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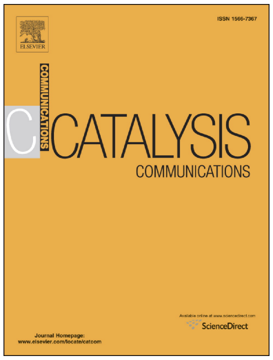

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Bis-*N,N*-aminophosphine (PNP) crosslinked poly(p-tert-butyl styrene) particles: A new support for heterogeneous palladium catalysts for Suzuki coupling reactions

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Abstract:

Crosslinked polymer particles carrying hemilabile bis-*N,N*-aminophosphine (PNP) moieties are obtained by the copolymerization of a PNP-derived monomer bearing four vinyl fragments as cross-linkers, with para-*tert*-butylstyrene and divinylbenzene, using free radical copolymerization in presence of AIBN, performed in aqueous dispersed medium. This new support was characterized by thermogravimetric analysis, elemental analysis, laser diffraction, solid state NMR. The PNP moiety could allow monochelation to palladium. The resulting insoluble Pd-catalyst revealed to be very active for Suzuki cross-coupling with several substrates, allowing separation of the product from the catalyst by filtration. The final palladium PS-PNP catalyst could be reused for several catalytic cycles.

Keywords: Free radical polymerization; aqueous dispersed media; C-C coupling; catalyst recycling

1. Introduction

The formation of the C–C bond is among the most useful synthetic transformations to conceive fine chemicals, pharmaceuticals, and agrochemicals [1]. In this field, catalytic Suzuki-Miyaura (S-M) coupling of aryl halides with arylboronic acids has become the dominant synthetic scheme. This technique is very efficient and easy to perform due to the stability toward air and non-toxicity of boronic acids used during this reaction [2, 3]. It has also found new applications for the preparation of advanced materials within optics and electronics [4]. Palladium is among the most applied element in the S-M coupling, under the form of soluble monometallic species derived from Pd(II) or Pd(0) complexes [5-9]. Several studies have suggested that the formation of colloidal nanoparticles can act as catalyst or, more likely, as precursor of the active species [10, 11]. On the other hand, uncontrollable growth of these aggregates will inevitably lead to the formation of insoluble black palladium, responsible of the deactivation during the C-C coupling reaction. In order to avoid this problem, tailored ligands are used to increase the stability of the catalyst and to trigger the reaction for less reactive substrates. However, these Pd catalysts are usually air sensitive, expensive, difficult to obtain and not available commercially. To resolve these problems, development of heterogeneous catalysts based on palladium is highly needed for practical, economic and environmental reasons [12-14]. Other advantages are the possibility of recovery and recycling of the solid catalyst, being crucial in view of up-scaling at industrial level. In addition, working with a supported Pd-catalyst offers the opportunity to conduct the reaction under continuous flow mode [15]. Different strategies have been used to obtain Palladium-based heterogeneous catalysts for C–C coupling reactions [3]. Compared to both inorganic or organic-inorganic supports [16], a rather promising approach is based on palladium(II) complexes grafted into organic polymer particles. Owing to their strong σ-donating ability and high versatility, phosphines [17, 18] and diphosphines [19] have been incorporated into organic polymer particles and the resulting products used as supports in heterogeneous transition metal catalysis [20, 21]. Among all the polymers that have been used to carry the Pd source, polystyrene (PS) incorporating phosphine ligands was extensively studied in particular, due to a ligand mobility as in homogeneous catalysis [22, 23]. Various heterogeneous systems have been developed to catalyze different chemical transformations such as alkylation [24], C-N bond formation [25] and the Suzuki cross coupling [16]. In many cases, using flexible linear polymer chains causes unfavorable steric environment around the Pd-active sites, resulting in deactivation and in reduced catalyst performances. Thus, it is crucial to incorporate a designed phosphine ligand on the PS backbone in order to increase the activity of Suzuki-Miyaura coupling. A fairly recent approach is to introduce a cross-linking mono-phosphine agent during the polymerization of styrenic monomers leading to the increase of the density of polystyrene chains around the phosphine center, and thereby reduce multidentate P-coordination to the metal [22]. This mono-phosphine functionalized crosslinked polymer particles can readily coordinate to palladium complexes and offer a stable and more active heterogeneous catalyst for S-M coupling and selective head-to-head dimerization of farnesene [26]. Furthermore, the insoluble Pd-catalyst obtained by this new strategy can easily be separated from the reaction crude by filtration. However, this catalyst gradually degrades upon several regeneration cycles by leaching of the metal due to low stability of the mono-coordinated Pd center. The same group has further extended their work on biphosphine ligand based on 1,2-bis(diphenylphosphino)benzene grafted into crosslinked polymer particles to further stabilize the active metal center [27]. This material has been used in amination of arylchloride and C-H/C-O coupling after functionalization with Ni, and alkene hydroboration after functionalization with Cu or Co. Extensive analyses for the metal coordination have revealed the importance of a monochelated system, as offered by the 1,2-bis(diphenylphosphino)benzene, compared to other bisphosphine ligands allowing multi-chelating systems. However, neither the S-M reaction nor recycling experiments were further investigated. Another strategy for the stabilization of active center is to use tridentate “pincer” ligands. In fact, these ligands provide a unique balance of versatility, stability and reactivity in organometallic chemistry and catalysis. The development of pincer PNP ligands has led to many applications in catalysis, including facile chemical transformations at transition metal centers with high stability during catalysis [28]. However, the catalytic activity of these systems with palladium is generally low probably due to the formation of bis-chelated single metal complexes or multinuclear complexes [27]. Herein, we report the synthesis of the first example of coordinated Palladium catalyst to PNP ligand-based cross-linked poly(para-tert-butyl styrene) (PS) particles obtained by free radical copolymerization performed in an aqueous dispersed medium. This is achieved by using an original soluble tetra-vinylated PNP ligand. The resulting support will be used for Suzuki type coupling reactions, catalyzed by Pd isolated center, leading to diphenyl compounds. The Pd-PNP-PS catalyst could be recycled demonstrating a good stability and recyclability of this new material during the S-M coupling catalytic process.

2. Experimental

*2.1. Synthesis of (methylamino)-bis[di(4-ethenylphenyl)phosphine] (PNP monomeric ligand) (**5**).*

A 5 mL solution of bromostyrene (2.0 g, 10.9 mmol, 4 eq) was added to an excess of Mg dissolved in THF at -20 °C. After 3h, the bromostyrene magnesium was filtrated by a cannula and transferred into another Schlenk containing a solution of $MeNP_2Cl_4$, **2**, (648 mg, 2.73 mmol, 1.0 eq) [29] dissolved in 3 mL THF and maintained at -20 °C. The reaction was stirred for 1 h at -20 °C and then at room temperature during 3 h. The solution was quenched by addition of deionized water (5 mL). Precipitate was filtrated and the liquid was extracted by dichloromethane. The combined organic phases were dried with $MgSO_4$, filtered and concentrated. The crude product was purified by chromatography (Eluent: pentane/ethyl-acetate = 98/2 to pentane/ethyl-acetate = 93/7) to give 415 mg of PNP ligand

5 (1.64 mmol, yield = 61%). NMR ^{1}H (ppm, CD_2Cl_2): 2.53 (3H, (t), ^3J = 3.0Hz, H1), 5.39 (4H, (d), ^3J = 11.1Hz, H3a), 5.92 (4H, (d), ^3J = 17.4Hz, H3b), 6.84 (4H, (dd), ^3J = 17.7Hz, ^3J = 11.1Hz, H2), 7.36 - 7.63 (16H, (m), H_{Ar}). NMR ^{13}C (ppm, CD_2Cl_2): 31.77, 113.66, 125.19, 131.72, 135.49, 137.13, 137.17. NMR ^{31}P (ppm, CD_2Cl_2): 71.89.

*2.2. Synthesis of PNP-PS crosslinked particles (**6**).*

A solution of NaCl (3.0 g) in water (120 mL) with acacia gum (4.8 g) was placed in a two-neck flask equipped with a magnetic stirring bar and deoxygenated by purging with Argon. On the other hand, a solution of para-tert-butylstyrene (5.5 mL, 30.0 mmol), divinylbenzene (72 μL, 0.50 mmol) and PNP ligand, **5**, (250 mg, 0.5 mmol) dissolved in chlorobenzene (6 mL) was rapidly injected into the aqueous solution under stirring. Azobisisobutyronitrile (AIBN) (98.5 mg, 0.60 mmol) was then added to this medium and the mixture was kept at 95 °C under stirring (24h). The reaction was then stopped by cooling at room temperature and the solid obtained was isolated by filtration under a reduced pressure, washed successively with water (700 mL), MeOH (600 mL), THF (600 mL) and toluene (600 mL) and then dried under vacuum at 90 °C for 24h in order to give the desired polymer as white beads (4.0 g).

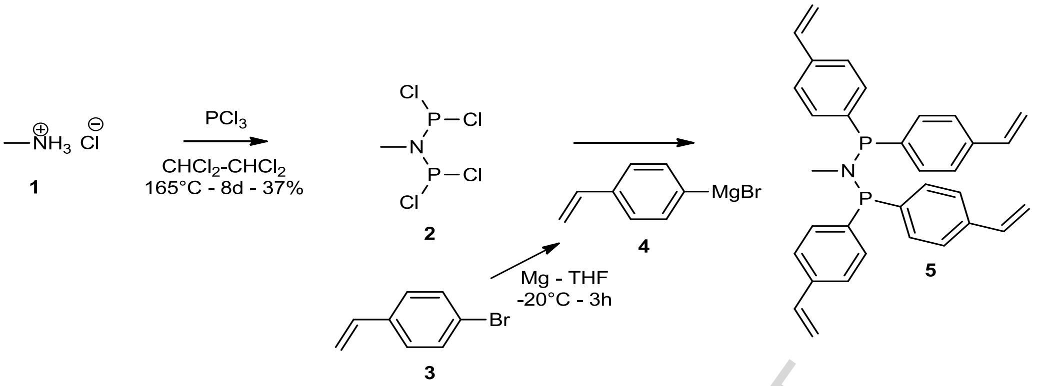
*2.3. Synthesis of Pd-PNP-PS (**7**).*

In a glovebox, the PNP and crosslinked PS particles **6** (0.5 g) were heated using a sand bath and contacted with a solution of $Pd(acac)_2$ (45 mg) in toluene at 70 °C during 4 h. The resulting suspension was filtrated and washed successively with toluene and pentane. The powder was dried under vacuum and stored in the glovebox.

2.4. General procedure *for a Suzuki-Miyaura coupling reaction*

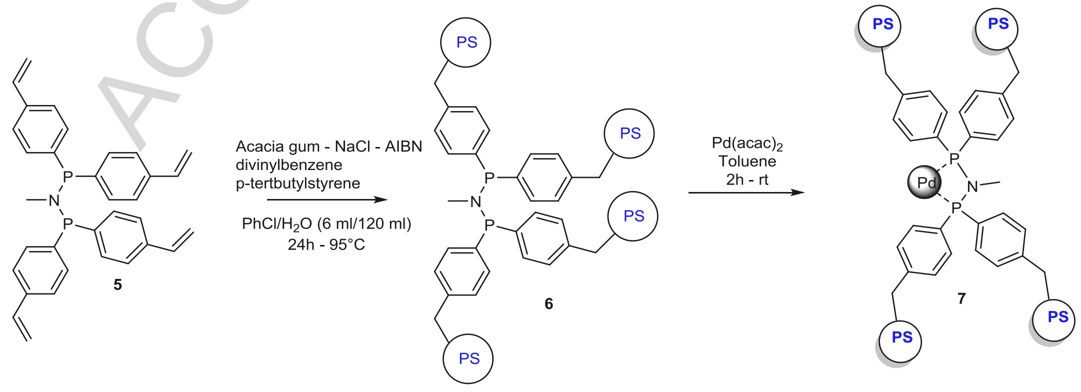
To a mixture of aryl halide (0.52 mmol), arylboronic acid (0.75 mmol), potassium phosphate (1.49 mmol) and solid catalyst, **7** (1,43 mol % Pd) was charged degassed THF (3 mL). The mixture was pumped and refilled with nitrogen three times. The resulting mixture was stirred at 60°C under argon for 15 h, and then cooled to room temperature, portioned with water (5 mL) and ethyl acetate (5 mL). The solid was filtrated, washed with water and ethyl acetate. The organic layer was separated, dried over magnesium sulfate, concentrated, and purified by silica gel column chromatography to provide biaryl compounds.[30, 31]

3. Results and discussions



Scheme 1: Synthesis of PNP monomeric ligand 5 in two steps from methylamino hydrochloride

An adaptable monomeric ligand should contain the following criteria: i) PNP moiety; ii) styrene fragment suitable for radical polymerization; iii) preferable sterical demand with moderate P-P proximity in a pyramidal-type space to facilitate the chelating effect and accessibility of the substrate. The simplest ligand satisfying the aforementioned criteria is depicted in Scheme 1 (**5**). However, this molecule has never been reported before. For the synthesis of this new tetravinylated PNP ligand **5**, methylamino hydrochloride, **1** and phosphorus trichloride are first brought together to reflux in 1,1,2,2-tetrachloroethane to give the phosphorus substituted amine, **2** (Scheme 1) [29]. Each of the four chlorine atoms was then substituted by an aryl group using styrene magnesium bromide, **4**, generated from commercially available bromostyrene, **3.** This led to the PNP ligand bearing four styrene units, obtained after purification with reasonably good yield (61%). It has been observed that **5** shows a small tendency to polymerize at room temperature and needs therefore to be kept cold. The material was then characterized by ^{1}H (Fig. A.1), ^{31}P (Fig. A.2) and ^{13}C NMR (Fig. A.3) to validate the structure (^{31}P NMR (CD_2Cl_2): 71.9 ppm) [32]. ^{1}H NMR in CD_2Cl_2 of the PNP ligand, **5**, shows two doublets at 5.39 and 5.92 ppm and a quadruplet at 6.84 ppm characteristic of the vinyl group of styrene fragment necessary to prepare the PNP-functionalized PS beads by free radical copolymerization.



Scheme 2: Synthesis of PNP-PS ligand and Pd-PNP-PS

The tetravinylated PNP ligand, **5**, was successif copolymerized in the presence of divinylbenzene (DVB) used as crosslinker in order to obtain more homogeneous and very uniform polymer beads [22], para-tert-butylstyrene (60 equivalents with respect to **5**), and acacia gum in a saturated aqueous solution containing a soluble amount of chlorobenzene. The polymerization was initiated with AIBN after a prolonged degassing under argon and heating at 95 °C. At the end of the polymerization, a solid, **6**, was harvested by filtration and thoroughly dried. The average volume equivalent sphere diameter D[4,3] is found to be 80.8 µm by laser diffraction (Fig. A.4, Table A.1). The polymer particles obtained are then smaller than those of monophosphine crosslinked PS triphenylphosphane particles (300-400 µm) reported by Iwai et al. [22]. The thermogravimetric analysis (Fig. A.5) of the dried PNP cross-linked PS showed that the organic support is highly stable (no weight loss below 250 °C). ^{1}H NMR spectrum (Figure 1) displayed two broad signals at 1.2 ppm (typically aliphatic CH, CH_2 and CH_3 groups from polystyrene and tert-butyl fragment) and 7.0 ppm (aromatic protons). ^{13}C NMR (Fig. A.6) showed several resonances localized at 31.3 and 33.9 ppm (originated from para-tert-butyl fragment), 39.4 and 44.8 ppm (usually observed for a polystyrene backbone, attributed to CH_2 and CH in between two aromatic cycles), 120.6-133.1 ppm (attributed to carbons from aromatic fragment). Finally, ^{31}P NMR spectrum (Figure 1) displayed an intense signal at 71.2 ppm, indicating that its electronic and steric properties are virtually the same as in the monomer **5** (^{31}P NMR: δ 71.9 ppm) and confirming the successful incorporation of the PNP units into the crosslinked PS matrix. The phosphorus loading value ([P] = 0.16 mmol g^{-1}) was determined by elemental analysis. Dried material was then swollen with toluene in order to allow the grafting of ($Pd(acac)_2$) on the PNP moieties of the polymeric material. The catalyst changed color and turned as expected from white to orange after the coordination of palladium.

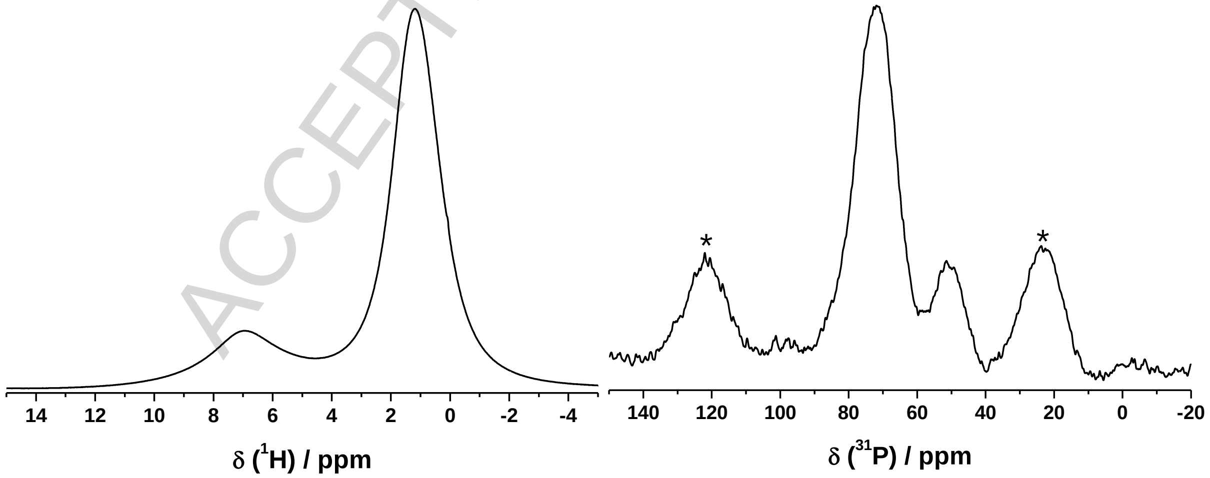
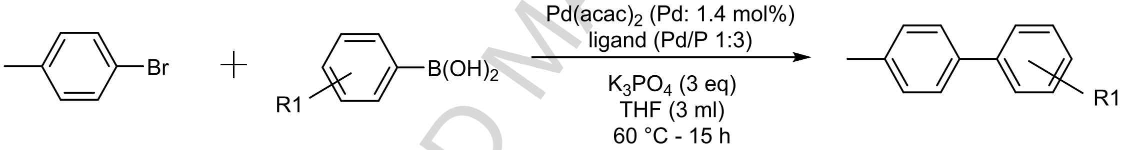


Figure 1: ^{1}H (500 MHz) and ^{31}P (202.4 MHz) NMR spectra of the polymeric support containing methyl *N,N*-bis(diarylphosphino) moieties (10 kHz; *: spinning side bands).

^{1}H and ^{13}C Solid state NMR characterizations of the Pd-coordinated PNP-functionalized and crosslinked PS gave virtually the same spectra as its Pd-free homologue (Fig. A.7, Fig. A.8). However, no ^{31}P NMR signal was detected in different acquisition modes

(CP MAS, $^{31}P\{H\}$ with different relaxation times). Only very weak resonances corresponding to the un-coordinated phosphorous was observed after very long accumulation (Fig. A.9). Absence of ^{31}P NMR signal is probably due to a combination of broadening of the peak and reduced mobility of phosphorous when Pd is coordinated. On the other hand, elemental analysis revealed that the concentration of phosphorus (0.48 wt%) and palladium (0.53 wt%) in the lattice, corresponds to [P] = 0.15 mmol g^{-1} and [Pd] = 0.05 mmol g^{-1}. The observed Pd/P ratio of ⅓ suggesting that 2/3 of the PNP fragment has coordinated to Pd, indicates that there are still un-coordinated phosphine moieties in the material, which is also confirmed by solid state ^{31}P NMR. The deficit of Pd concentration may be due to the inaccessibility of few PNP groups in the polymeric structure. In addition, IR spectroscopy reveals appearance of a new peak at 1583 cm^{-1} (Figure A.10), which corresponds to typical ν(C=O) vibration in acetylacetonate, suggesting successful coordination of $Pd(acac)_2$ complex onto the support.

We then chose to explore the use of such Pd-coordinated polymeric beads toward the Suzuki-Miyaura coupling of unactivated bromoarenes. For S-M reactions, the importance of the mono-ligation of two electron donor ligands has been established using electron rich phosphane [33, 34] and N-heterocyclic Carbenes ligands [35] in order to perform the catalytic reaction.



Scheme 3: The Suzuki coupling reactions of para-bromotoluene with phenylboronic acids using the polymer supported methyl amino *N,N*-bis(diarylphosphino) ligand.

The supported palladium complex was evaluated as precatalyst in the Suzuki reaction of para-bromotoluene with selected phenylboronic acids (Scheme 3). Following optimization of the reaction, a palladium loading of 7.5 μmol was employed together with K_3PO_4 as the base in THF at 60 °C. Control experiments showed that in the absence of the catalyst no reaction took place. However, in the presence of the catalyst (1.4 mol%), para-bromotoluene reacts cleanly with phenylboronic acids to give the appropriate cross-coupling products, generally in high yield (Table 1). As expected, the yields of the coupling product in reactions of para-bromotoluene with phenylboronic acids presenting a highly electron withdrawing group (CF_3) or an important steric hindrance are lower. Current material also couple chloro-toluene with selected arylboronic acid efficiently (Table 1) with similar conversion as the highly reactive bromotoluene.

Table 1. Suzuki-Miyaura cross-coupling reaction of para-bromotoluene[a] and para-chlorotoluene[b] with phenylboronic acid derivatives using the Pd supported complex as catalyst.

Boronic acid	% Conversion	% Isolated Yield
Phenylboronic Acid[a]	98	91
(o)-Tolylboronic Acid[a]	99	95
(m)-Tolylboronic Acid[a]	100	99
(p)-Tolylboronic Acid[a]	100	91
(p)-Ethylphenylboronic Acid[a]	99	95
(2)-Methoxyphenylboronic Acid[a]	87	81
(3)-Trifluoromethylphenylboronic Acid[a]	60	54
(4)-Methoxyphenylboronic Acid[a]	99	96
(4)-Vinylphenylboronic Acid[a]	84	68
(3)-Fluorophenylboronic Acid[a]	84	73
(4)-Fluorophenylboronic Acid[a]	86	66
(4)-Ethoxycarbonylphenylboronic Acid[a]	92	84
(2,4,6)-Trimethylphenylboronic Acid[a]	50	47
(2,4,6)-Triisopropylphenylboronic Acid[a]	22	15
Phenylboronic Acid[b]	84	79
(p)-Tolylboronic Acid[b]	87	79
(2)-Methoxyphenylboronic Acid[b]	87	80

Reaction conditions: THF, 0.15 g of the polystyrene supported Pd precatalyst, 7.5 µmol Pd (1.43 mol% Pd), 1.49 mmol K_3PO_4, 0.75 mmol $ArB(OH)_2$, 0.52 mmol PhBr, 60 °C, 15 h. Conversion of para-bromotoluene and Chlorotoluene determined by ^{1}H NMR analysis.

The supported palladium complex could be easily filtrated and reused at least six times for the coupling reaction of para-bromotoluene with phenylboronic acid, leading to 4-methyl-1,1'-biphenyl, without important decrease of activity between two runs.

Table 2. Suzuki-Miyaura cross-coupling reaction of para-bromotoluene with phenylboronic acid using the Pd supported complex as catalyst and reusing it.[a]

Run	% Conversion	% Isolated Yield
1 (first use)	98	91
2	95	80
3	92	87
4	92	78
5	98	87
6	97	94

[a] Reaction conditions: THF, 0.15 g of the polystyrene supported Pd precatalyst, 7.5 µmol Pd (1.43 mol% Pd), 1.49 mmol K_3PO_4, 0.75 mmol $C_6H_5B(OH)_2$, 0.52 mmol PhBr, 60 °C, 15 h. Conversion of para-bromotoluene determined by ^{1}H NMR analysis.

Importantly, no evident physical change of the Pd-coordinated PNP-functionalized and crosslinked PS, such as a black color, was observed after multiple recycling experiments, indicating the absence of metallic Pd. Moreover, no loss of activity was observed, strongly suggesting the absence of leaching. Hence, the PNP-functionalized polymer particles synthesized in this study seem to have/show enhanced stability compared to the previously published mono-coordinated Pd triphenylphosphine crosslinked PS particles [22].

4. Conclusion

In conclusion, a novel organic molecule bearing PNP-moiety and styrene fragments has been synthesized and characterized. This molecule can readily be polymerized through free radical polymerization performed in an aqueous dispersed medium to achieve micrometric polymer particles bearing bis(phosphino)amine functionality. This material can serve as support for heterogeneous catalysis. Indeed, it has been demonstrated that palladium can be coordinated to the PNP fragment, leading to a very efficient precatalyst for C–C coupling reactions in the Suzuki reaction. Moreover, it can be easily isolated from the reaction medium by filtration after reaction and could be reused at least five times without decrease of activity.

Acknowledgement

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:

References

[1] X.F. Wu, P. Anbarasan, H. Neumann, M. Beller, Angew. Chem.-Int. Edit. 49 (2010) 9047-9050.
[2] C. Torborg, M. Beller, Adv. Synth. Catal. 351 (2009) 3027-3043.
[3] A. Del Zotto, D. Zuccaccia, Catal. Sci. Technol. 7 (2017) 3934-3951.
[4] T. Yamamoto, K. Kobayashi, T. Yasuda, Z.H. Zhou, I. Yamaguchi, T. Ishikawa, S. Koshihara, Polym. Bull. 52 (2004) 315-319.
[5] J. Hassan, M. Sevignon, C. Gozzi, E. Schulz, M. Lemaire, Chem. Rev. 102 (2002) 1359-1469.
[6] A.F. Littke, G.C. Fu, Angew. Chem.-Int. Edit. 41 (2002) 4176-4211.
[7] R.J. Lundgren, M. Stradiotto, Chem.-Eur. J. 18 (2012) 9758-9769.
[8] N. Miyaura, A. Suzuki, Chem. Rev. 95 (1995) 2457-2483.
[9] S.C. To, F.Y. Kwong, Chem. Commun. 47 (2011) 5079-5081.
[10] M.T. Reetz, E. Westermann, Angew. Chem.-Int. Edit. 39 (2000) 165-168.
[11] A.H.M. de Vries, J. Mulders, J.H.M. Mommers, H.J.W. Henderickx, J.G. de Vries, Org. Lett. 5 (2003) 3285-3288.
[12] A. Dhakshinamoorthy, A.M. Asiri, H. Garcia, ACS Catal. 9 (2019) 1081-1102.
[13] I. Hussain, J. Capricho, M.A. Yawer, Adv. Synth. Catal. 358 (2016) 3320-3349.
[14] M. Lamblin, L. Nassar-Hardy, J.C. Hierso, E. Fouquet, F.X. Felpin, Adv. Synth. Catal. 352 (2010) 33-79.
[15] A. Kirschning, G. Jas, Immobilized Catalysts 242 (2004) 209-239.
[16] M. Guino, K.K.M. Hii, Chem. Soc. Rev. 36 (2007) 608-617.
[17] P.J.C. Hausoul, T.M. Eggenhuisen, D. Nand, M. Baldus, B.M. Weckhuysen, R. Gebbink, P.C.A. Bruijnincx, Catal. Sci. Technol. 3 (2013) 2571-2579.
[18] Y. Uozumi, H. Danjo, T. Hayashi, J. Org. Chem. 64 (1999) 3384-3388.

[19] P.J.C. Hausoul, C. Broicher, R. Vegliante, C. Gob, R. Palkovits, Angew. Chem.-Int. Edit. 55 (2016) 5597-5601.

[20] S. Chen, F. Gayet, E. Manoury, A. Joumaa, M. Lansalot, F. D'Agosto, R. Poli, Chem.-Eur. J. 22 (2016) 6302-6313.

[21] X.W. Zhang, A.F. Cardozo, S. Chen, W.J. Zhang, C. Julcour, M. Lansalot, J.F. Blanco, F. Gayet, H. Delmas, B. Charleux, E. Manoury, F. D'Agosto, R. Poli, Chem.-Eur. J. 20 (2014) 15505-15517.

[22] T. Iwai, T. Harada, K. Hara, M. Sawamura, Angew. Chem.-Int. Edit. 52 (2013) 12322-12326.

[23] R. Akiyama, S. Kobayashi, Angew. Chem.-Int. Edit. 40 (2001) 3469-3471.

[24] B.H.G. Swennenhuis, R.F. Chen, P. van Leeuwen, J.G. de Vries, P.C.J. Kamer, Eur. J. Org. Chem. (2009) 5796-5803.

[25] Y. Hirai, Y. Uozumi, Chem. Lett. 40 (2011) 934-935.

[26] M. Taoufik, K.C. Szeto, C. Rios Neyra, Pat. Appl. PCT/EP2016/050398 (2016).

[27] T. Iwai, T. Harada, H. Shimada, K. Asano, M. Sawamura, ACS Catal. 7 (2017) 1681-1692.

[28] D. Benito-Garagorri, K. Kirchner, Accounts Chem. Res. 41 (2008) 201-213.

[29] T. Agapie, M.W. Day, L.M. Henling, J.A. Labinger, J.E. Bercaw, Organometallics 25 (2006) 2733-2742.

[30] Q. Zhao, C.X. Li, C.H. Senanayake, W.J. Tang, Chem.-Eur. J. 19 (2013) 2261-2265.

[31] S.D. Walker, T.E. Barder, J.R. Martinelli, S.L. Buchwald, Angew. Chem.-Int. Edit. 43 (2004) 1871-1876.

[32] S.J. Schofer, M.W. Day, L.M. Henling, J.A. Labinger, J.E. Bercaw, Organometallics 25 (2006) 2743-2749.

[33] Q.S. Hu, Y. Lu, Z.Y. Tang, H.B. Yu, J. Am. Chem. Soc. 125 (2003) 2856-2857.

[34] G.A. Molander, B. Canturk, Angew. Chem.-Int. Edit. 48 (2009) 9240-9261.

[35] M.G. Organ, S. Calimsiz, M. Sayah, K.H. Hoi, A.J. Lough, Angew. Chem.-Int. Edit. 48 (2009) 2383-2387.

Highlights

- Novel ligand comprising PNP moiety and 4-fold styrene fragment is presented
- Crosslinked polymer particles carrying PNP are obtained by radical polymerization
- The crosslinked polymer particles can be used as support to immobilize Pd-complexes
- The materials were used as recyclable heterogeneous catalysts for C-C coupling