DOI: 10.1002/adsc.200606135

Poly(norbornene)-Supported N-Heterocyclic Carbenes as Ligands in Catalysis

William J. Sommer[a] and Marcus Weck[a,*]

[a] School of Chemistry and Biochemistry, Georgia Institute of Technology, 770 State Street, Atlanta, GA 30332-0400, USA
Fax: (+1)-404-894-7452; e-mail: marcus.weck@chemistry.gatech.edu

Received: March 24, 2006; Revised: June 18, 2006; Accepted: July 13, 2006

Abstract: In this contribution, we present the synthesis of norbornene-supported N-heterocyclic (NHC) carbenes. These functionalized norbornenes were polymerized *via* ring-opening metathesis polymerization in a controlled fashion either before or after metalation with a variety of palladium and ruthenium precursors resulting in the formation of polymer-supported NHC-based metal catalysts. The activities of the palladium-based catalysts in the Suzuki–Miyaura, Sonogashira and Heck coupling reactions were studied in detail. In all cases, the polymeric catalysts demonstrated the same activity as their small molecule analogues. Furthermore, we carried out preliminary investigations into the stability of these catalysts using poisoning studies. A clear dependence of the stability of the polymer-supported catalysts on their palladium precursor was observed with palladium acetate-based polymeric NHC catalysts being the most stable. Finally, we have studied the reactivity of our supported NHC ruthenium complexes as catalysts for ring-closing metathesis. Again, in all cases good conversions were observed with comparable activities to other supported NHC-ruthenium catalysts. Lastly, we were able to remove the ruthenium catalysts from the solution quantitatively demonstrating the possibility of metal removal.

Keywords: catalysis; coupling; N-heterocyclic carbene; palladium; polymer

Introduction

Transition metal-based catalysis has been a corner stone for the synthesis of specialty chemicals for diverse applications ranging from materials to pharmaceuticals.[1–3] The design of transition metal catalysts has to take into account several basic characteristics including high efficiencies and selectivities as well as economic and environmental considerations. An important prerequisite for the commercialization of most metal-containing catalysts in the pharmaceutical and fine chemical industries is the easy removal of any metal species from the product as well as, in some cases, the recyclability of these generally expensive metal-containing catalysts. One strategy to achieve these goals is the use of supported catalysts.[4]

Highly desirable would be to support a versatile ligand that has been employed extensively in catalysis and can be metalated with a wide variety of metal precursor thereby allowing for the formation of a library of catalysts for diverse applications. Moving towards this goal, we report the synthesis of norbornene-based monomers containing N-heterocyclic carbenes (NHC). These monomers can be metalated before or after polymerization with either ruthenium or palladium sources resulting in the formation of well-defined polymer-supported catalysts for a variety of transformations ranging from carbon-carbon bond formations such as the Heck reaction or the Suzuki–Miyaura coupling to ring-closing metathesis (RCM).[5,6] The use of these soluble polymer-supported catalysts in the carbon-carbon bond forming transformations resulted in comparable activities and selectivities to their small molecule analogues.[7–13] Furthermore, through the use of a highly controlled polymerization technique, ring-opening metathesis polymerization (ROMP),[14–19] we are able to tune the solubility of the catalysts as well as the metal loading *via* the formation of copolymers. This is the first reported supported NHC carbene system where the metal type as well as the metal loading along the support can be tuned in a systematic manner.

Stable N-heterocyclic carbenes, first synthesized by Arduengo, have been studied extensively over the past decade.[6,20–24] This class of ligands has several advantages over the closely related phosphine ligands including their increased stability to high temperatures and air.[6,24–29] Over the past decade, metal complexes containing NHC ligands have been utilized as catalysts for a variety of transformations.[6,9,10,16] The

majority of reports employ NHC-containing ruthenium complexes as catalysts in olefin metathesis, with RCM attracting the most attention.[7,16,20,30–33] Ruthenium-based olefin metathesis catalysts containing NHC ligands have the highest activities reported to date.[16,31] Furthermore, they are able to catalyze RCM reactions of sterically demanding compounds and are tolerant to a wide variety of functional groups resulting in the transformation of adducts that were unreactive to earlier olefin metathesis catalysts.[5,16]

The second carbon-carbon bond forming reaction using NHC ligands is based on palladium complexes that are able to catalyze coupling reactions such as the Heck or the Suzuki–Miyaura coupling reaction.[34–38] The NHC ligands in these palladium catalysts are outstanding σ-donors facilitating the oxidative reactions of aryl halides to the palladium center.[6,39–41] Furthermore, these catalysts do not require the addition of excess ligand during the reaction. Finally, the NHC ligands enhance the elimination of the final product from the palladium center as a result of their bulky nature.[6,11,23,29,42,43]

The above described versatility, stability and unique catalytic properties of NHC-containing transition metal catalysts make them interesting candidates for supported catalysis. Over the past five years, NHCs have been grafted onto different supports ranging from mesoporous silica to soluble poly(styrene)s.[44–53] While often successful, metal leaching and low metal loadings remain a major shortcoming for most supported catalysts. In particular the use of a soluble polymer support to immobilize N-heterocyclic carbene metal complexes has often been limited to one catalytic moiety per polymer chain.[50,54–57] One exception to this is the work by Buchmeiser et al., whose group reported the functionalization of insoluble monolithic polymer discs with a variety of ruthenium catalysts using elegant post-polymerization functionalizations.[58] In this contribution, we report the synthesis of supported NHCs using poly(norbornene) as soluble polymer support. Poly(norbornene) supports have the unique advantage that a) the support is often soluble during the catalytic reaction but can be removed from the reaction media and reused by simple precipitation methods, b) poly(norbornene)s can be synthesized *via* ROMP, a highly controlled, functional group-tolerant and often living polymerization method that allows for the formation of controlled architectures such as random and block copolymers thereby allowing us to control catalyst density,[14–19] and c) as a result of its functional group tolerance, ROMP can be carried out on fully functional and characterized monomers thereby eliminating low-yielding post-polymerization reactions.[59–63]

Results and Discussion

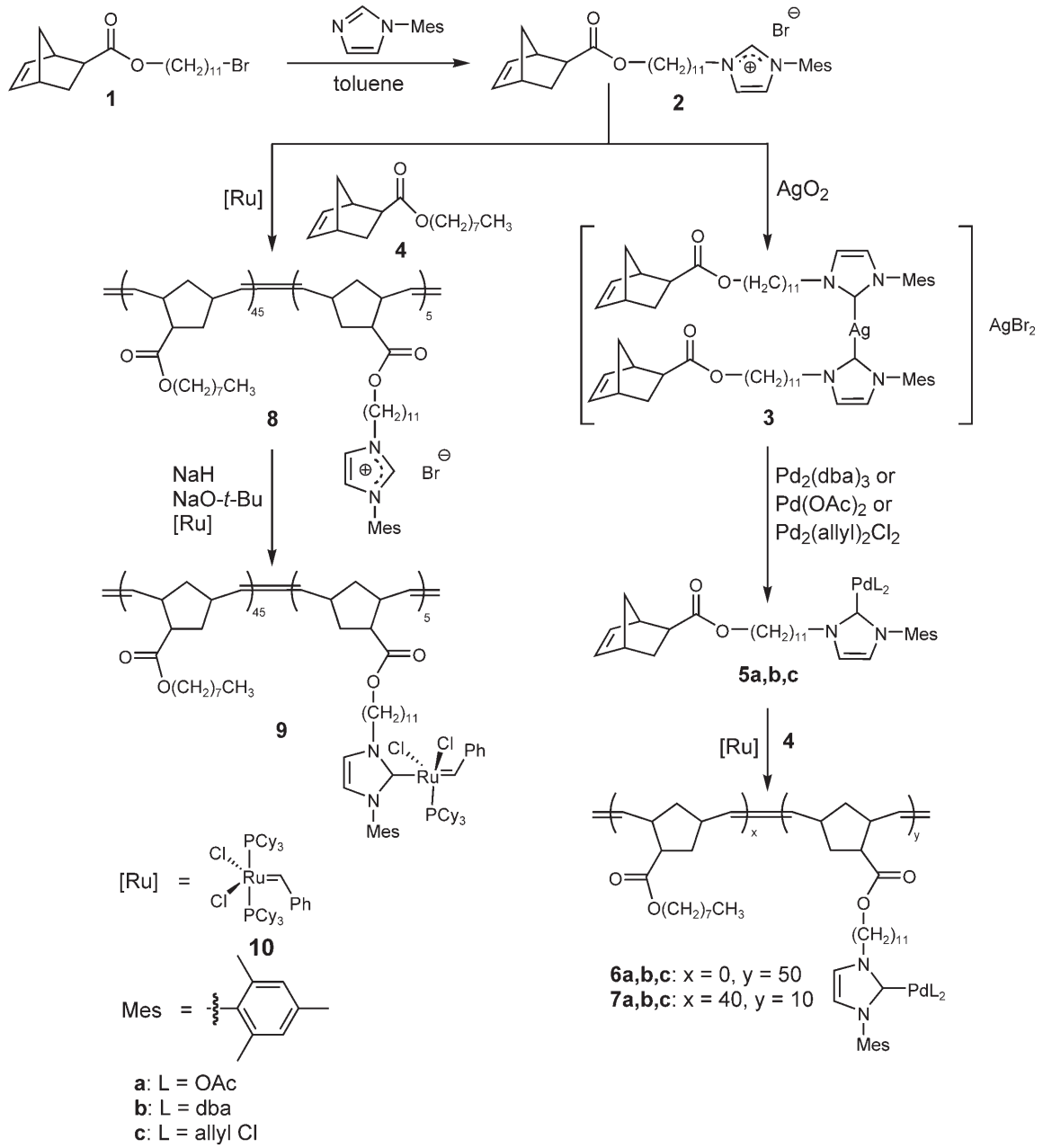
To demonstrate the versatility of our strategy to prepare supported catalysts, we investigated the catalytic activity of our novel polymer-supported catalysts in i) the Suzuki–Miyaura coupling of a library of aryl halides with phenylboronic acid, ii) the Sonogashira coupling of ethynyl(trimethyl)silane or 1-phenyl(trimethylsilyl)acetylene with bromobenzenes, iii) the Heck reaction of *n*-butyl acrylate with benzyl halides and iv) the ring-closing metathesis of diethyl diallylmalonate.

The synthesis of the four supported catalysts (Scheme 1) commences with the formation of **2** that was synthesized by reacting **1** with *N*-mesitylimidazole. The poly(norbornene)-supported Pd-NHC catalysts (**6** and **7**) were synthesized by treating **2** with silver oxide yielding **3**, followed by the addition of either $Pd(OAc)_2$, Pd_2dba_3, or $Pd_2allyl_2chloride_2$ to yield **5a–c**. Monomers **5a–c** and **4** were then co-polymerized in ratios of 1:4 and 1:0, respectively, using the first generation Grubbs catalyst **10** to yield copolymers **6a–c** and **7a–c**, respectively. For the synthesis of the poly(norbornene)-supported catalyst **9**, **2** and **4** were co-polymerized in ratios of 1:9 with **10**. A ruthenium monomer precursor for **9** could not be synthesized since this monomer would be polymerize *via* ROMP during the metallation step.

All catalytic reactions (Scheme 2) were carried out under inert atmospheres using screw-cap vials and were repeated at least three times. The products were characterized by GC-MS and ^1H and ^{13}C NMR spectroscopy.

First, we investigated the activity of our palladium-supported catalysts in the Suzuki–Miyaura transformation. The Suzuki–Miyaura transformation is an important tool for the synthesis of complex molecules with applications ranging from supramolecular chemistry[64] to natural product synthesis.[65,66] To evaluate the generality of our supported catalysts, aryl chlorides with electron-donating or electron-withdrawing groups as well as sterically hindered aryl chlorides were employed as reactants and coupled to aromatic phenylboronic acid derivatives. We carried out the Suzuki–Miyaura coupling reactions with all six different supported palladium catalysts (**6a–c** and **7a–c**) using a variety of reaction conditions to evaluate the different catalysts and to optimize reaction conditions.

The first system investigated consisted of a mixture of Pd_2dba_3 and **8**, with the carbene and ultimately the catalyst generated *in situ*. Cs_2CO_3 was used as the base and the reaction was carried out in dioxane at 80 °C using 4-chlorotoluene and phenylboronic acid as reactants. For all substrates, the Suzuki–Miyaura catalysis was complete within three hours with above 85 % of products isolated for all transformations,

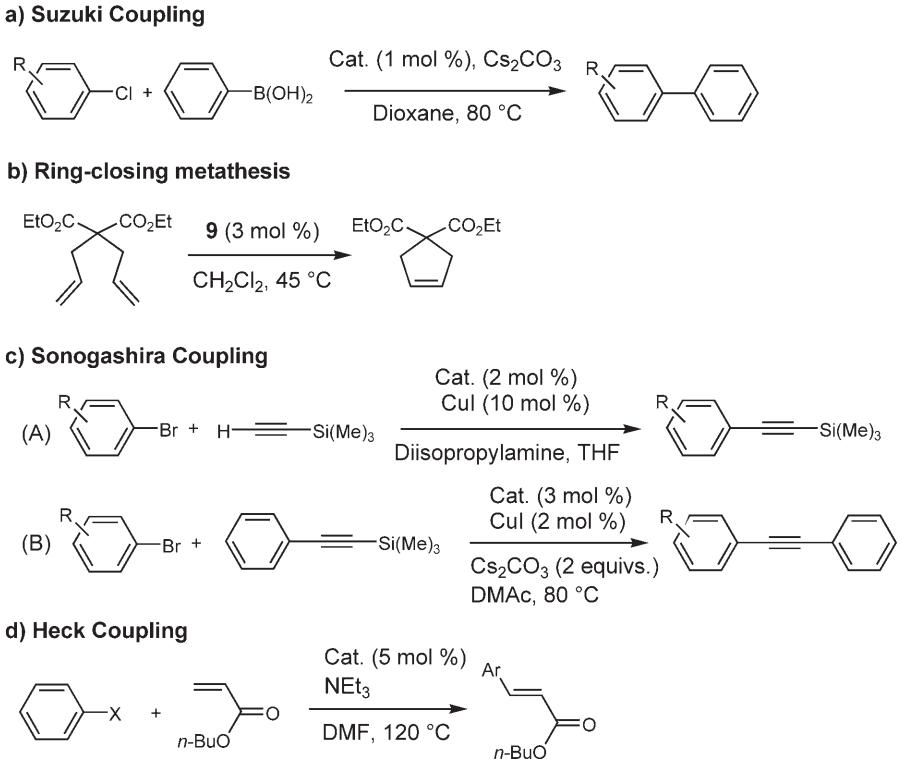


Scheme 1. Synthesis of the polymer-supported NHC-based catalysts **6**, **7** and **9** utilized in this study.

demonstrating the catalytic activity of our *in situ* generated catalyst. Control experiments using the same reaction conditions in the absence of either the palladium precursor or **8** did not result in the formation of any product.

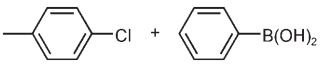
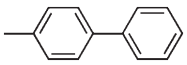
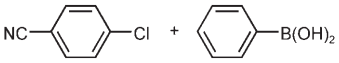
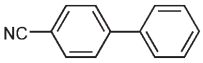
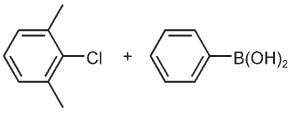
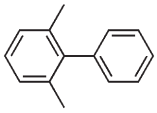
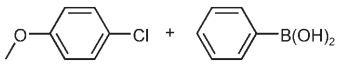
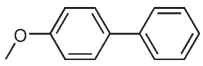
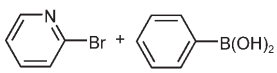
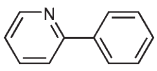
The second Suzuki–Miyaura system studied employed the fully palladated and characterized polymers **6** and **7**. We investigated these supported catalysts in the coupling of phenylboronic acid to a small library of chloroaryl compounds. The chloroaryl compounds were chosen to investigate the influence of electron-donating/withdrawing groups as well as bulky substrates on the catalytic activity of **6** and **7**. Initially, potassium *tert*-butoxide was used as the base and isopropyl alcohol as the solvent. When the reactions were carried out at room temperature, 70% conversions were observed after 24 h. Switching to cesium carbonate as the base and dioxane as the solvent and increasing the reaction temperature to 80 °C allowed us to optimize the isolated yields. The catalytic results of the reactions under these conditions are outlined in Table 1. For all substrates, isolated yields of 80–99%, with the vast majority of reactions giving above 90%, were obtained within hours.

The different functional groups on the phenyl chlorides affect the conversions only slightly. Substrates



Scheme 2. The catalytic reactions that have been employed to evaluate catalysts **6**, **7** and **9**.

Table 1. Catalytic results for the Suzuki–Miyaura coupling reaction.

Entry	Substrates	Product	Catalyst	Time [min]	Yield [%]
1			**6a**	30	99
			6b	30	97
			6c	30	99
			7a	45	99
			7b	45	94
			7c	45	97
2			**6a**	30	100
			6b	30	99
			6c	30	99
			7a	30	95
			7b	30	97
			7c	30	98
3			**6a**	130	93
			6b	130	88
			6c	130	84
			7a	130	90
			7b	130	88
			7c	130	81
4			**6a**	120	92
			6b	120	88
			6c	120	85
			7a	120	92
			7b	120	86
			7c	120	85
5			**6b**	180	84

containing electron-withdrawing groups such as CN react slightly faster. In contrast, electron-donating groups such as methoxy on the substrates slow down the conversions. Nevertheless, even with substrates containing electron-donating groups, quantitative reactions were still obtained within two to three hours. The sterically bulky substrates such as dimethylbromobenzene slowed down the reaction and quantitative conversions could not be obtained with any of the catalytic species.

Reactions using copolymers **7** yielded very similar results to the homopolymers suggesting that the spacing of the metal complex does not affect its activity. Overall the different polymer-supported catalysts showed very similar conversions compared to their small molecule analogues with catalysts **6a** and **6b** being the most active ones.

To investigate our catalytic system further, we performed kinetic studies on the most active polymer supported catalyst, **6a**, using chlorotoluene and phenylboronic acid as substrates. Samples of the reaction mixtures were taken every five minutes until complete conversion. The kinetic data are outlined in Figure 1. The data clearly show that no induction period is present.

Over the past two years, a variety of supported palladium catalysts have been shown to leach palladium

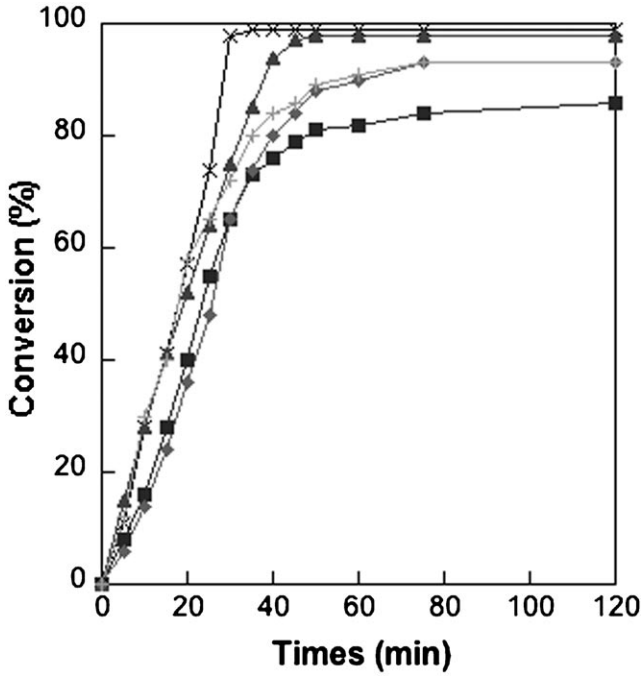


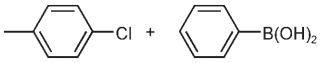
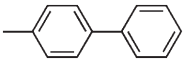
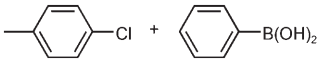
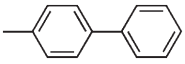
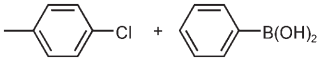
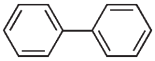
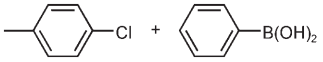
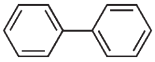
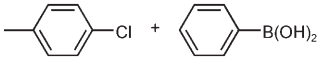
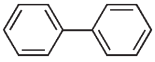
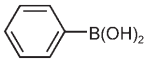
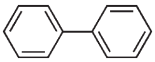
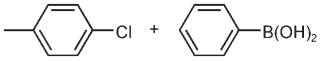
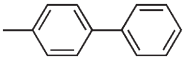
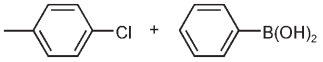
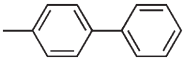
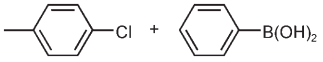
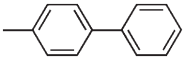
Figure 1. Kinetic study for **a**) the Suzuki–Miyaura reaction with **6a** (×), **b**) the Sonogashira reaction with **6a** (▲), **c**) the Suzuki–Miyaura reaction with **6a** in the presence of QuadraPure® (■), **d**) the Sonogashira reaction with **6a** in the presence of QuadraPure® (◆), and **e**) the Suzuki–Miyaura reaction with **6a** with the addition of QuadraPure® after 20 min (+).

during the catalysis.[48,61–63,67,68] We and others have shown for several of these cases that the supported palladium species do not catalyze any carbon-carbon bond formations but that the leached palladium species are the sole catalytically active species.[61–63,67] To identify if the same restrictions are true for our poly(norbornene)-supported NHC palladium complexes, we investigated whether or not palladium leaches during the reaction and if the polymer-supported species are active during the catalysis. To identify the nature of the catalytic species, we employed three catalyst poisons: a) highly cross-linked insoluble poly(vinylpyridine) (PVPy), b) Quadra-Pure®, a microporous resin metal scavenger that is especially sensitive to palladium, and c) mercury(0).[61–63] PVPy is known to interact only with molecular palladium(0) by coordinating to the metal center thereby removing the palladium from the reaction phase into the solid phase while Hg(0) has been reported to interact mainly with palladium nanoparticles by amalgamating the Pd particles thereby creating a catalytically inactive Hg/Pd amalgamate.[61–63,69–71] For both poisons, leached palladium species are the only metal species affected, *that is,* if the catalysis is due to a leached Pd(0) species, both poisons will shut down any catalytic activity. In contrast, ligand-protected Pd(0) species such as our supported NHC palladium complexes are untouched by both poisons and catalysis should be possible.[62]

We carried out leaching test for the Suzuki couplings using the same reaction conditions as outlined above. When carrying out the PVPy poisoning test (a ratio of 1:500 of Pd to PVPy was used) using catalyst **6a**, we observed a decrease in activity with only 15% conversions after 24 h (Table 2, Entry 1). Nevertheless, the catalyst stayed active during the whole experiment. To test if this decrease was due to palladium leaching off the supported NHC ligands or due to the lack of accessibility of the reactants to the catalyst sites, we carried out the same reaction using cross-linked poly(styrene) ($M_W = 25{,}000$). Poly(styrene) is not able to coordinate to leached palladium and should therefore not inhibit the catalysis from any leached metal species. When carrying out the catalysis in the presence of 500 equivalents of poly(styrene) for each catalytic moiety, we observed again a dramatic drop in catalyst activity with a conversion of approximately 15% after 24 h (Table 2, Entry 2), *that is,* the same drop in activity was observed as described above for the poly(vinylpyridine) poisoning experiment. This result suggests that the reduced activity in the poly(vinylpyridine) leaching test is most likely not due to metal leaching during the catalysis but reduced accessibility of the active sites in this case.

When carrying out the mercury test with our polymer-supported palladium NHC catalyst **6a**, we observed 90% conversions of the phenylboronic acid to the corresponding biphenyl, the homocoupling prod-

Table 2. Leaching tests results.

Entry	Substrates	Products	Catalyst	Poison	Yield [%]
1			**6a**	PVPy (500 mol%)	<15
2			**6a**	Poly(styrene) (500 mol%)	<15
3			**6a**	Mercury (500 mol%)	95
4			None	Mercury (500 mol%)	0
5			Pd(0)	Mercury (500 mol%)	0
6			**6a**	Mercury (500 mol%)	98
7			**6a**	QuadraPure® (2 equivs.)	89
8			**6b**	QuadraPure® (2 equivs.)	79
9			**6c**	QuadraPure® (2 equivs.)	0

uct (Table 2, Entry 3). To investigate this unexpected result we carried out a series of control experiments. First, we carried out the reaction without the supported palladium complex, *that is,* only the reactants and the mercury (Table 2, Entry 4) were added to the reaction flask. No conversions were observed. When using a non-supported Pd(0) source as catalyst, either Pd on carbon or Pd_2dba_3, and mercury (Table 2, Entry 5) we again observed no conversions. This proves that Pd(0) metal is not active in the presence of mercury. In the literature a variety of reductants including mercury(0) are described to catalyze the homocouplings of arylboronic acids as well as aryl iodides or bromides.[72–75] To investigate if the mercury acts as a reductant in our poisoning tests, we carried out the catalytic reaction without the addition of chlorotoluene, *that is,* only phenylboronic acid, the supported catalyst and mercury were present during the reaction. This experiment resulted in 95% conversion (Table 2, Entry 6) of the phenylboronic acid to the corresponding biphenyl. These results suggest that the mercury acts as a reductant in our poisoning tests but also that the supported palladium catalyst seems to be stable during the poisoning test and that no palladium leaches out. If leaching would have occurred and the catalysis (homocoupling) would have been due to a leached Pd species, the Hg should have amalgamized the leached Pd species resulting in no catalysis. Based on the PVPy and Hg(0) poisoning tests, no definite conclusions can be drawn regarding the stability and the potential palladium leaching of the polymer-supported catalyst **6a**. Following these results no further PVPy or Hg(0) leaching tests were carried out on any other supported catalysts **6b**, **c** or **7a–c**.

The next leaching tests that were carried out used QuadraPure® to trap leached palladium. QuadraPure® is a microporous resin that scavenges different metals and is especially efficient for trapping palladium.[76] When carrying out the Suzuki–Miyaura coupling reaction in the presence of QuadraPure®, 89% and 79% conversions were observed after 120 min (in comparison, the reactions without the addition of QuadraPure® gave 99% yields after 30 min) with **6a** and **6b**, respectively, while no conversions were obtained when using **6c** as catalyst. Kinetic studies using **6a** and QuadraPure® (Figure 1 squares and crosses) showed that the presence of QuadraPure® slows the reaction but does not inhibit conversion. The conversion obtained was 86% within 75 min. The presence of QuadraPure® slowed down the conversion but the kinetic curve looks very similar to the one without the poison present. By comparing the kinetic data with and without QuadraPure® present during the catalysis, one can clearly see that the poison, while slowing down the catalysis, does not prevent the catalytic transformation, suggesting that the active species for the catalysis is, at least in part, the polymer-supported palladium complex.

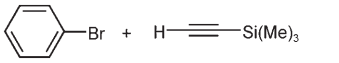
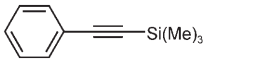
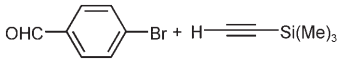
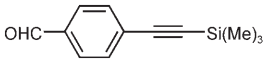
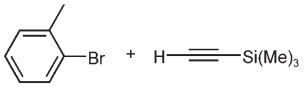
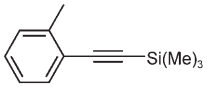
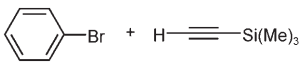
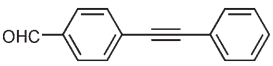
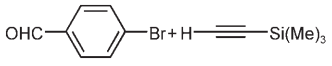
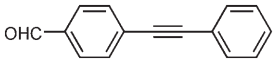
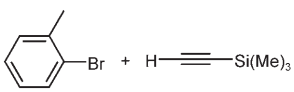
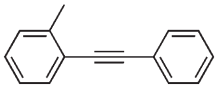
In summary, the poisoning studies show that **6c** leaches under the Suzuki–Miyaura reaction conditions and that the metal complex **6c** alone might not be a catalytically active species. More likely, the catalytic species is a leached palladium species off **6c** whereby **6c** serves only as a palladium reservoir. In contrast,

our studies suggest that the metal complexes supported on **6a** and **b** are catalytically active. While our leaching studies cannot exclude small amounts of leached species for **6a** and **b**, they show that QuadraPure® does not shut down the catalysis, proving that both polymers are catalytically active species in the Suzuki–Miyaura coupling.

We also carried out a recycling experiment for the Suzuki–Miyaura coupling of chlorobenzene with phenylboronic acid using similar conditions as described above. After complete reaction (confirmed by GC), the reactants and products were distilled off and the resulting polymeric residue dried. The polymeric residue was then reused for the same catalytic transformation using exactly the same reaction conditions. The polymer became less soluble after the first cycle yielding 80% conversions after 90 min. Following the same isolation procedure after the second cycle, the polymer became only slightly soluble in DMF for the third reuse and yielded only 44% conversions after 90 min. We have observed the same solubility problems with other poly(norbornene)-based catalyst supports.[77] To investigate if any changes of the polymer backbone during or after catalysis are the reason for this reduced solubility, we carried out a series of *in situ* ^{1}H and ^{13}C NMR experiments. The Suzuki–Miyaura transformation of phenylboronic acid with chlorotoluene was chosen for the *in situ* NMR studies. A preliminary spectrum of **6b** was taken in deuterated DMF at 85 °C. The reagents were then added using a catalyst loading of 50 mol% and a cesium carbonate loading of 150 mol%. The reaction was carried out for 24 h and monitored *via* NMR. No sign of polymer backbone degradation was noticed, *that is,* no changes in the olefin signals were observed which would be a sign of backbone degradation. The polymer was then recovered through precipitation into cold methanol and redissolved in DMF. A ^{1}H NMR was taken. Again, no sign of polymer degradation was noticed. While we cannot exclude a small percentage of backbone degradation or cross-linking, these studies demonstrate that the polymer backbone does not decompose significantly during the catalysis and/or the work-up. However, a weak coordination of leached metal species onto the polymer resulting in metal-based cross-linking cannot be detected with this method.

To expand the scope of our catalysts, we investigated the Sonogashira coupling using the most active polymeric catalysts **6a** (Table 3). Because of the importance of alkyne functionalities for a wide range of natural compounds as well as in the synthesis of highly conducting materials,[78–82] the Sonogashira reaction between an alkyl halide and a terminal alkyne is the method of choice to incorporate alkyne functionalities in aromatic systems. The reaction was developed in 1975 by Sonogashira using a mixture of palladium and copper iodide as the catalyst and has been improved steadily over the past 30 years.[83–86] In this work, we investigate two types of Sonogashira reactions. The first one consisted of the coupling of a silyl-terminated acetylene to an aryl bromide. As reactants, we employed a silane-protected acetylene and a small library of aryl bromides. Diisopropylamine (ten equivalents) was used as the base and tetrahydrofuran as the solvent. The base, solvent and CuI (10 mol%) were added to the reaction vessel at room temperature. When subjected to these conditions, all aryl halides were converted to the corresponding products in 83–100% isolated yields in 120–150 min (Table 3). As expected, the reaction using bromobenzaldehyde as reactant was the fastest with 100% conversions in 120 min. The more sterically hindered 2-bromotoluene reacted in 83% conversion within

Table 3. Catalytic results for the Sonogashira coupling reaction.

Entry	Substrates	Products	Catalyst	Time [min]	Yield [%]
1			**6a**	150	100
2			**6a**	120	100
3			**6a**	150	83
4			**6a**	45	96
5			**6a**	25	99
6			**6a**	60	95

150 min compared to the non-hindered bromobenzene which had quantitative conversion within the same time.

The second Sonogashira reaction consisted of the *in situ* deprotection of a silane-protected acetylene and the coupling of the resulting acetylene with a different aryl bromide.[13] Cesium carbonate (two equivalents) which was employed as the base and deprotection agent, dimethylacetamide (DMAc), and CuI (2 mol%) were added to a screw-cap vial and stirred at 80°C. Similar yields but faster reaction rates compared to method A were obtained. The 4-bromobenzaldehyde showed quantitative conversions within 25 min while the bromobenzene and the 2-bromotoluene had 96% and 95% conversions within 45 and 60 min respectively. These results compare favorably with those reported by Nolan et al. using the small molecule analogue to **6a**.[13]

To verify the robustness of our catalysts in the Sonogashira coupling reactions, leaching tests were carried out using **6a** and QuadraPure® as the poison. We employed benzyl bromide and silane-protected acetylene as reactants, CuI (10 mol%), diisopropylamine (ten equivalents) as the base and THF as the solvent. After 24 h, 100% conversions were observed. The second Sonogashira reaction tested consisted of bromobenzene and trimethyl(phenylethynyl)silane as reactants, cesium carbonate (2 equivalents) as the base, CuI (2 mol%) and dimethylacetamide. Again, the reaction yielded 100% conversions after 24 h. To determine the activity of **6a** in the presence of QuadraPure® in more detail, we carried out kinetic studies with and without the poison. The results are shown in Figure 1. As was the case for the Suzuki coupling poisoning studies, the Sonogashira reaction slows down slightly in the presence of QuadraPure®. The transformation takes 35 min to reach 80% conversions without the poison while in the presence of the poison the same conversions are obtained after 50 min. Therefore, in analogy to the Suzuki studies outlined above, the Sonogashira poisoning studies demonstrate the stability of our catalyst under Sonogashira reaction and suggest that the active species for the catalysis is at least partially the polymer-tethered palladium complex.

The third palladium-catalyzed transformation studied was the Heck coupling reaction. This reaction has been widely studied since its first report in the early 1970s.[87,88] Again, we employed our best catalyst, **6a** (2 mol%), for all studies. We used triethylamine (two equivalents) as the base and iodobenzene (one equivalent) and *n*-butyl acrylate (1.5 equivalents) as substrates. At 120°C, the catalysis proceeded in 30 min with 99% conversions. However, after the reaction, some palladium black was observed at the bottom of the flask indicating leaching of palladium from the complex. As these results clearly showed metal leaching, we wanted to investigate if the polymer-supported catalyst is catalytically active or if all activity stems from the leached palladium species. We carried out a Heck catalysis experiment in the presence of the QuadraPure® poison. The reaction conditions were: iodobenzene and *n*-butyl acrylate as reactants, triethylamine (two equivalents) as the base and DMF as the solvent. The reaction yielded 44% conversions after 24 h. While this result is inconclusive, the observed palladium black formation during the catalysis in combination with the lower conversions suggests that the vast majority of catalytic activity stems from leached palladium species and not from **6a**.

The second metal that was supported on our poly(norbornene) NHC polymers was ruthenium. The resulting polymer-supported ruthenium complex (**9**) was investigated as active catalysts for olefin metathesis, in particular ring-closing metathesis (RCM).[89] To study the activity of these supported catalysts, the RCM of diethyl diallylmalonate in dichloromethane at 45°C was investigated.[45,90,91] Under these reaction conditions, diethyl diallylmalonate was converted in 95% yield to its corresponding RCM product, cyclopent-3-ene-1,1-dicarboxylic acid diethyl ester, within 20 min using 5.0 mol% of **9** (Table 1, Entry 15). This activity is comparable to other supported Grubbs catalyst analogues of **10** that convert diethyl diallylmalonate using similar catalyst loadings with the same conversions in the same time frame,[45,90,91] demonstrating that our supported catalyst is an active olefin metathesis catalyst.

The polymeric catalyst **9** can be removed from the reaction mixture after complete catalysis using basic precipitation methods into cold methanol. To elucidate whether any ruthenium leached into the reaction solution and if the polymeric catalysts can be removed quantitatively, we carried out elemental analyses (ICP) of the reaction solutions after the removal of the polymeric catalysts. The elemental analyses showed no traces of ruthenium in the reaction solution demonstrating the quantitative recovery of the polymer and thereby the quantitative removal of the metal species from the reaction mixture. Blechert and co-workers using poly(oxanorbornene) as a support, reported similar results using a Grubbs-Hoveyda catalyst.[92]

Conclusions

In this contribution, we have reported the synthesis of a new class of polymer-supported N-heterocyclic carbene ligands, their metallation, before and after polymerization, and their use as supported catalysts for a variety of carbon-carbon bond formations. We demonstrated the versatility of our supported catalysts by investigating the catalytic activity of all complexes in

a wide array of reactions ranging from RCM to Suzuki couplings. For all transformations studied, our catalysts show high activities that are comparable to their small molecule analogues. We have shown by using poisoning studies that the stability of our palladium-based polymeric catalysts depends on the ligands around the palladium center. While for the polymer-supported palladium acetate-based NHC complexes the catalytic activity in the Suzuki and Sonogashira couplings stems mainly from the polymer-tethered complexes, palladium dba-based NHC complexes decompose under these reaction conditions. Finally, for the ring-closing metathesis we demonstrated the ability to remove the polymeric catalysts from the reaction mixture thereby ensuring the removal of any undesirable metal species from the product obviating extensive purification steps.

Experimental Section

General Experimental Conditions

All reactions with air- and moisture-sensitive compounds were carried out under a dry nitrogen/argon atmosphere using an MBraun UniLab 2000 dry box and/or standard Schlenk line techniques. THF, CH_2Cl_2, toluene, 1,4-dioxane and hexanes were distilled from sodium and benzophenone. Benzyl alcohol and methyl acetate were distilled from calcium hydride. $Pd(OAc)_2$, first generation Grubbs catalyst, and all bases were obtained from commercial sources and generally used without further purification. The syntheses of mesitylimidazole and **1** were carried out following published procedures.[93,94] Gas-chromatographic analyses were performed on a Hewlett Packard G1800 A GCD system GC-MS. ^1H (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Varian Mercury VX instrument. All spectra were referenced to residual proton solvent. Mass spectral analyses were provided by the Georgia Tech Mass Spectrometry Facility using a VG-70 se spectrometer. Gel-permeation chromatography (GPC) analyses were carried out using a Waters 1525 binary pump coupled to a Waters 2414 refractive index detector. The GPC was calibrated using poly(styrene) standards on a Styragel® HR 4 and HR 5E column set with CH_2Cl_2 as an eluent. All GPC experiments were carried out with a flow rate of 1 mL min^{-1}. Elemental analyses were carried out by either Atlantic Microlabs, Norcross GA (CHN analyses) or Galbraith Laboratories, Inc., TN (determination of the metal content).

Synthesis of *exo*-1-{11-(Bicyclo[2.2.1]hept-5-ene-2-carbonyloxy)undecyl}-3-(2,4,6-trimethylphenyl)-3*H*-imidazol-1-ium (2)

In a round-bottom flask equipped with a condenser, *N*-mesitylimidazole (950 mg, 5.1 mmol), **1** (1.9 g, 5.1 mmol) and toluene (50 mL) were combined. The reaction mixture was refluxed for 72 h. The solvent was removed yielding a brown oil which was purified using column chromatography (eluent: 1:20→1:1 ethanol:hexanes) to afford a yellow oil; yield: 1.6 g (68%). ^1H NMR ($CDCl_3$): $\delta = 10.57$ (s, 1H), 7.47 (s, 1H), 7.12 (s, 1H), 6.99 (s, 2H), 6.10 (m, 2H), 4.07 (t, $J = 6.6$ Hz, 2H), 3.03 (m, 1H), 2.33 (s, 5H), 2.07 (s, 9H), 1.91 (m, 1H), 1.75–1.58 (m, 5H), 1.54 (m, 1H), 1.51 (m, 1H), 1.46–1.19 (m, 14H); ^{13}C NMR ($CDCl_3$): $\delta = 176.2$, 139.4, 138.6, 135.2, 134.5, 129.2, 64.5, 51.7, 46.2, 43.0, 41.9, 31.2, 30.3, 29.5, 28.8, 26.0, 25.5, 21.2, 17.0; MS (ESI): $m/z = 477.53$ (M^+, calcd.: 477.35); anal. calcd. for $C_{31}H_{45}BrN_2O_2$: C 66.77, H 8.13, N 5.02; found: C 66.69, H 8.15, N 5.11.

Synthesis of *exo*-Ag-di-bicyclo[2.2.1]hept-5-ene-2-carboxylic Acid 11-[3-(2,4,6-Trimethylphenyl)-2,3-dihydroimidazol-1-yl]undecyl Ester Silver Dibromide (3)

In a screw-cap vial, **2** (306 mg, 0.54 mmol), silver oxide (64 mg, 0.27 mmol) and CH_2Cl_2 (10 mL) were combined. The solution was stirred for three hours during which a white precipitate formed. The solution was then filtered through celite and the solvent removed under vacuum to afford a brown oil; yield: 320 mg (89%). ^1H ($CDCl_3$): $\delta =$ 7.12 (m, 2H), 6.99 (s, 2H), 6.10 (m, 2H), 4.07 (t, $J = 6.6$ Hz, 2H), 3.03 (m, 1H), 2.33 (s, 5H), 2.07 (s, 9H), 1.91 (m, 1H), 1.75–1.58 (m, 5H), 1.54 (m, 1H), 1.51 (m, 1H), 1.46–1.19 (m, 14H); ^{13}C NMR ($CDCl_3$): $\delta = 177.2$, 139.4, 138.6, 135.5, 134.4, 129.2, 64.2, 51.1, 46.9, 43.5, 41.7, 31.4, 30.4, 29.0, 28.3, 26.6, 25.0, 23.5, 21.1, 17.1; MS (ESI): $m/z = 1061.92$ (M^+, calcd.: 1061.65); anal. calcd. for $C_{62}H_{90}Ag_2Br_2N_4O_4$: C 55.95, H 6.82, N 4.21; found: C 56.03, H 6.85, N 4.42.

Synthesis of *exo*-Bicyclo[2.2.1]hept-5-ene-2-carboxylic Acid Octyl Ester (4)

In a round-bottom flask equipped with a condenser, *exo*-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid (2.44 g, 17.6 mmol), 1-octanol (2.8 mL, 17.6 mmol), dicyclohexyldiamine (3.6 g, 17.6 mmol), a catalytic amount of diaminopyridine (100 mg) and CH_2Cl_2 (20 mL) were combined and refluxed overnight. The solution was then filtered through celite and the solvent removed under vacuum to yield a yellow solution which was further purified using column chromatography (eluent: hexanes) to afford a colorless oil; yield: 3.74 g (85%). ^1H NMR ($CDCl_3$): $\delta = 6.12$ (m, 2H), 4.07 (t, 2H, $J = 6.6$ Hz), 3.03 (m, 1H), 2.92 (m, 1H), 2.21 (m, 1H), 1.68–1.49 (m, 3H), 1.41–1.24 (m, 12H), 0.88 (t, 3H, $J =$ 7.1 Hz); ^{13}C NMR ($CDCl_3$): $\delta = 176.2$, 137.8, 135.6, 46.8, 46.2, 43.2, 41.5, 33.9, 29.2, 28.9, 28.5. MS (ESI): $m/z = 250.20$ (M^+, calcd.: 250.38); anal. calcd. for $C_{16}H_{26}O_2$: C 76.75, H 10.47; found: C 76.69, H 10.51.

Synthesis of *exo*-$Pd(OAc)_2$-bicyclo[2.2.1]hept-5-ene-2-carboxylic Acid 11-[3-(2,4,6-Trimethylphenyl)-2,3-dihydroimidazol-1-yl]undecyl Ester (5a)

Under an inert atmosphere, **3** (200 mg, 0.4 mmol), $Pd(OAc)_2$ (141 mg, 0.6 mmol) and CH_2Cl_2 (10 mL) were combined in a screw-cap vial. The solution was stirred overnight yielding a silver solid. The reaction mixture was filtered through celite to yield a yellow solution. The solvent was removed and the resulting yellow oil was further purified *via* column chromatography (eluent 1:1 hexanes:ethylacetate) to afford a yellow solid; yield: 190 mg (60%). ^1H NMR ($CDCl_3$): $\delta =$

6.88 (s, 2H), 6.10 (m, 2H), 4.07 (t, $J=6.6$ Hz, 2H), 3.03 (m, 1H), 2.33 (s, 5H), 2.07 (s, 9H), 1.91 (m, 1H), 1.75–1.58 (m, 5H), 1.54 (m, 1H), 1.51 (m, 1H), 1.46–1.19 (m, 20H); ^{13}C NMR ($CDCl_3$): $\delta=220.2$, 176.2, 139.7, 137.9, 135.1, 134.4, 129.6, 64.1, 51.2, 46.7, 43.4, 41.5, 31.6, 30.5, 29.9, 28.2, 26.4, 25.6, 21.5, 17.0. MS (ESI): $m/z=701.3$ (M^+, calcd.: 700.27); anal. calcd. for $C_{35}H_{50}N_2O_6Pd$: C 59.95, H 7.19, N 4.00; found: C 60.21, H 7.23, N 3.92.

Synthesis of *exo*-Pd(allyl)Cl-bicyclo[2.2.1]hept-5-ene-2-carboxylic Acid 11-[3-(2,4,6-Trimethylphenyl)-2,3-dihydroimidazol-1-yl]undecyl Ester (5b)

Under inert atmosphere, **3** (57 mg, 0.04 mmol), $Pd_2(allyl)_2Cl_2$ (16 mg, 0.04 mmol) and THF (5 mL) were combined in a screw-cap vial. The solution was stirred for five hours forming a silver precipitate. The reaction mixture was filtered through celite to yield a yellow solution. The solvent was removed under vacuum to yield yellow oil. The oil was washed three times with hexanes and dried under vacuum forming a yellow foam; yield: 16 mg (64%). ^{1}H NMR ($CDCl_3$): $\delta=7.06$ (d, 2H), 6.85 (m, 2H), 6.12 (m, 2H), 4.52 (m, 4H), 4.06 (t, $J=6.5$ Hz, 2H), 3.71 (m, 1H), 3.06 (d, 1H), 3.02 (m, 1H), 2.72 (d, 1H), 2.33 (s, 5H), 2.07 (s, 9H), 1.91 (m, 1H), 1.75–1.55 (m, 6H), 1.54 (m, 1H), 1.51 (m, 1H), 1.46–1.16 (m, 14H); ^{13}C NMR ($CDCl_3$): $\delta=180.1$, 174.5, 139.8, 136.7, 135.2, 132.6, 122.4, 121.5, 114.8, 68.5, 64.3, 49.5, 43.2, 42.4, 30.9, 29.4, 29.1, 28.5, 26.3, 25.9, 25.8, 25.5, 21.0; MS (ESI): $m/z=660.35$ (M^+, calcd.: 660.27); anal. calcd. for $C_{34}H_{51}ClN_2O_2Pd$: C 61.72, H 7.77, N 4.23; found: C 61.03, H 7.74, N 4.95.

Synthesis of *exo*-Pddba-bicyclo[2.2.1]hept-5-ene-2-carboxylic Acid 11-[3-(2,4,6-Trimethylphenyl)-2,3-dihydroimidazol-1-yl]undecyl Ester (5c)

Under inert atmosphere, **3** (76 mg, 0.06 mmol), Pd_2dba_3 (52 mg, 0.06 mmol) and THF (5 mL) were combined in a screw-cap vial. The solution was stirred for five hours forming a black precipitate. The reaction mixture was filtered through celite to yield a black solution. The solvent was removed under vacuum to yield a black solid. The solid was washed three times with hexanes and dried under vacuum to afford a brown solid; yield: 21 mg (45%). ^{1}H NMR ($CDCl_3$): $\delta=7.65$ (d, 4H), 7.31 (m, 6H), 7.12 (d, 2H), 6.95 (m, 2H), 6.86 (m, 2H), 6.82 (m, 2H), 6.11 (m, 2H), 4.08 (t, $J=6.4$ Hz, 2H), 3.05 (m, 1H), 2.33 (s, 5H), 2.07 (s, 9H), 1.93 (m, 1H), 1.75–1.58 (m, 5H), 1.55 (m, 1H), 1.51 (m, 1H), 1.46–1.20 (m, 14H); ^{13}C NMR ($CDCl_3$): $\delta=189.1$, 179.7, 145.8, 139.3, 136.2, 135.8, 135.3, 132.1, 129.5, 127.9, 125.3, 122.1, 115.4, 71.8, 50.8, 46.9, 43.2, 39.8, 36.3, 30.8, 30.0, 29.6, 25.3, 24.1; MS (ESI): $m/z=818.30$ (M^+, calcd.: 818.41); anal. calcd. for $C_{48}H_{59}N_2O_3Pd$: C 70.44, H 7.27, N 3.42; found C 70.33, H 7.32, N 3.15.

General Polymerization Procedure for the Synthesis of Polymers 6–9

The respective monomer(s) was dissolved in $CDCl_3$ followed by the addition of the desired amount of catalyst. The polymerization was monitored by NMR spectroscopy. After the polymerization was complete as determined by ^{1}H NMR, a few drops of ethyl vinyl ether were added to terminate the polymerization. The polymer was purified by repeated precipitations into cold methanol followed by centrifugation at 400 rpm for ten minutes. The purification procedure was repeated until the resulting methanol solution became colorless. The methanol was then decanted and the resulting polymer dried under vacuum.

Polymer 6a: ^{1}H NMR ($CDCl_3$): $\delta=6.89$–6.85 (br s, 2H), 5.53–5.21 (br m, 2H), 4.07–3.99 (br m, 2H), 3.03 (m, 1H), 2.33–2.30 (br s, 5H), 2.07–1.99 (br s, 9H), 1.91 (m, 1H), 1.75–1.58 (br m, 5H), 1.54 (m, 1H), 1.51 (m, 1H), 1.46–1.19 (br m, 20H); ^{13}C NMR ($CDCl_3$): $\delta=184.0$, 175.2, 175.0, 169.2, 145.5, 143.9, 137.4, 136.2, 128.4, 126.3, 126.0, 122.2, 114.4, 104.5, 50.2, 47.1, 43.1, 40.9, 36.4, 30.8, 29.7, 29.4, 25.2, 14.4, 9.2.

Polymer 6b: ^{1}H NMR ($CDCl_3$): $\delta=7.06$–7.03 (br m, 2H), 6.88–6.83 (br m, 2H) 5.55–5.20 (br m, 2H), 4.52–4.50 (br m, 4H), 4.07–4.02 (m, 2H), 3.71 (m, 1H), 3.07–3.05 (m, 1H), 3.02 (m, 1H), 2.74 (m, 1H), 2.33–2.28 (br s, 5H), 2.05 (br s, 9H), 1.91 (m, 1H), 1.75–1.53 (m, 6H), 1.52 (m, 1H), 1.50–1.48 (br m, 1H), 1.44–1.13 (br m, 14H); ^{13}C NMR ($CDCl_3$): $\delta=180.1$, 139.0, 136.4, 135.8, 135.5, 132.1, 128.9, 122.0, 121.1, 114.4, 73.2, 50.3, 47.4, 43.4, 40.2, 36.4, 30.2, 29.8, 29.4, 25.4, 14.3, 8.9.

Polymer 6c: ^{1}H NMR ($CDCl_3$): $\delta=7.67$–7.64 (br m, 4H), 7.34–7.30 (br m, 6H), 7.12–7.10 (br m, 2H), 6.95 (m, 2H), 6.86 (m, 2H), 6.84–6.81 (br m, 2H), 5.61–5.54 (br m, 2H) 4.10 (m, 2H), 3.05 (m, 1H), 2.33–2.29 (br s, 5H), 2.09–2.06 (br s, 9H), 1.95–1.93 (br m, 1H), 1.75–1.58 (m, 5H), 1.55–1.53 (m, 1H), 1.51–1.49 (m, 1H), 1.45–1.16 (m, 14H); ^{13}C NMR ($CDCl_3$): $\delta=189.1$, 179.8, 145.8, 139.2, 136.8, 135.8, 135.3, 132.1, 129.5, 128.9, 125.3, 122.1, 114.4, 71.2, 50.8, 46.9, 43.2, 39.8, 36.3, 30.8, 30.0, 29.6, 25.3, 13.5, 8.9.

Polymer 7a: ^{1}H NMR ($CDCl_3$): $\delta=6.89$–6.85 (br s, 2H), 5.53–5.21 (br m, 10H), 4.07–3.99 (br m, 10H), 3.03 (m, 5H), 2.33–2.26 (br s, 25H), 2.07–1.92 (br s, 45H), 1.91 (m, 4H), 1.75–1.58 (br m, 5H), 1.56–1.52 (m, 5H), 1.51–1.49 (m, 5H), 1.46–0.63 (br m, 100H); ^{13}C NMR ($CDCl_3$): $\delta=184.0$, 175.2, 175.0, 169.2, 151.8, 145.5, 143.9, 137.4, 136.2, 128.4, 126.5, 126.2, 122.2, 114.4, 104.8, 113.7, 64.8, 50.0, 48.7, 47.1, 43.1, 40.9, 36.4, 30.8, 29.7, 29.4, 26.3, 25.2, 14.4, 9.1.

Polymer 7b: ^{1}H NMR ($CDCl_3$): $\delta=7.08$–7.03 (br m, 2H), 6.89–6.80 (br m, 2H) 5.55–5.22 (br m, 2H), 4.52–4.50 (br m, 4H), 4.07–4.02 (m, 10H), 3.71 (m, 1H), 3.07–3.03 (m, 5H), 2.33–2.23 (br m, 25H), 2.05–1.89 (br m, 49H), 1.75–1.49 (br m, 6H), 1.48–1.43 (br m, 5H), 1.41–0.59 (br m, 100H); ^{13}C NMR ($CDCl_3$): $\delta=180.1$, 139.0, 136.4, 135.8, 135.5, 132.1, 128.9, 122.0, 121.1, 114.4, 73.2, 50.3, 48.3, 47.4, 43.4, 40.8, 40.2, 36.4, 31.1, 30.2, 29.8, 29.4, 26.7, 25.4, 14.3, 8.9, 8.6.

Polymer 7c: ^{1}H NMR ($CDCl_3$): $\delta=7.67$–7.64 (br m, 4H), 7.35–7.30 (br m, 6H), 7.12–7.10 (br m, 2H), 6.98–6.94 (br m, 2H), 6.86 (m, 2H), 6.84–6.81 (br m, 2H), 5.61–5.54 (br m, 2H) 4.10–4.01 (br m, 11H), 2.33–2.21 (br s, 25H), 2.09–1.98 (br s, 49H), 1.75–1.52 (m, 7H), 1.45–0.86 (m, 100H); ^{13}C NMR ($CDCl_3$): $\delta=189.1$, 179.8, 145.8, 139.2, 136.8, 135.8, 135.3, 132.1, 129.5, 128.9, 125.3, 122.1, 114.4, 71.2, 50.8, 46.9, 42.1, 43.2, 39.8, 37.3, 36.3, 35.2, 32.1, 31.4, 30.8, 30.0, 29.6, 28.4, 27.6, 25.3, 20.1, 13.5, 9.2, 8.7.

Polymer 9: ^{1}H NMR ($CDCl_3$): $\delta=7.20$–7.03 (br m, 4H), 6.86–6.82 (br m, 2H) 5.53–5.21 (br m, 2H), 4.55–4.50 (br m, 4H), 4.10–4.02 (m, 10H), 3.71 (m, 1H), 3.12–3.05 (m, 5H), 2.45–2.23 (br m, 25H), 2.04–0.59 (br m, 184H); ^{13}C NMR

($CDCl_3$): $\delta = 190.4$, 150.1,139.0, 136.4, 135.8, 135.5, 132.1, 128.9, 126.4, 123.4, 122.2, 121.1, 114.4, 73.1, 52.3, 49.1, 47.3, 42.7, 40.5, 40.1, 31.5, 30.1, 29.9, 29.4, 28.7, 25.1, 11.3, 9.3, 8.2.

General Procedure for the Suzuki–Miyaura Reaction

Under an atmosphere of nitrogen, a screw-cap vial was loaded with the desired catalyst, phenylboronic acid, chlorotoluene and DMF. After stirring for ten minutes, the cesium carbonate was added in one portion. The solution was heated to 80 °C until completion. The product was then purified *via* column chromatography.

General Procedure (A) for the Sonogashira Reaction

Under an inert atmosphere, a screw-cap vial was loaded with the desired catalyst, bromobenzene, ethynyltrimethylsilane, CuI, diisopropylamine and THF. The solution was stirred at room temperature until completion. The product was purified *via* column chromatography.

General Procedure (B) for the Sonogashira Reaction

Under an inert atmosphere, a screw-cap vial was loaded with the desired catalyst, bromobenzene, trimethyl(phenylethynyl)silane, CuI, cesium carbonate and dimethylacetamide. The solution was stirred at 80 °C until completion. The product was purified *via* column chromatography.

General Procedure for the Heck Reaction

Under an inert atmosphere, a screw-cap vial was loaded with the desired catalyst, iodobenzene, *n*-butyl acrylate, triethylamine and DMF. The solution was stirred at 120 °C until completion. The product was purified *via* column chromatography.

General Procedure for the Ring-Closing Metathesis Reaction

Under an inert atmosphere, a screw-cap vial was loaded with **9**, diethyl diallylmalonate and CH_2Cl_2. The solution was stirred at 45 °C until completion. The product was purified *via* column chromatography.

General Procedure for the Leaching Tests using QuadraPure®; Example: Suzuki–Miyaura Reaction

Under an inert atmosphere, a screw-cap vial was loaded with the desired catalyst (1 mol %), phenylboronic acid (1.2 equivalents), chlorotoluene (1 equivalent), QuadraPure® (2 mol %) and DMF. After stirring for 10 min, the cesium carbonate (1.5 equivalents) was added in one portion to the reaction mixture. The solution was heated to 80 °C and samples for GC analysis were taken every 5 min for the first 60 min, then every 30 min for the next 120 min.

General Procedure for the Leaching Tests using PVPy or Mercury. Example: Suzuki–Miyaura Reaction

Under an inert atmosphere, a screw-cap vial was loaded with the desired catalyst (1 mol %), phenylboronic acid (1.2 equivalents), chlorotoluene (1 equivalent), poison (500 equivalents) and DMF. After stirring for 10 min, the cesium carbonate (1.5 equivalents) was added in one portion to the reaction mixture. The solution was heated to 80 °C and samples for GC analysis were taken every 5 min for the first 60 min, then every 30 min for the next 120 min.

General Procedure for Precipitation Process

The precipitation of the polymer consists on reducing the amount of solvent to a minimum and adding cold methanol. The formed precipitate is then centrifuged for 10 min and the remaining solution decanted.

Acknowledgements

The US DOE Office of Basic Energy Sciences is acknowledged for financial support through Catalysis Science Contract No. DE-FG02–03ER15459. MW gratefully acknowledges a 3M Untenured Faculty Award, a DuPont Young Professor Award, an Alfred P. Sloan Fellowship, a Camille Dreyfus Teacher-Scholar Award and the Blanchard Assistant Professorship.

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