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Electron transfer in organonickel complexes of α-diimines: Versatile redox catalysts for C–C or C–P coupling reactions – A review

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Abstract

Organonickel complexes with α-diimine ligands play an important role in electrocatalytic C–C or C–P cross coupling reactions. The review summarises recent insights into the reaction mechanisms of such reactions obtained by electrochemical experiments, electrosynthesis and spectroelectrochemistry (UV–vis–NIR or EPR). The (formal) oxidations states of the involved nickel species range from Ni(0) to Ni(III).
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1. Introduction

Nickel catalyzed cross-coupling reactions to make new C–C and C–P bonds have become very powerful tools in synthetic organic chemistry [1–3]. Homogeneous catalysis has been increasingly used since it can offer valuable advantages, notably in terms of selectivity and efficiency. Electrochemistry is connected to this field in many ways [4–10]. Electrochemical methods enable one to synthesise many organometallic compounds, study the reactivity of coordination compounds and elucidate possible reaction mechanisms. In recent years, the use of electrochemically generated catalysts in reactions of organic compounds has assumed great importance both in organic synthesis and in thorough investigations into electron transfer, bond cleavage, substitution, addition and other reactions [4–17].

Understanding mechanistic details of catalyzed reactions may pave the way to the design of new and improved catalysts. Reactions catalysed by transition metals proceed through catalytic cycles involving metal complexes in different oxidation states. Consequently, they can be readily detected and characterised by electrochemical methods (voltammetry, amperometry, chronoamperometry, etc.). These methods also allow to estimate the reactivity of metal complexes. Presently, stationary and transient voltammetry are most readily available [18]. Cyclic voltammetry can also be used for generation of stable or short-lived organometallic species through successive electron transfers and chemical reactions in the redox process of metal complexes. Knowledge of the absolute number of electrons involved in an electrochemical process allows to determine oxidation states of a cascade of complexes, which can be generated from a particular stable complex. The kinetics of reactions of electrogenerated species with a particular substrate can be controlled by increasing the rate of the potential scan in cyclic voltammetry (or decreasing the pulse duration in chronoamperometry), thus reducing

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the time scale of the chemical reaction. Hence, intermediate species can be generated and/or identified and their reactivity can be characterised. However, although electrochemical methods provide a way of studying the kinetics and thermodynamics of reactions, they give no information on the structures of intermediates.

Electrochemical methods in combination with spectroscopy (spectroelectrochemistry) like NMR, IR, UV–vis–NIR absorption, EPR or EXAFS have shown to provide detailed characterization of species involved in sequential electrochemical and chemical reactions including structural data [19].

Fundamental information regarding the catalytic and electrochemical functionalisation of organic halides by nickel complexes of α-diimines such as 2,2′-bipyridine (bpy) to produce organics and organophosphorous compounds (Scheme 1) will be accumulated in this review. Based on a combination of electrochemical experiments, preparative electrochemistry, spectroelectrochemical methods (UV–vis–NIR) applied on isolated compounds and electrocatalytical investigations, a strong mechanistic foundation for carbon–carbon and phosphorus–carbon cross coupling reactions will be developed also addressing the frequent question of (formal and real) oxidation states [20] of involved complex species.

Apart from the lower price compared to the precious platinum metals palladium or platinum, the use of nickel is mainly motivated by the fact that nickel possesses a very favourable combination of properties to meet the requirements for an organic reaction to take place via coordination: sufficiently low ionization potential to favour oxidative addition; sufficiently weak metal–carbon bonds; tendency to form square-planar complexes and to reach penta-coordination to allow insertion; sufficiently high electron affinity to allow reductive elimination. Some properties are conflicting and a compromise has to be reached [21–23]. Thus, among the important properties of nickel complexes, which define their catalytic activity, it is necessary to term: high electron affinity of Ni(II) complexes (low reduction potential) and the ability to accept different oxidation states (0, +1, +2, +3, +4) at different stages of a catalytic cycle.

A mechanism for the C–C coupling reactions was initially proposed by Amatore and Jutand for corresponding diphosphine (dppe) complexes and the formation of biaryl
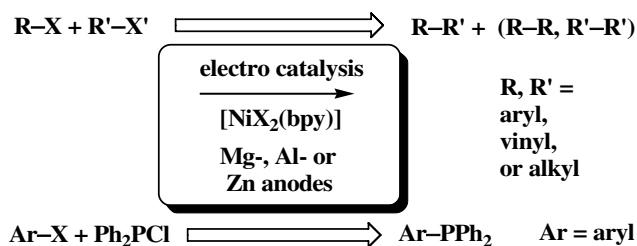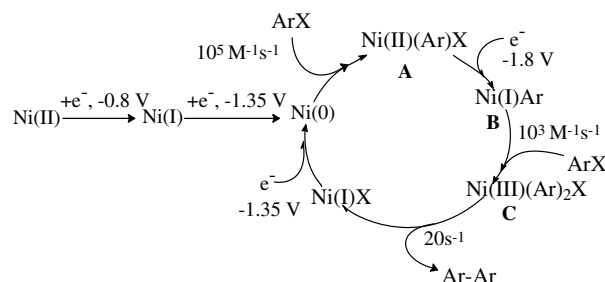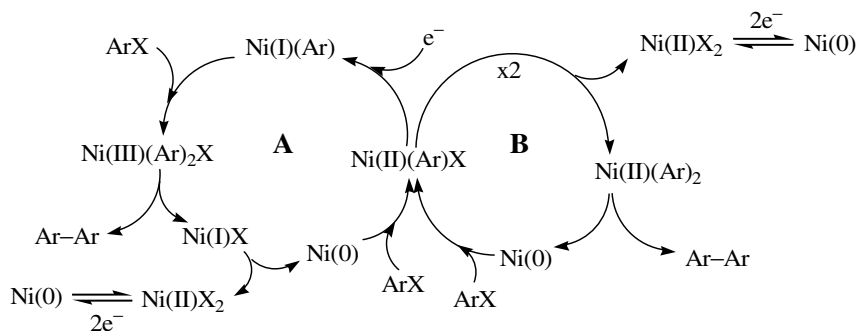

Scheme 2. Proposed mechanism for the C–C coupling reaction (Ar = aryl) for phosphine based Ni catalysts. Potentials are given vs. SCE [27].

from aryl halides ArX (Scheme 2) [10,24–26]. Under the reductive conditions the Ni(II) precursor complexes were successively reduced to Ni(0). The following oxidative addition, which is very often a key step in processes catalysed by nickel complexes, activates the substrate ArX. The thus formed σ-aryl-nickel intermediate **A** is then reduced to the corresponding Ni(I) complex **B** followed by the transformation into the diarylnickel(III) complex **C**. The complex **C** is subjected to reductive elimination to form the corresponding product and a Ni(I) complex from which Ni(0) is generated to restart the cycle [10,24–26]. Hence, homocoupling proceeds through intermediate paramagnetic [Ni(I) and Ni(III)] and diamagnetic [Ni(0) and Ni(II)] species. The threshold potential of −2 V with respect to a saturated calomel electrode (SCE), was demonstrated to be crucial for the formation of biphenyl. Note that for the conversion of potentials referenced to SCE to the nowadays frequently used ferrocene/ferrocenium couple a value of +0.46 V has to be added in DMF as solvent [27].

At less cathodic potentials, the reaction affords the phenylnickel derivative, which needs to be reduced for the cyclic process to occur. It should be noted that the proposed scheme proposed is mainly based on voltammograms [10,24–26] and lacks largely of experimental support because apart from [Ni(II)(Ph)Br(dppe)] [24] none of the postulated intermediates was isolated or identified. Equations describing the kinetical characteristics of the assumed sequence of reactions were derived and the rate constants of different steps were calculated. It is believed that reductive elimination is the rate-determining step.

By analogy with the reactions catalysed by Ni(dppe), two hypothetical catalytic cycles involving the formation of a σ-arylnickel intermediate were proposed for the reactions in the system containing 2,2′-bipyridine (bpy) (see Scheme 3). In the catalytic cycle A [10,12,28], the Ni(I)X complex, which is derived from the Ni(III) complex in the step of reductive elimination, undergoes disproportionation into Ni(0) and Ni(II). The resulting Ni(II) species is subject of reductive activation. In the next step of the catalytic cycle the Ni(0) species activates the aryl halide substrate ArX by oxidative addition. Subsequent electrochemical reduction and further oxidative addition leads to the Ni(III) complex which forms the starting point of these considerations. An alternative mechanism assumes

Scheme 1. Electrocatalytic C–C or C–P coupling reactions of aryl-, vinyl- or alkyl halides.

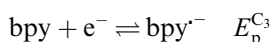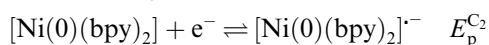Scheme 3. Proposed mechanisms for the C–C coupling reactions (Ar = aryl) for bpy-based nickel catalysts.
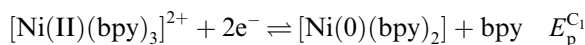
the formation of biaryl from diarylnickel species formed in the course of self-metathesis (transmetallation) of σ-aryl-nickel(II) complexes [Ni(Ar)X(bpy)]. The resulting dihalo-nickel(II) complexes were reduced to [Ni(0)(bpy)] and subsequent oxidative addition of ArX leads back to the haloarylnickel(II) complexes (catalytic cycle **B**) [12,29,30].

Many key steps of these proposed mechanisms of reactions were based singly on electrochemical and derived kinetic data [10,12,28–30], but remained largely without further sufficient substantiation from preparative chemistry or spectroscopy.

2. Results and discussion

2.1. Preparative (electro)chemistry and electrochemical investigations

The electroreduction of Ni(II) complexes [Ni(bpy)$_3$]X$_2$ (X = Br or BF$_4$) occurs via three reversible successive stages of electron transfer (Fig. 1) [10,12,16d,28]:

$$[\text{Ni(II)(bpy)}_3]^{2+} + 2e^- \rightleftharpoons [\text{Ni(0)(bpy)}_2] + \text{bpy} \quad E_p^{C_1}$$

$$[\text{Ni(0)(bpy)}_2] + e^- \rightleftharpoons [\text{Ni(0)(bpy)}_2]^{\cdot-} \quad E_p^{C_2}$$

$$\text{bpy} + e^- \rightleftharpoons \text{bpy}^{\cdot-} \quad E_p^{C_3}$$

The four-coordinated complex [NiBr$_2$(bpy)] shows essentially the same behaviour (Fig. 2) [28,31,32]. In the presence of aryl bromides, the anodic component of the first wave
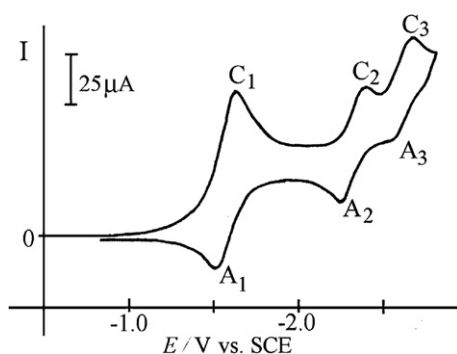
(C$_1$) disappears, and two new waves (C$_3$ and C$_4$) emerge at more negative potentials.

The waves C$_3$ and C$_4$ are supposed to correspond to the reduction of the products of oxidative addition, i.e. nickel σ-aryl complexes [Ni(Ar)Br(bpy)]. A number of such complexes have been prepared independently either by electrochemical means [28,32,33] or by chemical methods (see Scheme 4, reaction A) [34–37]. In this latter case also other α-diimine ligands were introduced and the complexes were submitted to detailed studies of their electrochemical properties using electrochemical and spectroelectrochemical (UV–vis–NIR and EPR) methods [38]. Also their general chemical and physical properties were investigated by optical spectroscopy, XRD and EXAFS spectroscopy in combination with quantum chemical calculations [35–37].

For the sake of completeness the preparative routes to aryl nickel complexes [Ni(Ar)X(bpy)] from [Ni(Et)$_2$(bpy)] and aryl halides ArX (Ar = Ph, 2-Tol, 3-Tol, 4-Tol and 2-ClPh, X = I, Br or Cl) [39], or using the oxidative addition reaction of aryl halides to [Ni(COD)$_2$] (COD = 1,5-cyclooctadiene) have to be quoted [30,32,40].

All these investigation have proved unequivocally the earlier assumptions and thus the first step of the catalytic cycle (oxidative addition to Ni(0) and formation stable arylnickel(II) complexes) is established. It also became evident, that *ortho*-substitution on the phenyl co-ligand is crucial for the stability of the organonickel complexes,
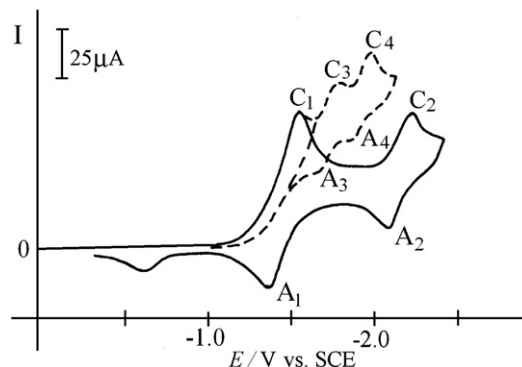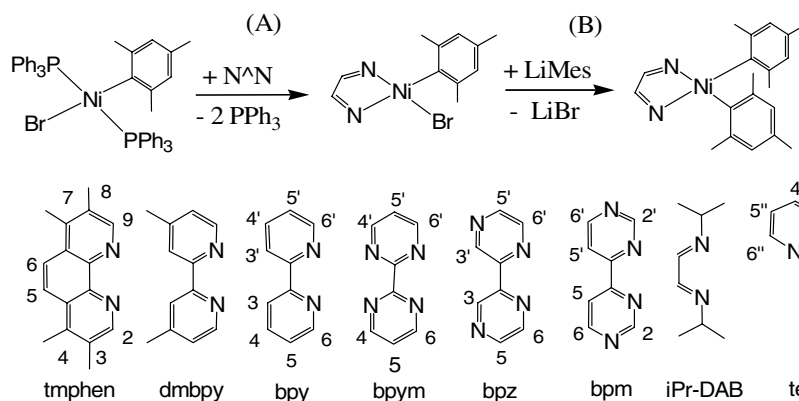

Fig. 1. Cyclic voltammogram for [Ni(bpy)$_3$](BF$_4$)$_2$ (10^{-2} M) in DMF/Et$_4$NBF$_4$ (10^{-1} M). Potentials vs. SCE.

Fig. 2. Cyclic voltammograms for [NiBr$_2$(bpy)] (10^{-2} M) in DMF/Et$_4$NBF$_4$ (10^{-1} M) in the absence (full line) and presence (dashed) of PhBr. Potentials vs. SCE.

Scheme 4. Preparation of mesitylnickel(II) complexes with various α-diimine ligands. Tmphen = 3,4,7,8-tetramethyl-1,10-phenanthroline, dmbpy = 4,4′-dimethyl-2,2′-bipyridine, bpy = 2,2′-bipyridine, bpym = 2,2′-bipyrimidine, bpz = 2,2′-bipyrazine, bpm = 4,4′-bipyrimidine, i-Pr-DAB = N,N′-diisopropyl-1, 4-diazabutadiene, terpy = 2,2′,6″-terpyridine.

but at the same time the rate of oxidative addition to electrogenerated [Ni(0)(bpy)] species decreases with increasing substitution: PhI > PhBr > 2-TolBr > MesBr [9a,33], a series which strongly reminds to Kochi's sequence of the rate of oxidative addition to Ni(0) phosphine complexes: PhBr > 2-TolBr > 2,6-XylBr > MesBr [41].

The σ-complex [Ni(II)(Mes)Br(bpy)] is very stable and exists in air for indefinitely long time. Recently the complex was shown to be an excellent catalyst precursor for the oligomerisation of ethylene [32]. It can be prepared by the reduction of [NiBr$_2$(bpy)] in the presence of MesBr (1:1) at a potential $E_p^{C_1}$ of −1.55 V (vs. SCE), passing of 2F (Fig. 3) [28,32].

In the presence of two equivalents MesBr the four-electron reduction of [NiBr$_2$(bpy)] results in the selective formation of the dimesityl nickel complex [Ni(Mes)$_2$(bpy)] [28], the electrochemical response is shown in Fig. 3. This complex could be isolated from the electrolysed solution and characterized by methods of spectroscopy and elemen-
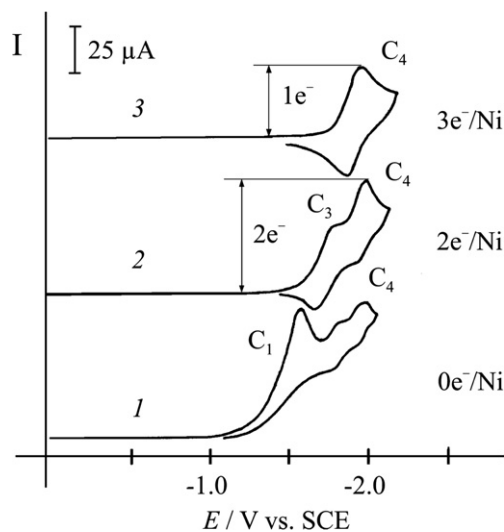

Fig. 3. Cyclic voltammograms for [NiBr$_2$(bpy)] (10^{-2} M) in DMF/Et$_4$NBF$_4$ in the presence of MesBr (2×10^{-2} M) before electrolysis (1), after 2e$^-$ per molecule of Ni complex (2), and after 4e$^-$ per molecule of nickel complex (3) Ni:MesBr = 1:2. Potentials vs. SCE.
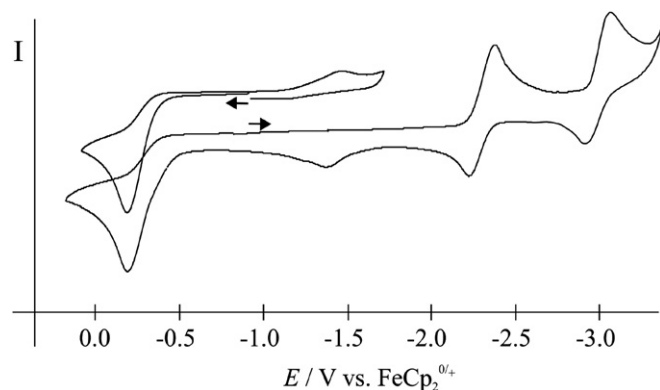

Fig. 4. Cyclic voltammograms of [Ni(Mes)$_2$(bpy)] in THF/n-Bu$_4$NPF$_6$, scan rate 100 mV/s at 298 K.

tal analysis. The independent chemical synthesis (Scheme 4, reaction B) fully confirmed its integrity [35–37].

The dimesityl complexes [Ni(Mes)$_2$(N^N)] (N^N = various α-diimine ligands) exhibit full reversibility on the first two reduction processes (Fig. 4) [37,38]. Quantum chemical calculations have revealed almost exclusively bpy π*-centred lowest unoccupied molecular orbitals (LUMO) for [Ni(Mes)$_2$(bpy)] [35] and spectroelectrochemical investigations (UV–vis–NIR and EPR, see also later) have unequivocally proved the bpy-centred character of the reduced species [Ni(II)(Mes)$_2$(bpy)]$^{n-}$ (n = 1 and 2) [37,38]. Oxidation of the complex leads to rapid decomposition. Since the 1e$^-$-oxidation is believed to occur mainly nickel-centred, we suppose that the corresponding Ni(III) species are not stable and undergo rapid disproportionation. We have tried to analyse the material from corresponding electrolysis experiments but we could not identify clear products so far. This is probably due to the sterically restricted ability of mesityl to undergo a clean biaryl elimination as depicted in Scheme 3 (cycle A). For further studies we will therefore switch to less hindered systems.

The bromo mesityl complexes [Ni(Mes)Br(N^N)] exhibit rather complex electrochemical behaviour at 298 K as shown in Fig. 5 for the bpy derivative.

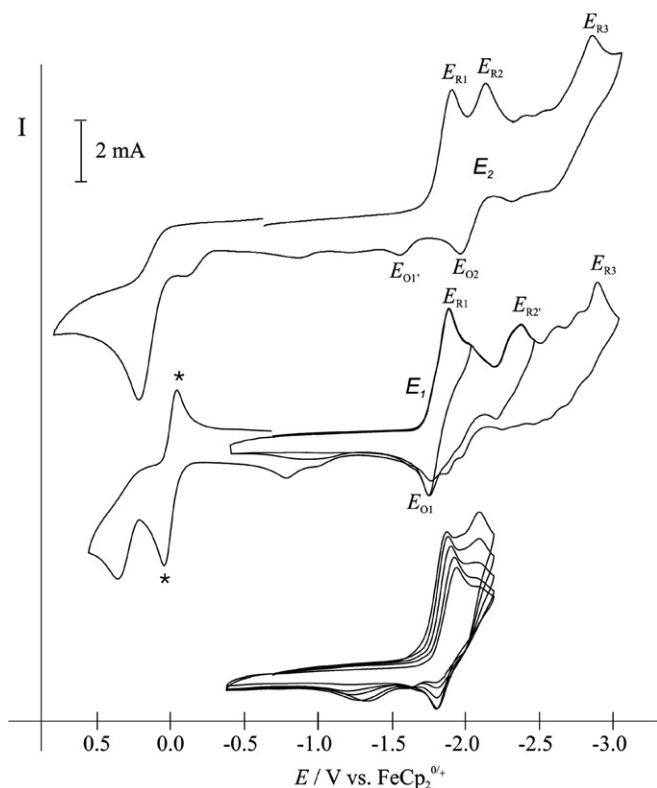Fig. 5. Cyclic voltammograms of [Ni(Mes)Br(bpy)] in THF/n-Bu$_4$NPF$_6$ at 298 K (top), in DMF/n-Bu$_4$NPF$_6$ at 238 K (middle), and DMF/n-Bu$_4$NPF$_6$ at temperatures varying between 238 K and 278 K (bottom), * marks redox waves of the ferrocen/ferrocenium standard.

A reversible wave E_2 (E_{R2}/E_{O2}) was observe after a first irreversible reduction wave (E_{R1}) for the more basic ligands tmphen, dmbpy or bpy. The cathodic peak potentials E_{R1} and E_{R2} increase (shift positively) along the series tmphen > dmbpy > bpy > bpym > bpz > iPr-DAB > bpm [38]. This series represents decreasing basicity or increasing π-accepting ability, which goes along with low lying π* LUMOs, of the diimine ligand. On the reverse scan a re-oxidation wave ($E_{O1'}$) is observed at around −1.5 V. The two reduction waves were followed by further waves. They are partly reversible (E_{R3}) for the less basic ligands. An exception for this complex behaviour can be observed for the terpy complex [Ni(Mes)(terpy)]$^+$ for which two reversible reduction waves were found [38].

At low temperatures (213 K) the situation is altered (Fig. 5). The process E_1 (E_{R1}/E_{O1}) is fully reversible already at normal scan rates. Compared to measurements at 298 K the peaks E_{R2} and E_{R3} are much smaller and further small reduction waves like e.g. $E_{R2'}$ were observed. We can therefore conclude that E_2 and E_3 are processes due to products emerging from the first electrochemical reduction (E) followed by a chemical reaction (C) (EC mechanism). Evidence that the C process is the cleavage of bromide comes from the reversible behaviour of the terpy complex and the dimesityl complexes (Fig. 4) as well as from increasing reversibility of the E_1 process upon addition of excess n-Bu$_4$NBr. The EC mechanism was also the conclu-

sion from the preparative electrochemistry described above [28,32,33] and has been established for a number of diimine complexes of other transition metals such as Ru, Os, Rh, Ir or Re with halide co-ligands [18b,42–44], and also for related phosphine complexes of Pd and Ni [4,25,45] .

For the diimine complexes [Ni(Mes)Br(N^N)] we may now draw a reaction scheme (see Scheme 5) to illustrate the proposed EC mechanism as well as the further feasible electrochemical or chemical reactions.

The first reduction (E_1) is followed by a rapid cleavage of bromide (C$_1$). The transient 15 VE species can be stabilised by coordinating a solvent molecule (C$_2$) or by dimerisation (C$_{2'}$). The solvent complexes can be described by two different canonical forms [Ni(II)(Mes)(Solv)(N^N$^{\cdot-}$)] ↔ [Ni(I)-(Mes)(Solv)(N^N)] either with a reduced diimine ligand or with monovalent nickel. The dimerisation occurs upon formation of a Ni–Ni bond with a formal Ni(I)–Ni(I) unit. The E_{R2} and E_{R3} processes might thus correspond to the reduction of the solvent complexes or dimers respectively. At low temperatures the chemical processes are hampered and therefore we can observe partially the second reduction wave of the parent complexes $E_{R3'}$.

To support the assumptions depicted in Scheme 5 it was tried to isolate defined products from solutions of [Ni(Mes)Br(bpy)] in THF/Bu$_4$NPF$_6$, which had been submitted to bulk electrolysis [38] or chemical reduction using sodium/benzophenone [46]. When the electrolysis was not driven to completeness, the main species isolated was the starting material together with the free ligand bpy as by-product. After exhaustive electrolysis mainly free bpy ligand and traces of the dimesityl complex [Ni(Mes)$_2$(bpy)] were found, as mentioned already above. The chemical reduction gave, after flash evaporation of the solvent, a heterogeneous material consisting of violet and green parts. Purification and analysis of the product revealed the violet product to be [Ni(Mes)$_2$(bpy)]. Under the work-up conditions (ambient temperature) we obtained violet solutions from the green material, containing the dimesityl complex and bpy in a 1:1 ratio. We assume that the green dimer [(bpy)(Mes)Ni–Ni(Mes)(bpy)] undergoes a rapid decomposition. This fits well into the observation that upon 4e$^-$-reduction of [NiBr$_2$(bpy)] in the presence of 2 equiv. of MesBr the dimesityl complex is obtained in high yields [28,33]. Very probably the formal Ni(I)–Ni(I) dimer complex decomposes to [Ni(II)(Mes)$_2$(bpy)] and [Ni(0)(bpy)] and the latter is not stable under these conditions. However in the presence of MesBr other pathways may be at work in the formation of [Ni(Mes)$_2$(bpy)].

2.2. Spectroelectrochemistry

In order to further support the above assignments the products were examined using spectroelectrochemical techniques (UV–vis–NIR or EPR) [38].

The UV–vis–NIR and EPR spectroelectrochemistry of the dimesityl complexes (e.g. see Fig. 6) revealed clearly the diimine(π*)-centred character of the first two reduc-
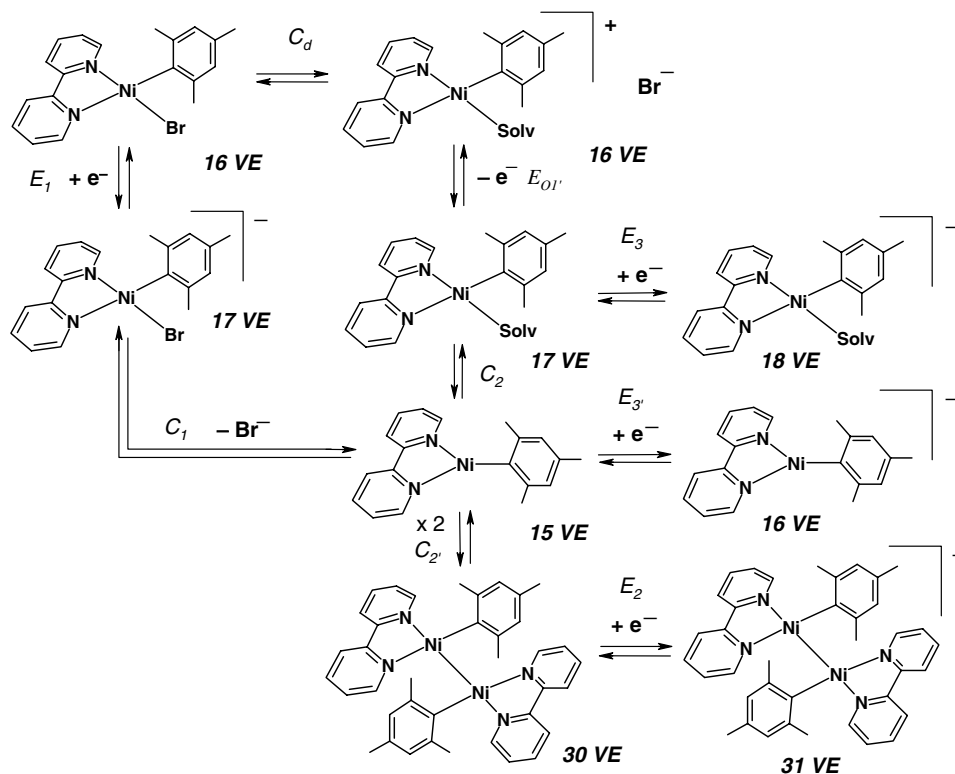
Scheme 5. Proposed mechanism scheme for electrochemical (E) and chemical reactions (C).

tions. The same spectroelectrochemical experiment for the bromo mesityl complex of bpy can be seen in Fig. 7. The first finding was, that the observed absorption bands of the 1e$^-$-reduced complex were concentration dependent. At high concentrations (about 5×10^{-2} M) the spectrum is characterised by a weak broad long-wavelength band around 1300 nm, two medium strong bands around 600 nm and 350 nm and a very strong band at 300 nm. In
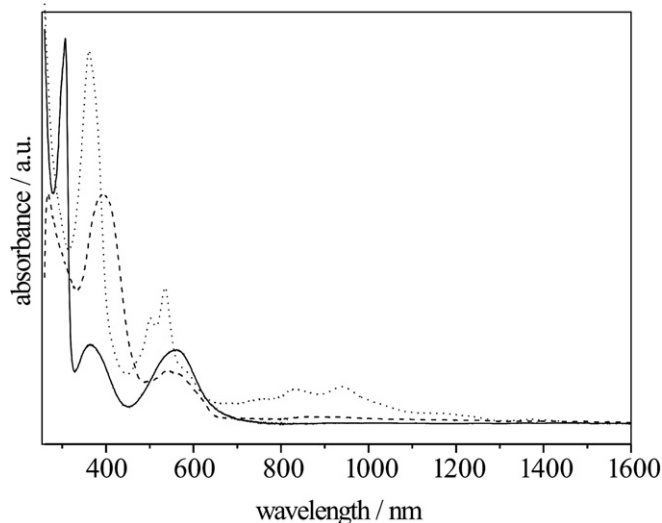

Fig. 6. Absorption spectra of [Ni(Mes)$_2$(bpy)]^n ($n = 0$: solid line, −1: dotted and −2: dashed) from UV–vis–NIR spectroelectrochemistry in DMF/n-Bu$_4$NPF$_6$. Note that in the last spectrum there is some residual absorption around 900 nm, which is due to incomplete second reduction.
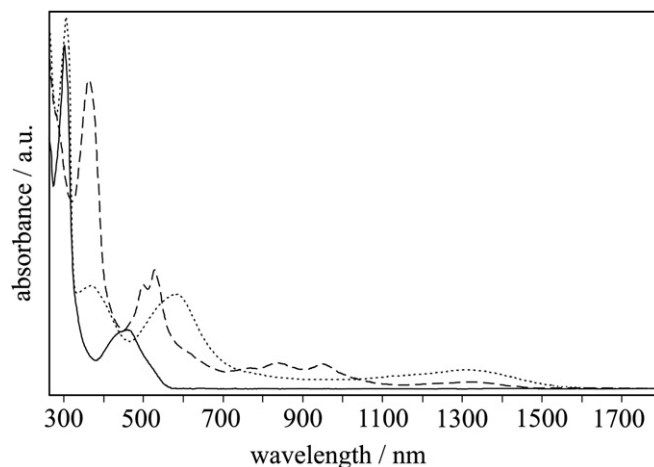

Fig. 7. UV–vis–NIR spectroelectrochemistry of [Ni(Mes)Br(bpy)] in DMF/n-Bu$_4$NPF$_6$. Absorption spectra of the parent compound (solid), after 1e$^-$-reduction, spectrum at higher concentration (about 5×10^{-2} M, dotted) and dilute solution (about 10^{-4} M, dashed).

dilute solutions ($<10^{-4}$ M) two structured band systems around 900 nm and 500 nm were visible together with a UV band around 350 nm. At 1300 nm there is only a very weak residual absorption. Medium concentrated solutions show all the so far described band systems simultaneously. In view of the dimesityl system (Fig. 6) and corresponding spectra of the free ligands [47], we can ascribe the spectral features of dilute solutions to a species containing a reduced bpy ligand and we assume this to be the radical complex [Ni(Mes)(Solv)(bpy$^{\bullet-}$)]$^{\bullet}$. Apart from the 1300 nm

band, the spectra of concentrated solutions resemble those of the starting complex. This species is tentatively assigned to the dimer [(bpy)(Mes)Ni–Ni(Mes)(bpy)], since it does not seem to contain reduced bpy as ligand [38,47]. The 1300 nm band might be ascribed to a transition arising from the Ni–Ni bond (probably a σ–σ* transition). Interestingly for the good acceptor ligands like bpz or bpm the spectra do not reveal any signal attributable to a dimer. Obviously the formation and stability is strongly dependent of the properties of the α-diimine ligand.

The spectral responses to further reduction confirm that the last obtained spectrum represents a mixture of the mononuclear species [Ni(Mes)Br(bpy·⁻)]⁺ and the dimer [(bpy)(Mes)Ni–Ni(Mes)(bpy)] [38] and are in agreement with the smaller size of the further reduction wave behind E_{R2}.

Reductive EPR-spectroelectrochemistry confirms these results. Firstly the EPR spectra of the anion radicals of the dimesityl nickel complexes [Ni(Mes)₂(N^N)]·⁻ all exhibit relatively narrow resonances with hyperfine splitting (HFS) in the range of 0.1–0.5 mT. Such HFS constants are typical for couplings of the unpaired electron to the protons and nitrogen atoms of the diimine ligand. Together with the g values, which are close to the free-electron value of 2.0023, this is a strong indication for an almost pure π* (diimine) character of the singly occupied molecular orbital (SOMO). At low temperatures in glassy frozen solutions a rhombic type spectrum was obtained for [Ni(Mes)₂(bpy)]⁻ with $g_1 = 2.014$, $g_2 = 2.004$ and $g_3 = 1.996$. The averaged value is in agreement with $g_{iso} = 2.0049$. The small g anisotropy $\Delta g = 0.018$ is indicative of a quite small metal contribution to the radical anion and a mainly diimine (π*)-centred SOMO.

For [Ni(Mes)Br(bpy)] the first reduction gives rise to a narrow signal at $g = 2.0016$, with partial HFS (Fig. 8, left). Electrolysis at more negative potential (second wave) first leads to an increase of the intensity of this signal and after a few minutes a second comparably broad signal appears (Fig. 8, right) which lies at far higher $g = 2.140$ and does not show any HFS. Measurements of this solution at 110 K (glassy frozen solution) reveal that the high-g species now exhibits as a rhombic type of spectrum, whereas the low-g species remains isotropic and narrow (Fig. 9).

The results for the complexes with the other α-diimine ligands were essentially the same and we can assign the signals with g values around the value of the free electron (2.0023) and detectable HFS to monomeric Ni(II) complexes containing reduced diimine ligands [Ni(Mes)L(N^N·⁻)] (L = Br or solvent). The broad and high-g signal after prolonged electrolysis for N^N = bpy point to a far higher nickel contribution to the unpaired electron in this species, which is in line with the assumption that the corresponding species is the proposed dimer in its reduced state [(bpy⁻)(Mes)Ni(I)–Ni(I)(Mes)(bpy)]·⁻. In agreement with the observations during the UV–vis–NIR spectroelectro-chemical investigations for the good acceptor ligands like bpz or bpm, no such broad signal, attributable to a dimer, was observed in corresponding EPR experiments.

Oxidation of the Ni(II) complexes [Ni(Mes)Br(N^N)] leads to very short-lived trivalent nickel species (see also Section 2.1) which have escaped spectroscopic characterization so far. However the related perfluorinated radical complex [Ni(Fmes)Br(PPh₃)₂]·⁺ has been characterised by EPR spectroscopy recently [38]. For this complex an almost pure metal-centred character for the SOMO can be concluded from the very high g anisotropy of the rhombic signal obtained at 4 K ($\Delta g = 0.878$). There is evidence that carbanionic ligands enhance the metal-centred character of formal Ni(III) species.

2.3. Electrocatalytic C–C coupling reactions

Because the model *o*-tolylbromide (2-TolBr) enters into all reactions of cross-coupling and, at the same time, it forms a stable σ-complex, [Ni(2-Tol)Br(bpy)], as a result of oxidative addition, it was broadly used to study mechanisms of electrocatalytic reactions. Thus, the pathways of catalytic cycle for cross-coupling process of aromatic and heteroaromatic halides were established. Mechanism of this process includes the stages of oxidative Ni(0) addition to organic halide with formation of σ-complex, [Ni(Ar)X(bpy)], its reduction to [Ni(Ar)(bpy)], reaction of the latter with other Ar'X molecule yielding presumably [Ni(Ar)(Ar')X(bpy)] and reductive elimination to the cross-coupling product (induced by electron transfer, in some instances) as depicted in Scheme 3. Thus the same
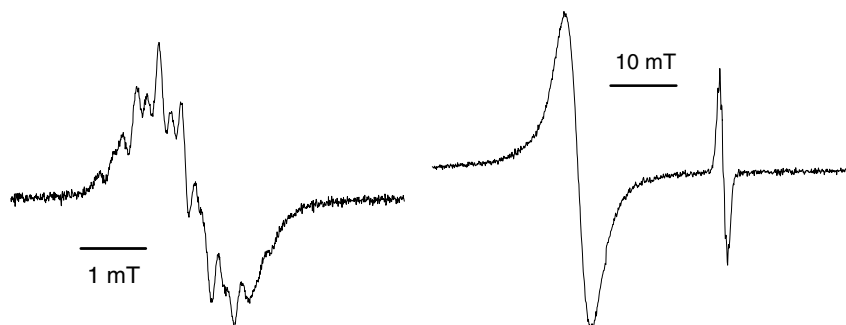

Fig. 8. EPR spectra obtained during electrochemical reduction of [Ni(Mes)Br(bpy)] in THF/*n*-Bu₄NPF₆ at 298 K. Signals obtained upon first reduction (left) and second reduction (right).
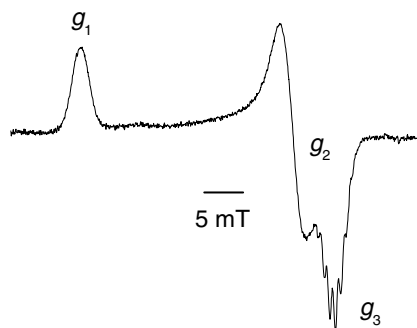
Fig. 9. EPR spectrum of a solution obtained at the second reduction wave, measured at 110 K (glassy frozen solution). Overlapping with the g_3 component of the main signal is the isotropic spectrum (with HFS) of the monomeric complex.

reaction as depicted in Fig. 3 was carried out with a number of substrates RX (R = aryl or alkyl) under limiting conditions [28,33]. As a result, the following sequence of substrate reactivity (k_0-rate constants for the oxidative addition) was derived from kinetic data: MesBr < n-BuBr < 2-TolBr < PhBr < 2-Cl-thiophene < PhI < i-C$_5$H$_{11}$I < i-C$_3$H$_7$I.

$$[\text{Ni(Ar)(bpy)}] + \text{RX} \xrightarrow[\text{oxidative addition}]{k_0} [\text{Ni(Ar)(R)Br(bpy)}]$$
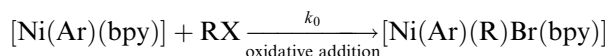
From these studies we can say that a particular complex can either serve as an efficient catalyst of homocoupling of organic halides or be poorly active or even inactive in cross-coupling of two different RX. In the general case, the efficiency of the catalyst depends on the following factors.

1. The possibility of rapid regeneration of the catalyst, i.e., the number of catalytic cycles.
2. The reaction rate of reductive addition of the aryl-nickel intermediate to aryl halide must be higher than the rates of its competitive decomposition, protonation, etc.
3. The reaction rate of reductive elimination of the complex [Ni(Ar^1)(Ar^2)X(N^N)] must be rather high for regeneration of the catalyst (conceivably, promoted by the electron transfer) to be successful.
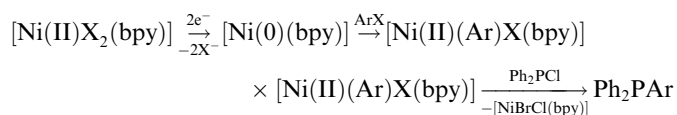
2.4. Electrocatalytic C–P cross-coupling reactions

A convenient method for electrosynthesis of tertiary phosphines from organic halides and chlorophosphines catalysed by nickel complexes was recently elaborated and the electrochemically synthesized stable σ-complex [Ni(2-Tol)Br(bpy)] proved to be a convenient model for studying the mechanism of the formation of phosphines [6,9,28]. Also unsymmetrical tertiary phosphines under mild conditions and with rather high yields were accessible by this method (including ligands for heterobinuclear and water-soluble complexes). Some of these compounds are not easily accessible and/or expensive when synthesised by usual classical methods. The method consists in electroreduction of

organic halide in the presence of mono- or dichlorophenyl phosphine added gradually using a Ni-bpy catalytic system in an undivided cell (see Scheme 6) [28].

The method is efficient both for aromatic halides with acceptor and donor substituents in the ring and for heteroaromatic species (pyridine, thiophene, pyrimidine and pyrazole halides). The advantages of it are a single-stage character and mild conditions (room temperature) of the process performance.

We suppose that the first stage of the catalytic cycle is an electrochemical reduction of the Ni(II) precursor to a Ni(0) complex. The latter is able to react with aryl bromide forming the organonickel compound [Ni(Ar)Br(bpy)] (Ar = aryl, see Scheme 6), which reacts with chlorophosphine resulting in formation of the desired product Ph$_2$PAr and regeneration of Ni(II) complex.
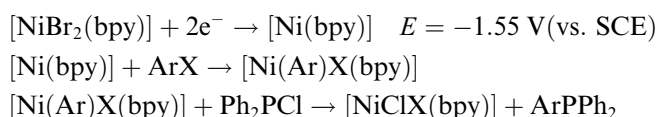
$$[\text{Ni(II)X}_2\text{(bpy)}] \underset{-2\text{X}^-}{\overset{2\text{e}^-}{\rightarrow}} [\text{Ni(0)(bpy)}] \overset{\text{ArX}}{\rightarrow} [\text{Ni(II)(Ar)X(bpy)}]$$
$$\times [\text{Ni(II)(Ar)X(bpy)}] \xrightarrow[-[\text{NiBrCl(bpy)}]]{\text{Ph}_2\text{PCl}} \text{Ph}_2\text{PAr}$$

To support the proposed scheme, chlorophosphine was added to the stable σ-complex, [Ni(2-Tol)Br(bpy)], prepared by electrochemical reduction of [NiBr$_2$(bpy)] in the presence of 2-TolBr. The addition lead to an instantaneous disappearance of the red nickel complex and emergence of green colouring of the solution characteristic for complexes [NiX$_2$(bpy)] (X = Cl or Br)]. Diphenyl(2-tolyl)phosphine and a minor amount of its oxide were isolated from the reaction mixture. We suppose that the triarylphosphines are formed by a transmetallation-like reaction in which the arylnickel(II) species act as arylation agents. In contrast to this, the diphenylphosphide complex [Ni(Ph$_2$P)Cl(bpy)], obtained by procedure analogous to the preparation of the 2-Tol complex, does not react with aryl halides. Furthermore, in order to obtain tertiary phosphines in high yields, it is necessary to carry out the process with uninterrupted addition of chlorophosphine, and at far higher potentials than necessary for the first reduction of the arylnickel(II) complexes [Ni(Ar)X(bpy)]. Therefore we can conclude, that the phosphines are generated by two different pathways. At lower potential (Scheme 7, cycle A) the Ni(0) species is generated and undergoes oxidative addition with aryl halides. They react with the chlorophosphines to give the product ArPPh$_2$.
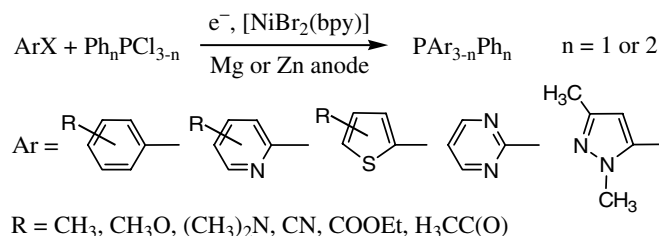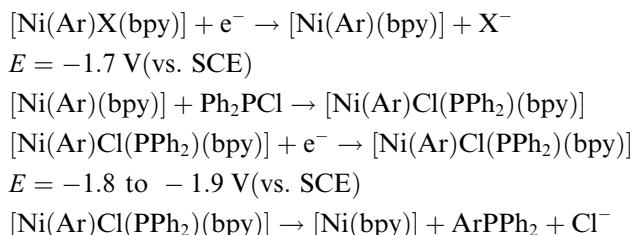

Scheme 6. Overall reaction for the electrocatalytic P–C cross-coupling reaction and substituents used in the study.
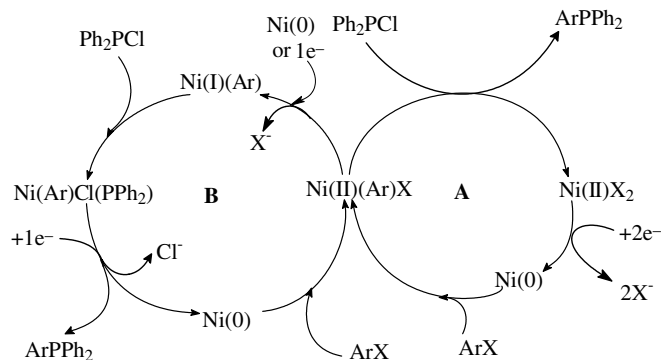
Scheme 7. Proposed mechanisms for the C–P coupling reactions for bpy-based nickel catalysts.

$$[NiBr_2(bpy)] + 2e^- \rightarrow [Ni(bpy)] \quad E = -1.55 \text{ V (vs. SCE)}$$
$$[Ni(bpy)] + ArX \rightarrow [Ni(Ar)X(bpy)]$$
$$[Ni(Ar)X(bpy)] + Ph_2PCl \rightarrow [NiClX(bpy)] + ArPPh_2$$

At higher potential (Scheme 7, cycle B) the products are formed much faster, presumably by the following sequence of reactions:

$$[Ni(Ar)X(bpy)] + e^- \rightarrow [Ni(Ar)(bpy)] + X^-$$
$$E = -1.7 \text{ V (vs. SCE)}$$
$$[Ni(Ar)(bpy)] + Ph_2PCl \rightarrow [Ni(Ar)Cl(PPh_2)(bpy)]$$
$$[Ni(Ar)Cl(PPh_2)(bpy)] + e^- \rightarrow [Ni(Ar)Cl(PPh_2)(bpy)]$$
$$E = -1.8 \text{ to } -1.9 \text{ V (vs. SCE)}$$
$$[Ni(Ar)Cl(PPh_2)(bpy)] \rightarrow [Ni(bpy)] + ArPPh_2 + Cl^-$$

The arylnickel(II) complexes [Ni(Ar)X(bpy)] are reduced and cleave X$^-$, as already discussed for the electrocatalytic C–C coupling. The aryl phosphide complexes [Ni(Ar)Cl-(PPh$_2$)(bpy)] formed by oxidative addition of the chlorophosphine are reduced under the applied conditions and undergo reductive elimination to afford the target compounds (Scheme 7, cycle **B**). As the catalyst is consumed, the reactions of the catalytic cycle **B** become dominant.

It is interesting to append that recently Le Gall et al. reported the advantages of bpy-based catalytic nickel systems over dppe-based analogues for C–P coupling reactions using zinc as reductant [48] or C–P cross coupling with organozinc reagents [49].

3. Conclusions and outlook

In view of our recent results we can substantiate the mechanistic model for the catalytic C–C and C–P coupling reaction catalysed by nickel complexes containing α-diimine ligands and draw some conclusions for the future search for effective catalyst systems.

(1) The oxidative addition of aryl halides ArX to Ni(0) species forming complexes [Ni(Ar)X(N^N)] (Ar = aryl; N^N = α-diimine ligands) has been established.

Derivatives with ortho-substituted aryl co-ligands R can be very stable. The use of electrochemical approach to generate Ni(0) and σ-organonickel complexes appears to have considerable promise. Firstly, this is a possibility to use a catalytic quantity of a complex which will be regenerated on the electrode and, in such a way, will be useful for various substrates. Secondly, it is possible to estimate quantitatively rates of catalytic reactions using an electrochemical approach, and, in some instances, to divide the overall process into separate stages and to evaluate reactivity of intermediates and stability of various forms of metal complex.

(2) Starting from the organometallic Ni(II) complexes [Ni(Ar)Br(N^N)] electrochemical reduction leads to highly reactive radicals which undergo follow-up chemical reactions. The nature of the products could not be established unambiguously, but strong evidence was found from optical and EPR spectroelectrochemistry that radical solvent complexes [Ni(Mes)(Solv)(N^N)]$^{\bullet}$ with a mainly α-diimine ligand-centred SOMO were formed in processes which start with ligand-centred 1e$^-$-reduction, followed by a splitting of the bromide ligand (EC process). Therefore the assumption of Ni(I) species after the first electrochemical reduction must be corrected towards a mainly α-diimine-centred reduction, nevertheless the splitting of the bromide occurs very rapidly, obviously regardless of the character of the SOMO.

(3) For highly sterically hindered systems the formation of the very stable diaryl complexes [Ni(Ar)$_2$(N^N)] may become predominant preventing effective catalysis. For the MesBr system additionally the formation of dimers [(N^N)(Mes)Ni–Ni(Mes)(N^N)] with monovalent nickel could occur, after the splitting of the bromide ligand. However in the presence of additional RX these species are very unlikely.

(4) Oxidation of the isolated Ni(II) complexes [Ni(Mes)Br(N^N)] or [Ni(Mes)$_2$(N^N)] leads very probably to very short-lived Ni(III) species. Therefore, the proposed monomeric Ni(III) species after oxidative addition of aryl halides have gained strong evidence as plausible transient states in the catalytic cycle(s). It seems that organo ligands favour nickel-centred radical states; however, this has been demonstrated for a complex containing phosphine instead of diimine ligands.

Future investigations will focus on the less sterically hindered aryl halides and other organohalides (alkyl, alkynyl), the preparation of corresponding organonickel complexes and their thorough investigations using the method combination described in this report. A second aim will be to examine the nickel-centred oxidation reactions in order to shed light on the reactivity of the formal Ni(III) species, which are supposed to be crucial for the

electrocatalysis, but have escaped spectroscopic characterisation so far.

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