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Polymer biquinolyl-containing complexes of Pd(II) as efficient catalysts for cyanation of aryl and vinyl halides with $K_4Fe(CN)_6$

Oleg M. Nikitin,[ab] Olga V. Polyakova,[a] Petr K. Sazonov,[a] Alexander V. Yakimansky,[c] Mikhail Ya. Goikhman,[c] Irina V. Podeshvo[c] and Tatiana V. Magdesieva*[a]

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A catalytic system for cyanation of aryl and vinyl halides with $K_4Fe(CN)_6$ based on a structurally tunable and nontoxic polymer backbone of polyamic type with biquinolyl fragments in the polymer chain capable of coordination to Pd^{II} ions is developed. The catalyst is eligible for thermal and microwave activation; in the latter case the reaction time is dramatically decreased. Cyanation of vinyl bromides occurs stereoselectively, and the configuration of the starting alkene is retained; even for *Z*-isomers the impact of configuration inversion is less than 5%. The polymer-based Pd catalyst is applicable for one-pot multi-step synthesis of the precursors of mesogenic structures of biphenyl type. Consecutive cross-coupling and cyanation reactions can be performed in the presence of the same portion of catalyst, in the same solvent, without isolation of intermediate products.

Introduction

Polymer backbones containing organic moieties capable of coordination to transition metal ions can be considered as polydentate macroligands which can be applied for the creation of homo- and heteropolymetallic catalytic systems. The usage of polymer catalysts provides important advantages such as easy separation from the reaction mixture, the possibility for immobilization on various supports as well as recycling. A bulky polymer ligand is prone to stabilize the nonequilibrium states of the coordination unit which are active in catalysis. All this provides a precondition for increasing interest in this type of catalytic systems and many efficient catalytic processes have been already elaborated using this approach (see, *e.g.*, ref. 1–8).

Polymers of polyamic type are widely used in various practical areas since they are easily accessible *via* facile synthetic procedures;[9–11] the simplest are commercially available. Recently,[12] new polymers of this type (PA, Scheme 1) which exhibit excellent thermal stability and good solubility in organic solvents were synthesized. The presence of the CH_2-group between two aromatic rings ensures plasticity, and imide fragments in the copolymer are responsible for the tensile strength of the polymer. The biquinolyl (biQ) fragments in the main chain of the polymer backbone provide an opportunity for coordination to transition metal ions, *e.g.*, Ni(II),[13,14] Cu(I),[15–18] Pd(II),[17,19] yielding polymer complexes which show excellent efficiency in electrocatalytic aerobic oxidation of aliphatic alcohols[15] and amines[16] to corresponding carbonyl compounds as well as in catalysis for C–C bond formation (Suzuki–Miyaura[19] and Sonogashira[17,18] couplings).

The present paper describes the further development of this research and is aimed at elaboration of an efficient catalytic process of cyanation of aryl and vinyl halides with $K_4Fe(CN)_6$ using Pd–polymer complexes of the aforementioned type (Scheme 2). Cyanation can be considered as one of the most synthetically important reactions since nitriles are valuable synthons in organic chemistry[20,21] as well as constitute key components of dyes, pharmaceuticals, herbicides, *etc.*[22] Currently, $K_4Fe(CN)_6$ is the reagent of choice in the majority of publications on this topic [see ref. 23 and references cited therein], since its first presentation in ref. 24.

Advantages of this reagent are very significant. $K_4Fe(CN)_6$ is non-toxic and cheap; all cyanide ions can be transferred to the halide providing an atom-economy strategy; the slow release of cyanide ions from $K_4Fe(CN)_6$ allows minimizing catalyst deactivation.[25,26] $K_4Fe(CN)_6$ utilization requires Pd or Cu catalysts and many catalytic systems have been already elaborated. The overwhelming part of publications describe catalytic cyanation of aryl halides (see ref. 23 and 27 and references cited therein) (mainly, iodides and bromides; examples of efficient cyanation of chlorides are rare[28–31]). As catalysts, Pd complexes with various phosphine ligands (which are very efficient but toxic and

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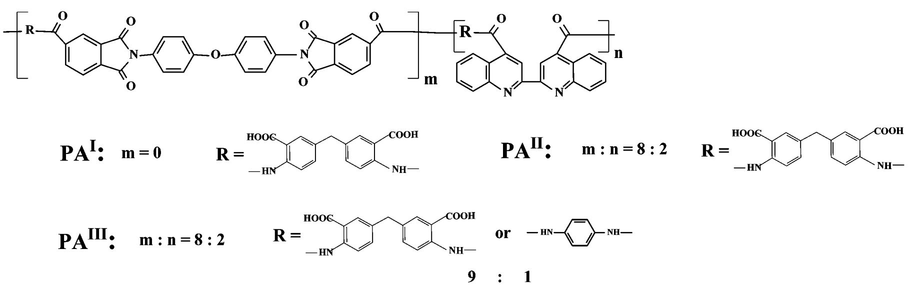
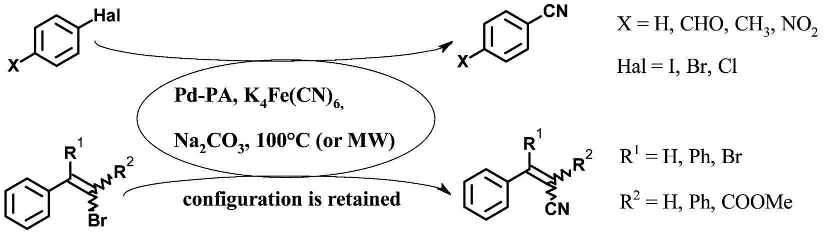
[a] Department of Chemistry, M.V. Lomonosov Moscow State University, Leninskie Gory, 1/3, Moscow, 119991, Russia. E-mail: tvm@org.chem.msu.ru; Tel: +7 (495) 939-30-65

[b] A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Science, Vavilova St, 28, Moscow, 119991, Russia

[c] Institute of Macromolecular Compounds, Russian Academy of Science, V.O., Bol'shoi pr. 31, St. Petersburg, 199004, Russia



Scheme 1 The structure of the polymer ligands.



Scheme 2 General scheme of aryl and vinyl cyanation.

expensive) are commonly used;[24,31–35] however, the current emphasis is gradually shifted to Pd nanocomposites[36–45] and polymer-bound Pd catalysts.[46–48] Copper containing catalysts are cheaper but usually less efficient, require harsh reaction conditions and usually have lower functional group tolerance.[49–51] Recently, combined Pd–Cu catalytic systems have been suggested for cyanation of aryl halides and have turned out to be rather efficient for iodides and activated bromides.[43,44]

As concerns cyanation of vinyl halides with $K_4Fe(CN)_6$, only few publications are available and the scope of halides is mainly limited to various styryl bromides.[50,52,53] Cyanation of aryl and vinyl halides usually requires elevated temperature. Currently, more and more publications are appearing in which microwave irradiation is used instead of commonly applied heating (see, *e.g.*, ref. 54–61). The use of microwave irradiation in homogeneous transition-metal catalyzed reactions leads to reduction of the reaction time producing high yields, higher selectivity and increased lifetime of the catalyst.

Thus, creation of Pd catalysts without toxic ligands which will be efficient for cyanation of both aryl halides (including cheap aryl chlorides) and vinyl halides and which are eligible for thermal and microwave activation is still a challenge.

Results and discussion

Pd–polymer complexes based on polyamic acids containing biquinolyl coordinating units can be obtained *via* Pd anode dissolution in the presence of the polymer ligand, as well as by the addition of a Pd salt, as it has been previously described.[19] The efficiency of catalytic systems obtained *via* two different approaches was previously tested in coupling reactions, and comparable yields of the products were obtained.[19] Since electrochemical Pd(0) deposition is quite a routine procedure[62] the electrochemical approach seems to be more convenient, due to the simplicity of the instrumental control over the reaction course and the absence of additional nucleophilic anions, which may play the role of extra ligands at the metal center and be harmful for catalysis.

The dissolution of the Pd anode was performed in a galvanostatic regime (I = 1 mA) in NMP solution containing a polymer (the amount of the polymer was calculated with respect to the required molar concentration of biQ units). The amount of electricity passed through the solution was estimated to provide the metal : biQ equimolar ratio. The composition of the catalytic centres obtained on the polymer chain was proved using cyclic voltammetry in combination with spectral methods and elemental analysis[19] indicating that $biQPdL_2$ coordination units (L = NMP) are formed. Pd content in the polymer can be determined by cyclic voltammetry. The characteristic peak corresponding to the PdII/0 redox couple in $biQPdL_2$ coordination units appears at a potential of −0.45 V[63] (*vs.* Ag/AgCl/KCl). A comparison of peak current values for the PdII/0 redox couple and for biQ reduction (−1.02 V) provides an estimation of the amount of catalytic units in the solution.

The thus obtained catalytic system was tested in the cyanation of aryl and vinyl halides.

Cyanation of aryl halides

One of the significant advantages of polymer-based catalysts is the possibility for fine-tuning of the structure of the polymer backbone to provide an optimal configuration and coordination environment of the catalytic center. To evaluate catalytic activity and to choose the best catalytic system, three polymer ligands were tested (Scheme 1). All of them are co-polymers which differ in the amount of biquinolyl units as well as in the presence of the phenylenediamine fragments which increase the conformational rigidity of the polymer. The reaction was performed in NMP

Table 1 The influence of the polymer type on the yield of the nitrile ($K_4Fe(CN)_6$, 0.04 mmol; p-$NO_2C_6H_4Br$, 0.2 mmol; Pd–PA (0.3 mol% of Pd); Na_2CO_3, 1 mmol; 2 ml of NMP, 8 h, 100 °C)

Catalyst	Pd–PA^{I}	Pd–PA^{II}	Pd–PA^{III}	Pd–biQ^{a}	Pd–bPy^{b}	$PdCl_2$^{c}
ArCN, %/conversion, %	90/91	52/55	21/26	14/16	11/12	24/25

[a] 8 h, 0.3 mol% of Pd[biQ(COOHex)$_2$]Cl_2 (biQ(COOHex)$_2$ = dihexyl ester of 2,2′-biquinolyl-4,4′-dicarboxylic acid). [b] 8 h, 0.3 mol% of Pd(bPy)Cl_2 (bPy = 2,2′-bipyridine). [c] 17 h, 1 mol% of $PdCl_2$.

solution (which turned out to be the best solvent for this type of polymers; it is also applicable both for microwave activation and for heating). First, *para*-$NO_2C_6H_4Br$ was selected as the model substrate and heating at 100 °C was used for activation. The catalyst was dissolved in NMP and its amount was calculated to provide 0.3 molar% of Pd. The reaction products were analyzed using a GC-MS system. The results obtained for three different polymers and for ligandless $PdCl_2$ taken for comparison are given in Table 1.

As follows from Table 1, the maximal yield of the nitrile was obtained using PA^{I}. This polymer is less rigid as compared to PA^{III} and contains biQ fragments in each monomer unit. This result is in line with the previously reported data when the same catalytic systems were used in Suzuki coupling.[19] Ligandless $PdCl_2$ gave poor results though the reaction time was doubled. The catalytic efficiency obtained for $PdCl_2$ in the presence of similar N-containing ligands of low-molecular weight (bPy and biQ) was higher but still sufficiently lower than that for the polymeric catalytic system. This emphasized the key role of the polymer ligand in the catalytic reaction.

For the screening of the reaction conditions, a series of experiments were performed varying the nature of the base. The role of the base is crucial to facilitate the reduction of the Pd(II) intermediate to catalytically active Pd(0)[64,65] as well as to provide a gradual release of the CN groups.[25] It was found that, among the common inorganic bases, application of Na_2CO_3 gave better yield of the nitrile (Table 2). K_2CO_3 is less efficient, in spite of similar basicity. Thus, Na_2CO_3 was used in all subsequent experiments.

Several experiments were conducted with some amount of water added into the reaction system to investigate its influence on catalytic efficiency. Rather inconsistent data on this subject can be found in the literature. It was shown that less than *ca.* 5% of water did not influence the cyanation[66] but addition of some amount of water can increase the solubility of hexacyanoferrate in organic solvents. Meanwhile, it has been demonstrated that hydrolysis of cyanide occurs to generate HCN which can compete with aryl halides for oxidative addition to Pd(0) catalyst and thus impair the catalysis.[26] Some examples of Pd-catalyzed cyanation with $K_4Fe(CN)_6$ in aqueous solution can be found in the literature.[41,53,67,68] To clarify the situation, the influence of water content was tested on a series of substrates including aryl bromides with electron-poor and electron-rich substituents as well as chlorobenzene. The results obtained indicate that the optimal NMP/H_2O ratio for our catalytic system is 9/1 (see Table 3). A further increase in water content dramatically decreases the yield of nitriles. One of the probable reasons might be a decrease in the solubility of the polymeric complex which leads to its coil-to-globule transition, thus decreasing the availability of the catalytic centers.

Table 2 The influence of the base nature on the yield of the nitrile ($K_4Fe(CN)_6$, 0.04 mol; p-$NO_2C_6H_4Br$, 0.2 mmol; Pd–PA^{I} (0.3 mol% of Pd); base, 1 mmol; 2 ml of NMP, 100 °C)

Base	Na_2CO_3	K_2CO_3	NaOAc	K_3PO_4	KF
Time, h	8	8	12	12	12
ArCN, %/conversion, %	90/91	62/62	55/57	6/8	6/20

Table 3 Effect of water on the yield of the nitriles ($K_4Fe(CN)_6$, 0.04 mmol; ArHal, 0.2 mmol; Pd–PA^{I} (0.3 mol% of Pd), Na_2CO_3, 1 mmol; 2 ml of H_2O–NMP mixture, 100 °C)

		NMP/H_2O (v/v)					
	ArCN yield/conversion, %	10/—	*t*, h	9/1	*t*, h	7/3	*t*, h
1	C_6H_5Br	73/73	12	81/84	12	6/8	12
2	p-OHC-C_6H_4Br	82/84	12	89/90	12	3/5	12
3	p-H_3C-C_6H_4Br	17/23	20	49/50	20		
4	C_6H_5Cl	12/12	20	39/40	20		

As follows from the tables presented above, PdPA^{I} exhibits sufficiently high catalytic activity in the cyanation of aryl bromides, but for aryl chloride the yield is moderate. The reaction was performed at an elevated temperature (100 °C) and for a prolonged reaction time (12–20 h). However, it was still not sufficient to provide complete conversion of the starting halide. To overcome the problem, microwave activation was tested. The use of microwave irradiation in homogeneous transition metal-catalyzed reactions is known to lead to remarkable reduction in the reaction time producing better yields and increased lifetime of the catalyst. Microwave activation has been successfully used in palladium-catalyzed cyanation of aryl halides in the previous reports.[54,56,57,61]

Application of the other type of activation (microwave irradiation instead of prolonged heating) required new experiments for optimization of the reaction conditions (Table 4). Iodobenzene was taken as a model substrate. Two different polymers were tested (PA^{I} and PA^{III}) and PA^{I} showed better results, as it has been previously observed under activation by heating. The bases were also varied and Na_2CO_3 was the best again. NMP, a microwave absorbing polar solvent, was used. However, water addition to NMP solution turned out to be harmful decreasing the yield of benzonitrile significantly (Tables 4 and 5). Furthermore, the best results were obtained when the salts were preliminary dried in vacuum and anhydrous solvent was used.

Comparison of the results obtained for halobenzenes under MW irradiation and under prolonged heating (see Table 5),

Table 4 Optimization of the reaction conditions for MW-assisted cyanation of iodobenzene ($K_4Fe(CN)_6$, 0.04 mmol; C_6H_5I, 0.2 mmol; Pd–PA^I (0.3 mol% of Pd); Na_2CO_3, 1 mmol; NMP, MW (70 W), 20 min)

	Catalyst				Base			NMP/H_2O	
	PdPA^I	PdPA^{III}	PdbiQ[a]	PdbPy[b]	Na_2CO_3	K_2CO_3	AcONa	10/—	9/1
ArCN/conversion, %	96/99	41/42	3/3	< 1/1	96/99	61/64	32/33	96/99	63/64

[a] PdbiQ(COOHex)$_2$Cl$_2$ was used as the catalyst (0.3 mol%, 20 min). [b] PdbPyCl$_2$ was used as the catalyst (0.3 mol%, 20 min).

Table 5 Halobenzene cyanation under MW irradiation (70 W, 20 min) and under prolonged heating (100 °C) ($K_4Fe(CN)_6$, 0.04 mmol; PhHal, 0.2 mmol; PdPA^I (0.3 mol% of Pd); Na_2CO_3, 1 mmol; 2 ml of NMP or H_2O–NMP mixture)

	ArCN/conversion, %				
	MW irradiation, 20 min			Heating, 100 °C	
	NMP	NMP/H_2O = 9/1	PdCl$_2$[a]	Time, h	NMP/H_2O = 9/1
C_6H_5Cl	46/46	9/10	2/3	20	49/50
C_6H_5Br	76/76	54/59	27/29	15	81/84
C_6H_5I	96/99	63/64		8	96/97

[a] Ligand-free PdCl$_2$ (1 mol%) in NMP was used as the catalyst.

with the other reaction parameters identical, showed that, for almost quantitative yield of benzonitrile to be obtained for phenyl iodide, 20 min and 8 h are required, respectively. This emphasizes the benefits of microwave activation in comparison with traditional heating methods and confirms that the polymer catalyst is stable under MW irradiation. The benzonitrile yields obtained for phenyl bromide and phenyl chloride after 20 min under MW irradiation are lower (76% and 46%, respectively) but incomplete conversion indicates that the yield can be increased by increasing the reaction time. To obtain similar yields in the case of thermal activation, prolonged heating of the reaction mixtures under optimized conditions is necessary (15 h and 20 h, respectively). To emphasize the role of the polymer ligand, both ligand-free PdCl$_2$ and PdCl$_2$ in the presence of similar N-containing ligands of low-molecular weight (biPy and biQ) were also tested as catalysts in the same reaction conditions. The dramatically lower yields (Tables 4 and 5) obtained confirmed the importance of the elaborated catalytic system.

Cyanation of vinyl halides

Cyanation of vinyl halides is much less investigated as compared to their aryl counterparts. Besides, the stereoselectivity issue arises. Having encouraging results for aryl halides, it was interesting to test the elaborated catalytic system for cyanation of vinyl bromides. Common heating and MW irradiation were applied. In a typical experimental procedure, a mixture of vinyl bromide, $K_4Fe(CN)_6$, Na_2CO_3 and PdPA^I (0.3 mol% of Pd) in NMP (or in NMP/H_2O = 9/1 v/v) was heated at 100 °C under Ar for the required period of time under intensive stirring. MW-activated reactions were performed in anhydrous NMP, with the same ratio of the reactants; the reaction time was 20 min. After the standard workup procedure, the products were analyzed using GC-MS (with the internal standard). *Z*–*E* configurations of the starting bromides and the corresponding nitriles were determined using ^1H and ^{13}C NMR. The chemical shifts of the signals of α- and β-protons in the bromides and nitriles with *Z*- and *E*-configurations differ significantly. This allows reliable control on the stereoselectivity of the process as well as the estimation of the conversion degree. Additional information can be obtained from the ^{13}C NMR signals of the nitrile carbon which are different for *Z*- and *E*-nitriles.

The first experiments were performed with *E*-bromostyrene. They demonstrated (Table 6) that with both ligand-free PdCl$_2$ and PdCl$_2$ in the presence of similar N-containing ligands of low-molecular weight (biPy and biQ) the reaction is very slow, as it has been observed also for aryl halides. Addition of 10% of water to NMP was found to have a profound effect on the yield of the nitrile. 12 h under common heating at 100 °C or 20 min under MW irradiation resulted in quantitative conversion of *E*-bromostyrene to the corresponding nitrile.

It was interesting to investigate the cyanation of vinyl bromides containing substituents at the α- and β-carbon atoms (Table 7). Cyanation of these substrates has not been investigated before; scarce publications are focused on styryl bromides with substituents in the aromatic ring.[50,52,53]

As follows from Table 7 (entry 7), cyanation of α-bromostyrene gave low yields of the nitrile, under both thermal and MW activation. In contrast to the other investigated compounds, the starting bromide was not detected in the reaction mixture but up to 20% of elimination product (alkyne) was present. One can suggest that a side-reaction of alkene or alkyne polymerization might take place. Dibromostylbene produced the corresponding dinitrile with good yield (entry 6) when two equivalents of $K_4Fe(CN)_6$ were taken. The brominated methyl ester of cinnamic acid gave good yield of the nitrile under prolonged heating whereas under MW irradiation the yield was low (Table 7, entry 5). Incomplete consumption of the starting bromide in the latter case indicates that the probable reason is a low reaction rate rather than side-reactions.

Table 6 *E*-Bromostyrene cyanation under MW irradiation (70 W, 20 min) and under prolonged heating (100 °C, 12 h) ($K_4Fe(CN)_6$, 0.04 mmol; *E*-bromostyrene, 0.2 mmol; Pd–PA^I (0.3 mol% of Pd); Na_2CO_3, 1 mmol; 2 ml of NMP–H_2O mixture)

	Heating, 100 °C NMP/H_2O ratio						MW irradiation
Conditions	10/—	9/1	7/3	9/1	9/1	10/—	NMP
Nitrile yield/ conversion, %	79/81	99	55/60	9/11[a]	10/12[b]	20/21[c]	100

[a] PdbiQ(COOHex)$_2$Cl$_2$ was used as the catalyst (0.3 mol%, 12 h). [b] PdbPyCl$_2$ was used as the catalyst (0.3 mol%, 12 h). [c] Ligand-free PdCl$_2$ (1 mol%) in NMP was used as the catalyst, 17 h.

Table 7 Cyanation of vinyl bromides under MW irradiation (70 W, 20 min) and under prolonged heating (100 °C, 14 h) ($K_4Fe(CN)_6$, 0.04 mmol; VinBr, 0.2 mmol; Pd–PA (0.3 mol%); Na_2CO_3, 1 mmol; 2 ml of NMP)

		Yield of VinCN[a], %	
No.	Vinyl bromide	Heating	MW irradiation
1	*Z*-PhCH=CHBr	99	99
2	*E*-PhCH=CHBr	99	100
3	*Z*-PhCH=CPhBr	97	97
4	*E*-PhCH=CPhBr	100	90 (100)
5	*Z*-PhCH=C(COOMe)Br	85 (89)	52 (53)
6	*Z*-PhBrC=CPhBr + 2 eq. $K_4Fe(CN)_6$	82 (84)	76 (79)
7	$PhBrC{=}CH_2$	5 (100)	24 (100)
8	$Ph_2C{=}CPhBr$	5 (8)	49 (52)

[a] The conversion is given in parentheses for the cases with incomplete transformation.

Reliable determination of the configurations of the starting bromide and the corresponding cyanation product was performed based on the NMR spectra, by comparison with the literature. Thus, *E*- and *Z*-cinnamonitriles can be distinguished due to the difference in the chemical shifts of the doublet signals corresponding to the α-protons (at 5.89 and 5.45 ppm, respectively[69]). In the case of 2-phenylcinnamonitrile, the signals of the *E*- and *Z*-isomers in ^{1}H NMR spectra are overlapped and the determination of the configuration of the product was based on ^{13}C NMR data, on the signals corresponding to the nitrile carbon atom which are well distinguished (chemical shifts are 120 ppm for the *E*-isomer and 118 ppm for the *Z*-isomer[70]). Differentiation between *E*- and *Z*-nitriles of 2-carbomethoxy cinnamon acid and determination of their relative amounts are more convenient to perform considering the singlets corresponding to the protons of the methyl group (chemical shifts are 3.76 ppm and 3.91 ppm for the *E*- and *Z*-isomer[71]).

In all cases *E*-bromides were stereoselectively converted to the corresponding nitriles with the retention of the starting alkene configuration. As concerns the *Z*-isomers, the traces (less than 5%) of the *E*-nitrile were detected in some cases. These results are in line with previously reported data[50,53] where cyanation of *Z*-styryl bromides provided a mixture of *Z*- and *E*-isomers (up to 20% of *E*-nitriles). The explanation given in ref. 53 seems reasonable. In the case of *Z*-styryl bromide, the NC–Pd–styryl intermediate may undergo β-elimination to form the alkyne–Pd–CN intermediate which can lead to a mixture of both *Z*- and *E*-isomers. Contrarily, the thermodynamically more stable *E*-bromide forms *E*-nitrile in a straightforward way. Detection of the alkyne in the reaction mixture (see above) serves as an indirect confirmation of the presented explanation. However, it should be emphasized that the polymer catalyst suggested in the present work provides extremely high stereoselectivity even for *Z*-isomers.

One-pot multi-step transformations

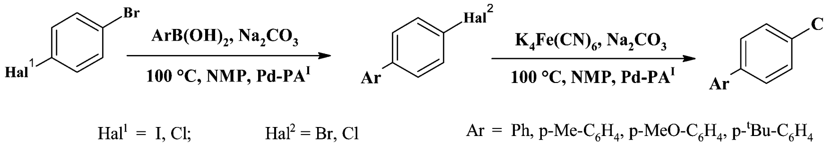
Synthesis of complicated organic molecules usually requires a large number of reaction steps involving separation and refining procedures. For economical reasons, it is necessary to reduce the number of steps, and one-pot synthesis is the best strategy. The applicability of the polymer-based Pd catalyst discussed in the present work for one-pot multi-step synthesis of the precursors of mesogenic structures of biphenyl type was tested.

Previously, we demonstrated that our catalytic system is efficient in Suzuki–Miyaura coupling.[19] Thus, cross-coupling and cyanation can be performed in the presence of the same catalyst. This enables catalysis of two different consecutive reactions in one-pot syntheses, in the same solvent, without separation of intermediate products (Scheme 3). However, this requires optimization and fine-tuning of reaction conditions with respect to the activity and selectivity of the catalyst for each reaction step.

As starting compounds, 4-iodo- and 4-chloro-bromobenzenes were taken. For catalysis, the PdPA^{I} complex was taken since this polymer ligand provides maximal efficiency in both coupling and cyanation reactions (see above). Suzuki–Miyaura coupling was performed first, to obtain the maximal selectivity. In this case we can be sure that only one halogen atom will be substituted in the first step for the aryl moiety (after one halogen atom is replaced, the product containing the phenyl ring with donor substituent becomes less active for further transformation as compared to the starting dihalide). Commonly, a small excess of boronic acid is used but we had to avoid it, to prevent substitution of the second halogen atom. If cyanation is performed first, formation of a dinitrile by-product can be expected (due to the activating effect of the electron-withdrawing CN-group). Thus, the possibility for selective substitution of the most active halogen atom for the aryl fragment was tested first. In the next step, $K_4Fe(CN)_6$ was added to the reaction mixture obtained in the first step without any purification; no additional portions of the catalyst were used to provide substitution of the second halide for the nitrile group.

To optimize the reaction conditions, Suzuki coupling was tested first. A number of boronic acids with different substituents were applied; the reaction was performed in NMP at 100 °C, using PdPA^{I} (0.3 mol% of Pd) in solution, with Na_2CO_3 as a base. The results obtained are given in Table 8.

Usually, the reaction is performed at higher temperatures (130 °C and more). To make the reaction more selective, the applied



Scheme 3 Consecutive one-pot cross-coupling and cyanation of aryl dihalides.

Table 8 The yields of 4-halobiphenyls in Suzuki–Miyaura coupling (ArHal, 0.2 mmol; $ArB(OH)_2$, 0.2 mmol; $PdPA^I$ (0.3 mol% of Pd); Na_2CO_3, 1 mmol; 2 ml of NMP, 100 °C, 6–10 h)

ArHal	Time, h	$ArB(OH)_2$	Biphenyl, %
p-I-C_6H_4-Br	6	$PhB(OH)_2$	>99
p-I-C_6H_4-Br	8	p-CH_3-$C_6H_4B(OH)_2$	>99
p-I-C_6H_4-Br	8	p-^{t}Bu-$C_6H_4B(OH)_2$	>99
p-I-C_6H_4-Br	8	p-CH_3O-$C_6H_4B(OH)_2$	95
p-Cl-C_6H_4-Br	10	$PhB(OH)_2$	>99
p-Cl-C_6H_4-Br	10	p-CH_3-$C_6H_4B(OH)_2$	98
p-Cl-C_6H_4-Br	10	p-^{t}Bu-$C_6H_4B(OH)_2$	96
p-Cl-C_6H_4-Br	10	p-CH_3O-$C_6H_4B(OH)_2$	96

temperature was 100 °C. As follows from Table 8, this allowed selective substitution of the more active halogen. The reaction time for iodo- and chloro-bromobenzenes was different (6–8 h and 10 h, respectively).

The products of the Suzuki coupling were isolated and subjected to the cyanation procedure, to optimize the reaction time. The results are given in Table 9. As follows from the data presented, 15 h for bromides is enough to get a good yield of the cyanated biphenyls. For the corresponding chlorides, the reaction time was increased to 24 h and the nitriles were obtained with moderate yields. Hence, the reaction time for these compounds should be prolonged.

Using these data, one-pot consecutive cross-coupling and cyanation reactions were performed. After allowing the time required for arylation, a probe for GC-MS analysis was taken (to test the completion of the coupling) and the cyanating agent with a new portion of the base was added to the reaction mixture which was subjected to additional heating at the same temperature for 15–24 h. After the work-up procedure, the products were analyzed using GC-MS. The yields of cyanated biphenyls are given in Table 10.

Unfortunately, after the work-up procedure the polymer catalyst becomes insoluble and it cannot be used twice. To overcome the problem, the immobilized form of the catalyst was applied. To prepare the immobilized catalyst, the graphite fabric was placed in the solution of $PdPA^I$ in NMP for 2 h; the graphite fabric impregnated with the catalyst (0.1 mol% of Pd) was taken off, dried and rinsed with MeCN to remove non-coordinated Pd ions and dried in vacuum. Afterwards, it was used for the one-pot two-step reaction described above.

After the reaction came to completion, the immobilized polymer catalyst was taken from the solution, rinsed and used again without purification with new portions of the reactants.

Table 9 The yields of cyanated biphenyls (ArBr, 0.2 mmol; $K_4Fe(CN)_6$, 0.04 mmol; $PdPA^I$ (0.3 mol% of Pd); Na_2CO_3, 1 mmol; NMP, 100 °C)

Ar-C_6H_4-Hal	Time, h	Yield of Ar-C_6H_4-CN, %	Conversion, %
Ph-C_6H_4-Br	15	87	87
p-CH_3-C_6H_4-C_6H_4-Br	15	86	88
p-Bu-C_6H_4-C_6H_4-Br	15	82	83
p-CH_3O-C_6H_4-C_6H_4-Br	15	75	76
Ph-C_6H_4-Cl	24	76	77
p-CH_3-C_6H_4-C_6H_4-Cl	24	81	82
p-Bu-C_6H_4-C_6H_4-Cl	24	48	52
p-CH_3O-C_6H_4-C_6H_4-Cl	24	63	65

Table 10 The yield of products in two-step one-pot synthesis (RHal, 0.2 mmol; $ArB(OH)_2$, 0.2 mmol; $K_4Fe(CN)_6$, 0.04 mmol; $PdPA^I$ (0.3 mol% of Pd); Na_2CO_3, 2 mmol; 2 ml of NMP, 100 °C)

ArHal	Ar in $ArB(OH)_2$	Time, h	Yield of biphenyl, %	Yield of Ar-C_6H_4-CN, %
p-I-C_6H_4-Br	Ph	6 + 15	>99	89
p-I-C_6H_4-Br	p-CH_3O-C_6H_4	8 + 15	>99	88
p-Cl-C_6H_4-Br	Ph	10 + 24	>99	76
p-Cl-C_6H_4-Br	p-CH_3O-C_6H_4	10 + 24	98	74

Recyclability of the catalyst was tested in the reaction of 4-iodobromobenzene with phenylboronic acid followed by one-pot cyanation with $K_4Fe(CN)_6$. Though the efficiency of the immobilized catalyst was gradually decreased, it was sufficiently active during at least three cycles. The yields of 4-cyanobiphenyl were 87%, 85% and 68% for three consecutive cycles (the total reaction time for the second and third cycles was increased from 30 to 36 h).

The possibility of Pd leaching from the immobilized polymer catalyst was also investigated. For this purpose, the first step (Suzuki–Miyaura coupling) was performed for 4-iodobromobenzene as the model substrate as described above using the immobilized $PdPA^I$ complex. After the reaction mixture was heated at 100 °C for 6 h, the immobilized catalyst was taken off and the cyanating agent was added. The reaction mixture was heated again for 24 h at 100 °C. GC-MS analysis of the products showed the presence of 4-biphenyl bromide (98%) and no cyanation product was detected. This indicated that the $PdPA^I$ polymer catalyst is strongly immobilized on the graphite surface and heterogeneous catalysis has been performed.

Conclusion

Thus, it was demonstrated that polyamic acids with biquinolyl fragments in the polymer backbone capable of coordination to Pd(II) ions can be used to prepare catalysts for cyanation of aryl and vinyl halides with $K_4Fe(CN)_6$. The structurally tunable and nontoxic polymer backbone allows creating an efficient catalytic system which can be applied in solution and in an immobilized form on the graphite fabric; cyanation of aryl halides (including chlorides) and vinyl bromides is possible. The catalyst is not destroyed under microwave irradiation. This allows performing cyanation not only under common heating but under MW activation as well; in the latter case the reaction time is dramatically decreased. The yields of nitriles are 40–90%. Cyanation of vinyl bromides occurs stereoselectively, and the configuration of the starting alkene is retained; even for *Z*-isomers, the impact of configuration inversion is less than 5%. The polymer-based Pd catalyst is applicable for one-pot multi-step synthesis of the precursors of mesogenic structures of biphenyl type. Consecutive cross-coupling and cyanation reactions can be performed in the presence of the same portion of catalyst, in the same solvent, without isolation of intermediate products. The immobilized catalyst can be reused for at least three runs; however, the reaction time for the second and third runs should be increased.

Experimental

The reaction mixtures obtained after the cyanation reactions were analyzed using a "Pegasus 4D" (LECO) GC/MS spectrometer (ionization energy 70 eV, a DB-5MS quartz capillary column (30 m), temperature mode: 50 °C (2 min)–280 °C (15 min), heating rate 20 deg min^{-1}).

^1H and ^{13}C NMR spectra were recorded using a Varian VXR 400 in $CDCl_3$. Chemical shifts were measured relative to TMS.

MW irradiation was performed using LG Intellowave MS-2322G, and the power used was 70 W.

N-Methylpyrrolidone (NMP, Aldrich, spectroscopic quality) was stirred over CaH_2 for 3 h and distilled under reduced pressure.

Polyamide ligands (PA) were synthesized as previously described.[12] The corresponding Pd-complexes were synthesized using preparative electrolysis with a Pd anode as described previously.[8,19] *p*-Iodobromobenzene and *p*-bromochlorobenzene were synthesized according to the literature protocol;[72] (*Z*)- and (*E*)-1-bromo-1,2-diphenylethylene were synthesized as described in ref. 73. Other investigated aryl and vinyl halides were commercially available from Aldrich and Acros Organics and used as received: iodobenzene (PhI, 99%, Aldrich), bromobenzene (PhBr, ≥99.5%, Aldrich), chlorobenzene (PhCl, 99.8%, Sigma-Aldrich), *Z*- and *E*-bromostyrene (97%, Sigma-Aldrich), α-bromostyrene (97%, Sigma-Aldrich), (*Z*)-1,2-dibromo-1,2-diphenylethylene (97%, Sigma-Aldrich), bromotriphenylethylene (98%, Sigma-Aldrich), 1-bromo-4-nitrobenzene ($4\text{-}NO_2C_6H_4Br$, 99%, Aldrich), *para*-bromoanisole (*para*-$CH_3OC_6H_4Br$, 98%, Acros Organics), sodium carbonate (Na_2CO_3, 98%, Reachem), potassium carbonate (98%, Reachem), sodium acetate (NaOAc, 98%, Reachem), tripotassium phosphate (K_3PO_4, ≥99.5%, Aldrich), potassium ferrocyanide ($K_4Fe(CN)_6$, ≥99.5%, Aldrich).

General procedure for cyanation of organic halides under heating

A mixture of 1 ml of NMP, organic halide (0.2 mmol), 14.7 mg of $K_4Fe(CN)_6$ (0.04 mmol), 106 mg of Na_2CO_3 (1 mmol) and 1 ml of the $PdPA^I$ solution in NMP (0.6 μmol of Pd) was deaerated with Ar flow. Afterwards, the reaction mixture was placed in a hermetic vessel of 10 ml volume and vigorously stirred using a shaker (J-KEM Scientific, 200 rpm) under an Ar atmosphere at 100 °C for several hours. After cooling to room temperature, 50 ml of water saturated with sodium chloride was added to the reaction mixture in NMP and the organic products were extracted with diethyl ether (3 × 20 ml). The ether extract was washed with water, dried over sodium sulfate and analyzed using gas chromatography-mass spectrometry (GC-MS, "Pegasus 4D", LECO) with naphthalene as an internal standard. The products were characterized by comparing their MS and ^1H, ^{13}C NMR spectra with those found in the literature. Configurations of the starting vinyl bromides and nitriles were determined using ^1H, ^{13}C NMR spectra.

Mass-spectra for cyanation products

$4\text{-}NO_2C_6H_4CN$. EI-MS, *m*/*z* (I, %): 148 $[M]^+$ (41), 102 $[M–NO_2]^+$ (100), 76 $[M–NO_2–CN]^+$ (26).

$4\text{-}MeOC_6H_4CN$. EI-MS, *m*/*z* (I, %): 133 $[M^+]$ (100); 107 $[M^+–CN]$ (37); 90 $[M^+–CN–OMe]$ (42).

PhCN. EI-MS, *m*/*z* (I, %): 103 $[M^+]$ (100); 76 $[M^+–CN]$ (32).

PhC(H)═C(H)CN. EI-MS, *m*/*z* (I, %): 129 $[M^+]$ (100); 103 $[M^+–CN]$ (28); 77 $[M^+–C_2H_2–CN]$ (11).

PhCH═CPhCN. EI-MS, *m*/*z* (I, %): 205 $[M^+]$ (100); 179 $[M^+–CN]$ (14), 178 $[M^+–H–CN]$ (16).

PhC(CN)═CH_2. EI-MS, *m*/*z* (I, %): 129 $[M^+]$ (100); 103 $[M^+–CN]$ (45).

Ph_2C═CPhCN. EI-MS, *m*/*z* (I, %): 281 $[M^+]$ (100); 255 $[M^+–CN]$ (31), 178 $[M^+–CN–Ph]$ (28).

PhCH═C(COOMe)CN. EI-MS, *m*/*z* (I, %): 187 $[M^+]$ (100); 161 $[M^+–CN]$ (78), 128 $[M^+–COOMe]$ (47).

^1H and ^{13}C NMR spectrum

***E*-PhCH═CHCN.** NMR ^1H (400 MHz, $CDCl_3$): δ, ppm: 7.46–7.38 (6H, m), 5.89 (1H, d, *J* = 16.7 Hz); lit.: 7.48–7.37 (6H, m), 5.87 (1H, d, *J* = 16.4 Hz).[69]

***Z*-PhCH═CHCN.** NMR ^1H (400 MHz, $CDCl_3$): δ, ppm: 7.83–7.78 (2H, m), 7.48–7.41 (3H, m), 7.13 (1H, d, *J* = 12.0 Hz), 5.45 (d, *J* = 12.1 Hz, 1H); lit.: δ, ppm: 7.84–7.76 (2H, m), 7.48–7.42 (3H, m), 7.13 (1H, d, *J* = 12.0 Hz), 5.45 (1H, d, *J* = 12.0 Hz).[69]

***E*-PhCH═CPhCN.** NMR ^1H (400 MHz, $CDCl_3$): δ, ppm: 7.39–7.29 (m, 9H), 7.16–7.10 (m, 2H); NMR ^{13}C (100 MHz, $CDCl_3$): δ, ppm: 144.2, 133.5, 132.7, 129.9, 129.8, 129.3, 129.1, 128.9, 128.6, 120.2, 114.4, lit.: NMR ^1H ($CDCl_3$, 400 MHz): δ 7.40–7.31 (m, 6H), 7.30–7.18 (m, 3H), 7.18–7.12 (m, 2H); NMR ^{13}C: δ 144.1, 133.5, 132.6, 129.8, 129.7, 129.2, 129.0, 128.8, 128.5, 120.1, 114.3.[70]

***Z*-PhCH═CPhCN.** NMR ^1H (400 MHz, $CDCl_3$): δ, ppm: δ 7.88–7.83 (m, 2H), 7.67–7.62 (m, 2H), 7.52 (s, 1H), 7.50–7.37 (m, 6H) NMR ^{13}C (100 MHz, $CDCl_3$): δ, ppm: 142.3, 134.5, 133.8, 130.6, 129.24, 129.20, 129.0, 128.9, 126.0, 118.0, 111.7; lit.: NMR ^1H ($CDCl_3$): δ, ppm = 7.92–7.86 (m, 2H), 7.70–7.65 (m, 2H), 7.53 (c, 1H), 7.50–7.36 (m, 6H); NMR ^{13}C ($CDCl_3$): δ, ppm: 142.2, 134.5, 133.7, 130.5, 129.24, 129.18, 129.0, 128.9, 126.0, 118.0, 111.7.[70]

***E*-PhCH═C(COOMe)CN.** NMR ^1H (400 MHz, $CDCl_3$): δ, ppm: 8.22 (1H, s), 7.96–7.91 (2H, m), 7.56–7.42 (3H, m), 3.93 (3H, s); lit.: NMR ^1H ($CDCl_3$), δ, ppm: 8.21s (1H, s), 7.97–7.92 (2H, m), 7.56–7.43 (3H, m), 3.90 (3H, s).[74]

General procedure for cyanation under microwave irradiation

The reaction mixture was prepared as described above. Instead of heating, it was subjected to MW irradiation (70 W) for 3 min periods which were alternated with cooling. The yields of nitriles were determined as described above.

One-pot synthesis of cyanated biphenyls

A mixture of aryl dihalogenide (0.2 mmol), $ArB(OH)_2$ (0.2 mmol), 106 mg of Na_2CO_3 (1 mmol) and 2 ml of the $PdPA^I$ solution in NMP (0.6 μmol of Pd) obtained *via* anode dissolution as described in ref. 8 and 19 was deaerated with Ar flow. Afterwards, the reaction mixture was placed in a hermetic vessel of 8 ml volume and vigorously stirred using a shaker (J-KEM Scientific, 200 rpm) under an Ar atmosphere at 100 °C for several hours. After cooling to room temperature, the vessel was opened and a sample for GC-MS analysis was taken. Afterwards, 14.7 mg of $K_4Fe(CN)_6$ (0.04 mmol) and 106 mg of Na_2CO_3 (1 mmol) were added and the solution was deaerated with Ar again. Then the vessel was hermetically closed and heated at 100 °C under stirring for the required period. After the reaction came to completion, 50 ml of water saturated with sodium chloride was added to the reaction mixture in NMP and the organic products were extracted with diethyl ether (3 × 15 ml). The ether extract was washed with water, dried over Na_2SO_4, and analyzed using GC-MS, with naphthalene as an internal standard. The products were characterized by comparing their MS and ^1H, ^{13}C NMR spectra with those found in the literature.

Recycling experiments

The graphite fabric of 1 cm × 1 cm (with an internal surface of 12 $m^2\ g^{-1}$; ''Ural'', St.-Petersburg) was weighed, placed on a glass plate and slowly impregnated with 200 μl of 1 mM (as calculated with respect to biQ units) solution of the Pd polymer complex using a micropipette. The fabric was dried in an oven at 200 °C for 3 h. The amount of the polymer adsorbed was determined by weighing.

The graphite fabric with the immobilized catalyst was placed in a hermetic vessel of 8 ml containing a mixture of aryl dihalogenide (0.2 mmol), $ArB(OH)_2$ (0.2 mmol), 106 mg of Na_2CO_3 (1 mmol) and 2 ml of toluene. The reaction mixture was vigorously stirred using a shaker (J-KEM Scientific, 200 rpm) under an argon atmosphere at 100 °C for several hours. After cooling to room temperature, the vessel was opened and 14.7 mg of $K_4Fe(CN)_6$ (0.04 mmol) and 106 mg of Na_2CO_3 (1 mmol) were added; the solution was deaerated with argon again. Then the vessel was hermetically closed and heated at 100 °C under stirring for the required period. After the reaction came to completion, the graphite fabric was taken off, and toluene was evaporated under reduced pressure. Water (50 ml) was added to the residue and the organic products were extracted with diethyl ether (3 × 15 ml) and analyzed using GC-MS. The graphite fabric was washed with acetonitrile, dried in vacuum and used again in the next run with a new portion of the reactants.

Mass-spectra for one-pot synthesis products

Ph-C_6H_4-Br. EI-MS, *m*/*z* (I, %): *m*/*z* (I, %): 234 [M^+] (98); 232 [M^+] (100); 153 [M^+–Br] (67); 157 [M^+–Ph] (22) 155 [M^+–Ph] (21).

***p*-CH_3-C_6H_4-C_6H_4-Br.** EI-MS, *m*/*z* (I, %): 248 [M^+] (8); 246 [M^+] (10); 167 [M^+–Br] (100); 157 [M^+–C_6H_4–CH_3] (34), 155 [M^+–C_6H_4–CH_3] (36).

***p*-Bu-C_6H_4-C_6H_4-Br.** EI-MS, *m*/*z* (I, %): 290 [M^+] (52); 288 [M^+] (48); 275 [M^+–Me] (100), 273 [M^+–Me] (98), 194 [M^+–Me–Br] (43), 157 [M^+–C_6H_4–Br] (14).

***p*-CH_3O-C_6H_4-C_6H_4-Br.** EI-MS, *m*/*z* (I, %): 264 [M^+] (27); 262 [M^+] (26); 183 [M^+–Br] (100), 157 [M^+–C_6H_4–Br] (18), 155 [M^+–C_6H_4–Br] (16).

Ph-C_6H_4-CN. EI-MS, *m*/*z* (I, %): 179 [M^+] (100); 153 [M^+–CN] (24); 76 [M^+–C_6H_4CN] (17).

***p*-CH_3-C_6H_4-C_6H_4-CN.** EI-MS, *m*/*z* (I, %): 194 [M^+] (100); 168 [M^+–CN] (37); 153 [M^+–CN–Me] (32).

***p*-^{t}Bu-C_6H_4-C_6H_4-CN.** EI-MS, *m*/*z* (I, %): 235 [M^+] (52); 220 [M^+–Me] (100); 179 [M^+–CN–2Me] (19).

***p*-MeO-C_6H_4-C_6H_4-CN.** EI-MS, *m*/*z* (I, %): 210 [M^+] (100); 184 [M^+–CN] (49); 169 [M^+–CN–Me] (51); 153 [M^+–CN–OMe] (26).

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