Carbon−Carbon Bond Formation with Electrogenerated Nickel and Palladium Complexes

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We report coupling reactions of organic derivatives through catalysis by nickel and palladium complexes combined with electrochemical methods. Arylation, carboxylation, carbonylation, cyclisation, alkylation, and other reductive C–C bond forming reactions of organic halide derivatives, unsaturated hydrocarbons, and carbonyl derivatives, are presented. This review highlights electrosynthesis as an alternative methodology in the field of synthesis and catalysis.

Introduction

In recent years there has been a growing search for novel, environmentally clean and catalytic routes for the synthesis of fine chemicals. In this context, electrochemistry represents a convenient synthetic method in which electrons constitute clean and energetically efficient reactants. Electrosynthesis in conjunction with organometallic catalysis has provided mild and selective processes that have been applied to organic synthesis,[1−3] and several industrial applications[4,5] have been developed in recent years.

Electrochemistry can provide an easy way to generate (and regenerate) a desired oxidation state of a metal complex that becomes the active catalytic species for an organic reaction. In the particular case of redox processes, the active catalytic species can be recycled continually by the electrode oxidation or reduction reactions. In these processes, the electrons are consumed stoichiometrically with respect to the substrate. Unlike classical organic reactions, the metallic oxidant or reducing reagent is used only in catalytic amounts, so it is the electrons that are used as clean, controlled, and nonpolluting redox agents.[6] In non-redox reactions, electrocatalytic processes are involved: electrochemistry is needed only to generate the catalytic system. It has been observed that electrogenerated species can be more reactive than their chemically prepared analogues.[1,7]

Coupling reactions involving organic substrates often require preparation of an organometallic reagent. Electro-

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Delphine Franco (bottom, left) was born in Privas (France), and received her Ph.D. in Organic Chemistry at the University of Nice − Sophia Antipolis in 2000 in the group of Dr. E. Duñach. She is now in a post-doctoral position at the University of Barcelona with Professor G. Muller, where she works on the synthesis of new chiral heterodonor ligands and on their applications in homogeneous enantioselective catalysis.

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MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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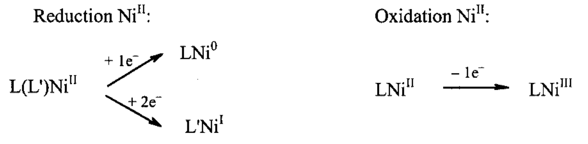
chemical reactions with catalytic amounts of low-valent nickel and palladium species, generated in situ from Ni^{II} or Pd^{II} precursors, allow for direct, one-step coupling processes. Electrolyses are conducted generally at relatively low reduction potentials, avoiding the direct reduction of the organic compounds.

In the particular case of electrochemical reactions involving nickel complexes, the catalyst precursors are generally stable and readily available Ni^{II} compounds. Many reductive coupling reactions of organic derivatives have been developed that involve the in situ generation of Ni^0 or Ni^I species. Whether either Ni^0 or Ni^I species are formed from Ni^{II} complexes depends on the nature of the ligands associated to the metal centre. Thus, tetraaza-macrocyclic ligands, such as cyclam, salen, or porphyrin-derived ligands,[8] generate Ni^I intermediates. The reduction of (phosphane)Ni^{II} complexes allows either the formation of Ni^I intermediates with further reduction to Ni^0 species, or the direct formation of Ni^0 complexes, depending on the nature of the phosphanes.[9] Other ligands, such as bidentate 2,2′-bipyridine, or mono- or diamines, undergo generally a direct two-electron reduction to Ni^0 complexes.[10]



Oxidative coupling reactions involving oxidised nickel complexes are less common. The electrogeneration of high oxidation states of nickel − for example Ni^{III} species − has been described, for example, with phosphane,[11] arsane,[12] salen,[13] cyclopentadienyl,[11] amine,[14] and thiolate-type[15] ligands, and electrochemical studies have been carried out.[16] Electrochemical reactions with oxidised nickel species have been reported for catalytic oxidation of various functional groups.[17,18] The use of these complexes, however, in catalytic C−C bond-forming reactions has, to the best of our knowledge, not yet been reported.

Electrosynthesis with palladium catalysts has been studied in several electroreductive coupling reactions. Pd^{II} complexes are usually the catalyst precursors and undergo a two-electron reduction to Pd^0 species,[19] although the electrochemical generation of Pd^I species has also been reported.[20] The use of Pd complexes in oxidative electrochemical C−C bond-forming reactions has been examined only in a few examples,[21] although other oxidative Pd-catalysed processes involving oxidation of functional groups have been studied.[22]

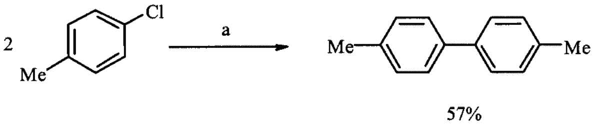
One- or two-compartment cells can be used for preparative organic electrosynthesis. Single-compartment cells, avoiding the use of membranes and compartment separators, offer simplicity and allow for easy scale-up of reactions. This methodology generally is associated with the use of sacrificial metal anodes.[23,24]

Most synthetic applications in electrochemically assisted nickel- and palladium-catalysed C−C bond-forming reactions have been carried out in the field of reductive coupling. This review concentrates on the C−C bond-forming reactions and does not report the electrochemical reduction or oxidation of functional groups or the formation of C−heteroatom bonds.

In each section of this review we first discuss the reactivity of aryl halides, followed by that of vinyl, allyl, benzyl and other activated halides, and finally that of alkyl halides. In each case, the use of nickel complexes is discussed before that of palladium complexes. In Section 6, which discusses the reaction of organic halides with olefins, we describe the reactivity of activated (conjugated) olefins before that of non-activated double bonds.

1) Homocoupling of Organic Halides

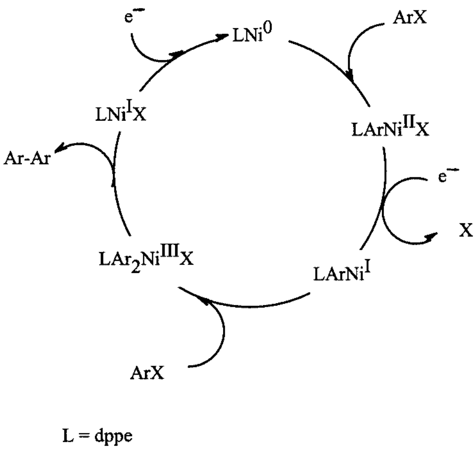
Among homocoupling reactions, aryl−aryl bond formation constitutes one of the most important tools in organic synthesis.[25] The electrochemical syntheses of biaryls from aryl chlorides, bromides, iodides, and triflates, are all possible.[26,27] Mono- and bidentate phosphane ligands [e.g., PPh_3, dppe = (diphenylphosphanyl)ethane] have been used in Ni^{II}-catalysed electrosyntheses of biaryls in variable yields (Scheme 1).[28−32] The preparation of bipyridines and quinolines from the reductive coupling of heteroaryl halides also has been reported.[33] Reactions proceed through Ni^0 in DMF or THF/HMPT as the solvent. Thus, the coupling of chlorobenzene led to biphenyl in 82% yield when 10% of $[Ni(PPh_3)_2Cl_2]$ was used as the catalyst.[10]



Scheme 1. a) e⁻, $[NiCl_2(PPh_3)_2]$ (10 mol %), HMPA/THF/$LiClO_4$, one-compartment cell, −2.0 to −2.5 V vs. Ag/AgCl, room temp.

Electrogenerated Ni^0 complexes associated with diamine-type ligands, such as 2,2′-bipyridine (bipy) or 2,2′-dipyridylamine (dpa), have shown high efficiency in the dimerisation of aryl[34] and heteroaryl[35] halides. *o*-Substituted aromatic halides also can be coupled.[36] The use of sacrificial anodes has allowed reactions to be conducted in undivided cells in either DMF or EtOH.[37,38] Thus, the system of $[NiBr_2(dpa)]$ and a stainless-steel anode led to 90% biaryl coupling for 4-bromofluorobenzene and 63% for 4-acetylbromobenzene.[39]

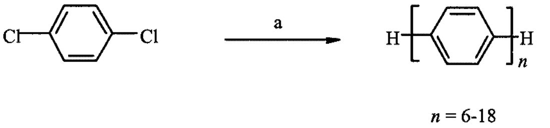
Electroanalytical studies on aryl homocoupling with Ni^{II} have reported[40,41] that they involve classical homogeneous catalytic processes: oxidative addition, reductive elimination, and ligand exchange (Scheme 2). The formation of a zero-valent nickel species from LNi^{II}, with ligands such as PPh_3 [42] or dppe,[40] is followed by oxidative addition of the aryl halide to afford σ-aryl−Ni^{II}−X intermediates. Their reduction to σ-aryl−Ni^I allows a second oxidative addition of aryl halide to occur with the formation of a diaryl−Ni^{III} intermediate. This process is followed by a reductive elimination to afford the biaryl compound and Ni^{I}, the reduction of which enables the regeneration of Ni^{0}. A different pathway is followed by (bipy)Ni^{II} complexes,[10,43] in which ligand exchange between two σ-aryl−nickel intermediates affords a biaryl with the regeneration of Ni^{II}.



Scheme 2

The electrochemical preparation of highly reactive nickel from a nickel anode and its further use in aryl halide homocoupling has been reported.[44]

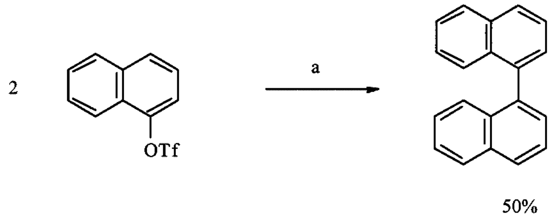
Electrochemical aryl coupling has been extended to the polymerisation of dihalides by several Ni^{II} complexes.[45,46] The polymerisation of 1,4-dibromobenzene to poly(1,4-phenylene) was catalysed by electrochemically reduced $[NiCl_2(dppe)]$.[47] The polymer was proposed to have regular *para* linkages and an average length of 6−18 phenylene units (Scheme 3).[48]



Scheme 3. a) e^-, $[NiCl_2(dppe)]$ (10 mol %), DMSO, −2.2 V, one-compartment cell, 65 °C

Electrogenerated (bipy)Ni^{0} complexes have been used as catalysts for the dehalogenative polycondensation of 4,4′-dihalobiphenyl and *N*-alkyl-3,6-dibromocarbazoles to form phenylene−carbazolylene copolymers,[49] which are electroactive materials with adjustable properties.[50]

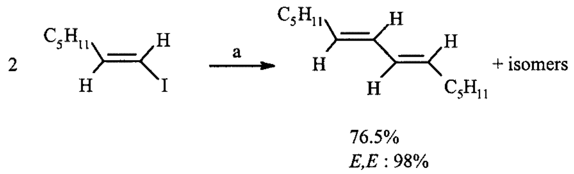
$[PdCl_2(PPh_3)_2]$ also has been used as a catalyst precursor for the electrosynthesis of biaryls from aryl iodide, bromide,[51] and triflate[52,53] derivatives, in yields of 34−78% (Scheme 4). Mechanistic studies with Pd^{II} associated to phosphane ligands have been reported.[41,54,55]



Scheme 4. a) e^-, $[PdCl_2(PPh_3)_2]$ (10 mol %), DMF/nBu_4NBF_4, −1.7 V vs. SCE, two-compartment cell, 90 °C

The activation of alkenyl halides is more difficult than that of aryl halides, but several electroreductive nickel-catalysed homo- and cross-coupling reactions involving alkenyl halides have been reported. These reactions lead to valuable target molecules, such aryl vinyl derivatives, conjugated dienes, and β,γ- or γ,δ-unsaturated compounds.[56] In classical organometallic chemistry, several nickel complexes have been tested stoichiometrically[57] and catalytically[58] for these coupling reactions.

Electrochemical homocoupling of alkenyl halides mediated by $[NiBr_2(bipy)]$ has been reported in NMP and DMF at 20 °C with a consumable magnesium anode (Scheme 5).[59] The mechanism of this dimerisation has been studied.[60]



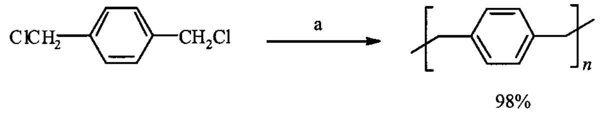
Scheme 5. a) e^-, $[NiBr_2(bipy)]$ (10 mol %), DMF, one-compartment cell, Mg anode, 20 °C

The electrosynthesis of conjugated symmetrical (*E*,*E*)-dienes can be performed from (*E*)-alkenyl halides in good yields and regioselectivities. A lack of stereoselectivity was observed for the preparation of conjugated (*Z*,*Z*)-dienes, which limits interest in this reaction.[60]

Polyacetylene has been prepared electrochemically from diiodacetylene reduction with catalysis by $[NiI_2(dppe)]$ to give an insoluble black powder that presumably corresponds to a polyyne derivative.[61]

Benzyl chloride has been reported to afford 50% of dimer $PhCH_2CH_2Ph$, and 50% of toluene, upon electroreduction in ethanol at room temperature in the presence of $[NiBr_2(PBu_3)_2]$ at −1.25 V vs. SCE.[62] The electroreductive dimerisation with $[NiBr_2(PPh_3)_2]$ at low temperature (−20 °C) gave 90% of the coupling product.[63] The dimerisation of benzal chloride catalysed by [Ni(salen)] {salen = 2,2′-[1,2-ethanediylbis(nitrilomethylidyne)]bis[phenolato]} in DMF also has been studied.[64]

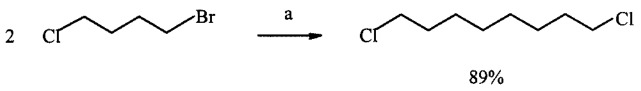
The electropolymerisation of 1,4-bis(chloromethyl)benzene, in the presence of catalytic amounts of $[NiCl_2L]$ (L = dppe or dppp), afforded poly-*p*-xylylenes in yields of 81−98% (Scheme 6).[65] Mechanistic aspects of the reaction have been examined.



Scheme 6. a) e$^-$, [$NiCl_2L$] (L = dppe) (10 mol %), DMSO, −2.2 V, one-compartment cell, 65 °C

Electrogenerated (bipy)-, (PPh_3)-, (Bu_3P)-, and (phenanthroline)Ni systems have been reported to catalyse the dimerisation of aliphatic mono- or dibromides with variable yields.[66,67] Using [$NiBr_2(PPh_3)_2$] as the catalyst, the dimerisation of alkyl and allyl halides gave R−R species and 1,5-hexadienes, respectively, in yields of up to 92%.[63,68]

The reductive coupling of alkyl halides has been reported with the use of electrogenerated nickel(I) complexes derived from [Ni^{II}(cyclam)] (cyclam = 1,4,8,11-tetraazzacyclotetradecane)[69] or [Ni^{II}(salen)] derivatives. Thus, under electrochemical conditions, [Ni^{II}(salen)] catalysed the reductive coupling of octyl bromide to the corresponding C-16 adduct,[70] as well as that of other alkyl bromides and iodides.[71] The kinetics and the mechanisms of these reactions have been examined, and radical intermediates have been proposed.[72] The electroreductive coupling of α,ω-dihaloalkanes catalysed by [Ni(salen)] complexes has also been explored.[71] Thus, electrolysis of 1-bromo-4-chlorobutane or of 1-chloro-4-iodobutane at a controlled potential in DMF led to 1,8-dichlorooctane in 80−90% yield, along with small amounts of 1-chlorobutane (7−10%) and 4-chloro-1-butene (2%) (Scheme 7).



Scheme 7. a) e$^-$, [Ni^{II}(salen)] (10 mol %), DMF/Me_4NClO_4, two-compartment cell, −1.0 V, vitreous carbon cathode

The reactivity of [Ni^{II}(salen)] complexes in the formation of polymeric films has been examined[73] and mechanistic studies have been reported.[74]

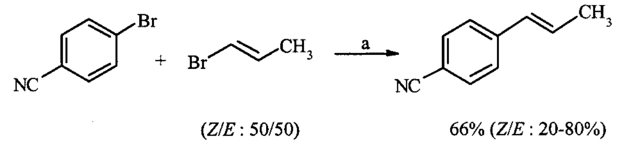
2) Heterocoupling of Organic Halides

The direct electrochemical synthesis of heterobiaryl derivatives has been reported for the coupling of an electron-rich aryl halide with an electron-poor one (Scheme 8).[75] These reactions were catalysed by [$NiBr_2$(bipy)], in an undivided cell in the presence of a magnesium anode, in NMP at room temperature. Selectivities of 15−70% were obtained. Heterocoupling of aryl halides with 2-chloropyridines, 2-chloropyrazines, and 2-chloropyrimidines, has also been described.[76,77]

Scheme 8. a) e$^-$, [$NiBr_2$(bipy)] (10 mol %), NMP, one-compartment cell, Mg anode, stainless steel cathode, I = 50 mA, room temp.

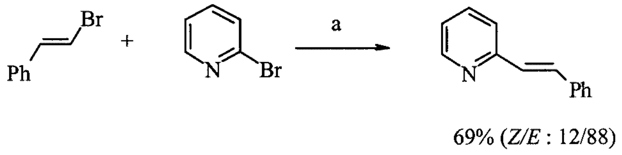
A two-step procedure for heteroaryl coupling has been described for [$PdCl_2(PPh_3)_2$]. The first step of stoichiometric preparation of a σ-aryl−palladium was followed by its electroreduction in the presence of a second aryl halide. The unsymmetrical biaryl compound was obtained quantitatively and Pd^0 was regenerated.[51,55] A combination of (bipy)Ni and (PPh_3)Pd catalysis with a zinc anode afforded yields of 83−90% for heteroaryl coupling in a two-step procedure.[78,79]

Heterocoupling of aromatic halides with allyl or vinyl halides has been reported using [$NiBr_2$(bipy)] with sacrificial anodes of Al in DMF at 40−70 °C (Scheme 9).[80] The substrates used were allyl chlorides or acetates and vinyl bromides or chlorides.



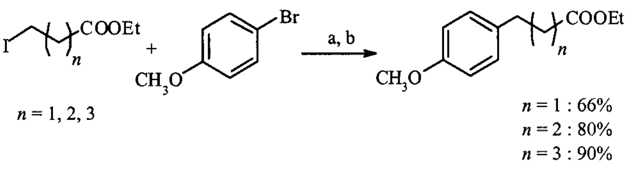
Scheme 9. a) e$^-$, [$NiBr_2$(bipy)] (10 mol %), one-compartment cell, DMF, Al anode, 40−70 °C

Similar cross-coupling reactions between heteroaromatic bromides and vinyl halides have been described with [$NiBr_2$(bipy)] catalysis in DMF solutions. The coupling of β-bromostyrene with 2-bromopyridine or 2-bromothiophene (Scheme 10) formed the nonsymmetrical diaryl olefins stereoselectively in yields of 40−69%.[79] (*E*)-β-Bromostyrene afforded the (*E*) adduct in 88% selectivity and (*Z*)-β-bromostyrene formed the (*Z*) adduct (95%). Competitive pathways for a first (vinyl)NiBr or (hetAr)NiBr formation were proposed.[79]



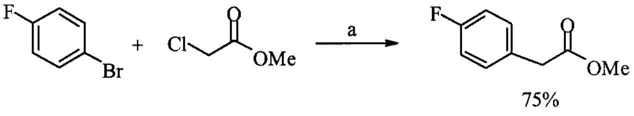
Scheme 10. a) e$^-$, [$NiBr_2$(bipy)] (10 mol %), one-compartment cell, DMF, Al anode, room temp.

Cross-coupling of aryl halides with alkyl iodides has been reported recently using [$PdCl_2\{P(o\text{-tol})_3\}_2$] catalysis (Scheme 11).[81] The reaction proceeded first by activation of the alkyl halide with electrogenerated reactive zinc. A further Pd-catalysed cross coupling of the organozinc intermediates with various aryl halides gave the corresponding cross-coupled products in yields of 48−98%.

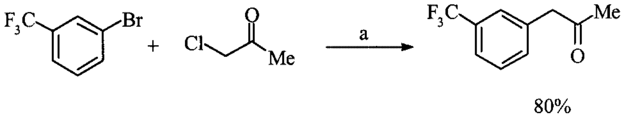


Scheme 11. a) Freshly electrodeposited Zn, DMF, 0 °C to room temp., 10−30 min; b) [$PdCl_2\{P(o\text{-tol})_3\}_2$] (5 mol %), THF

The electrochemical Ni^{II}-catalysed reductive coupling of aryl halides and α-halocarbonyl derivatives has been reported.[82] The electrosynthesis of aryl acetic and aryl propionic esters was first reported using Ni/PPh_3 catalytic systems in THF/HMPT or THF/NMP in yields of 30−85%.[83] Further cross coupling of aryl halides with α-chloropropionic acid, α-chloropropiononitrile and α-chloro ketones has been described in yields of 50−85% with the use of a sacrificial anode in the presence of $[NiBr_2(bipy)]$ as the catalyst (Schemes 12 and 13).[84,85] Heteroaryl halides, such as 2- and 3-bromothiophenes, also have been used.[86] The asymmetric version of the reaction using chiral 2-chloro esters also has been reported.[84b] Biaryl formation was a minor reaction. The slow addition of the activated α-halocarbonyl compounds to the aryl halide solution was necessary to minimise the direct reduction of the α-chlorocarbonyl derivative.

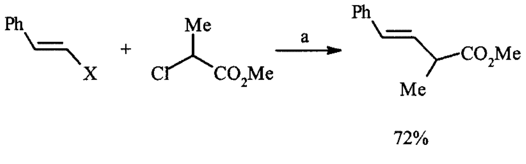


Scheme 12. a) 2 e^-, $[NiBr_2(bipy)]$ (10 mol %), DMF, one-compartment cell, Al or Zn anode



Scheme 13. a) e^-, $[NiBr_2(bipy)]$ (10 mol %), DMF, one-compartment cell, Al anode, 70 °C

Cross coupling between vinyl halides and α-halocarbonyl and -nitrile compounds allows the preparation of β,γ-unsaturated esters, ketones, and nitriles, products that are of high interest as precursors of natural and pharmaceutical products.[87] Electrolyses were performed in yields of 53−88% in DMF with $[NiBr_2(bipy)]$ as the catalyst, with the slow addition of the activated α-halocarbonyl derivative (Scheme 14). (*E*)-Alkenyl halides led to the (*E*) coupling products and (*Z*)-alkenyl halides led to the (*Z*) isomers in 74−98% selectivities.[84a]



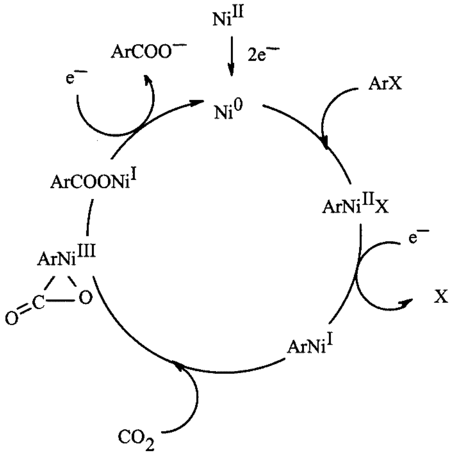
Scheme 14. a) e^-, $[NiBr_2(bipy)]$ (10 mol %), DMF, one-compartment cell, Al anode

3) Electrocarboxylation of Organic Halides

The direct electrocarboxylation of aryl halides, at room temperature and with CO_2 at atmospheric pressure, to afford the corresponding benzoic acid derivatives, has been reported to be efficient in undivided cells in the presence of sacrificial anodes (Mg or Al).[23,24,88] No catalyst was necessary to prepare aryl or benzyl carboxylic acids, but using Pd^{II} or Ni^{II} catalysts allowed the carboxylation of other halides, even in the presence of functional groups not compatible with the direct electroreductive process.

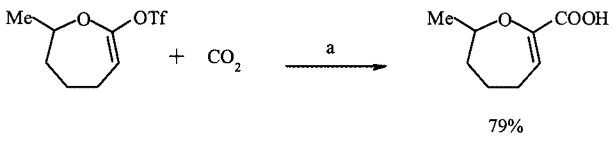
The electrochemical carboxylation of aryl halides (ArX; X = Br, Cl, I), in the presence of $[NiY_2(PPh_3)_2]$ (Y = Cl, Br) in THF/HMPA with an excess of ligand, has been reported to proceed through stable σ-aryl−nickel intermediate complexes of type $[ArNiYL_2]$. Under atmospheric pressure of CO_2 at room temperature, these Ni^{II} complexes were reduced and carboxylated to afford the corresponding arenecarboxylates with good faradaic and chemical yields.[89] The use of $[NiCl_2L_2]$ catalysts (L = PPh_3; dppe) for the electrocarboxylation of aryl bromides such as $4\text{-}RC_6H_4Br$ (R = F, OPh, CF_3) has been reported to give the corresponding benzoic acids with 56−84% selectivities.[90]

The detailed mechanism, including kinetic data, has been studied for the nickel-catalysed electrocarboxylation of bromobenzene in the presence of CO_2 and catalytic amounts of $[NiCl_2(dppe)]$ (Scheme 15).[91,92] The electrolysis afforded good yields of benzoic acid, with only traces (< 0.2%) of biphenyl. The reaction was shown to proceed through a sequence involving Ni^0, Ni^I, Ni^{II} and Ni^{III} intermediates, as in the case of Ni-catalysed biphenyl formation.[41]



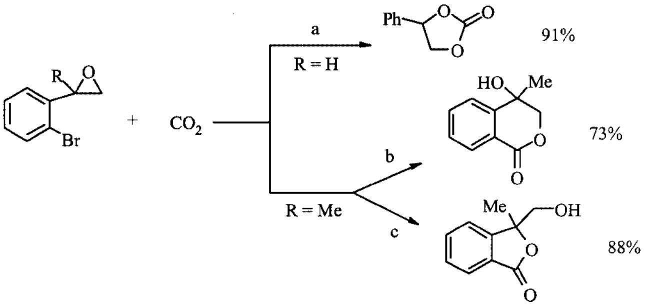
Scheme 15

The electrochemical carboxylation of alkyl-substituted vinyl bromides in the presence of $[NiBr_2(bipy)]$ and an Mg anode, in DMF under CO_2 at atmospheric pressure, gave the corresponding α,β-unsaturated carboxylic acids in yields of 53−82%.[93] With this system, 1-bromocyclooctene gave 82% cyclooctene-1-carboxylic acid, and lactone enol triflates afforded the corresponding cyclic α-alkoxy-α,β-unsaturated carboxylic acids, captodative cycloalkenes, in good yields (Scheme 16).[94]



Scheme 16. a) e^-, $[NiBr_2(bipy)]$ (20 mol %), DMF/nBu_4NBF_4, $p(CO_2)$ = 1 atm, T = 5 °C, one-compartment cell

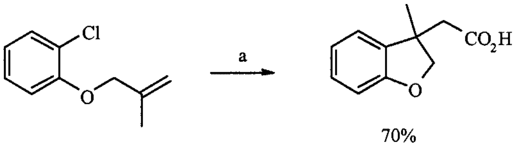
The Ni-catalysed electrocarboxylation of aryl halides has been applied to the synthesis of benzolactones from epoxide-functionalised aromatic halides, using one-compartment cells with an Mg anode.[95] Thus, CO_2 incorporation into 2-haloaryl epoxides led chemoselectively to carboxylated products that varied according to the nature of the substrate and of the catalytic system (Scheme 17).



Scheme 17. a) e^-, $[Ni(cyclam)]Br_2$ (10 mol %), DMF/KBr, one-compartment cell, Mg anode, stainless-steel cathode, $p(CO_2)$ = 1 atm, room temp.; b) e^-, $[Ni(bipy)_3](BF_4)_2$ (10 mol %), DMF/nBu_4NBF_4, one-compartment cell, Al anode, stainless-steel cathode, $p(CO_2)$ = 1 atm, room temp.; c) e^-, $[Ni(cyclam)_2](BF_4)_2$ (10 mol %), DMF/nBu_4NBF_4, one-compartment cell, Al anode, stainless steel cathode, $p(CO_2)$ = 1 atm, room temp.

Whereas terminal epoxides lead to cyclic carbonates in good yields,[96] 1,1-disubstituted epoxides react first through electrocarboxylation of a carbon−halogen bond followed by an oxirane ring opening. Five-membered-ring benzolactones were selectively formed with cyclam as the ligand on nickel, whereas six-membered-ring isocoumarin derivatives were obtained using 2,2′-bipyridine (Scheme 17).[95]

The electrochemical tandem $[Ni(bipy)_3](BF_4)_2$-catalysed cyclisation/carboxylation reactions of conveniently functionalised aryl halides, to afford carboxylic acids in cyclised structures, have been reported (Scheme 18).[97]



Scheme 18. a) e^-, $[Ni(cyclam)](BF_4)_2$ (10 mol %), DMF/nBu_4NBF_4, Mg anode [Ni cathode, one-compartment cell, room temp., $p(CO_2)$ = 1 atm]

The electrocarboxylation of benzyl halides affords arylacetic acid derivatives in excellent yields and can be performed without metal catalysis.[23,24] The electrocarboxylation has been reported, using either $[NiCl_2(dppe)]$ or $[NiCl_2(dppp)]$, for the synthesis of 2-arylpropionic acids such as the anti-inflammatory agents naproxen, fenoprofen and ibuprofen, which were prepared by electrocarboxylation of the corresponding ArCHMeCl at atmospheric pressure of CO_2, in yields of 76−90%.[98,99]

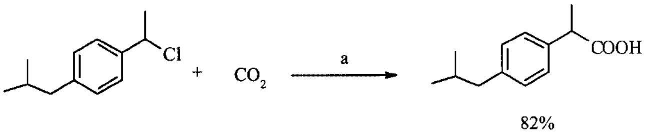
The electrochemical carboxylation of substituted benzyl chlorides, catalysed by $[Ni^{II}(salen)]$ derivatives in acetonitrile, yielded the corresponding arylacetic acids and substituted toluenes. The mechanism has been studied by cyclic voltammetry and controlled-potential electrolysis.[100] Remarkable catalytic currents were measured under CO_2. The results indicated the strong influence of the halide structure on reactivity. The electrogenerated $[Ni^{I}(salen)]^-$ reacted with the benzyl halide to form a benzyl radical; its further reduction to the carbanion was followed by electrocarboxylation, a process that was in competition with protonation by residual water.

The electroreductive carboxylation of aryl halides, α-bromostyrene, and allyl acetates in DMF saturated with CO_2 has been studied in the presence of catalytic amounts of $[PdCl_2(PPh_3)_2]$ and $[Pd(PPh_3)_4]$.[101] Thus, p-tBuC_6H_4I afforded p-tBu$C_6H_4CO_2H$ in 85% yield.

$[PdCl_2(PPh_3)_2]$ has been used also in the electrochemical carboxylation of aryl and vinyl triflates resulting in the formation of aromatic and α,β-unsaturated carboxylic acids, in yields of 32−86%.[54a,103]

The mechanism of the electrocarboxylation of aryl halides with $[PdCl_2(PPh_3)_2]$ was shown to be different from that involving Ni^{II}.[104] It proceeded by reduction of the divalent palladium to $[Pd^0(PPh_3)_2]$, followed by oxidative addition of the aryl halide to the resulting poorly ligated Pd^0, to afford the corresponding σ-aryl−Pd^{II} intermediate. Its two-electron reduction yielded an anionic σ-$[ArPd^0(PPh_3)_2]^-$, which dissociated reversibly to restore $Pd^0(PPh_3)_2$ and the σ-aryl anion, Ar^-. Nucleophilic attack of Ar^- on CO_2 gave the desired carboxylate.

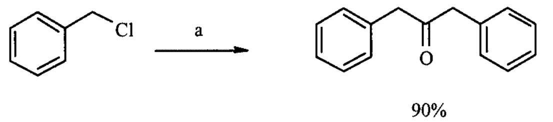
Electrochemical carboxylation of benzyl chlorides catalysed by (phosphane)Pd^{II} complexes afforded 2-arylpropionic acids in good yields under CO_2 at atmospheric pressure (Scheme 19).[105] Mechanistic and electrochemical studies revealed the cooperative role of reduced palladium species in the activation of the CO_2.



Scheme 19. a) e^-, $[PdCl_2(PPh_3)_2]$ (5 mol %), DMF/nBu_4NBF_4, i = 10 mA/cm^2, T = 5 °C, $p(CO_2)$ = 1 atm, Pt cathode, Mg anode

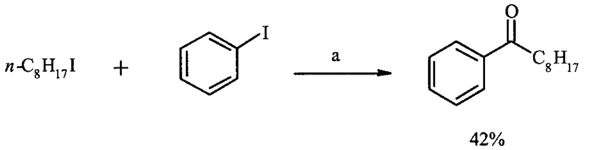
4) Carbonylation of Organic Halides

$[NiBr_2(bipy)]$ has been shown to be an efficient catalyst for the electrochemical carbonylation of organic halides to afford symmetrical and nonsymmetrical ketones in the presence of a carbonylmetal compounds, such as $[Fe(CO)_5]$, as the source of CO.[106] Thus, symmetrical ketones were obtained by electroreduction of an organic halide in DMF or MeCN in an undivided cell. The process is especially well adapted for primary benzyl chlorides and alkyl iodides; the corresponding ketones are obtained in yields of up to 90% (Scheme 20).[107]



Scheme 20. a) e$^-$, [Fe(CO)$_5$] (15 mol %), [NiBr$_2$(bipy)] (15 mol %), CO (1 atm), DMF/nBu$_4$NBF$_4$ (Ni cathode, stainless steel anode)

Nonsymmetrical aryl benzyl ketones or alkyl aryl ketones have been obtained in yields of 35−88%, by the direct electrolysis of a mixture of the two halides using the same catalyst system (Scheme 21). For example, benzyl *p*-methoxyphenyl ketone, derived from the coupling of benzyl chloride and *p*-methoxyphenyl iodide, was prepared in 88% yield.[108]



Scheme 21. a) e$^-$, [Fe(CO)$_5$] (30 mol %), [NiBr$_2$(bipy)] (30 mol %), DMF/nBu$_4$NBF$_4$, stainless steel anode, nickel grid cathode

The electrochemical formation of ketones from organic halides and carbon monoxide also has been reported. The dissolution of a stainless-steel anode provides a catalytic amount of a nickel species and enables the synthesis of ketones from organic halides in DMF in the presence of CO at atmospheric pressure.[109] The mechanism of this Ni^0-catalysed electrochemical carbonylation has been studied.[110] The [Ni(CO)(bipy)] complex was proposed as an intermediate.[111] Pathways leading to the formation of an active RCO−[Ni^{II}(bipy)]-type intermediate and of an inactive [Ni(CO)$_2$(bipy)] were proposed. The carbonylation required a careful control of the reaction conditions to avoid a loss of the catalytic activity.

The electrochemical carbonylation in the presence of CO$_2$ and [NiBr$_2$(bipy)] in NMP or DMF has been reported. [Ni(CO)$_2$(bipy)] was formed from an electroreduction process of CO$_2$ to CO.[112] The addition of benzyl chloride, or of an alkyl bromide or iodide, to the system resulted in the formation of a symmetrical ketone, RCOR, in yields of 60−85%.[113]

The electroreduction of [PdCl$_2$(PPh$_3$)$_2$] in the presence of carbon monoxide allowed the formation of lowly ligated [Pd(CO)(PPh$_3$)$_2$].[114] The further oxidative addition of 4-iodoanisole to this complex occurred readily, and 4-anisaldehyde and anisole were formed in yields of 14 and 46%, respectively.

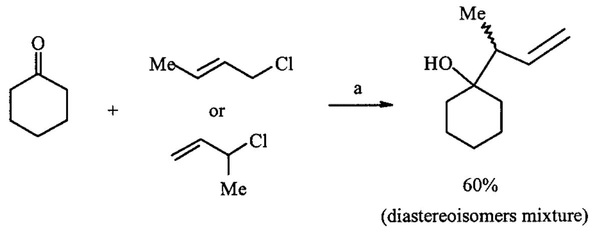
5) Reductive Coupling of Organic Halides with Carbonyl Derivatives

The electroreduction of an organic halide in the presence of a carbonyl compound affords the corresponding alcohol efficiently and under mild conditions. This electrochemical reaction works particularly well with activated, easily reducible organic halides, such as α-halo esters, allylic, propargylic and benzylic halides. The electrochemical processes complement the chemical alkylation of carbonyl compounds by Grignard, organolithium or other organometallic reagents,[115] but they avoid the need to prepare the organometallic reagents and can operate in various polar solvents at room temperature.

The electrochemical Reformatsky reaction of α-halo esters with carbonyl compounds to yield β-hydroxy esters has been reported with the use of a Zn anode in single-compartment cells.[116] The reaction was catalysed by [NiBr$_2$(bipy)] in DMF at room temperature. The coupling products were obtained selectively in yields of 55−89%. The mechanism of the reaction has been proposed to involve the insertion of electrogenerated Ni^0 into the α-halo ester, followed by an Ni^{II}/Zn^{II} transmetallation reaction, that leads to an organozinc Reformatsky-type reagent.[116] The electrosynthesis of various β-hydroxy esters, β-hydroxy nitriles and 2,3-epoxy esters was achieved successfully in DMF. Thus, the carbonyl coupling with methyl chlorodifluoroacetates allowed the preparation of a wide range of 2,2-difluoro-3-hydroxy esters in 20−79% yields (Scheme 22).[117] High yields were also obtained with enolizable aldehydes.

Scheme 22. a) e$^-$, [NiBr$_2$(bipy)] (10 mol %), DMF, ZnBr$_2$ (0.5 equiv./PhCHO), one-compartment cell, Zn anode, room temp.

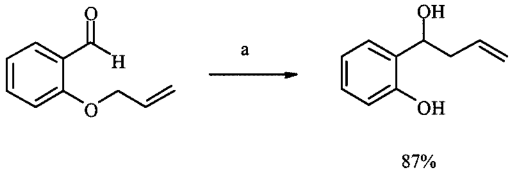
Electrochemical reactions involving the reduction of allyl halides or acetates in the presence of carbonyl compound — leading to the synthesis of homoallyl alcohols — have been studied extensively. In the absence of catalysts, mixtures of homoallylic alcohol, pinacol, aldol-type adducts, and reduced alcohols, were obtained.[118] Electrochemical allylation of both aldehydes and ketones in the presence of tin catalysts,[119] Sm^{III} species,[120] or [NiBr$_2$(bipy)],[121,122] has been reported to afford good yields of the corresponding homoallylic alcohols. The [NiBr$_2$(bipy)]-catalysed electrochemical allylation of carbonyl compounds was carried out in yields of 60−85% in DMF at room temperature using a sacrificial zinc anode (Scheme 23). Ni^0 was electrogenerated from Ni^{II} and (π^3-allyl)Ni^{II} species were proposed as intermediates.[122]



Scheme 23. a) e$^-$, [NiBr$_2$(bipy)] (10 mol %), DMF, Zn anode, one-compartment cell, room temp.

In nonelectrochemical allylations, stoichiometric Ni^0 reactions with aldehydes involving (π^3-allyl)nickel complexes have been reported to be slow reactions, with the (allyl)Ni^{II} complexes known also to undergo dimerisation.[123]

Allyl ethers have also been tested as sources of electrogenerated allyl species. Intramolecular allylation of carbonyl compounds with functionalised allyl aryl ethers in the presence of [Ni(bipy)$_3$(BF$_4$)$_2$] as the catalyst has been reported to afford the corresponding homoallyl alcohol−phenol products in good yields (Scheme 24).[124]

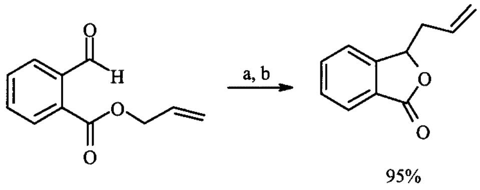


Scheme 24. a) e$^-$, [Ni(bipy)$_3$](BF$_4$)$_2$ (10 mol %), DMF/nBu$_4$NBF$_4$, one-compartment cell, Mg anode, room temp.

Aldehydes were efficiently converted into the corresponding homoallylic alcohols in yields of 42−87% in a one-compartment cell with a magnesium anode (Scheme 24). The intramolecular allyl transfer to ketones was most efficient with the use of a zinc anode.[125] Electrosynthesis was extended to the selective cleavage of aliphatic and benzylic allyl ethers and esters.[126,127] This interesting transformation is catalytic and a mild alternative method for allyl ether or ester deprotection.[128]

The mechanisms have been examined for the electrochemical allyl cleavage[129] and of the intramolecular allylation process[130] with allyl ether substrates. Ni^0 insertion into the C−O bond of the allyl ether leads to a π-allyl−Ni^{II} intermediate that undergoes a further reduction at the same Ni^{II}/Ni^0 reduction potential, with a rapid allyl transfer to the carbonyl group. Chemical and theoretical studies have confirmed the possibility of the reduction of the (π^3-allyl)nickel intermediates.[130]

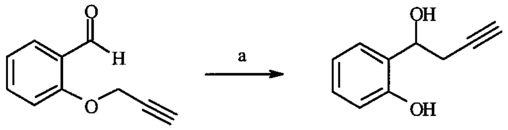
The Ni^{II}-catalysed electrochemical cleavage of allyl ethers has been extended to *ortho*-carbonylated allylic esters.[131] As described in Scheme 25, the allyl ester cleavage (also reported with allyl carbamates[132]) and further allyl transfer to the carbonyl group were followed by the lactonisation of the hydroxy acid intermediate, all in a one-pot reaction. The selectivity of the method has been highlighted by the synthesis of a series of bicyclic lactones with yields of up to 95%.[131]



Scheme 25. a) e$^-$, [Ni(bipy)$_3$](BF$_4$)$_2$ (10 mol %), DMF, Zn anode; b) hydrolysis

The nickel-catalysed electrochemical allyl transfer from allylic β-oxo esters has been examined, including the use of chiral ligands, with asymmetric inductions of up to 17%.[133]

The electrochemical cleavage of propargyl ethers[134] and the intramolecular propargyl transfer to carbonyl groups have been described in reactions catalysed by [Ni(bipy)$_3$](BF$_4$)$_2$, and an example is illustrated in Scheme 26.[135]



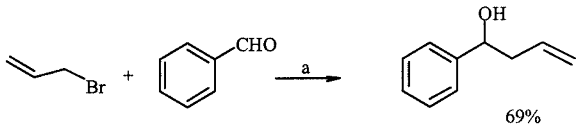
Scheme 26. a) e$^-$, [Ni(bipy)$_3$](BF$_4$)$_2$ (10 mol %), DMF/nBu$_4$NBF$_4$, one-compartment cell, Mg anode, room temp.

For nonsubstituted propargyl ethers, the reaction was chemoselective; only the homopropargyl alcohol was formed in yields of 41−71%. In the case of substituted propargyl ethers, a mixture of homopropargylic and allenic alcohols was obtained.[135] The direct electrochemical intermolecular propargylation of aldehydes or ketones also has been studied without a nickel or palladium catalyst, by using consumable Zn or Al anodes, to form mixtures of homopropargylic and allenic alcohols.[136]

The electrochemical Pd^{II}-catalysed reductive coupling of allyl acetates with carbonyl compounds to give the corresponding homoallylic alcohols has been described.[137][138] The reaction proceeds smoothly at room temperature using a catalytic amount of [PdCl$_2$(PPh$_3$)$_2$]. The proposed π-allyl−palladium intermediates required ZnCl$_2$ activation for addition to the carbonyl group.

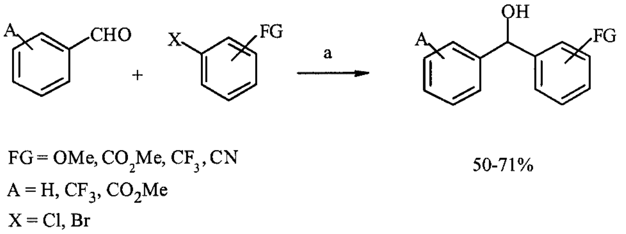
The Pd^{II}-catalysed intramolecular electrochemical allyl transfer reaction from allyl ethers to carbonyl compounds has been reported. Thus, the reduction of 2-allyloxybenzaldehydes (Scheme 24) catalysed by PdCl$_2$ in the presence of 2,2′-bipyridine afforded the allylated derivatives in yields of 25−52%.[139] Low enantioselectivity (≤ 6%) was obtained with several chiral pyridine−oxazoline ligands coordinated to the Pd^{II} complex.[139] In the electrochemical process, the reductive conditions allowed the umpolung of the (π^3-allyl)palladium species and their further addition to carbonyl groups. These (π^3-allyl)palladium intermediates, known chemically for their electrophilic character,[140] become nucleophilic under the electroreductive conditions.

The Nozaki−Hiyama−Kishi reaction, the coupling of organic halides with aldehydes mediated by Ni^0/Cr^{II} or Pd^0/Cr^{II} systems, also has been developed in an electrochemical version, with the use of catalytic amounts of Cr^{III} salts in combination with catalytic amounts Pd^0, to afford allylic alcohols in yields of 55−69% (Scheme 27).[141] The electrochemical reaction has been reported in DMF using a two-compartment cell. In some cases, the chromium salts were released by the oxidation of a chromium anode, thus avoiding the use of chromium chloride, which is toxic and sensitive to air and moisture. The proposed mechanism involves an oxidative addition of the vinyl or aryl halide to an electrogenerated Pd^0 complex, followed by a transmetallation by Cr^{III} and addition of the organochromate intermediate to the aldehyde. The Cr^{III} was regenerated after cleavage of the $O-Cr^{III}$ bond by an oxophile (Li^+ salt or TMSCl).



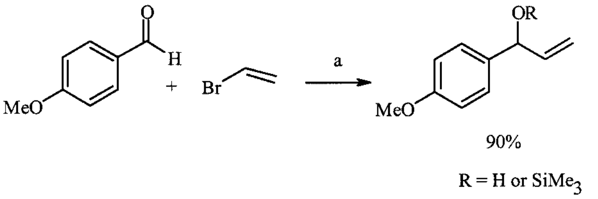
Scheme 27. a) e^-, $Pd(OAc)_2$ (0.4 mol %), PPh_3, $CrCl_2$ (10 mol %), DMF/$LiClO_4$, two-compartment cell

The Cr^{III}/(bipy)Ni^{II} system also has been tested in the electrochemical Nozaki−Hiyama−Kishi reaction for the arylation of aldehydes using an sacrificial iron anode.[142] With the use of a stainless-steel anode containing chromium, a large variety of benzaldehyde arylations have been effected, leading to substituted arylated secondary alcohols in 50−71% yields (Scheme 28).[143]



Scheme 28. a) e^-, $[NiBr_2(bipy)]$ (10 mol %), DMF, one-compartment cell, stainless steel anode containing Fe/Cr/Ni (72:18:10)

The alkenylation of carbonyl compounds with catalytic amounts of $CrCl_2$, $NiBr_2$ and Me_3SiCl has been performed by using a sacrificial Al anode.[144] The reaction proceeded in DMF in an undivided cell (Scheme 29). Alkenylation of substituted benzaldehydes afforded the corresponding allylic alcohols in yields of 5−90%. The nonelectrochemical reaction using an excess of Al or Zn led also to these alcohols in a wide range of yields (30−83%).[145]

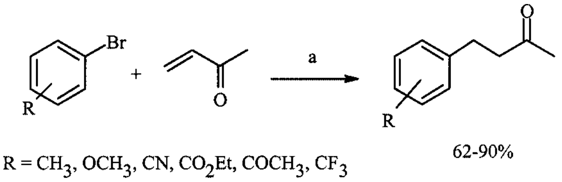


Scheme 29. a) e^-, $CrCl_2$ $NiBr_2$, Me_3SiCl, one-compartment cell, DMF, Al anode, room temp.

$CrCl_2$, $NiBr_2$, Me_3SiCl and Al were necessary for both the electrochemical and chemical reactions. Aluminium reacted as an electron source, $CrCl_2$ and $NiBr_2$ worked as the electron-transfer agents, and Me_3SiCl reacted with both the Cr^{III}−alkoxide intermediate, to release the Cr^{III} halide, and Al, to activate the metal surface.

6) Reductive Coupling of Organic Halides with C−C Double or Triple Bonds

The electrochemical version of a reductive Heck-type reaction has been examined both with Ni^{II} and Pd^{II} catalysts. The nickel-catalysed electrochemical arylation of activated olefins in the presence of an iron rod has been reported (Scheme 30).[146] Yields of 40−90% of the saturated adducts were obtained with $NiBr_2$ as the catalyst in DMF/pyridine.



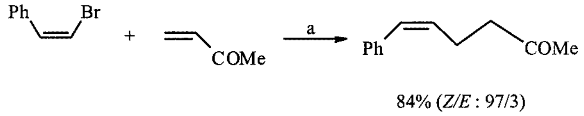
Scheme 30. a) e^-, $NiBr_2{\cdot}3H_2O$ (10 mol %), DMF/pyridine (9:1), 70 °C

The influence of the nature and the position of the substituents on the aromatic ring has been examined.[147] Both electron-donating and electron-withdrawing groups in *meta* or *para* positions gave good chemical yields of products (71−90%). For *ortho*-substituted derivatives, only electron-donating groups lead to satisfactory yields (62−67%). Aryl dihalides have been sequentially difunctionalised and dialkylated aryl derivatives were obtained in yields of 60−74%.

(PPh_3)Ni and [Ni(tet a)] (tet a = 5,7,7,12,14,14-hexamethylcyclam) catalytic systems have been reported to effect the intramolecular cyclisation of bromoaryl derivatives with *o*-acrylamides[31] or chlorovinyl substituents,[148] respectively.

The electrochemical version of the Pd-catalysed Heck reaction has been reported for the coupling of phenyl iodide and styrene using $Pd(OAc)_2$ and PPh_3 in DMF at room temperature.[149] The mechanism of the reaction has been examined in detail.[150]

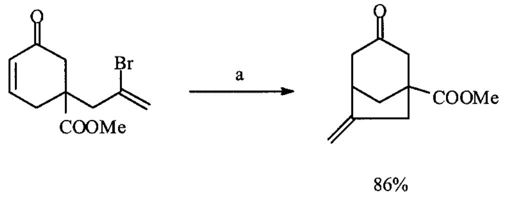
Organometallic alkenylation of electron-deficient olefins has been widely described and generally involves the introduction of the alkenyl moiety with organocopper,[151] organoboron,[152] organomanganese,[153] organozirconium,[154] or other reagents. One example of alkenylation of activated olefins using a nickel catalyst has been reported, with its regeneration by metallic Zn.[155] In contrast, the $NiBr_2$-catalysed electroreductive conjugate addition of (***Z***)- or (*E*)-alkenyl halides to electron-deficient olefins has been reported in a one-step reaction under mild conditions (Scheme 31).[156] The coupling was highly regio- and stereoselective, with retention of the stereochemistry on the alkenyl moiety.



Scheme 31. a) e^-, $NiBr_2{\cdot}3H_2O$ (10 mol %), DMF/CH_3CN (1:1), 60−80 °C

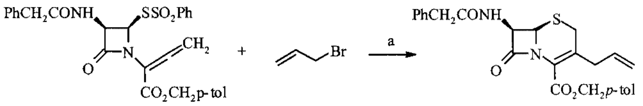
The utility of this procedure has been illustrated by the preparation of the Bontebok pheromone, which was obtained from methyl vinyl ketone and (*Z*)-1-iodo-1-heptene in 81% yield and with high stereoisomeric purity.[156]

The intramolecular version of a reductive addition of vinyl bromide to an enone has been reported in an [Ni(tet a)](ClO_4)$_2$-catalysed cyclisation in DMF, to give the 5,6-bicyclic structure in 86% (Scheme 32).[157]



Scheme 32. a) e$^-$, [Ni(tet a)](ClO_4)$_2$ (20 mol %), DMF/EtN_4ClO_4, carbon graphite cathode, two-compartment cell, 2.02 V vs. SCE

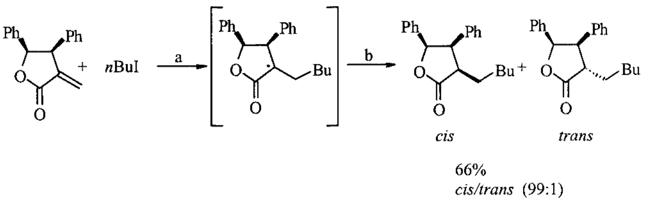
The electrochemical allylation of allenic esters with a combination of [$NiCl_2$(bipy)] and $PbBr_2$ as the catalytic system led to cephalosporin derivatives in moderate yields, as illustrated in Scheme 33.[158,159]



Scheme 33. a) e$^-$, [$NiCl_2$(bipy)] (10 mol %), $PbBr_2$, (5 mol %), Pt/Al, 6.7 mA/cm^2, 3.2 F/mol

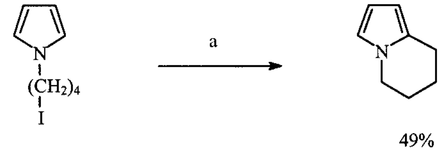
[Ni(cyclam)](ClO_4)$_2$ and other azamacrocyclic Ni^{II} complexes have been used as electron-transfer catalysts in the intermolecular addition of primary and secondary alkyl halides to activated olefins in radical-type reactions.[160] Tin hydrides have been used widely in radical additions to functionalised olefins.[161] However, the tin hydride method requires attention to avoid hydrogenation of the radical or hydrostannylation of the alkene; the tin hydride is used in stoichiometric amounts and is toxic. Electrogenerated [(salen)Ni^I]$^-$ has been reported to catalyse the reductive C−C coupling reactions between alkyl halides and ethyl acrylate to form ethyl alkanoate adducts in moderate yields (16−49%).[162] The reaction of 2-cyclohexen-1-one in the presence of alkyl halides catalysed by [Ni(salen)] has been investigated.[163] As a side-reaction, the reductive dimerization of 2-cyclohexen-1-one gave 2-(3-oxocyclohexyl)-2-cyclohexen-1-one. Using a macrocyclic Ni^{II} complex such as [Ni(tet a)](ClO_4)$_2$ as the catalyst, the electroreductive addition of alkyl bromides to activated olefins led to the adducts in yields of 13−72%.[148]

The synthesis of bicyclic ketones by the intramolecular 1,4-addition of alkyl bromides to enones has been described with several cobalt and nickel complexes as the catalysts.[164] The stereoselective *cis*-1,4-addition of butyl radicals to substituted α-methylenebutyrolactones has been reported in [Ni^{II}(tmc)]-catalysed (tmc = 1,4,8,11-tetramethylcyclam) electroreductions (Scheme 34).[165] Fused and spirocyclic carboxylic acid derivatives were prepared by the electrochemical reduction of bromoalkyl cyclohexenones using Co and Ni complexes as mediators.[164]



Scheme 34. a) e$^-$, [Ni(tmc)](ClO_4)$_2$ (10 mol %), DMF; b) e$^-$, H_2O

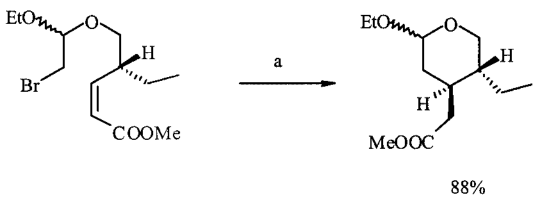
Cycloalkano[*a*]pyrroles have been obtained by the reductive cycloaddition of 1-(2-iodoethyl)pyrrole with activated olefins, using [Ni(tmc)](ClO_4)$_2$ as the catalyst.[166] The intramolecular cyclisation of 1-(ω-iodoalkyl)pyrroles was also studied (Scheme 35).



Scheme 35. a) e$^-$, [Ni(ClO_4)$_2$(tmc)] (20 mol %), DMSO, two-compartment cell, graphite cathode, zinc anode

Substituted (*Z*)-methylenecyclopentanes have been prepared from the coupling of ω-butynyl iodides and activated olefins with Ni(tmc)(ClO_4)$_2$, in a one-step electrolysis at room temperature by a sequence of radical addition then cyclisation on the alkyl moiety.[167]

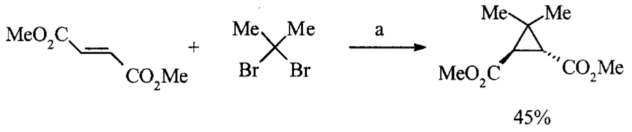
The electroreduction of 2-bromo acetals in the presence of unsaturated esters catalysed by [Ni(cyclam)](ClO_4)$_2$ afforded functionalised pyran derivatives in an intramolecular process, as shown in Scheme 36.[168]



Scheme 36. a) e$^-$, [Ni(cyclam)](ClO_4)$_2$ (10 mol %), −1.5 V vs. Ag/AgCl, DMF/Et_4NClO_4/NH_4ClO_4, vitreous carbon cathode, two-compartment cell

Synthetic intermediates of Ipecac and Corynanthe alkaloids were obtained in 88% yield in a highly stereoselective manner. A lactam precursor of tacamonine was prepared in 49% yield as a mixture of two diastereoisomers.[168]

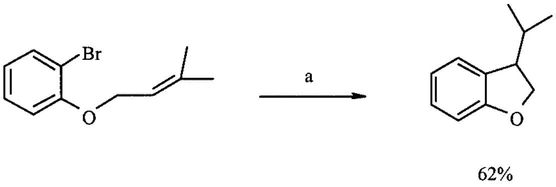
Cyclopropyl derivatives have been prepared from the electroreductive coupling of activated olefins and *gem*-dibromo derivatives in yields of 11−72%, using $NiBr_2$ and an Fe anode in DMF/pyridine (Scheme 37).[169] The procedure constitutes an alternative to the classical preparation of cyclopropyl derivatives from activated olefins.



Scheme 37. a) e$^-$, $NiBr_2$ (20 mol %), DMF/pyridine, two-compartment cell, Fe anode, 60 °C

Electrochemical additions of organic halide to non-activated double or triple bonds also have been described. The electroreductive coupling of aryl halides with C_2H_4 to give 1,1-diarylethanes was catalysed by $NiBr_2$ in THF/HMPA.[170,171] 1,1-Diphenylethane was obtained in up to 65% yield from the reaction with phenyl bromide.

Intramolecular electrochemical cyclisations of halogenated aromatic derivatives possessing an olefin in the *ortho* position have been reported. Thus, the [$NiBr_2$(cyclam)]-catalysed cyclisation of 2-allyloxyhalobenzenes led to dihydrobenzofuran derivatives in yields of 50−90% (Scheme 38).[172,173]



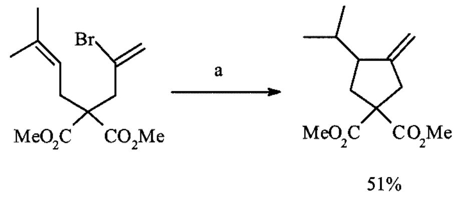
Scheme 38. a) e$^-$, [$NiBr_2$(cyclam)] (10 mol %), DMF/nBu$_4$NBF$_4$, Mg anode, carbon fibre cathode, one-compartment cell, 60 mA, room temp.

Unsaturated aryl chloride derivatives were also cyclised in yields up to 65%.[174] Cyclisation of analogous homoallylic alcohols afforded the corresponding dihydrobenzopyran structures in yields of 50−75%.[175] The analogous cyclisation of propargyl derivatives gave the benzofuran rings in 32% yield.[173] Electrochemical tandem cyclisation/carboxylation reactions of unsaturated aryl halides in the presence of CO_2 afforded carboxylic acids with bicyclic structures (Scheme 18).[97]

The mechanism of these cyclisations has been studied. Electrogenerated (cyclam)Ni^I species add oxidatively to the aryl−halogen bond to form ArNi^{III}X-type intermediates. The radical character of the aryl moiety allows for the addition to the side-chain double bond.[176] In the presence of (bipy)Ni^{II} catalysts, the same allyl aryl ether substrates did not undergo cyclisation, but a selective reductive cleavage of the ether C(allyl)−O bond instead.[129,177]

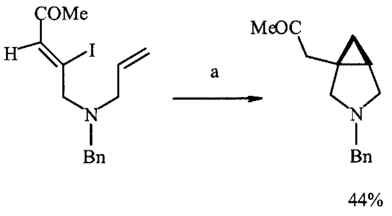
The [$PdCl_2(PPh_3)_2$]-catalysed reductive coupling of aryl halides with olefins and terminal acetylenes to give the corresponding saturated or vinylic coupling products, respectively, has been described in the presence of a Pb cathode.[178] The [$PdCl_2(PPh_3)_2$]-catalysed intramolecular electrochemical cyclisation of bromo- and iodoaryl derivatives with an allyl amide at the 2-position has been reported to afford indole derivatives in 33−81% yields.[179]

Intramolecular cyclisation of vinyl bromides or iodides in the presence of double bonds has been achieved in yields of 32−81% in [Ni(tet a)]$(ClO_4)_2$-catalysed reactions (Scheme 39).[157]



Scheme 39. a) e$^-$, [Ni(tet a)]$(ClO_4)_2$ (20 mol %), DMF, two-compartment cell

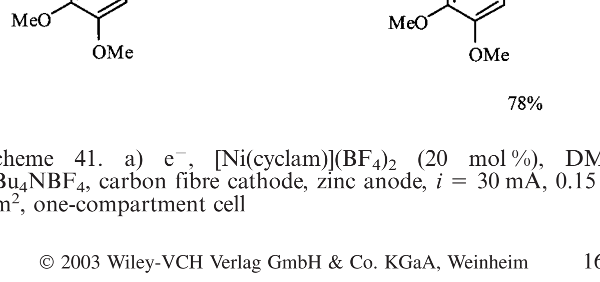
Bicyclic cyclopropane derivatives have been prepared in 10−66% yields by [Ni(tet a)]$(ClO_4)_2$- or [Ni(tmc)]$(ClO_4)_2$-catalysed electroreductions of vinyl bromides and iodides possessing an ω-double bond (Scheme 40).[180]



Scheme 40. a) e$^-$, [$Ni(ClO_4)_2$(tet a)] (20 mol %), DMF, one-compartment cell

The electroreduction of ω-unsaturated aliphatic halides using macrocyclic Ni^{II} complexes associated with salen or cyclam ligands as electron-transfer mediators has been achieved in DMF. The electrochemical reductive cyclisation of 6-bromo-1-hexene and citronellyl bromide in the presence of [Ni(cyclam)]$^{2+}$ and [Ni(salen)] complexes has been described; the reactions involve radical-type cyclisation. Cyclic compounds were obtained in yields of 13−65% under conditions that avoid the preparation of more classical organotin reagents.[181,182]

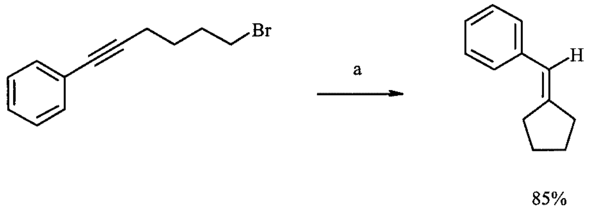
The intramolecular electrochemical cyclisation of α-bromo esters containing propargyl units (Scheme 41) has been reported in an [Ni(cyclam)]$^{2+}$-catalysed reaction to afford functionalised unsaturated cyclic ethers in yields of up to 93%.[183] Product distributions and selectivities were very dependent on the nature of the catalytic system and on the nature of the electrodes.



Scheme 41. a) e$^-$, [Ni(cyclam)]$(BF_4)_2$ (20 mol %), DMF/nBu$_4$NBF$_4$, carbon fibre cathode, zinc anode, i = 30 mA, 0.15 A/dm^2, one-compartment cell

Electrosynthesis of cyclic sulfides has been achieved in the [Ni(salen)]-catalysed intramolecular cyclisation of sulfides with acetylenic esters in 26−82% yields.[184]

The intramolecular addition of alkyl halides to nonactivated olefinic or acetylenic moieties afforded cycloalkenes in [Ni(salen)]-catalysed electrochemical cyclisations. Thus, the reduction of 6-iodo- or 6-bromo-1-phenyl-1-hexyne led to benzylidenecyclopentane in good yields, whereas the uncatalysed reaction led to reductive dehalogenation (Scheme 42).[185]



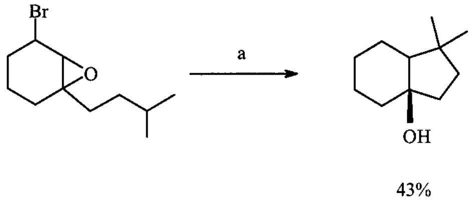
Scheme 42. a) e$^-$, [Ni^{II}(salen)] (10 mol %), DMF/Et_4NClO_4, two-compartment cell, −1.75 V vs. SCE, vitreous carbon cathode

Mechanistic studies have been performed on the catalytic reductive cyclisation of 6-iodo- and 6-bromo-1-phenyl-1-hexyne by [Ni(salen)] in acetonitrile.[186] Ni^I species were generated at a potential where the ω-haloalkynes were not electroactive. The substrates were reduced catalytically to form radical intermediates that cyclised to benzylidenecyclopentane in up to 84% yield.

Nickel(II)-catalysed indirect electroreduction of *N*-allyl- and *N*-propargyl-α-bromoamides and *o*-bromoacryloylanilides gave the corresponding five-membered-ring lactams. The electroreduction of *N*-allyl-*N*-(bromoacetyl)-*p*-toluenesulfonamide in DMF or acetonitrile provided 4-methylpyrrolidinone in 58% yield.[187] In contrast, the reaction of *N*-allyl-α-iodoamides in acetonitrile gave the iodinated pyrrolidinones.[188]

Electrochemical cyclisation of unsaturated 2-bromo ethers has been achieved under mild conditions using macrocyclic Ni^{II} complexes as catalysts; diphenyltetrahydrofuran was prepared in 85% yield.[189]

A tandem radical-mediated fragmentation of 2,3-epoxy bromides to form cyclopentanols and *cis*-fused bicyclic compounds in yields of up to 58% has been reported in a [Ni(tmc)]$(ClO_4)_2$-catalysed electroreduction in DMF (Scheme 43).[190] The reaction was proposed to proceed through the formation and rearrangement of alkyloxy radicals.



Scheme 43. a) e$^-$, [Ni(tmc)]$(ClO_4)_2$ (20 mol %), DMF/TEAP, CCE, graphite cathode, zinc anode, 80 °C

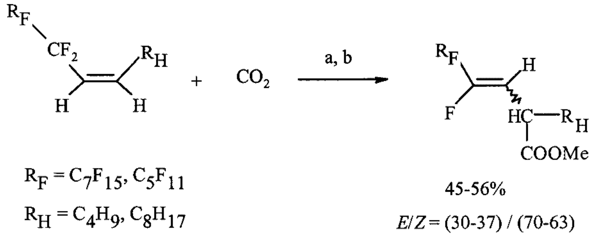
7) Homocoupling of Unsaturated Hydrocarbons

The electroreduction of $(PPh_3)Ni^{II}$ complexes in the presence of C_2H_4 afforded Ni^I intermediates that were able to dimerise ethylene mainly to 2-butenes, at room temperature in propylene carbonate at atmospheric pressure.[191] $NiCl_2$ also initiated the dimerisation−isomerisation processes of ethylene and propylene with consumable anodes (Zn, Cd, Al).[192] The oligomerisation of butadiene has been reported with various electrogenerated nickel species.[193,194] Thus, with $(PPh_3)Ni^{II}$ complexes, mixtures of 4-vinylcyclohexane and 1,5-cyclooctadiene were obtained from butadiene.

The $NiBr_2$-catalysed conversion of alkynes into polyacetylene has been reported to occur in acetonitrile.[195]

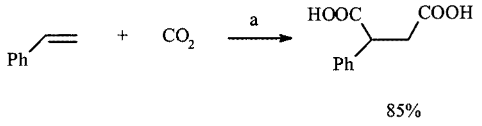
8) Carboxylation and Carbonylation of Unsaturated Hydrocarbons

The electrochemical [$NiBr_2$(cyclam)]-catalysed addition of CO_2 to (perfluoroalkyl)alkenes has been described to afford γ-fluoro-γ-(perfluoroalkyl)-β-alkenecarboxylic acids. The carboxylation process involved a double bond migration with loss of one allylic fluorine atom (Scheme 44).[196]



Scheme 44.a) e$^-$, [Ni(cyclam)]Br_2 (10 mol %), DMF/nBu_4NBF_4, stainless steel cathode, Mg anode, one-compartment cell, $p(CO_2)$ = 1atm, r.t.; b) K_2CO_3, MeI

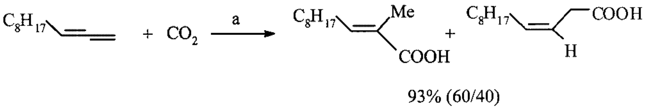
Electrogenerated (diamine)Ni^0 complexes have been reported as active catalyst precursors for the electrochemical incorporation of CO_2 into carbon−carbon double and triple bonds. Thus, the electrochemical reaction of styrene in DMF under 1 atm of CO_2 in the presence of [$NiBr_2$(PMDTA)] (PMDTA = pentamethyldiethylenetriamine) gave 85% of the 1,2-dicarboxylic acid (Scheme 45).[197]



Scheme 45. a) e$^-$, (PMDTA)Ni (10 mol %), DMF/nBu_4NBF_4, one-compartment cell, Mg anode, i = 50 mA, $p(CO_2)$ = 1 atm, room temp.

Different kinds of olefin derivatives, such as norbornene, acrylic esters, dienes, and enynes, were carboxylated to afford mono- or dicarboxylic acid derivatives in yields of 40−90%, depending on the olefin structure. The electrolyses were carried out in one-compartment cells fitted with an Mg anode under 1−5 atm of CO_2.[197]

The reductive electrocarboxylation of a series of substituted allenes with [$NiBr_2$(TMEDA)] and [Ni(bipy)$_3$](BF_4)$_2$ as catalysts afforded unsaturated monocarboxylic acids with high regioselectivities (Scheme 46). The influence of steric and electronic effects on the regioselectivity of CO_2 incorporation was discussed.[198]



Scheme 46. a) e^-, (PMDTA)Ni (10 mol %), DMF/nBu$_4$NBF$_4$, one-compartment cell, Mg anode, i = 50 mA, $p(CO_2)$ = 5 atm, room temp.

The incorporation of CO_2 into nonactivated alkynes catalysed by electrogenerated Ni^{II} complexes afforded α,β-unsaturated acids in moderate to good yields. The influence of a series of N and P ligands on the electrocarboxylation of 1-octyne was studied. Different carboxylic acids were obtained depending on the nature of the ancillary ligand, and the results represent an example of high ligand-directed product specificity.[199]

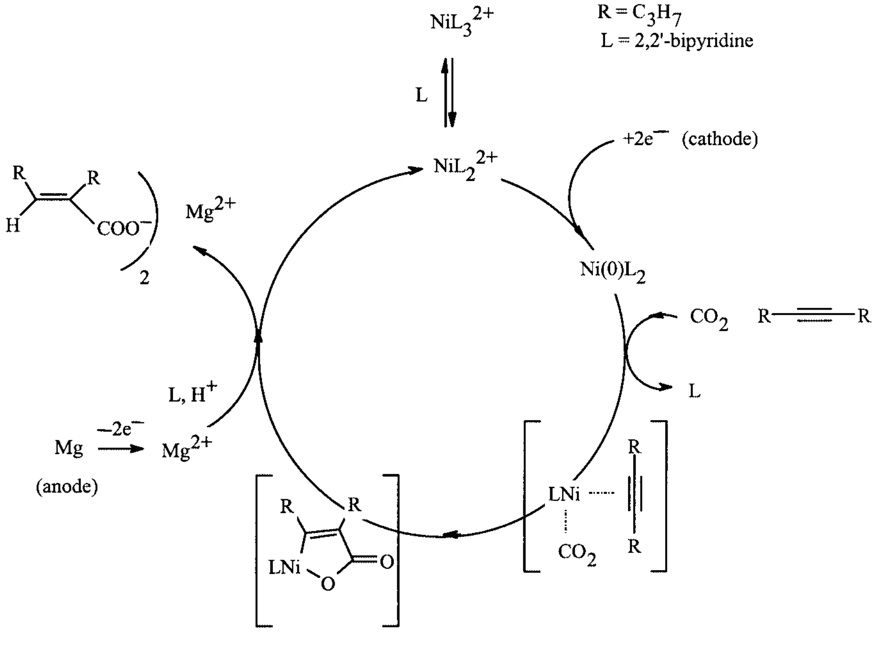
Electrochemically reduced [Ni(bipy)$_3$](BF_4)$_2$ catalyses the reaction of CO_2 with disubstituted alkynes to yield mono- and dicarboxylated derivatives. The reaction was carried out in DMF with CO_2 at atmospheric pressure in an undivided cell fitted with a sacrificial Mg anode.[200] The selective electrochemical carboxylation at the α-position of terminal alkynes at atmospheric CO_2 pressure also has been reported. A series of α-substituted acrylic acids was obtained in yields of 60−90% and regioselectivities of 65−90%.[201] (PMDTA)Ni systems also were described to be highly selective for the CO_2 incorporation into the 2-position of terminal alkynes.[202]

The mechanism of the electrocarboxylation of terminal alkynes with [Ni(bipy)$_3$](BF_4)$_2$ has been examined. An intermediate nickelacycle was isolated from the reaction (Scheme 47). Its cleavage by magnesium ions constitutes the key step in explaining Ni^{II} recycling and catalysis.[203] Cyclic voltammetry studies revealed that both carbon dioxide and the alkynes were able to coordinate to LNi^0-generated species in DMF.

The simultaneous activation of carbon dioxide and α,ω-diynes by electrogenerated LNi^0 complexes (L = bipy, PMDTA) afforded linear or cyclic adducts selectively depending on the nature of the ligand.[204] Diynes bearing both a terminal and an internal triple bonds gave exclusive CO_2 incorporation into the terminal alkynyl group, regioselectively at the 2-position.[205]

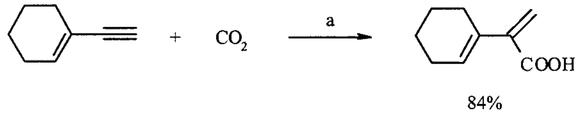
The electrocarboxylation of 1,3-diynes with the (PMDTA)Ni^{II} catalytic system yielded regio- and stereoselectively the (*E*)-2-vinylidene-3-ynecarboxylic acids in one step, resulting from the stereoselective *cis* addition of CO_2 to one triple bond.[206]

A series of 1,3-enynes has been electrocarboxylated by (bipy)- or (PMDTA)Ni^{II} catalytic systems. An overall hydrocarboxylation of the triple bond occurred through a stereoselective *cis* addition. Thus, the electroreductive carboxylation of 1-ethynylcyclohexene in DMF at 25 °C and 5



Scheme 47

atm of CO_2 afforded the corresponding dienecarboxylic acid in 84% yield (Scheme 48).[207]

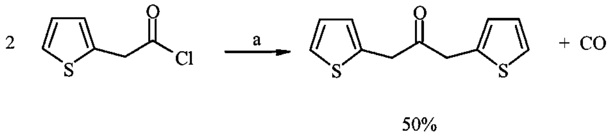


Scheme 48. a) e^-, [Ni(Br$_2$)PMDTA] (10 mol %), one-compartment cell, $p(CO_2)$ = 5 atm, Mg anode, room temp.

Electrochemical Pd^{II}-catalysed carbonylation of allylamines under a CO pressure of 50 atm at 110 °C afforded β,γ-unsaturated amides through carbonyl insertion into a π-allyl−Pd^{II}-type intermediate.[208]

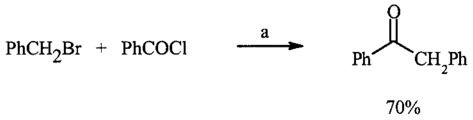
9) Homo- and Heterocoupling of Carbonyl and Carboxyl Derivatives

Chemical methods for the synthesis of ketones by the cross coupling between acid halides and alkyl or aryl halides have been reported, with the intermediate preparation of the corresponding organometallic species.[209−211] Symmetric ketones have been prepared by direct electrochemical homocoupling involving acid chlorides or anhydrides with loss of one CO unit, with a nickel or a stainless-steel anode and a nickel foam cathode (Scheme 49).[212,213] Good yields of symmetrical ketones were obtained with phenylacetyl halides (72−80%), moderate yields were observed with aryl, 1-naphthyl and 2-thiophenylacyl chlorides (30−50%), but the procedure did not work with alkyl chlorides. During the electrolyses, a release of carbon monoxide and/or carbonylmetal complexes occurred. In the proposed mechanism, nickel species were required for ketone formation and electrogenerated zerovalent iron was proposed to be involved in the carbon monoxide elimination process.



Scheme 49. a) 2 e^-, Ni or stainless steel anode (Ni/Cr 18:8), CH_3CN/nBu_4NBF_4, one-compartment cell

An [NiBr$_2$(bipy)]-catalysed electrochemical coupling of acid chlorides with aryl, benzyl or alkyl halides has been reported in undivided cells fitted with a zinc anode, affording nonsymmetrical ketones in 32−98% yields (Scheme 50).[214,215]

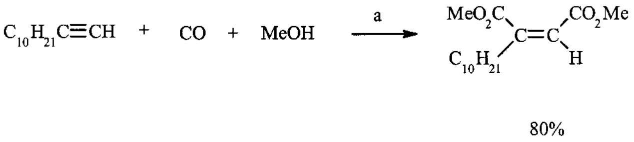


Scheme 50. a) e^-, [NiBr$_2$(bipy)] (20 mol %), bipy (10 mol %), CH_3CN, one-compartment cell, Mg anode, room temp.

Concerning catalyst activity, [NiBr$_2$(bipy)] gave the best results and the role of Zn^{2+} ions has been emphasised. The mechanism of this nickel-catalysed electrosynthesis of ketones has been examined in the case of the coupling of benzoyl chloride with benzyl bromide.[216] The electrogenerated Ni^0 complex added oxidatively to benzyl bromide, and the resulting Ni^{II} complex was further reduced at the potential of the Ni^{II}/Ni^0 reduction. The reduced complex reacted with benzoyl chloride to generate the ketone coupling product. Surprisingly, the oxidative addition of (bipy)Ni^0 to benzyl bromide was faster than the addition to benzoyl chloride, so that the formation of the symmetrical diketone was prevented. By this electrochemical method, the dimerisation of benzyl bromide also was avoided, allowing for the selective synthesis of the desired ketones.

10) Oxidative Coupling Reactions

The $PdCl_2$-catalysed oxidative C−C bond formation between alkynes and carbon monoxide at an atmospheric pressure of CO in MeOH has been reported to afford unsaturated 1,2-diesters in 33−99% current efficiencies.[217] The oxidation was well adapted to the carbonylation of terminal alkynes and gave predominantly the *cis*-diesters (Scheme 51).



Scheme 51. a) − e^-, $PdCl_2$ (10 mol %), MeOH/LiCl, two-compartment cell, 0.7 V vs. SCE, p(CO) = 1 atm, 50 °C

A selective oxidative monocarbonylation of terminal alkynes has been described with [Pd(OAc)$_2$(PPh$_3$)$_2$] as the catalyst. The reaction, carried out in MeCN/MeOH/NaOAc with CO at atmospheric pressure, led to α-alkynyl esters in 53−87% yields.[21]

The electrochemical Pd-catalysed carbonylation has been reported also for the synthesis of oxazolidin-2-ones from 2-amino-1-alkanols under mild conditions.[218] The Pd(OAc)$_2$ catalyst was anodically recycled at a graphite electrode. The electrooxidative carbonylation of methanol to dimethyl carbonate in the presence of [PdCl$_2$(bipy)] has been reported in yields of up to 64%.[219]

The electrooxidative carbonylation of arylamines to methyl carbamates in MeOH has been reported with a combination of Pd(OAc)$_2$ and Cu(OAc)$_2$ as the catalysts.[220]

Other electrochemical oxidative Ni^{II}- and Pd^{II}-catalysed reactions involving oxidation of functional groups have been reported, such as, for example, the conversion of olefins to ketones in a Wacker-type electrochemical process.[22] These oxidations have been catalysed mainly by $PdCl_2$ and Pd(OAc)$_2$. Methyl ketones were obtained from terminal olefins in yields of 70−85% with benzoquinone added as the mediator,[221] and in yields of 50−90% with tris(4-bromo-phenyl)amine as the mediator.[222] The Pd system has been described also for the electrooxidation of ethylene to acetaldehyde.[223]

The electrochemical Ni^{II}-catalysed oxidation of olefins to epoxides has been reported with electrogenerated Ni^{III} species derived from (salen)Ni^{II} complexes.[18,224] The electrooxidation of alcohols to carboxylic acids has been described through electrogenerated nickel hydroperoxides.[17]

Conclusions

The development of new methods for the controlled formation of C−C bonds lies at the heart of modern synthetic organic chemistry. Electrochemical methodology applied to the search for selective organic reactions has undergone important developments in recent years. Electrosynthesis offers an alternative methodology for generating C−C bonds from highly reactive intermediates. The selectivity and efficiency of electrochemically catalysed reactions gives evidence for the strong potential of this methodology as an interesting alternative for the synthesis of fine chemicals. The ease of electrochemical generation of active catalytic species under controlled conditions enables a very large spectrum of regio- and stereoselective syntheses, generally in single-step reactions under mild conditions. The scale-up of electrochemical reactions applied to the synthesis of fine organic chemicals, even on an industrial scale, has been proven possible, in particular by the use of undivided cells. At a laboratory scale, the equipment cost is reasonable, but on a larger scale the high level of the investment required makes this technology not yet largely developed in industry.

The combined use of transition metal complexes and electrosynthesis allows the generation of novel intermediates that can modulate and better control chemical reactivity. Moreover, electrosynthetic methods allow one to carry out redox processes in a catalytic way, without the need of stoichiometric chemical reagents. The search for electrochemical conditions that enable the clean and selective generation and regeneration of the active catalytic species, combined with the search of selective and efficient processes, constitute the essential efforts of modern electrosynthesis.

Electroanalytical studies are highly valuable tools that has been employed successfully to determine reaction mechanisms and to study redox reactions and mechanistic aspects of electron-transfer processes. The mechanistic knowledge provided by the electrochemical analysis may be a useful complement for the understanding of mechanistic pathways in classical organometallic chemistry.

The possibilities of development in the field of electrosynthesis associated with organometallic catalysis by transition-metal complexes are great, since the field still remains largely unexplored, particularly for anodically driven oxidative C−C coupling reactions.

Some of the examples reported have illustrated how fine tuning of the metal complexes' oxidation states and of the nature of the ligands or of the reaction conditions may determine the selectivity of the processes (including chemo-, regio- and stereoselectivity). Specifically controlling the reaction potential can generate unusual oxidation states of metal complexes. The possibilities of in situ generation and further reactivity of unstable (or lowly stable) oxidation states of a large series of metal complexes widens this promising field of research.

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[1] [1a] S. Torii in *Novel Trends in Electroorganic Synthesis*, Springer, Tokyo, **1998**. [1b] E. Steckhan, *Top. Curr. Chem.* **1987**, *42*. [1c] E. Steckhan, *Top. Curr. Chem.* **1997**, *185*.

[2] [2a] O. N. Efimov, V. V. Strelets, *Coord. Chem. Rev.* **1990**, *99*, 15−53. [2b] J. Y. Nédélec, J. Périchon, M. Troupel, *Top. Curr. Chem.* **1997**, *185*, 141−173. [2c] F. Battaglini, E. J. Calvo, F. Doctorovich, *J. Organomet. Chem.* **1997**, *547*, 1−21.

[3] [3a] T. V. Magdesieva, K. P. Butin, *Russ. Chem. Rev.* **2002**, *71*, 223−238. [3b] Y. H. Budnikova, *Russ. Chem. Rev.* **2002**, *71*, 111−139.

[4] L. Carlson, J. Bersier, *Top. Curr. Chem.* **1994**, *170*.

[5] H. Marzouk, *L'Actualité Chimique* **1998**, *10*, 37−56.

[6] M. A. Matthews, *Pure Appl. Chem.* **2001**, *73*, 1305−1308.

[7] [7a] A. Mortreux, J. C. Bavay, F. Petit, *New J. Chem.* **1980**, *4*, 671−676. [7b] H. Lehmkuhl, W. Leuchte, *J. Organomet. Chem.* **1970**, *23*, C30−C31. [7c] A. M. Allgeier, C. A. Mirkin, *Angew. Chem. Int. Ed. Engl.* **1988**, *37*, 895−908.

[8] F. C. J. M. VanVeggel, W. Verboom, D. N. Reinhouldt, *Chem. Rev.* **1994**, *94*, 279−299.

[9] M. Aresta, C. F. Nobile, A. Sacco, *Inorg. Chim. Acta* **1975**, *12*, 167−178.

[10] [10a] M. Troupel, Y. Rollin, O. Sock, G. Meyer, J. Périchon, *New J. Chem.* **1986**, *10*, 593−599. [10b] P. Le Floch, L. Ricard, F. Mathey, A. Jutand, C. Amatore, *Inorg. Chem.* **1995**, *34*, 11−12. [10c] M. Troupel, *Ann. Chim.* **1986**, *76*, 151−169.

[11] A. Louati, M. Huhn, *Inorg. Chem.* **1993**, *32*, 3601−3607.

[12] A. J. Downard, L. R. Hanton, R. L. Paul, *J. Chem. Soc., Chem. Commun.* **1992**, 235−237.

[13] B. Castro, C. Freire, E. Pereira, *J. Chem. Soc., Dalton Trans.* **1994**, 571−574.

[14] J. B. Chlistunoff, A. J. Bard, *Inorg. Chem.* **1992**, *31*, 4582−4587.

[15] [15a] G. Musie, P. J. Farmer, T. Tuntulani, J. H. Reibenspies, M. Y. Darensbourg, *Inorg. Chem.* **1995**, *35*, 2176−2183. [15b] C. Faulmann, P. Cassoux, E. B. Yagubskii, L. V. Vetoshkina, *New J. Chem.* **1993**, *17*, 385−391.

[16] D. De Montauzon, R. Poilblanc, P. Lemoine, M. Gros, *Electrochim. Acta* **1978**, *23*, 1247−1269.

[17] H. J. Schäfer, *Top. Curr. Chem.* **1987**, *142*, 101−129.

[18] H. Yoon, T. R. Wagler, K. J. O'Connor, C. J. Burrows, *J. Am. Chem. Soc.* **1990**, *112*, 4568−4570.

[19] [19a] C. Amatore, A. Jutand, M. M′Barki, *Organometallics* **1992**, *11*, 3009−3013. [19b] C. Amatore, A. Fuxa, A. Jutand, *Chem. Eur. J.* **2000**, *6*, 1474−1482.

[20] [20a] R. Van Asselt, C. J. Elsevier, C. Amatore, A. Jutand, *Organometallics* **1997**, *16*, 317−328. [20b] T. Tanase, K. Kawahara, H. Ukaji, K. Kobayashi, H. Yamazaki, Y. Yamamoto, *Inorg. Chem.* **1993**, *32*, 3682−3688.

[21] I. Chiarotto, I. Carelli, *Synth. Commun.* **2002**, *32*, 881−886.

[22] H. H. Horowitz, *J. Appl. Electrochem.* **1984**, *14*, 779−790.

[23] J. Chaussard, J. C. Folest, J.-Y. Nédélec, J. Périchon, S. Sibille, M. Troupel, *Synthesis* **1990**, *5*, 369−381.

[24] [24a] G. Silvestri, S. Gambino, G. Filardo, A. Gulotta, *Angew. Chem. Int. Ed. Engl.* **1984**, *96*, 978−979. [24b] G. Silvestri, S. Gambino, G. Filardo, *Acta Chem. Scand.* **1991**, *45*, 987−992.

[25] J. Hassan, M. Sévignon, C. Gozzi, E. Schulz, M. Lemaire, *Chem. Rev.* **2002**, *102*, 1359−1469.

[26] A. Yasuhara, A. Kasano, T. Sakamoto, *Organometallics* **1998**, *17*, 4754−4756.

[27] M. Tokuda, N. Kurono, S. Takasugi, A. A. Jalil, *Proc. Electrochem. Soc.* **2000**, 2000−2015.

[28] O. Sock, M. Troupel, J. Périchon, C. Chevrot, A. Jutand, *J. Electroanal. Chem.* **1985**, *183*, 237−246.

[29] M. Troupel, Y. Rollin, S. Sibille, J. F. Fauvarque, J. Périchon, *J. Organomet. Chem.* **1980**, *202*, 435−446.

[30] G. Schiavon, G. Bontempelli, B. Corain, *J. Chem. Soc., Dalton Trans.* **1981**, *5*, 1074−1081.

[31] M. Mori, Y. Hashimoto, Y. Ban, *Tetrahedron Lett.* **1980**, *21*, 631−634.

[32] M. A. Fox, D. A. Chandler, C. Lee, *J. Org. Chem.* **1991**, *56*, 3246−3255.

[33] M. Troupel, Y. Rollin, S. Sibille, J. F. Fauvarque, J. Périchon, *J. Chem. Res. Synop.* **1980**, *1*, 26−27.

[34] [34a] Y. Rollin, M. Troupel, G. D. Tuck, J. Périchon, *J. Organomet. Chem.* **1986**, *303*, 131−137. [34b] Y. Rollin, M. Troupel, O. Sock, G. Meyer, J. Périchon, *New J. Chem.* **1986**, *10*, 593−599.

[35] K. W. R. Franca, M. Navarro, E. Léonel, M. Durandetti, J. Y. Nédélec, *J. Org. Chem.* **2002**, *67*, 1838−1842.

[36] G. Meyer, Y. Rollin, J. Périchon, *J. Organomet. Chem.* **1987**, *333*, 263−267.

[37] T. M. Cassol, F. W. J. Demnitz, M. Navarro, E. A. D. Neves, *Tetrahedron Lett.* **2000**, *41*, 8203−8206.

[38] V. Courtois, R. Barhdadi, S. Condon, M. Troupel, *Tetrahedron Lett.* **1999**, *40*, 5993−5996.

[39] V. Courtois, R. Barhdadi, M. Troupel, *Tetrahedron Lett.* **1997**, *53*, 11569−11575.

[40] C. Amatore, A. Jutand, *Organometallics* **1988**, *7*, 2203−2214.

[41] [41a] C. Amatore, A. Jutand, *Acta Chem. Scand.* **1990**, *44*, 755−764. [41b] C. Amatore, A. Jutand, A. Suarez, *J. Am. Chem. Soc.* **1993**, *115*, 9531−9541.

[42] T. T. Tsou, J. K. Kochi, *J. Am. Chem. Soc.* **1979**, *101*, 7547−7560.

[43] M. Durandetti, M. Devaud, J. Périchon, *New J. Chem.* **1996**, *20*, 659−667.

[44] A. Yasuhara, A. Kasano, T. Sakamoto, *Yuki Gosei Kagaku Kyokaishi* **2000**, *58*, 192−198. *Chem. Abstr.* **2000**, *132*, 236828.

[45] [45a] A. Aboulkassim, C. Chevrot, *Polymer* **1993**, *34*, 401−405. [45b] C. Chevrot, T. Benazzi, M. Barj, *Polymer* **1995**, *36*, 631−638.

[46] G. Schiavon, G. Zotti, G. Bontempelli, F. Lo Coco, *J. Electroanal. Chem.* **1988**, *242*, 131−142.

[47] [47a] J. F. Fauvarque, M. A. Petit, F. Pfluger, A. Jutand, C. Chevrot, M. Troupel, *Makromol. Chem. Rapid Commun.* **1983**, *4*, 455−457. [47b] C. Amatore, F. Gaubert, A. Jutand, J. H. P. Utley, *J. Chem. Soc., Perkin Trans. 2* **1996**, *10*, 2447−2452.

[48] J. F. Fauvarque, A. Digua, M. A. Petit, J. Savard, *Makromol. Chem.* **1985**, *186*, 2415−2425.

[49] K. Faid, D. Ades, A. Siove, C. Chevrot, *Synth. Met.* **1994**, *63*, 89−99.

[50] K. Faid, D. Ades, A. Siove, C. Chevrot, *J. Chim. Phys. Phys.-Chim. Biol.* **1992**, *89*, 1019−1026.

[51] S. Torii, H. Tanaka, K. Morisaki, *Tetrahedron Lett.* **1985**, *26*, 1655−1658.

[52] A. Jutand, A. Mosleh, *J. Org. Chem.* **1997**, *62*, 261−274.

[53] A. Jutand, S. Negri, A. Mosleh, *J. Chem. Soc., Chem. Commun.* **1992**, 1729−1730.

[54] [54a] A. Jutand, S. Negri, *Eur. J. Org. Chem.* **1998**, 1811−1821. [54b] C. Amatore, M. Azzabi, A. Jutand, *J. Am. Chem. Soc.* **1991**, *113*, 8375−8384. [54c] A. Jutand, A. Mosleh, *Organometallics* **1995**, *14*, 1810−1817.

[55] C. Amatore, E. Carré, A. Jutand, H. Tanaka, Q. Ren, S. Torii, *Chem. Eur. J.* **1996**, *2*, 957−966.

[56] C. Cannes, S. Condon, M. Durandetti, J. Périchon, J.-Y. Nédélec, *J. Org. Chem.* **2000**, *65*, 4575−4583.

[57] [57a] I. Hashimoto, N. Tsuruta, M. Ryang, S. Tsutsumi, *J. Org. Chem.* **1970**, *35*, 3748−3752. [57b] A. S. Kende, L. S. Liebeskind, D. M. Braitsch, *Tetrahedron Lett.* **1975**, *39*, 3375−3378. [57c] M. F. Semmelhack, P. Helquist, L. D. Jones, L. Keller, L. Mendelson, L. S. Ryono, J. G. Smith, R. D. Stauffer, *J. Am. Chem. Soc.* **1981**, *103*, 6460−6471.

[58] [58a] M. Iyoda, H. Otsuka, K. Sato, N. Nisato, M. Oda, *Bull. Chem. Soc. Jpn.* **1990**, *63*, 80−87. [58b] K. Takagi, H. Mimura, S. Inokawa, *Bull. Chem. Soc. Jpn.* **1984**, *57*, 3517−3522. [58c] M. Zembayashi, K. Tamaoao, J. I. Yoshida, M. Kumada, *Tetrahedron Lett.* **1977**, *47*, 4089−4092.

[59] Y. Rollin, M. Troupel, D. G. Tuck, J. Périchon, *J. Organomet. Chem.* **1986**, *303*, 131−137.

[60] C. Cannes, E. Labbé, M. Durandetti, M. Devaud, J. Y. Nédélec, *J. Electroanal. Chem.* **1996**, *412*, 85−93.

[61] M. Kijima, Y. Sakai, H. Shirakawa, *Synth. Met.* **1995**, *71*, 1837−1840.

[62] S. Sibille, J. C. Folest, J. Coulombeix, M. Troupel, J. F. Fauvarque, J. Périchon, *J. Chem. Res. Synop.* **1980**, *8*, 268−269.

[63] G. Schiavon, G. Bontempelli, B. Corain, *J. Chem. Soc., Dalton Trans.* **1981**, *5*, 1074−1081.

[64] A. J. Fry, P. F. Fry, *J. Org. Chem.* **1993**, *58*, 3496−3501.

[65] C. Amatore, F. Gaubert, A. Jutand, J. H. P. Utley, *J. Chem. Soc., Perkin Trans. 2* **1996**, *11*, 2447−2452.

[66] [66a] W. H. Smith, Y. M. Kuo, *J. Electroanal. Chem.* **1985**, *188*, 189−202. [66b] W. H. Smith, Y. M. Kuo, *J. Electroanal. Chem.* **1985**, *188*, 203−218.

[67] [67a] S. Mabrouk, S. Pellegrini, J. C. Folest, Y. Rollin, J. Périchon, *J. Organomet. Chem.* **1986**, *301*, 391−400.

[68] G. Bontempelli, S. Daniele, M. Fiorani, *J. Electroanal. Chem. Interfacial Electrochem.* **1984**, *160*, 249−260.

[69] J. Y. Becker, J. B. Kerr, D. Pletcher, R. Rosas, *J. Electroanal. Chem.* **1981**, *117*, 87−89.

[70] C. Gosden, K. P. Healy, D. Pletcher, *J. Chem. Soc., Dalton Trans.* **1978**, *8*, 972−976.

[71] M. S. Mubarak, D. G. Peters, *J. Electroanal. Chem.* **1995**, *388*, 195−198.

[72] [72a] M. S. Ram, A. Bakac, J. H. Espenson, *Inorg. Chem.* **1988**, *27*, 4231−4235. [72b] C. E. Dahm, D. G. Peters, *J. Electroanal. Chem.* **1996**, *406*, 119−129. [72c] C. Gosden, J. B. Kerr, D. Pletcher, R. Rosas, *J. Electroanal. Chem. Interfacial Electrochem.* **1981**, *117*, 101−107. [72d] M. A. Hakrow, G. Christou, *Chem. Rev.* **1994**, *94*, 2421−2481.

[73] C. E. Dahm, D. G. Peters, *Anal. Chem.* **1994**, *66*, 3117−3123.

[74] A. L. Butler, D. G. Peters, *J. Electrochem. Soc.* **1997**, *144*, 4212−4217.

[75] G. Meyer, M. Troupel, J. Périchon, *J. Organomet. Chem.* **1990**, *393*, 137−142.

[76] C. Gosmini, J. Y. Nédélec, J. Périchon, *Tetrahedron Lett.* **2000**, *41*, 201−203.

[77] C. Gosmini, J. Y. Nédélec, J. Périchon, *Tetrahedron Lett.* **2000**, *41*, 5039−5042.

[78] C. Gosmini, J. Y. Nédélec, J. Périchon, *Tetrahedron Lett.* **2000**, *53*, 366−372.

[79] S. Sibille, V. Ratovelomanana, J. Y. Nédélec, J. Périchon, *Synlett* **1993**, 425−426.

[80] M. Durandetti, J. Y. Nédélec, J. Périchon, *J. Org. Chem.* **1996**, *61*, 1748−1755.

[81] N. Kurono, K. Sugita, S. Takasugi, M. Tokuda, *Tetrahedron* **1999**, *55*, 6097−6108.

[82] M. Durandetti, S. Sibille, J. Y. Nédélec, J. Périchon, *Synth. Commun.* **1994**, *24*, 145−151.

[83] J. C. Folest, J. Périchon, J. F. Fauvarque, A. Jutand, *J. Organomet. Chem.* **1988**, *342*, 259−261.

[84] [84a] A. Conan, S. Sibille, E. D'Incan, J. Périchon, *J. Chem. Soc., Chem. Commun.* **1990**, 48−49. [84b] M. Durandetti, J. Périchon, J. Y. Nédélec, *J. Org. Chem.* **1997**, *62*, 7914−7915.

[85] M. Durandetti, J. Y. Nédélec, J. Périchon, *J. Org. Chem.* **1996**, *61*, 1748−1755.

[86] M. Durandetti, J. Périchon, J. Y. Nédélec, *Tetrahedron Lett.* **1997**, *38*, 8683−8686.

[87] [87a] P. A. Grieco, Y. S. Hon, A. Perez-Medrano, *J. Am. Chem. Soc.* **1988**, *110*, 1630−1631. [87b] S. Knapp, A. T. Levorse, *J. Org. Chem.* **1988**, *53*, 4006−4014.

[88] S. Mcharek, M. Heintz, M. Troupel, J. Périchon, *Bull. Soc. Chim. Fr.* **1989**, *1*, 95−97.

[89] M. Troupel, Y. Rollin, J. Périchon, J. F. Fauvarque, *New J. Chem.* **1981**, *5*, 621−625.

[90] J. F. Fauvarque, C. Chevrot, A. Jutand, M. Francois, J. Périchon, *J. Organomet. Chem.* **1984**, *264*, 273−281.

[91] C. Amatore, A. Jutand, *J. Am. Chem. Soc.* **1991**, *113*, 2819−2825.

[92] C. Amatore, A. Jutand, *J. Electroanal. Chem. Interfacial Electrochem.* **1991**, *306*, 141−156.

[93] H. Kamekawa, H. Kudoh, H. Senboku, M. Tokuda, *Chem. Lett.* **1997**, *9*, 917−918.

[94] H. Senboku, H. Kanaya, M. Tokuda, *Synlett* **2002**, 140−142.

[95] P. Tascedda, E. Duñach, *Synlett* **2000**, 245−247.

[96] P. Tascedda, E. Duñach, *J. Chem. Soc., Chem. Commun.* **1995**, 43−44.

[97] S. Olivero, E. Duñach, *Eur. J. Org. Chem.* **1999**, 1885−1891.

[98] J. F. Fauvarque, A. Jutand, M. François, *J. Appl. Electrochem.* **1988**, *18*, 109−115.

[99] J. F. Fauvarque, A. Jutand, M. François, *New J. Chem.* **1986**, *10*, 119−122.

[100] A. Gennaro, A. A Isse, F. Maran, *J. Electroanal. Chem.* **2001**, *507*, 124−134.

[101] S. Torii, H. Tanaka, T. Hamatani, K. Morisaki, A. Jutand, F. Pfluger, J. F. Fauvarque, *Chem. Lett.* **1986**, *2*, 169−172.

[102] A. Jutand, S. Negri, *Eur. J. Org. Chem.* **1998**, 1811−1821.

[103] A. Jutand, S. Negri, *Synlett* **1997**, 719−721.

[104] C. Amatore, A. Jutand, F. Khalil, M. F. Nielsen, *J. Am. Chem. Soc.* **1992**, *114*, 7076−7085.

[105] J. Damodar, S. R. K. Mohan, S. R. J. Reddy, *Electrochem. Commun.* **2001**, *3*, 762−766.

[106] M. Troupel, M. Ocafrain, E. Dolhem, J. C. Folest, R. Barhdadi, *Can. J. Chem.* **1988**, *76*, 1013−1019.

[107] E. Dolhem, M. Ocafrain, J. Y. Nédélec, M. Troupel, *Tetrahedron* **1997**, *53*, 17089−17096.

[108] E. Dolhem, R. Barhdadi, J. C. Folest, J. Y. Nédélec, M. Troupel, *Tetrahedron* **2001**, *57*, 525−529.

[109] M. Ocafrain, M. Devaud, M. Troupel, J. Périchon, *J. Chem. Soc., Chem. Commun.* **1995**, 2331−2332.

[110] M Ocafrain, M. Devaud, J. Y. Nédélec, M. Troupel, *J. Organomet. Chem.* **1998**, *560*, 103−107.

[111] M. Ocafrain, E. Dolhem, J. Y. Nédélec, M. Troupel, *J. Organomet. Chem.* **1998**, *571*, 37−42.

[112] L. Garnier, Y. Rollin, J. Périchon, *J. Organomet. Chem.* **1989**, *367*, 347−358.

[113] L. Garnier, Y. Rollin, J. Périchon, *New J. Chem.* **1989**, *13*, 53−59.

[114] I. Chiarotto, I. Carelli, V. Carnicelli, F. Marinelli, A. Arcadi, *Electrochim. Acta* **1996**, *41*, 2503−2509.

[115] [115a] A. Fürstner, *Synthesis* **1989**, 571−590. [115b] M. W. Rathke, *Org. React.* **1975**, *22*, 423−460. [115c] M. Gaudemar, *Organomet. Chem. Rev.* **1972**, *8*, 183−233.

[116] [116a] A. Conan, S. Sibille, J. Périchon, *J. Org. Chem.* **1991**, *56*, 2018−2024. [116b] S. Sibille, J. Y. Nédelec, J. Périchon, *Electroorg. Synth.* **1990**, 361−367.

[117] S. Mcharek, S. Sibille, J. Y. Nédélec, J. Périchon, *J. Organomet. Chem.* **1991**, *401*, 211−215.

[118] M. Tokuda, S. Satoh, H. Suginome, *J. Org. Chem.* **1989**, *54*, 5608−5613.

[119] [119a] S. Torii, K. Uneyama, H. Matsuda, *Tetrahedron Lett.* **1984**, *25*, 6017−6020. [119b] A. Jutand, H. Kawafuchi, C. Amatore, M. Kuroboshi, S. Torii, *Novel Trends Electroorg. Synth.* **1997**, 349−350.

[120] H. Hebri, E. Duñach, J. Périchon, *Tetrahedron Lett.* **1993**, *34*, 1475−1478.

[121] S. Sibille, E. D'Incan, L. Leport, M. C. Massebiau, J. Périchon, *Tetrahedron Lett.* **1987**, *28*, 55−58.

[122] M. Durandetti, S. Sibille, J. Périchon, *J. Org. Chem.* **1989**, *54*, 2198−2204.

[123] [123a] L. S. Hegedus, S. D. Wagner, E. L. Waterman, K. Siirala-Hansen, *J. Org. Chem.* **1975**, *40*, 593−598. [123b] L. S. Hegedus, D. H. P. Thompson, *J. Am. Chem. Soc.* **1985**, *107*, 5663−5669. [123c] J. Ishizu, T. Yamamoto, A. Yamamoto, *Chem. Lett.* **1976**, 1091−1094. [123d] T. Yamamoto, J. Ishizu, A. Yamamoto, *J. Am. Chem. Soc.* **1981**, *103*, 6863−6869.

[124] D. Franco, S. Olivero, E. Duñach, *Electrochim. Acta* **1997**, *42*, 2159−2164.

[125] S. Olivero, D. Franco, J. C. Clinet, E. Duñach, *Collect. Czech. Chem. Commun.* **2000**, *65*, 844−861.

[126] S. Olivero, E. Duñach, *J. Chem. Soc., Chem. Commun.* **1995**, 2497−2498.

[127] D. Franco, S. Olivero, J. P. Rolland, E. Duñach, *Novel Trends Electroorg. Synth.* **1997**, 391−394.

[128] [128a] J. Gigg, R. Gigg, *J. Chem. Soc. Org.* **1966**, 82−86. [128b] E. J. Corey, J. W. Suggs, *J. Org. Chem.* **1973**, *38*, 3224−3226. [128c] R. Beugelmans, S. Bourdet, A. Bigot, J. Zhu, *Tetrahedron Lett.* **1994**, *35*, 4349−4350. [128d] H. X. Zhang, F. Guibé, G. Balavoine, *Tetrahedron Lett.* **1988**, *29*, 619−622. [128e] Y. Hayakawa, R. Kawai, S. Wakabayashi, M. Uchiyama, R. Noyori, *Nucleosides Nucleotides* **1998**, *17*, 441−449.

[129] S. Olivero, J. P. Rolland, E. Duñach, E. Labbé, *Organometallics* **2000**, *19*, 2798−2804.

[130] D. Franco, K. Wenger, S. Antonczak, D. Cabrol-Bass, E. Duñach, M. Rocamora, M. Gomez, G. Muller, *Chem. Eur. J.* **2002**, *8*, 664−672.

[131] D. Franco, E. Duñach, *Synlett* **2001**, 806−808.

[132] D. Franco, E. Duñach, *Tetrahedron Lett.* **2000**, *41*, 7333−7336.

[133] D. Franco, A. Riahi, F. Hénin, J. Muzart, E. Duñach, *Eur. J. Org. Chem.* **2002**, 2257−2259.

[134] S. Olivero, E. Duñach, *Tetrahedron Lett.* **1997**, *38*, 6193−6196.

[135] D. Franco, E. Duñach, *Tetrahedron Lett.* **1999**, *40*, 2951−2954.

[136] N. Kurono, K. Sugita, M. Tokuda, *Tetrahedron* **2000**, *56*, 847−854.

[137] [137a] P. Zhang, W. Zhang, T. Zhang, Z. Wang, W. Zhou, *J. Chem. Soc., Chem. Commun.* **1991**, 491−492. [137b] W. Qiu, Z. Wang, *J. Chem. Soc., Chem. Commun.* **1989**, *6*, 356−357.

[138] [138a] M. Minato, T. Nonaka, T. Fuchigami, *Chem. Lett.* **1986**, *7*, 1071−1074. [138b] S. Torii, H. Yanaka, T. Katoh, K. Morisaki, *Tetrahedron Lett.* **1984**, *25*, 3207−3210.

[139] D. Franco, D. Panyella, M. Rocamora, M. Gomez, J. C. Clinet, G. Muller, E. Duñach, *Tetrahedron Lett.* **1999**, *40*, 5685−5688.

[140] C. Amatore, A. Jutand, G. Meyer, L. Mottier, *Chem. Eur. J.* **1999**, *5*, 466−473.

[141] R. Grigg, B. Putnikovic, C. J. Urch, *Tetrahedron Lett.* **1997**, *38*, 6307−6308.

[142] M. Durandetti, J. Y. Nédélec, J. Périchon, *Org. Lett.* **2001**, *3*, 2073−2076.

[143] M. Durandetti, J. Périchon, J. Y. Nédélec, *Tetrahedron Lett.* **1999**, *51*, 9009−9013.

[144] M. Kuroboshi, M. Tanaka, S. Kishimoto, H. Tanaka, S. Torii, *Synlett* **1999**, 69−70.

[145] M. Kuroboshi, M. Tanaka, S. Kishimoto, K. Goto, H. Tanaka, S. Torii, *Tetrahedron Lett.* **1999**, *14*, 2785−2788.

[146] S. Condon-Gueugnot, E. Léonel, J. Y. Nédélec, J. Périchon, *J. Org. Chem.* **1995**, *60*, 7684−7686.

[147] S. Condon, D. Dupré, G. Falgayrac, J. Y. Nédélec, *Eur. J. Org. Chem.* **2002**, 105−111.

[148] S. Ozaki, H. Matsushita, H. Ohmori, *J. Chem. Soc., Perkin Trans. 1* **1993**, *6*, 649−651.

[149] C. Amatore, E. Carre, M. M'Barki, G. Meyer, *Organometallics* **1995**, *14*, 5605−5614.

[150] C. Amatore, A. Jutand, *Acc. Chem. Res.* **2000**, *33*, 314−321.

[151] P. Perlmutter in *Conjugate Addition Reactions in Organic Synthesis*, Pergamon Press, Oxford, **1992**.

[152] P. Jacob, H. C. Brown, *J. Am. Chem. Soc.* **1976**, *98*, 7832−7833.

[153] G. Cahiez, M. Alami, *Tetrahedron Lett.* **1989**, *45*, 4163−4176.

[154] M. K. Schwaebe, J. R. McCarthy, J. P. Whitten, *Tetrahedron Lett.* **2000**, *41*, 791−794.

[155] R. Sustmann, P. Hopp, P. Holl, *Tetrahedron Lett.* **1989**, *30*, 689−692.

[156] S. Condon-Gueugnot, D. Dupré, J. Y. Nédélec, J. Périchon, *Synthesis* **1997**, 1457−1460.

[157] S. Ozaki, I. Horiguchi, H. Matsushita, H. Ohmori, *Tetrahedron Lett.* **1994**, *35*, 725−728.

[158] H. Tanaka, S. Kameyama, S. Sumida, Y. Tokumaru, T. Shiroi, M. Sasaoka, M. Taniguchi, S. Torii, *Synlett* **1991**, 889−890.

[159] H. Tanaka, S. Kameyama, S. Sumida, S. Torii, *Tetrahedron Lett.* **1992**, *33*, 7029−7032.

[160] K. P. Healy, D. Pletcher, *J. Organomet. Chem.* **1978**, *161*, 109−120.

[161] [161a] B. Giese in *Radicals in Organic Synthesis: Formation of Carbon−Carbon Bonds*, Pergamon Press, Oxford, **1986**. [161b] D. P. Curran, *Synthesis* **1988**, 417−439, 489−513. [161c] P. Renaud in *Radicals in Organic Synthesis*, Wiley-VCH, **2001**, 2 vols.

[162] M. S. Mubarak, D. G. Peters, *J. Saudi Chem. Soc.* **1999**, *3*, 135−146.

[163] M. S. Mubarak, M. M. Pagel, M. Lawrence, D. G. Peters, *J. Org. Chem.* **1998**, *63*, 1319−1322.

[164] S. Ozaki, T. Nakanishi, M. Sugiyama, C. Miyamoto, H. Ohmori, *Chem. Pharm. Bull.* **1991**, *39*, 31−35.

[165] S. Ozaki, E. Matsui, H. Ohmori, *Chem. Pharm. Bull.* **1997**, *45*, 198−201.

[166] S. Ozaki, S. Mitoh, H. Ohmori, *Chem. Pharm. Bull.* **1996**, *44*, 2020−2024.

[167] S. Ozaki, S. Mitoh, H. Ohmori, *Chem. Pharm. Bull.* **1995**, *43*, 1435−1440.

[168] M. Ihara, A. Katsumata, F. Setsu, Y. Tokunaga, K. Fukumoto, *J. Org. Chem.* **1996**, *61*, 677−684.

[169] S. Sengmany, E. Léonel, J. P. Paugam, J. Y. Nédélec, *Tetrahedron* **2002**, *58*, 271−277.

[170] Y. Rollin, G. Meyer, M. Troupel, J. F. Fauvarque, *Tetrahedron Lett.* **1982**, *23*, 3573−3576.

[171] Y. Rollin, G. Meyer, M. Troupel, J. F. Fauvarque, J. Périchon, *J. Chem. Soc., Chem. Commun.* **1983**, *15*, 793−794.

[172] S. Olivero, E. Duñach, *Synlett* **1994**, 531−533.

[173] S. Olivero, J. C. Clinet, E. Duñach, *Tetrahedron Lett.* **1995**, *36*, 4429−4432.

[174] J. C. Clinet, E. Duñach, *J. Organomet. Chem.* **1995**, *503*, C48−C50.

[175] M. Gomez, G. Muller, D. Panyella, M. Rocamora, E. Duñach, S. Olivero, J. C. Clinet, *Organometallics* **1997**, *16*, 5900−5908.

[176] S. Olivero, J.-P. Rolland, E. Duñach, *Organometallics* **1998**, *17*, 3747−3753.

[177] S. Olivero, E. Duñach, *J. Chem. Soc., Chem. Commun.* **1995**, 2497−2498.

[178] S. Torii, H. Tanaka, K. Morisaki, *Chem. Lett.* **1985**, 1353−1354.

[179] H. Tanaka, Q. Ren, S. Torii, *Novel Trends Electroorg. Synth.* **1995**, 195.

[180] S. Ozaki, E. Matsui, J. Waku, H. Ohmori, *Tetrahedron Lett.* **1997**, *38*, 2705−2708.

[181] E. Duñach, A. P. Esteves, A. M. Freitas, M. J. Medeiros, S. Olivero, *Tetrahedron Lett.* **1999**, *40*, 8693−8696.

[182] [182a] A. P. Esteves, A. M Freitas, M. J. Medeiros, D. Pletcher, *J. Electroanal. Chem.* **2001**, *499*, 95−102. [182b] A. L. R Ataide, A. P. Esteves, A. M Freitas, M. J. Medeiros, V. Mota, D. Pletcher, P. Rodrigues, *Port. Electrochim. Acta* **1999**, *17*, 215−219.

[183] E. Duñach, A. P. Esteves, A. M. Freitas, M. A. Lemos, M. J. Medeiros, S. Olivero, *Pure Appl. Chem.* **2001**, *73*, 1−5.

[184] S. Ozaki, E. Matsui, H. Yoshinaga, H. Ohmori, *Tetrahedron Lett.* **1998**, *39*, 8121−8124.

[185] M. S. Mubarak, D. G. Peters, *J. Electroanal. Chem.* **1992**, *332*, 127−134.

[186] D. M. Fang, D. G. Peters, M. S. Mubarak, *J. Electrochem. Soc.* **2001**, *148*, E464−E467.

[187] S. Ozaki, H. Matsushita, H. Ohmori, *J. Chem. Soc., Perkin Trans. 1* **1993**, *19*, 2339−2344.

[188] S. Ozaki, H. Matsushita, M. Emoto, H. Ohmori, *Chem. Pharm. Bull.* **1995**, *43*, 32−36.

[189] S. Ozaki, H. Matsushita, H. Ohmori, *J. Chem. Soc., Chem. Commun.* **1992**, 1120−1122.

[190] S. Ozaki, Y. Urano, H. Ohmori, *Electrochim. Acta* **1997**, *42*, 2153−2158.

[191] S. Sibille, J. Coulombeix, J. Périchon, J. M. Fuchs, A. Mortreux, F. Petit, *J. Mol. Catal.* **1985**, *32*, 239−250.

[192] M. Troupel, Y. Rollin, S. Sibille, J. Périchon, J. F. Fauvarque, *J. Organomet. Chem.* **1980**, *202*, 435−446.

[193] [193a] N. Yamazaki, S. Murai, *J. Chem. Soc., Chem. Commun.* **1968**, 147−148. [193b] T. Ohta, K. Ebina, N. Yamazaki, *Bull. Chem. Soc. Jpn.* **1971**, *44*, 1321−1327.

[194] H. Lehmkuhl, W. Leuchte, *J. Organomet. Chem.* **1970**, *23*, C30−C31.

[195] [195a] W. A. Kornicher, Monsanto Co. US Pat. 3474012, **1969**. *Chem. Abstr.* **1970**, *72*, 22145. [195b] W. A. Kornicher, Monsanto Co. US Pat. 3578626, **1971**. *Chem. Abstr.* **1971**, *75*, 49875.

[196] E. Chiozza, M. Desigaud, J. Greiner, E. Duñach, *Tetrahedron Lett.* **1998**, *39*, 4831−4834.

[197] S. Derien, J. C. Clinet, E. Duñach, J. Périchon, *Tetrahedron* **1992**, *48*, 5235−5248.

[198] S. Derien, J. C. Clinet, E. Duñach, J. Périchon, *Synlett* **1990**, 361−364.

[199] E. Labbé, E. Duñach, J. Périchon, *J. Organomet. Chem.* **1988**, *353*, C51−C56.

[200] E. Duñach, S. Derien, J. Périchon, *J. Organomet. Chem.* **1989**, *364*, C33−C36.

[201] E. Duñach, J. Périchon, *J. Organomet. Chem.* **1988**, *352*, 239−246.

[202] E. Duñach, J. Périchon, *Synlett* **1990**, 143−145.

[203] S. Derien, E. Duñach, J. Périchon, *J. Am. Chem. Soc.* **1991**, *113*, 8447−8454.

[204] S. Derien, J. C. Clinet, E. Duñach, J. Périchon, *J. Org. Chem.* **1993**, *58*, 2578−2588.

[205] S. Derien, E. Duñach, J. Périchon, *J. Organomet. Chem.* **1990**, *385*, C43−C46.

[206] S. Derien, J. C. Clinet, E. Duñach, J. Périchon, *J. Chem. Soc., Chem. Commun.* **1991**, 549−550.

[207] S. Derien, J. C. Clinet, E. Duñach, J. Périchon, *J. Organomet. Chem.* **1992**, *424*, 213−224.

[208] S. I. Murahashi, Y. Imada, K. Nishimura, *Tetrahedron* **1994**, *50*, 453−464.

[209] [209a] G. Friour, A. Alexakis, G. Cahiez, J. F. Normant, *Tetrahedron* **1984**, *40*, 683−693. [209b] S. Inaba, R. D. Rieke, *J. Org. Chem.* **1985**, *50*, 1373−1381.

[210] T. Sato, T. Itoh, T. Fujisawa, *Chem. Lett.* **1982**, 1559−1560.

[211] Y. Tamaru, H. Ochiai, F. Sandra, Z. I. Yoshi, *Tetrahedron Lett.* **1985**, *26*, 5529−5562.

[212] J. C. Folest, E. Pereira-Martins, M. Troupel, J. Périchon, *Tetrahedron Lett.* **1993**, *34*, 7571−7574.

[213] [213a] T. Shono, I. Nishiguchi, H. Ohmizu, *Chem. Lett.* **1977**, 1021−1024. [213b] J. P. Gisselbrecht, H. Lund, *Acta Chem. Scand., Ser. B* **1985**, *39*, 823−827. [213c] E. d'Incan, S. Sibille, J. Périchon, *Tetrahedron Lett.* **1986**, *27*, 4175−4176.

[214] H. Marzouk, Y. Rollin, J. C. Folest, J. Y. Nédélec, J. Périchon, *J. Organomet. Chem.* **1989**, *369*, C47−C50.

[215] M. Troupel, M. Ocafrain, E. Dolhem, J. C. Folest, R. Barhdadi, *Can. J. Chem.* **1998**, *76*, 1013−1019.

[216] C. Amatore, A. Jutand, J. Périchon, Y. Rollin, *Monatsh. Chem.* **2000**, *131*, 1293−1304.

[217] F. W. Hartstock, L. B. McMahon, I. P. Tell, *Tetrahedron Lett.* **1993**, *34*, 8067−8070.

[218] I. Chiarotto, M. Feroci, *Tetrahedron Lett.* **2001**, *42*, 3451−3453.

[219] G. Filardo, A. Galia, F. Rivetti, O. Scaldone, G. Silvestri, *Electrochim. Acta* **1997**, *42*, 1961−1965.

[220] F. W. Hartstock, D. G. Herrington, L. B. McMahon, *Tetrahedron Lett.* **1994**, *35*, 8761−8764.

[221] J. Tsuji, M. Minato, *Tetrahedron Lett.* **1987**, *28*, 3683−3686.

[222] T. Inokuchi, L. Ping, F. Hamaue, M. Izawa, S. Torii, *Chem. Lett.* **1994**, 121−124.

[223] K. Otsuka, Y. Shimizu, I. Yamanaka, *J. Chem. Soc., Chem. Commun.* **1988**, 1272−1273.

[224] A. Böttcher, H. Elias, L. Müller, H. Paulus, *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 623−625.

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