



Threefold Cross-Linked Polystyrene–Triphenylphosphane Hybrids: Mono-P-Ligating Behavior and Catalytic Applications for Aryl Chloride Cross-Coupling and C(sp³)–H Borylation**

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Polystyrene (PS)-supported phosphanes are widely used for heterogeneous transition-metal catalysis, taking advantage of their practical merits as insoluble materials.^[1,2] Owing to the flexible nature of the PS backbone, the phosphane moieties have generally significant mobility even in cross-linked PS resins, and thus exhibit ligand properties generally similar to those of their homogeneous counterparts, except for their insoluble nature. Thus, such supported phosphanes are able to function not only as monodentate ligands (Figure 1, **A**) but also as bidentate or multidentate ligands (Figure 1, **B**) toward

emulsion polymerization of styrenes in the presence of tris(*p*-vinylphenyl)phosphane as a threefold cross-linker.^[3–5] Our scenario is as follows: The threefold cross-linking increases the density of the polymer chain around the Ph₃P core, and thus limits multidentate P-coordination to the metal, but the steric demand in proximity to the P atom is only moderate (Ph₃P-like) owing to the spacer effect of the three aromatic rings on the P atom, which projects toward trigonal pyramid directions; consequently, the resulting mono-P-ligated metal system allows effective access of substrates for catalysis. In fact, this simple technique yielded novel immobilized monodentate tertiary phosphane ligands that specifically formed mono-ligated transition-metal complexes (Figure 2). The

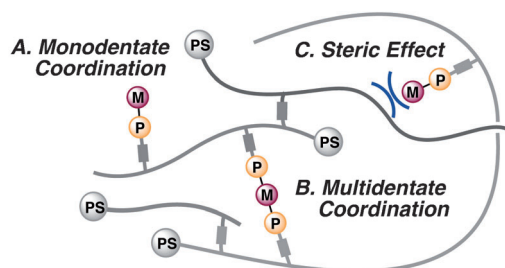


Figure 1. A conceptual view of various metal coordination modes of a PS-supported phosphane. The PS chains, which may cause steric effects toward the catalytic environment, are shown as gray lines.

transition metals. In many cases, however, the flexible polymer chain causes unfavorable steric effects in the catalytic environment, resulting in reduced catalyst efficiency (Figure 1, **C**). Thus, using the PS backbone for designing phosphane ligands to favor a specific structure desirable for an increase in catalytic activity is difficult.

Herein we report a new type of polystyrene–phosphane covalently bound hybrid, which was prepared through radical

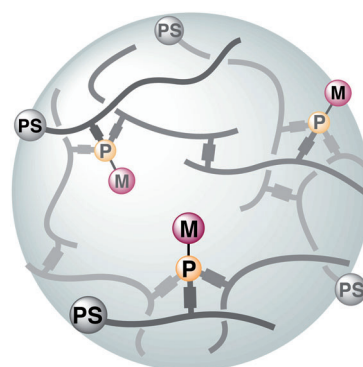


Figure 2. A conceptual view of metal mono-P-ligation of a networked PS resin prepared from a phosphane-centered threefold cross-linker. PS chains are shown as gray lines.

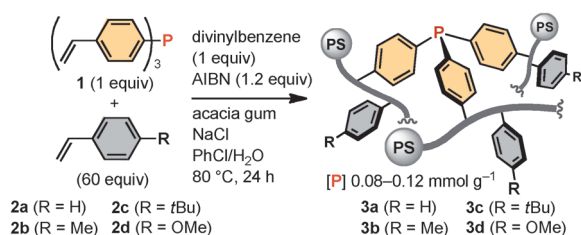
successful Pd-catalyzed C–Cl transformation reactions such as Suzuki–Miyaura coupling and Buchwald–Hartwig amination as well as the Ir- or Rh-catalyzed C(sp³)–H borylation reaction demonstrated the utility of this strategy, suggesting that steric hindrance of the polymer chain unfavorable for catalytic performance was successfully reduced in this system.

A solution of tris(*p*-vinylphenyl)phosphane (**1**), divinylbenzene (DVB), monofunctional styrenes (**2a–d**; R = H, Me, *t*Bu, OMe), and AIBN (azobis(isobutyronitrile); **1**/DVB/**2**/AIBN 1:1:60:1.2; stoichiometry not optimized) in chlorobenzene was dispersed in an aqueous phase containing acacia gum and NaCl.^[6] The mixture was vigorously stirred at 80 °C for 24 h for 70–90 % consumption of the vinyl monomers. The resultant solids were collected by filtration, washed with water, MeOH, THF, and toluene, and dried under vacuum to provide the Ph₃P cross-linked PS (**3a–d**) as white beads

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Scheme 1. Preparation of Ph_3P -cross-linked PS (**3a–d**).

(Scheme 1). The polymer beads did not contain any solvent molecules or unreacted monomers that were detectable by ^{13}C CP/MAS NMR spectroscopy. The phosphorus loading values ($[\text{P}]$ 0.08–0.12 mmol g^{-1}) were determined based on their abilities to capture transition-metal complexes.^[7] DVB (not shown in **3**) was used as a co-cross-linker to achieve uniform formation of bead-shape materials.

The dried beads of **3** have diameters of about 300–400 μm (Figure 3a), and exhibited ordinary swelling properties as polystyrene resins. Swelling was good with aprotic solvents, such as toluene, THF, and CH_2Cl_2 (Figure 3b), but poor with

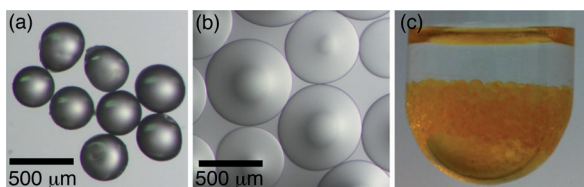
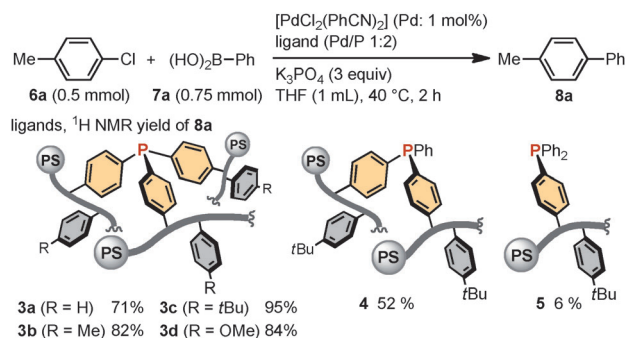


Figure 3. a) Dried beads of **3c** ($\text{R} = \text{tBu}$). b) Beads of **3c** swollen in toluene. c) Beads of $[\text{PdCl}_2(\text{PhCN})(\mathbf{3c})]$ (with a stirring bar) as prepared in THF (P/Pd 2:1).

aliphatic hydrocarbons and aprotic polar or protic solvents such as DMF, MeOH, and water.^[8] The degree of swelling was slightly dependent on the substituent (R) on the benzene ring of the PS backbone (5.0–5.8 mL g^{-1} in toluene).

The treatment of the THF-swollen polymer beads **3c** with $[\text{PdCl}_2(\text{PhCN})_2]$ at room temperature under magnetic stirring caused gradual coloring of the beads to orange over several minutes (Figure 3c). The ^{31}P CP/MAS NMR analysis was clearly indicative of the selective formation of the mono-P-ligated Pd^{II} complex $[\text{PdCl}_2(\text{PhCN})(\mathbf{3c})]$, irrespective of the stoichiometry of the P ligand and the Pd source (P/Pd 2:1, 1:2). In contrast, the homogeneous reaction between $[\text{PdCl}_2(\text{PhCN})_2]$ and 2 equiv of (*p*-Tol) $_3\text{P}$ in THF gave bis-P-ligated complex *trans*- $[\text{PdCl}_2\{(\text{p-Tol})_3\text{P}\}_2]$ as a single product. Similarly, the conventional PS-supported phosphane **5** (chemical structure shown in Scheme 2), in which the phosphane moiety was incorporated in the PS resin through the reaction of monovinylated triphenylphosphane, gave the bis-P-ligated complex $[\text{PdCl}_2(\mathbf{5})_2]$ as a major species when P was in excess (P/Pd 2:1).^[9]

Controlled mono-ligation in the Pd-**3** systems having been confirmed, we explored their applicability toward Suzuki–Miyaura coupling of unactivated chloroarenes, for which the importance of mono-ligation of two-electron donor ligands



Scheme 2. Effect of PS-supported triarylphosphanes in the Pd-catalyzed Suzuki–Miyaura cross-coupling reaction.

has been well-established through experiments with bulky and electron-rich phosphane^[10,11] or NHC^[12] ligands. Furthermore, Tsuji and co-workers achieved mono-ligation of Ph_3P -based ligands by introducing steric demands in the periphery of the dendrimer-type high-molecular-weight phosphane molecules.^[13–15] In fact, these “bowl-shaped” phosphanes also induced the Suzuki–Miyaura coupling with chloroarenes.^[13b]

The mono-P-ligated Pd^{II} complexes $[\text{PdCl}_2(\text{PhCN})(\mathbf{3a–d})]$ (1 mol % Pd) were evaluated for catalytic efficacy in the coupling reaction between *p*-chlorotoluene (**6a**, 0.5 mmol) and phenylboronic acid (**7a**, 0.75 mmol) in the presence of K_3PO_4 (1.5 mmol). To our delight, the reaction proceeded under mild conditions (THF, 40 °C, 2 h, Scheme 2). The yield of biaryl **8a** was apparently dependent on the substituents (R) on the benzene ring of the PS backbone of **3**. Relatively high yields were obtained with the substituted ligands (**3b**, $\text{R} = \text{Me}$, 82%; **3c**, $\text{R} = \text{tBu}$, 95%; **3d**, $\text{R} = \text{OMe}$, 84%) compared with the parent ligand (**3a**, $\text{R} = \text{H}$, 71%). The origin of these substituent effects are not clear; it is not explained by the difference in the swelling properties.^[8]

The threefold cross-linking is essential. The analogous twofold cross-linked PS- Ph_3P hybrid **4** ($\text{R} = \text{tBu}$) gave **8a** in only 52% yield under otherwise identical conditions, and the conventional single-point linked PS- Ph_3P hybrid **5** was even less efficient (6% yield; Scheme 2). A homogeneous catalyst system based on Ph_3P did not induce the reaction at all (data not shown).

The heterogeneous catalyst system prepared from $[\{\text{PdCl}(\eta^3\text{-cinnamyl})\}_2]$ (1 mol % Pd) and **3c** (2 mol % P) was examined for reusability in the coupling reaction between **6a** (1.0 mmol) and **7a** (1.5 mmol; K_3PO_4 , 60 °C, 2 h).^[16] After the first run, the catalyst beads were contaminated with inorganic salts, and the supernatant was colorless. The insoluble materials were filtered, washed with H_2O , and then with THF, and dried under vacuum to obtain orange-colored catalyst beads for use in the next run. The Pd-**3c** catalyst maintained most of its activity even in the fourth run, but the gradual color change from orange to brown over repeated uses (yield of **8a**: 1st 91%, 2nd 97%, 3rd 98%, 4th 94%, 5th 85%).^[17,18] HRTEM observation of the reused Pd-**3c** was indicative of gradual formation of Pd cluster species, which should be less active or inactive (Figure 4).^[19] Inductively coupled plasma atomic emission spectroscopy (ICP-

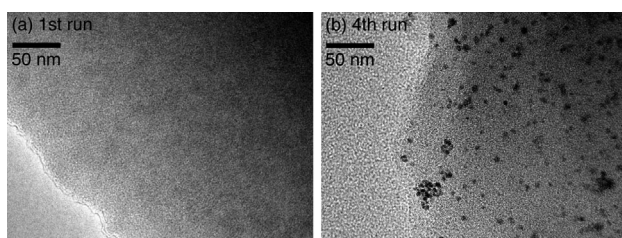
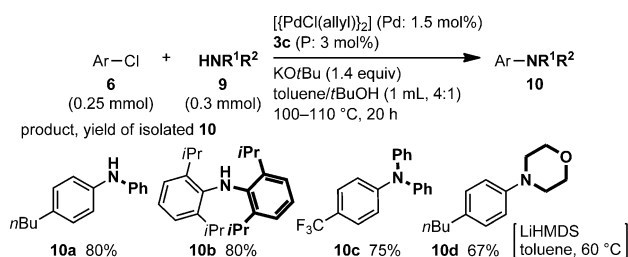


Figure 4. a,b) HRTEM images of part of the Pd-**3c** resins after 1st and 4th runs, respectively.

AES) analysis indicated that Pd leaching for each run was below the detection limit ($<0.02\%$ of the loaded Pd).^[20]

The chemical stability of the PS resin and the C–C bond linkage between the phosphane moiety and the resin is the advantage of the PS-Ph₃P hybrids **3** over heterogenized ligands based on oxide surfaces in the cases of using them under rather harsh reaction conditions. For example, a catalyst system prepared from $[\text{PdCl}(\eta^3\text{-allyl})_2]$ (1.5 mol % Pd) and **3c** (3 mol % P) was successfully applied to the amination of *p*-butylchlorobenzene (**6b**, 0.25 mmol) with aniline (**9a**, 0.3 mmol).^[21] The reaction was conducted under basic and high-temperature conditions employing KO^{*t*}Bu (0.35 mmol), which is stronger base than K₃PO₄, and a toluene-*t*BuOH (4:1) mixture as the base and solvent, respectively, at 100 °C over 20 h to afford the corresponding diarylamine **10a** in 80 % yield (Scheme 3).^[22] Notably, when the previously reported



Scheme 3. The C–N coupling reactions with the Pd-**3c** catalyst system.

silica-supported monophosphanes (silica-SMAP^[23] and silica-TRIP^[24]) with similar mono-P-ligating features were applied to this Pd catalysis instead of the PS-Ph₃P hybrid, the complete leaching of metal and P atoms owing to degradation of the oxide surface was evident, and no substrate conversion was observed, showing the merit of the PS resin over silica gel as a robust solid support. It is also to be noted that use of the twofold cross-linked phosphane **4**, the single-point linked phosphane **5**, and the homogeneous ligand **1** were again less efficient (22 %, 5 %, and 0 % yields, respectively).^[25]

This procedure was also applicable for the synthesis of a sterically congested diarylamine (**10b**) and a triarylamine (**10c**, from diphenylamine). The amination of the chloroarene **6b** with morpholine to give the *N,N*-dialkylaniline derivative **10d** was successfully performed under even more basic conditions using LiHMDS as a base.

The mono-ligating feature of the threefold cross-linked PS-Ph₃P hybrids (**3**) and their excellent performance in the

Pd-catalyzed coupling reactions prompted us to test the best-performing ligand **3c** in the heteroatom-directed borylation of unactivated C(sp³)–H bonds, for which the silica-supported cage-type trialkyl- or triarylphosphanes (silica-SMAP and silica-TRIP, respectively) were effective ligands in our recent studies.^[23c,e,f,24] We expected that such experiments might give us an answer to the question as to whether or not the cage in silica-SMAP and silica-TRIP is essential.

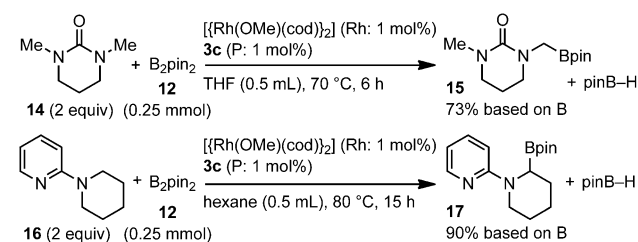
In fact, the PS-Ph₃P hybrid **3c** did promote these challenging catalyses. Specifically, the reaction of 2-pentylpyridine (**11**) with bis(pinacolato)diboron (**12**) in the presence of a catalytic amount of $[\{\text{Ir}(\text{OMe})(\text{cod})\}_2]$ (2 mol % Ir) and **3c** (2 mol % P) afforded secondary alkylboronate **13** in 82 % yield based on the diboron **12** (Table 1, entry 1).^[23f] Although the twofold cross-linked PS-Ph₃P ligand **4** and the single-point linked ligand **5** also induced the borylation, their efficacies were significantly lower than that of the threefold cross-linked ligand **3c** (entries 2 and 3). No reaction occurred under homogeneous conditions with Ph₃P (entry 4).

Table 1: Ir-catalyzed C(sp³)–H borylation.^[a]

Entry	Ligand	Yield [%] ^[b]
1	3c	82
2	4	61
3	5	45
4	Ph ₃ P	0

[a] Conditions: **11** (0.9 mmol), **12** (0.3 mmol), $[\{\text{Ir}(\text{OMe})(\text{cod})\}_2]$ (0.006 mmol Ir), ligand (0.006 mmol P), cyclopentyl methyl ether (CPME, 1 mL), 60 °C, 15 h. [b] Yield determined by ¹H NMR analysis based on **12**.

The threefold cross-linked PS-Ph₃P ligand **3c** was also effective for the Rh-catalyzed N-adjacent C(sp³)–H borylation of urea **14** and 2-aminopyridine **16** (1 mol % Rh, Scheme 4), for which the silica-TRIP triarylphosphane ligand was effective but the silica-SMAP trialkylphosphane was not in our previous study.^[24] As the pinB–H also served as a reagent for the C–H borylation, the α -aminoalkylboronates **15** and **17** were obtained in good or high yields (**15**, 73 %; **17**, 90 %) based on the boron atom used. These results clearly show that achieving mono-P-ligation and having moderate ligand steric effect together is important for producing a C(sp³)–H borylation catalyst (mono-P-ligating, homoge-



Scheme 4. Rh-catalyzed N-adjacent C(sp³)–H borylation.

neous bulky phosphanes were not useful^[23c,e,f,24]), and using a cage structure as in silica-SMAP and silica-TRIP is not always necessary. Advantages of the PS-Ph₃P hybrid system over the cage-type silica-supported phosphanes are found in the easiness of the synthesis and structural modification and in the flexibility for expanding the concept.

In summary, a new type of polystyrene(PS)-phosphane covalently bound hybrid was synthesized through radical emulsion copolymerization of styrenes, divinylbenzene, and a tris(*p*-vinylphenyl)phosphane threefold cross-linker. These hybrids were used for catalyst systems to favor a mono-P-ligated metal complex with minimal synthetic effort. The applicability of the PS-Ph₃P hybrids toward Pd-catalyzed cross-coupling reactions of unactivated chloroarenes as well as Ir- or Rh-catalyzed borylation reactions of C(sp³)-H bonds demonstrates the utility of this simple heterogeneous strategy. Expanding the applicability of this strategy for exploring new catalysis and the development of new functional polymer-phosphane hybrids will be the subject of future study in our laboratory.

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- [18] A hot filtration test of the Pd-**3c** catalyst indicated that no meaningful reaction occurred in the solution phase.
- [19] HRTEM observation after the 8th run (**8a**; 24% yield, 2 h) indicated the formation of larger Pd aggregates. See the Supporting Information for other HRTEM images (Figure S17) and the ³¹P CP/MS spectrum of the resins after the 8th run (Figure S18). The Pd cluster formation most likely occurred by dissociation of the Pd from the P atom.
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reaction were <0.02%, 3.6%, and <0.02% of the loaded metals, respectively.

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