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Introduction

Carbon–carbon cross coupling reactions are among the most widely studied metal-catalyzed chemical transformations. The various cross-coupling processes involving Mizoroki–Heck, Suzuki, Miyaura and Sonogashira reactions are catalyzed both by molecular catalysts that contain phosphine and *N*-heterocyclic carbene ligands and by colloidal palladium catalysts that are formed *in situ*.^{1–8} This chemistry has been widely used in synthesis in academic and industrial laboratories and its importance was recognized by the 2010 Nobel Prize in chemistry to professors Heck, Negishi and Suzuki.

The work described in this paper explores alternative more sustainable approaches to Pd-catalyzed cross coupling catalysis that proceed through Pd colloids. Two issues are addressed. First, we have prepared $Pd(\pi)$ complexes of colorimetric azo dyes attached to polyisobutylene (PIB) that serve as precatalysts that in turn form Pd colloids *in situ* that act as catalysts for cross coupling chemistry. We show here that the activity and recoverability of Pd in such Pd catalyzed processes can be influenced not just by the presence of a polymer support, but also by the presence of other soluble polymeric ligands that normally are used with molecular Pd complexes. Second, we

Recycling Pd colloidal catalysts using polymeric phosphine ligands and polyethylene as a solvent†

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Polyisobutylene (PIB)-bound azo dyes were prepared from aryl amine terminated polyisobutylene oligomers and used to form palladacycle precatalysts that can be used for catalytic carbon–carbon cross coupling reactions. The catalysts so formed were recyclable using thermomorphic heptane–DMF solutions that are monophasic at 80 °C and biphasic at room temperature. Under these conditions, the Pd catalyst can be recycled but some Pd leaches into the product solution. Using a low melting polyethylene oligomer as a solvent in place of the volatile heptane solvent reduces this leaching by roughly an order of magnitude. Further modification that involves using a second polyisobutylene (PIB)-bound phosphine ligand both increases the activity of the colloidal Pd catalyst and decreases the total Pd leaching by almost two orders of magnitude with 99.88% of the Pd being recovered. In this case, the Pd content in the solution of the product was *ca.* 0.3 ppm. These two modifications together lead to a much more sustainable strategy for the use of Pd colloidal catalysts in catalytic cross coupling chemistry.

> show that at least part of the solvent that is necessary for separation and recovery of these colloidal catalysts can be replaced by a low melting polyethylene wax. Using this polyethylene solvent and added ligands together leads to very efficient recovery of 99.88% of the Pd in a solid wax phase. This solid dispersion of the Pd can then be reused in subsequent catalytic reaction cycles. These two modifications together lead to a much more sustainable strategy for the use of Pd in these Pd colloidal catalyzed cross coupling reactions.

> Homogeneous molecular complexes of Pd ligated by phosphine and N-heterocyclic carbenes (NHC) are highly active and useful catalysts for Pd-catalyzed cross-coupling chemistry.4,7-15 However, it has become increasingly apparent that Pd colloids generated in a designed fashion or inadvertently through decomposition or in situ reduction of a Pd(II) species are comparably efficient as catalysts for cross coupling chemistry. The many examples that use what are variously described as colloidal or nanoparticle Pd species show the increasing importance of these types of catalysts.^{5,7,16-22} Thus, some of the attention previously devoted to recycling of homogeneous phosphine and NHC-ligated catalysts has now turned to recycling of colloidal catalysts.²³⁻²⁷ Diverse strategies where catalyst recycling and catalyst product separation are effected with dendrimer encapsulated Pd catalysts, 28-30 Pd catalysts on magnetic nanoparticles,³¹⁻³⁵ Pd nanoparticles in the presence of conventional or hyperbranched polymers,³⁶⁻³⁸ or Pd catalysts localized in a separable solid^{39,40} or liquid phase have all been described.⁴⁰⁻⁴³ Such catalysts are generally designed to achieve several goals - the formation of a highly active catalyst, an efficient catalyst/product separation process, and catalyst

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[†]Electronic supplementary information (ESI) available: Experimental procedures for the synthesis of the PIB-azobenzene Pd(II) complex, details of the catalytic reactions and recycling experiments, and ¹H and ¹³C NMR spectra of coupling products are provided. See DOI: 10.1039/c3gc36932c

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= polyethylene (Polywax) powder containing the catalyst

Fig. 1 (a) Thermomorphic liquid–liquid schemes for the use of cross-coupling catalysts using a polar and a nonpolar solvent (e.g. heptane and DMF) with a heptane soluble catalyst and products that separate into a polar phase after temperature perturbation generate a biphasic mixture after a reaction; (b) the use of polyethylene as a cosolvent in a thermomorphic catalyst separation where the catalyst is isolated as a dispersion in solid polyethylene wax and the products remain in solution after a hot monophasic reaction step is followed by phase perturbation and cooling.

recyclability with minimal Pd leaching into the productcontaining phase.

Our earlier work too has included such chemistry. For example, we along with a group at Georgia Tech showed that soluble polymer supported pincer S-C-S Pd complexes form highly active Pd colloidal catalysts for cross coupling chemistry that are easily recyclable and recovered.44-46 This chemistry is similar to our other chemistry involving recyclable and separable catalysts or dye-labelled catalysts that uses a biphasic separation after a monophasic reaction.^{47,48} This general strategy that we have used in catalyst recovery and separation is shown in Fig. 1a where a thermomorphic mixture of solvents that is miscible hot and immiscible cold is used to separate a polymer-bound catalyst and products into two liquid phases of different polarities and densities. This strategy was recently expanded to replace the volatile heptane solvent with a narrow dispersity, low melting polyethylene wax (Polywax) as shown in Fig. 1b.⁴⁹ The results below couple these separation strategies with the use of additional polyisobutylene bound phosphine ligands to separate and recycle the Pd colloidal cross coupling catalysts derived from PIB-bound azo dye ortho-metallated Pd(II) complexes.

Results and discussion

Our initial objective was to synthesize colorimetric polymerbound Pd catalysts that could be used in thermomorphic separations like those in Fig. 1(a). This was accomplished using polyisobutylene (PIB) bound azophenols like 3 (Scheme 1) as the starting material for the synthesis of a colored PIB-bound Pd(π) precatalyst. The PIB-bound aniline 1 is easily prepared on a multigram scale from polyisobutylene (PIB₂₃₀₀) 1 that is





 $\mbox{Scheme 1}$ Synthesis of the PIB-bound azophenol dye 3 (PIB = H–(CH_2C-(CH_3)_2)_{40}–).



Scheme 2 Synthesis of the PIB-azobenzene Pd(II) complex 5.

commercially available as a mixture of vinyl-terminated oligomers.⁵⁰ Diazotization was carried out using isoamyl nitrite in dichloromethane. The product of this reaction was a PIBbound diazonium salt, which was then allowed to react with an electron-rich arene to form a PIB-bound azo dye. For example, a diazonium salt formed from a 2,6-dimethylanilineterminated polyisobutylene forms an isolable electrophilic diazonium salt 2 that readily reacts with an excess of phenol to form the azo dye 3.⁵¹ While this reaction requires excess phenol, the excess phenol is easily separated from the heptane-soluble azo dye by a liquid–liquid biphasic extraction taking advantage of the heptane phase selective solubility of 3. This reaction can be carried out with PIB oligomers PIB₁₀₀₀, PIB₁₃₀₀, or PIB₂₃₀₀ on a multigram scale. We used PIB₂₃₀₀ to prepare the ligands and catalysts below.

We expected that the electron-rich aryl group of the PIBbound azo dye 3 would react with $Pd(\pi)$ to form an *ortho*palladated intermediate. However, palladation of 3 disappointedly led to a mixture of products based on ¹H NMR spectroscopy. Fortunately, the butyl ether 4 formed from 3 underwent facile metallation with $Pd(PhCN)_2Cl_2$ in chloroform at room temperature (Scheme 2) to afford the red chlorobridged PIB-bound palladium(π) complex 5 in quantitative yield (Scheme 2).

The formation of the PIB-palladacycle was followed by UVvisible and ¹H NMR spectroscopy. Ligand 4 has a λ_{max} of *ca*. 348 nm. On palladation the UV-visible spectrum changes and a new absorbance peak appears at 448 nm. These spectral changes are comparable to those seen in the formation of other similar palladium complexes.⁵² ¹H and ¹³C NMR spectra of 4 (Fig. 2) were also consistent with metallation in that the aryl protons of the electron rich aryl group in the butoxyarene ring changed from a doublet of doublets to a set of three



Fig. 2 ¹H NMR spectrum of the PIB-bound phenyl butyl ether azo dye 4 (above) and the PIB-Pd(II) palladacycle 5



Fig. 3 Visually evident phase selective solubility of the yellow phenyl butyl ether dye 4 or the red-orange PIB(II) palladacycle 5 in the less dense heptane phase of a biphasic thermomorphic heptane-DMF system.

resonances each integrating to one proton at 7.74, 6.67, and 6.61 δ with an ABX coupling pattern typical of that of a 2,4-disubstituted phenyl ether. ¹³C NMR spectroscopic analysis confirmed this result. As a result of the palladation, the two aryl C-H signals of the butoxyarene ring were replaced with three new aryl C–H signals and a new peak at 147.2 δ that is consistent with the formation of an aryl-Pd bond.^{44,52} A DEPT experiment confirmed that the peak at 147.2 δ was a quaternary carbon and that there were four aryl methine carbons. The PIB-bound Pd species 5 was also analyzed for Pd. For compound 5 containing a 2300 M_n PIB the calcd value for Pd is 3.92%. The found value by ICP-MS for Pd was 3.74%.

Our initial studies showed that the PIB-bound azo dye 4 as well as the $Pd(\pi)$ complex 5 were soluble in a hot equivolume mixture of DMF and heptane but were phase selectively soluble in the heptane phase of the biphasic mixture that formed on cooling based on the absence of color in the polar DMF phase (Fig. 3). DMF was used in these studies as a polar phase because it is a polar solvent that we have used previously as part of a thermomorphic liquid-liquid solvent mixture. Our expectation was that this PIB-bound Pd(II) complex 5 could be used as a precatalyst for C-C cross coupling reactions where the PIB-bound group would recycle the Pd catalyst in a heptane phase. To explore this, we carried out catalytic reactions at 100 °C in a 1:1 (vol:vol) mixture of heptane and DMF using 1 mol% of 5 as shown in Scheme 3. As expected, 5 was



Scheme 3 Carbon-carbon cross coupling reactions catalyzed by 5 in a thermomorphic heptane-DMF system where catalysts are separated from products and recycled using a liquid–liquid biphasic separation (cf. Fig. 1a).

Table 1 Recycling results using precatalyst 5 in a solvent system containing heptane and DMF where the catalyst is separated and recycled by thermomorphic liquid-liquid separation

Aryl halide	Acceptor	Product	Cycles	Yield ^a (%)
Ac	CO ₂ n-C ₄ H ₉	9	5	92
⟨Br	CO ₂ n-C ₄ H ₉	10	5	90
Ac-	С – в ОН ОН	15	5	96
CI	С – в ОН ОН	16	6	94
Br	MeO	17	5	89

The reactions were carried out with 1 mmol of the aryl halide and 1.2 mmol of butyl acrylate or 1.4 mmol of phenyl boronic acid using 2 mmol of K₂CO₃ as a base and 0.01 mmol of 5 in a mixture of 2 mL of heptane and 2 mL of DMF. The reaction was stirred under N2 at 100 °C for 6-12 h. ^a The yields are isolated average yields per cycle. ¹H NMR spectroscopic analyses of the product solution showed complete conversion of the limiting aryl halide in each cycle. Yields were obtained for each cycle in one experiment using *p*-iodoacetophenone and butyl acrylate. The yields after 12 h for each cycle were 81%, 80%, 71%, 78%, and 70%, in cycles 1-5, respectively. These studies used a lower catalyst loading (0.1 mol%) and did show that the initial reaction times with these lower loadings of Pd could be as short as 6 h. However, in these experiments, the time for complete conversion of starting material to product increased to 12 h by the fifth cycle. This longer reaction time is consistent with the observation of loss of Pd into product solutions seen by ICP MS.

competent at Mizoroki-Heck and Suzuki catalysis with a variety of substrates of varying reactivity although aryl chlorides are unreactive. In these reactions, the products were isolated from the DMF phase. Catalyst recycling was accomplished by adding a heptane-saturated solution of DMF containing fresh substrate to the recovered heptane catalystcontaining phase.

The results of a series of reactions where the catalyst was recycled through 5-6 cycles are summarized in Table 1. The

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results in this table show that the PIB-azobenzene Pd(II) precatalyst 5 has an activity for cross-coupling chemistry that is similar to that of other low molecular weight Pd precatalysts reported in the literature.⁵³

Visual observation of the formation of a colorless DMF phase on cooling indicated that no significant amount of the starting complex 5 remained in this phase. However, ICP-MS analysis showed that ca. 7% of the starting Pd leached into the polar product phase after the 4th cycle in a Mizoroki-Heck coupling that formed butyl cinnamate from iodoacetophenone and n-butylacrylate (entry 1, Table 1). Thus, while 5 is an effective precatalyst for cross coupling, the leaching of Pd from solutions of 5 is higher than desired. This leaching led to a product solution containing 37 ppm Pd. While fractionation during product isolation could reduce this Pd leaching in the final product through standard purification procedures or while a Pd sequestration reagent could be used to reduce the Pd content in the product to the 1-10 ppm range some reports suggest as a guideline for products,^{8,54} our interests here were in trying to minimize the total amount of Pd leaching to below 1 ppm by a simple physical phase separation of a phase that recycled the catalyst from a phase that contained the product a result we achieved as discussed below. While we also showed that a lower loading of Pd (e.g. 0.1 mol%) could effect these reactions, we used a higher 1 mol% Pd loading of catalysts in the remainder of these studies, as this higher Pd loading is often used in industry for catalyst robustness⁸ and affords a more rigorous platform for testing Pd recovery and the extent of Pd leaching to the product solution.

To address this problem of leaching as well as to make the overall catalytic reaction more sustainable we examined the use of 5 as a precatalyst in a mixture of THF and DMF replacing the heptane solvent used in Scheme 3 with a commercially available polyethylene oligomer (PE_{Olig}). This Polywax oligomer is a solid at room temperature. We recently reported that this low melting wax can serve as a solvent replacement for alkanes as it dissolves on heating with THF as well as with a 1 : 1 (vol : vol) mixture of THF and DMF at *ca.* 80 °C.⁴⁹ When these binary or ternary solvent mixtures are perturbed by the addition of water while hot, the Polywax phase separates as a low viscosity hydrocarbon liquid phase that PIB-bound species quantitatively partition into. This solvent system was used here as shown in Fig. 1b for the reactions shown in Scheme 4.



1 mol% 5

THF / DMF/ PE

OBL

Polywax, THF, and DMF solvent mixture where the catalyst is recycled as a solid dispersion in Polywax (cf. Fig. 1b).

Table 2Recycling results using precatalyst 5 in a solvent system consisting ofPolywax, THF, and DMF where the catalyst is isolated as a solid Polywaxdispersion

Aryl halide	Acceptor	Product	Cycles	Yield ^a (%)
Ac-	CO ₂ n-C ₄ H ₉	9	5	90
⟨Br	CO ₂ n-C ₄ H ₉	10	5	85
⟨	МеО-С	17	5	90

The reactions were carried out with 1 mmol of the aryl halide and 1.2 mmol of butyl acrylate or 1.4 mmol of phenyl boronic acid using 2 mmol of K_2CO_3 as a base and 0.01 mmol of 5 in a mixture of 2 mL of THF and 2 mL of DMF and 1.5 g of Polywax ($M_n \sim 400$). The reactions were stirred under N_2 at 90 °C for 12 h. ^{*a*} The yields are isolated average yields per cycle. ¹H NMR spectroscopic analyses of the product solution showed complete conversion of the limiting aryl halide in each cycle.

We initially prepared a suspension of 1.5 g of polyethylene oligomer (Polywax400) in 4 mL of a 1:1 mixture of THF-DMF containing substrate and 5. Polywax was used for this purpose since NMR studies showed that Polywax could be separated without contaminating the polar solutions of the product, avoiding the need for chromatography to remove traces of the polymeric solvent. At room temperature, no catalysis occurred and no 5 visually sorbed onto the suspended Polywax powder. However, on heating this mixture to 90 °C a solution formed and Mizoroki-Heck and Suzuki reactions could be effected (Table 2). After the reaction was complete, the Polywax could be separated as a solid on cooling. However, this quantitative separation of Polywax from the product solution led to precipitation of the Polywax without entrapment of the PIB-bound species. However, by using a THF-DMF mixture as the polar solvent, the addition of 1 mL of hot water to the homogeneous hot solution perturbed by the hot solvent mixture to form a liquid-liquid biphasic mixture with a colored low viscosity Polywax-rich phase and a polar THF-DMF rich phase. Cooling this biphasic mixture led to solidification of the Polywax to form a colored waxy solid that could then be physically separated from the colorless THF-DMF solution that contained the cross coupling product. This waxy catalyst containing Polywax solid was then added to a fresh THF-DMF solution to carry out subsequent reactions cycles. A total of 5 cycles of each Mizoroki-Heck and Suzuki reaction were carried out with isolated product yields of product (Table 2) that were equivalent to those in Table 1. Again, while visual observation indicated that there was no red color in the clear polar phase, Pd analysis after a Mizoroki-Heck reaction showed that 1.2% of the Pd leached into the polar product phase after the 4th cycle. This lower leaching in comparison to Pd leaching, seen in the reactions in Scheme 3, suggests that the formation of a solid solvent dispersion of the catalyst lowers the loss of Pd.

Based on the assumption that 5 is generating a Pd(0) species during these reactions, we examined 5 as a precatalyst



Scheme 5 Synthesis of PIB-azobenzene Pd(II) phosphine complex 18 and its use in an allylic amination reaction.

for an allylic amination reaction. However, a heptane-DMF solution of 5 did not form any detectable allylic substitution product from cinnamyl acetate and morpholine even after 24 h of stirring at 90 °C. To overcome this unexpected lack of reactivity of 5 in allylic substitution, we considered adding phosphine ligand since we had previously seen that phosphine ligands can enhance the reactivity of heterogeneous Pd(0) catalysts in a similar chemistry.55,56 Instead of simply adding a phosphine ligand to 5 and heating, we first sought to confirm that a phosphine ligand would form a complex with the Pd(n)center in 5 by treating the PIB-bound chloride bridged dinuclear complex 5 with 2 equiv. of triphenylphosphine (PPh₃) in dichloromethane at room temperature (Scheme 5). Gratifyingly this afforded a PIB-azophenol Pd(II) phosphine complex 18 (Scheme 5) based on ¹H, ¹³C, and ³¹P NMR spectroscopic analysis. Evidence for the formation of a phosphine complex from 5 includes the changes in the ¹H NMR spectrum of 18 wherein the resonance for H3 of 18 became a doublet due to ³¹P-¹H coupling. The chemical shift for this proton also changed from 6.5 to 5.9 δ consistent with phosphine complex formation.⁵⁷ When we examined the use of 18 in an allylic amination reaction using cinnamyl acetate and morpholine in heptane-DMF at 80 °C, complete conversion of the starting cinnamyl acetate to a mixture of structurally isomeric allylic amines occurred (Scheme 5). However, attempted recycling experiments of 18 failed, giving no conversion to products in the second cycle presumably due to the loss of phosphine to the DMF phase.

Encouraged by the observation that the presumed phosphine complex **18** is active in allylic amination in the presence of added phosphine and by our ability to recycle catalytic species derived from precatalysts like **5**, we next explored a more sustainable way to use colloidal Pd catalysts derived from **5** in the presence of phosphines. In this work we examined the use of a PIB-bound phosphine as a ligand to activate **5** for allylic substitutions. This study used a PIB-bound triarylphosphine (**21**) which we had previously used for organocatalysis. This phosphine was prepared using the chemistry shown in Scheme 6.⁵⁸

We then carried out an allylic substitution reaction of cinnamyl acetate by morpholine using 5 as a precatalyst in the presence of 2 equiv. of PIB-bound aryl phosphine **21** as an



Scheme 6 Synthesis of the PIB-bound triarylphosphine 21.

additive ligand. This reaction like that seen with the preformed phosphine complex 18 was successful. Moreover, in this scheme where the PIB-bound 5 and 21 were used in concert, recycling of an active catalyst was feasible because 21 is phase selectively soluble in heptane and does not detectably leach into a polar solvent phase.58 In these cases, the catalysis was carried out in heptane at 80 °C and catalyst recycling was accomplished by cooling to room temperature and extracting the product using acetonitrile. Under these conditions, both the catalyst and the PIB-bound phosphine ligand remain in the heptane phase. Additional reaction cycles were then effected by adding fresh substrates to this heptane solution for each subsequent reaction cycle. We carried out 8 cycles without any decomposition of the phosphine ligand and without any diminution of the product yield. These reactions show that an oligomeric phosphine can be an effective ligand for the presumed Pd colloidal catalyst formed from another oligomer bound species. A further feature of this chemistry is that ICP-MS analysis showed that Pd leaching further diminished by using 5 along with 21. A metal leaching experiment on the product phase of the 5th cycle using ICP-MS analysis showed 0.45 ppm Pd in the product phase showing that only 0.17% of the starting Pd was lost in this cycle.

The ability of 21 to lower leaching in the allylic substitution reaction described above suggested that 21 could be similarly useful in cross coupling chemistry. To test this hypothesis, we repeated the Mizoroki-Heck coupling reported in Table 2 that involved the reaction of 4-iodoacetophenone or bromobenzene and carried out this reaction using 1 mol% of 5 along with 2 equiv. of 21 using the more sustainable THF-DMF-Polywax solvent system used in Scheme 4 in place of the heptane used in Scheme 3. This Mizoroki-Heck reaction was carried out through 5 cycles under the conditions used in Table 2. The average yield of product in each cycle in this case was 89%, essentially equivalent to what was seen in Table 2 with the same substrates. Catalyst recycling was accomplished by perturbing the hot THF-DMF-Polywax monophasic mixture with water as described above. Cooling generated a solid Polywax phase that contained a dispersion of the PIB-bound Pd complex 5 and the PIB-bound phosphine 21 that was physically separated from the polar solution of product and then recycled with a fresh substrate in a subsequent cycle. ICP-MS analysis for Pd leaching in the 4th cycle showed that the polar phase contained 0.31 ppm Pd showing that only 0.12% of the Pd leached into the product phase. This Pd leaching is two orders of magnitude lower than the Pd leaching in a system



Fig. 4 (a) SEM image of Pd colloidal particles entrapped in Polywax, and (b) SEM image of Pd colloidal particles entrapped in Polywax solid from a Mizoroki–Heck reaction that included added PIB-bound phosphine **21**.

without Polywax or without a phosphine ligand. This result where we have eliminated one of the volatile organic solvents and shown the effectiveness of polymeric cofactor ligands suggests the possibility that it should be possible to significantly improve the sustainability of other homogeneous catalysts – something we are currently studying.

While the catalyst recycling experiments and metal leaching data show that we can recover the Pd catalyst in these various reactions and that high levels of Pd separation are possible using added ligands and a Polywax matrix as a cosolvent, the notion that the PIB-bound palladacycle is a precatalyst that forms colloidal palladium during the reaction was conjecture. To confirm that Pd colloidal species formed, we carried out scanning electron microscopy (SEM) experiments on the solid Polywax dispersion of the recycled catalyst isolated from cycle 5 in an experiment using the PIB-bound phosphine 21 as a cofactor and compared it with the recovered Polywax dispersion from an experiment in Table 2 where there was no added 21 present. Both studies examined the recovered Polywax from a Mizoroki-Heck reaction of 4-bromoacetophenone (Fig. 4a and 4b, respectively). These SEM images of the Polywax material that was recovered after 5 catalytic cycles showed that Pd colloidal particles with an approximate diameter of 50 nm were dispersed in the solid Polywax matrix in both cases.

Conclusion

We have shown that *ortho*-metallated PIB-bound azo dyes can be used to form Pd(II) complexes that serve as precatalysts useful for catalytic carbon–carbon cross coupling reactions. Good catalyst recyclability was seen. The extent of Pd leaching was reduced significantly when polyethylene oligomers were used as a solvent in place of heptane to separate the catalyst as a solid dispersion of Pd colloidal particles in a solid polyethylene matrix. These Pd colloids were also active in allylic amination reactions when triphenyl-phosphine was added as an auxiliary ligand. By using a PIB-bound triarylphosphine as an additive in place of triphenylphosphine, the enhanced reactivity resulting from the added triarylphosphine was still observed and the Pd catalyst was recyclable through eight cycles with very low Pd leaching. The latter systems that used an added PIB-bound triarylphosphine and polyethylene oligomers in place of heptane also showed the least Pd leaching both in allylic substitutions and in cross coupling chemistry, suggesting that the use of polymeric solvents coupled with multiple polymeric ligands could be a generally useful way to further enhance the sustainability of homogeneous catalysts.

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