DOI: 10.1002/masy.201051053

Polyphenylens, Cross-Linked Through Pd-Carbene Complexes Formation, for Catalysis in Suzuki-Miyaura Reactions

*Dmiry A. Rud, Natalia S. Kushakova, Alexey V. Shapovalov, Alexander V. Naumkin, Irina V. Zhidkova, Irina A. Khotina**

Summary: Polyphenylenes supported N-heterocyclic carbene Pd-complexes were synthesized for catalysis of cross-coupling Suzuki-Miyaura reactions. Starting polyphenylenes were prepared by cyclocondensation reaction of diacetylaromatic with monoacetylaromatic compounds. N-metylimidazole has been involved to the polymer through the mono-functional acetyl monomer, in which in *p*-position to acetyl group the group of haloalkyl was situated, and haloalkyl group interacted with N-methylimidazole. N-heterocyclic carbene complexes of Pd were synthesized usually by the reaction of imidazolium salts with the salts of transition metals in the presence of a base, obtaining the complex (N-heterocyclic carbene)$_2$PdX$_2$. The catalysis reaction was carried out between arylhalides (iodo- or bromobenzene) and phenylboronic acid with the presence of 1 mol% of Pd. The yields of biphenyl are from 70 to 95%, which is comparable with homogeneous catalysis.

Keywords: cross-linked matrix; organometallic catalysts; polycondensation

Introduction

A number of the modern methods of organic synthesis are based on the use of metal-complex catalysts. Pd-catalyzed reactions of C-C and C-heteroatom formation allow simplifying the synthesis of the compounds with complicated structure, such as the most biologically active compounds and synthetic pharmaceutical medications.

Big variety of the stable and effective metal-complex catalysts for homogenous catalysis was elaborated, but the course of the catalysis involves the rearrangement followed by the complex destruction and this leads to the irretrievable loss of the metal and contamination of substrate with the poison ligands. In this connection the immobilization of catalysts in solid polymer matrices with the covalent interaction of ligands is a very important task.[1] Polymer-supported catalysts offer many advantages for different applications due to their versatile processing capabilities and ease of separation and recycling. Several types of heterogeneous catalysts have recently been developed by anchoring the Pd complex onto a polymer matrix in order to decrease leaching of a metal, usually Pd.[2–4]

During the last decade the enhanced interest was shown to N-heterocyclic carbenes (NHCs) as ligands in Pd-catalyzed cross-coupling reactions due to the high Pd-(NHC) bonding strength. In case of Pd-(NHC), the active centers had an appreciable stability even at high temperatures.[5–10] The presented work is devoted to the synthesis of Pd-(NHC) complexes, connected with polyphenylene matrix, and their catalytic properties study.

Synthesis of the Polymer-Supported Catalysts

For the immobilization of the catalytic groups as the polymer matrices, polyphe-

---

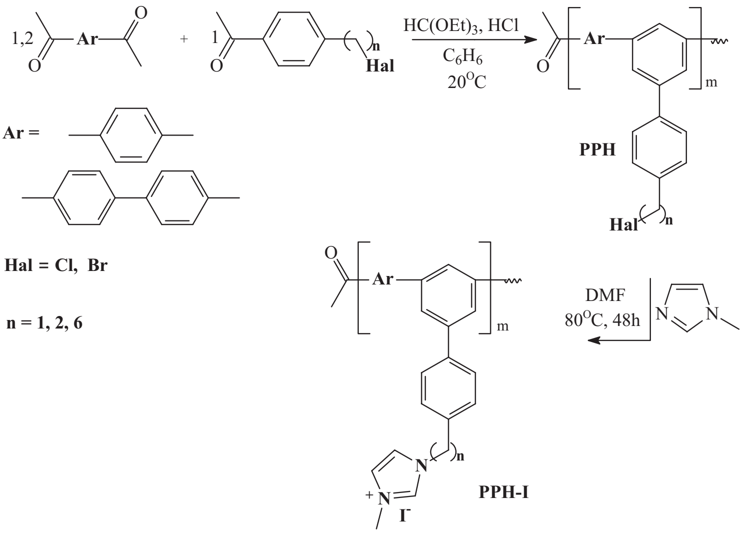
A. N. Nesmeyanov Institute of Organoelement Compounds Russian Academy of Sciences, Vavilova str. 28, 119991, Moscow, Russia
Fax: (+7)4991355085; E-mail: khotina@ineos.ac.ru

nylenes, synthesized by polycyclocondensation of acetylaromatic compounds, were chosen.[11,12]

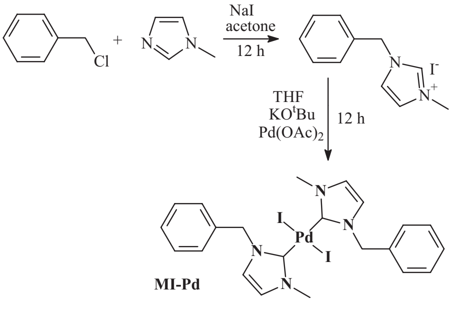
It was supposed, that the groups of NHC, based on N-metylimidazole have to be involved to the polymer through the monofunctional acetyl monomer, in which in *p*-position to acetyl group the group of haloalkyl is situated.

The family of mono- and bifunctional monomers for the polycyclocondensation (PCC) reaction was synthesized. Combinations of mono- with diacetylarylenes in this reaction have led to the formation of insoluble polyphenylene type polymers PPH with methylenehalide- or ethylenehalide groups at terminal phenylene rings.

As the polymers were insoluble, the characterization has been done using IR spectroscopy and elemental analysis, and that was compared with that of soluble analogs, when the synthesis was carried out up to gelation.[11,12] Polymer supported imidazolium salts were prepared by the interaction of polymers prepared with N-metylimidazole:



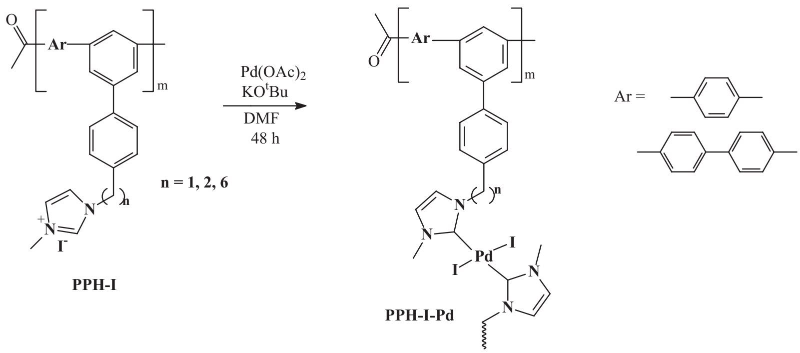
N-heterocyclic carbene complexes of the transition metals are synthesized usually by the reaction of imidazolium salts with the salts of transition metals in the presence of a base, obtaining the complex (N-heterocyclic carbene)$_2$PdX$_2$ (where X – anion). The procedure of polymer complexes preparation has been worked up on the synthesis of model compound **(MI-Pd)** based on benzylchloride and N-methylimidazole:



This compound MI-Pd was characterized with mass-spectrum (MS: m/z 704), ^{1}H NMR and elemental analysis.

The synthesis of polymer supported N-heterocyclic carbene complexes was carried out using the modified method.[14] As the maximum swelling for the polymers was observed in DMF, this solvent was used as a solvent for the reactions of polymer supported complexes formation. As a source of Pd, acetate palladium, and as a base, potassium *tret*-butylate were used.

Preparation of Pd-Complexes on Polyphenylenes (PPH-I-Pd)



The incorporation of Pd into the polymer matrix through the complex formation led to additional cross-linking of the polymer. As the polymer supported catalytic systems were insoluble, i.e. heterogeneous, to prove the formation of Pd-complexes was difficult. For the solution of this problem we used the method of X-ray photoelectronic spectroscopy, which allows estimation of the Pd chemical state in the compounds.

On Figure 1, X-ray photoelectronic spectra of model compound MI-Pd and polymer Pd-PPH-I-Pd-1 (the polymer with Ar = Ph, n = 2) are presented. In the spectra of the polymer and model compound two states of Pd with bond energies of the level Pd $3d_{5/2}$ are marked out: 337,9 and 335,7 eV. The bond energy of the level Pd $3d_{5/2}$ for complexes Pd^{II} - $Pd(PPh)_2Cl_2$, $Pd(PPh)_2Br_2$ are equal 337.9 eV and 337,9 eV, consequently. The reference data for $Pd(OAc)_2$ – 339.0 eV, for PdI_2 – 336.5 eV.[13]

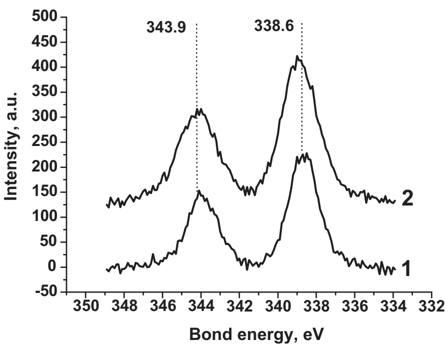
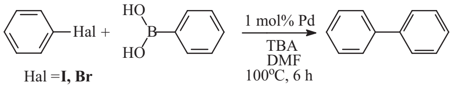


Figure 1.
Photoelectronic spectra Pd 3d (1 - MI-Pd; 2 - polymer with Ar = Ph, n = 2).

The first state indicates the formation of the complexes in case of the model compound and the polymer, as bond energies of the level Pd $3d_{5/2}$ in all complexes are equal to 338,0 and 337,9 consequently.

From the big variety of the cross-coupling reaction, to taste the catalytic properties of the polymer supported N-heterocyclic carbene complexes, Suzuki-Miyaura reaction was chosen.[14–20]



The catalysis reaction was carried out between arylhalides (iodo- or bromo-benzene) and phenylboronic acid in the presence of 1 mol% of Pd, tributylamine, in DMF at 100 °C for 6 hours. The results are presented in the Table 1.

In all cases the yields at use of polymer supported catalysis (heterogeneous) are comparable with that of model compound, i.e. for homogeneous catalysis. The better results were in cases of polyphenylenes with

Table 1.
The results of the catalysis for PPH-I-Pd, complexes in Suzuki-Miyaura reaction (1 - $\mathrm{Ar} = \mathrm{Ph}$, $n = 1$; 2 - $\mathrm{Ar} = \mathrm{biphenyl}$, $n = 1$; 3 - $\mathrm{Ar} = \mathrm{diphenyloxide}$, $n = 1$; 4 - $\mathrm{Ar} = \mathrm{Ph}$, $n = 2$; 5 - $\mathrm{Ar} = \mathrm{biphenyl}$, $n = 2$; 6 - $\mathrm{Ar} = \mathrm{diphenyloxide}$, $n = 2$).

Halide	MI-Pd	PPH-I-Pd					
		1	2	3	4	5	6
		yield in Suzuki-Miyaura reaction, %					
I	99	81	83	79	90	96	93
Br	94	73	82	71	68	91	74

Table 2.
The yields in Suzuki-Miyaura reaction after recycling for the polymer catalysts PPH-I-Pd series.

Cycle number	PPH-I-Pd-4	PPH-I-Pd-5	PPH-I-Pd-6
	yield, %		
1	90	96	93
2	53	64	60
3	58	60	53

diphenylene groups use, probably because of the best swelling – about 5 ml/g. For the best samples, the new reactions of catalysis (recycling) were carried out.

The data of elemental analysis after the carrying out of three cycles of catalytic reaction are evidenced of the Pd-content decrease from 8,6% to 5,1% (for the polymer PPH-I-Pd-1). So Pd is gradually going from the catalyst to the reaction solution and the catalytic activity of the polymer catalyst is decreasing from cycle to cycle.

Nevertheless, even after three cycles the metal is going from matrices no more then on 50%, which is impossible in case of homogeneous catalysis.

Conclusion

Pd-(NHC) complexes, connected with polyphenylene matrix, are synthesized. It has been shown that the results of the catalysis in model reaction are comparable with that for heterogeneous catalysis.

[1] L. Yin, J. Liebscher, *Chem. Rev.* **2007**, *107*, 133.
[2] D. Schönfelder, O. Nuyken, J. Weberskirch, *J. Organomet. Chem.* **2005**, *690*, 4648.
[3] J.-H. Kim, J.-W. Kim, M. Shokouhimehr, Y.-S. Lee, *J. Org. Chem.* **2005**, *70*, 6714.
[4] J.-H. Kim, D.-H. Lee, B.-H. Jun, Y.-S. Lee, *Tetrahedron Letters* **2007**, *48*, 7079.
[5] H. M. Lee, P. L. Chiu, J. Y. Zeng, *Inorg. Chim. Acta* **2004**, *357*, 4313.
[6] J. A. Loch, M. Albrecht, E. Peris, J. Mata, J. W. Faller, R. H. Crabtree, *Organometallics* **2002**, *21*, 700.
[7] V. Cesar, S. Bellemin-Laponnaz, L. H. Gade, *Organometallics* **2002**, *21*, 5204.
[8] M. Magill, D. S. McGuinness, K. J. Cavell, G. J. P. Britovsek, V. C. Gibson, A. J. P. White, D. J. Williams, A. H. White, B. W. Skelton, *J. Organomet. Chem.* **2001**, *617–618*, 546.
[9] S. Iyer, A. Jayanthi, *Synlett.* **2003**, 1125.
[10] D. Kremzow, G. Seidel, C. W. Lehmann, A. Furstner, *Chem. Eur. J.* **2005**, *11*, 1833.
[11] M. M. Teplyakov, *Uspekhi Chemistry*, **1979**, 2, 344.
[12] I. A. Khotina, O. E. Shmakova, D. Yu. Baranova, N. S. Burenkova, A. A. Gurskaja, P. M. Valetsky, L. M. Bronstein, *Macromolecules* **2003**, *36*, 8353.
[13] C. D. Wagner, A. V. Naumkin, A. Kraut-Vass, et al., ‘‘*NIST X-ray Photoelectron Spectroscopy Database. NIST Standard Reference Database 20*’’, Web Version 3.4, **2004**.
[14] M. Frank, G. Maas, J. Schatz, *Eur. J. Org. Chem.* **2004**, 607.
[15] F. Bellina, A. Carpita, R. Rossi, *Synthesis* **2004**, 2419.
[16] N. Miyaura, in: ‘‘*Metal-catalyzed Cross-Coupling Reactions*’’, Vol. *1*, 2nd ed., A., de Meijere, F. Diederich, Eds., J. Wiley-VCH Weinheim **2004**, p. 41–123, 164.
[17] M. Miura, *Angew. Chem.* **2004**, *116*, 2251.
[18] G. A. Grasa, M. S. Viciu, J. Huang, C. Zhang, M. L. Trudell, S. P. Nolan, *Organometallics*, **2002**, *21*, 2866.
[19] K. Arentsen, S. Caddick, F. G. N. Cloke, A. P. Herring, P. B. Hitchcock, *Tetrahedron Lett.* **2004**, *45*, 3511.
[20] C. Zhang, M. L. Trudell, *Tetrahedron Lett.* **2000**, *41*, 595.