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THE COUPLING OF ORGANIC GROUPS BY THE ELECTROCHEMICAL REDUCTION OF ORGANIC HALIDES: CATALYSIS BY 2,2′-BIPYRIDINENICKEL COMPLEXES

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Summary

The electrochemical reduction of a dilute solution of NiX_2bipy (bipy = 2,2′-bipyridine) in *N*-methylpyrrolidone gives the corresponding Ni^0 complex, which undergoes oxidative addition with an excess of an organic halide RX to form RNiX. Decomposition of RNiX gives the dimer R_2 in good yield and nickel(II). The nickel(0) species is regenerated to give an electrocatalytic process. The possible mechanism of these reactions is discussed briefly.

Introduction

There has been increasing interest in recent years in the homocoupling of the organic moieties of organic halides by reactions which are catalysed by nickel(0) complexes [1]:

$$2\,RX + Ni^0 \rightarrow R_2 + NiX_2$$

Semmelhack et al. [2] were the first to demonstrate the usefulness of nickel(0) in this respect by showing that the nickel(0)-cyclooctadiene complex catalyses the reductive dimerisation of aromatic or vinylic halides. In recent work nickel(0) complexes containing trialkyl- or triaryl-phosphine ligands have been widely used [1,3], but with very reactive substrates such as benzyl or vinyl halides, catalytic species can be obtained by the reduction of uncomplexed nickel(II) salts [4]. Similarly, catalytic quantities of nickel may suffice if a reducing agent such as zinc powder is added to regenerate the nickel(0) species [1,3–5], so that the overall reaction becomes:

$$2\,RX + Zn \xrightarrow{Ni} R_2 + ZnX_2$$

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The preparation and regeneration of the catalyst can also be conveniently carried out electrochemically [6]. In an earlier publication [6b,6c], it was reported that electroreductive coupling of aryl groups can be achieved by the following sequence:

$$NiX_2 \cdot (PPh_3)_2 + 2e \xrightarrow[THF/HMPA]{PPh_3} Ni^0(PPh_3)_n + 2\,X^- \qquad (1)$$

$$Ni^0(PPh_3)_2 + ArX \rightarrow ArNiX(PPh_3)_2 \qquad (2)$$

$$ArNiX(PPh_3)_2 + ArX + 2e \rightarrow Ar_2 + Ni^0(PPh_3)_n + 2\,X^- \qquad (3)$$

(THF = tetrahydrofuran; HMPA = hexamethylphosphoramide)

Reaction 1 corresponds to the electrochemical preparation of a zerovalent nickel complex, which then yields a stable species by oxidative addition (reaction 2); further reduction in the presence of excess ArX leads to the biaryl with regeneration of the Ni^0 catalyst (reaction 3).

The significant drawbacks in this system include the need to use a two-compartment cell with separate anode and cathode compartments, and the presence of a large excess of phosphine in order to avoid the deactivation of the catalytic system. The present paper reports a significant improvement to the method involving use of a single-compartment cell with a nickel complex of 2,2′-bipyridine (bipy) as the catalyst. A further advantage is that 2,2′-bipyridine is insensitive both to oxidation, and to side reactions as alkylation.

Experimental

General

The solvent, *N*-methylpyrrolidone (NMP) was distilled from alcoholic potassium hydroxide at reduced pressure. Other reagents were used as supplied. The supporting electrolyte was either Bu_4NClO_4 or Bu_4NBF_4 (0.1 *M*).

The complex $NiBr_2 \cdot$ bipy precipitated out on mixing solutions of $NiBr_2 \cdot 2H_2O$ and bipy in ethanol. This compound is reduced by a reversible two-electron process at -1.2 V (relative to the saturated aqueous calomel electrode) in a solution in NMP containing at least one molar equivalent of bipy in excess, giving the soluble dark green complex $[Ni(bipy)_2]^0$ [7,8].

Electrochemistry

The electrochemical cell consisted of a single compartment containing three electrodes (see Fig. 1). The anode was a cylindrical rod of magnesium, which was surrounded by a gold gauze cathode. Electrolysis was carried out at room temperature ($\cong$ 20°C) under an atmosphere of argon, with the cathode potential set versus a reference electrode at the potential of the Ni^{II}/Ni^0 transition.

The initial solution consisted of $NiBr_2 \cdot$ bipy (0.02 *M*) and bipy (0.02–0.04 *M*) in NMP, plus supporting electrolyte. When the organic halide (RX, 0.1–0.4 *M*) was added, electrolysis at potentials at which Ni^{II} is reduced yielded stable solutions of Ni^0 provided that the total charge exceeded approx. 1 mol of electron per mole of RX. Alternatively, the nickel could be first reduced to $[Ni(bipy)_2]^0$ before the addition of RX; in this case, approx. 50% of the element is recovered as Ni^{II} in the first stage of the experiment, implying a rapid reaction between RX and all the Ni^0.

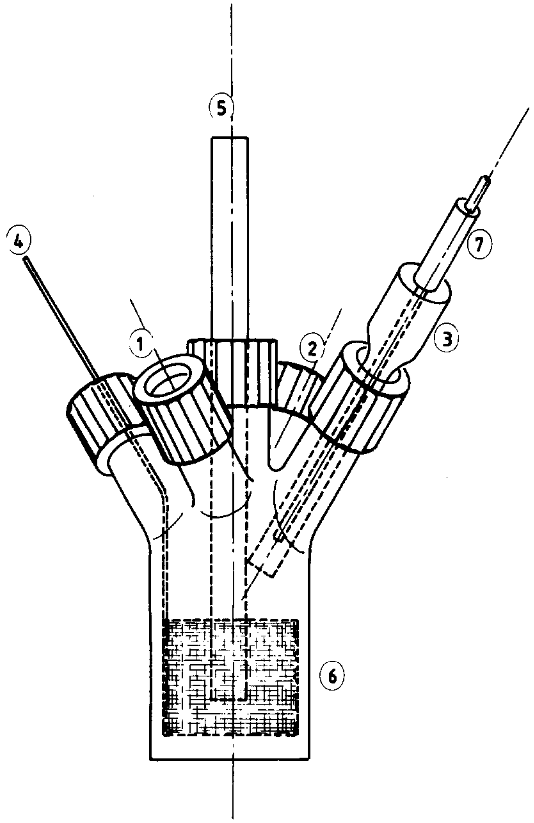

Fig. 1. Diagram of the electrochemical cell. Key: 1 and 2. Input and output of argon; 3. Tube with sintered glass cap to isolate the aqueous phase reference electrode; 4. Electrical lead connecting to gold gauze cathode; 5. Magnesium electrode; 6. Gold cathode; 7. Reference electrode.

The remaining 50% of the Ni^{II} is recovered more slowly, presumably from the decomposition of an organonickel complex to give R_2. The catalytic cycle then involves continuous electrolysis at the potential of the Ni^{II}/Ni^0 couple, with the cathodic process represented as follows:

$$2\,RX + 2e \xrightarrow{Ni} R_2 + 2\,X^-$$

Product identification

At the end of the electrolysis an aliquot of the solution was treated with an excess of dilute aqueous hydrochloric acid and the organic species were extracted into diethyl ether for identification by gas-liquid chromatography, and/or mass spectrometry, or NMR spectroscopy.

Results and discussion

Electrosynthesis

The results of the electrosynthesis experiments are summarised in Table 1. The

TABLE 1

ELECTROCHEMICAL COUPLING PRODUCTS

RX	% RX consumed	% R_2 formed vs. RX consumed
PhI	> 99	70
PhBr	> 99	75
PhCl	> 99	90
1-Br-naphthalene	> 99	75
$4\text{-BrC}_6H_4COCH_3$	> 99	[a]
$4\text{-ClC}_6H_4COCH_3$	> 99	[a]
$3\text{-ClC}_6H_4CH_3$	90	80
$2\text{-ClC}_6H_4COCH_3$	> 99	[b]
$2\text{-ClC}_6H_4OCH_3$	75	[b]
1-Br,1-butene	> 99	50 [c]
2-Br,2-butene	> 99	50 [c]
PhCH=CHBr	> 99	> 95 [c]
$PhCH_2Cl$	> 99	90
$3\text{-PhOC}_6H_4CHClCH_3$	> 99	[a,d]
1-Br-hexane	90	70
2-Cl-thiophene	> 99	[a]
2-Cl-quinoline	> 95	[a]
5-Br-indole	> 99	[a]
4-BrC_6H_4OH	> 99	0
$4\text{-ClC}_6H_4NO_2$	> 99	0

Solutions containing RX 0.3 M + $NiBr_2$bipy 2×10^{-2} M + bipy 4×10^{-2} M were electrolysed at -1.3 V vs. SCE until formation of stable Ni^0 or at most until the charge reached one mol-electron per mole of RX

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[a] Yield not calculated, but dimer identified as the main product. [b] Dimer only identified in trace quantities; main product is RH. [c] Starting material was a mixture of *Z*- and *E*-isomers; yield expressed as overall quantity of R_2, with no distinction between isomers. [d] Starting material was a racemic mixture; enantiomeric and *meso* forms of R_2 obtained in 1/1 ratio.

yields are generally satisfactory, especially in view of the simplicity of the techniques used. In experiments in which RX was completely consumed, the catalyst was almost completely recovered as the Ni^0 complex, and further dimerisation occurred on adding more RX. The electrochemical coupling can obviously be used with a wide variety of organic halides, with the exception of *ortho*-substituted aryl halides, and compounds which have protonic or other easily reduced substituents such as OH, COOH or NO_2.

Role of the magnesium anode

The sacrificial magnesium anode, whose weight loss corresponds to the process $Mg \rightarrow Mg^{2+} + 2e$ based on the quantity of electricity passed through the cell, does not appear to play a critical role in the coupling reaction, but rather allows anodic oxidation to proceed at a potential at which the reduced species, and especially Ni^0, are not re-oxidised. This is critical in using a single compartment cell, but we found that experiments in which anode and cathode compartments were separated by a glass sinter gave results identical to those with the apparatus described.

The magnesium may also act as a reducing agent in the catalytic cycle of the nickel-bipy complexes, as has been reported for the synthesis of polyphenylenes from aromatic dibromides [9], since the reaction

$$\mathrm{Mg^0 + Ni^{2+} \rightarrow Mg^{2+} + Ni^0}$$

is thermodynamically allowed. This may explain why we observed that the Faradaic yield for the conversion of RX was slightly greater than 100% in some cases. Tests carried out without electrolysis but with solution composition, time, etc, identical to those in the electrochemical experiments showed that such chemical reduction by magnesium metal can only account for at most, a 5–10% of the product yield.

The reductive coupling reaction is therefore seen as proceeding via the $\mathrm{Ni^{II}/Ni^0}$ catalytic cycle, and organometallic derivatives of magnesium are apparently not involved in the primary reaction. In keeping with this, magnesium can be satisfactorily replaced by other strongly electropositive metals such as aluminum or zinc.

The mechanism of the catalytic coupling process

The detailed mechanism of the electrochemical coupling which yields R_2 is not clearly understood, but the present results, and the preliminary results of electroanalytical measurements [8], lead to the following tentative model.

The nickel(0) catalyst is obtained by the two-electron reduction:

$$\mathrm{[Ni(bipy)_2]^{2+} + 2e \rightarrow [Ni(bipy)_2]^0} \qquad (4)$$

The addition of excess RX (RX = n-$C_6H_{13}Br$, C_6H_5Br, $C_6H_5CH_2Cl$, etc.) (see Table 1) to an Ni^0 solution prepared in this way causes total consumption of Ni^0, yielding Ni^{II} in quantities corresponding to 50% of the total nickel present. This excludes both the formation of a charge-transfer complex between Ni^0 species and RX and the formation of a stable reducible σ-organonickel RNiX complex, such as was found in the case of the analogous triphenylphosphine complexes (reactions 2 and 3) [6b,c,d]. We suggest that RNiX formed in the oxidative addition process

$$\mathrm{Ni^0 + RX \rightarrow RNiX} \qquad (5)$$

must react quickly by one of the following sequences, which are based on the mechanism proposed by Tsou and Kochi [10] for the synthesis of biaryls from triethylphosphine complexes of nickel.

SCHEME 1

$$\mathrm{2\ RNiX \rightleftharpoons R_2Ni + NiX_2} \qquad (6)$$

$$\mathrm{R_2Ni \rightarrow R_2 + Ni^0} \qquad (7a)$$

$$\mathrm{or\ R_2Ni + RX \rightarrow R_2 + RNiX} \qquad (7b)$$

There is ample evidence for each of these reactions, at least in the thermal decomposition of $ArNiX(PPh_3)_2$ [11], but in the present case one cannot exclude the reaction of RNiX with RX (Scheme 2) or with Ni^0 (Scheme 3).

SCHEME 2

$$\mathrm{RNiX + RX \rightarrow R_2NiX_2} \qquad (8)$$

$$\mathrm{R_2NiX_2 + Ni^0 \rightarrow NiX_2 + R_2Ni} \qquad (9)$$

SCHEME 3

$$RNiX + Ni^0 \rightarrow RNi^- + X^- + Ni^{II} \qquad (10)$$

$$RNi^- + RX \rightarrow R_2Ni + X^- \qquad (11)$$

In both of these schemes, the decomposition of R_2Ni to R_2 completes the sequence (eq. 7). Both require that eq. 5 is the rate-controlling process for the consumption of $[Ni(bipy)_2]^0$. We should point out that while Scheme 2 is consistent with the mechanism proposed for the metal-promoted coupling of organic halides [12], it appears to be inconsistent with the fact that stable ArNiX · bipy compounds were isolated in experiments using ArX itself as the solvent at room temperature (ArX = C_6H_5Cl, C_6H_5Br, *o*, *m*, *p*,-$CH_3C_6H_4Cl$) [13].

In any case, the overall rate of the electrocatalytic process is limited by the regeneration of nickel(II) via eq. 7 and subsequent reactions. Equation 7 probably proceeds via an interaction involving R_2Ni and RX, followed by the reductive elimination of R_2 (c.f. [14]) rather than by the first-order thermal decomposition of R_2Ni to R_2 and Ni^0. In agreement with this, we find that while *o*-substituted aryl halides such as *o*-bromoanisole do not yield the appropriate coupled biphenyl, the addition of a very reactive compound such as ethyl iodide results in the formation of 2,2′-dimethoxy-1,1′-biphenyl, with 1-methoxy-2-ethylbenzene as a minor product. The formation of this biaryl can also be brought about by blowing air through the solution of R_2Ni.

Mixed coupling reactions

In terms of the usefulness of this system in achieving the coupling of radicals from two organic halides, we find that the reactivity of the respective halides is critically important, at least in the case of aryl compounds. Thus if one halide is much more reactive than the other (e.g. $RX = C_6H_5I$, $R'X = p\text{-}CH_3C_6H_4Br$), the electrolysis of an equimolar mixture gives essentially R_2 in the early stages of the reaction, then R'_2 as RX is consumed. On the other hand, when RX and R′X are of similar reactivity (e.g., C_6H_5Br and $p\text{-}CH_3C_6H_4Br$), a mixture of the three products is found at all stages of the reaction in the statistically determined approximate ratio 25% R_2, 50% RR′, 25% R'_2. Unfortunately these results do not help in identifying the reaction mechanism, since all three schemes predict this same product distribution.

Conclusion

The method described provides a simple and efficient route to coupling products from a range of organic halides. The reactions are carried out at controlled potentials, and the catalytic precursor NiX_2 · bipy (X = Cl, Br) is recovered in almost quantitative yield at the end of the reaction. The mechanism is not clearly identified, and work on this aspect of the problem is proceeding, but this does not detract from the usefulness of the preparative method.

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