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New Hybrid Inorganic–Organic Polymers as Supports for Heterogeneous Catalysis: A Novel Pd(0) Metalated Cyclophosphazene-Containing Polymer as an Efficient Heterogeneous Catalyst for the Heck Reaction

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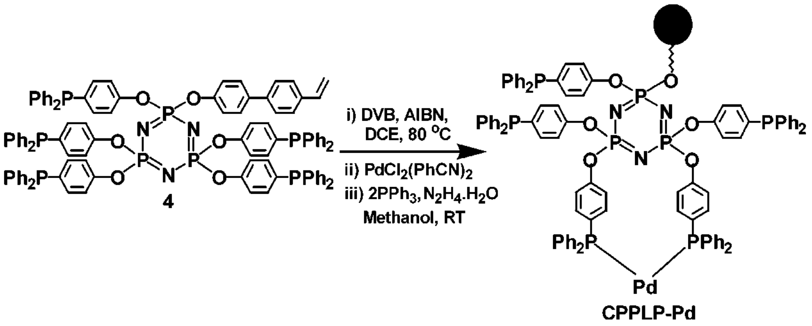
ABSTRACT



A new Pd(0) complex of a pendant cyclophosphazene-containing cross-linked polymer is found to be an effective heterogeneous catalyst for the Heck arylation reaction. The catalyst is robust and can be recycled without significant loss of activity.

Polyphosphazenes, $[\mathrm{N{=}PR_2}]_n$, constitute the largest and most diverse class of inorganic polymers.[1] The macromolecular substitution reaction involving the replacement of chlorine atoms[2] on polydichlorophosphazene $[\mathrm{N{=}PCl_2}]_n$ by an appropriate nucleophile (such as amino,[2a−c] alkoxy,[2d−e] or aryloxy[2f−h]) is the principal synthetic method that has been employed to prepare a large number of examples of this family. The recent discovery of an ambient temperature route to polydichlorophosphazene via the *living* cationic polymerization of the phosphoranimine $\mathrm{Cl_3P{=}NSiMe_3}$ provides an advanced method with molecular weight control and narrow polydispersities.[3] Despite their versatility, applications of polyphosphazenes as heterogeneous catalyst supports are fraught with difficulties. Thus, although polydichlorophosphazene can be prepared in the cross-linked form, substitution of chlorine atoms on the latter is a complex task. Consequently, designing a polymeric ligand with well-controlled

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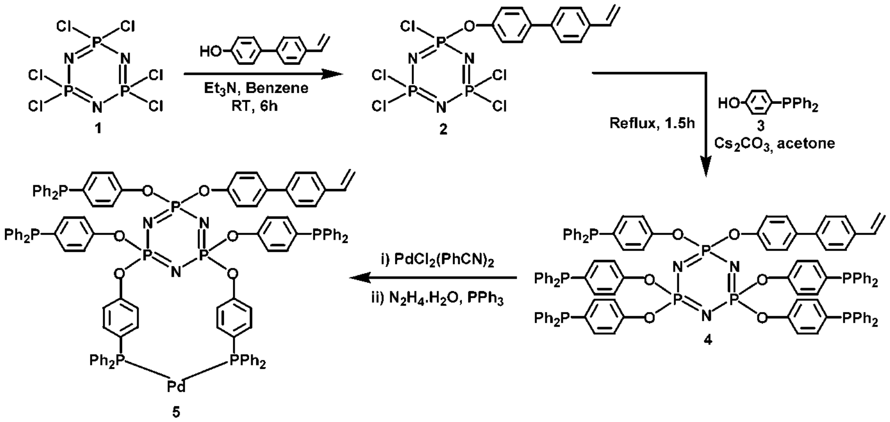
Scheme 1. Preparation of **5**



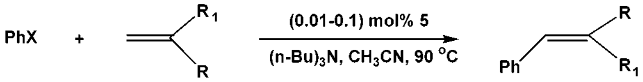
coordination sites in a cross-linked polyphosphazene remains a very difficult proposition. In this regard hybrid polymers[4] that contain the cyclophosphazene ring as a pendant group attached at regular intervals to the backbone of an organic polymer can be more versatile because of the following reasons: (a) cyclophosphazenes with appropriate coordinating groups can be assembled to afford ligands with definite coordinating capabilities and which can include a polymerizable vinyl group and (b) such suitably designed cyclophosphazene monomers can be readily cross-linked by copolymerization with divinylbenzene to afford cross-linked polymeric ligands with definite knowledge on the orientation and number of coordinating groups. Also, since the nature of the coordinating group can be varied quite readily in the pre-polymerization step, this methodology can be quite general and *polymeric ligand engineering* can be accomplished in a facile manner leading to a library of ligands.[5] In view of the importance of the Heck reaction in C−C bond formation, we have designed a cyclophosphazene-containing cross-linked polymeric ligand and have demonstrated its applicability in the standard Heck arylation reaction. These results are discussed herein.

The reaction of $N_3P_3Cl_6$ (**1**) with 4-hydroxy-4′-vinylbiphenyl afforded $N_3P_3Cl_5(O\text{-}C_6H_4\text{-}p\text{-}C_6H_4\text{-}p\text{-}CH{=}CH_2)$ (**2**). Compound **2** is the primary starting material for the assembly of the polymeric ligand as it possesses five reactive chlorines and also the polymerizable vinyl group. Reaction of **2** with $OH\text{-}C_6H_4\text{-}p\text{-}PPh_2$ **3** affords the fully substituted product **4** in a very good yield. The choice of **3** to introduce the phosphino groups in the cyclophosphazene is deliberate. This serves to keep the coordinating phosphino groups away from the cyclophosphazene ring, and the immediate environment around the phosphorus is analogous to a triphenylphosphine as found in the Merrifield−Wang resin. Compound **4** shows a molecular ion peak at 1717 in its FAB-MS. The $^{31}P\{^1H\}$ NMR of **4** shows that the phosphorus chemical shifts corresponding to the cyclophosphazene skeleton are isochronous and resonate at 9.25 ppm. Two phosphine resonances are seen at −6.54 and −6.59 ppm. Compound **4** was used as a ligand for the preparation of Pd(0) complex **5** as shown in Scheme 1.

The composition of complex **5** is confirmed from its analytical data. An exact structure of this compound must await an X-ray diffraction study. We were thus far unable to obtain single crystals of **5** that are suitable for X-ray diffraction. However, the $^{31}P\{^1H\}$ NMR of **5** shows two resonances at −6.46 and −5.16 ppm. These correspond to the *uncoordinated* phosphines. The phosphorus chemical shift for the cyclophosphazene ring occurs at 9.10 ppm. The *coordinated* phosphines resonate at 25.10 ppm.[6] On this basis we propose that two nongeminally substituted phosphines are involved in coordination to a dicoordinate palladium. Weakly bound solvent molecules and alternative coordination schemes involving for example geminally substituted phosphines cannot be ruled out. However, it is clear that the triphenylphosphine added during the reaction is not incorporated in the complex.

The catalytic activity of **5** has been tested under the standard Heck reaction conditions (Table 1). Compound **5**

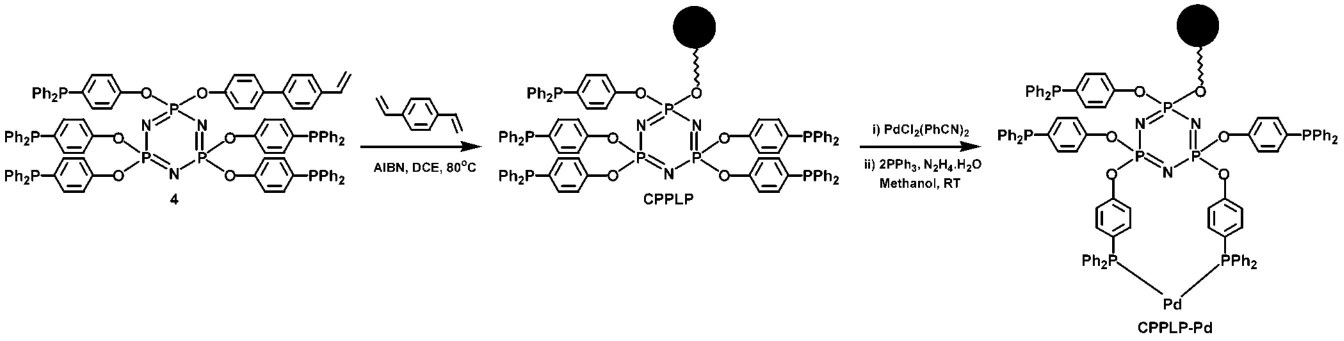
Table 1. Heck Arylation Reaction Catalyzed by **5**[a]



no.	X	catalyst	R	R_1	time (h)	product[d] yield (%)
1	I	$PdCl_2$	Ph	H	5	67[c]
2	I	$Pd(PPh_3)_4$[b]	Ph	H	5	61[c]
3	I	**5**	Ph	H	2	98
4	I	**5**	COOMe	H	3	99
5	I	**5**	COOEt	H	3	96
6	I	**5**[b]	COOMe	Me	20	72[c]
7	I	**5**[b]	CN	H	20	69[c]
8	Br	**5**[b]	Ph	H	60	99

[a] Reaction conditions: aryl halide (5 mmol), olefin (5 mmol), $(n\text{-Bu})_3N$ (5 mmol), and catalyst (0.01 mol %) are dissolved in acetonitrile (5 mL) and kept at a bath temperature 90 °C in an argon atmosphere. The reaction was monitored by thin-layer chromatography. [b] Aryl halide (5 mmol), olefin (6.25 mmol), $(n\text{-Bu})_3N$ (6.25 mmol), and catalyst (0.1 mol %). [c] Unreacted iodobenzene was removed by column chromatography. [d] A single product corresponding to the trans-arylation was obtained in each case. Yield represents isolated yield.

Scheme 2. Preparation of the Cross-Linked Polymeric Catalyst **CPPLP−Pd**



is more active than $PdCl_2$ or $Pd(PPh_3)_4$ as well as other recently reported homogeneous catalysts.[7] In all the cases, only the *trans* isomer is formed exclusively. Bromobenzene can also be used in the reaction with styrene although the reaction time is longer. Similarly a disubstituted olefin such as methyl methacrylate could also be arylated.

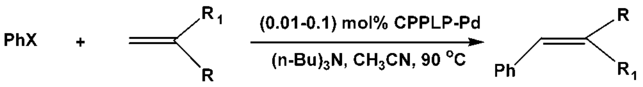
Encouraged by the results of **5**, we incorporated the structural motif of **4** in the cross-linked polymer **CPPLP** as shown in Scheme 2 by the copolymerization of **4** with divinylbenzene. A Pd(0) complex of **CPPLP** was prepared by adopting the procedure used for the preparation of the complex **5**. To ensure that the palladium incorporation in **CPPLP−Pd** is a result of coordination and not due to occlusion, the latter was washed thoroughly with dichloromethane, acetonitrile, methanol, and acetone and dried. The catalyst **CPPLP−Pd** was characterized by elemental analysis and infrared spectroscopy. The amount of palladium in **CPPLP−Pd** was determined by atomic absorption spectroscopy to be 18.9 mg/g of the polymer.

The catalytic activity of **CPPLP−Pd** has been tested by the same method as described in the Heck arylation reaction by **5**. The results obtained are summarized in Table 2. Although **CPPLP−Pd** is not effective with substrates such as acrylonitrile or bromobenzene, it is found to be quite efficient in catalyzing the Heck reaction in other situations. The isolated yields of the products are quite high.

Although slightly longer reaction times are involved with **CPPLP−Pd** in comparison to **5**, this is understandable in view of the heterogeneous nature of the former. It must be noted that hitherto the application of polymer-supported catalysts for the Heck reaction have not been very successful, and only a few examples have been published.[8] In some instances the actual catalytic species was shown to be some palladium species, leaching out into solution.[9]

To confirm that the activity of **CPPLP−Pd** arises from the polymer-bound metal, the following experiments were carried out. After the completion of the first cycle, the catalyst was removed by filtration, washed sequentially with dichloromethane, methanol, and acetone, and dried in a vacuum for 3 h at 40 °C and analyzed by elemental analysis

Table 2. **CPPLP−Pd** Catalyzed Heck Arylation Reaction[a]



no.	X	catalyst	R	R_1	time (h)	product yield[d] (%)
1	I	**CPPLP−Pd**	Ph	H	4	93
2	I	**CPPLP−Pd**	COOMe	H	5	99
3	I	**CPPLP−Pd**	COOEt	H	5	98
4	I	**CPPLP−Pd**[b]	COOMe	Me	30	79[c]
5	I	**CPPLP−Pd**[b]	CN	H	20	-
6	Br	**CPPLP−Pd**[b]	Ph	H	70	-
7	I	cycle-2	Ph	H	4	89
8	I	cycle-3	Ph	H	4	86
9	I	cycle-4	Ph	H	4	82

[a] The cross-linked polymer **CPPLP** was prepared by copolymerizing **4** with divinylbenzene in a 2.5:1 weight ratio. Reaction conditions of catalysis: aryl halide (5 mmol), olefin (6.25 mmol), $(n\text{-Bu})_3N$ (6.25 mmol), and catalyst (0.036 mol %) are dissolved in acetonitrile (5 mL) and heated at 90 °C in an argon atmosphere. The catalyst concentration is calculated with respect to the amount of palladium contained in the polymer. [b] Aryl halide (5 mmol), olefin (6.25 mmol), $(n\text{-Bu})_3N$ (6.25 mmol), and catalyst (0.1 mol %). [c] Unreacted iodobenzene was removed by column chromatography. [d] Yield represents isolated yield.

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and infrared spectroscopy. The results of these analyses showed that there is no change in the structural integrity of the polymeric catalyst. This can be attributed to the effective multisite coordinating capability of the polymeric cyclophosphazene ligand. To find whether palladium leaching occurs during the reaction as reported earlier,[10] we have estimated the amount of palladium of the recovered catalyst by atomic absorption spectroscopy. No significant change in the palladium content was found. Further, the recovered catalyst was tested in three successive cycles; the catalytic activity remains essentially undiminished (Table 2; entries 7, 8, and 9).

As a further test to ascertain that the reaction occurs due to the polymeric catalyst **CPPLP−Pd** and not due to any adventitious leached out palladium species, we filtered the catalyst after 2 h of the reaction between iodobenzene and styrene and allowed the reaction to continue. At this stage the conversion was about 53%. The reaction did not proceed to any significant extent even after 4 h as found by TLC.

In summary, we have synthesized and demonstrated the catalytic application of a new cross-linked Pd(0)-metalated polymeric catalyst. The major strength of this approach is the flexibility in obtaining a desired polymeric ligand whose coordination properties can be reliably determined by a simple model compound study. In our view this approach would considerably augment the existing methodologies available for polymer supports.

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