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Activation of the Carbon–Nickel σ-Bond by Cathodic Reduction of *trans*-Bromobis(triphenylphosphine)phenylnickel(II) in the Presence of Triphenylphosphine

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The complex trans-*[Ni(PPh$_3$)$_2$(Ph)Br] is found to be cathodically reduced in two steps in acetonitrile solution containing free PPh$_3$ at a platinum electrode. Both processes cause the activation of the σ-bonded organic group and the consequent formation of biphenyl along two quite different reaction pathways. In the first one the coupling product simply arises from the collapse of the metallorganic nickel(I) complex cathodically generated; in the second step biphenyl is formed in a reaction between a very reactive electrogenerated organometallic nickel(0) species and the parent nickel(II) complex.*

Unambiguous evidences of the occurrence of electrocatalyzed homo- and hetero-coupling are obtained when the cathodic reductions of the title complex are carried out in the presence of bromobenzene and benzyl chloride.

Introduction

The activation of a carbon–metal σ-bond in thermally stable organometallic species, *i.e.* the achievement of physicochemical conditions suitable for making the metal-coordinated organic group prone to chemical changes, can be carried through different procedures. Thus the employment of electrophylic reagents [1], the activation of π-acidic ligands able to promote reductive elimination [2], the cathodic reduction [3] and anodic oxidation [4, 6] of the metal can be successfully employed. It appears that a common feature of all the mentioned methods is the occurrence of a change in the actual oxidation state of the metal.

We are interested since some years both in the electroanalytical behaviour of nickel complexes in the oxidation states +2, +1, 0 [7–12] and in the cathodic behaviour of organometallic compounds of transition metals [3, 13]. As a common topic of our interests, we have investigated the cathodic behaviour of *trans*-bromobis(triphenylphosphine)phenylnickel(II), [Ni(PPh$_3$)$_2$(Ph)Br], in CH$_3$CN.

This complex combines a series of useful features: (i) it is a species thermally stable and well characterized from the physico-chemical point of view [14], (ii) it makes fully feasible the expectation to give reasonably stable nickel(I) and nickel(0) species [7, 8, 12], (iii) it appears to us a likely intermediate in the electrocatalyzed reudction of aryl halides promoted by the nickel(II)/PPh$_3$ system as catalyst precursor which is presently under investigation in our laboratories [15].

Experimental

Chemicals

All the chemicals employed were of reagent grade quality. Reagent grade acetonitrile was further purified by distilling repeatedly from phosphorous pentoxide and stored on molecular sieves (3 Å) under nitrogen atmosphere. The supporting electrolyte tetrabutylammonium perchlorate (TBAP) was prepared from perchloric acid and tetrabutylammonium hydroxide, recrystallized from methanol and dried in a vacuum oven at 50 °C.

Stock solutions of anhydrous nickel(II) perchlorate in acetonitrile were prepared by anodic oxidation of metallic nickel in TBAP–acetonitrile solutions as previously described [9]. Triphenylphosphine was crystallized from methanol and stored in a vacuum oven in the dark.

The complex [Ni(PPh$_3$)$_2$(Ph)Br] was synthesized as reported in the literature [14]. Nitrogen (99.99%), 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 disk 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 an H-shaped cell with cathodic and anodic compartments separated by a syntered glass disk. The working electrode was a platinum gauze while a mercury pool was used as counter electrode.

In all cases a silver/0.1 *M* silver perchlorate electrode in acetonitrile was used as reference electrode.

The employed voltammetric unit was a three-electrode system assembled with the MP-System 1000 equipment in conjunction with a digital logic function generator made up here [16]. 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 and the associated coulometer was an Amel integrator Model 558.

Gas chromatographic analyses were carried out with a Fractovap GU chromatograph, equipped with a OV17 silicone on chromosorb G AW-DMCS column, in conjunction with a Hewlett-Packard 3373 B integrator. For the quantitative evaluation of the organic products, the internal standard method was followed; the standard employed, naphthalene, was added to the solutions which have to be tested, before the beginning of the electrolyses.

All the electroanalytical measurements were made, unless otherwise stated, at 25 ± 0.1 °C.

Results and Discussion

The preliminary voltammetric tests carried out in this investigation have shown that the same results could be obtained employing both chemically prepared *trans*-$[Ni(PPh_3)_2(Ph)Br]$ in the presence of PPh_3 and the same species generated *in situ* upon addition of the stoichiometric amount of bromobenzene to solutions containing electrochemically prepared $[Ni(PPh_3)_4]$ [12]. The use of solutions obtained by the second method has been therefore preferred on the basis of its easier feasibility and hence it has to be noted that the solutions employed in this work normally contain the nickel(II) complex in the presence of a slight excess of PPh_3 (at least 2:1). Solutions of the so prepared $[Ni(PPh_3)_2(Ph)Br]$ complex display the cathodic behaviour depicted in Fig. 1 (full line).

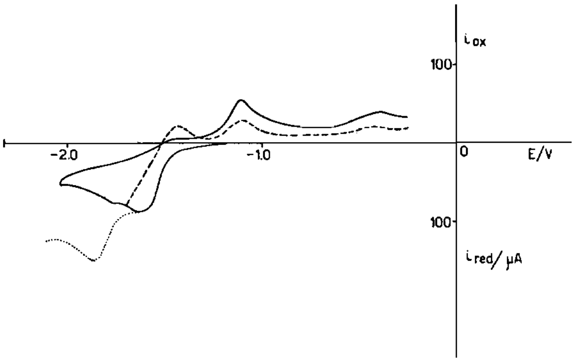


Fig. 1. Cyclic voltammetric curves at a platinum microelectrode in a (———) 3×10^{-3} *M* $[Ni(PPh_3)_2(Ph)Br]$, 6×10^{-3} *M* PPh_3, 0.1 *M* TBAP, CH_3CN solution; (-------) experimental conditions as above, less cathodic switching potential; (·········) experimental conditions as above, after addition of 10^{-2} *M* Ph–Br. Scan rate 0.2 V s^{-1}.

In the direct anodic scan (not reported in this figure) the only observed process is found to be the oxidation of free bromide ions in the presence of PPh_3, as checked by reference tests carried out on solutions containing convenient amounts of these species; this finding indicates an appreciable dissociation of the metal complex. In Fig. 1 two ill resolved reduction peaks occurring at potentials rather close each other can be observed, to which two or three anodic peaks are found to be associated depending on the potential at which the scan is reversed. Voltammetric tests carried out on solutions containing $[Ni(PPh_3)_4]$ electrogenerated [12] in the presence of free bromide ions let one to attribute the second and third anodic peaks to the oxidation processes nickel(0) → nickel(I) and nickel(I) → nickel(II) respectively [17].

Moreover, the first anodic peak observed in the reverse scan, appears to give rise to a quasi-reversible catho-anodic system with the first cathodic one, which is found to be associated to a diffusion controlled one-electron process as proved by chronoamperometric tests and by comparison of the peak height measured for solutions of the complex with that of $[Ni(CN)_2(PEt_2Ph)]$ for which the occurrence of a one-electron reduction process has been shown unambiguously [7].

All these findings indicate that this quasi-reversible catho-anodic system can be depicted by the following equation:

$$[Ni^{II}(PPh_3)_2(Ph)Br] + e^- \underset{+Br^-;\,-PPh_3}{\overset{+PPh_3;\,-Br^-}{\rightleftarrows}} [Ni^{I}(PPh_3)_3(Ph)] \qquad (1)$$

In this connection, it has to be pointed out that the addition of free bromide ions to $[Ni(PPh_3)_2(Ph)Br]$ solutions is observed to produce an appreciable cathodic shift of the first reduction peak which is fully consistent with the above mentioned halide dissociation of the nickel(II) complex. The observed presence of free bromide ions implies that PPh_3 (present in excess) or/and the solvent itself have to be involved in the coordination sphere of nickel(II). However, as in the cathodic reduction of $[Ni(PPh_3)_2(Ph)Br]$ no kinetic complication is apparent, all the ligand exchange equilibria involved have to be fast. Therefore, being all the nickel(II) species electrochemically undistinguishable, the notation $[Ni(PPh_3)_2(Ph)Br]$ will be employed henceforth to indicate the rather complex system Ni^{II}–(Ph), PPh_3, Br^-, CH_3CN.

Cyclic voltammetric tests have revealed that, for the quasi-reversible catho-anodic system depicted by equation (1), the ratio $(i_p)_a/(i_p)_c$ increases both by increasing the scan rate and by lowering the temperature; correspondingly, the height of the second and third anodic peaks decreases, in respect to that of the first cathodic one. These findings indicate that the complex $[Ni^I(PPh_3)_3(Ph)]$, produced in the reduction process, is scarcely stable and decays in a rather short time giving $[Ni^0(PPh_3)_4]$.

It has to be pointed out that the first anodic peak practically disappears when the scan direction is reversed after the second cathodic peak is traversed, at any scan rate employed. This has to be interpreted as the consequence of the apparent impossibility of reoxidizing the product of the second cathodic process (likely a nickel(0) species) to $[Ni^I(PPh_3)_3(Ph)]$ either electrochemically or by a chemical comproportionation reaction with the nickel(II) depolarizer.

The second cathodic peak appears almost undetectable, slightly emerging on the descending branch of the first one, at the lowest scan rates ($0.05\ V\ s^{-1}$), while it becomes more and more prominent by increasing the scan rate or by lowering the temperature. The circumstance that this trend strictly parallels that exhibited by the first anodic peak leaves little doubts on the fact that the depolarizer of both processes is the same lable species, *i.e.* $[Ni^I(PPh_3)_3(Ph)]$.

Chronoamperometric tests carried out on $[Ni^{II}(PPh_3)_2(Ph)Br]$ solutions directly at potential values corresponding to a diffusive control for the second reduction process (–2.0 V), reveal that the overall cathodic current ranges from the value expected for a two-electron process to that relative to a one-electron reduction, depending on time, as reported in Fig. 2.

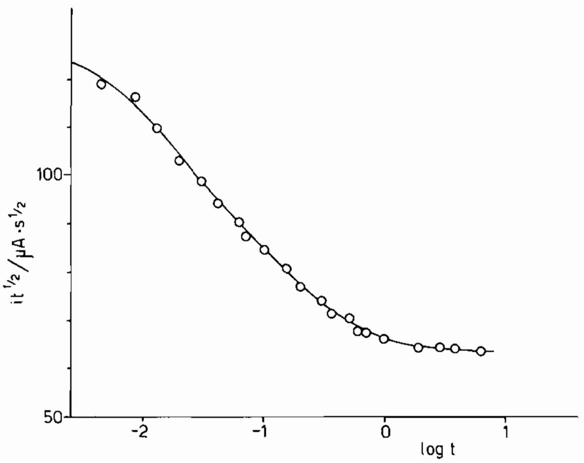


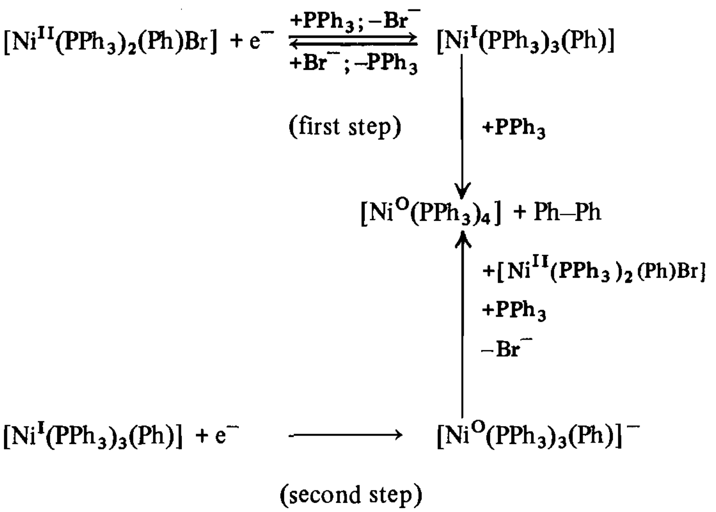
Fig. 2. Behaviour of the overall cathodic current as a function of time in chronoamperometric experiments. Experimental conditions: 2×10^{-3} *M* $[Ni(PPh_3)_2(Ph)Br]$, 8×10^{-3} *M* PPh_3, 0.1 *M* TBAP, CH_3CN solution; temperature = 0.0 °C; working potential = –2.0 V.

The observed lability of the nickel(I) intermediate (depolarizer for the second reduction step) cannot account for this chronoamperometric finding as, in these experimental conditions, this species is expected to uptake the second electron as soon as it is formed at the electrode surface to give, evidently, $[Ni^0(PPh_3)_3(Ph)]^-$. The trend depicted in Fig. 2 can be explained only by admitting a consumption of the depolarizer in a competing chemical reaction with the two-electron reduction product [18]. This chemical reaction can not be a valence comproportionation like:

$$[Ni^{II}(PPh_3)_2(Ph)Br] + [Ni^0(PPh_3)_3(Ph)]^- \xrightarrow{+PPh_3,\,-Br^-} 2[Ni^I(PPh_3)_3(Ph)] \qquad (2)$$

as the so formed nickel(I) species is reducible at the working potential, thus maintaining equal to two, the number of electrons involved for any time explored. This statement is in agreement with the results obtained in cyclic voltammetry when the switching potential is more negative than the second cathodic peak, as the peak attributable to the oxidation of the nickel(I) complex is not observed in the reverse scan (see above). By taking into account that the peaks due to the stepwise oxidation of $[Ni^0(PPh_3)_4]$ are associated to the second cathodic peak, an acid base reaction concomitant with a reductive elimination have to be, on the contrary, proposed.

The whole of the data presented so far can be rationalized on the basis of the following scheme:



(3)

In both the electrochemical steps nickel(O)* 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^-, originated by decomposition of the anionic nickel(O) species produced at the electrode surface, with the nickel(II) depolarizer.

The formation of the species $[Ni(PPh_3)_3(Ph)]^-$, expected to be very unstable, and its reaction with the parent nickel(II) depolarizer is supported by the results obtained by running voltammograms on $[Ni(PPh_3)_2(Ph)Br]$ solutions in the presence of electrophilic species able to react with the electrogenerated anionic species and to prevent hence, to some extent, the taking away of the depolarizer in the chemical step. When small amounts of a proton donor, such as phenol, are progressively added to solutions containing the phenyl-nickel(II) complex, it can be observed, in fact, that the second cathodic peak concomitantly increases, thus resembling the behaviour observed by increasing the scan rate or lowering the temperature. The same effect on the peak height can be obtained by carrying out the same tests in the presence of organic halides such as bromobenzene and benzyl chloride.

By carrying out controlled potential reductions on solutions of the phenyl-nickel(II) complex at potential values corresponding both to the rising portion of the first cathodic peak and to the range in which a diffusion control is operative for the second reduction process, the same results are obtained; that is the reductions are completed after one mol of electrons per mol of depolarizer is spent and both give, in quantitative yields (scheme 3), $[Ni(PPh_3)_4]$ and biphenyl as checked by voltammetric and gas-chromatographic tests respectively. This last finding is a further and decisive proof of the involvement of the nickel(II) depolarizer in a chemical reaction which has to follow the uptake of the second electron.

When the same experiments are carried out in the presence of a slight excess (3:1) of PhBr over nickel(II), the mol of electrons per mol of nickel(II) increase correspondingly as well as the amout of biphenyl produced**. These results are not suprising and they appear in full agreement with the reaction mechanism depicted in (3). In this mechanism, it appears that $[Ni(PPh_3)_4]$ is the final reduction product in any case and, on considering its ascertained great reactivity with PhBr, the cyclic chemical renewal of the depolarizer is expected and therefore also an electrocatalytic accumulation of biphenyl.

In connection with these last findings we have found that, by employing benzyl chloride, instead of PhBr, in the cathodic reductions carried out in correspondence to the second cathodic peak, the formation of the cross-coupling product $Ph{-}CH_2{-}Ph$, together with Ph–Ph and $Ph{-}CH_2{-}CH_2{-}Ph$ is observed**.

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*It is well known that the complex $[Ni(PPh_3)_4]$ undergoes, in the common organic solvents, partial loss of the phosphine ligand to give essentially the three coordinated species $[Ni(PPh_3)_3]$ [19]. Moreover, being CH_3CN a ligand of appreciable bonding ability towards nickel(O) [20], it is obvious that the presence of species like $[Ni(PPh_3)_3(CH_3CN)]$ has to be considered in the employed experimental conditions. However, as these equilibria are likely to be fast [19, 20], all these mentioned species result to be electrochemically 'undistinguishable' thus making the response referring to the metal center perfectly meaningful for any fixed concentration of PPh_3. For this reason, we will employ the notation $[Ni(PPh_3)_4]$ for indicating the system Ni^O, PPh_3, CH_3CN.

**Preliminary tests have shown that no coupling product is formed by a chemical reaction when $[Ni(PPh_3)_2(Ph)Br]$ and the employed organic halide are added to acetonitrile at room temperature.

Conclusions

The results reported in this paper clearly indicate that the decrease of the oxidation state of the metal in nickel complexes is an effective way for changing the reactivity of the metal coordinated σ-bonded organic radicals. In this way they are enabled, in fact, to react along different routes. Thus we have seen that the phenyl group can be driven to give homo- or hetero-coupling products depending on the controlled conditions employed.

It is apparent that in our experimental conditions the activation of the organic moiety is coupled with the formation of a nickel(O) complex, *i.e.* [Ni-$(PPh_3)_4$], which is able to react easily with organic halides thus regenerating σ-bonded organometallic nickel(II) complexes. From all these circumstances it appears clearly the possibility to achieve the nickel-(II) promoted electrocatalyzed coupling of organic halides [15, 21].

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