Pergamon

Tetrahedron Letters 40 (1999) 5993–5996

TETRAHEDRON
LETTERS

Catalysis by nickel–2,2′-dipyridylamine complexes of the electroreductive coupling of aromatic halides in ethanol

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Received 21 May 1999; accepted 15 June 1999

Abstract

Nickel–2,2′-dipyridylamine complexes are efficient catalysts for achieving in pure ethanol electroreductive dimerisation of aromatic halides or arylation of activated olefins. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: aryl halides; coupling reactions; nickel catalysis; electrochemical reactions.

Reductive couplings of organic halides catalysed by electrogenerated low valent transition metal complexes have been widely explored in aprotic solvents. Notably, zerovalent nickel–2,2′-bipyridine (Ni–bpy) complexes have proved to be very efficient catalysts in DMF or NMP to achieve either homocoupling reactions or cross-coupling reactions between organic halides and various electrophiles.[1]

Giving attention to economical and environmental considerations, we have recently shown that Ni–bpy catalysed electroreductive syntheses can also be carried out in alcoholic media such as EtOH/DMF or EtOH/MeOH mixtures.[2] Pure ethanol is not convenient since catalyst precursors NiX_2bpy (X=Br, Cl) are poorly soluble in this solvent.

The main aim of this work was to find conditions allowing the use of a cheap and safe solvent like EtOH, without any DMF or MeOH, and that is why we decided to replace bipyridine with another ligand. We selected 2,2′-dipyridylamine (dpa), a nitrogenous bidentate ligand, which would expectedly provide nickel complexes having catalytic properties similar to those of Ni–bpy complexes. Although 2,2′-dipyridylamine is known as a ligand of metallic cations,[3] little information related to nickel complexes is available.[4] Moreover, Ni–dpa complexes have never been used so far as catalysts in chemical or electrochemical syntheses.

We report here for the first time that the Ni–dpa system is an efficient catalyst to achieve various electroreductive couplings of aromatic halides in ethanol as solvent.

The first reaction we have studied is the electrosynthesis of biaryls according to Eq. 1.

$$2\,ArX \xrightarrow[EtOH]{Ni\text{-}dpa} Ar\text{-}Ar + 2\,X^- \qquad (1)$$

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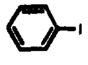
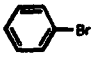
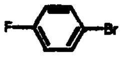
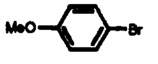
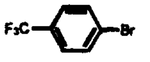
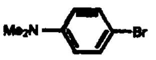
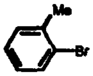
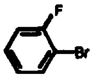
PII: S0040-4039(99)01157-0

Table 1
Ni–dpa catalysed electrosynthesis of biaryls in absolute EtOH

Entry	ArX	Ar-Ar : isolated yield / %
1		85[a] / 85[b]
2		95[a] / 84[b]
3		90[a] / 82[b]
4		32[a] / 46[b]
5		90[a] / 36[b]
6		63[a] / traces[b]
7		30[a] / traces[b]
8		43[a] / traces[b]
9		68[a] / traces[b]

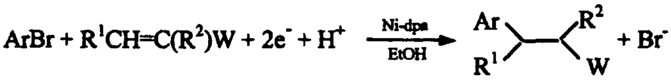
[a] : EtOH, $NiBr_2,3H_2O$ 1 mmol + dpa 1 mmol, ArX 10 mmol, I = 0.2 A, anode : stainless steel, room temperature.
[b] : For comparison results obtained from : EtOH/MeOH (1/1 v/v), $NiBr_2bpy$ 1.5 mmol, ArX 15 mmol, I = 0.3 A, anode : iron, temperature : 40 °C. (see ref 2)

Devices and procedures were the same as those previously used for Ni–bpy catalysed reactions in other solvents.[2,5] The undivided cell, described elsewhere,[6] was fitted with a stainless steel rod as the anode surrounded by a nickel grid as the cathode. In typical experiments the EtOH solution (50 ml) contained NaBr (2 mmol) as supporting electrolyte and the aromatic halide ArX (10 mmol). The catalytic precursor was formed in situ from equimolar amounts (1 mmol) of $NiBr_2$, $3H_2O$ and dpa. The electrolyses were conducted at room temperature and at constant current (0.6 $A.dm^{-2}$) until GC analysis of the samples indicated the full consumption of ArX, which required 1.5–2 electron mol per mol of halide. During the electrolyses, the potential of the cathode was around –0.9 V vs SCE, corresponding to the reduction of divalent nickel–dpa complexes as shown by cyclic voltametry.

After the electrolysis, most of the ethanol was evaporated and the residue was acidified with aqueous HCl (except in the case of 4,4′-dimethylaminobiphenyl). Most of the biaryls are solids. They were recovered by filtration, washing and drying, and characterised by MS, ^1H NMR and melting point. The results are reported in Table 1.

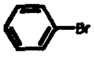
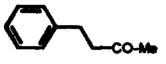
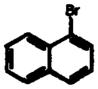
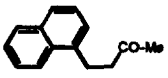
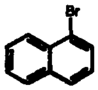
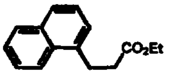
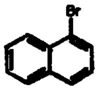
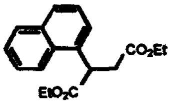
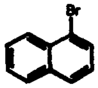
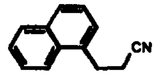
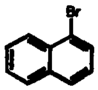
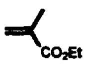
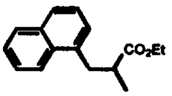
Depending on the starting compound, the yields in biaryls are either equal (Table 1, entries 1–4) or higher (Table 1, entries 5–9) than those previously obtained from Ni–bpy catalysis in EtOH/MeOH mixtures.[2] It is worth noting that *ortho*-substitued aromatic halides can be coupled in moderate yield in these new conditions, whereas the reaction was unsuccessful with a Ni–bpy catalyst.[7] In addition, with Ni–dpa in pure EtOH the faradaïc yields are higher (50–80%) than those obtained with Ni–bpy in EtOH/MeOH mixtures (~50%).

The other reaction we have investigated is the arylation of activated olefins (Eq. 2).



$$ArBr + R^1CH{=}C(R^2)W + 2e^- + H^+ \xrightarrow[EtOH]{Ni\text{-}dpa} Ar(R^1)CH{-}CH(R^2)W + Br^- \qquad (2)$$

Table 2
Ni–dpa catalysed conjugate addition of aryl bromides on activated olefins in ethanol

ArX	Activated olefin	Product	Isolated yield / %
			74[a] / 87[b]
			65[a] / 66[b]
			40[a] / 50[b]
			59[a] / 59[b]
			traces[a] / 61[b]
			traces[a] / 27[b]

[a] : EtOH, $NiBr_2,3H_2O$ 1 mmol + dpa 1 mmol, ArX 10 mmol, olefin 20 mmol, anode : stainless steel, I = 0.2 A, temperature : 20°C.

[b] : for comparison, results obtained from : DMF/pyr (9/1 v/v), $NiBr_2$, $3H_20$ 1.5 mmol, ArX 15 mmol, olefin 40 mmol, anode : iron, I = 0.08 to 0.2 A, temperature : 60 °C. (see ref. 8)

This reaction has been recently performed[8] by electrolysis of a solution of an arylbromide and an excess (2.5 equiv.) of activated olefin, at 60°C in an undivided cell using a sacrificial Al or Fe anode. The solvent was a mixture of DMF and pyridine (9/1 v/v). The catalytic precursor was $NiBr_2$ (5–10% vs ArBr), pyridine and the activated olefin acting as labile ligands of low valent nickel.

We have now achieved the reaction in absolute ethanol with experimental conditions identical to those described above for the synthesis of biaryls. The initial solution contains: ArBr (10 mmol), the activated olefin (20 mmol), $NiBr_2,3H_2O$ (1 mmol) and dpa (1 mmol). The reaction is best conducted at room temperature. After the electrolysis, evaporation of EtOH and addition of aqueous HCl, the product was extracted with diethylether, dried over $MgSO_4$, purified on silica gel and characterised by MS, ^1H and ^{13}C NMR. The results are presented in Table 2.

Yields of arylated olefins are roughly similar to those obtained in DMF–pyridine. However, in the case of acrylonitrile, the consumption of the aryl bromide was suppressed, possibly because the reactivity of the catalyst was too low due to overligation by both dpa and acrylonitrile. With ethyl methacrylate, poor yields were obtained in either reaction media. The side reaction is usually the reduction of ArBr into ArH. In these new conditions, no biaryl was formed providing that only one equivalent excess of the activated olefin was used.

In conclusion we have shown that the association of nickel and 2,2′-dipyridylamine gives a new and efficient catalytic system to achieve with simple and mild conditions, reductive couplings of aromatics halides in an unusual solvent, ethanol.

Acknowledgements

We wish to thank the Société Rhône Poulenc Rorer and Electricité de France for their financial support of this work.

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