Synthesis of heteropolynuclear Cu^I and Pd^{II} complexes with polymeric 2,2´-biquinoline-containing ligands and investigation of their catalytic activity in the Sonogashira couplings

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A method for electrosynthesis of heteropolynuclear biquinoline-containing Cu^I and Pd^{II} complexes using sacrificial Cu and Pd anodes was developed. The sequence of anode dissolution (first Pd and then Cu) was important for the synthesis of the complex. The opposite sequence of dissolution resulted in oxidation of the initially formed Cu^I ions to Cu^{II}. The obtained Cu^I and Pd^{II} complexes with polymer ligands had high catalytic activity in the reaction of aryl halides with phenylacetylene giving rise to a $C(sp^2)$—C(sp) bond. The yield of arylphenylacetylene in the presence of 0.1 mol.% of Pd catalyst in relation to the starting halide was 50—90% depending on the nature of the aryl halide.

Key words: Cu^I- and Pd^{II}-containing polymers, biquinoline complexes, sacrificial anodes, metal complex catalysis, cross-coupling, Sonogashira reaction.

The development of effective catalytic systems in which several catalytic sites of different nature are immobilized on the same support is quite topical nowadays. The interest in these systems is due to a number of reasons, in particular, the ability to perform one-pot successive transformations (tandem or cascade reactions[1—5]), the possibility of catalytic processes that require both a catalyst and a co-catalyst (for example, Sonogashira and Stille reactions, *etc.*)[6—8] and some other. Catalyst regeneration by filtration and its low consumption are important parameters determining the compliance of catalytic processes to the requirements of "green chemistry". Currently, only a few examples of "multifunctional" catalysts are known. The catalytic sites can be supported on graphite materials, polymer substrates, polydentate ligands, *etc.*

Recently,[9] novel polymer systems containing biquinoline (biQ) or quinolyl-pyridine (QPy) fragments located in the backbone or side chain and able to coordinate transition metal ions were synthesized. Using these polymeric macroligands, polynuclear Cu^I complexes were synthesized;[10] they showed high catalytic activities in oxidative processes involving molecular O_2 (see Refs 11, 12). The coordination of Pd^{II} ions to the biQ fragments of the polymers gave rise to effective catalysts for the Suzuki reaction.[13] As a continuation of these studies, it is reasonable to study the electrosynthesis of heteropolynuclear complexes with polymer macroligands and their use in catalysis.

The purpose of this work is to develop and optimize the electrosynthesis of heteropolynuclear Cu^I- and Pd^{II}-containing complexes with polyamide ligands (PA) and to study the catalytic activities of the obtained polymeric complexes in the Sonogashira reaction, *i.e.*, coupling of aryl halides with terminal alkynes. This reaction is widely used in the synthetic practice, as it is a convenient method for the $C(sp^2)$—C(sp) bond formation in the synthesis of some pharmaceuticals, polyconjugated systems, and organic materials.[14—16] The experimental knowledge of synthetic applications of the Sonogashira reaction is fully reflected in a number of reviews.[6,17] However, the search for new catalysts of this reaction that are effective at minor loads (≤0.1 mol.% of catalyst) and suitable for recycling is still a topical task.

Electrosynthesis with sacrificial anodes is widely used for preparing transition metal chelates (see Ref. 18 and references cited therein). A considerable advantage of this method is the absence of additional anions in solution (which cannot be avoided in the syntheses with transition metal salts). The presence of some anions is often undesirable, as they can function as extra ligands in the metal coordination sphere. This is especially topical for the synthesis of catalytic systems, as the presence of a vacant coordination site (or a ligand that is easily eliminated, *e.g.*, a solvent molecule) is often a necessary condition for the catalytic process to occur.

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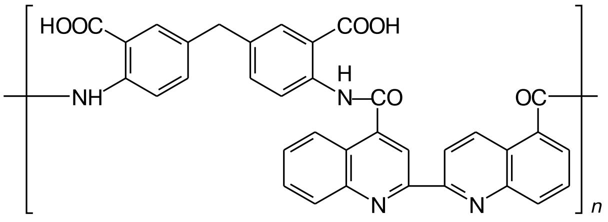
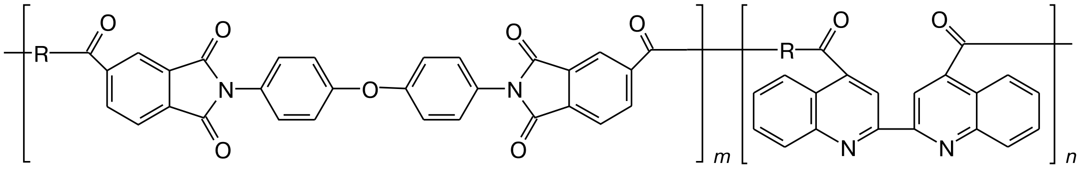


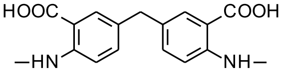
PA^{I}



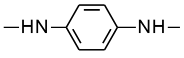
PA^{II}, PA^{III}

$m : n = 8 : 2$ (PA^{II}, PA^{III})
PA^{II} : R = R^1, PA^{III} : R = R^1 or R^2, R^1 : R^2 = 80 : 20,

R^1 =



, R^2 =



The interest in the complexes with polydentate sterically crowded macroligands is related to their ability to stabilize non-equilibrium coordinatively unsaturated states (which are normally most active in catalysis). In addition, polymers are less expensive and generally more processable than inorganic crystalline materials.

Experimental

N-Methylpyrrolidone (NMP) (Aldrich) was dehydrated with calcium hydride and distilled, the fraction boiling at 80 °C (7 Torr) being collected.

The electrochemical oxidation and reduction potentials were measured using an IPC-Win digital potentiostat/galvanostat connected to a personal computer. The cyclic voltammetry (CV) curves were recorded on a stationary platinum electrode at different potential sweep rates in the presence of 0.05 *M* $Bu_4{}^nNBF_4$ in *N*-methylpyrrolidone at 20 °C in a 10-mL electrochemical cell. Oxygen was removed by purging the cell with dry argon. Electrolysis was carried out using a P-5827 M potentiostat in a 10-ml undivided cell. A Pd wire 1 mm in diameter or a copper plate with an area of 2.4 cm^2 served as the working electrode (anode). A Pt wire functioned as the auxiliary electrode. The reference electrode was represented by a saturated silver chloride electrode (–0.48 V *vs.* Fc/Fc$^+$ in NMP). The measured potentials were corrected for ohmic losses.

The reaction mixtures obtained after the Sonogashira reaction were analyzed on a Finigan MAT SSQ 7000 GC/MS spectrometer (ionization energy 70 eV, a DV-5 quartz capillary column (30 m), temperature mode: 70 °C (2 min): –280 °C (10 min), heating rate 20 deg min^{-1}.

Electrosynthesis of the complexes [Pd^{II}PA][BF$_4$]$_2$ in solution. The Pd-wire was dissolved under galvanostatic conditions ($I = 1 \cdot 10^{-3}$ A) in 10 mL of a 10^{-3} *M* solution of PA (in relation to biQ fragments) in NMP in the presence of 0.05 *M* Bu_4NBF_4. The process was stopped after passage of a specified quantity of electricity (2.1 F per mole of biQ fragments). The composition of the obtained polymeric complexes was determined by CV based on the characteristic peak[13,19] of the Pd$^{II/0}$ redox transition accompanying the formation of the biQPdL$_2$ coordination units (–0.45 V *vs.* Ag/AgCl/KCl, L = NMP) whose concentration was 10^{-3} mol L^{-1}.

Electrosynthesis of the complex [Cu^{I}Pd^{II}PA][BF$_4$]$_3$ in solution. First, the Pd wire was dissolved under galvanostatic conditions ($I = 1 \cdot 10^{-3}$ A) in 10 mL of a $2 \cdot 10^{-3}$ *M* solution of PA in NMP in the presence of 0.05 *M* Bu_4NBF_4. The process was terminated after passage of a specified quantity of electricity (0.55 F per mole of biQ fragments of the starting polymer). After that, the Pd wire was replaced by a Cu plate, which was also dissolved under galvanostatic conditions ($I = 1 \cdot 10^{-3}$ A) in the same solution that contained the dissolved polymer and Pd^{II} ions. The process was terminated after passage of a specified quantity of electricity (0.25 F per mole of biQ fragments of the initial polymer). The composition of the obtained polymeric complexes was determined by CV based on the characteristic peaks[11] corresponding to the Pd$^{II/0}$ and Cu$^{I/II}$ redox transitions accompanying the formation of the biQPdL$_2$ (–0.45 V), biQCuL$_2$ (0.44 V), L = NMP, and (biQ)$_2$Cu (0.69 V) coordination units.

Sonogashira reaction (general procedure). Aryl halide ($1.9 \cdot 10^{-4}$ mol) was dissolved in NMP (5 mL), and phenylacetylene ($3.9 \cdot 10^{-4}$ mol) and Bu_3N ($5.8 \cdot 10^{-4}$ mol) were added. A dry argon flow was passed through the reaction mixture for 15 min to remove oxygen. Then a specified amount of a 10^{-3} *M* solution of a Pd (or Pd and Cu) catalyst in NMP was added. The reaction mixture was heated under argon at a specified temperature for a definite period of time. Then NaCl- and NaHCO$_3$-saturated water (100 mL) was added to the reaction mixture, and the reaction products were extracted with diethyl ether. The yield of arylphenylacetylene was determined by GC/MS (with naphthalene as the internal standard).

Results and Discussion

Electrosynthesis of Cu^I- and Pd^{II}-containing polymers with sacrificial anodes

One of the goals of this work was to employ metal anodic dissolution for the synthesis of biquinoline (biQ) containing polymers coordinated to Cu^I and Pd^{II} ions. This method is widely used for the synthesis of metal complexes; however, only few publications deal with the preparation of heterobimetallic complexes and clusters (see, for example, Ref. 20). In order to optimize the conditions of synthesis of the Cu^I- and Pd^{II}-containing polymeric complexes, it was necessary to (1) determine the order of dissolution of metallic anodes of different nature; (2) select the relative amounts of Cu^I and Pd^{II} ions coordinated to the polymeric ligands; and (3) study the effect of the nature of the polymeric ligand on the stability and the catalytic activity of heteropolymetallic complexes.

The complexes were synthesized in an undivided cell under either potentiostatic or galvanostatic conditions. The resulting polynuclear complexes were studied by CV. Previously, it was found**[13]** that Pd^{II} coordination to the biQ fragments of a polymer chain gives rise to an intense peak at −0.45 V (*vs.* Ag/AgCl/KCl) in the voltammogram, which corresponds to the Pd^{II}/Pd^0 transition, indicating the formation of $biQPdL_2$ (L is the solvent molecule, for example, NMP). The complexation with Cu^I ions was detected by appearance of peaks at 0.44 and 0.69 V (*vs.* Ag/AgCl/KCl) corresponding to the Cu^I/Cu^{II} redox transition accompanying the formation of coordination units with one or two biQ ligands in the copper coordination sphere, $biQCu^IL_2$ and $(biQ)_2Cu^I$, respectively (see Refs 10, 11, 12). Figure 1 shows the CV curve recorded for the heteropolynuclear complex containing Cu^I and Pd^{II} ions coordinated to the polymeric ligand PA^{II} in the molar ratio Cu : Pd : biQ = 1 : 1 : 4.* This shows two redox transitions corresponding to the $biQPdL_2$ and $(biQ)_2Cu^I$ complexes.

The variation of electrolysis conditions (polymer concentration, potential, current) provides complexes with different Cu^I to Pd^{II} ratios, which can be estimated from the relative current values corresponding to redox transitions involving these ions. However, an increase in the amount of generated Cu^I ions with respect to the biQ fragments remaining vacant does not entail a considerable increase in the number of active coordination units such as $biQCu^IL_2$, as excessive copper ions can replace Pd^{II} ions in the polymeric ligand. Meanwhile, an increase in the conformational rigidity of the polymer (replacement of PA^{II} by PA^{III} containing rigid *para*-phenylenediamine units in the polymer chain) favors the formation of coordination active sites $biQCu^IL_2$, as indicated by the feebly defined additional peak for Cu^I/Cu^{II} oxidation appearing in the CV curve at 0.44 V (Fig. 2).**[11]** The variation of the Pd^{II} : Cu^I : biQ molar ratio showed that approximately equal amounts of Pd^{II} and Cu^I ions and a three- to fourfold excess of the total number of biQ fragments of the initial polymer are optimal for catalytic reactions.

Variation of the sequence of dissolution of Cu and Pd anodes indicates that the initial generation of Pd^{II} ions followed by replacement of the Pd anode by the Cu anode after which the biQ units that remain vacant are coordinated to the Cu^I ions is optimal. The opposite sequence of metal dissolution results in Cu^I oxidation to Cu^{II} and the subsequent electrogeneration of Pd^{II} ions. Figure 3 shows the voltammogram of the heteropolynuclear complex with the PA^I polymer measured for successive dissolution of the Cu anode and Pd anode. It follows from the Figure that the potential of the $Pd^{II/0}$ redox couple remains unchanged and that the redox transition in the anodic region corresponds to $Cu^{II/III}$ oxidation (*cf.* Refs 11, 21).

The heteropolymetallic system $[Cu^IPd^{II}PA]$ is the first example of polynuclear Cu- and Pd-containing polymeric system obtained by electrosynthesis.

Catalytic activity of Cu^I- and Pd^{II}-containing polymers in the Sonogashira reaction

The catalytic properties of the synthesized heteropolynuclear complexes were estimated in the Sonogashira reaction, *i.e.*, coupling of aryl halides **1** with terminal alkynes. It is known**[6]** that implementation of the catalytic cycle requires the presence of a co-catalyst, Cu^I salt, which

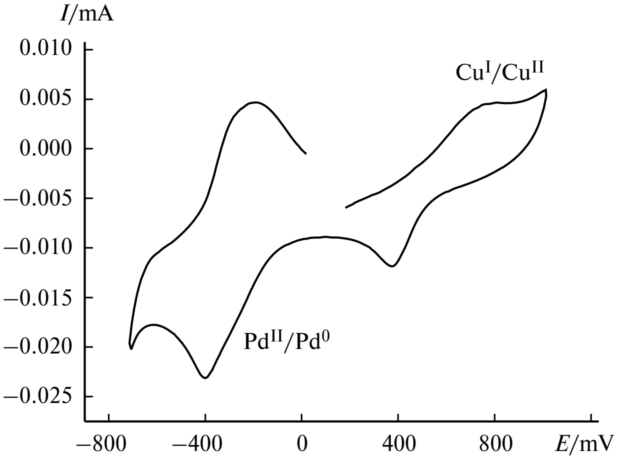


Fig. 1. Voltammogram of the heteropolynuclear complex containing Cu^I and Pd^{II} ions coordinated to the PA^{II} polymeric ligand (Pt, NMP, 0.05 *M* Bu_4NBF_4, molar ratio Cu : Pd : biQ = = 1 : 1 : 4).

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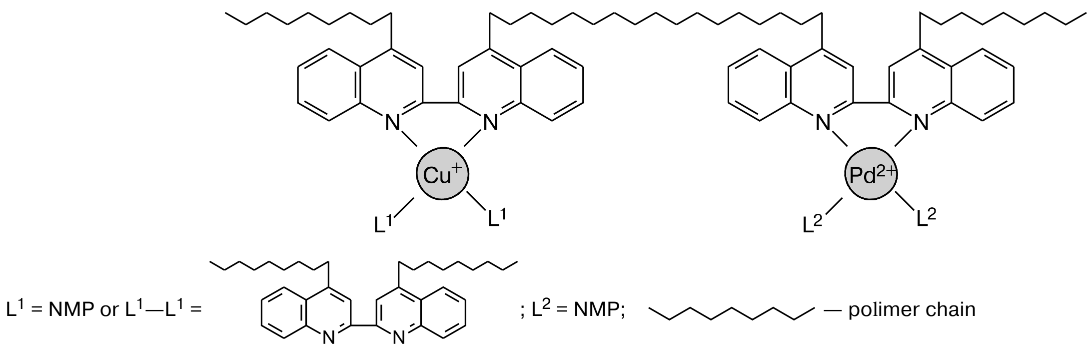
* The required ratio was attained by selecting the concentration of the polymer (and biQ fragments) and conditions of galvanostatic electrolysis (the current and the process duration, which determine the number of generated metal ions).

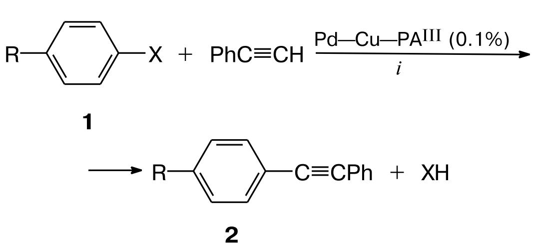


activates the alkyne giving rise to copper acetylenide, which then participates in transmetallation. Examples of Sonogashira reaction carried out without the copper co-catalyst were reported.[6] However, according to a publication,[22] palladium salts ($PdCl_2$, $Pd(OAc)_2$) used most often to prepare catalysts always contain minor copper impurities.

As the model reaction, we chose the reaction of aryl halides with phenylacetylene in the presence of Bu_3N as the base (Scheme 1). The reaction was carried out in NMP as this is the most suitable solvent for these polymeric systems. Both palladium and heteropolynuclear Cu^I/Pd^{II} complexes with various polymeric ligands (PA^I, PA^{II}, PA^{III}) were used as catalysts. The amount of the catalyst relative to the initial halide was varied from 7% to 0.1 mol.%. The results are summarized in Table 1.

The use of a large amount of the catalyst (7 mol. %) results in a quantitative yield of diphenylacetylene (see Table 1). The decrease in the amount of the catalyst to 1 mol.% and the decrease in the reaction time and temperature reduces the product yield to 64%. However, the introduction of Cu^I-containing coordination units into the polymeric ligand markedly increases the yield of diphenylacetylene. A tenfold decrease in the amount of the catalyst (to 0.1 mol. %) sharply decreases the efficiency of the process carried out with the catalytic system based on PA^I.

Scheme 1



i. NMP, 100 °C, 5 h.

In order to study the effect of the nature of the polymeric ligand on the efficiency of the catalytic process, heteropolynuclear Cu^I/Pd^{II} complexes with the ligands PA^I, PA^{II}, and PA^{III} were synthesized and added to the reaction mixture under identical conditions. The complex based on PA^{III} was most active, giving diphenylacetylene in 56% yield even with the use of 0.1 mol. % of the cata-

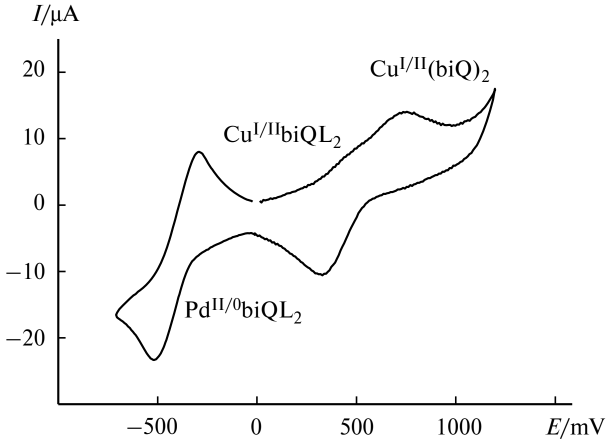


Fig. 2. Voltammogram of the heteropolynuclear complex containing Cu^I and Pd^{II} ions coordinated to the PA^{III} polymeric ligand (Pt, NMP, 0.05 *M* Bu_4NBF_4, molar ratio Cu : Pd : biQ = = 1 : 1 : 4).

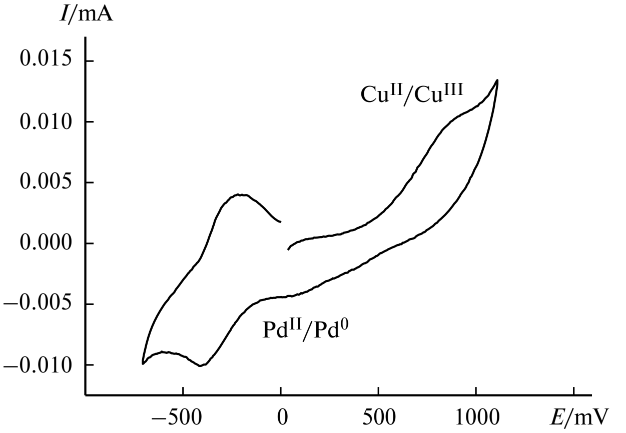


Fig. 3. Voltammogram of the heteropolynuclear complex containing Cu^I and Pd^I ions coordinated to the PA^I polymeric ligand (Pt, NMP, 0.05 *M* Bu_4NBF_4, molar ratio Cu : Pd : biQ = 1 : 1 : 4). The Cu-polymer complex was obtained first, and the Pd anode was dissolved in the presence of this complex.

Table 1. Yields of ArC≡CPh in the coupling of ArX ($1.9 \cdot 10^{-4}$ mol) with PhC≡CH ($3.9 \cdot 10^{-4}$ mol)[a]

Run	ArX	*T* /°C	*t* /h	Catalyst[b]	Yield ArC≡CPh (%)
1	PhI	130	4	$PdPA^{I}$ (7%)	>99
2	PhI	130	4	$PdPA^{II}$ (7%)	>99
3	PhI	110	2.5	$PdPA^{I}$ (1%)	64
4	PhI	110	2.5	$PdCuPA^{I}$ (1 : 1 : 3)[c] (1%)	76
5	PhI	100	2.5	$PdCuPA^{I}$ (1 : 1 : 3)[c] (0.1%)	19
6	PhI	100	2.5	$PdCuPA^{II}$ (1 : 1 : 3)[c] (0.1%)	22
7	PhI	100	2.5	$PdCuPA^{III}$ (1 : 1 : 3)[c] (0.1%)	56
8	PhI	100	5	$PdCuPA^{III}$ (1 : 1 : 3)[c] (0.1%)	88
9	$4\text{-}O_2NC_6H_4I$	100	5	$PdCuPA^{III}$ (1 : 1 : 3)[c] (0.1%)	86
10	$4\text{-}O_2NC_6H_4Br$	100	5	$PdCuPA^{III}$ (1 : 1 : 3)[c] (0.1%)	68
11	$4\text{-}CH_3OC_6H_4Br$	100	5	$PdCuPA^{III}$ (1 : 1 : 3)[c] (0.1%)	58
12	PhI	100	5	$Pd(BF_4)_2$(0.1%), $Cu(BF_4)$ (0.1%)	2

[a] Reaction conditions: NMP, Bu_3N $5.8 \cdot 10^{-4}$ mol, heating.

[b] Amount of the catalyst relative the starting halide.

[c] The molar ratio of the Pd, Cu ions and biQ fragments in the polymer is indicated.

lyst. An increase in the reaction time with the PA^{III}-based catalytic system resulted in the cross-coupling product in an about 90% yield at a low concentration of the Pd catalyst (0.1%). A control experiment with palladium and copper salts used without the polymeric ligand confirmed the key role of the ligand for implementation of the catalytic process.

It follows from the Table that the efficiency of the polymeric ligand changes in the sequence $PA^{I} < PA^{II} < PA^{III}$. The change in the catalytic activity is apparently related to the nature of the coordination Pd^{II} and Cu^{I} sites in the polymer. In our earlier studies,[13] the highest activity in the cross-coupling (Suzuki reaction) was found for palladium complexes ($biQPd^{II}L_2$) with the PA^{I} ligand containing biQ fragments in all monomer units of the chain; this may be related to the lack of additional units in the copolymer that would hamper the approach of the substrate to the catalytic site. In turn, the activity of the copper sites in the oxidation of organic substrates with O_2 proved to be the highest when PA^{III} was used as the ligand (see Ref. 12). This is caused by the fact that this polymer, which has the highest conformational rigidity, promotes the formation of the $biQCu^{I}L_2$ coordination units, which are most active in catalysis. These coordination sites contain solvent molecules that are easily eliminated, thus providing vacant coordination sites for introduction of reagents into the coordination sphere of a metal ion (unlike the $[(biQ)_2Cu^{I}]$ coordination units, which are much more stable).[12] The obtained activity sequence of the polymeric ligands indicates that the ability to form $biQCu(I)L_2$ active sites, which depends most appreciably on the nature of the polymeric ligand and is maximum for PA^{III}, is more important for the cross-coupling reaction.

Thus, an electrochemical route to heteropolynuclear biquinoline-containing Cu^{I} and Pd^{II} complexes, which allows combining catalytic sites of different nature on the same polymeric ligand, was developed using sacrificial Cu and Pd anodes. The order of anode dissolution (first Pd and then Cu) was found to be important for the synthesis of the target complexes. When the anodes are used in the opposite order, the initially formed Cu^{I} ions are oxidized to Cu^{II}. The resulting Cu^{I} and Pd^{II} complexes with polymeric ligands had high catalytic activities in the coupling of aryl halides with phenylacetylene. The catalytic system based on the more conformationally rigid PA^{III} polymer was most efficient.

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