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Pd(0)-CATALYZED ELECTRO-REDUCTIVE COUPLING OF ARYL HALIDES

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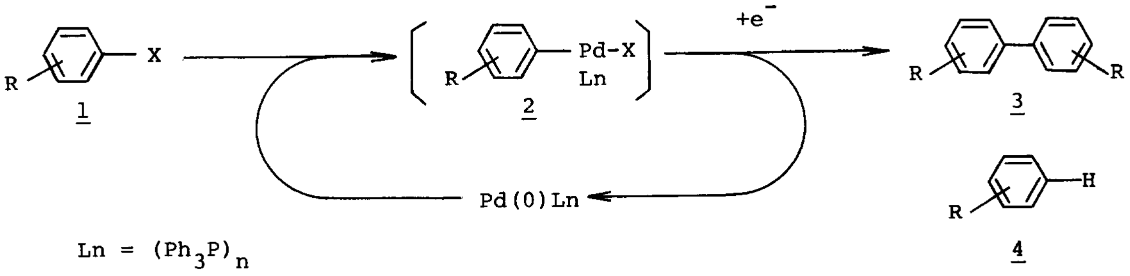
ABSTRACT: An efficient electro-reductive coupling of aryl bromides and iodides into biaryls has been performed by the electrolysis with Pd(0)- and/or Pd(II)-catalysts in a DMF-Et_4NOTs-(Pb cathode) system. 4-Bromo- and 2-bromopyridines were also converted into the corresponding bipyridyls, respectively.

Electro-reductive removal of halogen atom of aryl halides has been intensively investigated, particularly from a mechanistic viewpoint.1) It has been reported that in the electro-reduction of aryl halides, the replacement of halogen atom with hydrogen atom takes place predominantly and difficulties have been encountered in obtaining tha aryl-aryl coupling products in good yields. Recently, Ban2) and Perichon3) have reported Ni(0)-catalyzed electro-reductive coupling of aryl halides, in which, however, yields of biaryls (16-56%) and/or turnover of the catalysts (3 times) are not yet satisfactory.

In the course of our investigation on electro-reductive Pd(0)-recycling systems,4) we found an efficient coupling reaction of aryl halides 1 (X = Br and I) by use of Pd(0) and/or Pd(II)-catalysts in the electrolysis media.

Scheme 1



Electrolysis was carried out in an H-type divided cell fitted with Pb cathode (1.5 × 2 cm^2) and Pt anode (1.5 × 2 cm^2). A mixture of **1a** (R = *p*-*t*-Bu; X = I; 0.3 mmol) and Pd(0)$(Ph_3P)_4$ (0.02 mmol) in *N*,*N*-dimethylformamide (DMF, 10 ml) containing Et_4NOTs (0.5 g) was charged into the cathode chamber and a DMF solution (10 ml) of Et_4NOTs (0.5 g) into the anode chamber. After the cell was purged with argon gas, regurated dc power (2.5 mA/cm^2) was supplied (3.3 F/mol) at room temperature until most of the starting material was consumed. Usual workup of the catholytes afforded the corresponding biaryl **3a** (R = *p*-*t*-Bu) in 98% yield (entry 1 in the Table). In place of the Pd(0)-catalyst, Pd(II)$Cl_2(Ph_3P)_2$ could be used for this purpose (entry 2). Presence of the Pd-catalysts in the electrolysis media is indispensable for the aryl-aryl coupling reaction since electrolysis in the absence of the catalyst resulted in the formation of hydrogenolysis product **4a** (R = *t*-Bu, 57%) along with the recovered **1a** (42%) (entry 3).

In a similar manner, *p*-*t*-butylphenyl bromide **1b** (R = *p*-*t*-Bu; X = Br) was converted to the corresponding biaryl **3a** in 99% yield (entry 4), while chloride **1c** (R = *p*-*t*-Bu; X = Cl) gave no coupling product **3a** but yielded only 11% yield of hydrogenolysis product **4a** after passage of 4.1 F/mol of electricity (entry 5). Electro-reductive coupling of various para and/or meta-substituted phenyl halides **1** (X = Br and I) and 4-bromo- and 2-bromopyridines proceeded smoothly in the same electrolysis media (entries 6-11). In contrast, when ortho-substituted phenyl bromides **1** were submitted to the same electrolysis conditions, hydrogenolysis products **4** were obtained exclusively (entries 12 and 13). Electro-reduction of naphthyl halides resulted in the competitive formation of binaphthyls and naphthalenes (entries 14 and 15). The dramatical change of the products depending on the substrates would be due to the steric and/or electronic reasons.

It is interesting to note that the cross-coupling between two different aryl iodides **1** (R = *p*-Me_2N and *p*-*t*-Bu; X = I) could be achieved by using stoichiometric amounts of Pd(0)-complex in the electrolysis media (Scheme 2). Thus, after treatment of **1e** (R = Me_2N; X = I; 0.3 mmol) with Pd(0)$(Ph_3P)_4$ (0.3 mmol) in DMF (5 ml) containing Et_4NOTs (0.5 g) for 2.5 h, **1a** (0.3 mmol) was added and the mixture was electrolyzed in a similar manner as described above, yielding the cross-coupling product **5** (77%) exclusively.[5] Absence of appreciable amounts of homo-coupling products **3** (R = *p*-Me_2N and *p*-*t*-Bu) in

Scheme 2

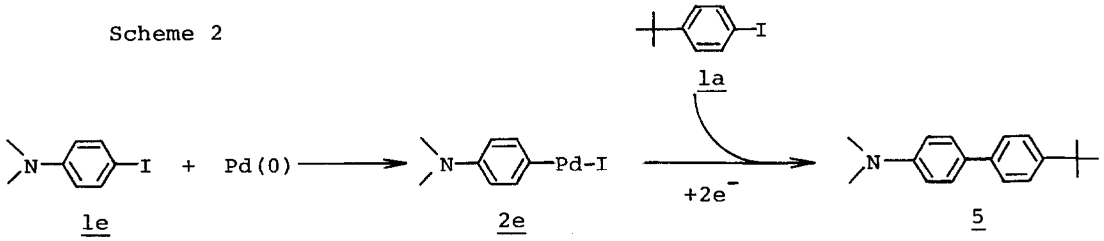
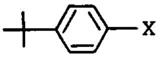
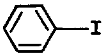
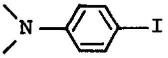
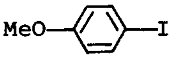
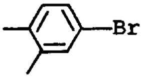
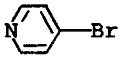
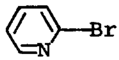
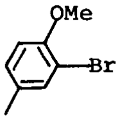
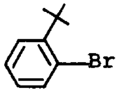
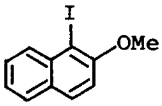
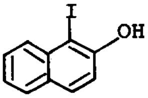


Table Electro-reduction of Aryl Halides with Pd-Catalysts[a)]

entry	substrate	Pd cat.[b)]	electricity (F/mol)	products, yield %[c)]		
				biaryl 3	arene 4	recov. 1
						
1	X = I	(0)	3.3	98	—	—
2		(II)	5.3	97	—	—
3		—	3.3	—	57	42
4	X = Br	(0)	4.1	99	—	—
5	X = Cl	(0)	4.1	—	11	78
6		(0)	2.9	94	—	—
7		(0)	4.7	93	—	—
8		(0)	3.7	87	—	—
9		(0)	2.8	78	—	—
10		(II)	2.4	91	—	—
11		(II)	2.8	91	—	—
12		(II)	2.2	—	96	—
13		(II)	4.1	—	99	—
14		(II)	4.9	53	43	—
15		(II)	2.8	16	53	—

a) Carried out in the presence of 7 mol % of Pd-catalysts at 2.5 mA/cm^2.

b) (0): $Pd(0)(Ph_3P)_4$; (II): $Pd(II)Cl_2(Ph_3P)_2$.

c) Isolated yields after column chromatography (SiO_2).

the electrolysis products suggests that an aryl-Pd complex formed *in situ* would be accumulated and coupled with iodide 1a in a highly selective manner, presumably *via* two electron reduction with loss of 2 equiv. I$^-$.

Although the mechanism of the Pd(0)-catalyzed electro-reductive aryl-aryl coupling has not been clarified, it is likely that in the early stage of the reaction, oxidative addition of Pd(0)-complex to aryl halides 1[6] would take place, affording 2, which would, in turn, suffer from discharge at the cathode (→6) as illustrated in Scheme 3.[7] This assumption is in good accordance with current-potential curves in Figure 1. Subsequent coupling of radical anion 6 with 1 would involve further one-electron reduction and successive elimination of 2 equiv. halide ions, leading to biaryl Pd-complex 7, a reductive elimination of which affords biaryls 3 with regeneration of Pd(0)-complex.[8]

Scheme 3

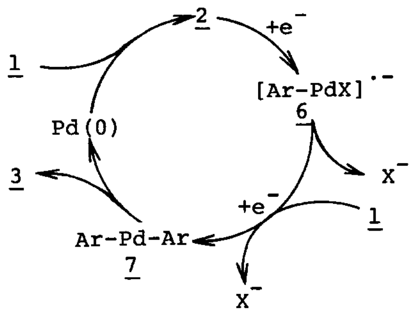
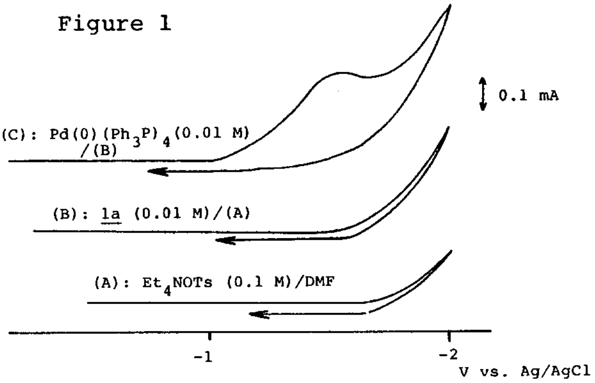


Figure 1



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4) S. Torii, H. Tanaka, T. Katoh, and K. Morisaki, Tetrahedron Lett., 25, 3207 (1984).
5) No detectable amounts of homo-coupling products 3 could not be isolated after column chromatography (SiO$_2$; hexane).
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