Contents lists available at ScienceDirect







journal homepage: www.elsevier.com/locate/elecom

# Reduction of aryl halides at transition metal cathodes. Conditions for aryl-aryl bond formation The Ullmann's reaction revisited

# Viatcheslav Jouikov<sup>a</sup>, Jacques Simonet<sup>b,\*</sup>

<sup>a</sup> UMR 6510, Université de Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex, France

<sup>b</sup> Laboratoire MaSCE, UMR 6226, Université de Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex, France

### ARTICLE INFO

Article history: Received 9 March 2010 Received in revised form 26 March 2010 Accepted 26 March 2010 Available online 31 March 2010

Keywords: Electrochemical Ulmann's reaction Cathodic reduction Aryl iodides Homo-coupling

#### ABSTRACT

The cathodic reduction of some aryl halides ArX (1-naphthyl halides NpI and NpBr, iodo benzene and bromobenzene PhI and PhBr taken as model substrates) was achieved essentially in propylene carbonate (PC) considered for its high dielectric permittivity. Different electrode materials such as copper, silver, palladium, silver palladium alloy and nickel were used. Such conditions permit the activation of the C-X bond by metal (the step featuring similarity with Ullmann's reaction). Electron transfer to organometallic intermediates generated at the metal interface activates the formation of Ar–Ar linkages often in good yields, especially in the case of aryl iodides.

© 2010 Elsevier B.V. All rights reserved.

# 1. Introduction

The easy formation of aryl-aryl linkages is an important goal in chemistry, particularly in supramolecular chemistry or in the preparation of redox oligomers. There exist efficient methods for building aryl-aryl bonds. Thus, metals such as Mg<sup>0</sup>, Pd<sup>0</sup> and Ni<sup>0</sup> may react with C-X bonds of aromatic halides forming, via oxidative insertion (mainly in the presence of appropriate ligands), organometallic linkages e.g. C-Pd<sup>II</sup>-X known to promote a large palette of C-C couplings by the reaction with electrophiles like RX or Ar'X [1]. Worth quoting is Gattermann's method of dediazotation (reduction of diazonium salts by Cu in acids) which remains a great method for creating aryl radicals, which was used with success for building Ar-Ar' linkages or for the functionalization of radicalophilic surfaces [2]. Similarly, ArX (when X = I) can be converted into bi-aryls in the presence of copper (Ullmann's reaction [3]). The proposed key intermediate is an organometallic complex that could be written as ArCu<sup>1</sup>,X<sup>-</sup>. The species of this kind were formed [4] by contact of RBr with highly activated copper (formation of RCu<sup>1</sup>). These intermediates are often considered as nucleophilic species for reacting with organic halides. It is worth underlining that Ullmann's reaction is essentially performed with activated ArI (Scheme 1, Eq. (2)) at high temperatures.

In general, direct electrochemical reductions do not yield Ar–Ar linkages [5]. Until now, the data concerning ArXs deal mostly with the

C–X bond scission under electron transfer when using carbon electrode materials. Studies on dissociative electron transfer were carried out in polar organic solvents [6]. The transient aryl radical Ar<sup>•</sup> is very easy to reduce ( $E^{0}_{R/R}$ <sup>-</sup> of phenyl radical is 0.05 V vs. SCE [7]) so the overall process yields the anion Ar<sup>-</sup>. Recently [8], the voltammetric reduction of a large palette of ArBrs was achieved at smooth silver and the interest of using transition metals as electrode material was underlined. Large increases in reduction potentials were expected to be due to the selective affinity of Br<sup>-</sup> toward silver.

The studies [9,10] using metals as cathode materials (copper, nickel, silver and all these materials often associated to palladium in form of alloys) prompted us to re-consider the electrochemical aryl–aryl bond formation. This approach was based on the oxidative insertion involving metals now also used as a cathodic material: more precisely, electro-active species chemically formed according to Eq. (1) (Scheme 1) could be electrochemically activated for creating more efficient nucleophiles. Additionally, in order to boost the reactivity of ArX towards this nucleophile, the use of solvents of high dielectric constants is proposed for stronger polarization of the C–X bond increasing its electrophilicity. For this, PC possessing dielectric constant  $\varepsilon$ =66, – much higher than that of DMF ( $\varepsilon$ =37), – was successfully used. This preliminary work is focused on the capacities of ArXs to form dimers under changing such experimental conditions as solvents and electrode materials.

# 2. Experimental

All electrochemical studies were conducted in freshly prepared 0.1 M solution of tetra *n*-butylammonium tetrafluoroborate (TBABF<sub>4</sub>)

<sup>\*</sup> Corresponding author. Tel.: +33 23236292; fax: +33 23236732. *E-mail address:* jacques.simonet@univ-rennes1.fr (J. Simonet).

<sup>1388-2481/\$ -</sup> see front matter © 2010 Elsevier B.V. All rights reserved. doi:10.1016/j.elecom.2010.03.032

ich	eme	1.
~	CHIC	

in dimethylformamide (DMF), acetonitrile (AN), and PC. All potentials refer to aqueous saturated calomel electrode (SCE). The electrochemical instrumentation was previously reported [10].

Glassy carbon (GC), nickel, gold, copper and silver disks used as solid substrates had a surface area of 0.8 mm<sup>2</sup>. Prior to use, all electrodes were carefully polished with Norton polishing paper (type 02 and 03). Metals could be also deposited galvanostatically onto GC from acidic solutions of their salts. By this way, electrodes denoted as GC-M were obtained. Such depositions were carried out with electricity amounts of  $2 \times 10^{-3}$  °C mm<sup>-2</sup> at a current density of 500 µA mm<sup>-2</sup> (average thickness ≪0.1 µm). Before use, the electrodes were thoroughly rinsed with alcohol and acetone.

Ag–Pd alloy electrodes were prepared according to a specific procedure fully described in a previous report [10].

#### 3. Results

The voltammetric reduction of aryl iodides in PC is summarized by the data shown in Fig. 1. At a glassy carbon electrode (curve A), two main reduction steps (I and II) are obtained with NpI, corresponding to the two-electron cleavage of the C–I bond (step I) and the reversible reduction of the produced naphthalene (step II); these steps have  $E_{p/2} = -1.78$  V and -2.48 V, respectively. With palladium, silver, copper, nickel and gold electrodes, a catalytic step (IIIc) is then observed and all these materials display very large positive potential shifts relative to the potentials at carbon. Thus, at Ag–Pd, smooth



**Fig. 1.** Voltammetry of ArIs at solid electrodes  $(0.8 \text{ mm}^2)$  in PC + TBABF<sub>4</sub>. Scan rate 50 mV s<sup>-1</sup>. (A) – reduction of NpI (5.5 mmol L<sup>-1</sup>) at GC and (B) – at Ag–Pd (a), smooth silver (b), and at modified carbon surfaces: GC–Ni (c) and GC–Cu (d). (C) – reduction of PhI (6.3 mmol L<sup>-1</sup>) at GC and (D) – at Ag–Pd electrode (a), GC–Cu (b), GC–Ni (c), and GC–Pd (d) electrodes.

silver and smooth gold stationary electrodes, half-peak potentials of -1.24 V, -1.30 V and -1.40 V are respectively observed. Fig. 1 (curves B a, b, c and d) exhibits the reductions obtained at Ag–Pd and Ag electrodes, and those at glassy carbon surfaces modified by very thin ( $\delta$ <0.05µm) deposits of nickel and copper. Those catalytic steps are immediately followed by a reversible step (IV) that was identified as resulting from the reaction of aryl anion with organic carbonates (e.g. with PC, it is ring opening with the formation of an aromatic ester moiety reversibly reducible under these conditions).

PhI behaves quite similarly: Fig. 1 (curves C and D) shows that the reduction process is more complex than in DMF or AN. At a GC electrode, a two-electron step I ( $E_{p/2} = -1.93$  V) corresponds to the cleavage of the C–I bond. With Ag–Pd, a catalytic reduction peak (IIIc) (diffusion controlled) is obtained ( $E_{p/2} = -1.19$  V) while deposits of Cu, Ag, Pt, Pd and Ni onto GC show half-peak potentials equal to -1.38 V, -1.46 V, -1.46 V, -1.40 V and -1.47 V, therefore within a rather narrow potential range. Fig. 1, curves D b and c display the responses of the organic iodide at GC–Ni and GC–Cu surfaces. At more negative potentials, the reversible step (IV at -2.11 V) specific for the addition of the aryl anion to PC is observed.

ArBrs display similar results at transition metal surfaces. So at an Ag–Pd electrode, NpBr exhibits the step IIIc at -1.38 V and PhBr shows this step at -1.40 V. Voltammetry data obtained at solid surfaces modified by the deposits of Cu, Ag, and Pd are rather close to those obtained with parent ArIs.

One might expect that the materials clearly leading to potential shifts in voltammetry, in particular Ag, Ag–Pd, Cu or Pd, preliminarily react with ArXs (Scheme 1, Eq. (1)). Indeed, the solutions of ArXs in DMF and PC put in contact with smooth Cu or Ag plates clearly provoke (as shown in Fig. 2) a form of corrosion of the latter. Copper surface shows pinholes and copper crystallites, suggesting then a reaction of the halide with Cu followed by a disproportionation (in fact a mechanism already evoked for the Ullmann's reaction). At silver, a similar feature is obtained. The material is hollowed with a lot of channels of very small size scattered among Ag nano-particles. Additionally, the formation of an organometallic transient (Eq. (1)) is corroborated by reduction of organic halides in the presence of fine metal powders when taking a bare carbon electrode as a cathode and polarizing it at the potential at which ArX is not cleaved in the absence of catalyst. Stirring the solution allows the formation of a 3D electrode with metal particles playing the role of vector in this process. Thus, by a preceding reaction of ArX at their surfaces followed by a discharge of modified grains at the cathode, metal nano-particles of copper or silver could be deposited at the GC surface.

Lastly, potentiostatic electrolyses with different cathode materials were performed in a solvent like PC (or other organic carbonates) but also in DMF and AN in order to check the solvent effect. Most striking results obtained in PC are gathered in Table 1. Especially, reductions of NpI in PC lead to 1,1'-binaphthyl in quite high yields (runs 2 and 3). Electrolyses with different concentrations and in the presence of several tetraalkyl ammonium salts confirm these results. It was also found that fairly dry PC (kept under activated alumina) allowed higher yields of Np–Np without formation of naphthalene. Small amounts of a 1-naphthoate ester correspond to the addition of the anion Ar<sup>-</sup> to PC. This side reaction occurs whatever the experimental conditions. PhI similarly affords Ph-Ph (entry 1) as major product and certainly in a good yield. Still with NpI, the use of smooth Cu and Ag also led to the dimer but unexpectedly, quite large amounts of NpH were concomitantly obtained (entries 4 and 5). Entry 6 confirmed that the use of less dry PC (not maintained under activated neutral alumina) favors the two-electron scission at Ag with an increase in the relative amount of NpH. Additionally, reductive cross-couplings of mixtures of [NpI + PhI] were successfully achieved (entry 7). Phenyl acetylene considered as a radical trap (entry 8) could not confirm free aryl radicals as transients (no addition across the triple bond was observed). All experiments performed with ArBrs in PC yielded dimers in trace amounts only



**Fig. 2.** MEB images showing the reactivity of ArXs with metals. (A) – smooth copper in the contact with NpI during 4 h. (B) – smooth commercial silver after the contact with 4-iodobiphenyl ( $5 \times 10^{-3} \text{ mol } \text{L}^{-1}$ ) in PC during 6 h in the dark. (C) – smooth silver in contact with pure NpBr in the dark during 6 h. After reaction, all samples were consecutively rinsed with ethanol and acetone.

(NpBr, entry 9). The use of ethylene carbonate EC (with 20% of PC added to maintain the solution liquid) only allowed 2% of Np–Np. PhBr did not lead to any traces of biphenyl (entry 10). Lastly, it has been checked that DMF and AN under the conditions of Table 1 were unable to afford any coupling products with the studied ArIs, leading instead to the quasi-selective formation of ArHs.

# 4. Conclusion

This preliminary report emphasizes that the electro-coupling of ArX can be achieved by using metallic electrodes such as Ag–Pd, Ag, Ni

Potentiostatic electrolyses of ArX in PC and in mixtures of diethylcarbonate (DEC) with DMF in a divided cell. Electrolyte: TBABF<sub>4</sub>. Amounts of ArX: about 0.2 mmol. Applied potential: -1.6 V vs. SCE. Average amount of electricity for a total conversion of ArI: 1.5 F mol<sup>-1</sup>. (a) – the relative proportion of reduction products was obtained by ether extractions followed by GC/MS analyses. (b) – the reaction with solvent (here essentially a cyclic carbonate, PC) corresponds to the nucleophilic attack of the electrogenerated Nu (Ar<sup>-</sup>) on the C O of the carbonate group concomitantly with the ring opening. Here, the predominant isomer is ArC(O)OCH<sub>2</sub>CH(CH<sub>3</sub>)OH (c) – PC not kept over activated alumina. (d) – equimolar mixture of two ArXs. (e) – PAC: phenylacetylene in a 1:3 molar ratio to ArX. (f) – the reaction was not totally completed and a large amount of the starting compound left. (g) – formation of ethylbenzoate.

Run Electrode/		Substrate	Products, % <sup>a</sup>			
	solvent	ArX	ArH	Ar–Ar	Ar-solv- OH <sup>b</sup>	Other products, %
1	Ag-Pd/PC	PhI	-	87	13	-
2	Ag–Pd/ PC <sup>c</sup>	NpI	6	72	22	-
3	Ag-Pd/PC	NpI	-	78	20	Di- and tetrahydro forms of Np–Np <2
4	Smooth Cu/PC <sup>c</sup>	NpI	53	21	26	-
5	Smooth Ag/PC	NpI	42	43	14	-
6	Smooth Ag/PC <sup>c</sup>	NpI	68	18	13	-
7	Ag-Pd/PC	PhI + NpI <sup>d</sup>	NpH 24	(Ph) 4 (Np) 27	(Ph) 22 (Np) 11	Cross-coupling Np–Ph 12
8	Ag-Pd/PC	NpI + PAC <sup>e</sup>	24	52	20	(1-naphthyl)-phenyl- acetylene 3 Dihydro forms <1
9 10	Ag-Pd/PC Ag-Pd/ DEC-DMF (90:10)	NpBr <sup>f</sup> PhBr	68 -	0.1 -	32 100 <sup>g</sup>	-

and Cu. Best yields are obtained with Ag-Pd presumably because of a synergy of the concomitant action of two metals. If the use of such metallic surfaces is necessary, employing organic solvents of high dielectric permittivity such as PC appears essential. It has been shown that the coupling process does not involve aryl radicals as intermediates. It is expected that the key reaction is the one given by Eq. (4) although the intrinsic mode of reactivity remains unclear. The activation of the organometallic intermediate by electron transfer seems strongly increasing its nucleophilicity (decreasing  $\Delta G^{\neq}$ ) to allow its much faster reactivity on the starting halide. Thus, electrochemical activation has been already used for accelerating the reaction of Pd-aryl complexes [11]. Along with this activation, the ArX electrophilicity must be concomitantly boosted and this is apparently achieved by higher dissociative ability of PC. For the moment, this kind of "electrochemical" Ullmann's reaction remains valid for aryl iodides only.

#### References

- E. Negishi, General Discussions and Organomatallics of Main Group Metals in Organic Synthesis, Organometallics in Organic Synthesis, Vol. 1, John Wiley and Sons, N.Y, 1980.
- [2] J. Pinson, F. Podvorica, Chem. Soc. Rev. 34 (2005) 429.
- [3] M. Sainsbury, Tetrahedron 36 (1980) 3327.
- [4] R.D. Rieke, D.E. Stack, B.T. Dawson, T.-C. Wu, J. Org. Chem. 58 (1993) 2483.
- [5] D.G. Peters, in: H. Lund, O. Hammerich (Eds.), Organic Electrochemistry, Fourth Edition, Marcel Dekker, N.Y, 2001, p. 343.
- [6] J.M. Saveant, in: T.T. Tidwell (Ed.), Advances in Physical Organic Chemistry, Academic Press, N.Y, 2000, p. 117.
- [7] C.P. Andrieux, J. Pinson, J. Amer. Chem. Soc. 125 (2003) 14801.
- [8] A. Isse, P.R. Mussini, A. Gennaro, J. Phys. Chem. C 113 (2009) 14983.
- [9] J. Simonet, P. Poizot, L. Laffont, Platinum Metals Rev. 52 (2008) 84.
- [10] P. Poizot, L. Laffont-Dantras, J. Simonet, J. Electroanal. Chem. 624 (2008) 52.
- [11] C. Amatore, E. Carré, A. Jutand, H. Tanaka, D. Qinghua, S. Torii, Chem. Eur. J. 2 (1996) 957.