# Coupling of Organic Halides electrocatalyzed by the $Ni^{II}/Ni^{I}/Ni^{0}$–$PPh_3$ System. A Mechanistic Study based on an Electroanalytical Approach

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The coupling of the organic halides bromobenzene, 1-iodobutane, 1-iodo-2,2-dimethylpropane, and benzyl chloride has been carried out by electrochemically generating and continuously recycling the nickel(0) complex promoter [$Ni(PPh_3)_4$]. This species undergoes oxidative addition by organic halides leading to σ-bonded organometallic nickel(II) derivatives. In these complexes the metal–carbon bond can be cleaved either by a straightforward thermal decomposition or by a cathodic reduction, depending upon whether the co-ordinated organic group is an alkyl or an aryl one. In the former case a high yield of the coupling product is obtained only by employing organic halides not bearing hydrogen atoms in the β position; when a β-elimination reaction can occur, the yield of the coupling product is, on the contrary, very low and can be significantly improved only by carrying out the reductive process at more negative potentials, at which a proposed nickel hydride intermediate can be reduced. When the co-ordinated organic group is an aryl one, reductive elimination of the organic group does not occur by thermal decomposition and the coupling product can be formed only by means of a cathodic reduction of the relevant organometallic nickel(II) derivative. An overall mechanism is proposed which is consistent with the data.

THE coupling reaction of organic halides can be achieved by employing inorganic reducing agents, usually nickel or copper compounds.[1-4] However, these syntheses appear to be strictly stoicheiometric [equation (1)] and

$$R'X + R''X + M^n \longrightarrow R'-R'' + M^{n+2}X_2 \quad (1)$$

the only chemical means of renewing the promoter in its original low oxidation state ($M^n$) are the use of Grignard reagents [1] or of zinc powder [5] as the ultimate reductant.

An obvious way of regenerating $M^n$ appears to be the electrochemical reduction of the oxidized species $M^{n+2}X_2$, if such a process can be carried out without reducing the organic reactant and the coupling product. These reactions are unlikely to occur very often, owing to the high overvoltage generally exhibited by organic halides and hydrocarbons in their cathodic reduction. Moreover, the electrochemical reduction offers the advantage of generating the reduced species without at the same time generating an electrophile.

The catalytic coupling of organic halides appears to have been carried out recently by employing nickel species cyclically regenerated by cathodic reduction. It has been reported that, in the cathodic reduction of nickel pentane-2,4-dionate at a copper electrode in the presence of triphenylphosphine and organic halides, coupling products have been obtained in good yield.[6] In this study, although the continuous recycling of the promoter is suggested on the basis of the results presented, no investigation of the mechanism involved is performed.

More recently the coupling reaction of organic halides promoted by nickel(I) complexes with macrocyclic quadridentate ligands was described;[7] the promoters were continuously generated *in situ* by cathodic reduction of the corresponding square-planar nickel(II) complexes formed in the coupling process. A very interesting feature of this paper lies in the fact that it appears to be the first report which offers a methodological and conceptual approach to the understanding of the mechanism by which a metal centre, repeatedly interacting with an electrode surface, can act as a promotion site for a carbon–carbon bond-forming process.

The electrochemical method allows one not only to regenerate cyclically the promoter of the coupling reaction, but also offers the best approach for investigating reaction mechanisms involving redox processes. It can be observed that the synthesis of organic compounds promoted in the homogeneous phase by metal complexes occurs through at least one redox step, involving the metal, in which one of the reagents is activated. In particular, it is well known that in the coupling of organic halides this activation step is their oxidative addition to the metal promoter, originally present in a low oxidation state.

In this connection, it should be noted that on these conceptual bases alone the mechanism of the coupling of aryl halides promoted by [$Ni(PPh_3)_2R(X)$] (R = aryl group) has been recently advanced in the literature.[8]

With the aim of contributing to the emerging trend of employing electrochemical methods for the generation *in situ* of catalytically active metal complexes, we report an electrochemical investigation on the coupling of organic halides carried out by cathodic reduction of nickel(II) in the presence of triphenylphosphine, with particular attention to the mechanistic aspects of the process.

## EXPERIMENTAL

*Chemicals.*—All the chemicals employed were of reagent grade quality. Reagent grade acetonitrile was further purified by distilling repeatedly from phosphorus pentaoxide and afterwards storing on molecular sieves (3 Å) under an atmosphere of nitrogen. The supporting electrolyte tetrabutylammonium perchlorate was prepared from perchloric acid and tetrabutylammonium hydroxide, re-

crystallized from methanol and dried in a vacuum oven at 50 °C.

Stock solutions both of anhydrous nickel(II) perchlorate and of anhydrous perchloric acid were prepared by anodic oxidation in $[NBu_4][ClO_4]$–acetonitrile solutions of metallic nickel [9] and of hydrogen [10] respectively. Triphenylphosphine was recrystallized from methanol and stored in a vacuum oven in the dark.

The complex $[Ni(PPh_3)_2Ph(Br)]$ was synthesized as reported in the literature.[11] Stock solutions of $[Ni^0(PPh_3)_4]$ and $[Ni^I(PPh_3)_4][ClO_4]$ were electrochemically prepared as reported previously.[12]

Fully deoxygenated nitrogen, previously equilibrated to the vapour pressure of acetonitrile, was used in the removal of dissolved oxygen.

*Apparatus and Procedure.*—Voltammetric experiments were carried out in a three-electrode cell. The working electrode was a platinum sphere (geometric area *ca.* 0.05 $cm^2$) surrounded by a Pt spiral counter-electrode. The potential of the working electrode was probed by a Luggin capillary-reference electrode compartment whose position was made adjustable by mounting it on a syringe barrel.

Coulometric and preparative tests were carried out in a H-shaped cell with cathodic and anodic compartments separated by a sintered glass disc. The working electrode was a platinum gauze while a mercury pool was used as counter-electrode.

In all cases a silver–0.1 mol $dm^{-3}$ silver perchlorate electrode in acetonitrile was used as reference electrode.

The voltammetric unit used was a three-electrode system consisting of the MP-System 1000 equipment in conjunction with a digital logic function generator, assembled here.[13] The recording device was either a Hewlett–Packard 7040 A *X-Y* recorder or a Hewlett–Packard Memory Scope 1201 A.

In the controlled-potential electrolyses an AMEL model 552 potentiostat was used with an AMEL integrator model 558 coulometer.

Gas chromatographic analyses were carried out with a Fractovap GU chromatograph equipped with OV 17 silicone on a Chromosorb GAW-DMCS column (high-boiling hydrocarbons), or Carbowax 20 M on a Chromosorb W column (low-boiling hydrocarbons). For quantitative evaluation, the internal standard method was followed; the standards employed were naphthalene in the evaluation of biphenyl and bibenzyl, n-octane for benzene and toluene, and n-hexane for other hydrocarbons.

Gas chromatographic–mass spectrometric (g.c.–m.s.) experiments were performed by using a Fractovap 2150 chromatograph in conjunction with a Hitachi–Perkin-Elmer RMU 6 mass spectrometer.

The electroanalytical measurements were performed, unless otherwise stated, at 20 °C and in all cases with a $PPh_3$ to $Ni[ClO_4]_2$ molar ratio of 5 : 1.

## RESULTS AND DISCUSSION

In a previous paper [12] we reported the cathodic behaviour of nickel(II) perchlorate in the presence of triphenylphosphine in acetonitrile at a platinum electrode.

The obtained voltammetric profile is shown in Figure 1. Nickel(II), present in this case as $[Ni(PPh_3)_2(NCMe)_4]^{2+}$, appears to be directly reduced, in a two-electron irreversible process, to the zerovalent complex $[Ni(PPh_3)_4]$. This species is oxidized to $[Ni(PPh_3)_4]^+$ at the first anodic peak associated with the cathodic one and the so formed nickel(I) complex can be oxidized to nickel(II) or reduced to nickel(0) at the second anodic peak and at the cathodic one, indicated by a dashed line, in Figure 1 respectively. The addition of organic

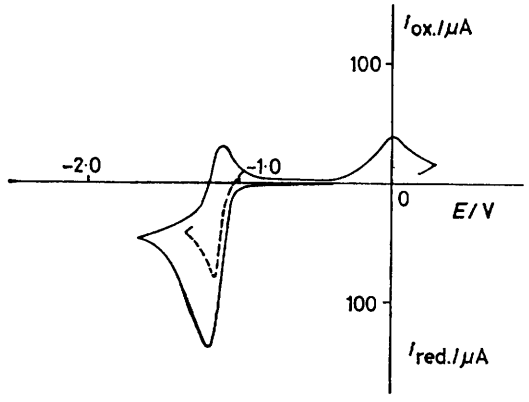



FIGURE 1 Cyclic voltammetric curve recorded with a platinum microelectrode on a $CH_3CN$ solution containing nickel(II) ($3 \times 10^{-3}$ mol $dm^{-3}$), $PPh_3$ (0.1 mol $dm^{-3}$), and $[NBu_4][ClO_4]$ (0.1 mol $dm^{-3}$). Scan rate 0.1 V $s^{-1}$

halides causes profound changes in the reported voltammetric behaviour which is found to depend markedly on the nature of the organic substrate employed. For this reason, the different cases will be examined in the following sections.

*Bromobenzene.*—When cyclic voltammograms were run for nickel(II)–$PPh_3$ solutions to which $C_6H_5Br$ was added stepwise, the behaviour illustrated in Figure 1 was progressively modified until the profile shown in Figure 2

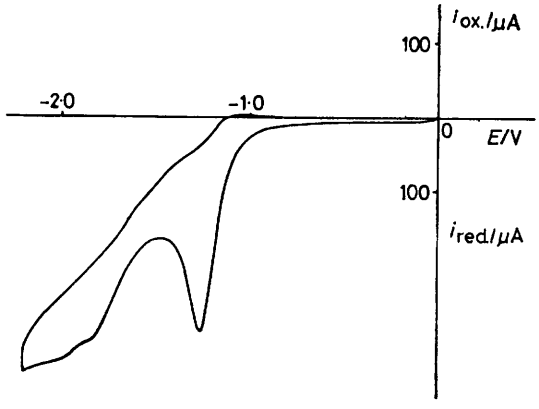



FIGURE 2 Cyclic voltammetric curve recorded with a platinum microelectrode on a $CH_3CN$ solution containing nickel(II) ($6 \times 10^{-3}$ mol $dm^{-3}$), $PPh_3$ ($3 \times 10^{-2}$ mol $dm^{-3}$), $C_6H_5Br$ (0.6 mol $dm^{-3}$), $[NBu_4][ClO_4]$ (0.1 mol $dm^{-3}$). Scan rate 0.1 V $s^{-1}$

was obtained (the direct reduction of $C_6H_5Br$ occurs at *ca.* −2.5 V). The nickel(II) reduction peak remained unchanged, while the anodic peaks due to the stepwise nickel(0) oxidation appeared to be no longer associated with this process. Moreover, two additional reduction peaks, which merge into a broad distorted one and

whose height increased with bromobenzene concentration, appeared at more negative potentials.

Controlled-potential coulometric experiments carried out on $PPh_3$-containing nickel(II) solutions at −1.3 V [first peak for nickel(II) reduction in the presence of

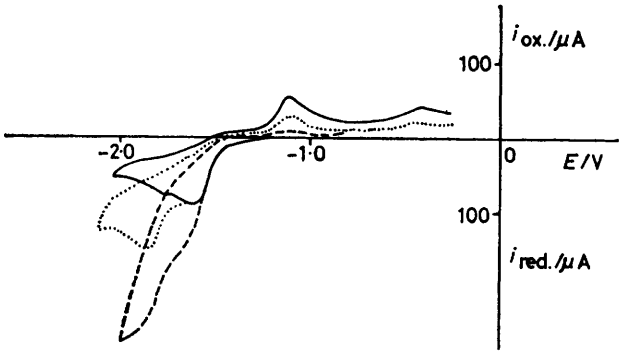



FIGURE 3 Cyclic voltammetric curves recorded with a platinum microelectrode on a $CH_3CN$ solution containing $[Ni(PPh_3)_2Ph(Br)]$ ($2.5 \times 10^{-3}$ mol $dm^{-3}$), $PPh_3$ ($1.25 \times 10^{-2}$ mol $dm^{-3}$), and $[NBu_4][ClO_4]$ (0.1 mol $dm^{-3}$) (——); experimental conditions as above after addition of $C_6H_5Br$ ($10^{-2}$ mol $dm^{-3}$) (· · · ·); same experimental conditions after addition of $C_6H_5Br$ ($10^{-1}$ mol $dm^{-3}$) (— — —). Scan rate 0.1 V $s^{-1}$

PhBr] show that two moles of electrons per mole of nickel(II) were required, as in the absence of the organic halide. The voltammetric profile recorded on the electrolyzed solutions corresponded closely to that exhibited in $CH_3CN$ by the $[Ni(PPh_3)_2Ph(Br)]$ complex, in the presence of PhBr, which is reported in Figure 3. The two merged cathodic peaks, also shown in Figure 2, were observed, with which the anodic one due to the oxidation of nickel(0) appeared to be associated only for fairly low PhBr : $Ni^{II}$ molar ratios (<50 : 1). The ratio between the height of this anodic peak and that of the cathodic ones increased with increasing scan rate.

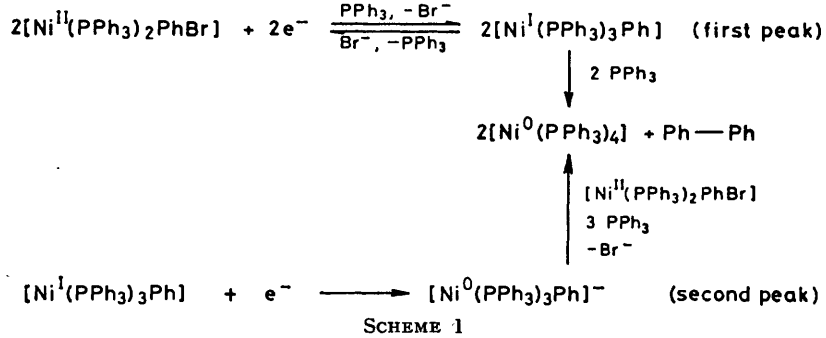
These findings show that the nickel(0) species obtained in the reduction of nickel(II) (first cathodic peak in Figure 2) is involved, in this case, in a chemical reaction with PhBr giving the stable organometallic species $[Ni(PPh_3)_2Ph(Br)]$,[11] the cathodic reduction of which occurs at potentials corresponding to the merged peaks. The reduction processes relative to this species have been reported previously [14] and are summarized in Scheme 1.

In both the electrochemical steps nickel(0) and biphenyl are formed; in the first step they are originated by thermal decomposition of the electrode product, while in the second one they are formed by reaction of $Ph^-$, from decomposition of the anionic nickel(0) species produced at the electrode surface, with the nickel(II) depolarizer. This mechanism evidently holds in the presence of PhBr too, the only difference being that the complex $[Ni^0(PPh_3)_4]$ produced in the reduction steps reacts with PhBr thus renewing the $[Ni^{II}(PPh_3)_2Ph(Br)]$ species and allowing an electrocatalytic cycle to take place.

Controlled-potential electrolyses carried out at potentials corresponding to the two merged peaks (−2.0 V) confirmed this view, since the electrolysis current decreased very slowly with time even for $n_e$ (number of moles of electrons) values higher than one {$n_e = 1$ in the exhaustive reduction of $[Ni(PPh_3)_2Ph(Br)]$ when PhBr is absent [14]}. Moreover, g.c.–m.s. analyses of the electrolyzed solutions revealed the presence of the coupling product, biphenyl, together with small amounts of benzene with the yields reported in the Table.

It must be noted, however, that when these controlled-potential electrolyses were carried out on $[Ni(PPh_3)_2Ph(Br)]$ solutions in the presence of increasing ratios of PhBr to nickel complex, the apparent $n_e$ value ($n_{app.}$) decreased (see the Table) thus indicating an incomplete renewal of the catalytically active species. This observation was made by monitoring the cathodic peaks and the charge during the electrolysis; plots of $i_p$ against charge passed made possible the evaluation by extrapolation of the apparent number of moles of electrons transferred per mole of nickel complex.

This observation suggests that not only $[Ni^0(PPh_3)_4]$ but also $[Ni^0(PPh_3)_3Ph]^-$ undergoes an oxidative addition




SCHEME 1

by PhBr as shown in Scheme 2 (for the sake of simplicity, the stoicheiometric coefficients and the free phosphine involved have been omitted).

In path (i) PhBr reacts in favour of its catalytic reduction, undergoing oxidative addition to $[Ni^0(PPh_3)_4]$ and regenerating cyclically the depolarizer $[Ni^{II}(PPh_3)_2Ph(Br)]$, the reduction of which yields the coupling product. Reaction (ii), on the other hand, removes the nickel species from the electrocatalytic cycle giving an organometallic complex electrochemically ineffective at

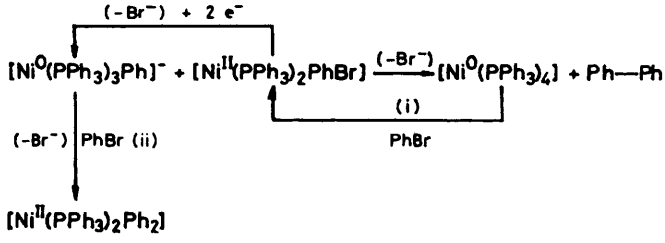
Coupling reactions of organic halides

| Organic halide | $\theta_c$/°C | Cathodic step | Initial molar ratio RX : $Ni^{II}$ | Fraction of promoter consumed in each cycle [a] | Coupling product (yield [b]) | Other products (yield [b]) |
|---|---|---|---|---|---|---|
| 1-Iodobutane | 25 | first | 20 : 1 | 0.00 | n-octane (*ca.* 2%) | n-butane (36%)<br>but-1-ene (57%)<br>hydrogen [c] |
| | | second | 20 : 1 | 0.00 | n-octane (75%) | n-butane (10%)<br>but-1-ene (15%)<br>hydrogen [c] |
| 1-Iodo-2,2-dimethylpropane | 25 | single | 20 : 1 | 0.00 | 2,2,5,5-tetramethylhexane (92%) | 2,2-dimethylpropane (2.5%)<br>1,1-dimethylcyclopropane (2.5%) |
| Benzyl chloride | 25 | first | 20 : 1 | 0.00 | | |
| | −20 | second | 50 : 1 | 0.20 | bibenzyl (90%) | toluene (2%) |
| | −35 | third | 60 : 1 | 0.30 | | |
| Bromobenzene | 25 | second | 15 : 1 | 0.03 | | |
| | | or third | 50 : 1 | 0.08 | biphenyl (82%) | benzene (4%) |
| | | | 150 : 1 | 0.25 | | |

[a] Given by $1/(n_{app.} - 2)$. [b] Referred to the amount expected on the basis of quantitative efficiency of the redox process. [c] Qualitatively determined.

the working potential. This reaction, in which the electrophilic depolarizer is replaced by the phenyl bromide, evidently becomes increasingly important with increasing PhBr : nickel complex molar ratio.

The proposed mechanism for the formation of the diaryl nickel complex is confirmed by adding anhydrous perchloric acid to the solutions exhaustively electrolyzed.




SCHEME 2

The complex $[Ni(PPh_3)_2Ph(Br)]$ was quantitatively regenerated (voltammetric tests) after the addition of $HClO_4$ in a stoicheiometric amount (1 : 1) with respect to the nickel initially present. It is well known, in fact, that strong proton donors added in this molar ratio cleave the carbon–nickel bond in diorganonickel compounds to afford the free hydrocarbon,[15] according to reaction (2).

$$[Ni(PPh_3)_2Ph_2] + H^+ \xrightarrow{Br^-} [Ni(PPh_3)_2Ph(Br)] + C_6H_6 \quad (2)$$

On the basis of the reduction mechanism (Scheme 1), it appears that the troubling side reaction (ii) would not take place at potential values corresponding to the first reduction step {which does not give $[Ni(PPh_3)_3Ph]^-$}. Unfortunately the two cathodic peaks shown in Figure 3 appear to be sufficiently separated only at the beginning of the electrolyses, since they tend to merge more and more, with the progressive release of bromide ions during the catalytic cycle. The effect of the bromide ions was checked by adding tetrabutylammonium bromide to $[Ni(PPh_3)_2Ph(Br)]$ solutions since the bromide dissociation, which is known to occur in this organometallic species,[14] progressively decreases in the presence of increasing amounts of bromide ions.

*1-Iodobutane.*—The behaviour of the $Ni^{II}$–$PPh_3$ system was rather different when the alkyl halide 1-iodobutane, in place of $C_6H_5Br$, was used. By running cyclic voltammetric tests on $PPh_3$-containing nickel(II) solutions to which n-$C_4H_9I$ was added stepwise, the nickel(II) reduction peak shown in Figure 1 increased progressively and took on a sigmoidal shape, while a concomitant lowering of the anodic peak due to the nickel(0) oxidation takes place in the reverse scan. Moreover, the addition of n-$C_4H_9I$ caused, as shown in Figure 4, the appearance of

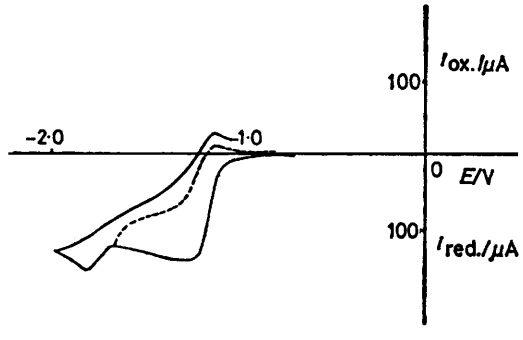



FIGURE 4 Cyclic voltammetric curve recorded with a platinum microelectrode on a $CH_3CN$ solution containing nickel(II) ($2 \times 10^{-3}$ mol $dm^{-3}$), $PPh_3$ ($10^{-2}$ mol $dm^{-3}$), $C_4H_9I$ (0.1 mol $dm^{-3}$), and $[NBu_4][ClO_4]$ (0.1 mol $dm^{-3}$). Scan rate 0.1 V $s^{-1}$

a new reduction peak, with a low height, located at potentials more negative than those corresponding to the nickel(II) reduction, but more positive than those at which the direct reduction of the organic halide occurs (*ca.* −2.3 V).

Voltammetric and chronoamperometric measurements

carried out at potential values corresponding to the first cathodic process revealed a decrease in the value of $i_p/v^{\frac{1}{2}}$ with increasing scan rate (0.03—5 V $s^{-1}$) and an increase with time in the value of $it^{\frac{1}{2}}$ respectively, as expected for a catalytic electrochemical process. Moreover, by electrolyzing the nickel(II) solutions in the presence of a large excess (100 : 1) of butyl iodide at −1.4 V, it was observed that the electrolysis current remained practically unchanged until the organic substrate was present (catalytic current). The g.c.–m.s. tests carried out on the electrolyzed solutions revealed the presence of but-1-ene, n-butane, and hydrogen, in addition to small traces of n-octane, with the yields reported in the Table. The same tests performed on the solutions during the electrolysis showed that one mole of electrons per mole of organic halide was involved in the reduction process.

All these results can be explained by the fact that, as in the presence of PhBr, the nickel(0) obtained in the reduction of nickel(II) (first cathodic peak in Figure 4) undergoes oxidative addition by the organic halide to give the organometallic species $[Ni(PPh_3)_2R(X)]$ which is known to be thermally unstable when R is an alkyl group.[2] Its decomposition evidently provides a nickel species reducible at the working potential, thus allowing the renewal of the nickel(0) complex $[Ni(PPh_3)_4]$ and, hence, the achievement of a catalytic cycle. Moreover, the high yield of olefin obtained in this case, at the expense of the coupling product, compared with the alkane one, also suggests that the decay of the intermediate organometallic complex $[Ni(PPh_3)_2R(X)]$ has to occur through a β-elimination reaction.

In order to shed light on the nature of the nickel species obtained in the thermal decomposition of $[Ni(PPh_3)_2R(X)]$, butyl iodide was added (in a 1 : 1 molar ratio) to a $CH_3CN$ solution containing electrochemically

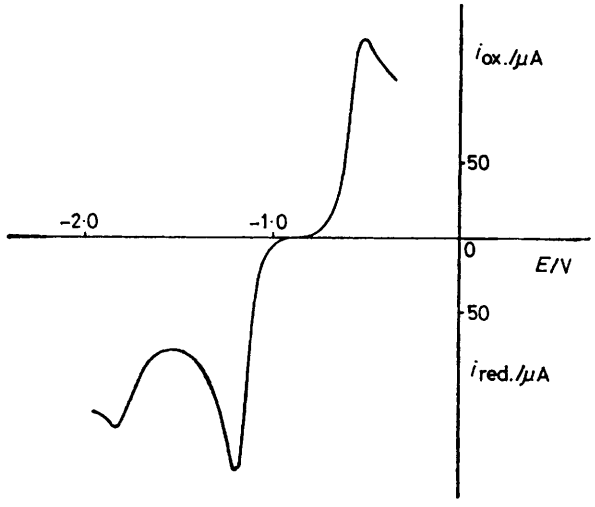
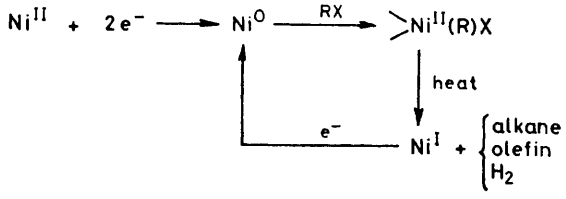



FIGURE 5 Voltammetric curves recorded with a platinum microelectrode on a $CH_3CN$ solution containing $[Ni(PPh_3)_4]$ ($5 \times 10^{-3}$ mol $dm^{-3}$) and $[NBu_4][ClO_4]$ (0.1 mol $dm^{-3}$), after addition of $C_4H_9I$ ($5 \times 10^{-3}$ mol $dm^{-3}$). Scan rate 0.1 V $s^{-1}$. Potentials are scanned from −0.9 V both in the cathodic and anodic directions

generated [12] $[Ni(PPh_3)_4]$. A fast discharge of the red colour of the nickel(0) solution was observed, while the voltammetric behaviour corresponded to that shown in Figure 5. The presence in the voltammetric picture of the anodic peak and of the first cathodic peak has allowed us to identify the nickel(I) complex $[Ni(PPh_3)_2I]$ as a reaction product because this complex had been found to undergo anodic and cathodic processes just at these potentials when free phosphine is present; [16] on the other hand, the cathodic reduction of this complex to $[Ni(PPh_3)_4]$ is operative, in fact, at the working potential employed in the electrocatalyzed reduction of butyl iodide (see above). Therefore, Scheme 3 summarizes the course of the n-$C_4H_9I$ reduction in the presence of nickel(II).




SCHEME 3

However, the nickel(I) obtained in the chemical test was less than that expected for a quantitative conversion of the nickel(0) initially present (in typical tests it was only *ca.* 80—85% on the basis of peak height measurements). The remainder went on to be the depolarizer of the second cathodic process shown in Figure 5 (which is the same as the second reduction peak shown in Figure 4). When the solution obtained in this chemical test was left to stand at room temperature, the height of this second cathodic peak decreased slowly with time (typically it completely disappeared in *ca.* 12 h), while the anodic and the cathodic peaks due to the presence in solution of nickel(I) species concomitantly increased up to the height expected on the basis of Scheme 3. Moreover, when an activated olefin such as acrylonitrile was added to the solution, this conversion occurred immediately thus suggesting that a nickel hydride complex is the depolarizer of the second cathodic process. On the other hand, as the thermal decomposition of the organonickel(II) species giving nickel(I) (see Scheme 3) has been shown to occur through a β-elimination reaction, it is conceivable that a nickel hydride complex may be considered as an intermediate. Therefore, we suggest that this thermal decomposition occurs *via* the reaction sequence given by equations (3)—(5).

$$[Ni^{II}(PPh_3)_2(C_4H_9)I] \xrightarrow{\text{heat}} [Ni^{II}(PPh_3)_2H(I)] + \text{but-1-ene} \quad (3)$$

$$[Ni^{II}(PPh_3)_2H(I)] \xrightarrow[PPh_3]{\text{heat}} [Ni^{I}(PPh_3)_3I] + \tfrac{1}{2}H_2 \quad (4)$$

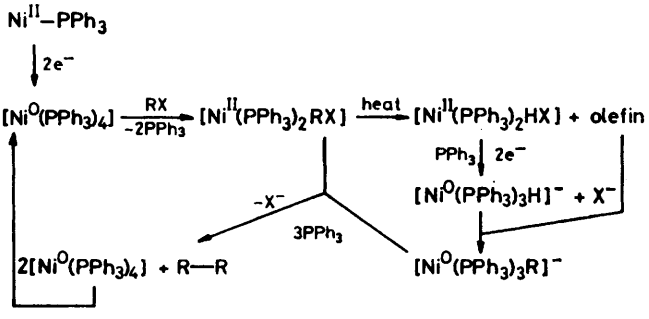
$$[Ni^{II}(PPh_3)_2H(I)] + [Ni^{II}(PPh_3)_2(C_4H_9)I] \xrightarrow[2PPh_3]{} 2[Ni^{I}(PPh_3)_3I] + \text{n-butane} \quad (5)$$

In particular, reaction (5) can account both for the

high yield of alkane obtained in this ' β-elimination process ' and for the observed non-accumulation in the solution of the hydride complex (responsible for the second cathodic peak) during the electrocatalytic cycle.

The proposed reaction sequence also accounts for the results obtained by reducing the nickel(II)–$PPh_3$ solutions in the presence of a large excess (100 : 1) of butyl iodide directly, at the potentials of the second cathodic peak. At this potential, in fact, the electrochemical process again appeared to be catalytic in nature, although the yields of the organic products were quite different, as shown in the Table. In particular, the yield of the coupling product n-octane was significantly increased at the expense of those of but-1-ene and n-butane. These findings suggests that the reduction of the nickel(II) hydride complex leads to such an increase of electron density at the metal that a reinsertion of the olefin, from the β-elimination process [reaction (3)], into the nickel–hydrogen bond has to be expected. In this way, near the electrode surface, an anionic organometallic nickel(0) species is obtained which is able, as in the case of PhBr, to involve the parent organometallic complex (which also formed near the electrode surface) in a reaction to give the coupling product (see Scheme 1).

According to this view, for the electrocatalytic process occurring at the second peak, Scheme 4 can be advanced, which partially resembles that formulated for the electrocatalytic reduction of PhBr.




SCHEME 4

1-*Iodo*-2,2-*dimethylpropane*.—The formation of olefin in the electrocatalytic cycle which takes place at potentials corresponding to the nickel(II) reduction (first cathodic peak in Figure 4) in the presence of 1-iodobutane has been attributed by us to a β-elimination reaction involving the relevant organometallic intermediate. In order to substantiate this view, neopentyl iodide [$(CH_3)_3CCH_2I$], *i.e.* an organic halide without hydrogen atoms in the β position, was also employed.*

All the electrochemical results were found to be similar to those obtained in the previous case, with the exception of the absence of the second cathodic peak shown in Figure 4.

To gain information on the chemical reaction, following the charge-transfer step, which cyclically generates nickel(I), the organic halide was added to a $[Ni^0(PPh_3)_4]$ solution in a 1 : 1 molar ratio. The two peaks (anodic and cathodic), due to the presence of the nickel(I) depolarizer, could in this case be detected with the height expected on the basis of a quantitative $Ni^0 \longrightarrow Ni^I$ oxidation (see Scheme 3).

The g.c.–m.s. analyses of the $(CH_3)_3CCH_2I$-containing nickel(II) solutions electrolyzed at potential values corresponding to the single cathodic peak indicated that the predominant product was the coupling one as shown in the Table.

*Benzyl Chloride*.—Benzyl chloride was used in the hope of substantiating the hypothesis, based on an analogy with the case of PhBr, for the formation of an organometallic complex in the catalytic cycle when alkyl halides are employed.

In this organic halide there is no hydrogen atom in the β position and hence it is expected to give predominantly the coupling product, as in the case of neopentyl iodide. However, the electron-withdrawing effect of the aromatic ring should stabilize to some extent the metal–carbon bond in the corresponding organonickel derivative thus giving a somewhat more stable nickel(II) organometallic complex. The behaviour of nickel(II) in the presence of $PhCH_2Cl$ approaches, in fact, that obtained in the presence of either PhBr or neopentyl iodide, depending on the temperature employed. The voltammetric picture obtained at low temperature (−30 °C) on $PPh_3$-containing nickel(II) solutions to which benzyl chloride had been added closely resembled that shown in Figure 2 for the case of PhBr. By carrying out controlled-potential electrolyses at this temperature (at the first peak), it could be observed that, as in the case of PhBr, the reduction of one mole of nickel(II) involved two moles of electrons and made possible the formation of a nickel species {evidently $[Ni(PPh_3)_2(CH_2Ph)Cl]$}, the reduction of which occurred at more negative potential values.

At 25 °C, on the contrary, although the cyclic voltammetric profile was the same as that at low temperature, the electrolysis current relative to nickel(II) reduction (large excess of $PhCH_2Cl$) decreased only at the initial times, while subsequently its value remained practically unchanged, thus suggesting that, as in the presence of neopentyl iodide, the depolarizer was continuously regenerated in a chemical reaction which, in this case, appeared to be slow.

Gas chromatographic tests carried out on these electrolyzed solutions showed that the main organic product was bibenzyl as shown in the Table.

By carrying out controlled-potential electrolyses at −30 °C directly at potential values corresponding to the two merged peaks, results similar to those observed in the

* The simplest organic halides unable to undergo the β-elimination reaction are methyl halides. However they could not be employed here due to the presence in solution of triphenylphosphine. It is well known that the quaternization reaction of tertiary phosphine with methyl halides, in particular in polar solvents, occurs readily. We have voltammetrically checked that this reaction does not occur to any appreciable extent on the time scale of our experiments for all the substrates employed.

case of PhBr were obtained. That is, the coupling product was again produced (with the yield reported in the Table) and the number of electrons involved in the exhaustive electrolyses increased with decreasing RX : $Ni^{II}$ molar ratio thus indicating that, at this temperature, a side reaction takes away the nickel promoter from the catalytic cycle.

In this case, in contrast with the one in which PhBr was used, the anodic oxidation of the side reaction product could be observed. The voltammetric profile exhibited by the solutions exhaustively electrolyzed at −30 °C, shown in Figure 6, showed the presence of a

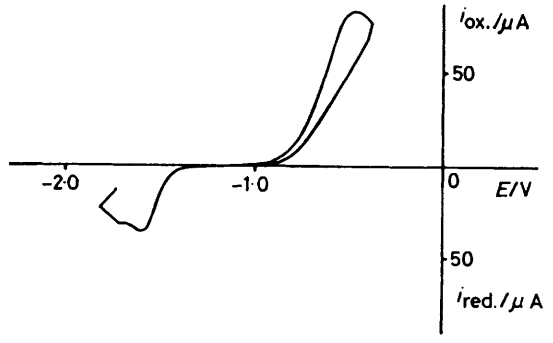



FIGURE 6 Cyclic voltammetric curve recorded at −30 °C with a platinum microelectrode on a $CH_3CN$ solution containing $[Ni(PPh_3)_2PhBr]$ ($2 \times 10^{-3}$ mol $dm^{-3}$), $PPh_3$ ($10^{-2}$ mol $dm^{-3}$), and $[NBu_4][ClO_4]$ (0.1 mol $dm^{-3}$), after exhaustive electrolysis at −2.0 V. Scan rate 0.1 V $s^{-1}$. Potentials are initially scanned from −1.07 V in the anodic direction

one-electron irreversible anodic peak with which were associated the cathodic ones displayed by the complex $[Ni(PPh_3)_2(CH_2Ph)Cl]$. This latter complex could be quantitatively regenerated by one-electron anodic oxidation, at the potential of the mentioned anodic peak, of the exhaustively electrolysed solutions as well as by addition of one molar equivalent of anhydrous perchloric acid [as in the case of PhBr, reaction (2)]. These two results strongly suggest [15,17-19] that in this case also the side reaction product is the non-reducible diorganocomplex $[Ni(PPh_3)_2(CH_2Ph)_2]$.

*Conclusions.*—In the electrochemical system set up and investigated by us, effective electrocatalytic processes can be carried out owing to the fact that (*i*) the activation energy required is lowered and (*ii*) the inorganic promoter of the synthesis is cyclically regenerated. The latter aspect represents the crucial improvement of the previously well known stoicheiometric organic halide coupling reaction promoted by transition-metal complexes which was the original aim for this research. The lowering of the activation energy for the organic halides reduction process produces an important change in the pattern of RX electrochemical reduction. When this process is carried out directly on RX solutions, it is affected by so large an overvoltage that it occurs at potential values at which the radical, generated in the primary one-electron uptake, is further reduced to the corresponding carboanion, leading, therefore, to the related hydrocarbon instead of the coupling product. [20,21]

All the results reported in this paper show that the electrocatalyzed reduction of organic halides promoted by phosphine complexes of nickel can be rationalized on the basis of simple steps, operative in all cases, in spite of the variety of behaviour observed. In all cases, we clearly identify (*i*) an electrochemical step in which the oxidation state of the metal centre in the nickel complex is lowered to zero, (*ii*) a step involving the organic halide activation through its oxidative addition to the nickel(0) complex electrochemically generated, and (*iii*) a step in which the metal–carbon bond is cleaved (reductive elimination) either by straightforward thermal decomposition or after a further cathodic reduction.

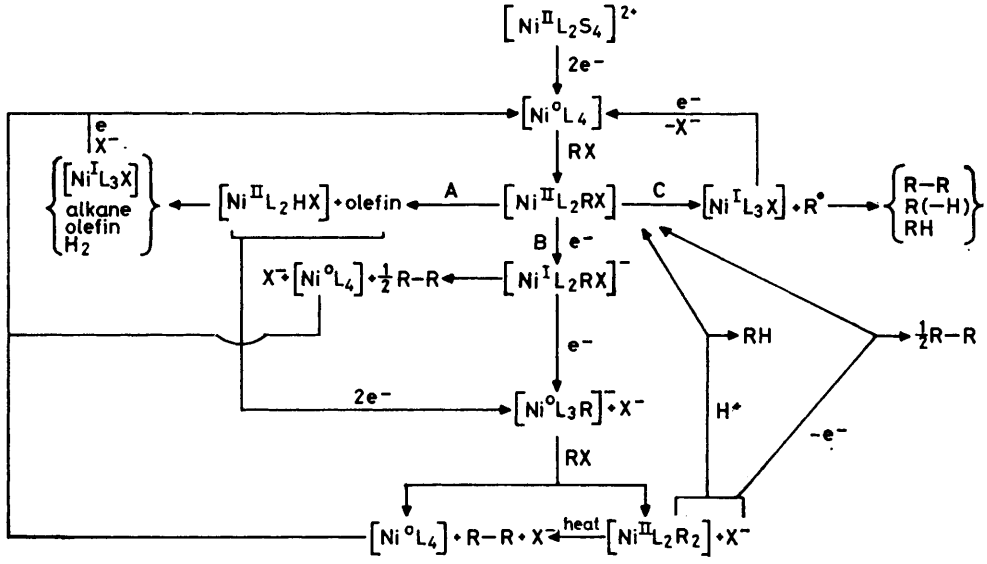



FIGURE 7 Reaction scheme operative in the presence of an excess of RX (L = $PPh_3$; S = $CH_3CN$; X = I, Br, or Cl; R = alkyl or aryl group)

To summarize all the electrochemical and chemical events, we propose the reaction scheme shown in Figure 7.

Route B is allowed when the nickel–carbon derivative [$NiL_2R(X)$] is sufficiently stable, as in the case of bromobenzene and benzyl chloride at low temperature. In these cases the electrocatalytic process occurs only at potentials at which the elimination from the organonickel species can be induced by cathodic reduction; during this elimination-by-reduction a zerovalent nickel species is formed which immediately reacts with the organic substrate thus allowing the electrocatalytic cycle to take place.

As far as route C is concerned (neopentyl iodide and benzyl chloride at 25 °C), the coupling product is produced by dimerization of the radical formed in the homolytic fission of the nickel–carbon bond in the [$NiL_2R(X)$] derivative. The organic product distribution observed can be explained on the basis of a radical decay.[22]

Route A accounts for the findings of the experiments in which butyl iodide is employed. In this case the thermal decomposition of the organonickel intermediate occurs *via* a β-elimination reaction involving a nickel hydride complex as intermediate. It accounts for the possibility of obtaining the coupling product, when working at more negative potential values, in an electrocatalytic pathway overlapping with route B (see Scheme 4). In this case it is therefore possible to pilot the process towards the generation of the desired products by choosing the appropriate working potential.

Finally, the slow step of all the electrocatalytic cycles discussed so far appears to be the oxidative addition of the organic halide to the zerovalent complex [$NiL_4$], since this species can be detected as an intermediate in all cases. Consequently, the differing increases of the catalytic reduction current observed in the presence of various organic halides, employed under the same experimental conditions, enables one to compare the rate of the oxidative addition reactions. Our results indicate the following sequence for the rate of such a reaction: $C_4H_9I > (CH_3)_3CCH_2I > PhCH_2Cl > PhBr$; this parallels that of the decreasing dipolar moments exhibited by these organic halides.

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