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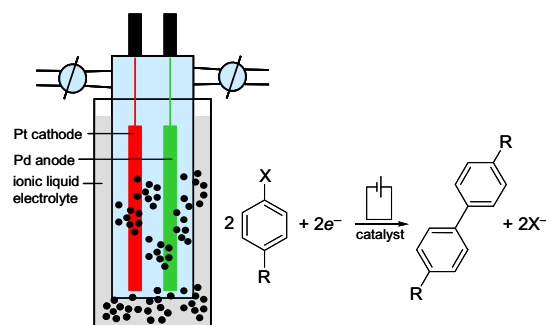
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*Electroreductive palladium-catalyzed
Ullmann reactions in ionic liquids*

Chapter 4



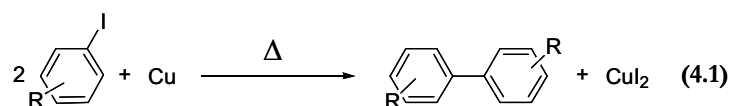
Abstract

A room-temperature catalytic alternative to the Ullmann reaction is presented based on electroreductive homocoupling of haloaryls catalyzed by palladium nanoparticles. The particles are generated *in situ* in an electrochemical cell, and electrons are used to close the catalytic cycle and provide the motivating force for the reaction. This system gives good yields using iodo- and bromoaryls, and requires only electric current and water as reagents. Using an ionic liquid solvent combines the advantages of excellent conductivity and cluster stabilising. The solvent is reusable at least five times. Kinetics experiments at different electrode potentials show that the two-electron oxidation of water closes the catalytic cycle by regenerating the Pd⁰. A mechanism involving radical anion formation is proposed. The advantages and limitations of this new system for carbon–carbon homocoupling and cross-coupling are discussed.

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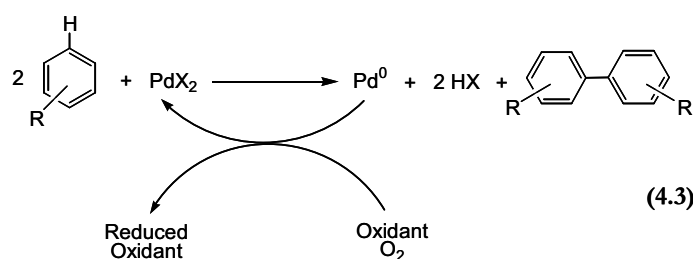
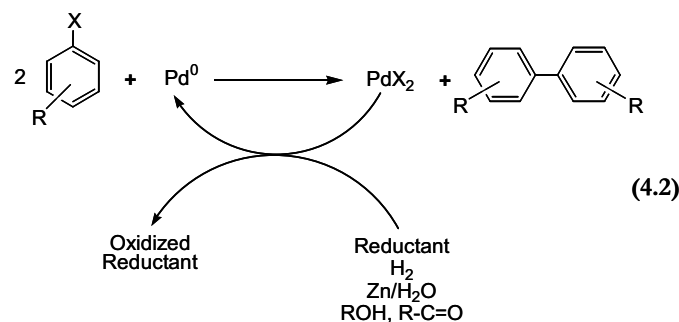
4.1. Introduction

Symmetrical biaryls are important intermediates for synthesizing agrochemicals, pharmaceuticals and natural products.^{1,2} One of the simplest protocols to make them is the Ullmann reaction,³ the thermal homocoupling of aryl iodides in the presence of copper metal. This reaction, though over a century old, it still used today without industrial alternative despite two main disadvantages: First, it uses stoichiometric copper, generating stoichiometric amounts of CuI_2 waste (**Equation 4.1**). Second, it only works with aryl iodides. This is a problem because chemicals react by their molarity, but are quantified by their mass, e.g. one tonne of iodobenzene contains 620 kg of 'iodo' and only 380 kg of 'benzene'. Aryl iodides are both expensive and wasteful in this respect.⁴

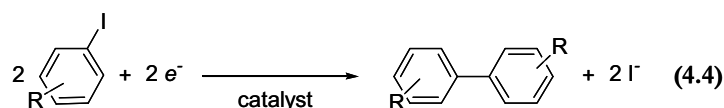


In the past five years, we showed that heterogeneous Pd/C catalyzes Ullmann-type reactions of aryl iodides, bromides, and chlorides. Two reaction pathways are possible: Reductive coupling (**Equation 4.2**), where Pd^{2+} is generated and reduced back to Pd^0 using an external reducing agent, and oxidative coupling (**Equation 4.3**), which starts with Pd^{2+} and needs an oxidizing agent. Different reagents can be used for closing the reductive coupling cycle, including HCO_2^- ,⁵ H_2 gas,⁶ $\text{Zn}/\text{H}_2\text{O}$,⁷ and alcohols.⁸ The two pathways can even be joined, giving a tandem system that converges on one product.⁹ All of these examples, however, require an additional chemical reagent.

Using electrochemistry is an interesting alternative, because in principle the reductive coupling requires only two electrons for closing the catalytic cycle. Ullmann-type reactions using a combination of electrochemistry and Ni^0 , Pd^0 or Co^0 complexes as well as sacrificial Mg anodes have been reported.^{10,11}



In this chapter, we present a different approach that combines electrochemical reduction and palladium nanoparticles catalysts in an ionic liquid solvent¹² (Equation 4.4). The catalytic cycle is closed by electrochemical regeneration of the Pd⁰ species.



4.2. Results and discussion

4.2.1. Palladium nanocluster-catalyzed electrosynthesis of biphenyl

The initial experiments were run with iodobenzene. In a typical reaction, PhI was stirred [octylmethylimidazolium]⁺[BF₄]⁻ in a specially constructed electrochemical cell (Figure 4.1, left) containing a Pd anode and a Pt cathode. Using an ionic liquid as solvent¹³ has two main advantages: First, it is a good conductor of electricity; second, it can stabilize metal nanoparticles *via* an ion bilayer mechanism, avoiding additional electrolytes or stabilizers.

This type of ‘ligand-free’ catalysis has gained considerable importance, as it avoids using expensive ligands and allows catalyst recycling.^{14,15}

The solution was kept at 25 °C under a constant current intensity of 10 mA (1.6 V) and the reaction progress was monitored by gas chromatography (GC). After 20 min, the reaction mixture turned from a light yellow solution to a dark brown suspension. However, no conversion was observed by GC analysis at this stage. The color change reflects the anodic oxidation of Pd⁰ to Pd²⁺ ions (**Equation 4.5**). These are in turn reduced to ad-atoms at the Pt cathode, and finally form stabilized Pd⁰ nanoparticles (**Figure 4.1, middle**).¹⁶ After 8 h, the PhI was totally consumed, giving 80% biphenyl and 20% benzene. Weighing the electrodes before and after the reaction showed a difference of ~ 2.5 mg in the Pd anode, equivalent to 0.1 mol% relative to the initial amount of PhI. This corresponds to a minimum TON of 1000 (assuming that all the ‘missing’ Pd participates in the catalysis).

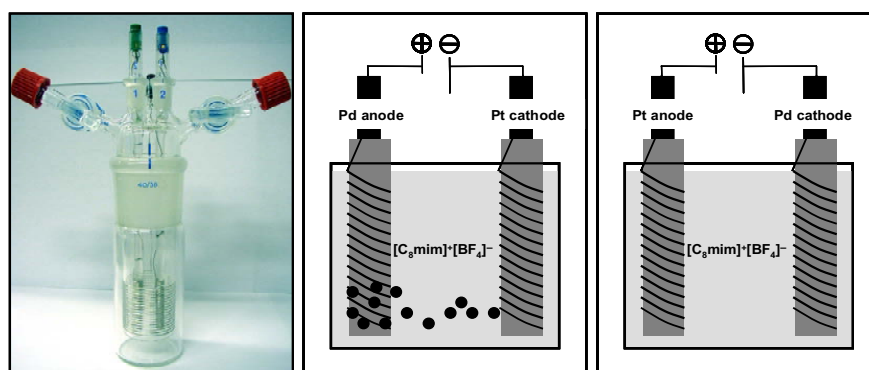
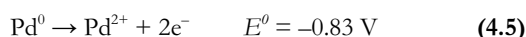


Figure 4.1. Photo of the two-electrode cell (*left*) and cartoons showing the generation of Pd clusters using a Pd anode and a Pt cathode (*middle*) and the reverse configuration (*right*).

To investigate the role of palladium nanoparticles in this system, we switched the current between the two electrodes, so that now the Pd electrode was the cathode and the Pt electrode was the anode (**Figure 4.1, right**). The rationale behind this experiment was that in theory, the catalysis could occur on the cathode surface (**Figure 4.2**).⁵ Direct electron transfer from a Pd⁰ atom on the cathode surface to PhI would give a [PhI]^{•-} radical anion,

that would then dissociate to Ph^\bullet and I^- .¹⁷ The constant supply of electrons to the cathode would ensure the electron transfer (**Figure 4.2**). However, we did not observe any reaction in this case, and no Pd nanoparticles formed. Thus, we conclude that in our system, Pd nanoparticles are necessary for catalyzing the homocoupling of aryl halides.

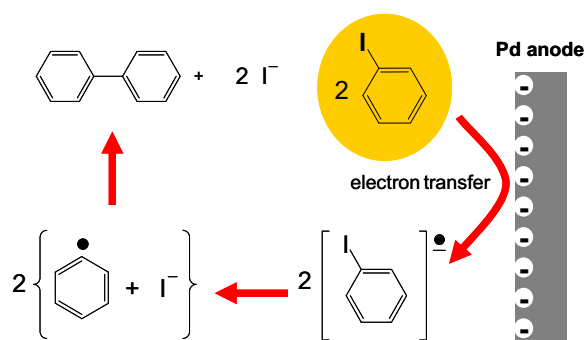

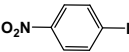
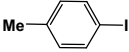
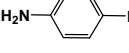

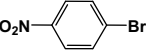
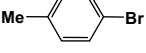
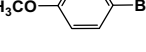
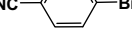
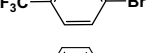
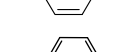
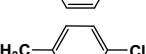
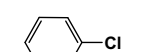



Figure 4.2. Testing the direct electro-transfer hypothesis, where the PhI^\bullet radical anion forms directly at the Pd cathode (this experiment was done using the reverse configuration, cf. Figure 4.1, *right*).

To examine the scope of this catalytic system, we tested a variety of *p*-substituted halo aryls (**Equation 4.6** and **Table 4.1**). Aryl iodides gave good yields (**Table 4.1**, entries 1–3) with the exception of the electron-donating iodoaniline. Aryl bromides were also active, but surprisingly less conversion was observed for the electron-withdrawing bromobenzotrifluoride. The corresponding chloride substrates showed little or no activity. The ionic liquid $[\text{omim}]^+\text{BF}_4^-$ was recycled after the reaction and re-used as solvent five times without change in activity (see experimental section for details).

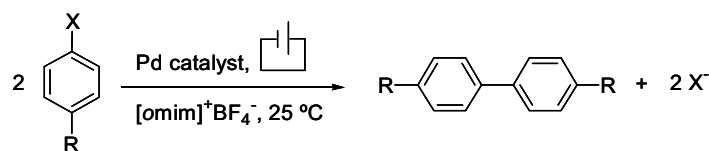
Table 4.1. Pd-catalyzed electroreductive homocoupling of various haloaryls.^a

Entry	Aryl halide	Conversion (%) ^b	Yield (%) ^b	TON ^c	Time (h)
1		99	80 (55)	800	8
2		99	82	820	8
3		83	76	760	9
4		56	35	350	9
5		99	75	750	14
6		74	61	610	20
7		83	59 (38)	590	24
8		80	65	650	24
9		78	61	610	24
10		20	14	140	24
11		5	4	40	24
12		5	3	30	24
13		< 1	-	-	-
14		< 1	-	-	-

[a] Reaction conditions: 20 mmol halide, 50 ml [omim]⁺[BF₄]⁻, 25 °C.

[b] Based on GC analysis, corrected for the presence of an internal standard. The numbers in the parentheses represent isolated yields.

[c] Minimum TON based on the difference in weight in the Pd anode before and after the reaction. This electrode weight difference was independent from the reaction time.

**1 a–h**

- 1a** R = H, X = I
1b R = NO₂, X = I
1c R = CH₃, X = I
1d R = NH₂, X = I
1e R = H, X = Br
1f R = NO₂, X = Br
1g R = CH₃, X = Br
1h R = OCH₃, X = Br
1i R = CN, X = Br
1j R = CF₃, X = Br
1k R = OH, X = Br
1l R = NO₂, X = Cl
1m R = CH₃, X = Cl
1n R = H, X = Cl

2 a–h

- 2a** R = H
2b R = NO₂
2c R = CH₃
2d R = NH₂
2e R = OCH₃
2f R = CN
2g R = CF₃
2h R = OH

3 a–c

- 3a** X = I
3b X = Br
3c X = Cl

(4.6)

4.2.2. Mechanistic studies

Palladium-catalyzed systems have been described as an alternative to the stoichiometric Ullmann protocol with copper. The reaction mechanism, however, is still unclear. One proposal involves the formation of a radical anion through a single electron transfer (SET) process that give a $[\text{PhX}]^{\cdot-}$ radical anion that then dissociates, forming a Ph^{\cdot} radical and ultimately the biaryl product.^{5,18} To understand the mechanism in our system, we must first clarify what closes the catalytic cycle and what role do the Pd clusters play in this reaction.

First, we monitored the kinetics of the model reaction for PhI coupling (**Figure 4.3**). An induction period of almost 3 h was observed.^{19,21} This induction period supports the involvement of palladium clusters in the cycle, because if the Pd⁰ atoms or ad-atoms alone are responsible for the catalysis, there would not be such a long induction period.

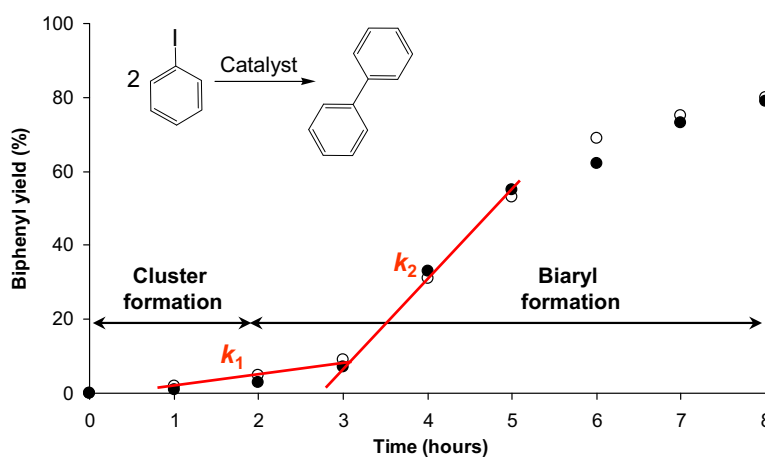


Figure 4.3. Time-resolved reaction profiles for the Pd cluster-catalyzed coupling of PhI. Reaction conditions are as in Table 1. The ‘o’ and ‘•’ symbols represent duplicate experiments.

After 3 h, the reaction rate increased from $k_1 = 0.0542 \text{ min}^{-1}$ ($R^2 = 0.979$) to $k_2 = 0.383 \text{ min}^{-1}$ ($R^2 = 0.999$, both R^2 values pertain to six observations in duplicate experiments). We think this is due to the “optimal particle size” formation during the induction period, as proposed by Finke and co-workers in the case of hydrogenation.²⁰ The unusual kinetic profile for such reactions, where an induction period was also found, was interpreted by Schmidt and Smirnov using the concept of a “cluster magic number”.^{20,22} We used transmission electron microscopy (TEM) to characterize the particle size at the end of the induction period. Spherical well-dispersed particles were observed (**Figure 4.4, left**) with a size distribution of $2.5 \pm 0.5 \text{ nm}$. This corresponds to a ‘magic number’ of ~ 300 atoms.

The TOF for these 2 h was 230 h^{-1} , more than double the average TOF during the entire reaction (100 h^{-1}). This also fits well with the ‘active cluster’ concept. Another interesting point is the reaction order for this period. We fitted the kinetic data and the best R^2 value was obtained for a first-order reaction ($k_2 = 0.383 \text{ min}^{-1}$, $R^2 = 0.999$; cf. with $R^2 = 0.977$ for second-order). This agrees with a first-order rate-determining step, e.g. the dissociation of the $[\text{PhX}]^{\cdot-}$ radical anion.

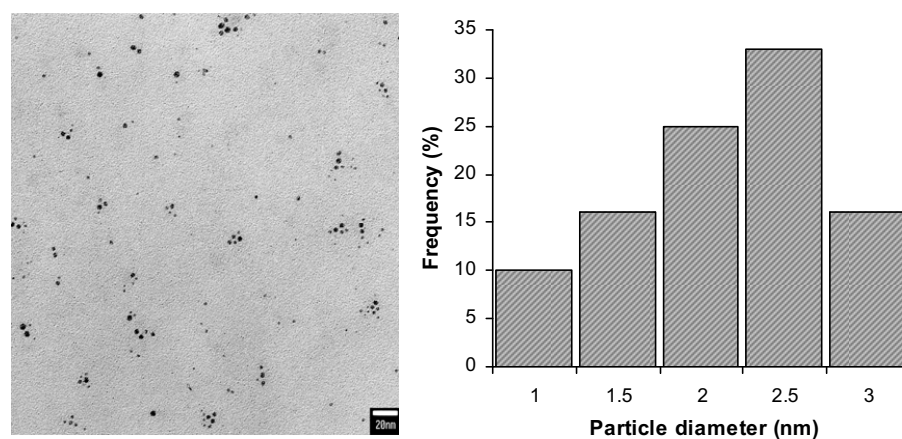


Figure 4.4. Transmission electron micrograph (*left*) and Pd cluster size distribution (*right*, based on 600 particles counted).

An important mechanistic question is: “what closes the catalytic cycle?” We think that it is oxidation of water into dioxygen (**Equation 4.7**), recovering the Pd⁰ catalyst and neutralizing the halide anions in the media. A similar reaction was observed by Raynal *et al.* in their elegant Ni complex-catalyzed electrosynthesis of biaryls in water.²³ Ionic liquids are notoriously hygroscopic, and a small water impurity would suffice for closing the cycle.²⁴ To test this hypothesis, we ran control experiments in the presence of one molar equivalent of water. The reaction was indeed faster (complete conversion after 6 h, *cf.* with 8 h for the ‘dry’ system). However, no difference in reactivity was found when more equivalents of water were added.



To obtain further evidence for the water oxidation, we performed a simple experiment varying the potential during the reaction (**Figure 4.5**). For the same model reaction, the applied potential (1.60 V) was decreased after a given time to below the potential necessary for water oxidation (1.23 V). Again, we observed an induction period of 3 h. Subsequently, the reaction rate increased, reaching ~30% conversion in 1 h. As expected, the same *k* value was found as before at this point ($k_3 = 0.383 \text{ min}^{-1}$, $R^2 = 0.999$ for four observations in duplicate experiments). After 4 h, the potential was decreased to 1.00 V for 3 h. GC analysis

showed that almost no reaction occurred. After 7 h, we increased the potential back to 1.60 V and the reaction re-started immediately, reaching the maximum conversion after ~10 h ($k_4 = 8.25 \times 10^{-3} \text{ min}^{-1}$, $R^2 = 0.920$ for 12 observations in duplicate experiments). This experiment shows that water oxidation indeed closes the cycle. Furthermore, the reaction can be controlled by simple variation of the potential.

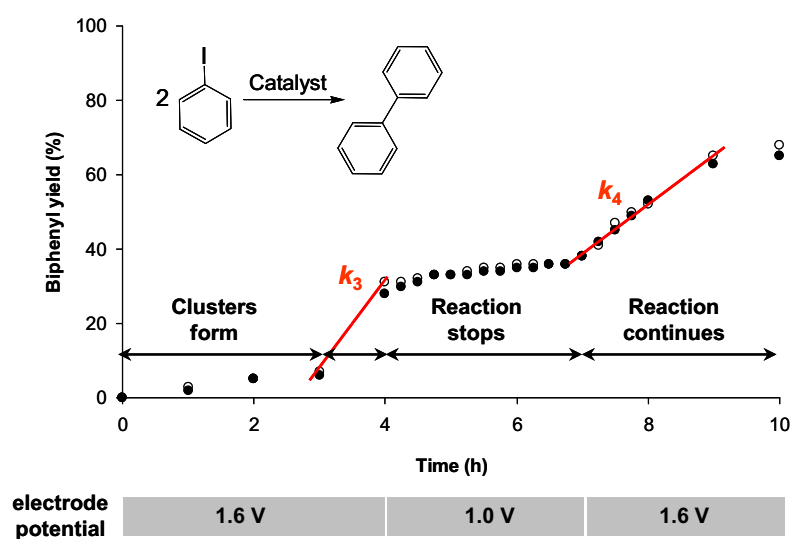


Figure 4.5. Time-resolved reaction profiles observed for the coupling of PhI to biphenyl using palladium clusters catalyst. Reaction conditions are as in Table 1. The ‘o’ and ‘•’ symbols represent duplicate experiments.

From these studies we conclude that two processes take place in this system. First, the *in situ* formation of the palladium nanoparticles. Second, the Pd-catalyzed electroreductive homocoupling of biaryls with a first-order rate-determining step. Based on this we propose a catalytic cycle (**Figure 4.6**) wherein a SET occurs from a Pd cluster to an ArX molecule, forming a $[\text{ArX}]^{\cdot-}$ radical anion and a positively charged Pd^+ cluster. In case of a single Pd atom, this would be unstable, but the charge on the cluster would be stabilized by the electron cloud of the neighboring Pd^0 atoms. First-order dissociation of $[\text{ArX}]^{\cdot-}$ to Ar^{\cdot} and X^- followed by coupling of two aryl radicals would give the biaryl product. Simultaneously, oxidation of water to dioxygen and 2H^+ regenerates the Pd^0 clusters and closes the catalytic cycle.

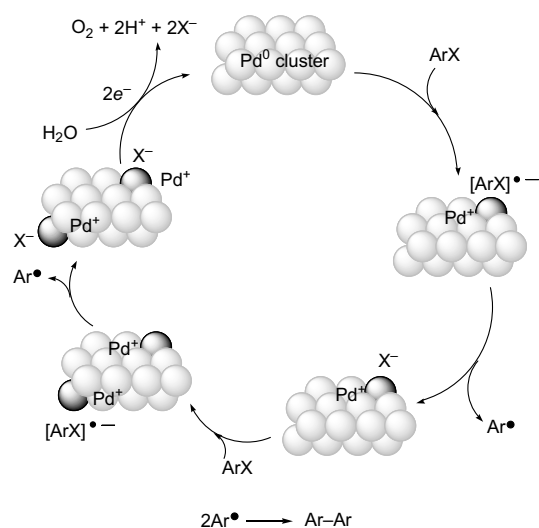


Figure 4.6. Proposed catalytic cycle for the electroreductive palladium-catalyzed homocoupling of aryl halides. The dark grey spheres represent Pd^+ ions. This cycle shows for clarity two single electron-transfers from the same cluster, but in principle these processes could also occur on different clusters.

4.3. Conclusions

We show that palladium nanoparticles generated *in situ* catalyze efficiently Ullmann-type reactions. To the best of our knowledge, this is the first time this reaction is performed using electro-reductive palladium catalysis. Room-temperature ionic liquids are good solvents for preparing and stabilising palladium nanoparticles. The kinetic data supports a cycle involving the formation of a phenyl radical anion that coordinates on the surface of the palladium nanoparticles. This attractiveness of this system lies in the fact that only electrons and water are necessary for closing the catalytic cycle. However, any practical large-scale application would have to include recovery of the ‘lost’ palladium catalyst.

4.4. Experimental section

4.4.1. Materials and instrumentation

^1H NMR spectra were recorded on a Varian Mercury vx300 instrument at 25 °C. GC analysis was performed on an Interscience GC-8000 gas chromatograph with a 100% dimethylpolysiloxane capillary column (DB-1, 30 m \times 0.325 mm). GC conditions (pentadecane internal standard): isotherm at 105 °C (2 min); ramp at 30 °C min^{-1} to 280 °C; isotherm at 280 °C (5 min). TEM images were obtained with a JEOL JEM-1200 EXII instrument, operated at an accelerating voltage of 120 kV. Samples were prepared by placing 150 μl of 0.1 mM Pd cluster suspension on carbon-coated copper grids. The solvent was then evaporated at 50 °C and 250 mm Hg. At least four images were taken for each sample. Electrochemical experiments were done using a special home-made cell coupled to a dual current supply with a maximum output of 10 V/40 mA. A detailed technical description of this system is published elsewhere.²⁵ The ionic liquid $[\text{omim}]^+[\text{BF}_4]^-$ was prepared following a published procedure and dried prior to use.²⁶ All other chemicals were purchased from commercial sources (> 98% pure). The ionic liquid solvent was recycled following a published procedure.²⁷

4.4.2. Procedure for Pd-catalyzed electroreductive Ullmann coupling

Example (1): Biphenyl (2a) from iodobenzene (1a). The electrochemical cell was charged with PhI (4.09 g, 20.0 mmol) and 50 ml $[\text{omim}]^+[\text{BF}_4]^-$. After stirring for 5 min, a constant current (10 mA, 1.6 V) was applied and the mixture was further stirred for 8 h at 25 °C. Reaction progress was monitored by GC. After 8 h, the product was extracted with ether (3 \times 50 ml). The ether phases were combined and evaporated under vacuum to give 0.81 g (55 mol% based on PhI) as colourless crystalline platelets, mp = 71–73 °C (lit.,²⁸ 69–72 °C). The solvent was recycled by washing with aqueous NaBF_4 . ^1H NMR (Me_4Si): δ = 7.36–7.42 (m, 2H), 7.45–7.51 (m, 4H), 7.62–7.68 (m, 4H). Good agreement was found with the literature values.¹⁵

Example (2): 4,4'-dimethyl-biphenyl (2c) from 1-bromo-4-methylbenzene (1f). The electrochemical cell was charged with MePhBr (3.50 g, 20.0 mmol) and 50 ml $[\text{omim}]^+[\text{BF}_4]^-$.

Chapter 4

Electroreductive palladium-catalyzed Ullmann reactions in ionic liquids

The reaction was performed as above to give 0.71 g (38 mol% based on MePhBr) as light yellow crystalline needles, mp = 118–121 °C (lit.,²⁹ 119–121 °C). The solvent was recycled by washing with aqueous NaBF₄. ¹H NMR (Me₄Si): δ = 2,51 (m, 6H), 7.41–7.49 (m, 2H), 7.53–7.57 (m, 4H), 7.60–7.66 (m, 4H). Good agreement was found with the literature values.²⁹

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