand, H. Kawafuchi, C. Amatore, M. Kuroboshi, S. Torii in *Novel Trends in Electroorganic Synthesis* (Ed.: S. Torii), Springer, 1997, pp. 349–350; c) S. Durandetti, S. Sibille, J. Périchon, *J. Org. Chem.* 1989, 54, 2198–2204.

- [15] S. Derien, E. Duñach, J. Périchon, J. Am. Chem. Soc. 1991, 113, 8447– 8454.
- [16] S. Olivero, J. P. Rolland, E. Duñach, E. Labbé, Organometallics 2000, 19, 2798 – 2804.
- [17] a) L. S. Hegedus, S. D. Wagner, E. L. Waterman, K. Siirala-Hansen, J. Org. Chem. 1975, 40, 593–598; b) E. J. Corey, M. F. Semmelhack, J. Am. Chem. Soc. 1967, 89, 2755–2759; c) L. S. Hegedus, S. Varaprath, Organometallics 1982, 1, 259–263.
- [18] a) L. S. Hegedus, J. Organomet. Chem. Libr. 1976, 1, 329–331; b) J. Ishizu, T. Yamamoto, A. Yamamoto, Chem. Lett. 1976, 1091–1092.
- [19] J. J. Eisch, K. R. Im, J. Organomet. Chem. 1977, 139, C45-C47.
 [20] a) H. F. Klein, A. Bickelhaupt, B. Hammerschmitt, U. Flörke, H. J. Haupt, Organometallics 1994, 13, 2944-2950; b) H. F. Klein, T. Dal, S. Braun, C. Röhr, U. Flörke, H. J. Haupt, Eur. J. Inorg. Chem. 1998, 621-627; c) Y. J. Kim, K. Osakada, A. Takenawa, A. Yamamoto, J.
- Am. Chem. Soc. 1990, 112, 1096–1104; d) D. W. Dockter, P. E. Fanwick, C. P. Kubiak, J. Am. Chem. Soc. 1996, 118, 4846–4852.
 [21] P. D. Hampton, S. Wu, T. M. Alam, J. P. Claverie, Organometallics
- **1994**, *13*, 2066–2074. [22] J. Campora, M. L. Reyes, T. Hackl, A. Monge, C. Ruiz, *Organo-*
- metallics 2000, 19, 2950-2952.
 [23] H. G. Colguhoun, J. Holton, D. J. Thompson, M. V. Twigg, Practical Applications of Transition Metals, New Pathways for Organic Synthesis, Plenum Press, New York, p. 389.
- [24] L. L. Merrit, E. D. Schroeder, Acta. Cryst. 1956, 9, 801-804.
- [25] E. Duñach, J. Périchon, J. Organomet. Chem. 1988, 352, 239-246.
- [26] A. D. Becke, J. Chem. Phys. 1993, 98, 5648-5652.
- [27] C. Lee, W. Yang, R. G. Parr, Phys. Rev. B 1988, 37, 785-789.
- [28] P. J. Hay, W. R. Wadt, J. Chem. Phys. 1985, 82, 299-310.
- [29] W. J. Hehre, L. Radom, P. von R. Schleyer, J. A. Pople in *Ab initio Molecular Orbital Theory*, Wiley, New York, **1986**, pp. 226–261.
- [30] NBO, version 3.1, E. D. Glendening, A. E. Reed, J. E. Carpenter, F. Weinhold.
- [31] Gaussian 98, Revision A.7, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1998**.

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