

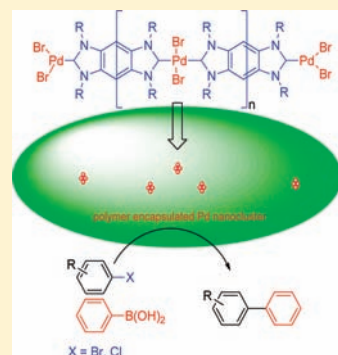
# A Study on Applications of *N*-Substituted Main-Chain NHC-Palladium Polymers as Recyclable Self-Supported Catalysts for the Suzuki–Miyaura Coupling of Aryl Chlorides in Water

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**S** Supporting Information

**ABSTRACT:** The preparation and characterization of a number of main-chain organometallic polymers (NHC-Pd MCOP) with different *N*-alkyl substituted groups such as benzyl (3a), *n*-hexyl (3b), and *n*-dodecyl (3c) are described. Among these polymers, 3c bearing the more lipophilic group *n*-dodecyl was found to be a more reactive and recoverable catalytic system in the Suzuki–Miyaura cross-coupling reaction of chloroarenes, including both deactivated and hindered aryl chlorides with different types of arylboronic acids under aqueous conditions. While the catalysts seem to be highly recyclable, on the contrary, we have provided much compelling evidence, such as kinetic monitoring, poisoning experiments, and average molecular weight determination before and after catalysis, that shows that the described organometallic polymers might be indeed the source of production of active soluble Pd species in the form of either Pd nanoparticles or fragmented NHC-Pd complexes. Our studies showed that in order to assess whether the catalysts are functioning in a heterogeneous pathway or they are simply a source of production of active Pd species, it is crucial to devise a suitable and highly efficient poison that could capture essentially soluble catalytic species. In this regard, we interestingly found that among a variety of well-known catalyst poisons such as Hg(0), SBA-15-PrSH, and cross-linked poly(4-vinylpyridine) (PVP), only PVP could efficiently quench catalysis, thus providing clear evidence of the formation soluble Pd species in our protocol. In addition, several experiments such as bright-field microscopy, dynamic light scattering (DLS) of the reaction mixture, and kinetic monitoring of the reaction at an early stage confirm not only that the described organometallic polymers could be a source of production of trace amounts of Pd nanoparticles but the capsular structures of these lipophilic polymers in water provides a means of entrapment of nanoclusters in a hydrophobic region, thus accelerating the reaction in pure water in the absence of any co-organic solvent.



## INTRODUCTION

Palladium-catalyzed carbon–carbon coupling reactions of aryl halides with arylboronic acids are very important routes to constructing biaryl units in organic synthesis. Although significant progress for these reactions has been achieved in recent years, they are suffering from difficult separation from reaction media and nonreusability. This reaction is one of the most general and powerful tools for the synthesis of pharmaceuticals, herbicides, natural products, conducting polymers, liquid crystalline materials, and ligands for catalysis.<sup>1</sup> While most of the palladium catalysts can be used for the activation of aryl iodides and bromides, in recent years, there has been an increasing challenge in the Suzuki reaction of aryl chlorides since these starting materials are cheaper and more easily available. However, chloroarenes exhibit much less reactivity than aryl bromides and iodides. Recently, several remarkable catalyst systems have been explored, which mainly employ either bulky electron-rich phosphines or palladacycles as ligands under homogeneous reaction conditions.<sup>2,3</sup> However, not only are most of these ligands air-sensitive but they are also relatively difficult to prepare. Meanwhile, *N*-heterocyclic carbenes (NHCs) have also received increasing attention as possible alternatives to the widely used

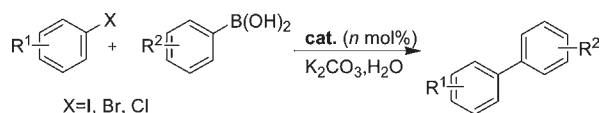
air-sensitive phosphorus ligands in Pd-catalyzed cross-coupling reactions, led primarily by the groups of Hermann, Nolan, and others.<sup>4</sup> These ligands have several advantages over the closely related phosphine ligands. They exhibit strong  $\sigma$ -donation and low  $\pi$ -acceptor ability. These NHCs also have excellent air and moisture stability and higher dissociation energies.

Despite significant achievement in improving catalytic activity and substrate scope, most of the developed catalyst systems are homogeneous and cannot be efficiently separated from the product; thus they contaminate the product. To address the recyclability issue of homogeneous catalysts, numerous heterogeneous supported palladium catalysts such as Pd/SiO<sub>2</sub>,<sup>5</sup> Pd/charcoal,<sup>6</sup> Pd/TiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub>,<sup>7</sup> Pd/MCM-41,<sup>8</sup> oxime-carbopalladacycle,<sup>9</sup> Pd-supported polymers,<sup>10</sup> Pd/fluoroapatite,<sup>11</sup> Pd/metal–organic frameworks,<sup>12</sup> and Pd/PMO-IL<sup>13</sup> were successfully utilized in the Suzuki cross-coupling reactions of aryl bromides and iodides. Nevertheless, only a few such Pd catalysts have been realized to display acceptable activity for cross-coupling with aryl chlorides.<sup>12–15</sup>

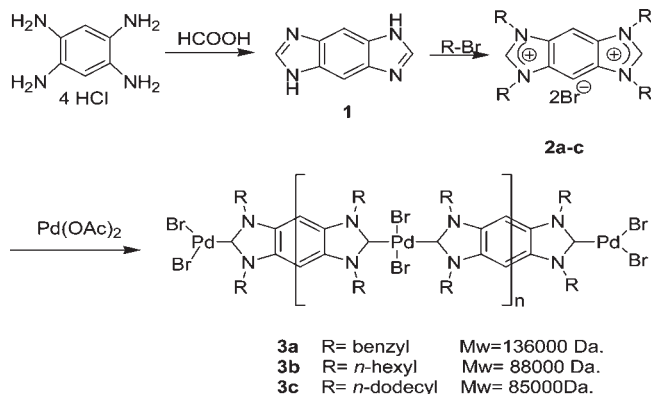
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**Scheme 1. Suzuki Coupling of a Variety of Aryl Halides in Water in the Presence of NHC-Pd-MCOP**



**Scheme 2. Synthesis of Main Chain NHC-Pd Polymers 3a–c**



Moreover, most of these catalyst systems still use organic (co)-solvents and/or require high catalyst concentrations (up to 1 mol %) and a rather large excess of boronic acids. In addition, many of the existing heterogeneous catalysts suffer from the poor recyclability, owing to the aggregation of nanoparticles into less reactive large particles (palladium black) because of the high surface energy of small nanoparticles generated during the catalytic reactions. Therefore, there has been extensive interest in the development of novel recoverable catalytic systems that can be efficiently reused while keeping the original activity of the catalytic centers.

Recently, the Bielawski research group has developed a variety of novel main-chain NHC-based organometallic polymers (NHC-MCOPs) which exhibit high thermal stability and versatile electronic properties.<sup>16</sup> Following this interesting discovery, in particular, a number of the described polymers have been shown to be promising materials for the preparation of conducting polymers,<sup>16a,e</sup> self-assembled materials,<sup>17</sup> and phosphorescent<sup>18</sup> and luminescent complexes.<sup>19</sup>

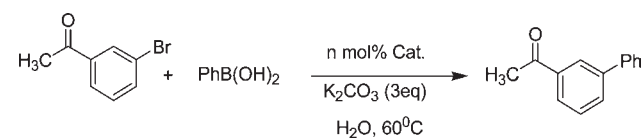
Quite recently, we explored the use of NHC-Pd-MCOP as an efficient and recyclable self-supported catalyst for the Suzuki–Miyaura coupling of a variety of aryl halides in water (Scheme 1).<sup>20</sup>

In continuation of this study, herein, we present the preparation and characterization of a variety of NHC-Pd-MCOP catalysts, in which NHC ligands bear different alkyl chain functionalities, and discuss more fully the effect of alkyl chains on catalyst activity and the nature of catalytic active species (sites) during the reaction process.

## RESULTS AND DISCUSSION

The preparation procedure to obtain NHC-Pd MCOP (3a–c) is outlined in Scheme 2. Initially, ligand precursors (2a–c) bearing different *N*-substituted alkyl groups such as benzyl (2a), *n*-hexyl (2b), and *n*-dodecyl (2c) were synthesized

**Table 1. Suzuki Coupling of 3-Bromoacetophenone with PhB(OH)<sub>2</sub> in the Presence of Catalysts 3a–c in Water<sup>a</sup>**



entry	catalyst <sup>a</sup>	<i>n</i>	time (h)	yield (%)
1	3a	5 × 10 <sup>−4</sup>	18	92
2	3a	0.05	7	92
3	3b	5 × 10 <sup>−4</sup>	18	42
4	3b	0.05	18	79
5	3c	5 × 10 <sup>−4</sup>	10	91
6	3c	0.05	4	90
7	3c	0.05	10	10 <sup>b</sup>
8	3c	0.05	10	55 <sup>c</sup>
9	3a	0.05	18	17 <sup>b</sup>

<sup>a</sup> Reaction conditions for the Suzuki reaction of 3-bromoacetophenone: 1.0 mmol of 3-bromoacetophenone, 1.1 mmol of benzenboronic acid, 3.0 mmol of K<sub>2</sub>CO<sub>3</sub>, 3.0 mL of water, 60 °C. <sup>b</sup> Toluene was used as a solvent. <sup>c</sup> THF was used as a solvent.

from the condensation of 1,2,4,5-tetraaminobenzene with freshly distilled formic acid followed by the alkylation of the resulting bis(benzimidazole) (1) with benzyl, *n*-hexyl, and *n*-dodecyl bromide, respectively. To this end, the obtained bis(imidazolium) bromides (2a–c) were then allowed to separately react with stoichiometric Pd(OAc)<sub>2</sub> in DMSO at 110 °C following the reported procedure with slight modification to give the corresponding NHC-Pd polymers 3a–c.<sup>16a</sup>

The obtained NHC-Pd polymers were well characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, elemental microanalysis, and gel-permeation chromatography (GPC). All of the polymers are soluble in polar solvents such as DMF and DMSO, whereas 3c also exhibits good solubility in CH<sub>2</sub>Cl<sub>2</sub> and CHCl<sub>3</sub> possibly owing to the presence of a long C-12 alkyl chain.

We next compared the ability of the obtained NHC-Pd-MCOPs to actually catalyze the Suzuki–Miyaura coupling reaction of aryl halides with that of arylboronic acids. Initially, we tested the Suzuki coupling of 3-bromoacetophenone with phenylboronic acid using catalysts 3a–c under the reaction conditions (60 °C, H<sub>2</sub>O as solvent, K<sub>2</sub>CO<sub>3</sub> (3 equiv) as a base) reported in our preliminary communication (Table 1, entries 1–6).<sup>20</sup> Although catalysts 3a and 3c with *N*-benzyl and *N*-dodecyl substituents, respectively, were able to furnish the corresponding biaryl in excellent yields within the indicated time (Table 1, entries 1, 2, 5, 6), obviously, catalyst 3b with the *N*-hexyl group gave unsatisfactory results under the same reaction conditions (Table 1, entries 3, 4).

Remarkably, 3c bearing *n*-C12 is a more efficient catalyst than 3a and 3b and afforded the product in 91% yield, even with a low catalyst loading (0.0005 mol %), and within a shorter reaction time of 10 h (Table 1, entries 5). Our preliminary studies demonstrated that the coupling of 3-bromoacetophenone as a model substrate with phenylboronic acid did not proceed well with 3c in usual organic solvents such as toluene and THF (Table 1, entries 7–9), and water was the optimum choice of solvent under the presented reaction conditions.

Table 2. Suzuki Coupling of Various Aryl Chlorides with Arylboronic Acid in the Presence of 3c in Water

Entry	Aryl chloride	Arylboronic acid	Time(h)	Yield(%) <sup>a, b</sup>
1			13	90
2			20	89
3			16	94
4			18	91
5			22	90
6			10	91
7			16	93
8			12	95
9			16	92
10			20	88
11			24	45 <sup>c</sup>

<sup>a</sup> Reaction conditions for the Suzuki reaction: aryl chloride (1.0 mmol), arylboronic acid (1.2 mmol), K<sub>2</sub>CO<sub>3</sub> (3.0 mmol), water (3.0 mL), 80–90 °C.

<sup>b</sup> Isolated yield after flash chromatography. <sup>c</sup> A total of 0.3 mol % of 3c was used at 90 °C.

On the basis of the fact that the Suzuki coupling catalyzed by most of the present heterogeneous palladium catalyst does not properly work with aryl chlorides, in the next stage, the abilities of 3a and 3c were compared in the Suzuki coupling of these highly challenging substrates (Tables 2, 3). With regard to catalyst 3a, we reported in an earlier communication that at 0.05 mol %, it is an efficient and recyclable catalyst for the Suzuki reaction of a wide range of aryl chlorides in water at 80–90 °C.<sup>20</sup> These promising results encouraged us to investigate and/or compare the performance of 3c in the Suzuki coupling of aryl chlorides under our earlier established reaction conditions using 3a. Along these lines, a range of aryl chlorides including electron-rich (deactivated) and electron-poor (activated) substrates were

tested in the Suzuki coupling reaction with phenylboronic acid using our new catalyst, giving the corresponding biaryls in excellent yields (Table 2, entries 1–5).

Similarly, we found that the coupling reaction of the same aryl chlorides with 4-methylphenylboronic acid afforded the respected biphenyls in excellent yields (Table 2, entries 6–10).

For the purpose of comparison, Table 3 also summarizes the results of the coupling of various aryl chlorides with either phenylboronic acid or 4-methylphenylboronic acid in the presence of 3a under essentially identical reaction conditions (Table 3).<sup>20</sup>

These results clearly confirm that higher isolated yields and activities, especially in the case of deactivated aryl chlorides, were

Table 3. Suzuki Coupling of Various Aryl Chlorides with Arylboronic Acid in the Presence of 3a in Water

Entry	Aryl chloride	Arylboronic acid	Time(h)	Yield(%) <sup>a, b</sup>
1			20	94
2			29	88
3			25	91
4			28	91
5			30	85 <sup>c</sup>
6			18	93
7			26	91
8			25	92
9			25	89
10			27	81 <sup>c</sup>
11			30	17 <sup>c, d</sup>

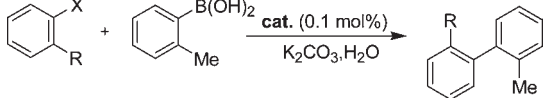
<sup>a</sup> Reaction conditions for the Suzuki reaction: aryl chloride (1.0 mmol), arylboronic acid (1.2 mmol), K<sub>2</sub>CO<sub>3</sub> (3.0 mmol), water (3.0 mL), 80–90 °C.


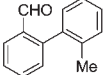

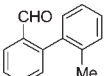

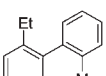

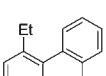

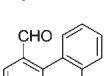

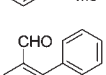

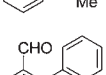

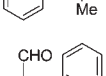
<sup>b</sup> Isolated yield after flash chromatography. <sup>c</sup> *n*-Bu<sub>4</sub>NBr (0.5 equiv.) was added. <sup>d</sup> A total of 0.3 mol % of 3a was used at 90 °C.

consistently obtained within shorter reaction times when using 3c rather than 3a under the described reaction conditions without the need of any added auxiliary such as *n*-Bu<sub>4</sub>NBr. The results also show that the electronic effects do not seem to have a significant effect on the isolated yields for electron-rich and electron-deficient aryl chlorides (Table 2). Taking into account the consistently higher catalytic performance of 3c in the Suzuki coupling reactions and the fact that the same reaction in the usual organic solvent did not efficiently give the expected products, it would be logical to speculate that the increase in hydrophobic character of *N*-alkyl groups in close proximity to the catalytic centers might be one of the reasons for this favorable behavior.

It is also noteworthy that in the case of coupling reactions of highly challenging 2-substituted aryl bromides with hindered 2-substituted arylboronic acid, the corresponding biaryl products were obtained in good yields using 3c (0.1 mol %; Table 4 entries 2, 4), whereas the same reaction using 3a (Table 4, entries 1, 3) was unsatisfactory under the same reaction conditions. Moreover, considering the significant difficulty of this type of reaction, the same coupling using 2-chlorobenzaldehyde with 2-methylboronic acid in the presence of both 3a and 3c only resulted in low yields of 4% and 15%, respectively, under similar reaction conditions (Table 4, entries 5, 6).

Interestingly, we found that by increasing the 3c loading to 0.3 mol %, this coupling reaction gave the corresponding biaryls

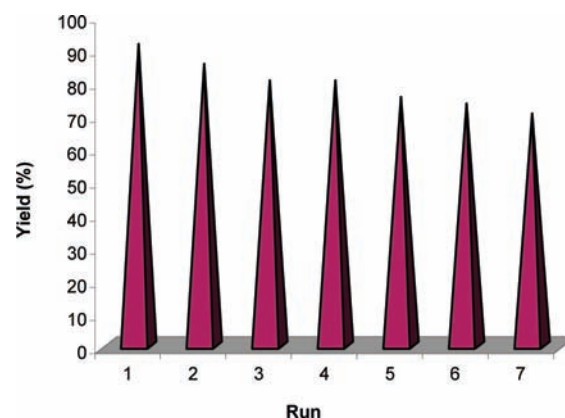
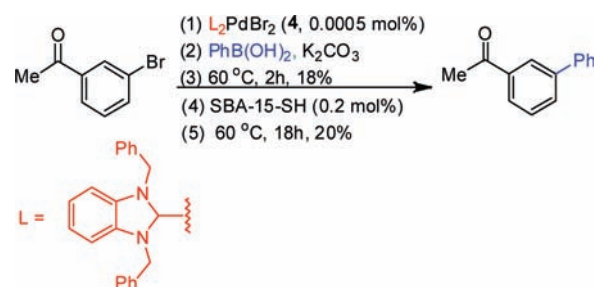
**Table 4.** Miyaura Coupling of 2-Substituted Aryl Halides with 2-Substituted Arylboronic Acid


Entry	Aryl Halide	Product	Catalyst	Time(h)	Yield (%) <sup>a, b</sup>
1			3a	24	47
2			3c	20	70
3			3a	30	50
4			3c	25	71
5			3a	24	4
6			3c	24	15
7			3a	30	29 <sup>c</sup>
8			3c	24	74 <sup>c</sup>

<sup>a</sup> Reaction conditions for the Suzuki reaction: aryl halide (1.0 mmol), 2-methylboronic acid (1.2–1.3 mmol), K<sub>2</sub>CO<sub>3</sub> (3.0 mmol), water (3.0 mL), 80–90 °C. <sup>b</sup> Isolated yield after flash chromatography. <sup>c</sup> A total of 0.3 mol % of catalyst was used.

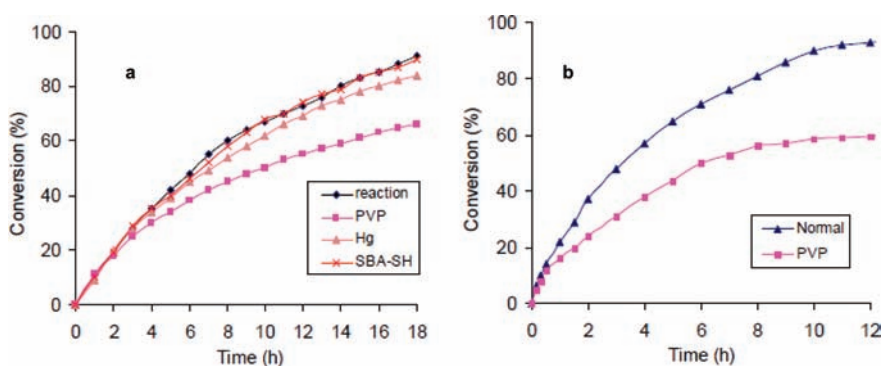
in 74% yield (Table 4, entry 8). However, under this new reaction condition, the catalytic activity of 3a was not good enough to activate the coupling reaction even after 30 h (Table 4, entry 7 vs 8).

For practical purposes, the lifetime and recycling of the catalyst are important problems to resolve. On the basis of our previous studies, we found that catalyst 3a could be consistently applied in six consecutive coupling reactions of 4-chlorobenzaldehyde with phenylboronic acid to give the corresponding biphenyl in an average 92% chemical yield. Similarly, by using the coupling reaction of phenylboronic acid and 4-chlorobenzaldehyde as a test reaction in the presence of 3c (0.05 mol %), it was found that recycling can be successfully achieved in seven reaction runs (Figure 1). While this experiment clearly verified that virtually no significant deactivation occurred during the catalysis and recovery, it was necessary to increase the reaction times after the fourth run to ensure suitable conversion.

**Figure 1.** Reusability of the 3c catalyst in the Suzuki coupling of 4-chlorobenzaldehyde.**Scheme 3.** Strong Poisoning Effect of SBA-15-Pr-SH in a Typical Homogeneous Suzuki Reaction Catalyzed with 4

To assess whether the catalyst is actually functioning in a heterogeneous pathway, or whether it is merely a precatalyst for more active soluble species (or naked palladium nanoparticles), a variety of different control experiments have been performed.<sup>21</sup> First, we conducted a hot-filtration test using 3a as a catalyst after the reaction of 3-bromoacetophenone with phenylboronic acid was initiated and before the substrates were completely consumed. The hot filtrates were then rapidly transferred to another flask containing K<sub>2</sub>CO<sub>3</sub> (3 equiv) in water at 60 °C. However, upon the further heating of a catalyst-free solution for 18 h, no considerable progress (4% by GC analysis) was observed.<sup>20</sup> Nevertheless, a negative hot-filtration test could not be a strong indication of the actual catalytic activity attributed solely to heterogeneity. This is due to the fact that in many circumstances the leached and soluble Pd species could be redepositing back on the insoluble support (polymer backbone) during the hot-filtration.<sup>21</sup> Therefore, while the negative hot-filtration test may indicate that the catalyst could be to some extent recyclable, it should not be used as a unique tool for heterogeneity of the solid catalysts.

In our initial studies, we also found that catalyst 3a (0.0005 mol %) maintains its activity in the Suzuki coupling of 3-bromoacetophenone and phenyl boronic acid in the presence of a large excess of Hg(0) (Hg/Pd, 400:1) under vigorous stirring, affording the corresponding biphenyl in excellent conversion without any detectable induction period (60 °C, 85%, 18 h). The high degree of activity of catalyst 3a even in the presence of Hg(0) provides at least interesting evidence that catalyst 3a is not a precatalyst for the formation of naked PdNPs.<sup>21</sup> However, it is



**Figure 2.** Reaction progress as a function of time on the Suzuki coupling of 3-bromoacetophenone with phenylboronic acid by using (a) **3a** in water under normal conditions (black diamond), in the presence of 400 equiv of Hg(0) (brown triangle), in the presence of 400 equiv of PVP (pink square), and in the presence of 400 equiv of SBA-propyl-SH (red cross) and using (b) **3c** as a catalyst in water under normal conditions (blue triangle) and in the presence of 400 equiv of PVP (pink circle).

well-known that Hg(0) has no poisoning effect on molecular homogeneous (ligand-protected) Pd species.<sup>22</sup>

On the other hand, it is nicely documented that polymer-bound thiophenol is an effective insoluble metal poison where palladium-containing provskites are actually sources for active and soluble palladium species.<sup>23</sup> Encouraged by the work of Kang et al.<sup>24</sup> and Crudden et al.,<sup>25</sup> who showed that thiol-modified mesoporous materials also have a high affinity for heavy metals, we decided to examine the ability of SBA-15-Pr-SH<sup>26</sup> (one of the best metal scavengers) to hopefully catch and poison any Pd soluble, thereby blocking access of the substrates to the active sites of any possible homogeneous ligand-protected Pd species. In order to better probe how much homogeneous ligand-protected complexes could participate in our protocol, we also managed to prepare a sample of a complex such as (1,3-dibenzylbenzimidazole-2-ylidene)<sub>2</sub>PdBr<sub>2</sub> (**4**),<sup>27</sup> which is structurally analogous to **3a**, and then compare its activity and poisoning behavior with that of the catalyst **3a** (Scheme 3).

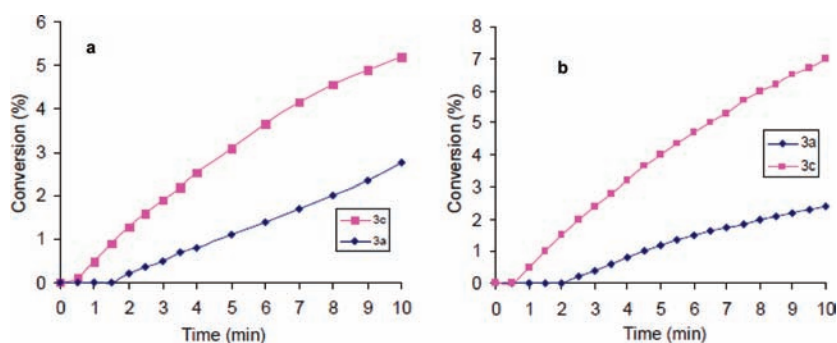
To make a clear comparison, a new experiment in which an excess of SBA-15-PrSH (S/Pd 400:1) is added to the coupling reaction of 3-bromoacetophenone with phenyl boronic acid using **4** under our optimal reaction conditions was investigated (Scheme 3). This reaction was conducted for 2 h until a conversion of 18% was reached, after which time SBA-15-PrSH (400 equiv) was added to the reaction mixture. To this end, the reaction was then allowed to stir, and no further catalytic activity was seen after 18 h at 60 °C. For comparison, a separate coupling experiment using **4** in which no SBA-15-SH was added led to the corresponding biaryl in good yield of 75% after 18 h under the same reaction conditions.

It is worth noting that adding mercury (0.2 mol %) to a third catalytic run using **4** was also investigated to further shed light on this issue. In this case, no further conversion was detected, indicating that Hg had immediately inhibited the function of the catalyst. Therefore, on the basis of the above-mentioned observations, the high catalytic activity of catalyst **3a** in the presence Hg(0) provides at least interesting evidence that catalyst **3a** is not a precatalysts for the formation of either “naked” Pd nanoparticles or small, soluble NHC-protected Pd species like **4**.

To further clarify whether the coupling reaction we are observing here using NHC-Pd-MCOP catalyst systems was simply heterogeneous in nature or not, we then designed a three-phase experiment in which the reagents were added to a

premixed sample of catalyst **3a** and SBA-15-Pr-SH (S/Pd 400:1) at 60 °C under an argon atmosphere. Interestingly, under these conditions, no apparent suppression of catalysis by SBA-15-Pr-SH has been observed for catalyst **3a** (90% yield, 18 h). Taking into account the negative poisoning effect of Hg(0) and three-phase test using SBA-15-PrSH, we may conclude that our system is working heterogeneously in nature. However, it is very important to note that a negative result from the poisoning test by considering the final yield alone can sometimes result in an erroneous conclusion. Thus, the use of a suitable and strong enough scavenger is necessary in order to be sure that all soluble catalytic species are selectively cached from the reaction mixture, while the immobilized sites on the polymer backbone remain unaffected. Along these lines, Richardson and Jones have recently demonstrated that poly(4-vinylpyridine) (PVP) is an efficient poison for the Pd-catalyzed Suzuki coupling reaction using a poly(urea)-entrapped palladium catalyst (Pd-En-Cat 40).<sup>28</sup> This successful study encouraged us to use the same poison to ascertain whether our catalysts were operating by a homogeneous or heterogeneous mechanism. To do this, a new three-phase poisoning test was designed for the coupling reaction of 3-bromoacetophenone with phenyl boronic acid using **3a** in the presence of PVP (PVP/Pd 400:1) under our optimal reaction conditions. It is gratifying that this new control experiment led to a gradual (but not still remarkable) decrease in catalytic activity upon the addition of PVP, giving the respected biaryl in 66% conversion after 18 h at 60 °C. Although the addition of PVP merely slowed down the reaction rate, it is a clear indication that catalyst **3a** is at least partly operating in an *incompletely heterogeneous* pathway.

Another powerful tool used to assess the nature of the true active species is the study of reaction kinetics, both in the presence and in the absence of poisons. Our experimental observations provided a lot of clear kinetic evidence for the generation of a soluble Pd species, in our protocol. The kinetic experiments were conducted using 3-bromoacetophenone and phenylboronic acid as coupling partners under our optimized reaction conditions in the presence of **3a** and **3c** (Figure 2). One of the most interesting observations from kinetic studies was that while the reaction rates were not significantly affected in the presence of poisons like Hg(0) and SBA-15-PrSH, upon the addition of PVP as a poison, the reaction progress would remarkably slow down from the point of addition. Once again, this study demonstrates the importance of devising a suitable



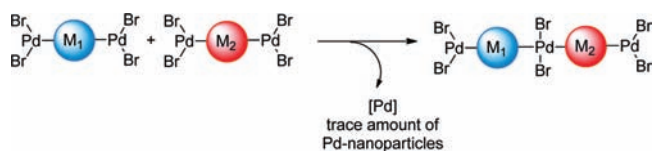
**Figure 3.** Induction period of (a) a Suzuki coupling reaction of 3-bromoacetophenone with phenylboronic acid by using **3a** (blue diamond) and **3c** (pink square) as catalysts in water and (b) a Suzuki coupling reaction of 4-chlorobenzaldehyde with phenylboronic acid using **3a** (blue diamond) and **3c** (pink square) as catalysts in water.

poison for efficient removal of a typical solution-phase Pd species. The PVP effect on the rate may be attributed to either the complexing of inactive soluble fragments that results in a lowered concentration of catalyst or catching active soluble Pd species. At a first glance, this observation highlights the notion that the MCOPs are decomposing during the reaction, and thus it is unlikely to proceed through a true heterogeneous pathway.

Another observation we made was that careful kinetic monitoring of the coupling reaction of 3-bromoacetophenone with phenylboronic acid under standard Suzuki conditions using **3a** as a catalyst demonstrated a very short induction period of about 2 min (Figure 3). In another experiment, to show the effect of PVP as a poison in the induction period, the reaction of 3-bromoacetophenone with phenylboronic acids using **3c** at an early stage has also been investigated under the conditions described in Table 3. The results show that while PVP effectively retards the reaction, no apparent change has been observed in the induction period upon the addition of PVP. This clearly indicates that PVP can only catch the *in situ* generated soluble Pd species, and the generation of the active species is independent of the presence of PVP (Supporting Information, Figure 7S). Although, no considerable color change has been detected in the reaction solution, even such a short induction period is indicative of the formation of soluble metal species in our protocol. Unfortunately, an inspection of TEM images of a sample of catalyst **3a** after recovery from the cross-coupling reaction of 3-bromoacetophenone with phenylboronic acid did not show any Pd clusters in the samples. However, on the basis of both the observed induction period and also positive poisoning experiments, it would be impossible to exclude the generation of a trace and nonobservable amount of Pd nanoparticles, which could react through a homogeneous reaction pathway.

To gain better insight into how our catalytic system changes during the reaction on a molecular level, we have also studied catalyst evolution by means of Gel-Permeation Chromatography (GPC). Along these lines, the average molecular weight of the organometallic polymer **3a** was measured using GPC.<sup>29</sup> The value for the fresh catalyst was found to be  $MW_A \sim 136\,000$  Da. Interestingly, we found that the average molecular weight for the recovered **3a** from the Suzuki coupling of 3-bromoacetophenone with phenylboronic acid slightly decreased to a value of 105 400 Da. Furthermore, by careful analysis of molecular weight distribution of the recovered catalyst, we interestingly observed that a small amount of  $\sim 3.5\%$  organometallic polymers with a  $MW_A$  ranging from 500 000 to 600 000 Da was generated during the

#### Scheme 4. Formation of MCOP with High Molecular Weight, Only Achieved through Combination of Smaller MCOPs

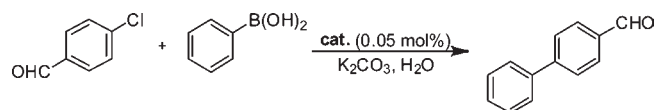


reaction. The fact that a majority of the polymer was reduced in molecular weight and that a small amount increased provides at least two notable facts. First, the total change of average molecular weight supports the notion that organometallic polymers are partly decomposing during the catalysis, so these polymers might (could) be the source of production of active Pd species in the form of either Pd nanoparticles or fragmented NHC-Pd complexes. Second, the formation of MCOP with high molecular weight could only be achieved through the combination of smaller MCOPs, which necessarily required breaking of the Pd–C bond (Scheme 4). This result clearly demonstrates that MCOP might be indeed a source of a trace amount of (of course unobservable) palladium nanoparticles.

However, it is very important to note that depending on the catalyst loading the concentration of halide (bromide or chloride) will be 100 to 10 000 times that of the polymer by the end of the reaction, and this may indeed involve in the fragmentation process. However, in order to assess how the halide concentration could actually participate in our catalytic system, we established two new experiments by adding an equimolar amount of NaBr (1 equiv) to the coupling reaction of 4-chlorobenzaldehyde with phenylboronic acid in the presence of either **3a** or **3c** under optimal reaction conditions in Table 3 (Table 5, entries 1, 2). Interestingly, we found that no apparent changes had occurred upon the addition of a high initial concentration of  $\text{Br}^-$ , thus confirming that the concentration of halide ions does not seem to significantly participate in catalyst performance in our protocol.

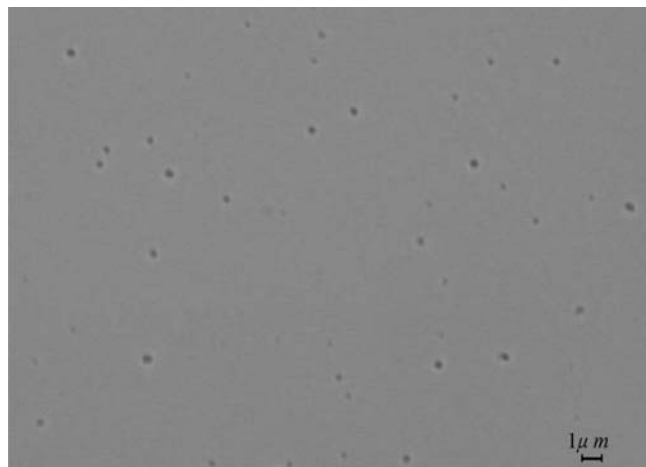
**The Effect of *N*-Alkyl groups.** It is known that organic–metal frameworks could be assembled into capsular structures that provide a nanoenvironment with a specific chemical behavior different from the exterior surroundings.<sup>30</sup> An interesting property of these container-like structures is that they can act as catalytic reaction chambers, thus affording a highly concentrated

**Table 5. Study of Suzuki–Miyaura Coupling of 4-Chlorobenzaldehyde with Phenylboronic Acid under Different Conditions**



Entry	Aryl chloride	Product	Catalyst	Time(h)	Yield (%) <sup>a, b</sup>
1			<b>3a</b>	20	90 <sup>c</sup>
2			<b>3c</b>	13	95 <sup>d</sup>
3			Pd(OAc) <sub>2</sub>	24	5
4			<b>4</b>	24	7

<sup>a</sup> GC yield using internal standard method. <sup>b</sup> Reaction conditions for the Suzuki reaction: aryl halide (1.0 mmol), phenylboronic acid (1.3 mmol), K<sub>2</sub>CO<sub>3</sub> (3.0 mmol), water (3.0 mL), 90 °C. <sup>c</sup> NaBr (1 mmol) was added according to the conditions in Table 3. <sup>d</sup> NaBr (1 mmol) was added according to the conditions in Table 4.



**Figure 4.** A bright-field microscope image of the reaction mixture.

reaction site that lowers the energy barrier for chemical reactions. Bright-field microscopy of the reaction mixture indicates the involvement of numerous polydisperse capsular structures in the region of ~500 nm (Figure 4). Moreover, the formation of capsular aggregates was also further confirmed by dynamic light scattering (DLS) of the reaction solution.<sup>27</sup> On the basis of these observations and our previous compelling evidence concerning the nature of the actual active species, we may conclude that not only could the described organometallic polymers be a source of

production trace amounts of Pd nanoparticles but the capsular structures of these polymers in water provides a means of entrapment of nanoclusters in the hydrophobic region. Therefore, one reason the Suzuki coupling reactions are somewhat more prominent in the case of **3c** than in the cases of **3a** and **3b** presumably is owed to a combination of lipophilic character of capsular chambers of **3c** and the hydrophobic effect of water, which results in an increased concentration of coupling partners inside the capsular structures where Pd species are located.

This proposal can be further supported by the fact that both ligand-free Pd(OAc)<sub>2</sub> and monomeric complex (1,3-dibenzylbenzimidazol-2-ylidene)<sub>2</sub>PdBr<sub>2</sub> (complex **4**) were unable to catalyze the coupling reaction between 4-chlorobenzaldehyde as a model for chloroarene with phenylboronic acid under our optimal reaction conditions (Table 5, entries 3, 4).

Another explanation for the observed enhanced reactivity of **3c** might be inferred by a careful comparison of the reaction kinetics of **3c** versus those of **3a** in the reaction between 3-bromoacetophenone and phenylboronic acid at an early stage. These kinetic investigations clearly demonstrated that the induction period for **3c** was shorter (but still measurable) than that for **3a**. In separate experiments, the kinetics of the Suzuki reaction between 4-chlorobenzaldehyde and phenylboronic acid in the presence of 0.05 mol % **3a** and **3c** were also investigated following the conditions demonstrated in Table 3, to show any possible effect of the reaction constituents (type of substrate, catalyst loading, and the reaction temperature) on the induction period at an early stage. As can be seen using the new reaction constituents (4-chlorobenzaldehyde, reaction temperature 80–90 °C, and catalyst loading 0.05 mol %), a shorter induction period for **3c** than for **3a** was obtained (Figure 3a vs b). Therefore, the higher reactivity of **3c** than **3a** might also be due, to some extent, to the faster production of active Pd species (probably entrapped Pd nanoclusters) when using **3c** as catalysts (Figure 3).

## CONCLUSION

In conclusion, we present, herein, the preparation and characterization of a variety of NHC-Pd-MCOP materials with different *N*-alkyl functionalities such as benzyl (**3a**),<sup>20</sup> *n*-hexyl (**3b**), and *n*-dodecyl (**3c**). Among the described MCOPs, the polymer bearing *N*-dodecyl group **3c** was found to be more reactive in catalyzing the Suzuki–Miyaura coupling of chloroarenes, including deactivated and hindered substrates under aqueous conditions without the need of any co-organic solvent. While the catalysts seem to be highly recyclable, on the contrary, we have provided a great deal of compelling evidence, such as kinetic studies, poisoning experiments, and average molecular weight determination before and after catalysis, which show that the described organometallic polymers might indeed be the source of production of active soluble Pd species in the form of either Pd nanoparticles or fragmented NHC-Pd complexes. Our studies showed that in order to attain reliable insight to whether the catalysts are functioning in a heterogeneous pathway or they are simply a source of production of active Pd species, it is crucial to devise a suitable and highly efficient poison that could capture essentially soluble catalytic species. In this regard, we interestingly found that among a variety of well-know catalyst poisons such as Hg(0), SBA-15-PrSH, and cross-linked PVP, only PVP could efficiently quench catalysis, thus providing clear evidence of the formation soluble Pd species in our protocol.



It should also be pointed out that a range of complementary tests are required to clearly probe how the catalyst operates in practice. Although the exact mechanism for the Suzuki reaction over the MCOP is still unclear, the high catalytic performance may be attributed to the *in situ* formation of trace amounts of Pd nano-clusters inside the hydrophobic capsular structure of MCOP in water. Work is underway to expand the application of this novel catalyst system in other important chemical transformations.

## ■ ASSOCIATED CONTENT

**S Supporting Information.** Procedure for formation of benzo-bis(imidazole); procedures for the formation of tetrabenzyl benzo-bis(imidazolium) bromide (**2a**), tetrahexyl benzo-bis(imidazolium) bromide (**2b**), and tetradodecyl benzo-bis(imidazolium) bromide (**2c**); typical procedure for the preparation of organometallic polymer **3a–c**; procedures for the formation of 1,3-dibenzylbenzimidazolium bromide and (1,3-dibenzylbenzimidazole-2-ylidene)<sub>2</sub>PdBr<sub>2</sub> (**4**); general procedure for the Suzuki coupling reaction using **3a–c** catalysts; procedure for reusability test of **3c** catalyst; general procedure for the study of the effects of Hg(0), poly-(4-vinylpyridine) (PVP), and SBA-propyl-SH on **3a** catalyst reactivity; analysis of the polymers by gel permeation chromatography; dynamic laser light scattering data; thermal gravimetric analysis (TGA) of polymers **3**; <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## ■ REFERENCES

- (1) (a) Diederich, F.; de Meijere, A. *Metal-Catalyzed Cross-Coupling Reaction*; Wiley-VCH: Weinheim, Germany, 2004. (b) Corbet, J.-P.; Mignani, G. *Chem. Rev.* **2006**, *106*, 2651. (c) Hassan, J.; Sevignon, M.; Gozzi, C.; Schulz, E.; Lemaire, M. *Chem. Rev.* **2002**, *102*, 1359. (d) Suzuki, A. *J. Organomet. Chem.* **1999**, *576*, 147. (e) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457.
- (2) For a review on the Pd-catalyzed coupling reaction of aryl chlorides, see: (a) Littke, A. F.; Fu, G. C. *Angew. Chem., Int. Ed.* **2002**, *41*, 4176. For coupling reactions of aryl chlorides using Pd–phosphine complexes, see: (b) Billingsley, K.; Buchwald, S. L. *J. Am. Chem. Soc.* **2007**, *129*, 3358. (c) Ohta, H.; Tokunaga, M.; Obara, Y.; Iwai, T.; Iwasawa, T.; Fujihara, T.; Tsuji, Y. *Org. Lett.* **2007**, *41*, 89. (d) Kudo, N.; Perseghini, M.; Fu, G. C. *Angew. Chem., Int. Ed.* **2006**, *45*, 1282. (e) Anderson, K. W.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2005**, *44*, 6173. (f) Barder, T. E.; Walker, S.; Martinelli, J. R.; Buchwald, S. L. *J. Am. Chem. Soc.* **2005**, *127*, 4685. (g) Zapf, A.; Jackstell, R.; Rataboul, F.; Riermeier, T.; Monsees, A.; Fuhtmann, C.; Digerdissen, U.; Beller, M. *Chem. Commun.* **2004**, 38.
- (3) For coupling reactions of aryl chlorides using palladacycle complexes, see: (a) Botella, L.; Nájera, C. *Angew. Chem., Int. Ed.* **2002**, *41*, 179. (b) Bedford, R. B.; Cazin, C. S. J.; Hazelwood, S. L. *Angew. Chem., Int. Ed.* **2002**, *41*, 4120.
- (4) For coupling reactions of aryl chlorides using NHC–Pd complexes, see: (a) Marion, N.; Navarro, O.; Mei, J.; Stevens, E. D.; Scott, N. M.; Nolan, S. P. *J. Am. Chem. Soc.* **2006**, *128*, 4101 and references cited therein. (b) Hadei, N.; Kantchev, E. A. B.; O'Brien, C. J.; Organ, M. G. *Org. Lett.* **2005**, *7*, 1991. (c) Gstottmayr, C. W. K.; Böhm, V. P. W.; Herdtweck, E.; Grosche, M.; Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1363. (d) Meise, M.; Haag, R. *Chem. Sus. Chem.* **2008**, *1*, 637. For an excellent review on the application of N-heterocyclic carbene complexes of palladium as catalysts for cross-coupling reactions, see: (e) Kantchev, E. A. B.; O'Brien, C. J.; Organ, M. G. *Angew. Chem., Int. Ed.* **2007**, *46*, 2768.
- (5) Crudden, C. M.; Sateesh, M.; Lewis, R. J. *Am. Chem. Soc.* **2005**, *127*, 10045.
- (6) Hallberg, A.; Westfelt, L. *J. Chem. Soc., Perkin Trans. 1* **1984**, 933.
- (7) Wali, A.; Pillai, S. M.; Kaushik, V. K.; Satish, S. *Appl. Catal., B* **1996**, *135*, 83.
- (8) Augustine, R. L.; O'leary, S. T. *J. Mol. Catal. A* **1995**, *95*, 277.
- (9) Baleizao, C.; Corma, A.; Garcia, H.; Leyva, A. *Chem. Commun.* **2003**, 606.
- (10) For Pd supported polymers, see: (a) Uozumi, Y.; Danjo, H.; Hayashi, T. *J. Org. Chem.* **1999**, *64*, 3384. (b) Uozumi, Y.; Kikuchi, M. *Synlett* **2005**, 1775. (c) Uozumi, Y.; Nakai, Y. *Org. Lett.* **2002**, *4*, 2997. (d) Yamada, Y. M. A.; Maeda, Y.; Uozumi, Y. *Org. Lett.* **2006**, *8*, 4259. (e) Bai, L.; Wang, J.-X. *Adv. Synth. Catal.* **2008**, *350*, 315. (f) Uozumi, Y.; Matsuura, Y.; Arakawa, T.; Yamada, Y. M. A. *Angew. Chem., Int. Ed.* **2009**, *48*, 2708. (g) Chen, W.; Li, R.; Wu, Y.; Ding, L. S.; Chen, Y. C. *Synthesis* **2006**, 3058. (h) Kim, J.-W.; Kim, J.-H.; Lee, D.-H.; Lee, Y.-S. *Tetrahedron Lett.* **2006**, *47*, 4745. (i) Solodenko, W.; Schçn, U.; Messinger, J.; Glinschert, A.; Kirschning, A. *Synlett* **2004**, 1699. (j) Nájera, C.; Gil-Molto, J.; Karlstrçm, S. *Adv. Synth. Catal.* **2004**, *346*, 1798. (k) Gil-Molto, J.; Nájera, C. *Eur. J. Org. Chem.* **2005**, 4073. (l) Wen, F.; Zhang, W.; Wei, G.; Wang, Y.; Zhang, J.; Zhang, M.; Shi, L. *Chem. Mater.* **2008**, *20*, 2144. (m) Colacot, T. J.; Carole, W. A.; Neide, B. A.; Harad, A. *Organometallics* **2008**, *27*, 5605. (n) Colacot, T. J.; Gore, E. S.; Kuber, A. *Organometallics* **2002**, *21*, 3301.
- (11) Kantam, L. M.; Kumar, K. B. S.; Srinivas, P.; Sreedhar, B. *Adv. Synth. Catal.* **2007**, *349*, 1141.
- (12) Yuan, B.; Pan, Y.; Li, Y.; Yin, B.; Jiang, H. *Angew. Chem., Int. Ed.* **2010**, *44*, 4054.
- (13) Karimi, B.; Elhamfar, D.; Clark, J. H.; Hunt, A. J. *Chem.—Eur. J.* **2010**, *16*, 8047.
- (14) (a) Yin, L.; Liebscher, J. *Chem. Rev.* **2007**, *107*, 133. (b) Sommer, W. J.; Weck, M. *Coord. Chem. Rev.* **2007**, *251*, 860. (c) Yamada, Y. M. A.; Takeda, K.; Takahashi, H.; Ikegami, S. *J. Org. Chem.* **2003**, *68*, 7733. (d) Tsuji, Y.; Fujihara, T. *Inorg. Chem.* **2007**, *46*, 1895.
- (15) For more recent examples of Pd supported catalysts for the Suzuki coupling, see: (a) Baleizão, C.; Corma, A.; Garcia, H.; Leyva, A. *Chem. Commun.* **2003**, 606. (b) Kantam, M. L.; Shiva Kumar, K. B.; Srinivas, P.; Sreedhar, B. *Adv. Synth. Catal.* **2007**, *349*, 1141. (c) Sayah, R.; Glegola, K. *Adv. Synth. Catal.* **2007**, *349*, 373. (d) Sommer, W. J.; Weck, M. *Adv. Synth. Catal.* **2006**, *348*, 2101. (e) Schweizer, S.; Becht, J.-M.; Le Drian, C. *Org. Lett.* **2007**, *9*, 3777. (f) Gallon, B. J.; Kojima, R. W.; Kaner, R. B.; Diaconescu, P. L. *Angew. Chem., Int. Ed.* **2007**, *46*, 7251. (g) Jin, M.-J.; Lee, D.-H. *Angew. Chem., Int. Ed.* **2010**, *49*, 1119.
- (16) (a) Boydston, A. J.; Williams, K. A.; Bielawski, C. W. *J. Am. Chem. Soc.* **2005**, *127*, 12496. (b) Khoramov, D. M.; Boydston, A. J.; Bielawski, C. W. *Angew. Chem., Int. Ed.* **2006**, *45*, 6186. (c) Boydston, A. J.; Khoramov, D. M.; Bielawski, C. W. *Tetrahedron Lett.* **2006**, *47*, 5123. (d) Khoramov, D. M.; Boydston, A. J.; Bielawski, C. W. *Org. Lett.* **2006**, *8*, 1831. (e) Boydston, A. J.; Rice, J. D.; Sanderson, M. D.; Dykhon, O. L.; Bielawski, C. W. *Organometallics* **2006**, *25*, 6087. (f) Boydston, A. J.; Bielawski, C. W. *Dalton Trans.* **2006**, 4073. (g) Williams, K. A.; Boydston, A. J.; Bielawski, C. W. *Chem. Soc. Rev.* **2007**, *36*, 729. (h) Tennyson, A. G.; Norris, B.; Bielawski, C. W. *Macromolecules* **2010**, *43*, 6923. (i) Williams, K. A.; Bielawski, C. W. *Chem. Commun.* **2010**, *46*, 5166. (j) Tennyson, A. G.; Khoramov, D. M.; Varnado, C. D., Jr.; Creswell, P. T.; Kamplain, J. W.; Lynch, V. M.;

Bielawski, C. W. *Organometallics* **2009**, *28*, 5142. (k) Lynch, V. M.; Bielawski, C. W. *Dalton Trans.* **2009**, 7253. (l) Powell, A. B.; Bielawski, C. W.; Cowley, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 18232. (m) Kamplain, J. W.; Bielawski, C. W. *Chem. Commun.* **2006**, 1727. (n) Williams, K. A.; Boydston, A. J.; Bielawski, C. W. *J. R. Soc. Interface* **2007**, *4*, 359. (o) Norris, B. C.; Bielawski, C. W. *Macromolecules* **2010**, *43*, 3591.

(17) Hahn, F. E.; Radloff, C.; Pape, T.; Hepp, A. *Organometallics* **2008**, *27*, 6408.

(18) Tennyson, A. G.; Rosen, E. L.; Collins, M. S.; Lynch, V. M.; Bielawski, C. W. *Inorg. Chem.* **2009**, *48*, 6924.

(19) (a) Coady, D. J.; Norris, B. C.; Khramov, D. M.; Tennyson, A. G.; Bielawski, C. W. *Angew. Chem., Int. Ed.* **2009**, *48*, 5187. (b) Tennyson, A. G.; Kamplain, J. W.; Bielawski, C. W. *Chem. Commun.* **2009**, 2124. (c) Er, J. A. V.; Tennyson, A. G.; Kamplain, J. W.; Lynch, V. M.; Bielawski, C. W. *Eur. J. Inorg. Chem.* **2009**, 1729. (d) Boydston, A. J.; Vu, P. D.; Dykhno, O. L.; Chang, V.; Wyatt, A. R., II; Stockett, A. S.; Ritschdorff, E. T.; Shear, J. B.; Bielawski, C. W. *J. Am. Chem. Soc.* **2008**, *130*, 3143. (e) Boydston, A. J.; Pecinovsky, C. S.; Chao, S. T.; Bielawski, C. W. *J. Am. Chem. Soc.* **2007**, *129*, 14550.

(20) Karimi, B.; Fadavi Akhavan, P. *Chem. Commun.* **2009**, 3570.

(21) (a) Widegren, J. A.; Finke, R. G. *J. Mol. Catal. A: Chem.* **2003**, *198*, 317. (b) Phan, N. T. S.; Van der Sluy, M.; Jones, C. W. *Adv. Synth. Catal.* **2006**, *348*, 609.

(22) Yu, K.; Sommer, W.; Richardson, J. M.; Weck, M.; Jones, C. W. *Adv. Synth. Catal.* **2005**, *347*, 161.

(23) Andrews, S. P.; Stepan, A. F.; Tanaka, H.; Ley, S. V. *Adv. Synth. Catal.* **2005**, *347*, 697.

(24) (a) Kang, T.; Park, Y.; Park, J. C.; Cho, Y. S.; Yi, J. *Stud. Surf. Sci. Catal.* **2003**, *146*, 527. (b) Kang, T.; Park, Y.; Yi, J. *Ind. Eng. Chem. Res.* **2004**, *43*, 1478.

(25) (a) Mercier, L.; Pinnavaia, T. J. *Adv. Mater.* **1997**, *9*, 500. (b) Feng, X.; Fryxell, G. E.; Wang, L.-Q.; Kim, A. Y.; Liu, J.; Kemner, K. M. *Science* **1997**, *276*, 923. (c) Crudden, C. M.; Sateesh, M.; Lewis, R. *J. Am. Chem. Soc.* **2005**, *127*, 10045.

(26) (a) Karimi, B.; Zareyee, D. *Org. Lett.* **2008**, *10*, 3989. (b) Margolese, D.; Merelo, J. A.; Christiansen, S. C.; Chmelka, B. F.; Stucky, G. D. *Chem. Mater.* **2000**, *12*, 2448.

(27) See Supporting Information for experimental details

(28) Richardson, J. M.; Jones, C. W. *Adv. Synth. Catal.* **2006**, *348*, 1207.

(29) The GPC chromatography was performed using a water column, 10 000 Å-DVB, a refractive index detector, and DMF as the eluent at 40 °C.

(30) (a) Hof, F.; Rebek, J., Jr. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 4775. (b) Conn, M. M.; Rebek, J., Jr. *Chem. Rev.* **1997**, *97*, 1647. (c) Rebek, J., Jr. *Acc. Chem. Res.* **1999**, *32*, 278. (d) Friedler, D.; Bergman, R. G.; Raymond, K. N. *Angew. Chem., Int. Ed.* **2004**, *43*, 6748. (e) Lee, M.; Jang, C.-J.; Ryu, J.-H. *J. Am. Chem. Soc.* **2004**, *126*, 8082. (f) Pluth, M. D.; Bergman, R. G.; Raymond, K. N. *Angew. Chem., Int. Ed.* **2007**, *46*, 8587. (g) Ryu, J.-H.; Hong, D.-J.; Lee, M. *Chem. Commun.* **2008**, 1043.