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Polyisobutylene-supported *N*-heterocyclic carbene palladium catalysts

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ABSTRACT

This paper describes how the nonpolar polymer polyisobutylene (PIB) can be used as a handle to prepare PIB-bound NHC ligands that are soluble in monophasic mixtures of mixed solvents but phase separable when such solvent systems are perturbed to be biphasic. The results here show that such PIB-bound NHC ligands can be used to synthesize useful palladium catalysts. In this paper, both PIB-bound analogs of an *N*,*N*′-bis(2,6-diisopropylphenyl) heterocyclic carbene and simpler *N*,*N*′-dialkyl heterocyclic carbene ligand were prepared and were successfully used to form palladium cross-coupling catalysts. The reactivity, recycling and reusability of these catalysts has been examined.

1. Introduction

Since Arduengo isolated the first stable *N*-heterocyclic carbene (NHC) in 1991 [1], NHCs have become of increasing interest in organometallic chemistry, catalysis, and materials science [2]. Their use as stabilizing ligands for highly oxidized transition metals [3] and late transition metals has been widespread [4,5]. As neutral excellent two-electron σ-donors with little π-accepting character, NHCs are a class of ligands that are often compared to phosphine ligands [6]. In 1995, Herrmann first noted the similarity between NHCs and electron-rich trialkylphosphines in metal coordination chemistry [6h]. These properties led to many other studies that demonstrated that NHC-metal complexes have reactivities similar to those of phosphine–metal complexes, often with better air and moisture stability . NHC ligands can form stable bonds with metals and phosphine–metal complexes are sometimes used as precursors for NHC-metal complexes [7,8]. These properties of NHC ligands have led to many examples of metal complexes of these electron-rich ligands, NHC ligated complexes that are often used in homogeneous catalysis using transition metals like palladium, ruthenium, rhodium, gold, copper, and nickel [2].

We were interested in using polymer-bound NHC ligands for catalyst reuse, recycling and separation. While we have already begun to explore these questions in connection with Ru-metathesis catalysts [9], we were intrigued by reports that show that NHC–Pd complexes are useful in Pd-catalyzed cross-coupling chemistry that leads to the formation of carbon–carbon and carbon–nitrogen bonds.

Many palladium catalysts have been designed for cross-coupling chemistry using phosphine ligands. However, while these catalysts can be exceptionally active, such catalysts are often sensitive to air and moisture and require air-free conditions to minimize ligand oxidation. These problems and/or catalyst instability can lead to problems in the design of recyclable catalysts [6,10,11] NHC ligated metal complexes used in this chemistry have been suggested to be more stable yet are also highly active. This has led us to explore ways to use these sorts of ligands to prepare recyclable NHC–palladium complexes. In planning this approach, we had many potential cross-coupling NHC-complexed Pd catalysts we could study [12]. These included Pd complexes with simpler *N*,*N*′-dialkyl NHC ligands or more elaborate Pd complexes prepared from sterically encumbered *N*,*N*′-diaryl NHC ligands. For example, Pd complexes with NHC ligands with alkyl groups were first described in 1995 by Herrmann who showed that the NHC–palladium complex **1** (Fig. 1) was effective as a catalyst for Heck chemistry [6(h)]. Later, palladium complexes with sterically hindered *N*-aryl substituents were designed and studied by Nolan's group. Their work showed that the Pd complex **2** (Fig. 1), (IPr)PdCl(allyl), was able to catalyze aryl animation [13,14], Suzuki-Miyaura cross-couplings [14], and α-arylation of ketones [15]. Below we describe our efforts to prepare polymeric versions of these NHC-complexed Pd catalysts and our results in attempted recycling of these catalysts in cross-coupling chemistry.

While the organometallic chemistry of NHC-metal complexes and the studies of NHC–Pd complexes in cross-coupling chemistry

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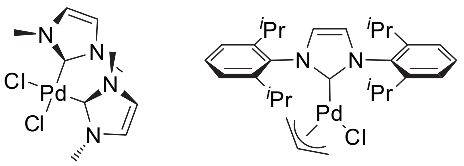


1 **2**

Fig. 1. Prior examples of NHC–Pd catalysts useful in cross-coupling chemistry.

in particular has made significant progress, strategies that facilitate separation, recovery and reuse of these catalysts have received less attention. NHC ligands and Pd catalysts have been immobilized in various ways including in ionic liquids [16a,16b], in water, and in fluorous phases [16c]. Various sorts of solid supports including polymer supports have also been used. These examples mostly used insoluble cross-linked polymers [17a–g] and nanoparticles [17h,17i]. Studies using soluble polymers have largely been restricted to the use of polar polymers like poly(ethylene glycol) [18].

The reports of immobilized NHC ligands and of their metal complexes as noted above have mainly focused on insoluble supports or always biphasic systems. An alternative approach that we have emphasized is the use of soluble polymers as catalyst supports. Polyisobutylene (PIB) is of particular interest since ligands and transition metal complexes formed with this polymer as a phase handle can partition into nonpolar solutions with products remaining in a more polar phase after catalyst recovery in a post-reaction separation step. Thus, catalysts and products can be separated by a simple biphasic liquid/liquid separation after a monophasic reaction.

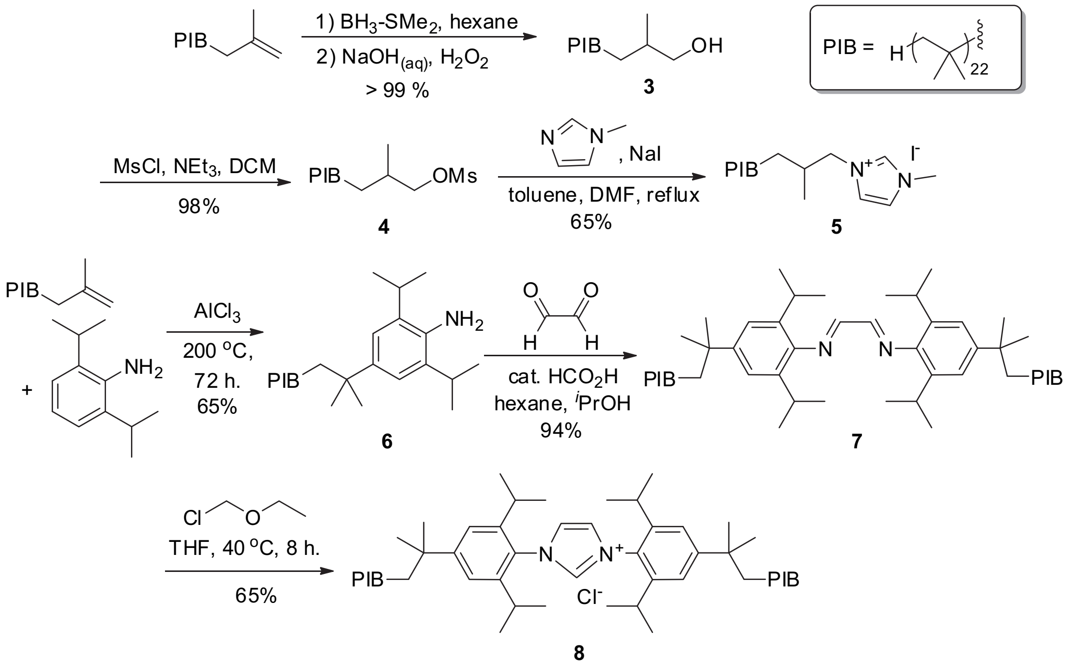
PIB oligomers are readily available commercial materials [19] that are used in various applications including as oil or fuel additives. These PIB derivatives have the advantage that they have a structurally simple and chemically inert alkane backbone. Functional groups attached to such polymers can be readily analyzed by solution state spectroscopy. For example, ^{1}H NMR spectroscopic analyses of PIB are simplified because there are only two major types of protons present on the polymer and because these protons appear in the 2.00–1.00 ppm region of the ^{1}H NMR spectrum. a region that does not obscure signals from most functional groups. The commercially available PIB derivatives used in this work have a vinyl terminus [19] that can be modified by simple chemistry to prepare many sorts of soluble polymeric reagents and ligands including PIB-bound phosphine ligands, olefin metathesis catalysts, salen catalysts, organocatalysts, Cu(I) catalysts for atom transfer radical polymerizations, azide–alkyne cyclizations, Rh(II) and Cu(I) cyclopropanation catalysts, and vinyl ether sequestring agents [9,20]. Because PIB is a noncrystalline polymer, it is soluble even at low temperatures in nonpolar and weakly polar solvents like alkanes, chlorinated alkanes, arenes, and ethers. However, it is generally not soluble in polar solvents like acetonitrile, DMF, ethanol, and water though it does dissolve in many solvent mixtures containing these solvents at elevated temperature. This phase selective solubility makes PIB and its derivatives attractive because the polymer and species attached to it can be easily separated from reaction mixtures by extraction or by a gravity based separation of an immiscible mixture of polar and nonpolar liquid phases of different density.

Previous work from our group has shown that PIB is a useful support for ligands, that ligands attached to PIB behave like their low molecular weight counterparts in metal coordination, and that such ligands are useful in catalysis [9,20]. Here we describe the synthesis of two types of imidazolium salt precursors of NHC ligands that contain PIB polymers. These heptane-soluble NHC ligands can be used to form active Pd catalysts for cross-coupling chemistry. The utility and limitations of the resulting PIB-bound NHC–Pd catalysts are described.

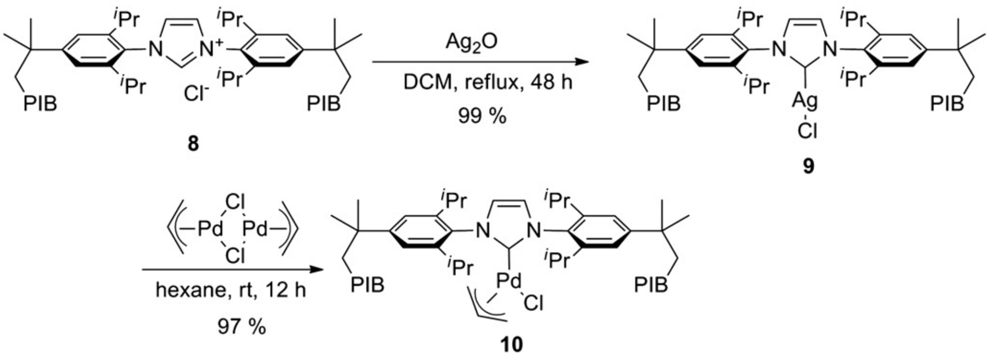
2. Results and discussion

2.1. Synthesis of PIB-bound imidazolium salts

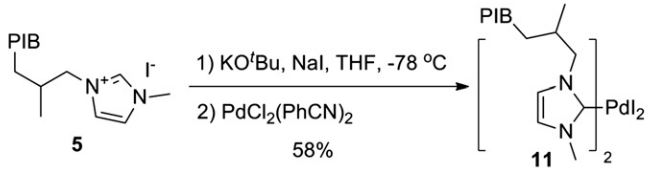
Synthesis of the PIB supported imidazolium salt **5** is straightforward and proceeds via a S_N2 reaction of an *N*-methylimidazole on an appropriately substituted PIB derivative (Scheme 1).The necessary PIB substrate was obtained by hydroboration–oxidation



Scheme 1. Synthesis of the PIB-bound imidazolium salts **5** and **8**.



Scheme 2. Synthesis of the PIB-bound (IPr)PdCl(allyl) catalyst **10**.



Scheme 3. Synthesis of the PIB-bound palladium catalyst **11**.

reaction of an alkene-terminated polyisobutylene. While the ligands herein were prepared with PIB whose average molecular weight was 1300 Da, the same chemistry works with higher molecular weight PIB derivatives. The product hydroxy-terminated polyisobutylene was then converted into a mesylate [20b]. This PIB mesylate was then allowed to react with *N*-methylimidazole in the presence of sodium iodide to form the desired imidazolium salt **5**. This product was characterized by ^{1}H and ^{13}C NMR spectroscopy. The ^{1}H NMR spectrum was diagnostic in that it contained a peak at 10.59 ppm which was assigned as the acidic proton at the 2-position of the imidazolium ring.

The synthesis of the imidazolium salt **8** followed a general procedure used in our prior work where we prepared an *N*,*N*′-bis(4-polyisobutyl-2,6-dimethyl)imidazolium chloride NHC ligand precursor [9(a)]. In this case, the initial step involved the reaction of polyisobutylene with 2,6-diisopropylaniline at 200 °C in the presence of aluminum chloride. Under these conditions, the Friedel–Crafts reaction of the alkene-terminated PIB and the 2,6-disubstituted aniline was successful leading to a 65% yield [20f] of the desired 4-polyisobutyl-2,6-diisopropylaniline. Two more synthetic steps were carried out using the chemistry described previously. This chemistry could be carried out to afford the desired imidazolium salt **8** on a two-gram scale.

2.2. PIB-bound NHC–Pd catalyst synthesis

We first opted to examine the activity, separability, and recyclability of catalyst **10**. In this case, the desired PIB-bound (IPr)PdCl(allyl) catalyst was prepared via a PIB-bound Ag–NHC intermediate **9** (Scheme 2). This silver complex was prepared in quantitative yield from **8** using silver oxide following procedures reported in our earlier work [9(a)]. The silver complex was then used in a transmetallation reaction with the allylpalladium chloride dimer to form the PIB-bound (IPr)PdCl(allyl) catalyst **10**.

A second sort of PIB-bound NHC–Pd complex was prepared by treating imidazolium salt **5** first with potassium *t*-butoxide and then with bis(benzonitrile)dichloropalladium(II) (Scheme 3). This deprotonation–metalation reaction was carried out in the presence of NaI and led to a 58% yield of the product **11**. This reaction was monitored by ^{1}H NMR spectroscopy. The disappearance of the peak at 10.59 ppm (which was assigned to the proton at the 2-position of the imidazolium ring) was followed to determine when this reaction was complete. Complex **11** was then isolated and characterized spectroscopically.

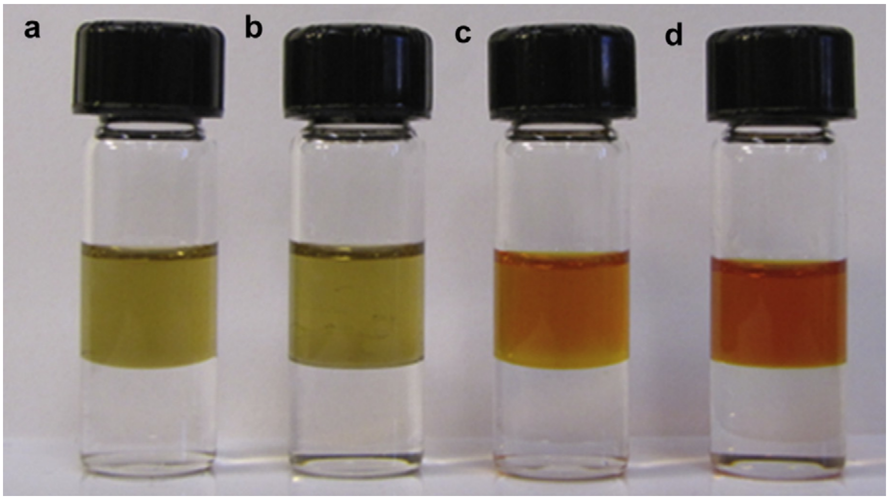
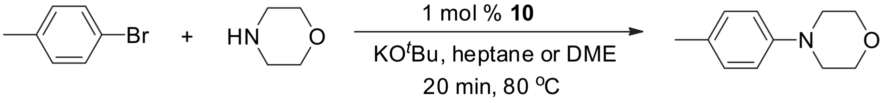
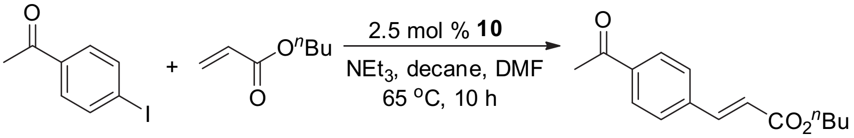


Fig. 2. The phase selective solubility of **10** and **11** in heptane vs. polar solvents at room temperature: (a) **10** in heptane vs. acetonitrile; (b) **10** in heptane vs. DMF; (c) **11** in heptane vs. acetonitrile; and (d) **11** in heptane vs. DMF.



Scheme 4. The use of the PIB-bound palladium complex **10** as a catalyst for a Buchwald–Hartwig reaction.



Scheme 5. The use of the PIB-bound palladium complex **10** as a catalyst for a Heck reaction.

2.3. Separability of PIB-bound NHC–Pd complexes

The PIB-bound NHC complexes **10** and **11** were found to be stable for up to a year when stored on a bench top and were visually phase selectively soluble in heptane versus polar solvents. This phase selective solubility is illustrated in Fig. 2. This figure shows that both **10** and **11** are phase selectively soluble in heptane versus acetonitrile or DMF.

2.4. Studies of the reactivity and recyclability of PIB-bound NHC–Pd complexes in Pd-catalyzed cross-coupling reactions

The PIB-bound catalyst **10** was first examined in a Buchwald–Hartwig aryl amination reaction (Scheme 4). With 1 mol% catalyst, 4-bromotoluene underwent complete conversion to *N*-(4-methylphenyl)morpholine within 20 min at 80 °C in heptane or 1, 2-dimethoxyethane. However, we also observed that the solution discolored during the reaction forming a dark brown solution. In the case of the heptane reaction, we separated the active catalyst by using acetonitrile to extract the reaction product from this dark brown solution. This led to a biphasic mixture of a solution of the *N*-(4-methylphenyl)morpholine product and a heptane phase that we presume contained the PIB-NHC complexed Pd catalyst. This heptane solution was successfully used in a second reaction cycle. However, complete conversion of 4-bromotoluene to the product required that the reaction time be extended to 8 h. Attempts to separate product from the catalyst phase and reuse the catalyst in a third cycle were even less successful with the reaction not proceeding to completion after 16 h at 80 °C.

We also examined the use of **10** as a catalyst for a Heck coupling reaction (Scheme 5). Recycling of **10** in this Heck reaction led to similar results as seen above for recycling **10** in amination chemistry. The coupling between 4-iodoacetophenone and *n*-butyl acrylate in the presence of Et$_3$N in the mixture of decane and DMF at 65 °C required 10 h in the first cycle. However, the catalyst reactivity decreased in a second and third cycle with complete formation of a Heck product only occurring after 36 h at 100 °C in the third cycle.

To understand why recycling of **10** was ineffective, we examined the stability of **10** under the reaction conditions. First, complex **10** was dissolved in benzene-d$_6$ and its ^{1}H NMR spectrum was measured. Then potassium *tert*-butoxide (50 equivalents) was added. After 3 h at 60 °C, the solution became brown. ^{1}H NMR spectroscopic analysis of this solution showed that the peaks in the 4.90–2.50 ppm region of **10** (which were assigned to the allylic protons of **10**) became broad. This suggested some decomposition of **10** had occurred. If an acrylate ester and an aryl iodide were added at this point, no conversion to a Heck product was seen in 10 h at 60 °C. Darkening of Pd catalyst solutions is often associated with formation of Pd colloids. To determine if this was the case, **10** was dissolved in decane and the solution was placed in capillary tubes that were examined under a microscope. In the absence of base, no discoloration and no precipitation was apparent after heating at 100 °C for 60 h. However, when another solution of **10** was prepared containing 10 equivalents of Et$_3$N, the solution formed some black precipitate after several days at room temperature or after heating at 60 °C for 1 h. Fig. 3 shows the black precipitate that was observed. We presume this precipitate is a Pd colloid. We believe this decomposition of **10** is why solutions of **10** darken and become increasingly inactive in both the Buchwald–Hartwig and Heck reactions.

Given the problems in recycling **10**, we next turned to studies using the simpler *N*,*N*′-dialkyl NHC–Pd complex **11** since this NHC–Pd complex could be recycled (cf. Fig. 2) if the catalyst formed using **11** were stable. This premise was tested by examining the use of **11** in the Heck coupling of 4-iodoacetophenone and *n*-butyl acrylate in the presence of Et$_3$N in a thermomorphic mixture of heptane and DMF at 75 °C. Recycling was examined with various catalyst loading levels. While the reactivity of the catalyst is unexceptional, the results in Scheme 6 show that recycling was successful. These recycling experiments used a thermomorphic mixture of heptane and DMF that is miscible hot but immiscible at room temperature. In this case, when the reaction mixture was cooled to room temperature, a biphasic mixture forms. In this

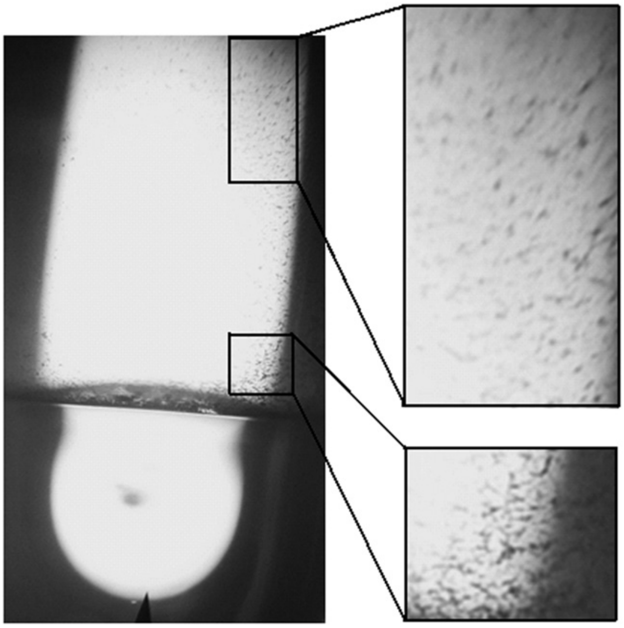
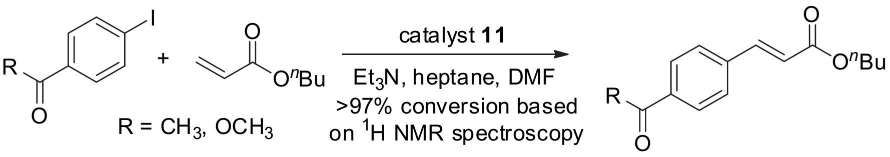


Fig. 3. Complex **10** was dissolved in decane in a capillary tube and examined microscopically after the addition of Et$_3$N and heating at 60 °C for 1 h. The black precipitate observed is believed to be palladium colloid formed in decomposition of 10.



catalyst loading	Temperature	reaction time	cycle tested
5 mol %	75 °C	14 h	10
1 mol %	75 °C	46 h	10
1 mol %	130 °C (MW)	0.5 h	6

Scheme 6. The use of **11** as a reusable catalyst for a Heck reaction.

mixture, the upper heptane-rich phase contained the PIB-bound catalyst, some DMF, and some product. No starting material was present. The lower DMF phase contained most of the product. The absence of starting material in this phase and in the upper phase allowed us to estimate that the conversion was >97%. As is true in other themomorphic systems, some extractable product remains in the catalyst-containing upper phase. While we did not demonstrate this here, prior work has shown that the product concentration in the upper phase rapidly becomes constant because the this heptane-rich phase becomes saturated in product [21]. Thus, high yields of product can be isolated from the polar phase after several cycles of such separations. Just as was done previously, we separated the lower polar product-containing phase by a gravity separation. Recycling simply involved the addition of fresh substrates, base and DMF to the heptane-rich phase. This procedure was used for 10 cycles without any change in measured conversion of substrate to product.

^{1}H NMR spectroscopy was used to determine the extent of conversion of 4-iodoacetophenone to product. We also showed that this catalyst could be used with a different aryl iodide substrate. In this experiment, methyl 4-iodobenzoate was substituted as a substrate after four cycles of a Heck coupling of *n*-butyl acrylate and 4-iodoacetophenone. The subsequent catalytic reaction led to 100% conversion of methyl 4-iodobenzoate to the expected Heck product based on ^{1}H NMR spectroscopy. We also briefly examined microwave conditions. At 130 °C in a microwave reactor, the reaction time was considerably shortened. Catalyst recycling was still equally effective. These results are summarized in Scheme 6.

While we have not tried to determine whether **11** is a precatalyst leading to an active Pd(0) catalyst or if Pd colloids are formed in these experiments using **11**, we did carry out an ICP-MS (inductively coupled mass spectroscopy) analysis of the DMF phase from a Heck coupling of 4-iodoacetophenone and *n*-butyl acrylate with 1 mol% of **11**. That analysis showed that a modest amount of metal leaching occurred with ca. 1% of the charged Pd metal loading being lost in cycle 2 and 3 and 0.2% in cycle 10.

3. Conclusion

Two imidazolium salts bound to a nonpolar solvent-soluble polymer, polyisobutylene, were prepared. On deprotonation, either can bind to palladium(II) to form NHC–Pd(II) complexes that can be phase isolated in the heptane phase of a mixture of heptane and an immiscible polar solvent. We have examined these complexes' catalytic properties and the abilities of the PIB support for recycling and reuse of these Pd catalysts. Using a PIB-bound NHC–Pd aryl amination catalyst, we were able to successfully carry out an aryl amination even with a relatively unreactive aryl bromide and were able to show that the PIB-bound allylpalladium complex **10** had activity in a heptane solution like that of its low molecular weight counterpart. However, the instability of this complex in the reaction mixture made recycling this catalyst more than two cycles problematic in aryl amination or even in reactions with very reactive Heck substrates. Catalyst recyclability was more successful with simpler PIB-bound NHC-complexed Pd catalyst **11**.

4. Experimental section

All reactions were carried out under an inert atmosphere unless otherwise noted. ^{1}H and ^{13}C NMR spectra spectra were recorded on Inova 499.9 MHz or 299.9 MHz spectrometers. Chemical shifts were reported in parts per million (δ) relative to residual proton resonances in the deuterated chloroform (CDCl$_3$). Integrations of the chemically different protons on pendant groups on PIB-bound intermediates reflect the normal accuracy associated with integration in ^{1}H NMR spectroscopy. The large signal due to the PIB protons in the 1–2 δ region of the ^{1}H NMR spectrum of these PIB-bound products can also be integrated. A typical value for the polymers we use is 180/1 since the PIB used has a M_n of ca. 1300. However, since samples of PIB vary in M_n and since the normal ca. 5–10% errors in integration are exaggerated in NMR analyses of a very large (e.g. a 180 proton signal in this case) and a very small signal (e.g. a 1 proton signal), we have not listed these integrations in the ^{1}H NMR spectra below. ICP-MS (inductively coupled mass spectroscopy) data were obtained using a Perkin Elmer DRC II instrument. Acetonitrile, heptane, DMF, ethanol, CH$_2$Cl$_2$, THF, and toluene were purchased from EMD and used as received. Polyisobutylene was a gift from BASF [19]. All other chemicals were purchased from Sigma–Aldrich and used as received.

4.1. *Hydroxy-terminated polyisobutylene (**3**)*

In a 250-mL round-bottomed flask, equipped with a magnetic stir bar and a rubber septum, the vinyl-terminated PIB (39 g, 39 mmol) was dissolved in 50 mL of hexanes. Then a 2.0 M solution of BH$_3$·SMe$_2$ (7.7 mL, 15.4 mmol) in THF was slowly added. After 18 h, the reaction mixture was cooled to 0 °C and 12 mL of a 4 N aqueous NaOH solution and 100 mL of water were added to the hydroboration product. Then 7 mL of a 30% H$_2$O$_2$ solution was slowly added and the mixture was stirred for overnight at room temperature. At this point, the two phases were separated and the organic phase was washed with H$_2$O (3 × 50 mL) and brine (50 mL), and then dried over MgSO$_4$. After filtration, the solvents were removed under reduced pressure and the product was dried under vacuum for 24 h, a total yield of 40.0 g of product was obtained. ^{1}H NMR (299.9 MHz, CDCl$_3$), δ: 3.48 (dd, J = 5.4, 10.2 Hz, 1H), 3.31 (dd, J = 7.5, 10.2 Hz, 1H), 0.75–1.46 (PIB protons).

4.2. Polyisobutyl mesylate (**4**)

In a 250-mL round-bottomed flask, equipped with a magnetic stir bar a rubber septum, the hydroxy-terminated polyisobutylene (10 g, 9.8 mmol) and methanesulfonyl chloride (2.3 mL, 29 mmol) were dissolved in 100 mL of CH_2Cl_2 and cooled to 0 °C. Then Et_3N (4.3 mL, 31 mmol) was added dropwise. The reaction mixture was allowed to stir for 3 h after warming to room temperature. The solvent was removed under reduced pressure to yield a crude viscous oil. This oil was dissolved in 300 mL of hexane and this hexane solution was washed with water (3 × 100 mL), dried over $MgSO_4$ and filtered. The solvent was removed under reduced pressure to yield 10.5 g (98%) of product. ^{1}H NMR (299.9 MHz, $CDCl_3$), δ: 4.06 (dd, $J = 5.4$, 9.3 Hz, 1H), 3.88 (dd, $J = 7.5$, 9.3 Hz, 1H), 2.96 (s, 3H), 1.95 (m, 2H), 1.39–0.88 (PIB protons).

4.3. N-Methyl-N′-polyisobutylimidazolium iodide (**5**)

In a 50-mL round-bottomed flask, equipped with a magnetic stir bar and a rubber septum, polyisobutyl mesylate (1.21 g, 1.1 mmol), *N*-methylimidazole (0.49 g, 5.9 mmol) and sodium iodide (0.32 g, 2.2 mmol) was mixed with 15 mL of toluene and 10 mL of DMF. After refluxing for 2 d, the reaction mixture was cooled to room temperature. At this point, the upper phase of the two-phase mixture that formed was separated and washed with water (3 × 50 mL) and dried over $MgSO_4$. After filtration, the solvents were removed under reduced pressure to yield a crude product which contained the excess *N*-methylimidazole and the desired product. This mixture was further purified by column chromatography (elution first with CH_2Cl_2 and then with 9:1 solution of CH_2Cl_2 and methanol) to yield 0.7 g (59%) of product. ^{1}H NMR (299.9 MHz, $CDCl_3$), δ: 10.59 (s, 1H), 7.18 (s, 2H), 4.30–4.00 (br, 5H), 2.40–0.80 (PIB protons). ^{13}C NMR (75.43 MHz, $CDCl_3$), δ: 138.10, 123.13, 121.71, multiple poorly resolved peaks between 60.00–58.00, 49.68, multiple poorly resolved peaks between 40.00–30.00.

4.4. 2,6-Diisopropyl-4-(polyisobutyl)aniline (**6**)

In a 100-mL pressure vessel, a mixture of 2,6-diisopropylaniline (23 g, 130 mmol), polyisobutylene (10 g, 10 mmol), and aluminum trichloride (4.0 g, 30 mmol) was stirred in a sand bath at 200 °C. After 3 days, the deep purple solution was cooled to approximately 100 °C and added to 200 mL of hexane. After cooling to room temperature, the mixture was filtered and washed with water (3 × 150 mL) and CH_3CN (3 × 150 mL). The solvent was removed under reduced pressure to yield a crude product which contained the desired product and unreacted starting materials. This mixture was purified by column chromatography (eluted first with hexane and then with CH_2Cl_2). Solvent removal afforded the product as a light yellow viscous liquid (7.5 g, 63% yield). ^{1}H NMR (299.9 MHz, $CDCl_3$), δ: 7.03 (s, 2H), 3.60 (s, 2H), 2.96 (m, 2H), 1.77 (s, 2H), 1.60–0.80 (PIB protons).

4.5. N,N′-Bis(2,6-diisopropyl-4-polyisobutylphenyl) ethylenediimine (**7**)

In a 100-mL round-bottomed flask, equipped with a magnetic stir bar and a rubber septum, a mixture of 2,6-diisopropyl-4-(polyisobutyl)aniline (6.6 g, 5.6 mmol) and a catalytic amount of formic acid in 20 mL of hexane was prepared. To this stirring solution, a solution of glyoxal (0.41 g of a 40% aqueous solution, 2.8 mmol) in 5 mL of isopropanol was added. The reaction mixture initially turned cloudy for roughly 5 min and then became a clear yellow solution. The reaction mixture was allowed to stir for 20 h. At this point, the bright yellow solution was dried with Na_2SO_4 and the solvent was removed under reduced pressure, affording a dark yellow viscous liquid (6.5 g, 99% yield). ^{1}H NMR (299.9 MHz, $CDCl_3$), δ: 8.10 (s, 2H), 7.17 (s, 4H), 2.97 (m, 4H), 1.83 (s, 2H), 1.60–0.80 (PIB protons). ^{13}C NMR (125.72 MHz, $CDCl_3$), δ: 163.88, 146.44, 145.55, 136.00, 121.55, multiple poorly resolved peaks between 60.00–58.00 and 40.00–30.00, 18.90.

4.6. 1,3-Bis(2,6-diisopropyl-4-(polyisobutyl)phenyl)imidazolium chloride (**8**)

In a 100-mL round-bottomed flask, equipped with a magnetic stir bar and a rubber septum, *N,N*′-bis(2,6-diisopropyl-4-polyisobutylphenyl)ethylenediimine (6.3 g, 2.6 mmol) was dissolved in 25 mL of THF. Chloromethyl ethyl ether (0.25 g, 2.6 mmol) was added and the mixture was heated to 40 °C for 20 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography (eluted first with CH_2Cl_2 and then with 9:1 solution of CH_2Cl_2 and methanol). Solvent removal afforded the product as a light brown viscous liquid (2.0 g, 31% yield). ^{1}H NMR (299.9 MHz, $CDCl_3$), δ: 8.63 (s, 1H), 8.41 (s, 2H), 7.33 (s, 4H), 2.46 (m, 4H), 1.90 (s, 6H), 1.60–0.80 (PIB protons). ^{13}C NMR (125.72 MHz, $CDCl_3$), δ: 154.44, 144.00, 137.88, 127.77, 127.22, 122.22, multiple poorly resolved peaks between 60.00–58.00 and 40.00–30.00, 18.90.

4.7. 1,3-Bis(2,6-diisopropyl-4-(polyisobutyl)phenyl)imidazo-2-ylidenesilver(I) chloride (**9**)

In a 25-mL round-bottomed flask, equipped with a magnetic stir bar and a rubber septum, 1,3-bis(2,6-diisopropyl-4-(polyisobutyl) phenyl)imidazolium chloride **8** (0.86 g, 0.40 mmol) was dissolved in 6 mL of hexane. Silver oxide (0.058 g, 0.25 mmol) was added and the mixture was fluxed for 24 h. After cooling to room temperature, the reaction mixture was filtered through celite to remove excess Ag_2O and the celite was washed with hexane. The solvent was removed from the combined hexane solution under reduced pressure, affording 0.85 g (95%) of a viscous oilproduct. ^{1}H NMR (499.9 MHz, $CDCl_3$), δ: 7.26 (s, 4H), 7.11 (s, 2H), 2.58–2.46 (m, 4H), 1.84 (s, 6H), 1.60–0.80 (PIB protons). ^{13}C NMR (125.72 MHz, $CDCl_3$), δ: 184.74 (dd, $J^{13\,107}_{\mathrm{C-\;Ag}} = 236$ Hz, $J^{13\,109}_{\mathrm{C-\;Ag}} = 271$ Hz), 152.22, 144.20, 131.88, 123.63, 122.14, multiple poorly resolved peaks between 60.00–58.00 and 40.00–30.00, 28.72, 24.84, 24.03.

4.8. (1,3-Bis(2,6-diisopropyl-4-(polyisobutyl)phenyl)imidazo-2-yliidene)(allyl)palladium(II) chloride (**10**)

To a 25-mL round-bottomed flask, equipped with a magnetic stir bar and a rubber septum was added $(allylPdCl)_2$ (12.4 mg, 0.34 mmol) along with a solution of 1,3-bis(2,6-diisopropyl-4-(polyisobutyl)phenyl)imidazol-2-ylidene silver(I) chloride **9** (0.85 g, 0.38 mmol) in 5 mL of CH_2Cl_2. After 12 h, the reaction mixture was filtered through celite and the celite was washed with hexane. The solvent was removed from the combined hexane solutions under reduced pressure to yield 0.85 g (96%) of a brown residue of product as a viscous oil. ^{1}H NMR (499.9 MHz, $CDCl_3$), δ: 7.23 (s, 4H), 7.06 (s, 2H), 4.85–4.7 (m, 1H), 3.87 (d, $J = 6.8$ Hz, 1H), 3.13–3.00 (m, 4H), 2.90–2.78 (m, 2H), 2.69 (d, $J = 13.3$ Hz, 1H), 1.84 (s, 6H), 1.75–0.7 (PIB protons). ^{13}C NMR (125.72 MHz, $CDCl_3$), δ: 186.17, 151.09, 144.94, 144.67, 133.14, 124.31, 121.69, 114.08, 72.31, multiple poorly resolved peaks between 60.00–58.00, 49.18, multiple poorly resolved peaks between 40.00–30.00, 28.51, 28.41, 26.66, 25.91, 22.97, 22.91.

4.9. Bis(N-methyl-N′-polyisobutylimidazo-2-ylidene)palladium(II) iodide (**11**)

N-Methyl-*N*′-polyisobutylimidazolium iodide **5** (0.52 g, 0.48 mmol) and sodium iodide (0.47 g, 3.1 mmol) were dissolved in 10 mL of THF in a 50-mL round-bottomed flask, equipped with a magnetic stir bar and a rubber septum. This THF solution was cooled to −78 °C and potassium *tert*-butoxide (62.3 mg, 0.55 mmol) was added. After stirring at −78 °C for 40 min, a solution of bis(benzonitrile)dichloropalladium(II) (82.4 mg, 0.22 mmol) in 3 mL of THF was added. The mixture was allowed to stir at −78 °C for 30 min and then warmed to room temperature. After stirring at room temperature for another 14 h, the solvent was removed under reduced pressure. The residue was dissolved in 20 mL of hexane and washed with 90% ethanol (3 × 15 mL). The hexane phase was concentrated and purified by column chromatography (hexane first and then CH_2Cl_2) to yield 0.35 g (58%) of an orange viscous liquid. ^{1}H NMR (299.9 MHz, $CDCl_3$): 6.88 (s, 2H), 6.85 (s, 2H), 4.6–4.3 (br, 2H), 4.3–4.1 (br, 6H), 4.1–3.9 (br, 2H), 2.8–2.4 (br, 2H), 2.0–0.80 (PIB protons).

*4.10. Aryl amination with catalyst **10** and recycling*

In a 10-mL Schlenk flask, equipped with a magnetic stir bar and a rubber septum, a mixture of 4-bromotoluene (87 mg, 0.50 mmol), morpholine (61 mg, 0.70 mmol), potassium *tert*-butoxide (84 mg, 0.75 mmol), and the catalyst **10** (13 mg, 0.005 mmol) were dissolved in 2 mL of heptane. After 20 min at 80 °C, the reaction was complete in the first cycle of an aryl amination using **10**. At this point, 3 mL of CH_3CN was added to the reaction mixture. After vigorous stirring, the mixture was allowed to settle and the two phases separated. The CH_3CN layer containing the product was removed and fresh substrates and base were added to the heptane phase to start a new catalytic cycle.

*4.11. Heck reaction with catalyst **10** and recycling*

A substrate solution containing 4-iodoacetophenone (8.19 g, 33.3 mmol) and *n*-butyl acrylate (4.86 g, 37.9 mmol) dissolved in 51.4 g of heptane-saturated DMF was prepared and added to a 10-mL Schlenk flask equipped with a magnetic stir bar and a rubber septum, that contained catalyst **10** (11 mg, 4.2 μmol) dissolved in 1 mL of decane. After addition of Et_3N (0.1 g, 1 mmol), the resulting mixture was stirred at 65 °C for 10 h. The reaction mixture was cooled to room temperature and became two phases. The bottom phase was removed using a syringe. Fresh substrate solution and Et_3N (0.05 g, 0.46 mmol) were added to the remaining heptane phase to start the second cycle and the recovered polar phase was analyzed for product by ^{1}H NMR spectroscopy.

*4.12. Heck reaction with catalyst **11** and recycling*

In a 10-mL Schlenk flask, equipped with a magnetic stir bar and a rubber septum, catalyst **11** (12 mg, 4.8 μmol) was dissolved in 1 mL of heptane. 4-Iodoacetophenone (0.123 g, 0.5 mmol), *n*-butyl acrylate (0.077 g, 0.6 mmol) and 1 mL of heptane-saturated DMF were added followed by 0.2 mL of Et_3N. The resulting mixture was stirred at 75 °C for 2 d. After cooling to room temperature, the solution became biphasic. The bottom phase was removed using a syringe. Fresh substrates and base were added to the remaining heptane solution in the flask to start the second cycle.

*4.13. Microwave-assisted Heck reaction with catalyst **11** and recycling*

The palladium catalyst **11** (29.3 mg, 11.6 μmol) was dissolved in 2 mL of heptane in a microwave reaction tube. Then 2 g of a substrate solution (prepared using 4-iodoacetophenone (8.19 g, 33.3 mmol) and *n*-butyl acrylate (4.86 g, 37.9 mmol) in 51.4 g of heptane-saturated DMF) and 0.4 mL of Et_3N were added to the solution of **11**. The reaction mixture was heated at 130 °C for 30 min in a microwave reactor. On cooling to room temperature the reaction mixture became biphasic. The two phases were separated and fresh substrate solution and Et_3N were added to the top phase to start the second cycle and the bottom polar phase was analyzed for product by ^{1}H NMR spectroscopy.

4.14. Sample digestion and sample preparation for ICP-MS analysis

All solvent was removed from the product-containing DMF-rich phase of a catalytic reaction. Then 2 mL of concentrated nitric acid was added to this residue at 25 °C and the resulting mixture was heated in a sand bath at 132 °C for 48 h. Another 2 mL of concentrated nitric acid was added and the mixture was heated at 132 °C for a further 55 h. At this point, 2 mL of concentrated sulfuric acid was added and the sample was heated at 132 °C a further 48 h. At this point, the solution was cooled to room temperature and diluted with 1% aqueous HNO_3 and the diluted solution was analyzed by ICP-MS.

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