

# Access to Well-Defined Heterogeneous Catalytic Systems via Ring-Opening Metathesis Polymerization (ROMP): Applications in Palladium(II)-Mediated Coupling Reactions

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**Abstract:** The preparation of a new heterogeneous palladium(II)-based catalyst and its homogeneous analogue and their use for Heck-type, alkyne and amine couplings are described. The heterogeneous catalytic system is based on a polymer-bound dichloropalladium di(pyrid-2-yl)amide and was prepared via ring-opening metathesis copolymerization of norborn-2-ene-5-(*N,N*-di(pyrid-2-yl))carbamide with 1,4,4a,5,8,8a-hexahydro-1,4,5,8-*exo-endo*-dimethanonaphthalene and subsequent loading of the resulting resin with palladium(II) chloride. The heterogeneous catalyst is air, moisture, and temperature stable up to 150 °C and highly active (94–99% yields) in the vinylation of aryl iodides and aryl bromides (Heck-type couplings) with turn-over numbers (TONs) of up to 210000. Even higher TON's (up to 350000) may be achieved in the arylation of alkynes. High yields ( $\leq 95\%$ ) and TONs ( $\leq 24000$ ) may additionally be achieved in the tetrabutylammonium bromide (TBAB) assisted vinylation of aryl chlorides. Moderate yields ( $< 65\%$ ) and TONs ( $< 4000$ ) are observed in the amination of aryl bromides. A soluble analogue of the heterogeneous system, *N,N*-di(pyrid-2-yl)acetamide palladium dichloride (**2**), was prepared from palladium(II) chloride and *N,N*-di(pyrid-2-yl)acetamide (**1**) and characterized by X-ray analysis. **2** crystallizes in the monoclinic space group  $P2_1/n$ ,  $a = 835.0(1)$  pm,  $b = 1494.3(4)$  pm,  $c = 1199.3(2)$  pm,  $\alpha = 90^\circ$ ,  $\beta = 109.05(2)^\circ$ ,  $\gamma = 90^\circ$ ,  $Z = 4$ . It served as a model compound for the elucidation of the actual geometry of the catalytic species. The unstrained geometry of **2** with almost ideal angles and bond lengths explains the high stability of the catalytic center. The significantly higher catalytic activity of the heterogeneous system compared to the homogeneous one suggests well-defined ligand-bound catalytic sites rather than polymer-supported palladium colloids.

## Introduction

Palladium-mediated polymerizations<sup>1,2</sup> and couplings<sup>3</sup> have attracted significant interest during the last years as they represent versatile tools in synthetic chemistry. Besides modern applications, e.g., the catalytic formation of hydrogen peroxide,<sup>4</sup> classical reactions such as the vinylation of aryl halides, commonly called the Heck reaction, as well as cross-coupling reactions involving alkynes<sup>5</sup> or the arylation of arylamines<sup>6</sup> are still in the center of interest, in particular when these reactions are carried out in an enantioselective way.<sup>7–10</sup> Despite the significant progress in homogeneous catalysis which has been

made so far,<sup>11–14</sup> the demand for highly active and stable heterogeneous systems is still high.<sup>15–18</sup> Only a few reports exist on the synthesis of heterogeneous palladium catalysts,<sup>19</sup> e.g., based on palladium-loaded porous glass,<sup>20</sup> palladium-loaded carbon, or alumina,<sup>21</sup> palladium colloids,<sup>22–24</sup> zeolite (NaY-type)-entrapped Pd complexes,<sup>25</sup> or Pd-grafted MCM-41.<sup>26</sup> Recently, Bräse et al. described a heterogeneous system<sup>27</sup> based

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on a Merrifield polymer using a permanently "renewable" triazene-linker. Generally speaking, the most striking advantages of heterogeneous catalytic systems is their easy removal from the reaction mixture which, in case of sufficient stability, allows their reuse as well as the formation of catalyst and ligand-free products. Besides a lack of knowledge about the exact chemical structure of a heterogeneous catalytic system, a major drawback in the synthesis of stable heterogeneous palladium(II) systems is often related to the rather low durability of the corresponding complexes. Generally, the high temperatures which are required to promote the coupling reaction lead to the fast formation of palladium black. In general, such heterogeneous coupling reactions are characterized by low to moderate TONs ( $\leq 5000$ ) and low to moderate yields in the case where aryl chlorides are used.<sup>22,24,26</sup> Consequently, to obtain acceptable yields, comparably large amounts of palladium(II) (usually 0.5–3 mol %) are required. The problem of temperature-induced catalyst degradation may somehow be reduced if microwave<sup>28</sup> or high pressure<sup>29</sup> are used to promote the corresponding coupling reaction. While phosphine-based ligands possess excellent binding properties for palladium(II) and allow the preparation of highly active systems,<sup>30</sup> they are easily transformed into the corresponding phosphine oxides. This reaction results in a slow but permanent release of palladium (catalyst bleeding) which significantly aggravates their industrial use. To circumvent this problem, more stable catalytic systems have been elaborated for homogeneous catalysis.<sup>31–33</sup> Phosphapalladacycles,<sup>34–40</sup> which may also be used in nonaqueous ionic solvents,<sup>41</sup> and more recently an aza-analogue were reported<sup>32</sup> to be a highly active Heck-type catalysts. Finally, homoleptic chelating N-heterocyclic carbene complexes<sup>17,42–45</sup> have to be mentioned. Other cyclic, chelating N- and P-based ligands<sup>31,46</sup> such as dipyrindyl, phenantroline, etc. are well-known in homogeneous catalysis<sup>47,48</sup>

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as they form stable complexes with a large variety of metal ions. Nevertheless, due to the nonselectivity of binding, the catalytically active metal ion is often replaced by traces of other metal ions present in technical grade chemicals such as iron, copper, nickel, etc., leading to a fast deterioration of the catalyst. In this contribution, the use of a palladium-selective ligand, its heterogenization by ring-opening metathesis polymerization (ROMP), and the synthesis of the catalysts as well as some applications are presented.<sup>49</sup>

## Results and Discussion

**Preparation of the Heterogeneous Catalyst.** Standard procedures for the preparation of polymer-supported ligands usually entail the surface modification of commercially available polymer supports, e.g. polystyrene-divinylbenzene (PS-DVB) or chloromethylated PS-DVB (Merrifield polymer). Nevertheless, this synthetic route is characterized by some disadvantages. To achieve a maximum derivatization capacity (usually expressed in mmol of functional group/g of resin) porous materials with high surface areas have to be chosen. As a major part of the specific surface area ( $\sigma$ ) results from internal pores, large amounts of the desired ligand are located at the interior of the particle. This leads to a diffusion-controlled reaction during catalysis which usually significantly reduces the overall reaction rate constant.<sup>15</sup> Another critical point lies in the usually employed divergent synthetic approach for surface derivatizations. The synthetic protocol often consists of at least two to three steps. Due to the heterogeneous character of such transformations, each step may not be accomplished in a quantitative way. In contrast to homogeneous reactions, the resulting "byproducts" are not removed. This leads to a situation, where a significant amount of the initial functionality is not transformed into the desired ligand. Poor definitions in terms of chemical structure and problems of catalyst poisoning are often the consequence.

Ring-opening metathesis polymerization (ROMP) has been demonstrated to present a powerful tool in the preparation of functionalized polymer supports.<sup>49–64</sup> Even complex functionalities may be introduced with high reproducibility and without

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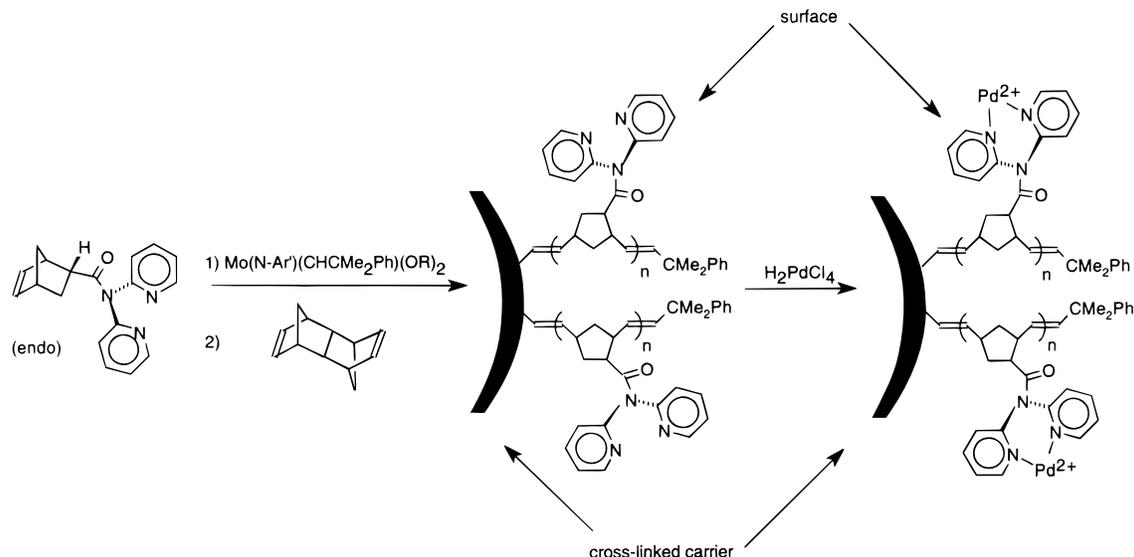
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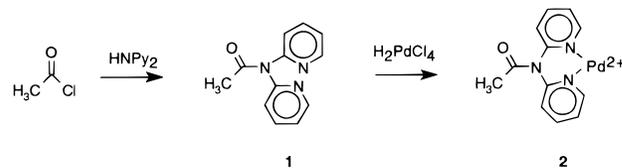
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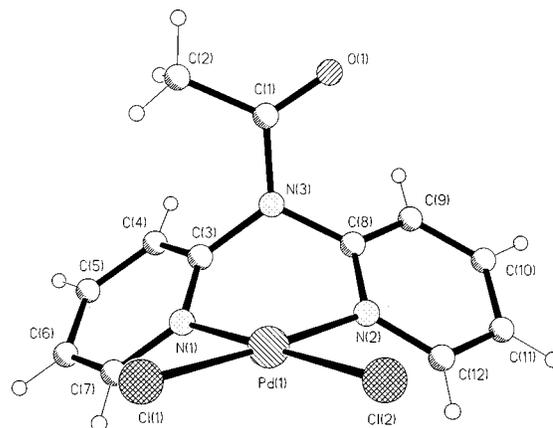
**Figure 1.** Heterogenization of the ligand and preparation of the catalyst ( $\text{Ar}' = 2,6\text{-}i\text{-Pr}_2\text{-C}_6\text{H}_3$ ,  $\text{R} = \text{C}(\text{CH}_3)(\text{CF}_3)_2$ ).

any change in the chemical nature, geometry, and even chirality of the corresponding functional group. Previously, we reported on the synthesis of a new material for the selective enrichment of palladium and mercury via ROMP using Schrock-type initiators.<sup>52,60</sup> For the present investigation, a beaded ROMP-based polymer containing the palladium-selective ligand was loaded with the transition metal and used for Heck-type couplings and the amination of aryl halogenides. The synthesis of the support and loading of the resin is summarized in Figure 1. The norborn-2-ene-bound palladium-selective ligand *N,N*-di(pyrid-2-yl)carbamide was polymerized in a living way by the Schrock catalyst  $\text{Mo}(\text{N}-2,6\text{-}i\text{-Pr}_2\text{-C}_6\text{H}_3)(\text{CHCMe}_2\text{Ph})(\text{OCMe}(\text{CF}_3)_2)_2$ . The living polymer chains were cross-linked using 1,4,4a,5,8,8a-hexahydro-1,4,5,8-*exo-endo*-dimethanonaphthalene. As a consequence of the polymerization order, the linear polymer chains bearing the functional groups form tentacles which are attached to the surface of the cross-linked carrier. The resulting material represents a typical small particle catalyst.<sup>15</sup> The carrier particles have a mean diameter of 20–40  $\mu\text{m}$ , possess only macropores ( $>1000 \text{ \AA}$ ), and are therefore characterized by a low specific surface area (4–6  $\text{m}^2/\text{g}$ ) both in the dry as well as in the wetted state. Consequently, swelling is a minor problem. As the palladium-loaded chelating groups are located exclusively at the surface of the particle,<sup>52,60</sup> they are easily accessible; diffusion plays a minor role and coupling reactions proceed within the interphase.<sup>65,66</sup> As a consequence of the high selectivity of the ligand for palladium, no substitution by other metal ions which might be present in technical grade chemicals occurs. The high affinity of the ligand for palladium also leads to a high-temperature stability of up to 150  $^\circ\text{C}$  and to an extraordinary pH stability of the resulting complex. Thus, palladium may not be removed from the ligand within a pH range of 0–12.

**Preparation of the Homogeneous Catalyst.** To obtain more information about the actual geometry of the catalytic center, to estimate any potential loss of activity that results from heterogenization, and to make a statement about the actual catalytically active species, a homogeneous analogue, **2**, was prepared (Figure 2). Reaction of acetyl chloride with dipyridyl-



**Figure 2.** Preparation of **2**.



**Figure 3.** X-ray structure of **2**.

amine leads to the formation of *N,N*-di(pyrid-2-yl)acetamide (**1**). Reaction of **1** with  $\text{H}_2\text{PdCl}_4$  in methanol yields the corresponding complex **2**. It was characterized by X-ray analysis and shows the expected square-planar conformation of the palladium center (Figure 3). The carbonyl group shows no additional interaction with the metal center. A comparison between the palladium-containing ligand **2** and the similar free ligand norborn-2-ene-5-(*N,N*-dipyrid-2-yl)carbamide<sup>60</sup> reveals no significant differences in the relevant bond distances and angles. The surrounding of the  $\text{sp}^2$ -hybridized amide-nitrogen atom N(3) is virtually the same within standard deviations, consequently the angle C3–N3–C8 ( $116.5(3)^\circ$ ) is nearly identical with the corresponding one in the free ligand ( $116.1(2)^\circ$ ) (Table 2). The two angles of C3–N1–C7 and C8–N2–C12 ( $118.3(4)^\circ$  and  $118.8(4)^\circ$ , respectively) are only slightly increased compared to the corresponding angles in the free ligand ( $116.9(3)^\circ$  and  $115.6(3)^\circ$ , respectively). The reason for this increase in the C–N bond lengths in the range of 1 pm is the movement of the N1 (N2) atoms in direction of C5 (C10) of about the same range. This

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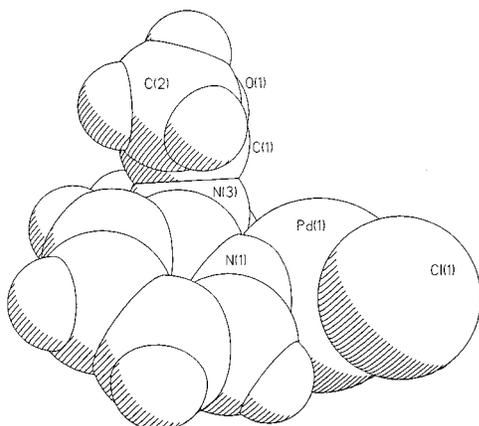
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**Table 1.** Selected X-ray Data for **2**

2	
mol formula	C <sub>12</sub> H <sub>11</sub> Cl <sub>2</sub> N <sub>3</sub> OPd
fw	390.54
cryst syst	monoclinic
space group	<i>P2<sub>1</sub>/n</i>
<i>a</i> (pm)	835.0(1)
<i>b</i> (pm)	1494.3(4)
<i>c</i> (pm)	1199.3(2)
$\alpha$ (deg)	90
$\beta$ (deg)	109.05(2)
$\gamma$ (deg)	90
vol (nm <sup>3</sup> )	1.4145(5)
<i>Z</i>	4
temp (K)	218.(2)
density (calcd) (Mg/m <sup>3</sup> )	1.834
abs coeff (mm <sup>-1</sup> )	1.683
color, habit	yellow plate
no. of rflns with $I > 2\sigma(I)$	1779
goodness-of-fit on $F^2$	1.068
<i>R</i> indices $I > 2\sigma(I)$	<i>R</i> 1 = 0.0305; <i>wR</i> 2 = 0.0702

**Table 2.** Selected Bond Lengths [pm] and Angles [deg] for **2**

Pd(1)–N(2)	203.9(3)	Pd(1)–Cl(1)	228.77(12)
Pd(1)–N(1)	204.1(3)	Pd(1)–Cl(2)	229.26(12)
N(2)–Pd(1)–N(1)	87.80(14)	N(1)–Pd(1)–Cl(2)	177.96(10)
Cl(1)–Pd(1)–Cl(2)	91.17(5)	N(2)–Pd(1)–Cl(1)	176.93(10)
N(1)–Pd(1)–Cl(1)	90.70(10)	C(8)–N(2)–Pd(1)	118.6(3)
N(2)–Pd(1)–Cl(2)	90.37(10)	C(8)–N(3)–C(3)	116.5(3)

**Figure 4.** Geometry of the relevant binding sites of **2**.

distortion may be explained by the Gillespie–Nyholm rules.<sup>67</sup> The high selectivity of this ligand for palladium results from its geometry (Figure 4). As the distance of the N3–C1 axis to the palladium atom is in the range of 260 pm, this leads to a repulsion between the amide group and any other ligand that would approach to form an octahedrally coordinated system. Consequently, the ligand prefers to form square-planar complexes and discriminates the building of octahedral complexes. The selectivity of the ligand for palladium versus other transition metal ions which preferably form square-planar complexes may lie in the thermodynamic or kinetical stability of the corresponding starting compounds. Thus, platinum is known to form extraordinarily stable chloro complexes, which may prevent recomplexation by this ligand.

**Coupling Reactions.** Both the heterogeneous as well as the homogeneous catalyst **2** were used for Heck-type reactions, alkyne couplings, polymerizations, and aminations of a series of differently substituted aryl halogenides with various vinyl

and alkyne compounds. An overview is given in Table 3. Each coupling sequence was carried out with different amounts of both the homogeneous and the heterogeneous palladium catalyst using different solvents and bases.

**(a) Aryl Iodides.** Aryl iodides are known to be the most reactive compounds in Heck-type couplings. As shown in Table 3 (entries 1–12), coupling yields of up to 99% (entry 5) may easily be obtained with extremely low amounts (0.2  $\mu$ mol) of the heterogeneous catalyst. Generally speaking, the system dimethylacetamide (DMAC)/K<sub>2</sub>CO<sub>3</sub>/Na<sub>2</sub>CO<sub>3</sub> was found to work best. Reactions were additionally carried out with extremely low amounts of catalyst (0.00038 mol %, entry 3) to characterize the new system in terms of the maximum achievable TONs. It is worth noting that TONs of up to 210000 may be achieved in these systems. Tetrabutylammonium bromide (TBAB), which is known to promote Heck-type couplings,<sup>33,38,68,69</sup> was used for comparative studies in the coupling reaction of styrene with iodobenzene (entry 6). Addition of 20 mol % of NBu<sub>4</sub>Br with respect to iodobenzene led to a significant increase in the overall reaction rate constant (Figure 5, graph B). Additionally, a significant increase in yield (98%) was observed. The elevated overall coupling rate constant and the high stability of the catalytic system may give access to a permanent system. As a consequence of the high stability of the heterogeneous system (Figure 5, graph A), the catalytic system for *trans*-stilbene employing  $3 \times 10^{-3}$  mol % palladium may be refed with educts without any further addition of catalyst (Figure 5, graphs, B, C, and D). The combination of the present heterogeneous system with such promoters therefore offers an attractive access to fast and efficient Heck-type couplings which may be of certain interest in industry.

Another demonstration of the versatility and applicability of the new heterogeneous system is given by the effective coupling of iodobenzene with vinylferrocene (Table 3, entry 11). While these reactions have been reported previously<sup>70</sup> to require 11 mol % of the catalyst to obtain yields larger than 85%, the present coupling system leads to similar yields with only  $4.4 \times 10^{-3}$  mol % palladium(II) (Table 3, entry 11). An interesting approach to ethynyl-based systems represents the use of trimethylsilylacetylene (TMS-acetylene). If the reaction is carried out in an autoclave under basic conditions (tri-*N*-butylamine, NBu<sub>3</sub>) and in the presence of traces of water, the TMS groups are cleaved off during coupling with iodobenzene to form a mixture of tolan (diphenylacetylene) and (partially TMS-protected) ethynylbenzene (Table 3, entry 12).

**(b) Aryl Bromides.** Coupling of activated bromoaryls such as 4-cyanobromobenzene with styrene leads to yields and TONs (170000) similar to those observed in the corresponding coupling reactions with iodoarenes (Table 3, entries 14–17). The system DMF/tri-*N*-butylamine allows yields of up to 94%. Nonactivated systems, e.g. bromobenzene/styrene, work best with DMAC/K<sub>2</sub>CO<sub>3</sub>/Na<sub>2</sub>CO<sub>3</sub> (entry 13). *p*-Fluorobromobenzene- and *p*-methoxybromobenzene-based systems may be coupled with moderate yields of up to 70%.

**(c) Aryl Chlorides.** The use of the easily accessible and cheap aryl chlorides in coupling reactions represents a major point of interest in industries. Unfortunately, coupling yields of vinyl compounds with aryl chlorides are often low. The same applies to the current system if it remains unmodified. Thus, no or little

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**Table 3.** Summary of Heck-Couplings, Polymerizations, and Pd-Mediated Aminations<sup>f</sup>

no.	Ar-I	g	H <sub>2</sub> C=CHR	g	product	resin <sup>d</sup> [mg]	Pd [μmol]	yield <sup>e</sup> [%]	solvent	10 <sup>3</sup> TON
1	iodobenzene	5.0	styrene	2.8	<i>trans</i> -stilbene	100	210	86.6	DMF <sup>b</sup>	1.0
2	iodobenzene	34.8	styrene	16.8	<i>trans</i> -stilbene	1.6 <sup>f</sup>	69.3	DMF <sup>c</sup>	73.9	
3	iodobenzene	11.3	styrene	5.7	<i>trans</i> -stilbene	1	0.2	78.3	DMF <sup>c</sup>	206.5
4	iodobenzene	9.0	styrene	4.6	<i>trans</i> -stilbene	3	1	90.0	DMAC <sup>c</sup>	40.2
5	iodobenzene	9.0	styrene	4.6	<i>trans</i> -stilbene	1.2	0.4	99.0	DMAC <sup>k</sup>	111.0
6	iodobenzene/TBAB <sup>a</sup>	3 × 1.5/0.5	styrene	3 × 0.77	<i>trans</i> -stilbene	1	0.2	98	DMF <sup>b</sup>	93.2
7	iodobenzene	5.5	ethylacrylate	2.7	ethyl cinnamate	20	4.2	79.3	DMF <sup>b</sup>	5.1
8	iodobenzene	9.1	ethylacrylate	4.5	ethyl cinnamate	20	6.7	<10	DMAC <sup>k</sup>	
9	iodobenzene	20.0	ethylacrylate	9.8	ethyl cinnamate	2	0.4	75.0	DMF <sup>b</sup>	175.1
10	iodobenzene	17.0	ethylacrylate	8.1	ethyl cinnamate	1.6 <sup>f</sup>	27.0	DMF <sup>b</sup>	14.1	
11	iodobenzene	0.92	vinylferrocene	0.94	1-ferrocenyl-2-phenylethene	1	0.2	81.1	DMF <sup>b</sup>	17.4
12	iodobenzene	14.8	TMS-acetylene	3.55	tolan/TMS-ethynylbenzene	1	0.2	75 (2:1)	DMF	432

no.	Ar-Br	g	H <sub>2</sub> C=CHR	g	product	resin <sup>d</sup> [mg]	Pd [μmol]	yield <sup>e</sup> [%]	solvent	10 <sup>3</sup> TON
13	bromobenzene	7.0	styrene	4.7	<i>trans</i> -stilbene	11 <sup>i</sup>	3.9	72.0	DMF <sup>c</sup>	9.4
14	bromobenzene	7.0	styrene	4.6	<i>trans</i> -stilbene	3	1	90.0	DMAC <sup>k</sup>	40.0
15	4-bromobenzonitrile	4.5	styrene	2.55	4-cyano- <i>trans</i> -stilbene	18	3.8	94.0	DMF <sup>b</sup>	6.1
16	4-bromobenzonitrile	6.7	styrene	3.8	4-cyano- <i>trans</i> -stilbene	5	1.1	62.1	DMF <sup>b</sup>	20.6
17	4-bromobenzonitrile	6.7	styrene	3.8	4-cyano- <i>trans</i> -stilbene		1.6 <sup>f</sup>	51.2	DMF <sup>b</sup>	11.7
18	4-bromobenzonitrile	12.3	styrene	8.5	4-cyano- <i>trans</i> -stilbene	1 <sup>9)</sup>	0.35	83.0	DMF <sup>b</sup>	157.7
19	4-bromo-1-fluorobenzene	15.3	styrene	9.1	4-fluoro- <i>trans</i> -stilbene	2	0.4	26.0	DMF <sup>c</sup>	54.1
20	4-bromo-1-fluorobenzene	7.8	styrene	4.6	4-fluoro- <i>trans</i> -stilbene	2	0.7	58.5	DMAC <sup>k</sup>	34.4
21	4-methoxybromobenzene	8.3	styrene	4.6	4-methoxy- <i>trans</i> -stilbene	105	36	70.0	DMAC <sup>k</sup>	0.9

no.	Ar-Cl	g	H <sub>2</sub> C=CHR	g	product	resin <sup>d</sup> [mg]	Pd [μmol]	yield <sup>e</sup> [%]	solvent	10 <sup>3</sup> TON
22	chlorobenzene	5.0	styrene	4.7	<i>trans</i> -stilbene	10 <sup>j</sup>	3.5	0.0	DMF <sup>c</sup>	0.0
23	chlorobenzene/TBAB	5.0/3.0	styrene	4.7	<i>trans</i> -stilbene	10 <sup>j</sup>	3.5	60.0	DMF <sup>c</sup>	8.2
24	chlorobenzene/TBAB	5.0/3.0	styrene	4.6	<i>trans</i> -stilbene	10 <sup>j</sup>	1.5	89.0	DMAC <sup>k</sup>	23.6
25	chlorobenzene/TBAB	5.0/3.0	styrene	4.6	<i>trans</i> -stilbene	5	1.7	16.0	DMF, 70° <sup>c</sup>	4.1
26	4-chloroacetophenone	13.5	styrene	9.1	4-acetyl- <i>trans</i> -stilbene	10	0.2	<10	DMF <sup>c</sup>	-
27	4-chloroacetophenone/TBAB	7.5/3.0	styrene	5.0	4-acetyl- <i>trans</i> -stilbene	20 <sup>9)</sup>	6.9	19.0	DMF <sup>c</sup>	1.4
28	4-chloroacetophenone/TBAB	6.9/3.0	styrene	4.6	4-acetyl- <i>trans</i> -stilbene	20	6.9	95.0	DMAC <sup>k</sup>	6.1

no.	Ar-Br	g	H <sub>2</sub> C=CHR	g	product	resin <sup>d</sup> [mg]	Pd [μmol]	yield <sup>e</sup> [%]	solvent	10 <sup>3</sup> TON
29	dibromobenzene	2.0	divinylbenzene	1.14	polyphenylenevinylene (M <sub>w</sub> = 1970, PDI = 1.63)	2	0.7	>99	DMAC <sup>k</sup>	18

no.	ArBr	g	amine	g	product	resin <sup>d</sup> [mg]	Pd [μmol]	yield <sup>i</sup> [%]	solvent	10 <sup>3</sup> TON
30	bromobenzene/KO- <i>t</i> -Bu	4.2/3.5	<i>N</i> -methylaniline	2.8	<i>N</i> -methyl-diphenylamine	15	3.2	45.2	THF <sup>g</sup>	3.8
31	bromobenzene/KO- <i>t</i> -Bu	4.2/3.5	<i>N</i> -methylaniline	2.8	<i>N</i> -methyl-diphenylamine	22 <sup>h</sup>	5.5	63.0	toluene	3.7
32	bromobenzene/KO- <i>t</i> -Bu <sup>h</sup>	5.0/4.0	piperidine	2.7	<i>N</i> -phenylpiperidine	22 <sup>j</sup>	7.7	18.0	toluene	0.8
33	bromoanisole/KO- <i>t</i> -Bu	2.2/3.0	diphenylamine	2.0	4-methoxytriphenylamine	15	3.2	10.0	THF <sup>g</sup>	0.4

<sup>a</sup> TBAB = tetrabutylammonium bromide. <sup>b</sup> 30 mL tri-*n*-butylamine. <sup>c</sup> 50 mL tri-*n*-butylamine. <sup>d</sup> Containing 0.21 mmol/g immobilized Pd<sup>2+</sup> (+0.4 mmol free ligand). <sup>e</sup> Isolated yields <sup>f</sup>Soluble, homogeneous analogue, Cl<sub>2</sub>PdL<sub>2</sub> 865 °C. <sup>h</sup> 2 h at 110 °C. <sup>i</sup> by NMR. <sup>j</sup> Containing 0.35 mmol/g of immobilized Pd(0) (+0.65 mmol free ligand). <sup>k</sup> K<sub>2</sub>CO<sub>3</sub>/Na<sub>2</sub>CO<sub>3</sub>. <sup>l</sup> Unless stated otherwise, Heck-couplings were carried out at *T* = 140 °C, *t* = 90 h.

reaction (<10%) is observed between styrene and chlorobenzene or the more activated 4-chloroacetophenone using 1 × 10<sup>-2</sup> mol % of the heterogeneous catalyst (entries 21 and 25). Nevertheless, upon addition of TBAB, conversions of up to 89% and 96%, respectively, may be achieved (entries 22, 23, 24, and 27–28). As for the aryl iodides and bromides, the system DMAC/K<sub>2</sub>CO<sub>3</sub>/Na<sub>2</sub>CO<sub>3</sub> works best.

**Polymerizations.** The use of the heterogeneous catalyst in combination with the system DMAC/K<sub>2</sub>CO<sub>3</sub>/Na<sub>2</sub>CO<sub>3</sub> allows the quantitative polymerization of dibromobenzene/divinylbenzene (containing 20% of ethylvinylbenzene, which serve as chain terminating substrates) to form yellow poly(*p*-phenylenevinylene) (PPV). Molecular weights as determined by GPC (M<sub>n</sub> = 1200) fit well the calculated values (M<sub>n</sub> = 2000) which may be deduced from the average chain length of PPV in the presence of 20% of ethylvinylbenzene. Polydispersities (PDIs) are as low as 1.6 (entry 29).

**Amination of Aryl Bromides.** There exist several methods for the amination of aryl compounds. While standard procedures

entailed the use of organotin compounds<sup>71,72</sup> or aryltriflates,<sup>73,74</sup> coupling reactions of aryl iodides and bromides may now be accomplished by phosphine-based palladium catalysts<sup>13,14,75</sup> in the presence of a sterically hindered base such as sodium or potassium-*tert*-butylate.<sup>11</sup> Nickel-based systems or the use of particular phosphines (e.g. di-*tert*-butylbiphen-2-ylphosphine) even allow the use of aryl chlorides.<sup>12,76–78</sup> More recently, highly

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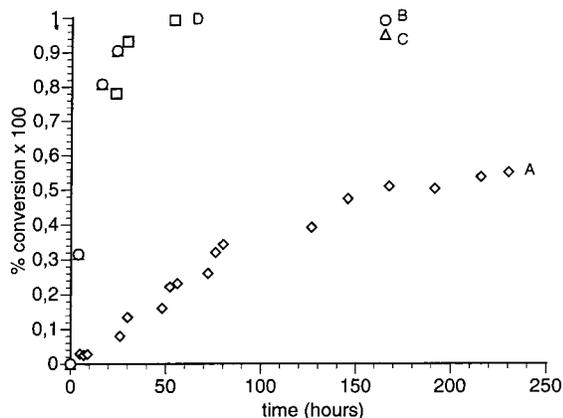
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**Figure 5.** (A) Time profile for the formation of *trans*-stilbene from iodobenzene (1.5 g) and styrene (0.77 g) using 1 mg of immobilized Pd catalyst corresponding to 0.0027 mol % (21  $\mu$ g) palladium(II) based on styrene. (B–D) Time profile for the “refeeding” of the coupling system iodobenzene (1.5 g), styrene (0.77 g), tetrabutylammonium bromide (0.5 g), and immobilized Pd catalyst (1 mg): (B) first run, (C) second run, (D) third run. (All experiments were performed in DMF at 140 °C,  $\text{NBu}_3$ .)

active homogeneous systems, which allow the amination of aryl halogenides at room temperature, have been reported.<sup>76,79</sup> In general, transition metal-catalyzed aminations of aryl halogenides are still characterized by low to moderate TONs (<5000).<sup>80</sup> To demonstrate the applicability of the heterogeneous system to the field of aminations, coupling reactions were carried out with *N*-methylaniline, diphenylamine, and piperidine (Table 3, entries 30–33). As expected, these aminations require larger amounts of catalyst compared to Heck-type reactions. Especially in the case of sterically hindered amines such as diphenylamine, TONs and yields are significantly lowered. Nevertheless, coupling yields may be improved by performing the reaction at  $T = 110$  °C in toluene.

**Reactivity and Stability.** A comparison of the heterogeneous system with the homogeneous analogue in terms of TONs reveals some interesting aspects (Table 3, e.g. entries 2, 5, 6, 9, and 10). Surprisingly, yields and TONs obtained with the homogeneous catalyst are generally lower than those obtained with the heterogeneous system. An additional observation was that couplings carried out with the homogeneous analogue resulted in the formation of minor, yet detectable amounts of palladium(0). One explanation for these findings may be that the palladium(0) intermediate, which is now commonly accepted as the active species both in homogeneous<sup>75,81–83</sup> and heterogeneous Heck-type couplings,<sup>25</sup> stays immobilized at the surface of the particle. This may either occur in form of a Pd(0) colloid or as a ligated Pd(0) species. Formation of the former one would result in a significant loss of activity. As roughly only 35% of the ligands present at the surface form a palladium(II) complex, the large excess of uncomplexed dipyriddy amide ligands may serve as complementary complexing sites, which significantly reduce the formation and/or release of uncomplexed palladium black. In contrast, any release of palladium from the ligand

(dipyriddy amide) of the homogeneous catalyst would result in the formation of a nonstabilized palladium(0) colloid, which may further aggregate and become inactive. This assumption of the existence of a heterogeneous ligand-stabilized species was supported by the following experiments. The palladium(II)-loaded resin was treated with an aqueous solution of ascorbic acid, leading to a palladium(0)-loaded resin. If, as proposed, palladium(0) is still complexed by the dipyriddy ligand, no formation of palladium colloids will occur. Consequently, the palladium(0) system will still exhibit similar activities in the Heck-coupling of bromo- and chloroarenes which are known to preferably proceed with ligand-stabilized palladium systems. A coupling sequence using 4-cyanobromobenzene and styrene was carried out under similar conditions which were chosen for the heterogeneous palladium(II) system. Thus, 4-cyano-*trans*-stilbene was formed in 62% yield using 1.1  $\mu$ mol of the heterogeneous Pd(II) system (entry 16), while even higher yields (83%) were obtained with 0.35  $\mu$ mol of the reduced species. In contrast, the same reaction sequence carried out with a homogeneous Pd(II) catalyst resulted in the formation of 4-cyano-*trans*-stilbene in only 51% yield (entry 17). Finally, the constant catalytic activity of the heterogeneous system which must be expected in the case of a ligand-stabilized system was demonstrated by the recording of a time profile for the reaction of styrene with iodobenzene (Figure 5, graph A). An almost constant rate of reaction was observed within the investigated reaction time (250 h).

## Summary

A new heterogeneous catalytic system has been prepared by polymerization and subsequent cross-linking of a polymerizable chelating ligand using ROMP. Subsequent loading with palladium(II) results in a polymer-immobilized palladium catalyst. The entire system is characterized by a straightforward synthesis as well as by a high temperature, pH and chemical stability. It may be used effectively for Heck-type reactions and for the amination of aryl bromides. As a direct consequence of the palladium-loaded ligand:free ligand ratio, the heterogeneous system exceeds the homogeneous one in catalytic activity due to enhanced stability.

## Experimental Section

**General Details.** NMR data were obtained in the indicated solvent at 30 °C on a Bruker AM 300 and Varian EM 360L unless stated otherwise and are listed in parts per million downfield from tetramethylsilane for proton and carbon. Coupling constants are given in hertz. IR spectra were recorded on a Midac FT-IR. Further instrumentation for the determination of the specific surface area ( $\sigma$ ) by means of the BET method and GPC, respectively, and for ICP-OES experiments is described elsewhere.<sup>60</sup> The GPC equipment has also been described previously.<sup>60</sup> Purchased starting materials were used without any further purification. Reagent grade tetrahydrofuran and toluene were distilled from sodium benzophenone ketyl under nitrogen.  $\text{Mo}(\text{N}-2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)(\text{CHCMe}_2\text{Ph})(\text{OCMe}(\text{CF}_3)_2)_2$  was synthesized as described in the literature.<sup>84</sup>

**Preparation of the Resin.** The preparation of the resin (0.6 mmol of dipyriddy amide,  $\sigma = 4$  m<sup>2</sup>/g,  $40 \pm 10$   $\mu$ m) was performed under an argon atmosphere by standard Schlenk techniques according to a previously published procedure.<sup>60</sup> Loading with palladium(II) was achieved by stirring the resin (1.045 g) in an aqueous solution of  $\text{H}_2\text{-PdCl}_4$  (1000  $\mu$ g/mL in 5% HCl, 83.3 mL) (pH 0) at room temperature for 20 h. The actual amounts of palladium(II) sorbed onto the resin as determined by ICP-OES were 0.21 and 0.34 mmol/g, respectively.

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**Reduction of Palladium.** The resin (0.5 g) was stirred overnight in an aqueous solution of ascorbic acid (10%) containing 20% of methanol. The resin was then filtered off, extensively washed with water, and dried in vacuo. Subsequent chlorine analysis revealed the absence of any halogen.

**Heck-Couplings.** Unless stated otherwise, couplings were carried out at  $T = 140\text{ }^{\circ}\text{C}$  in the solvent indicated in Table 3. Solvents and reagents were used as purchased. The educts were dissolved in 70–100 mL of solvent and the base (tri-*n*-butylamine,  $\text{K}_2\text{CO}_3$ ,  $\text{Na}_2\text{CO}_3$ ) as well as the catalyst were added. Reaction times as well as a summary of the experiments including the corresponding scales and molar ratios are given in Table 3. For workup, the reaction mixture was poured on water, acidified with hydrochloric acid (2 N), and extracted with diethyl ether (3–5  $\times$  50 mL). The combined organic phases were dried over sodium sulfate. Finally, the solvent and (where applicable) the reactants were evaporated in vacuo. The coupling products were isolated by flash chromatography (silica G-60, 4  $\times$  30 cm, pentane:diethyl ether = 90:10) and repeated crystallization. Purity of the corresponding crops was determined by  $^1\text{H}$  NMR.

**Time Profiles.** Time profiles of the reaction of iodobenzene with styrene were determined by withdrawing 1 mL aliquots from the reaction mixture. The time-dependent yield was calculated from the educts:product ratio which was determined by  $^1\text{H}$  NMR spectroscopy via integration of the *o*-H signals of *trans*-stilbene and iodobenzene, respectively.

**Polymerization.** 1,4-Dibromobenzene, divinylbenzene (DVB, containing 20% of ethylvinylbenzene), the catalyst, and the base were placed in a round-bottomed flask. For the corresponding amounts of educts refer to Table 3. DMAC (60 mL) was added and the mixture was heated to  $140\text{ }^{\circ}\text{C}$  for 90 h. The polymer formed was extracted with THF, and the solution was filtered to remove catalyst and inorganic salts and precipitated by adding pentane.

**Aminations.** In a 150 mL Schlenk tube, the aryl halide and the amine were dissolved in dry toluene and the base as well as the catalyst were added. Reactions were carried out at  $65\text{ }^{\circ}\text{C}$  in THF and at  $110\text{ }^{\circ}\text{C}$  in toluene, respectively. The reaction time was 24 h throughout. For workup, the reaction mixture was poured on water and extracted with diethyl ether (3–5  $\times$  50 mL). The combined organic phases were dried over sodium sulfate and the amine was isolated by flash chromatography (silica G-60, 4  $\times$  30 cm, pentane:diethyl ether = 70:30). Purity of the corresponding fractions was determined by  $^1\text{H}$  NMR.

***N,N*-Dipyrid-2-ylacetamide (1).** A solution of acetyl chloride (5.04 g, 4.56 mL, 64.2 mmol) in methylene chloride was added dropwise to a well-stirred solution of dipyrid-2-ylamine (10.0 g, 58.5 mmol) in 20 mL of the same solvent at  $T = -20\text{ }^{\circ}\text{C}$ . The reaction mixture was warmed to room temperature and extracted twice with saturated aqueous sodium bicarbonate solution. Finally the solvent was removed in vacuo. The residue was recrystallized from diethyl ether to yield 4.34 g (34.7%) of pure **1**. IR (KBr): 1688 s ( $\nu_{\text{C=O}}$ ), 1586 s, 1571 s, 1468 vs, 1364 s, 1314 s, 1279 vs ( $\nu_{\text{C-O}}$ ), 1148 s, 985 s, 783 s, 743 m, 513 m, 415 m, 409m.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  8.43 (m, 2 H), 7.74 (d  $\times$  d  $\times$  d, 2 H,  $J_1 = 7.9$ ,  $J_2 = 2.3$ ,  $J_3 = 0.1$ ), 7.48 (d, 2 H,  $J = 7.9$ ), 7.17 (m, 2 H), (s,

3 H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  170.8 (CO), 154.7, 149.0, 138.1, 122.1, 24.6 ( $\text{CH}_3$ ). Elemental analysis calcd for  $\text{C}_{12}\text{H}_{11}\text{N}_3\text{O}$  ( $M_w = 213.239\text{ g/mol}$ ): C 67.59; H 5.20 N19.71. Found: C 67.17; H 4.91; N 19.73.

***N*-Acetyl-*N,N*-dipyrid-2-yl Palladium Dichloride (2).** To a solution of anhydrous palladium(II) chloride (203 mg, 1.14 mmol) in 5 mL of 32% hydrochloric acid is added a solution of sodium hydroxide (15%) just before palladium hydroxide starts to precipitate. A solution of **1** (285 mg, 1.44 mmol) in methanol (10 mL) was added. A red precipitate formed that dissolved upon addition of a few drops of hydrochloric acid. A yellow crystalline solid formed which was filtered off, washed with water and methanol, and dried in vacuo. Yield: 314 mg (70.7%). IR (KBr): 1713 s ( $\nu_{\text{C=O}}$ ), 1602 m, 1480 s, 1466 s, 1439 s, 1366 s, 1312 s, 1268 vs ( $\nu_{\text{C-O}}$ ), 1225 s, 791 m, 780 m, 760 s, 741 s, 581 s.  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ ):  $\delta$  8.80 (d, 2 H,  $J = 4.9$ ), 8.28 (m, 2 H), 8.02 (bs, 2 H), 7.67 (m, 2 H), 2.28 (s, 3 H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{DMSO-}d_6$ ):  $\delta$  168.5, 152.6, 148.2, 142.4, 125.4, 22.6 ( $\text{CH}_3$ ). Elemental analysis calcd for  $\text{C}_{12}\text{H}_{11}\text{N}_3\text{OPdCl}_2$  ( $M_w = 390.565\text{ g/mol}$ ): C 36.90; H 2.84; N 10.76. Found: C 36.88; H 2.77; N 10.59. Single crystals suitable for X-ray analysis may be obtained by recrystallization from methylene chloride/diethyl ether (CCDC No. 136902, Cambridge Crystallographic Data Centre).

***trans*-1-Ferrocenyl-2-phenylethene [Registry No. 12094-24-5].** The compound was prepared according to the general coupling procedure described above. Analytical data (IR,  $^1\text{H}$  NMR) were identical with those described in the literature.<sup>85–87</sup> Additional data are as follows:  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  67.1, 69.2, 69.4, 83.5, 126.0, 126.2, 127.0, 128.2, 128.8, 138.1.

**X-ray Measurement and Structure Determination of 2.** A Siemens P4 diffractometer with graphite-monochromatized Mo  $K\alpha$  radiation ( $\lambda = 71.073\text{ pm}$ ) was used for data collection. Intensities were measured via  $\omega$ -scans and corrected for Lorentz and polarization effects. The structure was solved by direct methods (SHELXS-86)<sup>88</sup> and refined by full-matrix least-squares against  $F^2$  (SHELXL-93).<sup>89</sup> The function minimized was  $\Sigma[w(F_o^2 - F_c^2)^2]$  with the weight defined as  $w^{-1} = [\sigma^2(F_o^2) + (xP)^2 + yP]$  and  $P = (F_o^2 + 2F_c^2)/3$ . All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located by difference Fourier methods, but in the refinement they were generated geometrically and refined with isotropic displacement parameters 1.2 and 1.5 (for the methyl-group) times higher than  $U(\text{eq})$  of the attached C atoms. Further relevant crystallographic data are summarized in Tables 1 and 2.

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